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K. H. Büchel, H.-H. Moretto, P. Woditsch

Industrial Inorganic Chemistry

Second, Completely Revised Edition

Karl Heinz Büchel
Hans-Heinrich Moretto
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Translated by
David R. Terrell

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Professor Dr. Dr. h. c. mult. Karl Heinz Büchel
Member of the Board of Directors of Bayer AG
D-51368 Leverkusen

Professor Hans-Heinrich Moretto
Bayer AG
Central Research
D-51368 Leverkusen

Professor Dr. Peter Woditsch
Bayer AG
CH-BS
D-47829 Krefeld

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Preface to the Second English Edition

In the more than 10 years, since the publication of the first edition of the book "Industrial Inorganic Chemistry", the structure of inorganic industrial chemistry has not changed fundamentally.

In most sectors the "state of the art" has been expanded and refined. This is addressed together with the updating of the economic data in this new edition.

The pressure for change in the meantime was due in particular to globalization of the World economy and the resulting pressure for cost reduction through new and optimalized processes and to an expanding knowledge of ecological requirements e.g. energy saving and new production and development principles such as quality assurance and responsible care.

To the extent that it is discernible in the products and processes, appropriate aspects have been incorporated in the revision, for example see membrane technology in the chloralkali and hydrochloric acid electrolysis.

Expansion of the sections on the products of silicon chemistry, silanes, heavy duty ceramics and photovoltaics reflects their increased importance.

Chapter 6 over the Nuclear Fuel Cycle has been updated as regards technical developments and in particular as regards its societal and political context.

In inorganic chemistry there have been important changes particularly in inorganic materials such as new composite materials and so-called nano-materials, in the area of photovoltaics and in catalysis. Since these have not yet been widely used industrially, they have not been covered in the second edition of this book.

In the revision of this book numerous colleagues have assisted us, we particularly wish to thank:

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Leverkusen, Autumn 1999 The Authors

Preface to the First English Edition

"Industrial Inorganic Chemistry" was first published in German in 1984. The book was well received by students and teachers alike, leading to the publication of a second German edition in 1986. The publishers, VCH Verlagsgesellschaft, were convinced that a wide circle of readers would welcome the appearance of our book in the English language, and their encouragement has led to the preparation of the present up-dated and revised edition in English.

The basic structure of the German Edition has been retained. Changes in the industrial importance of some compounds and processes since the appearance of the German edition have been taken into account and data relating to the US market have been emphasised. Thus the chapter on potassium permanganate has been considerably abridged and that on the membrane process for the manufacture of chlorine and sodium hydroxide expanded.

We are indebted to Dr Podesta and Dr Heine from Bayer AG for their assistance in the revision of the German edition in addition to the institutions and colleagues mentioned in the preface to the German edition.

The book was translated by Dr D. R. Terrell from Agfa-Gevaert NV, to whom we are particularly grateful for the patience and care he devoted to this difficult task. We also wish to acknowledge the contribution of VCH Verlagsgesellschaft in producing this edition.

Leverkusen, Autumn 1988 K. H. Büchel

Preface to the First German Edition

The book "Industrielle Anorganische Chemie" will fill a long term need, which has become even more apparent since the appearance of "Industrielle Organische Chemie" by Wessermel and Arpe*. Although there are comprehensive chapters on this branch of chemistry in a number of encyclopedias and handbooks, a single volume text is lacking that describes concisely the current state of industrial inorganic chemistry.

The authors have been made aware of this need in discussions with students, young chemists, colleagues in neighboring fields, teachers and university lecturers and willingly accepted the suggestion of the publishers to write this text. Changes in the supply of raw materials and their markets and economic and ecological requirements are responsible for the continual reshaping of the inorganic chemical industry. As a result the treatment of industrial processes in the available textbooks seldom keeps pace with these developments.

The inorganic chemical industry is an important branch of industry and its structure is particularly diverse: including a large number of finished products (mineral fertilizers, construction materials, glass, enamels and pigments to name but a few) and basic products for the organic chemical industry such as mineral acids, alkalis, oxidizing agents and halogens. Modern developments in other branches of industry, such as chips for microelectronics, video cassettes and optical fibers have only been possible due to the continuous development of the inorganic chemical industry.

This book emphasises the manufacturing processes, economic importance and applications of products. In the sections on production the pros and cons are considered in the context of the raw material situation, economic and ecological considerations and energy consumption, the different situations in different countries also being taken into account. Processes which are no longer operated are at most briefly mentioned. The properties of the products are only considered to the extent that they are relevant for production or applications.

It was necessary to restrict the material to avoid overextending the brief. Metallurgical processes have not been included, except for the manufacture of "chemical" metals (e.g. alkali metals) which is briefly described. Several borderline areas with organic chemistry are considered (e.g. organophosphorus, -silicon and -fluoro products), others are deliberately excluded. A whole chapter is devoted to the nuclear fuel cycle, since it involves so much industrial scale inorganic chemistry and is currently so important.

The layout follows that of its sister book "Industrielle Organische Chemie" with the main text being supplemented by marginal notes. These are essentially summaries of the main text and enable the reader to obtain a rapid grasp of the most important facts. The equations are printed on a gray background for the same reason.

At the end of each main section a generally subtitled list of references is provided. This should enable the reader to obtain more detailed information on particular matters with the minimum of effort. In addition to references to original papers and reviews, readers are referred to the important handbooks: Ullmann, Winnacker-Küchler and Kirk-Othmer. The Chemical Economic Handbook of the Stanford Research Institute has frequently been used for economic data.

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Contents

1 Primary Inorganic Materials 1

1.1 Water 1
1.1.1 Economic Importance 1
1.1.2 Production of Potable Water 2
1.1.2.1 Break-Point Chlorination and Ozonization 3
1.1.2.2 Flocculation and Sedimentation 4
1.1.2.3 Filtration 5
1.1.2.4 Removal of Dissolved Inorganic Impurities 5
1.1.2.5 Activated Charcoal Treatment 7
1.1.2.6 Safety Chlorination 8
1.1.2.7 Production of Soft or Deionized Water 8
1.1.3 Production of Freshwater from Seawater and Brackish Water 10
1.1.3.1 Production by Multistage Flash Evaporation 10
1.1.3.2 Production using Reverse Osmosis 11
References for Chapter 1.1: Water 13

1.2 Hydrogen 14
1.2.1 Economic Importance 14
1.2.2 Hydrogen Manufacture 15
1.2.2.1 Petrochemical Processes and Coal Gasification 15
1.2.2.2 Electrolysis of Water 16
1.2.2.3 Other Manufacturing Processes for Hydrogen 17
1.2.2.4 Production of Hydrogen as a Byproduct 18
1.2.3 Hydrogen Applications 18
References for Chapter 1.2: Hydrogen 19

1.3 Hydrogen Peroxide and Inorganic Peroxo Compounds 20
1.3.1 Economic Importance 20
1.3.1.1 Hydrogen Peroxide 20
1.3.1.2 Sodium Perborate and Sodium Carbonate Perhydrate 20
1.3.1.3 Alkali Peroxodisulfates and Sodium Peroxide 21
1.3.2 Production 21
1.3.2.1 Hydrogen Peroxide 21
1.3.2.2 Sodium Perborate 24
1.3.2.3 Sodium Carbonate Perhydrate 25
1.3.2.4 Alkali Peroxodisulfate 26
1.3.2.5 Sodium Peroxide 26

1.3.3 Applications 27
1.3.3.1 Hydrogen Peroxide, Sodium Perborate and Sodium Carbonate Perhydrate 27
1.3.3.2 Alkali Peroxodisulfates and Sodium Peroxide 28
References for Chapter 1.3: Hydrogen Peroxide and Inorganic Peroxo Compounds 28

1.4 Nitrogen and Nitrogen Compounds 29
1.4.1 Ammonia 29
1.4.1.1 Economic Importance 29
1.4.1.2 Synthetic Ammonia Manufacture 29
1.4.1.2.1 General Information 29
1.4.1.2.2 Ammonia Synthesis Catalysts 30
1.4.1.2.3 Synthesis Gas Production 32
1.4.1.2.4 Conversion of Synthesis Gas to Ammonia 39
1.4.1.2.5 Integrated Ammonia Synthesis Plants 41
1.4.1.3 Ammonia Applications 43
References for Chapter 1.4: Nitrogen and Nitrogen Compounds 43
1.4.2 Hydrazine 43
1.4.2.1 Economic Importance 43
1.4.2.2 Manufacture of Hydrazine 44
1.4.2.2.1 Raschig Process 44
1.4.2.2.2 Urea Process 45
1.4.2.2.3 Bayer Process 46
1.4.2.2.4 H_2O_2 Process 47
1.4.2.3 Applications of Hydrazine 48
References for Chapter 1.4.2: Hydrazine 49
1.4.3 Hydroxylamine 50
1.4.3.1 Economic Importance and Applications 50
1.4.3.2 Manufacture 50
1.4.3.2.1 Raschig Process 51
1.4.3.2.2 Nitrogen(II) Oxide Reduction Process 51
1.4.3.2.3 Nitrate Reduction Process (DSM/HPO-Stamicarbon) 52
References for Chapter 1.4.3: Hydroxylamine 53
1.4.4 Nitric Acid 53
1.4.4.1 Economic Importance 53
1.4.4.2 Manufacture 53
1.4.4.2.1 Fundamentals of Nitric Acid Manufacture 53
1.4.4.2.2 Plant Types 57
1.4.4.2.3 Process Description 58
1.4.4.2.4 Manufacture of Highly Concentrated Nitric Acid 59
1.4.4.2.5 Tail Gases from Nitric Acid Manufacture 62
1.4.4.3 Nitric Acid Applications 64
References for Chapter 1.4.4: Nitric Acid 65

1.5 Phosphorus and its Compounds 65
1.5.1 Phosphorus and Inorganic Phosphorus Compounds 65
1.5.1.1 Raw Materials 65

1.5.1.2 Products 67
1.5.1.2.1 Phosphoric Acid 67
1.5.1.2.2 Phosphoric Acid Salts 75
1.5.1.2.3 Phosphorus 80
1.5.1.2.4 Products Manufactures from Phosphorus 85
References for Chapter 1.5.1: Phosphorus and Inorganic Phosphorus Compounds 90
1.5.2 Organophosphorus Compounds 91
1.5.2.1 Neutral Phosphoric Acid Esters 91
1.5.2.2 Phosphoric Ester Acids 94
1.5.2.3 Dithiophosphoric Ester Acids 94
1.5.2.4 Neutral Esters of Thio- and Dithio-Phosphoric Acids 95
1.5.2.5 Neutral Di- and Triesters of Phosphorous Acid 97
1.5.2.6 Phosphonic Acids 99
References for Chapter 1.5.2: Organophosphorus Compounds 101

1.6 Sulfur and Sulfur Compounds 101
1.6.1 Sulfur 101
1.6.1.1 Occurrence 101
1.6.1.2 Economic Importance 102
1.6.1.2.1 Sulfur from Elemental Sulfur Deposits 102
1.6.1.2.2 Sulfur from Hydrogen Sulfide and Sulfur Dioxide 102
1.6.1.2.3 Sulfur from Pyrites 103
1.6.1.3 Economic Importance 104
1.6.1.4 Applications 104
1.6.2 Sulfuric Acid 104
1.6.2.1 Economic Importance 104
1.6.2.2 Starting Materials for Sulfuric Acid Manufacture 105
1.6.2.2.1 Sulfuric Acid from Sulfur Dioxide 105
1.6.2.2.2 Sulfuric Acid from Waste Sulfuric Acid and Metal Sulfates 113
1.6.2.3 Applications of Sulfuric Acid 115
1.6.3 100% Sulfur Dioxide 116
1.6.4 100% Sulfur Trioxide 117
1.6.5 Disulfur Dichloride 118
1.6.6 Sulfur Dichloride 118
1.6.7 Thionyl chloride 119
1.6.8 Sulfuryl Chloride 119
1.6.9 Chlorosulfonic Acid 120
1.6.10 Fluorosulfonic Acid 120
1.6.11 Sulfurous Acid Salts 120
1.6.12 Sodium Thiosulfate, Ammonium Thiosulfate 121
1.6.13 Sodium Dithionite and Sodium Hydroxymethanesulfinate 122
1.6.14 Hydrogen Sulfide 124
1.6.15 Sodium Sulfide 124
1.6.16 Sodium Hydrogen Sulfide 125
1.6.17 Carbon Disulfide 126
References for Chapter 1.6: Sulfur and Sulfur Compounds 126

1.7 Halogens and Halogen Compounds 127
1.7.1 Fluorine and Fluorine Compounds 127
1.7.1.1 Fluorspar 127
1.7.1.1.1 Fluorspar Extraction 128
1.7.1.1.2 Qualities and Utilization of Fluorspar 128
1.7.1.1.3 Fluorapatite 130
1.7.1.2 Fluorine and Inorganic Fluorides 130
1.7.1.2.1 Fluorine 130
1.7.1.2.2 Hydrogen Fluoride 132
1.7.1.2.3 Aluminum Fluoride 138
1.7.1.2.4 Sodium Aluminum Hexafluoride (Cryolite) 140
1.7.1.2.5 Alkali Fluorides 141
1.7.1.2.6 Hexafluorosilicates 142
1.7.1.2.7 Uranium Hexafluoride 142
1.7.1.2.8 Boron Trifluoride and Tetrafluoroboric Acid 142
1.7.1.2.9 Sulfur Hexafluoride 143
1.7.1.3 Organofluoro Compounds by Electrochemical Fluorination 144
References for Chapter 1.7.1: Halogens and Halogen Compounds 145
1.7.2 Chloralkali Electrolysis, Chlorine and Sodium Hydroxide 146
1.7.2.1 Economic Importance 146
1.7.2.2 Starting Materials 148
1.7.2.3 Manufacturing Processes 151
1.7.2.3.1 Mercury Process 152
1.7.2.3.2 Diaphragm Process 154
1.7.2.3.3 Membrane Process 157
1.7.2.3.4 Evaluation of Mercury, Diaphragm and Membrane Processes 158
1.7.2.4 Applications of Chlorine and Sodium Hydroxide 159
1.7.2.4.1 Chlorine 159
1.7.2.4.2 Sodium Hydroxide 160
References for Chapter 1.7.2: Chloralkali-Electrolysis 161
1.7.3 Hydrochloric Acid – Hydrogen Chloride 162
1.7.3.1 Manufacture of Hydrogen Chloride 162
1.7.3.2 Economic Importance of Hydrogen Chloride and Hydrochloric Acid 163
1.7.3.3 Electrolysis of Hydrochloric Acid 163
1.7.3.4 Non-Electrolytic Processes for the Manufacture of Chlorine from Hydrogen Chloride 164
References for Chapter 1.7.3: Hydrochloric Acid – Hydrogen Chloride 165
1.7.4 Chlorine-Oxygen Compounds 166
1.7.4.1 Economic Importance 166
1.7.4.2 Manufacture of Chlorine-Oxygen Compounds 167
1.7.4.2.1 Hypochlorite 167
1.7.4.2.2 Chlorites 170
1.7.4.2.3 Chlorates 170
1.7.4.2.4 Perchlorates and Perchloric Acid 172
1.7.4.2.5 Chlorine Dioxide 173
1.7.4.3 Applications of Chlorine-Oxygen Compounds 174

References for Chapter 1.7.4: Chlorine-Oxygen Compounds 175
1.7.5 Bromine and Bromine Compounds 175
1.7.5.1 Natural Deposits and Economic Importance 175
1.7.5.2 Manufacture of Bromine and Bromine Compounds 176
1.7.5.2.1 Bromine 176
1.7.5.2.2 Hydrogen Bromide 178
1.7.5.2.3 Alkali Bromides, Calcium Bromide, Zinc Bromide 179
1.7.5.2.4 Alkali Bromates 179
1.7.5.3 Applications for Bromine and Bromine Compounds 179
References for Chapter 1.7.5: Bromine and Bromine Compounds 181
1.7.6 Iodine and Iodine Compounds 181
1.7.6.1 Economic Importance 181
1.7.6.2 Manufacture of Iodine and Iodine Compounds 182
1.7.6.2.1 Iodine 182
1.7.6.2.2 Hydrogen Iodide 183
1.7.6.2.3 Alkali Iodides 183
1.7.6.2.4 Alkali Iodates 184
1.7.6.3 Applications of Iodine and Iodine Compounds 184
References for Chapter 1.7.6: Iodine and Iodine Compounds 185

2 Mineral Fertilizers 187

2.1 Phosphorus-Containing Fertilizers 187
2.1.1 Economic Importance 187
2.1.1.1 General Information 187
2.1.1.2 Importance of Superphosphate 188
2.1.1.3 Importance of Triple Superphosphate 188
2.1.1.4 Importance of Ammonium Phosphates 189
2.1.1.5 Importance of Nitrophosphates 189
2.1.1.6 Importance and Manufacture of Thermal (Sinter, Melt) and Basic Slag (Thomas) Phosphates 189
2.1.2 Manufacture of Phosphorus-Containing Fertilizers 190
2.1.2.1 Superphosphate 190
2.1.2.2 Triple Superphosphate 191
2.1.2.3 Ammonium Phosphates 192
2.1.2.4 Nitrophosphates 195

2.2 Nitrogen-Containing Fertilizers 196
2.2.1 Economic Importance 196
2.2.1.1 General Information 196
2.2.1.2 Importance of Ammonium Sulfate 197
2.2.1.3 Importance of Ammonium Nitrate 197
2.2.1.4 Importance of Urea 198
2.2.2 Manufacture of Nitrogen-Containing Fertilizers 199
2.2.2.1 Ammonium Sulfate 199

2.2.2.2 Ammonium Nitrate 200
2.2.2.3 Urea 201

2.3 Potassium-Containing Fertilizers 205
2.3.1 Occurrence of Potassium Salts 205
2.3.2 Economic Importance of Potassium-Containing Fertilizers 206
2.3.3 Manufacture of Potassium-Containing Fertilizers 208
2.3.3.1 Potassium Chloride 208
2.3.3.2 Potassium Sulfate 210
2.3.3.3 Potassium Nitrate 210
References for Chapter 2: Mineral Fertilizers 211

3 Metals and their Compounds 213

3.1 Alkali and Alkaline Earth Metals and their Compounds 213
3.1.1 Alkali Metals and their Compounds 213
3.1.1.1 General Information 213
3.1.1.2 Lithium and its Compounds 213
3.1.1.2.1 Natural Deposits and Economic Importance 213
3.1.1.2.2 Metallic Lithium 214
3.1.1.2.3 Lithium Compounds 214
3.1.1.3 Sodium and its Compounds 216
3.1.1.3.1 General Information 216
3.1.1.3.2 Metallic Sodium 217
3.1.1.3.3 Sodium Carbonate 218
3.1.1.3.4 Sodium Hydrogen Carbonate 222
3.1.1.3.5 Sodium Sulfate 223
3.1.1.3.6 Sodium Hydrogen Sulfate 225
3.1.1.3.7 Sodium Borates 225
3.1.1.4 Potassium and its Compounds 227
3.1.1.4.1 General Information 227
3.1.1.4.2 Metallic Potassium 227
3.1.1.4.3 Potassium Hydroxide 227
3.1.1.4.4 Potassium Carbonate 228
References for Chapter 3.1.1: Alkali Metals and their Compounds 229
3.1.2 Alkaline Earth Metals and their Compounds 230
3.1.2.1 General Information 230
3.1.2.2 Beryllium and its Compounds 231
3.1.2.3 Magnesium and its Compounds 231
3.1.2.3.1 Natural Deposits 231
3.1.2.3.2 Metallic Magnesium 232
3.1.2.3.3 Magnesium Carbonate 234
3.1.2.3.4 Magnesium Oxide 235
3.1.2.3.5 Magnesium Chloride 236
3.1.2.3.6 Magnesium Sulfate 237

3.1.2.4 Calcium and its Compounds 237
3.1.2.4.1 Natural Deposits 237
3.1.2.4.2 Metallic Calcium 238
3.1.2.4.3 Calcium Carbonate 238
3.1.2.4.4 Calcium Oxide and Calcium Hydroxide 239
3.1.2.4.5 Calcium Chloride 240
3.1.2.4.6 Calcium Carbide 240
3.1.2.5 Strontium and its Compounds 242
3.1.2.6 Barium and its Compounds 242
3.1.2.6.1 Natural Deposits and Economic Importance 242
3.1.2.6.2 Barium Carbonate 243
3.1.2.6.3 Barium Sulfide 245
3.1.2.6.4 Barium Sulfate 245
References for Chapter 3.1.2: Alkaline Earth Metals and their Compounds 245

3.2 Aluminum and its Compounds 246
3.2.1 General Information 246
3.2.2 Natural Deposits 247
3.2.3 Metallic Aluminum 248
3.2.3.1 Economic Importance 248
3.2.3.2 Manufacture 248
3.2.3.3 Applications 249
3.2.4 Aluminum Oxide and Aluminum Hydroxide 250
3.2.4.1 Economic Importance 250
3.2.4.2 Manufacture 250
3.2.4.3 Applications 251
3.2.5 Aluminum Sulfate 252
3.2.5.1 Economic Importance 252
3.2.5.2 Manufacture 252
3.2.5.3 Applications 253
3.2.6 Aluminum Chloride 253
3.2.6.1 Economic Importance 253
3.2.6.2 Manufacture 253
3.2.6.3 Applications 254
3.2.7 Sodium Aluminate 254
References for Chapter 3.2: Aluminum and its Compounds 255

3.3 Chromium Compounds and Chromium 255
3.3.1 Chromium Compounds 255
3.3.1.1 Economic Importance 255
3.3.1.2 Raw Material: Chromite 257
3.3.1.3 Manufacture of Chromium Compounds 258
3.3.1.3.1 Chromite Digestion to Alkali Chromates 258
3.3.1.3.2 Alkali Dichromates 260
3.3.1.3.3 Chromium(VI) Oxide ("Chromic Acid") 262
3.3.1.3.4 Chromium(III) Oxide 264

3.3.1.3.5 Basic Chromium(III) Salts (Chrome Tanning Agents) 265
3.3.1.4 Applications for Chromium Compounds 266
3.3.2 Metallic Chromium 266
3.3.2.1 Economic Importance 266
3.3.2.2 Manufacture of Chromium Metal 267
3.3.2.2.1 Chemical Reduction 267
3.3.2.2.2 Electrochemical Reduction of Chrome Alum 267
3.3.2.2.3 Electrochemical Reduction of Chromium(VI) Oxide 268
References for Chapter 3.3: Chromium Compounds and Chromium 268

3.4 Silicon and its Inorganic Compounds 269
3.4.1 Elemental Silicon 269
3.4.1.1 General Information and Economic Importance 269
3.4.1.2 Manufacture 270
3.4.1.2.1 Ferrosilicon and Metallurgical Grade Silicon 270
3.4.1.2.2 Electronic Grade Silicon (Semiconductor Silicon) 272
3.4.1.3 Silicon Applications 278
3.4.2 Inorganic Silicon Compounds 279
References for Chapter 3.4: Silicon and its Inorganic Compounds 281

3.5 Manganese Compounds and Manganese 282
3.5.1 Manganese Compounds 282
3.5.1.1 Economic Importance 282
3.5.1.2 Raw Materials 283
3.5.1.3 Manufacture of Manganese Compounds 284
3.5.1.3.1 Manganese(II) Compounds 284
3.5.1.3.2 Manganese(II,III) Oxide (Mn_3O_4) and Manganese(III) Oxide (Mn_2O_3) 286
3.5.1.3.3 Manganese(IV) Oxide 286
3.5.1.3.4 Potassium Permanganate 289
3.5.1.4 Applications of Manganese Compounds 292
3.5.2 Manganese - Electrochemical Manufacture, Importance and Applications 292
References for Chapter 3.5: Manganese Compounds and Manganese 293

4 Organo-Silicon Compounds 295

4.1 Industrially Important Organo-Silicon Compounds, Nomenclature 295

4.2 Industrially Important Silanes 296
4.2.1 Organohalosilanes 296
4.2.2 Industrial Important Silicon-functional Organo-Silanes 298
4.2.2.1 Organoalkoxysilanes 299
4.2.2.2 Acyloxysilanes 300
4.2.2.3 Oximino- and Aminoxy-Silanes 300
4.2.2.4 Amidosilanes, Silazanes 301
4.2.2.5 Organohydrogensilanes 301

4.2.3 Organofunctional Silanes 302
4.2.3.1 Alkenylsilanes 302
4.2.3.2 Halo-organosilanes 303
4.2.3.3 Organoaminosilanes 303
4.2.3.4 Organomercaptosilanes, Organosulfidosilanes 304
4.2.3.5 Other Organofunctional Silanes 304
References for Chapter 4.1 and 4.2: Organo-Silicon Compounds 305

4.3 Silicones 305
4.3.1 Structure and Properties, Nomenclature 305
4.3.2 Economic Importance 306
4.3.3 Linear and Cyclic Polyorganosiloxanes 307
4.3.3.1 Manufacture 307
4.3.3.2 Hydrolysis 307
4.3.3.3 Methanolysis 309
4.3.3.4 Cyclization 310
4.3.3.5 Polymerization 310
4.3.3.6 Polycondensation 312
4.3.3.7 Industrial Realization of Polymerization 313
4.3.4 Manufacture of Branched Polysiloxanes 314

4.4 Industrial Silicone Products 307
4.4.1 Silicone Oils 307
4.4.2 Products Manufactured from Silicone Oils 316
4.4.3 Silicone Rubbers 317
4.4.3.1 Room Temperature Vulcanizable Single Component Silicone Rubbers 317
4.4.3.2 Two Component Room Temperature Vulcanizable Silicone Rubbers 319
4.4.3.3 Hot Vulcanizable Peroxide Crosslinkable Silicone Rubbers 320
4.4.3.4 Hot Vulcanizable Addition Crosslinkable Silicone Rubbers 320
4.4.3.5 Properties of Silicone Rubber 322
4.4.4 Silicone Resins 322
4.4.5 Silicone Copolymers, Block Copolymers and Graft Copolymers 323
References for Chapters 4.3 and 4.4: Silicones 324

5 Inorganic Solids 325

5.1 Silicate Products 325
5.1.1 Glass 325
5.1.1.1 Economic Importance 325
5.1.1.2 Structure 325
5.1.1.3 Glass Composition 326
5.1.1.4 Glass Manufacture 329
5.1.1.4.1 Glass Raw Materials 329
5.1.1.4.2 Melting Process 331
5.1.1.4.3 Melting Furnaces 332

5.1.1.5 Forming 334
5.1.1.6 Glass Properties and Applications 336
References for Chapter 5.1.1: Glass 337
5.1.2 Alkali Silicates 338
5.1.2.1 General and Economic Importance 338
5.1.2.2 Manufacture of Alkali Silicates 338
5.1.2.3 Applications 340
References for Chapter 5.1.2: Alkali Silicates 340
5.1.3 Zeolites 340
5.1.3.1 Economic Importance 340
5.1.3.2 Zeolite Types 341
5.1.3.3 Natural Zeolites 344
5.1.3.4 Manufacture of Synthetic Zeolites 344
5.1.3.4.1 From Natural Raw Materials 344
5.1.3.4.2 From Synthetic Raw Materials 344
5.1.3.4.3 Modification of Synthetic Zeolites by Ion Exchange 346
5.1.3.5 Forming of Zeolites 346
5.1.3.6 Dehydration of Zeolites 347
5.1.3.7 Applications for Zeolites 347
5.1.3.7.1 As Ion Exchangers 347
5.1.3.7.2 As an Adsorption Agent 347
5.1.3.7.3 For Separation Processes 348
5.1.3.7.4 As Catalysts 349
5.1.3.7.5 Miscellaneous Applications 349
References for Chapter 5.1.3: Zeolites 350

5.2 Inorganic Fibers 351
5.2.1 Introduction 351
5.2.1.1 Definitions, Manufacture and Processing 351
5.2.1.2 Economic Importance 352
5.2.1.3 Properties 352
5.2.1.4 Classification and Applications 354
5.2.1.5 Physiological Aspects 354
5.2.2 Asbestos Fibers 356
5.2.2.1 General and Economic Importance 356
5.2.2.2 Occurrence and Extraction 359
5.2.2.3 Applications of Asbestos Fibers 361
5.2.3 Textile Glass Fibers 364
5.2.3.1 General and Economic Importance 364
5.2.3.2 Manufacture 366
5.2.3.3 Applications 369
5.2.4 Optical Fibers 370
5.2.5 Mineral Fiber Insulating Materials 372
5.2.5.1 General Information and Economic Importance 372
5.2.5.2 Manufacture 373
5.2.5.3 Applications 377

5.2.6 Carbon Fibers 377
5.2.6.1 General Information and Economic Importance 377
5.2.6.2 Manufacture and Applications 380
5.2.7 Metal Fibers 384
5.2.7.1 Steel and Tungsten Fibers 384
5.2.7.2 Boron Fibers 386
5.2.8 Ceramic Reinforcing Fibers 388
5.2.8.1 General information and Economic Importance 388
5.2.8.2 Oxide Fibers 389
5.2.8.3 Non-oxide Fibers 391
5.2.8.4 Whiskers 394
References for Section 5.2: Inorganic Fibers 395

5.3 Construction Materials 396
5.3.1 General Introduction 396
5.3.2 Lime 397
5.3.2.1 Economic Importance 397
5.3.2.2 Raw Materials 398
5.3.2.3 Quicklime 398
5.3.2.4 Slaked Lime 400
5.3.2.4.1 Wet Slaking of Quicklime 400
5.3.2.4.2 Dry Slaking of Quicklime 401
5.3.2.4.3 Lime Hydrate from Calcium Carbide 401
5.3.2.5 Steam-Hardened Construction Materials 402
5.3.2.6 Applications of Lime 402
5.3.3 Cement 403
5.3.3.1 Economic Importance 403
5.3.3.2 Composition of Cements 404
5.3.3.3 Portland Cement 405
5.3.3.3.1 Raw Materials 405
5.3.3.3.2 Composition of Portland Cement Clinkers 405
5.3.3.3.3 Manufacture of Portland Cement 405
5.3.3.3.4 Applications of Portland Cement 409
5.3.3.4 Slag Cement 409
5.3.3.5 Pozzolan Cements 410
5.3.3.6 Alumina Cement 411
5.3.3.7 Asbestos Cement 411
5.3.3.8 Miscellaneous Cement Types 411
5.3.3.9 Processes in the Solidification of Cement 412
5.3.4 Gypsum 415
5.3.4.1 Economic Importance 415
5.3.4.2 Modifications of Calcium Sulfate 416
5.3.4.3 Natural Gypsum 418
5.3.4.4 Natural Anhydrite 420
5.3.4.5 Fluoroanhydrite 420
5.3.4.6 Byproduct Gypsum 420

5.3.4.6.1 Byproduct Gypsum from the Manufacture and Purification of Organic Acids 420
5.3.4.6.2 Byproduct Gypsum from Flue Gas Desulfurization 421
5.3.4.6.3 Phosphogypsum 421
5.3.4.7 Processes in the Setting of Plaster 423
5.3.5 Coarse Ceramic Products for the Construction Industry 424
5.3.6 Expanded Products 425
5.3.6.1 General Information 425
5.3.6.2 Expanded Products from Clays and Shales 425
5.3.6.2.1 Raw Materials 425
5.3.6.2.2 Gas-forming Reactions in the Manufacture of Expanded Products 428
5.3.6.2.3 Manufacture of Expanded Products 429
5.3.6.3 Expanded Products from Glasses (Foam Glass) 430
5.3.6.4 Applications of Expanded Products 430
References for Chapter 5.3: Construction Materials 431

5.4 Enamel 430
5.4.1 General Information 432
5.4.2 Classification of Enamels 433
5.4.3 Enamel Frit Manufacture 437
5.4.3.1 Raw Materials 437
5.4.3.2 Smelting of Frits 437
5.4.4 Enameling 438
5.4.4.1 Production of Coatable Systems 438
5.4.4.2 Coating Processes 439
5.4.4.2.1 Wet Application Processes 439
5.4.4.2.2 Dry Application Processes 440
5.4.4.3 Stoving of Enamels 441
5.4.5 Applications of Enamel 442
References for Chapter 5.4: Enamel 442

5.5 Ceramics 443
5.5.1 General Information 443
5.5.2 Classification of Ceramic Products 443
5.5.3 General Process Steps in the Manufacture of Ceramics 444
5.5.4 Clay Ceramic Products 445
5.5.4.1 Composition and Raw Materials 445
5.5.4.2 Extraction and Treatment of Raw Kaolin 447
5.5.4.3 Manufacture of Clay Ceramic Batches 447
5.5.4.4 Forming Processes 448
5.5.4.4.1 Casting Processes 449
5.5.4.4.2 Plastic Forming 450
5.5.4.4.3 Forming by Powder Pressing 451
5.5.4.5 Drying Processes 452
5.5.4.6 Firing of Ceramics 452
5.5.4.6.1 Physical-Chemical Processes 452

5.5.4.6.2 Firing Conditions 454
5.5.4.6.3 Glazes 455
5.5.4.7 Properties and Applications of Clay Ceramic Products 455
5.5.4.7.1 Fine Earthenware 455
5.5.4.7.2 Stoneware 456
5.5.4.7.3 Porcelain 456
5.5.4.7.4 Rapidly Fired Porcelain 457
5.5.4.8 Economic Importance of Clay Ceramic Products 458
5.5.5 Specialty Ceramic Products 458
5.5.5.1 Oxide Ceramics 458
5.5.5.1.1 General Information 458
5.5.5.1.2 Aluminum Oxide 460
5.5.5.1.3 Zirconium Oxide 461
5.5.5.1.4 Beryllium Oxide 462
5.5.5.1.5 Uranium Oxide and Thorium Oxide 462
5.5.5.1.6 Other Oxide Ceramics 463
5.5.5.2 Electro- and Magneto-Ceramics 464
5.5.5.2.1 Titanates 464
5.5.5.2.2 Ferrites 465
5.5.5.3 Refractory Ceramics 468
5.5.5.3.1 Definition and Classification 468
5.5.5.3.2 Alumina-Rich Products 470
5.5.5.3.3 Fireclay Products 470
5.5.5.3.4 Silicate Products 471
5.5.5.3.5 Basic Products 472
5.5.5.3.6 Specialty Refractory Products 473
5.5.5.3.7 Economic Importance 473
5.5.5.4 Nonoxide Ceramics 474
5.5.5.4.1 Economic Importance 475
5.5.5.4.2 Manufacturing Processes for Silicon Carbide 475
5.5.5.4.3 Refractory Silicon Carbide Products 477
5.5.5.4.4 Fine Ceramic Silicon Carbide Products 477
5.5.5.4.5 Fine Silicon Nitride Ceramic Products 478
5.5.5.4.6 Manufacture and Properties of Boron Carbide 480
5.5.5.4.7 Manufacture and Properties of Boron Nitride 481
5.5.5.4.8 Manufacture and Properties of Aluminum Nitride 482
References for Chapter 5.5: Ceramics 482

5.6 Metallic Hard Materials 484
5.6.1 General Information 484
5.6.2 General Manufacturing Processes and Properties of Metal Carbides 485
5.6.3 Carbides of the Subgroup of the IVth Group 487
5.6.3.1 Titanium Carbide 487
5.6.3.2 Zirconium Carbide and Hafnium Carbide 488
5.6.4 Carbides of the Subgroup of the Vth Group 488
5.6.4.1 Vanadium Carbide 488

5.6.4.2 Niobium Carbide and Tantalum Carbide 488
5.6.5 Carbides of the Subgroup of the VIth Group 489
5.6.5.1 Chromium Carbide 489
5.6.5.2 Molybdenum Carbide 489
5.6.5.3 Tungsten Carbide 489
5.6.5.4 Cemented Carbides Based on Tungsten Carbide 490
5.6.6 Thorium Carbide and Uranium Carbide 491
5.6.7 Metal Nitrides 492
5.6.8 Metal Borides 493
5.6.9 Metal Silicides 494
References for Chapter 5.6: Metallic Hard Materials 495

5.7 Carbon Modifications 496
5.7.1 Introduction 496
5.7.2 Diamond 496
5.7.2.1 Economic Importance 496
5.7.2.2 Mining of Natural Diamonds 497
5.7.2.3 Manufacture of Synthetic Diamonds 498
5.7.2.4 Properties and Applications 500
5.7.3 Natural Graphite 500
5.7.3.1 Economic Importance 500
5.7.3.2 Natural Deposits and Mining 502
5.7.3.3 Properties and Applications 503
5.7.4 Large Scale Production of Synthetic Carbon and Synthetic Graphite 505
5.7.4.1 Economic Importance 505
5.7.4.2 General Information about Manufacture 505
5.7.4.3 Manufacture of Synthetic Carbon 506
5.7.4.3.1 Raw Materials 506
5.7.4.3.2 Processing 507
5.7.4.3.3 Densification and Forming 507
5.7.4.3.4 Carbonization 508
5.7.4.4 Graphitization of Synthetic Carbon 509
5.7.4.4.1 General Information 509
5.7.4.4.2 Acheson Process 509
5.7.4.4.3 Castner Process 510
5.7.4.4.4 Other Graphitization Processes 510
5.7.4.4.5 Purification Graphitization 511
5.7.4.5 Impregnation and Processing of Carbon and Graphite Articles 511
5.7.4.6 Properties and Applications 512
5.7.5 Special Types of Carbon and Graphite 513
5.7.5.1 Pyrolytic Carbon and Pyrolytic Graphite 513
5.7.5.2 Glassy Carbon and Foamed Carbon 515
5.7.5.3 Graphite Foils and Membranes 516
5.7.6 Carbon Black 517
5.7.6.1 Economic Importance 518
5.7.6.2 Manufacture 518

5.7.6.2.1 General Information 518
5.7.6.2.2 Pyrolysis Processes in the Presence of Oxygen 519
5.7.6.2.3 Pyrolysis Processes in the Absence of Oxygen 522
5.7.6.2.4 Posttreatment 523
5.7.6.3 Properties and Applications 524
5.7.7 Activated Carbon 527
5.7.7.1 Economic Importance 527
5.7.7.2 Manufacture 528
5.7.7.2.1 General Information 8
5.7.7.2.2 Activated Carbon by “Chemical Activation” 529
5.7.7.2.3 Activated Carbon by “Gas Activation” 530
5.7.7.3 Reactivation and Regeneration of Used Activated Carbon 532
5.7.7.4 Applications of Activated Carbon 532
References for Chapter 5.7: Carbon Modifications 534

5.8 Fillers 535
5.8.1 General Information 535
5.8.2 Economic Importance 536
5.8.3 Natural Fillers 536
5.8.3.1 Silicon-Based Fillers 536
5.8.3.2 Other Natural Fibers 538
5.8.3.3 Beneficiation of Natural Fillers 538
5.8.4 Synthetic Fillers 539
5.8.4.1 Silicas and Silicates 539
5.8.4.1.1 Pyrogenic Silicas 539
5.8.4.1.2 Wet Chemically Manufactured Silicas and Silicates 540
5.8.4.1.3 Posttreatment of Silicas 541
5.8.4.1.4 Glasses 542
5.8.4.1.5 Cristobalite 542
5.8.4.2 Aluminum Hydroxide 542
5.8.4.3 Carbonates 543
5.8.4.4 Sulfates 544
5.8.4.5 Other Synthetic Fillers 545
5.8.5 Properties and Applications 545
References for Chapter 5.8: Fillers 546

5.9 Inorganic Pigments 548
5.9.1 General Information and Economic Importance 548
5.9.2 White Pigments 552
5.9.2.1 General Information 552
5.9.2.2 Titanium Dioxide Pigments 553
5.9.2.2.1 Economic Importance 553
5.9.2.2.2 Raw Materials for TiO_2 Pigments 553
5.9.2.2.3 Manufacturing Processes for TiO_2 Pigments 555
5.9.2.2.4 Applications for TiO_2 Pigments 558
5.9.2.3 Lithopone and Zinc Sulfide Pigments 559

5.9.2.4 Zinc Oxide White Pigments 560
5.9.2.4.1 Manufacture 560
5.9.2.4.2 Applications 561
5.9.3 Colored Pigments 561
5.9.3.1 Iron Oxide Pigments 561
5.9.3.1.1 Natural Iron Oxide Pigments 561
5.9.3.1.2 Synthetic Iron Oxide Pigments 563
5.9.3.2 Chromium(III) Oxide Pigments 567
5.9.3.2.1 Manufacture 567
5.9.3.2.2 Properties and Applications of Chromium(III) Oxide 569
5.9.3.3 Chromate and Molybdate Pigments 570
5.9.3.4 Mixed-Metal Oxide Pigments and Ceramic Colorants 571
5.9.3.5 Cadmium Pigments 573
5.9.3.6 Cyanide Iron Blue Pigments 575
5.9.3.7 Ultramarine Pigments 577
5.9.4 Corrosion Protection Pigments 578
5.9.5 Luster Pigments 580
5.9.5.1 Metal Effect Pigments 580
5.9.5.2 Nacreous Pigments 581
5.9.5.3 Interference Pigments 581
5.9.6 Luminescent Pigments 581
5.9.7 Magnetic Pigments 582
5.9.7.1 General Information and Properties 582
5.9.7.2 Manufacture of Magnetic Pigments 584
References for Chapter 5.9: Inorganic Pigments 586

6 Nuclear Fuel Cycle 587

6.1 Economic Importance of Nuclear Energy 587

6.2 General Information about the Nuclear Fuel Cycle 591

6.3 Availability of Uranium 592

6.4 Nuclear Reactor Types 594
6.4.1 General Information 594
6.4.2 Light-water Reactors 594
6.4.2.1 Boiling Water Reactors 594
6.4.2.2 Pressurized Water Reactors 595
6.4.3 Graphite-Moderated Reactors 595
6.4.3.1 Gas-Cooled 595
6.4.3.2 Light-Water Cooled 597
6.4.4 Heavy-Water Reactors 597
6.4.5 Fast Breeder Reactors 598

6.5 Nuclear Fuel Production 599
6.5.1 Production of Uranium Concentrates ("Yellow Cake") 600
6.5.1.1 Uranium from Uranium Ores 600
6.5.1.1.1 Leaching Processes 600
6.5.1.1.2 Separation of Uranium from the Leaching Solutions 602
6.5.1.1.3 Manufacture of Marketable Uranium Compounds ("Yellow Cake") 603
6.5.1.2 Uranium from Phosphate Ores and Wet Phosphoric Acid 605
6.5.1.3 Uranium from Seawater 606
6.5.2 Conversion of Uranium Concentrates to Uranium Hexafluoride 607
6.5.2.1 General Information 607
6.5.2.2 Wet Process for Uranium(VI) Fluoride Manufacture 607
6.5.2.3 Dry Process for Uranium(VI) Fluoride Manufacture 609
6.5.3 ^{235}U-Enrichment 609
6.5.4 Reconversion of Uranium(VI) Fluoride into Nuclear Fuel 610
6.5.4.1 Into Uranium(IV) Oxide 610
6.5.4.1.1 General Information 610
6.5.4.1.2 Uranium(IV) Oxide by Wet Processes 611
6.5.4.1.3 Uranium(IV) Oxide by the Dry (IDR) Process 612
6.5.4.1.4 Manufacture of Uranium(IV) Oxide Pellets 612
6.5.4.2 Other Uranium Nuclear Fuels 613
6.5.5 Fuel Element Manufacture 614

6.6 Disposal of Waste from Nuclear Power Stations 615
6.6.1 General Information 615
6.6.2 Stages in Nuclear Waste Disposal 617
6.6.2.1 Interim Storage of Spent Fuel Elements 617
6.6.2.2 Reprocessing of Spent Fuel Elements 617
6.6.2.3 Further Processing of Uranium and Plutonium Solutions 620
6.6.2.4 Treatment of Radioactive Waste 621
6.6.2.5 Permanent Storage of Radioactive Waste 623
References for Chapter 6: Nuclear Fuel Cycle 624

Company Abbreviations Index 627

Subject Index 631

Industrial inorganic Chemistry
Karl Heinz Büchel, Hans-Heinrich Moretto & Peter Woditsch

1 Primary Inorganic Materials

1.1 Water

1.1.1 Economic Importance

Water: a raw material in principle available in unlimited quantities, since used water is fed back into the Earth's water circulation

Water is a raw material which is available on Earth in unlimited quantities. Water is not consumed since, after use, it is fed back sooner or later into the Earth's water circulation. The local availability of water (e.g. in arid regions), especially with the purity necessary for the particular application, is another matter. Cheap high purity water is required for many applications.

FRG 1991:

- Public supply of water: $6.1 \cdot 10^9$ m^3 = 80 m^3 per inhabitant per year
- Total water extraction: $46.44 \cdot 10^9$ m^3

Statistics for the Federal Republic of Germany serve to illustrate the origin and production of water for an industrialized country. In 1991 a total of $6.1 \cdot 10^9$ m^3 of water was produced (corresponding to about 80 m^3 per inhabitant) which comprises:

- $4015 \cdot 10^6$ m^3 ground- and spring water, of which
  $399 \cdot 10^6$ m^3 is spring water
- $1725 \cdot 10^6$ m^3 surface water, of which
  $387 \cdot 10^6$ m^3 is filtered through river banks,
  $529 \cdot 10^6$ m^3 is augmented ground water and
  $586 \cdot 10^6$ m^3 from reservoirs

$46.44 \cdot 10^9$ m^3 of water was extracted (= demand) in 1990 (of which ca. 84 % was surface water) which was mainly (ca. 70%) used as a coolant in power stations. The utilization of water is, however, slightly more than double this quantity, reflecting the multiple usage of the cooling water.

In rain starved regions (southern Mediterranean, northern desert belt) potable water is produced on an industrial scale from sea- and brackish water using distillation plants (older technology), reverse osmosis (newer technology) and to a small extent electrodialysis plants (brackish water).

In 1995, just in Saudi Arabia (45 % of Arabia) more than $1.9 \cdot 10^9$ m^3 of water was produced from seawater. By early

1995 8900 plants worldwide, with a capacity of $10 \cdot 10^6$ m^3/a, produced $5.7 \cdot 10^9$ m^3/a of potable water. Geographically this capacity is distributed as follows:

- 60 % in the Middle East
- 13 % in North America
- 10 % in Europe including the former States of the USSR

60 % of the capacity is in multistage (typically 18 to 24 stage) vacuum distillation plants (MSF, multistage flash), ca. 35 % of the capacity is in plants utilizing the more recent reverse osmosis (RO) technology and 5% in plants using electrodialysis technology. RO-plants dominate because they are more compact to build and consume much less energy, although this is expensive electrical energy, than MSF-plants which essentially use thermal energy.

1.1.2 Production of Potable Water

Only good spring water can be used as potable water without further treatment.

The untreated water is more or less contaminated depending upon the source. To obtain potable water some or all of the following steps have to be carried out:

- Break-point chlorination (alternatives are ozone and chlorine dioxide)
- Flocculation
- Sedimentation
- Filtration
- Treatment with activated charcoal
- Safety chlorination
- pH adjustment

In obtaining potable water some or all of the following steps have to be carried out:

- Break-point chlorination or ozonization
- Flocculation
- Sedimentation
- Filtration
- Treatment with activated charcoal
- Safety chlorination
- pH adjustment

The number of steps carried out in practice depends entirely upon the quality of the untreated water. In the case of spring water only safety chlorination is necessary, to prevent infection from mains water. In the case of strongly polluted water (e.g. water filtered through the banks of the Rhine or Ruhr) almost all the steps are necessary. In this way potable water can be obtained even from strongly contaminated water. However, industrial water with lower purity, e.g. for cooling purposes, requires fewer purification steps.

Additional purification steps are necessary if the water contains large quantities of hardeners (calcium and magnesium ions), unbound carbon dioxide and iron and manganese ions.

Certain applications require deionized water. This can be obtained by ion exchange.

Further purification steps may also be necessary to:

- reduce the concentration of water hardeners (calcium and magnesium ions)
- remove free carbon dioxide and iron and manganese ions

1.1.2.1 Break-Point Chlorination and Ozonization

In the case of strongly polluted surface water, chlorination is the first purification step and is carried out after removal of any coarse foreign matter. Sufficient chlorine is added to ensure a free chlorine concentration of ca. 0.2 to 0.5 mg/L in the water after treatment (break-point chlorination). Chlorine reacts with water forming hydrochloric acid and the hypochlorite anion, depending upon the pH.

Break-point chlorination:

- addition of sufficient chlorine to ensure 0.2 to 0.5 mg/L of free chlorine in the water after treatment

Chlorination results in:

- elimination of pathogenic germs, deactivation of viruses,
- oxidation of cations such as iron(II) or manganese(II) to higher valency states,
- chlorination of ammonia to chloramines or nitrogen trichloride,
- chlorination of phenols to chlorophenols, and
- chlorination of organic impurities, particularly humic acid, e.g. to aliphatic chlorohydrocarbons.

Chlorination results in:

- elimination of pathogenic organisms
- chlorination of ammonia
- formation of undesirable organochloro-compounds!

The last two processes are undesirable: chlorophenols have a very strong taste and some of the aliphatic chlorohydrocarbons (e.g. chloroform) are also suspected of being carcinogenic. It is therefore usual to perform the chlorination only up to the chloramine stage and to carry out the further elimination of impurities, e.g. microbiological degradation processes, on activated charcoal.

The most important alternative to chlorination of water is ozonization in which the above-mentioned disadvantages occur to a much lesser extent. However, the higher cost of ozonization is a problem. Ozonization helps subsequent flocculation and biological degradation on activated charcoal. About 0.2 to 1.0 g of ozone is required per m^3 of water, in exceptional cases up to 3 g/m^3. A further alternative is treatment with chlorine dioxide (from sodium chlorite and chlorine), in which there is less formation of organochloro-compounds than in the case of chlorination (see Section 1.7.4.2.5).

Ozonization as an alternative to chlorination:

- advantages:
  - no formation of organochloro-compounds
  - subsequent flocculation made easier
- disadvantages:
  - higher costs

In the Federal Republic of Germany ozonization, as pre-ozonization – a post ozonization step being inserted before flocculation (see Section 1.1.2.2) – has largely supplanted break-point chlorination.

Aeration is sufficient to oxidize and thereby flocculate out iron and manganese ions in the treatment of groundwater, as well as serving to increase the pH by expelling the unbound carbon dioxide.

1.1.2.2 Flocculation and Sedimentation

Flocculation:

removal of inorganic and organic colloids by adsorption on (in situ produced) aluminum and iron(III) hydroxide flakes. If necessary flocculation aids are added

Preliminary purification by flocculation is necessary, if the untreated water has a high turbidity, particularly as a result of colloidal or soluble organic impurities. Iron or aluminum salts are added to the water, so that iron(III) or aluminum hydroxide is precipitated:

$$\begin{aligned} Al_2(SO_4)_3 + 6\,H_2O &\longrightarrow 2\,Al(OH)_3\downarrow + 3\,H_2SO_4 \\ FeSO_4Cl + 3\,H_2O &\longrightarrow Fe(OH)_3\downarrow + H_2SO_4 + HCl \\ Fe_2(SO_4)_3 + 6\,H_2O &\longrightarrow 2\,Fe(OH)_3\downarrow + 3\,H_2SO_4 \end{aligned}$$

The optimum pH for flocculation is about 6.5 to 7.5 for aluminum salts and about 8.5 for iron salts. If the natural alkali content of the untreated water is insufficient to neutralize the acid formed, alkali has to be added (e.g. calcium hydroxide or sodium hydroxide). In addition flocculation aids such as poly(acrylamide) or starch derivatives may be added (not in the case of potable water production). When aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$ is used 10 to 30 g/m^3 is added. The very fine hydroxide flakes which precipitate are positively charged and adsorb the negatively charged colloidal organic materials and clay particles.

A variety of industrial equipment has been used to carry out the flocculation process and the separation of the flocculated materials producing a well-defined sludge suspension layer, which can be removed. Some plant operates with sludge feedback to enable more efficient adsorption. Sludge flocks can also be separated by flotation.

1.1.2.3 Filtration

Water having undergone flocculation then has to be filtered. The water is generally filtered downwards through a 1 to 2 m high sand filter with 0.2 to 2 mm sand particles at a rate of 3 to 5 mm/s. When the filter is covered with impurities this increases the filter resistance and it is then cleaned by flushing upwards together with air, if necessary. Alternatively, a multiple-layer filter can be used, optionally combined with a 0.5 m high anthracite layer (Fig. 1.1-1).

Filtration:

separation of undissolved solids over a sand filter, optionally combined with an anthracite filter. Flushing with water or water/air when the filter is covered.

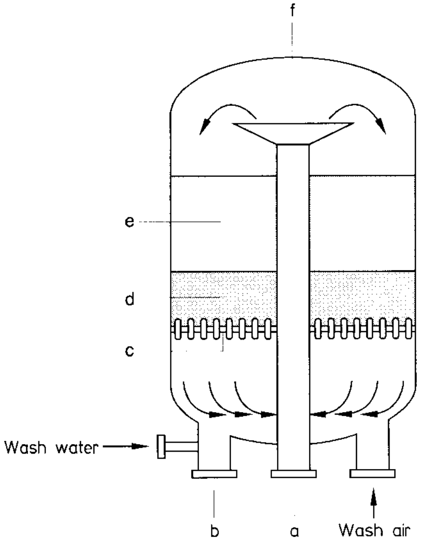


Figure 1.1-1. Construction of a two layer filter.
a) inlet; b) outlet; c) bottom; d) sand; e) filter charcoal; f) water distribution

1.1.2.4 Removal of Dissolved Inorganic Impurities

Untreated water containing much dissolved hydrogen carbonate forms, upon heating, a precipitate consisting mainly of calcium carbonate (carbonate hardness, boiler scale):

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$

The carbonate hardness can be removed by adding acid, whereupon the more soluble calcium sulfate is formed:

Hardeners, especially calcium and magnesium hydrogen carbonates rendered untroublesome by addition of:

- sulfuric acid and expulsion of carbon dioxide,
- calcium hydroxide and separation of the carbonates formed

$$Ca(HCO_3)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2\,CO_2 + 2\,H_2O$$

The resulting carbon dioxide has to be expelled, as carbon dioxide-containing water is corrosive. The hydrogen carbonate can be removed by the addition of calcium hydroxide:

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2\,CaCO_3 + 2\,H_2O$$

In an industrial variant of this process the calcium hydroxide, as a solution or a suspension, is added to hydrogen carbonate-containing water and the mixture passed over calcium carbonate beads, upon which the freshly formed calcium carbonate is deposited. Fresh beads form on the crystal nuclei added and those beads which become too large are separated off.

Carbon dioxide must also be expelled from soft water containing a high concentration of carbonic acid, a simultaneous hardening can be obtained by filtering over semi-calcined dolomite.

Removal of iron(II) and manganese(II) ions by oxidation of the bivalent ions with air, or if necessary, with chlorine and separation of the oxide hydrates formed. Dissolved carbon dioxide also expelled during air oxidation

Iron and manganese are present as bivalent ions in many waters. They are removed by oxidation to their oxide hydrates, preferably with air, and if necessary after increasing the pH. These are then filtered off. Treatment with air expels the dissolved carbon dioxide at the same time. If air is an insufficiently powerful oxidation agent, e.g. when considerable quantities of humic acid (which acts as a complexing agent) is present, stronger oxidizing agents such as chlorine or ozone are used.

Small quantities of phosphates are desirable in household effluent to protect household equipment from corrosion by suppressing heavy metal dissolution. Reservoirs can contain too much phosphate due to run off from intensively used agricultural areas. This is then precipitated by flocculation with iron or aluminum salts.

Dedicated nitrate removal is hardly used despite known processes for denitrification, the mandatory minimum concentrations being obtained by mixing. Decomposition of ammonium salts is carried out on biologically colonized activated charcoal filters.

1.1.2.5 Activated Charcoal Treatment

If after the above-mentioned treatment steps, water still contains nonionic organic impurities e.g. phenolic matter or chloro/bromohydrocarbons from chlorination, adsorption by treatment with activated charcoal is advisable.

Activated charcoal provides an additional safety element for dealing with sporadic discharges, e.g. accidental, into river-water of organic substances e.g. mineral oil, tempering oils.

So-called absorber resins based on poly(styrene) are recommended as an alternative to activated charcoal, but have as yet found little application. Chlorohydrocarbons and phenols are efficiently adsorbed by activated charcoal. Humic acid is less well adsorbed, its detection being a sign of activated charcoal filter exhaustion.

If powdered charcoal is added (widely used in the USA) adsorption can be carried out simultaneously with flocculation, but passing through a bed of granular activated charcoal beds is more widely used in Europe.

Use of powdered charcoal has the advantage that the amount used can be easily adjusted to the impurity level of the water and that the investment costs are low. Powdered charcoal is, however, not easy to regenerate, whereas granular activated charcoal can be regenerated thermally. Since the composition of the impurities varies from water to water, the conditions required for the treatment of water with granular activated charcoal (e.g. number of filters, contact time) have to be established empirically. The release of already adsorbed compounds e.g. chloro-alkanes into the eluant due to displacement by more easily adsorbed compounds (chromatographic effect) has, however, to be avoided.

Between 50 and 150 g TOC/m^3 water removed by activated carbon per day

About 50 to 150 g TOC/m^3 (TOC = total organic carbon) of organic carbon are on average removed from water per day. This value is higher, if the water is not break-point chlorinated (see Section 1.1.2.1) or is pretreated with ozone.

Regeneration of charcoal by back flushing and periodic thermal reactivation

Back flushing is used to remove the sludge from the activated charcoal filter. Thermal reactivation of the filters under similar conditions to activated charcoal production has to be performed periodically to avoid break-through of pollutants. This can be carried out either at the waterworks or by the manufacturer of the activated charcoal.

The activated charcoal treatment also has effects other than the elimination of dissolved organic impurities:

Activated charcoal treatment also leads to:

- decomposition of excess chlorine
- biological oxidation of ammonia and organic compounds by microbiological processes on the activated charcoal surface
- removal of iron and manganese ions

- excess chlorine is decomposed
- ammonia and some of the organic compounds are biologically oxidized
- iron and manganese oxide hydrates are removed.

1.1.2.6 Safety Chlorination

Safety chlorination:

avoidance of reinfection of potable water in the distribution network by adding 0.1 to 0.2 mg/L chlorine

After the water treatment is finished a safety chlorination is carried out to prevent reinfection of the potable water in the distribution network. This is also necessary after prior ozonization. Potable water contains about 0.1 to 0.2 mg/L chlorine.

1.1.2.7 Production of Soft or Deionized Water

Treatment of water with cation exchangers:

Water with a lower hardener content than that produced according to the process described in Section 1.1.2.4 is required for a range of industrial processes. This can be accomplished by ion exchange with solid polymeric organic acids, the "ion exchangers".

Exchange of Ca^{2+} and Mg^{2+} for Na^+ or H^+

When the sodium salt of sulfonated poly(styrene) is used as the cation exchanger, calcium and magnesium ions are exchanged for sodium ions:

$$PS\text{–}SO_3^-Na^+ + 0.5\ Ca^{2+} \longrightarrow PS\text{–}SO_3^-Ca^{2+}_{0.5} + Na^+$$

[PS poly(styrene)]

Regeneration of ion exchangers charged with calcium and magnesium ions (1L of ion exchange material can be charged with ca. 40 g of CaO) can be accomplished by reversing the above equation by (countercurrent) elution with 5 to 10% sodium chloride solution. If the hardeners are present as hydrogen carbonate, the eluant becomes alkaline upon heating:

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + CO_2\uparrow + H_2O$$

If ion exchangers are used in the acid form, then the eluant will be acidic:

$$PS\text{–}SO_3^-H^+ + M^+ \longrightarrow PS\text{–}SO_3^-M^+ + H^+$$

(M^+: monovalent metal ion or equivalent of a multivalent ion)

If (weakly acidic) resins containing carboxy-groups are used, only those hardeners present as hydrogen carbonates are removed, as only the weak carbonic acid can be released:

$$\text{PS–(COOH)}_2 + \text{Ca(HCO}_3)_2 \longrightarrow \text{PS–(COO}^-)_2\text{Ca}^{2+} + 2\ \text{CO}_2\uparrow + 2\ \text{H}_2\text{O}$$

For very high purity water (for applications such as high performance boilers or in the electronics industry) virtually ion-free water is required. This is achieved in alternate layers of cation and anion exchangers or so-called "mixed bed exchangers". In these, both strongly acid cationic exchangers in the proton form and basic ion exchangers based on poly(styrene) modified with amino- or ammonium-groups are present, e.g.

Water with less than 0.02 mg/L can be obtained by stepwise treatment over cation and anion exchange beds or in "mixed beds". Residual organic impurities can be removed by reverse osmosis

$$\text{PS–N(CH}_3)_2 \quad \text{or} \quad \text{PS–N(CH}_3)_3{}^+\text{OH}^-$$

Basic ion exchangers remove anions and are regenerated with sodium hydroxide, e.g.

$$\text{PS–N(CH}_3)_3{}^+\text{OH}^- + \text{Cl}^- \longrightarrow \text{PS–N(CH}_3)_3{}^+\text{Cl}^- + \text{OH}^-$$

Upon passing salt-containing water through a mixed bed, the cations are replaced by protons and the anions by hydroxide ions. Protons and hydroxide ions together form water, making the resulting water virtually ion-free with an ion residue of 0.02 mg/L. The higher density of anion exchangers (than cationic exchangers) makes the regeneration of mixed beds possible. The mixed bed ion-exchange columns are flushed from the bottom upwards with such a strong current of water that the resins are transported into separate zones, in which they can be regenerated independently of one another.

For the electronics industry etc. a further purification using reverse osmosis (see also Section 1.1.3.2) is necessary to remove dissolved nonionic organic compounds. Distillation ("distilled water") is no longer economic.

1.1.3 Production of Freshwater from Seawater and Brackish Water

1.1.3.1 Production by Multistage Flash Evaporation

Seawater contains on average 3.5% by weight of dissolved salts, for the most part sodium chloride. Calcium, magnesium and hydrogen carbonate ions are also present. Potable water should not contain more than 0.05% of sodium chloride and less than 0.1% of dissolved salts.

Important process for the production of freshwater from seawater:

The removal of such quantities of salt from seawater using ion exchangers would be totally uneconomic. Distillation processes are currently mainly used in the production of potable and irrigation water from seawater.

Multistage (vacuum) flash evaporation

Distillation is carried out by multistage (vacuum) flash evaporation (MSF), Fig. 1.1-2.

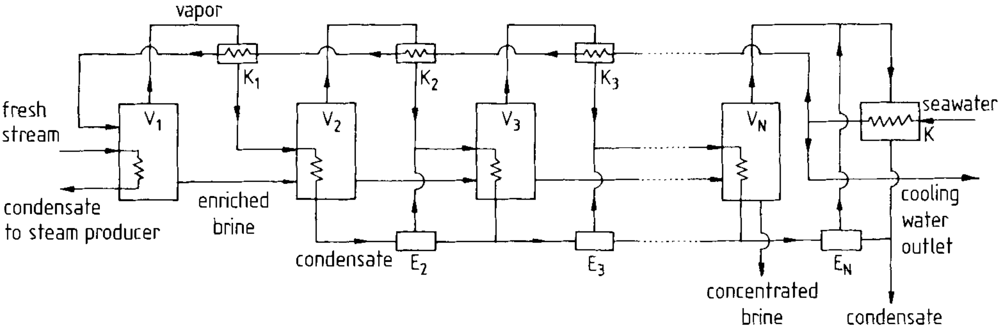


Fig. 1.1-2. Flowchart of a multistage distillation plant.
V evaporator; K heat exchanger (preheater); E expansion valve

Seawater freed of particulate and biological impurities is evaporated at temperatures of 90°C up to 120°C in a number - generally 18 to 24 - of stages in series. The seawater feed is also the coolant for condensing the stream produced and in so doing is heated up as it proceeds from stage to stage. In the first (hottest) stage the energy required for the complete system is supplied by stream using a heat exchanger. The temperature of the ever more concentrated salt solution decreases from stage to stage as does the prevailing pressure. Additional seawater is necessary in a supplementary circuit for cooling the steam produced in the last (coolest) stages. This is returned directly to the sea, which represents a considerable energy loss. The rest of the prewarmed water is used as feed-water and is heated by the final heater and subjected to evaporation. The concentrate, which is not recycled to the final heater, is run off. The "concentration factor" of the run off concentrate is about 1.6 with respect to the seawater. Disposal of this concentrate also represents an energy loss.

The quality of the seawater has to fulfill certain requirements: in addition to the removal of coarse foreign matter and biological impurities, hardener removal or stabilization is necessary. Calcium carbonate and magnesium hydroxide (Brucite) are deposited from untreated seawater onto the heat exchanger surfaces with loss of carbon dioxide, resulting in a strong decrease in the distillation performance of the plant.

Precipitation of hardeners is prevented by adding:

- molar quantities of sulfuric acid
- polyphosphate or poly(maleic acid) derivatives in under-stoichiometric quantities

Hardener precipitation can be prevented by adding sulfuric acid, whereupon the fairly soluble calcium and magnesium sulfates are formed. However, considerable quantities of acid are required and desalination plants are often poorly accessible. Furthermore, exact dosing is necessary, underdosing leading to encrustation and overdosing leading to corrosion. Therefore polyphosphates are currently used for hardener stabilization in under-stoichiometric quantities in the first (hottest) stage at temperatures of up to ca. 90°C. Above 90°C polyphosphates (sodium tripolyphosphate) hydrolyze too rapidly, thereby losing their activity and forming precipitates. In plants operating above 90°C, poly(maleic acid) is almost exclusively used for hardener stabilization. It is usual to use sludge balls for removing encrustation. Above 120°C calcium sulfate precipitates out as anhydrite (the solubility of calcium sulfate decreases with increasing temperature), which in practice limits the final heater temperature to 120°C.

The cost of potable water production from seawater is mainly dependent upon the cost of the energy consumed. It is, however, considerably higher than that for potable water produced from freshwater, a factor of 4 in Europe.

1.1.3.2 Production using Reverse Osmosis

Production of potable water from brackish water or seawater by reverse osmosis:

permeation of water with a low salt content through a semipermeable membrane by applying pressure to the side containing saltwater

Currently another process for the production of potable water from seawater is becoming established: reverse osmosis (RO). The RO-process is particularly suitable for small plants. Therefore almost 70% of all plants operate according this principle, but they account for only 35% of the desalination capacity. In osmosis, water permeates through a semipermeable membrane from a dilute solution to a concentrated solution resulting in a hydrostatic pressure increase in the concentrated solution. This process proceeds spontaneously. In reverse osmosis, water with a low salt content is produced by forcing a salt-containing solution through a semipermeable membrane under pressure. To produce a usable quantity of water, the pressure applied must be substantially higher than the equilibrium osmotic pressure. This is 3.5 bar for a 0.5% by weight salt solution. Pressures of 40 to 70 bar are necessary for water production, the higher the pressure on the feed water side the higher the permeation of water. However, the salt concentration in the water thus produced increases with increasing pressure, as the membrane is unable to retain the salt completely. A multistep process has sometimes to be used.

Membranes mostly made of acetylcellulose or more preferably polyamide. Large pressure differences mean complicated desalination plant construction (in some cases multistage). Pretreatment of water necessary as for distillation plants

The membranes are manufactured from acetylcellulose or, more preferably, polyamide. The technical construction is complicated and made expensive by the large pressure differences and the need for thin membranes. Bundles of coiled thin hollow capillaries (external diameter 0.1 mm, internal diameter 0.04 mm) are, for example, placed in a pressure cylinder (Fig. 1.1-3). These capillaries protrude from the ends of the cylinder through plastic sealing layers. Of the (high salt content)-water fed into the cylinder from the other side, 30% passes through the capillary walls into the capillaries and the rest is run off as concentrate and disposed of. An intensive and expensive pretreatment of the feed water is also necessary: in addition to the removal of all colloidal and biological impurities, treatment of the feed water is also necessary e.g. by acid addition. The use of feed water from wells in the neighborhood of beaches is particularly favored.

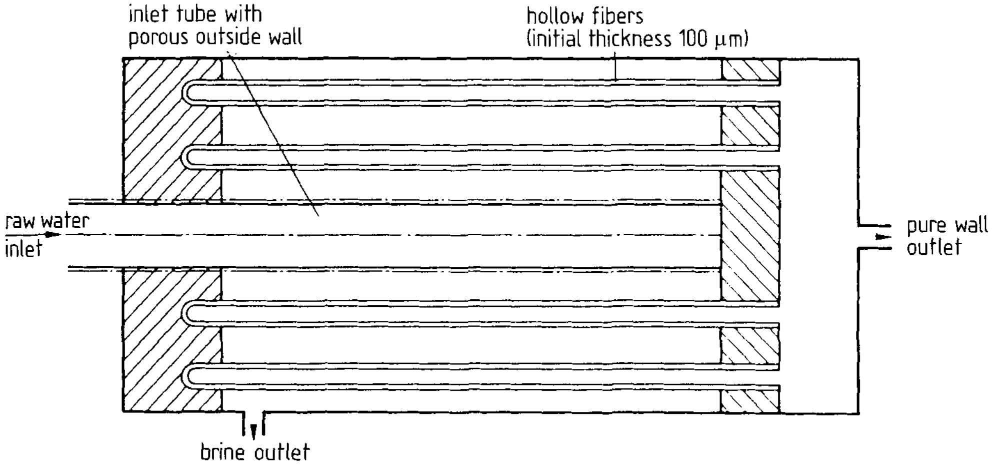


Fig. 1.1.3. Schematic lay-out of a RO-module.

In water production, reverse osmosis requires less than 50% of the energy required by multistage flash distillation (8 to 10.6 kWh for freshwater for a capacity of $19 \cdot 10^3$ m^3/d).

Freshwater production by reverse osmosis is considerably cheaper than flash distillation

References for Chapter 1.1: Water

Water supply in the Federal Republic of Germany:
Statistisches Jahrbuch der BR Deutschland. 1994. *Öffentliche Wasserversorung und Abwasserbeseitigung 1991*, **26**/Umwelt, 737.
Flinspach, D. 1993. *Stand der Trinkwasseraufbereitungstechnik*, Stuttg. Ber. Siedlungswasserwirtschaft, 157 – 182.
Bundesverband der deutschen Gas- und Wasserwirtschaft e. V. (BGW), (Hrsg). 1997. *108. Wasserstatistik Bundesrepublik Deutschland, Berichtsjahr 1996*, Wirtschafts- und Verlagsgesellschaft Gas und Wasser, Bonn.
Schleyer, R. u. Kerndorff, H. 1992. *Die Grundwasserqualität westdeutscher Trinkwasserressourcen*, VCH Verlagsgesellschaft, Weinheim.
Der Wasserbedarf in der Bundesrepublik Deutschland bis zum Jahre 2010 – Studie erstellt im Auftrage des Umweltbundesamtes, Berlin, 1981.

Reviews:
Ullmann's Encyclopedia of Industrial Chemistry. 1996. 5. Ed., Vol. A 28, 1 – 101, VCH Verlagsgesellschaft, Weinheim.
Kirk-Othmer, Encyclopedia of Chemical Technology. 1998. 4. Ed., Vol. 25, 361 – 569, John Wiley & Sons, New York.
Chemie und Umwelt, VCI – *Wasser* (Verband der Chemischen Industrie, Frankfurt/Main, Hrsg.).

Adsorption:
Sontheimer, H., Crittenden, J. C., Summers, R. S. 1988. *Activated Carbon for Water Treatment*, 2. Ed., DVGW-Forschungsstelle, Karlsruhe.

Demineralization:
Applebaum, S. B. 1968. *Demineralization by Ion Exchange*, Academic Press, New York - London.

Flocculation:
Jekel, M., Ließfeld, R. 1985. *Die Flockung in der Wasseraufbereitung*, DVGW-Schriftenreihe Wasser **42**.

Filtration:
Degremont. 1991. Water Treatment Handbook, Vols. 1 + 2, Lavoisier Publ., Paris.

Treatment of Seawater:
Coghlan, A. 1991. *Fresh water from the sea*, New Scientist 31, 37 – 40.
Finan, M. A., et. al. 1989. *Belgard® EV – 15 years experience in scale control*, Desalination **73**, 341 – 357.
Heitmann, H. G. (Ed.). 1990. *Saline Water Processing*, VCH Verlagsgesllschaft, Weinheim.

Mulder, M. 1991. *Basic Principles of Membrane Technology*, Kluwer Academic Publ., Dordrecht.

Desalination of Water:

International Desalination Association. 1995. *Proceedings, IDA World Congress on Desalination and Water Sciences, Abu Dhabi*, Topsfield, Mass., USA

A. Coghlan, A. 1991. *Fresh Water from the Sea,* New Scientist 31, 37 – 40.

1.2 Hydrogen

1.2.1 Economic Importance

Hydrogen is the most widespread element in the Universe, but only the ninth most common element in the Earth's crust

Hydrogen is by far the most widespread element in the universe, but on Earth (litho-, bio- and atmosphere) it is only the ninth most common element with 1% by weight (or 15 atomic %). Hydrogen is almost exclusively present as water, hydrates, in the biomass and in fossilized raw materials.

Further development of hydrogen technology requires cheap primary energy sources

Commercially hydrogen has only been utilized as a chemical raw material and industrial chemical. However, particularly since the 1973/74 oil crisis, there has been increasing, if largely speculative, interest in hydrogen as an almost inexhaustible (secondary) energy source (for power and combustion purposes). This instead of, or in addition to, electricity, due to its high energy density per unit mass (121 kJ/g compared with 50.3 kJ/g for methane), its high environmental compatibility, its being nonpoisonous and the ease of its transport and storage.

1996 Consumption of hydrogen	in 10^9 m^3
USA	79
Western Europe	51
Japan	16
Rest of the World	251

Its world consumption in 1996 was about 400 · 10^9 m^3 (ca. 37 · 10^6 t). Further growth in consumption is expected, in certain application up to 10% per year. The recorded consumption in Western Europe in 1996 was about 50 · 10^9 m^3, although the actual consumption was certainly somewhat higher, since the quantities produced as a byproduct in refineries and used in other sites are not included in these figures.

Only a small part of the hydrogen produced is marketed, most is directly utilized by the producer

In the USA only about 5% of the total consumption of hydrogen was marketed, most of the hydrogen produced, e.g. as a byproduct, being directly used by the producer as in Western Europe. Since refineries are increasingly using hydrogen from the plants of third parties rather than from their own hydrogen plants, the proportion of marketed hydrogen should increase in the future.

Liquid hydrogen has a small but important market e.g. for rocket fuels and industrial applications. The USA consumption was ca. $0.5 \cdot 10^9$ m^3 of gaseous hydrogen in 1996.

1.2.2 Hydrogen Manufacture

Industrially hydrogen is mainly produced by two fundamentally different processes:

- by petrochemical processes including gasification of coal (> 90%)
- by the electrolysis of water

Hydrogen is also formed in large quantities as a byproduct in petrochemical processes, refineries, coking plants (coke oven gas) and in chemical and electrochemical processes e.g. chloralkali-electrolysis. Other processes such as the photochemical production of hydrogen or thermal dissociation of water are only used in special applications and are currently industrially unimportant.

Raw material sources for H_2:

- fossil raw materials (natural gas, oil, coal) account for > 90% of H_2 production
- water

H_2 as a byproduct in:

- refineries
- petrochemical plants
- coking plants
- chemical industry

1.2.2.1 Petrochemical Processes and Coal Gasification

The industrially most important and currently cheapest hydrogen production process is the catalytic steam reforming process in which steam is reacted with natural gas (methane) or light crude oil fractions (propane, butane, naphtha with b.p.'s ≤ 200°C). The hydrogen produced comes partly from the steam utilized and partly from the hydrocarbons, in the case of methane 1/3 from water and 2/3 from the methane:

$$CH_4 + H_2O \longrightarrow 3\,H_2 + CO \qquad \Delta H = 205\ \text{kJ/mol}$$

About 80% of the hydrogen used is produced petrochemically, which includes the thermal or catalytic cracking of hydrocarbons e.g. in refineries.

In the USA over 90% of the hydrogen is currently produced from natural gas using this very economic process.

In addition to steam-reforming of low boiling point hydrocarbons, the partial oxidation of heavy fuel oil and

Hydrogen production worldwide:

77%	from natural gas/crude oil fractions
18%	from coal
4%	from water electrolysis
1%	from other sources

crude oil residues is also industrially important. It can be represented by the following equation:

$$2\,C_nH_{2n+2} + nO_2 \longrightarrow 2\,(n+1)H_2 + 2\,nCO$$

This is a self-sustaining noncatalytic thermal reaction.

In countries with cheap coal (e.g. South Africa) hydrogen is being increasingly produced by coal and coke gasification (before World War II 90% of hydrogen was produced in this way). This reaction proceeds as follows:

$$3\,C + O_2 + H_2O \longrightarrow H_2 + 3\,CO$$

Since over half of the hydrogen is utilized in the production of ammonia (fertilizer production) and is carried out in the modern ammonia plants (hydrogen production and utilization in integrated plants), all three processes will be dealt with in detail in Section 1.4.1.2.

1.2.2.2 Electrolysis of Water

Electrolysis of water is very energy intensive

The efficiency including electricity production is 20 to 25%

Hydrogen production by the electrolysis of water is currently less important, accounting for less than 3% of the hydrogen produced, due to the low overall efficiency of 20 to 25% including the electricity production. Large plants are only constructed where favorable conditions obtain, mainly near dams e.g. in Egypt (a plant at the Assuan dam has an ammonia capacity of 33 000 m^3/h), India, Peru and in countries with low electricity prices or where there is a favorable demand for the byproduct oxygen e.g. in Norway.

Water electrolysis is currently only of interest where favorable conditions hold (accounts for < 3% of hydrogen production), but could become important in a future hydrogen-based economy

Hydrogen produced by electrolysis is also used where particularly pure hydrogen is required such as in food technology (margarine production) or for small users. The process could in the long term become important in a hydrogen-based economy in the post-oil era.

At present, electrolysis cells basically consist of two electrodes separated by an asbestos diaphragm impermeable to gases. 20 to 30% potassium hydroxide is dissolved in the electrolyte to increase its conductivity. The electrolysis is carried out at 80 to 85°C. The theoretical decomposition potential is 1.24 V with 1.9 to 2.3 V being used in practice due to overvoltage effects etc. Oxygen is produced at the anode and hydrogen at the cathode:

$$\begin{array}{lcll}
2\,OH^- & \longrightarrow & H_2O + 0.5\,O_2 + 2e^- & \text{anode} \\
2\,H_2O + 2e^- & \longrightarrow & H_2 + 2\,OH^- & \text{cathode} \\
\hline
H_2O & \longrightarrow & H_2 + 0.5\,O_2 &
\end{array}$$

The specific energy consumption per m^3 of hydrogen (and $0.5 m^3$ oxygen) produced is about 4.5 to 5.45 kWh.

Industrial cells are mainly bipolar consisting of a large number of individual plate cells connected back to back and coupled in blocks according to the filter press principle. If the electrolysis is carried out under pressure, the energy consumption can be reduced by 20%. Further recent developments are the use of porous electrodes, high temperature steam electrolysis and the SPE-process (solid polymer electrolyte). Heavy water, D_2O, can be produced as a byproduct in water electrolysis through enrichment in the electrolyte.

1.2.2.3 Other Manufacturing Processes for Hydrogen

The direct thermal dissociation of water:

$$H_2O \longrightarrow H_2 + 0.5\,O_2 \qquad \Delta H = 285\ \text{kJ/mol}$$

is industrially and commercially impractical due to the >2000°C temperatures required.

However, multistep thermochemical cyclic processes, of which a number are thermodynamically possible, can be carried out at lower temperatures. In such processes the splitting of water is assisted by an auxiliary agent which is fed into the cycle and the reaction products, in part via intermediates, are thermally split. One example from the so-called "Iron-Chlorine-Family" is the following three step process:

$$\begin{array}{lcl}
6\,FeCl_2 + 8\,H_2O & \longrightarrow & 2\,Fe_3O_4 + 12\,HCl + 2\,H_2 \\
2\,Fe_3O_4 + 12\,HCl + 3\,Cl_2 & \longrightarrow & 6\,FeCl_3 + 6\,H_2O + O_2 \\
6\,FeCl_3 & \longrightarrow & 6\,FeCl_2 + 3\,Cl_2 \\
\hline
\text{overall: } 2\,H_2O & \longrightarrow & 2\,H_2 + O_2
\end{array}$$

Material and corrosion questions as well as the realization of the necessary high temperatures (possibly nuclear process heat or solar energy) have hindered their application.

Photochemical, photoelectric and thermochemical processes currently have no commercial significance.

For particular purposes, hydrogen is produced by catalytic decomposition of ammonia (by contact with nickel at 900°C for hydrogenation or metallurgical purposes) or methanol in cracking plants.

1.2.2.4 Production of Hydrogen as a Byproduct

H_2 produced as a byproduct in refineries and photochemical companies particularly from:

- reforming
- aromatization
- production of olefins from saturated hydrocarbons

Hydrogen-containing gases (refinery gas) are formed in large quantities as a byproduct in the processing of crude oil in refineries by cyclization and aromatization e.g. by catalytic reforming.

This hydrogen is, however, mostly used in house. Hydrogen is also produced in other petrochemical and chemical processes (synthesis of olefins, ethyne, styrene, acetone). Coke oven gas contains over 50 volume % of hydrogen, from which it can be isolated. Finally hydrogen occurs as a valuable byproduct in chloralkali-electrolysis (directly with the diaphragm process or indirectly with the amalgam process and hydrochloric acid hydrolysis) see Section 1.7.3.3. The electrolysis processes account for less than 5% of the worldwide production of hydrogen.

H_2 from chloralkali-electrolysis:

$2\,NaCl + 2\,H_2O \rightarrow H_2 + Cl_2 + 2\,NaOH$

1.2.3 Hydrogen Applications

Consumption of hydrogen in the USA in 1996:

in total $79 \cdot 10^9$ m^3, comprising:

ammonia production	40.3%
methanol reforming	10.0%
refinery processes	42.9%
food (fats and oils)	0.3%
metal refining	0.2%
electronics industry	0.1%
miscellaneous	6.1%

In the USA of the ca. $79 \cdot 10^9$ m^3 hydrogen produced in 1996, 40% was utilized in ammonia production, 43% in refinery processes (e.g. hydrocracking to improve the quality of crude oil products, hydrotreating e.g. hydrodesulfurization and 10% in methanol production.

The rest was utilized in the hydrogenation of organic chemicals (hydrogenation of fats and aniline and cyclohexane synthesis), in the electronics industry (protective gas in the manufacture of semiconductors), in metallurgy (e.g. the use of synthesis gas in the direct reduction of iron ore, as reduction or protective gas in tempering and recasting processes), in the glass industry, in hydrogen chloride production and in autogenic welding and cutting (oxyhydrogen blowpipe) and in protective gas welding technology (e.g. with argon-hydrogen).

In Western Europe of the ca. $51 \cdot 10^9$ m^3 hydrogen produced in 1996, 47% was utilized in ammonia production, 31% in the refining of crude oil, 8% in methanol production and 14% for other applications.

Worldwide of the $400 \cdot 10^9$ m^3 hydrogen produced in 1996, 63% was utilized in ammonia production, 25% in the refining of crude oil, 9% in methanol production and 3% for other applications.

Utilization in crude oil refining is currently growing very strongly. This is due to environmental protection laws in industrialized countries which require greater hydrogen utilization and an increasing proportion of high boiling point hydrocarbons which contain less hydrogen than lower boiling point hydrocarbons.

H_2-demand in refineries is increasing strongly with the working up of heavier crude and in the future oil shale, oil sands and coal oils (compensation of the H/C ratio)

Hydrogen is marketed as a gas or a liquid. It is transported as a compressed gas (e.g. 200bar) in steel cylinders or clusters of bottles or as a liquid (cryogenic) under pressure in highly insulated tankers at -253°C. Hydrogen can also be distributed by pipeline. In the Federal Republic of Germany, a 200 km (pressure) pipeline network has operated for decades in the Rhine-Ruhr region (so-called Wasserstoffverbund Rhein-Ruhr), which connects hydrogen producing plants and hydrogen consuming plants.

H_2-transport:

- as a gas in gascylinders or pipelines
- as a liquid in pressurized cryogenic containers
- possibly as a solid in the form of hydrides

Similar pipeline networks have been set up in other European countries e.g. in The Netherlands, Belgium and France.

Further developments in the storage and transport of hydrogen concern hydrogen in the form of hydrides of titanium/iron hydride $TiFeH_{1.95}$ or magnesium/nickel hydride $MgNiH_{4.2}$.

References for Chapter 1.2: Hydrogen

Ullmann's Encyclopedia of Industrial Chemistry. 1989. *Hydrogen.* 5. Ed., Vol. A 13, 297 – 442, VCH Verlagsgesellschaft, Weinheim.

Ullmann's Encyclopedia of Industrial Chemistry. 1989. *Hydrides.* 5. Ed., Vol. A 13, 199 – 226, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1995. 4. Ed., Vol. 13, 838 – 949, John Wiley & Sons, New York.

Chemical Week, 6 July 1994, 118

Chemical Marketing Reporter, 20 June 1994, 20.

Hydrocarbon Processing, July 1993, 27.

Oil & Gas Journal, March 1993, 45.

Chemical Marketing Reporter (24.8.92), 9.

Chemical Business, June 1990, 44.

Chemical Economics Handbook 1994. *Hydrogen.* Stanford Research Institute, Menlo Park, California.

1.3 Hydrogen Peroxide and Inorganic Peroxo Compounds

1.3.1 Economic Importance

1.3.1.1 Hydrogen Peroxide

Commercially hydrogen peroxide is available in a variety of concentrations. The most important are aqueous solutions with 35, 50 and 70% by weight H_2O_2. The following statistics refer to "100% hydrogen peroxide".

World capacity in 1991: 1.5 · 10^6 t/a

Table 1.3-1. Hydrogen Peroxide Capacities in 1991 in 10^3 t/a.

World	Europe	USA/ Canada	Latin America	Aus- tralia	Asia excl. Japan	Japan	Africa
1492	715	422	45	17	99	184	10

H_2O_2 commercially mainly available in concentrations of 35, 50 and 70% by weight

Hydrogen peroxide demand is currently increasing comparatively strongly, the production capacity having increased by 70% between 1979 and 1991 from 882 · 10^3 to 1492 · 10^3 t/a. Further growth is expected.

Producers of hydrogen peroxide are e.g. Degussa, DuPont, EKA Nobel, FMC, Kemira, Mitsubishi Gas Chemical, Oxysynthese and Solvay-Interox.

1.3.1.2 Sodium Perborate and Sodium Carbonate Perhydrate

Sodium perborate is produced in almost all Western industrialized countries, but particularly in Europe (mainly utilized in washing powders).

The world capacity for sodium carbonate perhydrate is about 20% of that of sodium perborate, both products being alternately produced in some plants. About 40% of the hydrogen peroxide production of Western Europe is utilized in the production of sodium perborate and sodium carbonate perhydrate.

Estimated consumptions for 1991 are given in tables 1.3-2 and 1.3-3 respectively:

Table 1.3-2.. Sodium Perborate consumption in 1991 (estimated) in 10^3 t.

Europe	USA
400	15

World capacity in 1991: 415 · 10^3 t/a

Table 1.3-3. Sodium Carbonate Perhydrate consumption in 1991 (estimated) in 10^3 t.

Europe	USA
110	10

1.3.1.3 Alkali Peroxodisulfates and Sodium Peroxide

Details over the production capacity for peroxodisulfates are to be found in Table 1.3-4.

World capacity for alkali peroxodisulfate in 1991: 62 · 10^3 t/a

Table 1.3-4. Capacity for Peroxodisulfates in 1991 in 10^3 t.

World	Europe
62	18

The most important compound is the ammonium salt, followed by the potassium and sodium salts. Production capacities for sodium peroxide are not available.

1.3.2 Production

1.3.2.1 Hydrogen Peroxide

The industrial production of hydrogen peroxide is possible using the following processes:

- oxidation of isopropanol
- electrochemical oxidation of sulfuric acid or ammonium sulfate
- cathodic reduction of oxygen
- anthraquinone process

Of these processes, the first has only historical interest: the plants which produced 15 000 t/a of hydrogen peroxide and 30 000 t/a of acetone were shut down in 1980. Only in the former States of the USSR are such plants still in use. The electrochemical oxidation process is also of limited importance. Over 95% of the hydrogen peroxide is produced with the anthraquinone process. Electrochemical

Production of H_2O_2:

- oxidation of isopropanol
- electrochemical oxidation of sulfuric acid or ammonium sulfate - currently only of limited interest
- anthraquinone process: used for production of > 95% of H_2O_2

reduction can, under particular circumstances, be advantageous for small stand-alone units. Formerly practiced processes such as production from barium peroxide, have not been used for some time.

Isopropanol Oxidation Process

Isopropanol oxidation process:

isopropanol is oxidized with air to acetone and H_2O_2 at 90 to 140°C and 15 to 20 bar and the reaction mixture worked up by distillation. The acetone byproduct must be utilized.

Acetone and hydrogen peroxide are produced with a selectivity of 80% upon multistage oxidation of isopropanol with air at 15 to 20 bar and 90 to 140°C:

$$CH_3CH(OH)CH_3 + O_2 \longrightarrow CH_3COCH_3 + H_2O_2$$

The degree of conversion is limited to about 30% to suppress side reactions. After the oxidation and diluting the reaction mixture with water, the acetone, unreacted isopropanol and water are distilled off. A ca. 20% hydrogen peroxide solution is run off from the sump (sump temperature ca. 120°C). Acetone is separated from the distillate and the isopropanol-water solution fed back into the process. The 20% hydrogen peroxide solution is then purified over ion exchangers and concentrated by distillation. The process has one disadvantage: the weight of acetone produced is double that of the hydrogen peroxide. This must either be utilized in situ or reduced back to isopropanol with hydrogen.

Electrochemical Process

Electrochemical process:

- anodic oxidation
- from sulfuric acid to peroxodisulfuric acid
- or from ammonium sulfate to ammonium peroxodisulfate,

subsequent hydrolysis and separation of H_2O_2 by distillation

In the electrochemical processes, an aqueous solution of sulfuric acid (550 to 570 g/L) (Degussa-Weißenstein Process) or of sulfuric acid (260 g/L) and ammonium sulfate (210 to 220 g/L) (Löwenstein-Riedel Process) is electrochemically oxidized at the anode to peroxodisulfuric acid or ammonium peroxodisulfate respectively and reduced at the cathode producing hydrogen.

Small quantities of ammonium thiocyanate of hydrochloric acid are added to increase the anode potential. The peroxo compound obtained is subsequently hydrolyzed, the hydrolysis proceeding by way of the peroxomonosulfate. (Caro's acid):

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$$
$$H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$$

The hydrogen peroxide formed is distilled off, the sulfuric acid or sulfuric acid-ammonium sulfate solutions being recycled. The total yield for both processes relative to the electricity consumed is about 70%.

The disadvantage of the electrochemical processes are the high plant and production costs, due to the high cost of the electricity used.

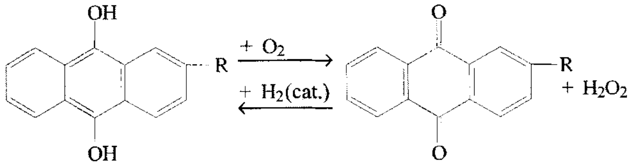
Disadvantage of anodic oxidation: high electricity costs, moderate yields

Anthraquinone Process

The anthraquinone process is based on the following processes:

- oxidation of a 2-alkyl-anthrahydroquinone with air to the corresponding 2-alkyl-anthraquinone and hydrogen peroxide and
- catalytic (back)-reduction of the 2-alkyl-anthraquinone to the 2-alkyl-anthrahydroquinone with hydrogen

In this cyclic process hydrogen peroxide is formed from hydrogen and oxygen:



The alkyl-group substituent R on the anthraquinone differs from manufacturer to manufacturer. In addition to 2-ethyl- (mainly used), 2-tert-butyl-, 2-tert-amyl- and 2-sec-amyl-anthraquinones are also utilized. Mixtures of different alkyl anthraquinones can also be used.

The solvent mixture, in which both the quinone- and hydroquinone-compounds must dissolve, is complex. The "working solution" contains, as a solvent for the quinone, mainly a mixture of aromatic compounds such as naphthalene or trimethylbenzene. Polar compounds such as tris-(2-ethylhexyl)-phosphate, diisobutylcarbinol or methylcyclohexanol-acetate are suitable solvents for the hydroquinone.

The anthraquinone process requires a complex solvent mixture:

- "quinone dissolver": mainly mixtures of aromatic solvents
- "hydroquinone dissolver": polar solvents, especially esters

The solvent mixture has to fulfill a number of requirements: low solubility in water, low volatility, good dissolving properties, chemical stability under the reaction conditions used, low viscosity etc.

In the first step of the process the anthraquinone is hydrogenated to the hydroquinone with palladium as the preferred catalyst: on carriers, such as gauze, or in suspension. The reaction is carried out at about 40°C and at pressures up to ca. 5 bar with cooling and only to ca. 50% hydrogenation to suppress side reactions (see below).

The subsequent oxidation proceeds with air at 30 to 80°C and pressures up to 5 bar, if necessary after catalyst separation and a precautionary filtration. It can be carried out in co- or countercurrent mode, in a single step or multistep process. The hydrogen peroxide formed during the oxidation is extracted from the reaction mixture with water e.g. in pulsating packed towers. The extraction yield is ca. 98%. The hydrogen peroxide solutions obtained are 15 to 35% by weight and must be freed from residual organic compounds before they can be concentrated by distillation.

Commercial hydrogen peroxide solutions always contain stabilizers, such as diphosphates, organic complexing agents or tin compounds, to prevent their decomposition to oxygen and water

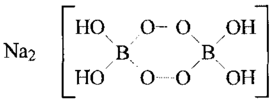
Formation of byproducts - particularly during hydrogenation - complicates the anthraquinone process

After separating off the hydrogen peroxide, the working solution has to be dried and freed of byproducts e.g. with active aluminum oxide. This occurs in a bypass.

In practice, the anthraquinone process is much more complicated than has been described above, in that byproducts such as 1,2,3,4-tetrahydroanthraquinone are formed, particularly in the hydrogenation step. These behave similarly to anthrahydroquinones, but their further hydrogenation leads to octahydroanthrahydroquinones which are unusable in this process. Other byproducts such as oxanthrones and anthrones can only be partially regenerated. These unusable byproducts have to be removed from the process.

1.3.2.2 Sodium Perborate

Sodium perborate (more correctly sodium peroxoborate) ($NaBO_2(OH)_2 \cdot 3\ H_2O$)



is produced from borax in a two-step process:

1. $Na_2B_4O_7 + 2\ NaOH \longrightarrow 4\ NaBO_2 + H_2O$
2. $NaBO_2 + H_2O_2 + 3\ H_2O \longrightarrow NaBO_2(OH)_2 \cdot 3\ H_2O$

Sodium perborate production:
Step 1: Formation of metaborate from borax and sodium hydroxide
Step 2: Reaction of metaborate with H_2O_2 forming perborate, which is then filtered off from the cooled solution and dried

The first step, the formation of sodium metaborate from borax and sodium hydroxide, is carried out at temperatures up to 90°C. When impure borax is used the solution is filtered. The second step is carried out at 25°C and the mixture subsequently cooled to 15°C and the precipitated sodium peroxoborate hexahydrate filtered off. Stabilizers for the perborate, such as silicates or magnesium salts, may be added to the reaction mixture. Residual moisture (3 to 10%) is removed in a hot air drier. The mother liquor from the second step can be returned to the first step.

The end product contains ca. 10.1 to 10.4% "active oxygen" (theoretically 10.38%). The bulk density of the perborate is adjusted to that of the other components in detergents ("light perborate") by special steps in the process. Older manufacturing processes, which started from sodium peroxide or use electrochemical processes, are no longer used.

Active oxygen content: 10.1 to 10.4% (theoretically 10.38%)

1.3.2.3 Sodium Carbonate Perhydrate (Sodium Percarbonate)

In contrast with sodium perborate, which is a genuine peroxo compound. Sodium percarbonate is only a perhydrate. It has the composition $Na_2CO_3 \cdot 1.5H_2O_2$. It can be manufactured using "dry" and "wet" processes. In a modern dry process, hydrogen peroxide and a sodium carbonate solution are sprayed onto a fluidized bed of sodium percarbonate which is fluidized with warm air. The *fines are returned to the process and the oversized particles* are ground.

In the wet process, sodium carbonate solution and hydrogen peroxide are reacted together in stoichiometric proportions. The percarbonate precipitates out upon cooling after vacuum concentration, if required.

Sodium percarbonate: from soda and H_2O_2
- "dry" in fluidized bed
- "wet" in solution with subsequent cool crystallization

Stabilizers have to be added to sodium percarbonate, because it decomposes easily

Active oxygen content ca. 13.5% (theoretically 15.28%)

Since percarbonate is much less stable than perborate, stabilizers such as alkali silicates or phosphates are used in both processes. For its use in detergents it can also be coated with an organic or inorganic material to increase its stability. Its active oxygen content is ca. 13.5% (theoretically 15.28%).

1.3.2.4 Alkali Peroxodisulfate

Diammonium peroxodisulfate produced electrochemically from solutions of sulfuric acid and ammonium sulfate on platinum electrodes

Diammonium peroxodisulfate is produced by electrolyzing solutions of ammonium sulfate and sufuric acid, in cells with or without diaphragms, using the Löwenstein-Riedel Process (see Section 1.3.2.1):

$$(NH_4)_2SO_4 + H_2SO_4 \longrightarrow (NH_4)_2S_2O_8 + H_2$$

The voltage used is between 5 and 7 V (theor.: 2.1 V) and the current density between 0.5 and 1 A/cm^2. Graphite or lead cathodes and platinum anodes are used. During electrolysis the solution becomes enriched with peroxodisulfate up to a concentration of 1 to 1.5 mol/L. Pure diammonium peroxodisulfate (purity >99%) precipitates out upon cooling. After adding ammonium sulfate and sulfuric acid to the mother liquor, it is returned to the electrolysis cell.

Disodium and dipotassium peroxodisulfate manufacture:

electrochemically or from diammonium peroxosulfate with $KHSO_4$, NaOH or Na_2CO_3 respectively

Disodium and dipotassium peroxodisulfates can also be produced in cells without diaphragms by the electrolysis of the corresponding disulfates. Alkali peroxodisulfates can also be produced by a metathesis reaction with diammonium peroxodisulfate:

$$(NH_4)_2S_2O_8 + 2\ KHSO_4 \longrightarrow K_2S_2O_8 + 2\ NH_4HSO_4$$
$$(NH_4)_2S_2O_8 + 2\ NaOH \longrightarrow Na_2S_2O_8 + 2\ NH_3 + H_2O$$

1.3.2.5 Sodium Peroxide

Sodium peroxide production:

Step 1: Formation of Na_2O
Step 2: Further oxidation to Na_2O_2

Sodium peroxide is produced from sodium metal and oxygen (from air) in two steps:

$$2\ Na + 0.5\ O_2 \longrightarrow Na_2O$$
$$Na_2O + 0.5\ O_2 \longrightarrow Na_2O_2$$

Sodium monoxide is first produced by adding sodium metal intermittently to sodium monoxide in a rotary tube reactor while passing air through it countercurrently. The sodium metal rapidly distributes itself over the surface of the monoxide and in doing so is oxidized. The reaction temperature is 200 to 700°C and the heat of reaction is sufficient to maintain this temperature. In this way a noncaking material is obtained. The monoxide formed, containing a few per cent of peroxide and less than 1% sodium is withdrawn from the reactor intermittently.

Reaction temperature of 2nd step: 350°C

Purity of Na_2O_2: 97 to 98%

The oxidation of the monoxide to sodium peroxide is carried out in a similar reactor at 350°C. As this step is only slightly exothermic (-79.5 kJ/mol) heating is needed. The end product is formed as beads with a diameter of 0.5 to 1 mm and a purity of 97 to 98%.

1.3.3 Applications

1.3.3.1 Hydrogen Peroxide, Sodium Perborate and Sodium Carbonate Perhydrate

H_2O_2 applications: vary considerably from region to region. Minimal use in the USA for the manufacture of per-compounds

The fields in which hydrogen peroxide is utilized vary considerably from region to region. This is due to different washing temperatures. In Europe, the household wash is carried out at relatively high temperatures. Therefore, the detergents contain perborate or percarbonate, whose manufacture accounts, in Europe and the Federal Republic of Germany, for ca. 40% of the hydrogen peroxide produced. Detergents in Europe contain about 15 to 30% perborate with ca. 23% in the Federal Republic of Germany.

The consumption of hydrogen peroxide in several important regions is shown in Table 1.3-5.

The heading "production of chemical products" includes the conversion of allyl alcohol to glycerine with hydrogen peroxide, the production of epoxy-compounds such as epoxy soya oil (plasticizer for PVC) and organic peroxides (e.g. methyl-ethyl-ketone-peroxide, dibenzoylperoxide), which are used as free radical initiators in polymerization processes. The production of amine oxides such as lauryl-dimethyl-amine-oxide with hydrogen peroxide (used as a rinsing agent in dishwashers) is also included.

Table 1.3-5. Hydrogen Peroxide Consumption in Different Regions in 1990 in 10^3 t.

	Western Europe	USA/ Canada	Japan
Perborate & percarbonate production	170	13	10
Bleaching of paper	142	127	66
Bleaching of textiles	40	23	18
Production of chemical products	84	28	52
Miscellaneous	8	44	1

The consumption of hydrogen peroxide in the manufacture of high quality paper is expected to increase strongly, at least in the USA. In the textile industry, hydrogen peroxide is mainly used for the bleaching of cotton, although it is also used for the bleaching of wool.

The consumption of hydrogen peroxide in the treatment of effluent, especially for the removal of phenols, cyanides and sulfur compounds (hydrogen sulfide), is also expected to increase strongly.

1.3.3.2 Alkali Peroxodisulfates and Sodium Peroxide

Peroxodisulfates:

over 65% used as a polymerization initiator

Most of the peroxodisulfate produced (>65%) is used as a polymerization initiator in the production of poly(acrylonitrile), emulsion-polymerized PVC etc. The rest is utilized in numerous applications (etching of printed circuit boards, bleaching processes etc.).

Sodium peroxide is mainly used for bleaching of paper and textile raw materials and competes thereby with sodium hydroxide/hydrogen peroxide.

References for Chapter 1.3: Hydrogen Peroxide and Inorganic Peroxo Compounds

Reviews:

Ullmann's Encyclopedia of Industrial Chemistry. 1989. 5. Ed., Vol. A 13, 443-466, VCH Verlagsgesellschaft, Weinheim.

Ullmann's Encyclopedia of Industrial Chemistry. 1991. 5. Ed., Vol. A 19, 177 – 197, VCH Verlagsgesellschaft, Weinheim.

Winnacker-Küchler. Chemische Technologie. 1982. Anorganische Technologie I, Bd. 2, 563-606, Carl Hanser Verlag, München.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1995. 4. Ed., Vol. 13, 961-995, John Wiley & Sons, New York.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1996. 4. Ed., Vol. 18, 202-229, John Wiley & Sons, New York.

Crampton C.A. et al 1977. *The Manufacture, Properties and Uses of Hydrogen Peroxide and Inorganic Peroxy Compounds*, in: Thompson, R. (ed), The Chemical Society, Burlington House, London.

Wasserstoffperoxid und seine Derivate. 1978. Weigert, W. (Hrsg.), Hüthig Verlag, Heidelberg.

Commercial Information:

Chem. Ind., XXXIII, Dec. 1981, 806.

Chemical Week, 4 November 1981, 49.

Chemical Week, 16 September, 19
Chem. Ind., XXXII, Oct. 1980, 698.
Chemical Week, 17 November 1982, 29-30.
Chemical Week, 3 August 1994, 36
Chemical & Engineering News, 30 January 1995, 15.
Chemical Engineering, 7/1995, 67.
European Chemical News, 25 April 1983, 11.
Hydrogen Peroxide. 1980. 1992. 1994. Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California.

Technical Information:
Weigert, W., Delle, H., Käbisch, G., 1975. *Herstellung und Eigenschaften von Wasserstoffperoxid*, Chem. Z. **99**, 101-105

1.4 Nitrogen and Nitrogen Compounds

1.4.1 Ammonia

Ammonia is an important primary inorganic material. 85% of the worldwide production is utilized in the manufacture of synthetic fertilizers. Ammonia production therefore represents an indicator of the size of the fertilizer industry in a particular country.

1.4.1.1 Economic Importance

In recent years the worldwide production capacity for synthetic ammonia has increased slowly to its current high level from $102 \cdot 10^6$ t in 1983 to $112 \cdot 10^6$ t in 1993. Growth has mainly occurred in developing countries, the capacity in the Western World having largely stagnated or in the case of Western Europe decreased. The proportion of worldwide capacity in Western Europe has fallen from 15% in 1983 to 12% in 1993. Some increase in worldwide capacity is expected in the near future.

Ammonia is produced as a byproduct in coking plants, but this accounts for less than 1% of the worldwide capacity for ammonia.

NH_3 Worldwide production capacity (10^6 t):

1983:	102
1993:	112

1.4.1.2 Synthetic Ammonia Manufacture

1.4.1.2.1 General Information

Large scale manufacture of synthetic ammonia is exclusively carried out with "synthesis gas" ($N_2 + 3H_2$; this term is also used for the gas mixtures of carbon monoxide and hydrogen used for the synthesis of organic products):

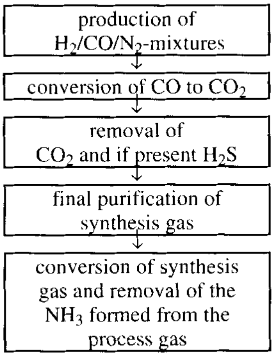
$$N_2 + 3\,H_2 \longrightarrow 2\,NH_3 \quad \Delta H = -91.6\ \text{kJ/mol}$$

which is based on the investigations of Haber in 1904 into the equilibrium between nitrogen, hydrogen and ammonia. The industrial manufacture of ammonia resulted from a later cooperation with Bosch and Mittasch (both from BASF). The first Haber-Bosch plant was commissioned at BASF in 1913.

Formation of ammonia from nitrogen and hydrogen in the Haber-Bosch process is favored by:

- high pressure
- low temperature
- active catalyst
- pure gas (as little inert gas as possible)

NH_3-synthesis consists of the following process steps:



The exothermic reaction between nitrogen and hydrogen occurs in the presence of suitable catalysts and results in volume reduction, the highest ammonia concentrations being obtained at the highest possible pressure and the lowest possible temperature. The upper limit for the applied pressure is determined by the cost of compression of the gas mixture and the cost of the high pressure plant. The reaction temperature is determined by the type and activity of the catalyst. The removal of ammonia from the reaction gas should be as complete as possible to favor the fresh formation of ammonia. Other important parameters are the contents of inert gas and oxygen compounds in the unreacted synthesis gas.

All ammonia production plants in the world operate according to the same basic principles i.e. reaction of nitrogen and hydrogen in a catalyst-filled pressure reactor at temperatures between 400 and 500°C, pressures between 100 and 1000 bar (depending upon the plant) and removal of the ammonia formed from the reaction gas. The plants differ in their design, catalyst composition and production and purification of the synthesis gas.

α-Iron is formed from magnetite

1.4.1.2.2 Ammonia Synthesis Catalysts

Catalysts for NH_3-synthesis: promoter-containing α-iron

Promoters increase the activity, lifetime and temperature stability of the catalyst and reduce its susceptibility to poisoning.

Promoters:

K_2CO_3	increases activity, decreases temperature stability
Al_2O_3, SiO_2, CaO	protect against pre-sintering and thereby increases temperature stability
CaO	reduces susceptibility to sulfur and chlorine compounds

Ammonia synthesis catalysts consist of α-iron with small quantities of different oxides, so-called promoters, which increase the activity of the catalyst, increase its lifetime and decrease its susceptibility to poisoning.

The starting material for α-iron is magnetite, Fe_3O_4, which is mixed with the promoter substances, which are essentially:

- potassium carbonate, which in the presence of acidic and amphoteric oxides such as silicon dioxide or aluminum oxide increase the catalytic activity, but decreases the temperature stability

- aluminum oxide, silicon dioxide and calcium oxide, which under the catalyst production conditions form aluminosilicates, which protect the catalyst particles from presintering and thereby increase the temperature stability of the catalyst. Calcium oxide also increases the resistance of the catalyst to poisoning by, for example, sulfur and chlorine compounds.

Some catalysts contain oxides of lithium, beryllium and vanadium as promoters.

The catalysts can therefore be tuned to the particular conditions pertaining in the particular ammonia reactor, which accounts for the differences in composition between industrially utilized catalysts.

Production of catalysts by melting magnetite and promoter oxides together, followed by cooling, pulverizing, sieving

Catalysts are produced by melting together a mixture of magnetite with the promoters at temperatures of ca. 1500°C in an electric furnace or an electric arc furnace, followed by rapid cooling, pulverizing and sieving. A particle size of 6 to 10 mm is normally required, but there are also ammonia plants for which 1 to 2 mm particles are preferred.

Reduction of magnetite:

- conventional by synthesis gas in a pressure reactor
- prereduction in a separate plant preferred

The subsequent reduction of the magnetite is of crucial importance to the quality of the catalyst. It is normally carried out with synthesis gas in the pressure reactor of the ammonia plant at not too high pressures (70 to 300 bar, depending on the plant type) and at temperatures between 350 and 400°C, whereupon highly porous α-iron is formed:

$$Fe_3O_4 + 4\ H_2 \longrightarrow 3\ Fe + 4\ H_2O$$

The oxide promoters are not themselves reduced, but their presence decreases the reduction rate. The concentration of the water resulting from the reduction must be kept low to prevent its coming into contact with the freshly reduced catalyst, otherwise premature aging takes place. As a result high gas velocities are used. Modern ammonia furnaces contain up to 100 t of catalyst and the reduction lasts several days.

An alternative process in which catalysts have been prereduced in separate plants, has become favored in recent years. These catalysts are pyrophoric and are therefore stabilized by exposure to nitrogen containing 0.2% oxygen at 100°C. Only a short reaction time is required to reduce the thereby partially oxidized catalyst in the ammonia reactor.

Catalyst poisons:

O-, S-, P- and As-compounds; hydrocarbons and inert gases such as argon also interfere

These catalysts are extremely sensitive to catalyst poisons, which reduce chemisorption of hydrogen and nitrogen on the active surfaces of the catalyst and thereby reduce its activity. Gaseous oxygen-, sulfur-, phosphorus- and chlorine compounds, such as water, carbon monoxide, carbon dioxide, the latter being reduced to water under ammonia synthesis conditions, are particularly troublesome in this regard. Catalyst poisoned with oxide compounds can be reactivated by reduction with pure synthesis gas.

Catalysts containing sulfur-, phosphorus- or arsenic-compounds cannot be regenerated under the conditions of ammonia synthesis. A catalyst filling can have a lifetime of 5 years or more, if a highly purified synthesis gas with less than 10 ppm of oxygen-containing compounds is used. Hydrocarbons such as methane and inert gases such as argon also interfere with the process, since they interact with the catalyst surface and hinder the diffusion of nitrogen and hydrogen into the catalyst pores.

1.4.1.2.3 Synthesis Gas Production

Raw Materials

The production of one ton of ammonia requires a mixture of 2400 m^3 of highly purified hydrogen and 800 m^3 of highly purified nitrogen (at 0°C and 1000 mbar). It is produced using different processes depending upon the raw materials utilized.

Synthesis gas:

- N_2 – from air or natural gas
- H_2 – from reaction of natural gas or naphtha with H_2O (by steam reforming)
  - from heavy fuel oil and H_2O (by partial oxidation)
  - from coal and water (by coal gasification)

Nitrogen is taken from air or from the nitrogen content of natural gas. This is carried out by low temperature fractionation of air, which is preferred when pure oxygen is required as an oxidizing agent in the production of synthesis gas. Alternatively air is employed directly in the production of synthesis gas and the oxygen is removed by the to be oxidized reaction partners.

Hydrogen is produced from hydrocarbons or coal and water:

- from natural gas (methane) and naphtha (raw gasoline) using the steam-reforming process
- from crude oil products (e.g. heavy heating oil)
- from coal (coal gasification) by partial oxidation

80% of the hydrogen produced is produced on the basis of natural gas/crude oil

The choice of process depends upon the availability of raw materials. Hydrogen for ammonia synthesis is currently rarely produced by water electrolysis, except in countries with cheap electricity. Before World War II ca. 90% of the hydrogen production for ammonia synthesis was produced by coal gasification. With the availability of the cheap raw materials natural gas and crude oil, this process is unimportant. In the event of increased natural gas and crude oil prices, coal gasification could become more attractive, particularly in countries with cheap coal.

About 80% of the World's production of hydrogen is produced from natural gas and crude oil. The rest is mainly produced from coal or coke with, 4% being produced by water electrolysis.

These proportions vary from region to region, natural gas being mainly used in the USA and Europe, whereas coal is mainly used in South Africa and India.

Manufacture of Mixtures of Hydrogen, Nitrogen and Carbon Monoxide

Steam-Reforming (from natural gas and naphtha)

In the steam-reforming process, natural gas or naphtha are reacted in the presence of catalysts at temperatures between 700 and 830°C and pressures of up to 40 bar in an endothermic process with steam to hydrogen, carbon monoxide (and carbon dioxide):

$$C_nH_{2n+2} + nH_2O \longrightarrow nCO + (2n + 1)H_2$$

The reaction mixture still contains, depending upon the reaction temperature, 7 to 9% by weight of methane.

These reactions are carried out in primary reformers containing a number of vertical catalyst-filled tubes. The heat of reaction is supplied externally e.g. by an allothermal process.

The catalyst is nickel oxide on a carrier such as α-aluminum oxide or magnesium oxide-aluminum oxide-spinels reduced by hydrogen to nickel under the conditions obtaining in the steam-reforming process. These nickel catalysts are very susceptible to poisoning, in particular by sulfur compounds, but halogens and arsenic compounds also interfere.

The sulfur-compound containing natural gas and naphtha utilized in the steam-reforming process, have therefore to undergo prior desulfurization. This is accomplished by

Steam reforming:

- methane or naphtha are cracked in a "primary reformer" at 700 to 830°C under pressure on NiO-Al_2O_3- or NiO-MgO-Al_2O_3-catalysts

- preliminary hydro-desulfurization of raw materials on CoO- or NiO- and MoO_3-containing catalysts at 350 to 450°C; H_2S is adsorbed on ZnO

contacting the raw materials with cobalt- or nickel-molybdenum oxide-containing catalysts in the presence of hydrogen at 350 to 450°C, whereupon the sulfur-carbon compounds are reduced to hydrogen sulfide which is adsorbed on zinc oxide.

- in a "secondary reformer" CH_4 is converted into H_2 and CO at 1000 to 1200°C in the presence of Cr_2O_3-containing catalyst
- temperature increase by input of air and combustion of part of the cracking gas
- the quantity of air is regulated so that 3 moles H_2 and 1 mole N_2 is present

After desulfurization, steam is added and the mixture heated to 480 to 550°C before it is fed into the primary reformer. The gas leaving the primary reformer contains between 7 and 10% methane. This is removed in so-called "secondary reformers" in which the gas leaving the primary reformer is partially burnt with air in nickel catalyst-filled shaft furnaces (autothermal process), whereupon the temperature increases to ca. 1000°C. Under these conditions the methane reacts with the steam reducing the methane content in the synthesis gas to ca. 0.5 mole %. The quantity of air is adjusted to give the nitrogen to hydrogen ratio required for the stoichiometry of the ammonia synthesis.

Partial Oxidation of Heavy Heating Oil

In partial oxidation, the raw materials, e.g. heavy heating oil, are oxidized to hydrogen and carbon monoxide with insufficient oxygen for total combustion:

$$2\ C_nH_{2n+2} + nO_2 \longrightarrow 2\ nCO + 2\ (n + 1)H_2$$

If oxygen-enriched air is used, its quantity is adjusted to give the nitrogen to hydrogen ratio required for the stoichiometry of the ammonia synthesis.

- the partial oxidation is autothermal

Partial oxidation:

- different crude oil fractions are oxidized incompletely at 1200 to 1500°C and 30 to 40 bar with insufficient oxygen for complete combustion
- desulfurization of raw materials is unnecessary

The partial oxidation is autothermal and in contrast to steam reforming does not require a catalyst.

It proceeds at temperatures between 1200 and 1500°C and at a pressure of 30 to 40 bar (plants operating at a pressure up to 80 bar are rare). To avoid exceeding this temperature range, the starting gas mixture is spiked with a little hydrogen.

The advantage of the partial oxidation process is that sulfur does not interfere and therefore desulfurization is unnecessary. Disadvantageous compared with steam-reforming is, however, that an air fractionation plant for oxygen production is necessary (utilization of air giving a limitedly usable nitrogen/hydrogen-ratio of 4/1 instead of the required ratio of 3/1).

The soot formed as a byproduct in the partial oxidation process has to be scrubbed out with water and recycled in a fairly complex process.

Industrial processes are operated by Shell and Texaco.

- the soot formed as a byproduct has to be scrubbed out with water

Coal Gasification

A mixture of hydrogen, carbon monoxide, carbon dioxide, methane and sometimes nitrogen is formed upon the partial oxidation of coal (hard or soft coal) with oxygen or air and steam at high temperatures. The main reaction taking place during the gasification is the reduction of water with carbon to hydrogen and carbon monoxide:

Coal gasification:

- autothermal reaction of coal with O_2 and H_2O-vapor at high temperatures

$$C + H_2O \rightleftharpoons H_2 + CO$$

and the exothermic partial combustion of carbon to carbon monoxide:

$$2\,C + O_2 \rightleftharpoons 2\,CO$$

Under these conditions water and carbon monoxide react forming hydrogen and carbon dioxide, and methane is formed by the reduction of carbon monoxide or carbon with hydrogen.

All the industrial processes are autothermal, 30 to 40% of the coal utilized being burnt to attain the required high reaction temperatures. This is also the case for the Lurgi pressure gasification process carried out in a mechanically agitated solid bed at ca. 1200°C (as used e.g. in Sasolburg in South Africa), for the Koppers-Totzek process in which the coal is used in the form of flyash (atmospheric pressure, 1400 to 1600°C) and for the Winkler process operating with a pressureless fluidized bed at 800 to 1100°C.

Industrial processes:

- Lurgi
- Koppers-Totzek
- Winkler

These gasification processes are, on the basis of invested capital and energy consumption, still inferior to the processes for producing hydrogen-carbon monoxide mixtures from hydrocarbons.

The utilization of nuclear process heat in (allothermal) coal gasification plants e.g. with 950°C helium from high temperature nuclear reactors has been postponed to the distant future, due to the stopping of development work in the Federal Republic of Germany.

Conversion of Carbon Monoxide

CO-conversion to H_2 + CO with steam

The next step in the manufacture of synthesis gas is the removal of carbon dioxide by oxidizing it with steam to carbon dioxide, the steam being reduced to hydrogen:

$$CO + H_2O \longrightarrow CO_2 + H_2$$

As this water gas conversion reaction is exothermic, low temperatures favor the formation of carbon dioxide and hydrogen.

High temperature conversion at 350 to 380°C:

- on iron oxide/chromium oxide catalysts or
- on sulfur-insensitive Co/Mo-containing catalysts

Low temperature conversion at 200 to 250°C on very sulfur-sensitive CuO/ZnO-catalysts

Selection of different conversion processes is dependent upon the sulfur-content of the gas mixtures:

- for steam-reforming: low temperature conversion or a combination of high temperature and low temperature conversion
- for partial oxidation: only high temperature conversion

Iron-chromium oxide catalysts, reduced with hydrogen-containing in the conversion plants, permit reactions temperatures of 350 to 380°C (high temperature conversion), the carbon monoxide content in the reaction gas is thereby reduced to ca. 3 to 4% by volume. Since, these catalysts are sensitive to impurities, cobalt- and molybdenum-(sulfide)-containing catalysts are used for gas mixtures with high sulfur contents. With copper oxide/zinc oxide catalysts the reaction proceeds at 200 to 250°C (low temperature conversion) and carbon monoxide contents of below 0.3% by volume are attained. This catalyst, in contrast to the iron oxide/chromium oxide high temperature conversion catalyst, is, however, very sensitive to sulfur compounds, which must be present in concentrations of less than 0.1 ppm.

Gas mixtures from the steam reforming process are without further treatment sulfur-free, since they have already been desulfurized at the raw material (natural gas and naphtha) stage due to the sensitivity of the steam-reforming catalysts to poisoning by sulfur compounds. On the other hand reaction gases from the partial oxidation process contain sulfur compounds, since the starting materials have not been subjected to prior desulfurization. Such gas mixtures can therefore only be subjected to high temperature conversion with sulfur-resistant catalysts and the hydrogen sulfide formed has to be removed with the carbon dioxide afterwards. The reaction gases from the steam-reforming process can, by contrast, be worked up in low temperature conversion plant or, preferably, worked up by a combination of high temperature and low temperature conversion.

Removal of Carbon Dioxide and Hydrogen Sulfide

In the next step the carbon dioxide, mostly from the conversion reaction, and the hydrogen sulfide, if present, are removed from the gas mixture. This is accomplished either by physical or chemical absorption in appropriate solvents.

Removal of the acidic gases CO_2 and H_2S by physical or chemical absorption

In the physical absorption processes such as the Rectisol process (carried out at low temperatures with methanol as solvent) the gas mixture under pressure is brought into contact with solvent in absorption columns, the solvent being regenerated by pressure release or high temperature stripping. In this process carbon dioxide and hydrogen sulfide can be jointly scrubbed or selectively by using a small quantity of methanol, whereupon only hydrogen sulfide is absorbed with only a little carbon dioxide. The residual carbon dioxide can then be absorbed separately. The Fluor-Solvent (propylene carbonate), Purisol (N-methylpyrrolidone) and Selexol [poly(ethyleneglycol dimethyl ether)] processes operate with lower vapor pressure solvents than that used in the Rectisol process.

Physical absorption:

with methanol, propylene carbonate, N-methylpyrrolidone, poly(ethyleneglycol dimethyl ether)

Chemical absorption processes use different absorption agents e.g. organic amines such as mono-, di-, triethanolamine, N-methyldiethanolamine or diisopropanolamine (Shell). BASF's alkazide process uses the potassium salt of monomethylaminopropionic acid. Aqueous solutions of potassium carbonate with added corrosion inhibiting and reaction activating agents (e.g. Benfield process) are widely used as absorption agents.

Chemical absorption:

with mono-, di- and triethanolamine, N-methyldiethanoloamine, diisopropanolamine, potassium salt of monomethylamino-propionic acid, solutions of potassium carbonate

Combinations of physical and chemical absorption are also used, as in Shell's Sulfinol process in which a mixture of diisopropanolamine and sulfolane in water is utilized. For the hydrogen sulfide-free gases from the steam-reforming process, chemical scrubbing with activated potassium carbonate solutions or alkanolamines is preferred. In the case of hydrogen sulfide-containing gases from the partial oxidation process, physical absorption alone or in combination with chemical absorption is preferred.

For H_2S-free gases:

chemical scrubbing

For H_2S-containing gases:

physical absorption alone or in combination with chemical absorption

Final Purification of Synthesis Gases

To protect the ammonia synthesis catalysts from premature poisoning the nitrogen-hydrogen-mixture, after the removal of the acidic components carbon dioxide and hydrogen sulfide,

Final purification of synthesis gas by removal of oxygen-containing impurities has to be subjected to further intensive purification to remove quantitatively any oxygen-containing impurities present.

Scrubbing with liquid N_2 under pressure and at low temperatures for high temperature conversion gases; H_2O, CO_2 and hydrocarbons are removed beforehand

The large quantities of carbon monoxide present after high temperature conversion (3 to 5% by volume), are removed by liquid nitrogen scrubbing. The formerly practiced copper lye-scrubbing is no longer used due to the higher costs and possible environmental contamination with copper. In liquid nitrogen scrubbing, the gas mixture is scrubbed with liquid nitrogen in columns at -190°C under pressure (up to 80 bar). Formerly residual water, carbon dioxide and methane were removed by adsorption on zeolites to prevent ice formation during liquid nitrogen scrubbing and the hydrocarbons removed by condensation. Liquid nitrogen scrubbing also serve to make up any nitrogen deficit in the gas mixture, particularly when pure oxygen had been used for the production of the synthesis gas.

N_2 is added to the gas mixture during the liquid nitrogen scrubbing

Low temperature conversion gases are subjected to methanation on Ni-catalysts at high temperatures under pressure

Nitrogen-hydrogen mixtures resulting from low temperature conversion contain only 0.1 to 0.3% by volume of carbon monoxide. In this case the ca. 0.01 to 0.1% by volume of carbon monoxide and carbon dioxide present after carbon dioxide scrubbing is hydrogenated to methane (methanation) in the presence of nickel catalysts on a carrier in an exothermic reaction at 30 bar and 250 to 350°C:

Composition of synthesis gas after methanation (% by volume):

H_2	74.0%
N_2	24.7%
CH_4	1.0%
Ar	0.3%
$CO + CO_2$	5 ppm

$$CO + 3\,H_2 \longrightarrow CH_4 + H_2O$$
$$CO_2 + 4\,H_2 \longrightarrow CH_4 + 2\,H_2O$$

The water formed in this reaction is removed from the synthesis gas by condensation, the synthesis gas then containing less than 10 ppm of carbon-oxygen compounds and about 1.3% by volume of inert gases (methane and argon).

Removal of CH_4, Ar (partial) and surplus N_2 by condensation

In some ammonia plants, the residual methane (ca. 1% by volume) and some of the residual argon (ca. 0.3% by volume) are completely removed by low temperature condensation, as is surplus nitrogen from the secondary reforming process (Braun purifier concept).

1.4.1.2.4 Conversion of Synthesis Gas to Ammonia

General Information

The industrial scale reaction of synthesis gas to ammonia in pressure reactors takes place in a cyclic process in which the ammonia formed is removed from the reaction gas and the unreacted synthesis gas returned to the reactor. In addition to the ammonia formed, inert gases and the liberated reaction heat have to be continuously removed from the cyclic process. The excess heat of the product gas is used to heat the feed synthesis gas to the reaction temperature in a heat exchanger integrated into the reactor. Additional waste heat can be utilized for steam generation. The pressure loss in the synthesis gas due to its passage through the synthesis loop is compensated for and the fraction of synthesis gas converted replaced by fresh compressed synthesis gas ("fresh gas").

NH_3 synthesis is a cyclic process:
- removal of:
  - NH_3
  - inert gas
  - reaction heat (utilized for heating up cold synthesis gas)
- recycling of unused synthesis gas into the reactor
- supply of fresh gas
- compensation of pressure losses

The most important part of an ammonia synthesis plant is the pressure reactor, which is filled with catalyst and in which ammonia formation takes place at temperatures between 400 and 500°C. A maximum temperature of 530°C must not be exceeded, otherwise catalyst damage will ensue.

Compression in the larger plants is currently carried out with turbocompressors. Plants with capacities <600 t/d still use the previously widely used piston pumps. With turbocompressors, which are almost always driven by steam turbines, plants with a capacity of 1500 t/d can operate in the preferred and economically optimal pressure range of 250 to 350 bar, a single turbocompressor providing the fresh gas compression and the circulation.

Compression with the help of:
- turbocompressors
- piston pumps (for smaller plants)

Reactor Types

Different reactor types are used in the individual ammonia-synthesis plants. They have in common, that the catalyst mass is to be found in a separate container inside the reactor chamber. Between the catalyst holder and the reactor wall there is a gap through which the cold synthesis gas can be fed in, such that the reactor wall is not heated to the same temperature as the catalyst holder.

The NH_3-synthesis proceeds in reactors in which the catalyst is present in a separate container. The cooling in the reactor is carried out with cold synthesis gas

The cold synthesis gas fed into the cycle is, heated with the help of the hot reaction gases inside or outside the catalyst holder, depending upon the reactor type either in countercurrent or in co-current.

In the cooling of the reactor with the cold synthesis gas, the temperature control is so designed, that upon exit of the reaction gas from the reactor a lower temperature prevails than at the synthesis gas input into the catalyst. This arrangement is aided by a separate stream of cold synthesis gas.

Reactor classes:

- tubular reactors
  - co-current
  - countercurrent
- multiple bed reactors
  - cooling by cold gas
  - heat exchange cooling
  - catalyst arranged in separate beds

In principle there are two classes of reactor: tubular reactors and multiple bed reactors. The former group is split into co-current and countercurrent reactors, the latter into those with cold gas cooling and heat-exchange cooling. In the frequently used Casale reactor, a countercurrent reactor, the heat is transferred from the hot reaction gas to the cold synthesis gas by a ring heat-exchanger round the whole catalyst bed. This reactor type is started up by heating the synthesis gases to 400°C with a centrally positioned electrically heated rod just before their entry into the catalyst mass, In other reactors this heating up takes place indirectly outside the reactor using heat from oil or gas combustion.

Most popular reactor type:

multiple bed reactors directly cooled with cold gas (quench reactor)

In cross flow (layer) reactors catalyst beds, gas flow radial

In multiple bed reactors the catalyst is arranged in separate beds. Between the layers the gas is either cooled with a heat exchanger or by adding cold synthesis gas. The ÖSW-reactor, developed by Österreichischen Stickstoff-Werken (now Chemie Linz) together with Uhde is an example of the first type. Reactors, directly cooled by the feeding of cold gas (so-called "quench reactors") are the most widely used type. A representative of this category is the Kellogg quench reactor. Multiple bed reactors in which the gas stream passes radially through the catalyst beds (cross flow reactors) are frequently used. They are cooled by heat exchangers or with cold gas. There are also horizontal versions of such cross flow reactors (ÖSW and Kellogg).

Reactor materials:

Cr- and Mo-containing steels

Reactors are multilayer constructions, e.g. produced by to the Schierenbeck process

Tempered steel is used for the construction of all these pressure reactors, alloyed with chromium and molybdenum to make them resistant to hydrogen under pressure, so that no decarburization, embrittlement and grain boundary splitting occurs. These pressure reactors are more and more being constructed out of several layers. In this way the total reactor wall is built up of a multitude of individual layers, which are wound round a central tube. The advantage of such a multiple layer construction, as against pressure chambers with a plate-girder construction, is that the central tube is subject to chemical demands and the adjacent layers can consist of simpler steels. These multilayer chambers constructed according to the BASF Schierenbeck-winding process are easier to repair than welded plate-girder chambers. A red-hot profiled steel winding-strip is wound helically round a thin-walled (20 to 40 mm) central tube forming multiple layer, the profiles mating with each another. Pressure chambers are currently being built up to 30 m in length and greater than 2 m in diameter.

Ammonia Separation

The separation of the ammonia formed from the circulating gas is mainly carried out by condensation at low temperatures, water cooling being augmented by the evaporation of liquid ammonia. The evaporated ammonia is either utilized as an intermediate or is liquefied by compression and subsequent cooling. In the case of low synthesis pressures and a demand for aqueous ammonia, separation of ammonia formed in the synthesis gas is carried out by absorption in water. Water vapor which thereby enters the cycling gas is removed by scrubbing with liquid ammonia, to avoid deterioration of the catalyst by water vapor.

Separation of NH_3 from the circulating gas by condensation at low temperatures

1.4.1.2.5 Integrated Ammonia Synthesis Plants

In modern ammonia plants the individual process steps of gas production, conversion of the carbon monoxide to carbon dioxide, purification of the synthesis gas and ammonia synthesis is performed in single-train plants. Plants for synthesis gas production e.g. with steam-reforming (Fig. 1.4.1-1) or partial oxidation (Fig. 1.4.1-2) operate economically, since personnel requirements are low and optimal energy exchange between heat-consuming and heat-producing steps enables a high level of waste heat utilization to be achieved. In addition, steam is produced in steam reforming units e.g. from the flue gas of the primary reformers or in waste heat boilers connected to the secondary reformer, high temperature conversion and methanation units. This steam is used both as a gasification agent in synthesis gas production and as a propellant for the compressors and pumps. In this way much of the total energy requirements (up to 85% in steam-reforming) of an

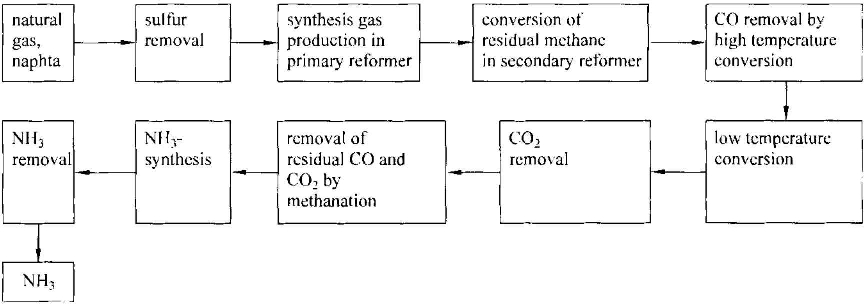
Integrated NH_3-plants include:

- gas production
- CO- and CO_2-conversion
- synthesis gas purification
- NH_3-synthesis

Single train plants are economic to operate, since the waste heat can be optimally utilized and the personnel requirements are low

The economics of NH_3-plants is very dependent upon the plant size

integrated plant can be supplied by the heat produced. The economics of an ammonia plant is in addition strongly dependent upon the size of the plant. Plants with a capacity under 600 t/d are barely competitive. Many plants have a capacity of 1500 t/d.



Storage and transport of NH_3 occurs at various pressures and temperatures

Fig. 1.4-1. Flow chart of a single-train plant for the synthesis of ammonia using the Steam-Reforming process.

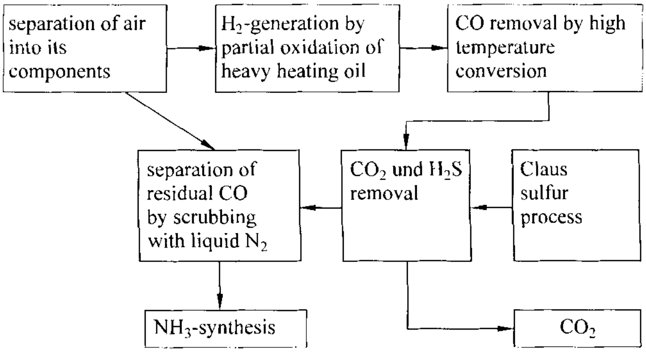


Fig. 1.4-2. Flow chart of a single-train plant for the synthesis of ammonia using the partial oxidation process.

In single-train plants it is necessary to store a certain amount of ammonia to cover production breakdowns. The ammonia is either stored at atmospheric pressure and low temperatures (-33°C), or under moderate pressures at +5 to -5°C. Ammonia is also transported under these different conditions.

1.4.1.3 Ammonia Applications

Ammonia is the starting material for the manufacture of nitric acid, urea and ammonium phosphate, as well as for the production of precursors for fibers, plastics, pesticides and many other organic products.

By far the most important consumer of ammonia is the fertilizer sector.

NH_3 is used in the manufacture of:

- HNO_3
- urea
- ammonium phosphates
- plastics and fibers

References for Chapter 1.4: Nitrogen and Nitrogen Compounds

Ullmann's Encyclopedia of Industrial Chemistry. 1985. 5. Ed., Vol. A 2, 143 – 242, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 2, 638-691, John Wiley & Sons, New York.

Winnacker-Küchler. Chemische Technologie. 1994. 4. Ed., Vol. 2, 94-148, Carl Hanser Verlag, München.

1.4.2 Hydrazine

1.4.2.1 Economic Importance

Hydrazine is commercially available as aqueous solutions and, in smaller quantities, in the form of salts. Hydrazine forms a high boiling point azeotrope with water, whose composition is close to a 1:1 molar ratio, corresponding to 64% hydrazine. This solution is known as "hydrazine hydrate". The capacity statistics in table 1.4-1 relate to "hydrazine hydrate". Anhydrous hydrazine is only produced in very small quantities for special applications in satellite technology.

Table 1.4-1. Estimated Hydrazine Hydrate Capacities in Western Producer Countries* in 1992 in 10^3 t/a.

	Company	Capacity	Process
USA	Olin	10	sodium hypochlorite/acetone
USA	Bayer Corp.	10	sodium hypochlorite/acetone
FRG	Bayer A.G.	10	sodium hypochlorite/acetone
France	Atochem	10	H_2O_2/methyl ethyl ketone
Far East	Mitsubishi	10	H_2O_2/methyl ethyl ketone
Far East	Otsuka		sodium hypochlorite(Raschig)

* other fairly small Raschig process plants are operated in the former Iron Curtain Countries

1.4.2.2 Manufacture of Hydrazine

Manufacture of hydrazine:
oxidation of ammonia or urea with sodium hypochlorite or hydrogen peroxide

Hydrazine is formed in a multitude of chemical reactions. Only a few processes have acquired commercial importance. These all oxidize ammonia or urea, an ammonia derivative, to hydrazine. Sodium hypochlorite or hydrogen peroxide is used as the oxidizing agent. Certain processes (Bayer-, H_2O_2-processes) operate in the presence of ketones.

1.4.2.2.1 Raschig Process

Raschig process:
oxidation of ammonia with sodium hypochlorite to hydrazine and sodium chloride. Distillative separation of hydrazine from solid sodium chloride. Yield ca. 70%

In the Raschig process, ammonia is oxidized with sodium hypochlorite:

$$\begin{array}{lcl}
2\,NaOH + Cl_2 & \longrightarrow & NaOCl + NaCl + H_2O \\
NaOCl + NH_3 & \longrightarrow & NH_2Cl + NaOH \\
NH_2Cl + NaOH + NH_3 & \longrightarrow & N_2H_4 + NaCl + H_2O \\
\hline
2\,NaOH + Cl_2 + 2\,NH_3 & \longrightarrow & N_2H_4 + 2\,NaCl + 2\,H_2O
\end{array}$$

Sodium hypochlorite is obtained as a ca. 4.7 mol/L solution by mixing chlorine and sodium hydroxide with cooling in a molar ratio of 1:2 (see Fig, 1.4.-3). This is diluted to ca. 1 mol/L and reacted with an aqueous ammonia solution (ca. 15%) at temperatures around 0°C (with cooling) forming chloramine and sodium hydroxide. The yield is almost quantitative.

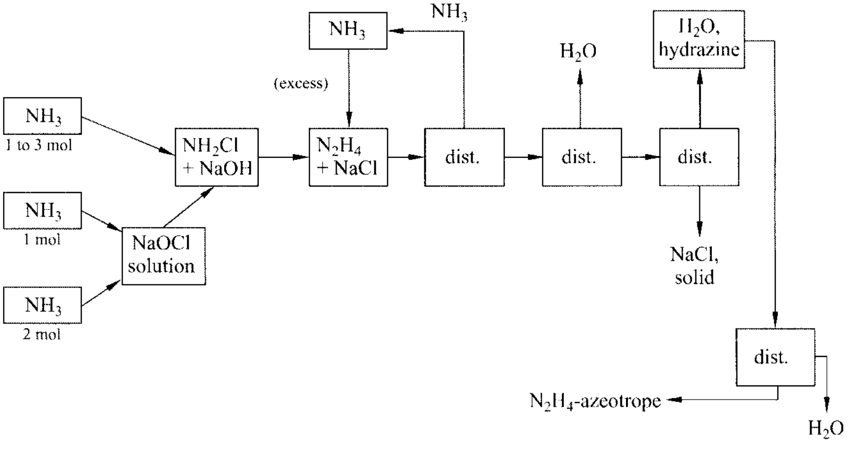


Fig. 1.4-3. Schema of the Raschig process.

The alkaline chloramine solution is then reacted, at ca. 130°C under pressure, with a 20- to 30-fold molar excess of anhydrous ammonia. The excess ammonia then separated from the reaction mixture, is recycled. Water and the hydrazine-water azeotrope (b.p. 120.5°C) are distilled off leaving solid sodium chloride. The aqueous hydrazine solution obtained is finally concentrated by distillation. Ca. 70% of the theoretical yield is obtained. Important side reactions are:

- reaction of chloramine with the hydrazine formed:

$$2\,NH_2Cl + N_2H_4 \longrightarrow N_2 + 2\,NH_4Cl$$

This reaction is particularly catalyzed by copper. A large excess of ammonia and the addition of complexing agents such as ethylenediaminetetra-acetic acid (EDTA) are used as countermeasures.

- decomposition of hydrazine during its evaporation from solid sodium chloride

If hydrazine hydrate is not required, hydrazine can be precipitated out from the Raschig synthesis reaction mixture as the sparingly soluble hydrazine sulfate ($N_2H_6^{2+}SO_4^{2-}$, solubility in water: 2.96 g/L).

1.4.2.2.2 Urea Process

In this process a mixture of urea, sodium hypochlorite and sodium hydroxide is converted into hydrazine, sodium chloride and sodium carbonate.

Urea process:

oxidation of urea with sodium hypochlorite to hydrazine, sodium chloride and sodium carbonate. Working up same as in the Raschig process. Yield: 60 to 70%

$$H_2NCONH_2 + NaOCl + 2\,NaOH \longrightarrow N_2H_4 + NaCl + Na_2CO_3 + H_2O$$

The reaction components are mixed cold in the above molar ratios and the mixture rapidly heated to 100°C. The working up is the same as with the Raschig process, giving 60 to 70% of the theoretical yield of hydrazine. The advantages of this process are the avoidance of a large excess of ammonia and working at atmospheric pressure, which must be set against the serious disadvantage of using two moles of sodium hydroxide per mole of hydrazine.

Furthermore, the production of a sodium chloride-sodium carbonate-mixture poses an additional ecological problem.

1.4.2.2.3 Bayer Process

Bayer process:

oxidation of ammonia with sodium hypochlorite in the presence of acetone to acetone azine and sodium chloride, distillative separation of the acetone-azine from the sodium chloride solution, hydrolysis of the acetone azine to hydrazine and acetone, Hydrazine yield: 80 to 90%

Of a number of hydrazine syntheses based on the oxidation of ammonia with sodium hypochlorite in the presence of ketones (acetone, methyl ethyl ketone) (see Fig. 1.4-4), only that of Bayer A.G. appears to have graduated to a commercial process.

The two main reactions are the formation and hydrolysis of acetone azine:

$$NaOCl + 2\ NH_3 + 2\ CH_3COCH_3 \longrightarrow (CH_3)_2C{=}N{-}N{=}C(CH_3)_2 + NaCl + 3\ H_2O$$

$$(CH_3)_2C{=}N{-}N{=}C(CH_3)_2 + 2\ H_2O \longrightarrow 2\ CH_3COCH_3 + N_2H_4$$

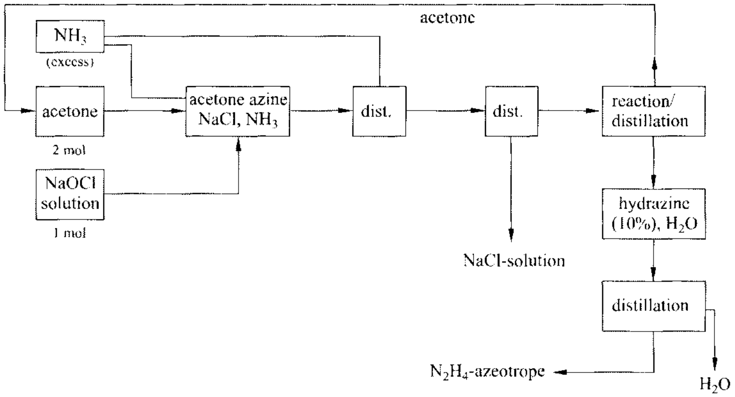
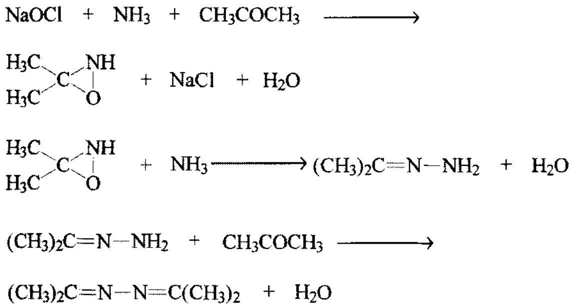


Fig. 1.4-4. Schema of hydrazine manufacture by the Bayer process.

The formation of azine is not a means of trapping the hydrazine formed in the Raschig process with acetone, the reaction proceeding by way of two distinct intermediates: dimethyl oxazirane and acetone hydrazone, as follows:



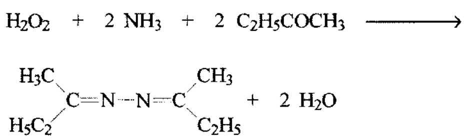
Sodium hypochlorite solution (ca. 1.5 mol/L), ammonia and acetone in a molar ratio of 1:15 to 20:2 are reacted together at 35°C. A solution results consisting of 5 to 7% by weight of acetone azine together with sodium chloride and excess ammonia. This ammonia is distilled off and returned to the reaction. Next, the acetone azine-water-azeotrope (b.p. 95°C) is distilled off leaving the sodium chloride solution. Herein lies the essential difference from the Raschig process in which the hydrazine water mixture has to be separated from solid sodium chloride.

Finally, the acetone azine is hydrolyzed with water in a reaction distillation tower into acetone (head product) and a 10% aqueous hydrazine solution (sump product) at temperatures up to 180°C and pressures of 8 to 12 bar. The hydrazine solution is concentrated to its azeotrope composition of 64% by weight of hydrazine. The hydrazine yield is 80 to 90%, based on the hypochlorite utilized.

1.4.2.2.4 H_2O_2 Process

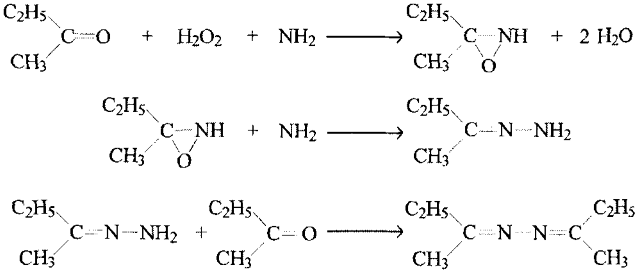
This process is similar to the Bayer process except that hydrogen peroxide is used as the oxidizing agent and the ketone used is methyl ethyl ketone:

H_2O_2 process:
oxidation of ammonia with H_2O_2 in the presence of methyl ethyl ketone to methyl ethyl ketone azine and sodium chloride, distillative separation of methyl ethyl ketone azine from the sodium chloride, hydrolysis of the methyl ethyl ketone azine to hydrazine and methyl ethyl ketone. 80 to 90% yield of hydrazine



$$H_2O_2 + 2\,NH_3 + 2\,C_2H_5COCH_3 \longrightarrow (H_3C)(H_5C_2)C{=}N{-}N{=}C(CH_3)(C_2H_5) + 2\,H_2O$$

Since the reaction with hydrogen peroxide is too slow, an activator is added as a catalyst, which in the process variant published by ATOCHEM is a mixture of acetamide, ammonium acetate and sodium hydrogen phosphate. Other catalysts can also be used. The presumed reaction mechanism is similar to that of the Bayer process:



The methyl ethyl ketone azine formed, which is poorly soluble in water, is separated and hydrolyzed to hydrazine and ketone. The catalyst-containing aqueous solution is returned to the synthesis.

This process is operated commercially by ATOCHEM in France and in a very similar process by Mitsubishi Gas Chemicals in Japan. The advantage of this process over the Bayer and Raschig processes is that sodium chloride is not formed as a byproduct.

1.4.2.3 Applications of Hydrazine

Applications of hydrazine:

- as a corrosion inhibitor
- in the manufacture of:
  - blowing agents
  - polymerization initiators
  - herbicides
  - pharmaceuticals

The presence of hydrazine in ppm quantities in boiler feed water prevents corrosion, due to its promotion of a protective magnetite layer. Derivatives of hydrazine are particularly important as blowing agents in the manufacture of foamed plastics and rubbers, as free radical polymerization initiators, as herbicides and as pharmaceutical products. The hydrazine products used as blowing agents or polymerization initiators decompose upon heating into nitrogen and free radicals: the nitrogen acting as a blowing agent, the free radicals as polymerization initiators.

Amongst the commonly used blowing agents are:

- Azodicarbonamide
- Benzene sulfonic acid hydrazide

A typical polymerization initiator is α,α'-azobisisobutyronitrile.

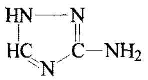
Azodicarbonamide can, for example, be produced as follows:

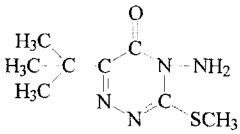
$$2\ NH_2CONH_2 + N_2H_4 + H_2SO_4 \longrightarrow NH_2CONHNHCONH_2 + (NH_4)_2SO_4$$

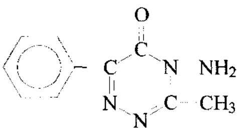
$$NH_2CONHNHCONH_2 + Cl_2 \longrightarrow NH_2CON{=}NCONH_2 + 2\ HCl$$

Another blowing agent which has become important of late is sodium azide, which in addition to being synthesized from sodium amide and chloramine can also be produced from methyl nitrite and hydrazine hydrate. Sodium azide is utilized in the airbags installed in motor vehicles.

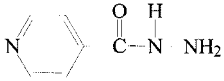
Important herbicides based on hydrazine are Weedazol®, Sencor® and Goltix®:







A typical hydrazine derivative in the pharmaceuticals sector is the anti-tubercular agent Neoteben®:



References for Chapter 1.4.2: Hydrazine

Ullmann's Encyclopedia of Industrial Chemistry. 1989. 5. Ed., Vol. A 13, 177 –191, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1980. 4. Ed., Vol. 13, 560-606, John Wiley & Sons, New York.

Winnacker-Küchler. Chemische Technologie. 1982. 4. Ed., Vol. 2, *Anorganische Technologie I*, Carl Hanser Verlag, München.

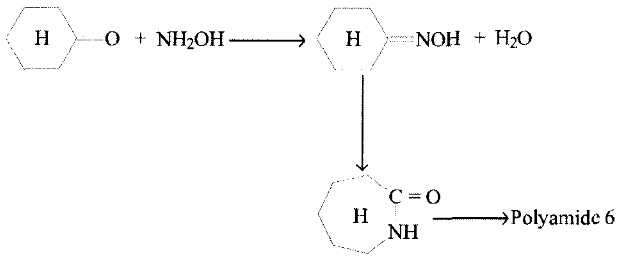
Schmidt, E. W. 1984. *Hydrazine and its Derivatives - Preparation, Properties, Applications*, John Wiley & Sons, New York.

1.4.3 Hydroxylamine

1.4.3.1 Economic Importance and Applications

Hydroxylamine: > 97% used in production of caprolactam

The commercial importance of hydroxylamine is coupled to its use (up to 97%) in the manufacture of caprolactam, a precursor in the manufacture of polyamide 6 (however, not all caprolactam is manufactured using it):



1996 worldwide capacity for hydroxylamine: > $1 \cdot 10^6$ t

In 1996 the worldwide capacity caprolactam capacity was ca. $4400 \cdot 10^3$ t. Over 90% of plants operate with hydroxylamine as an intermediate. The hydroxylamine capacities are not recorded separately, but in total must be at least $1 \cdot 10^6$ t/a (calculated on the basis of NH_2OH), assuming 100% synthesis yield, in order to provide this caprolactam capacity.

Hydroxylamine is also used in much smaller quantities as a reducing agent and in the manufacture of oximes for use in paints (skin prevention agents), pharmaceuticals and pesticides.

1.4.3.2 Manufacture

Production of hydroxylamine:

- Raschig process
- NO reduction process
- nitrate reduction process

There are three commercially operated processes for the manufacture of hydroxylamine:

- (modified) Raschig process
- NO reduction process (BASF, Inventa)
- nitrate reduction process (DSM/HPO-Stamicarbon)

1.4.3.2.1 Raschig Process

Nitrogen(II) oxide from ammonia combustion is reacted with ammonium hydrogen carbonate solution and air:

$$2\,NO + 0.5\,O_2 + 2\,NH_4HCO_3 \longrightarrow 2\,NH_4NO_2 + 2\,CO_2 + H_2O$$

Raschig process:

1st step: preparation of ammonium nitrite from ammonium hydrogen carbonate, nitric oxide and oxygen (in solution)

The resulting ammonium nitrite solution is reacted with sulfur dioxide at 0 to 5°C and pH 2 to 4.5 forming ammonium hydroxylamine disulfonate:

$$NH_4NO_2 + 2\,SO_2 + NH_3 + H_2O \longrightarrow HON(SO_3NH_4)_2$$

2nd step: formation of hydroxylamine disulfonate by reaction with sulfur dioxide

3rd step: hydrolysis to hydroxylamine sulfate and ammonium sulfate

The yield based on nitrite is ca. 90%. Finally, the disulfonate is hydrolyzed at 100°C in a relatively slow reaction:

$$2\,HON(SO_3NH_4)_2 + 4\,H_2O \longrightarrow (NH_3OH)2\ SO_4 + (NH_4)_2SO_4 + 2\,NH_4HSO_4$$

Ammonium sulfate byproduct: 1.8 kg/ kg caprolactam

The hydroxylamine content in this solution, which also contains ammonium sulfate, is ca. 70g/L. In an integrated caprolactam manufacturing plant using the Raschig process for hydroxylamine production, ca. 1.8 kg of ammonium sulfate is produced per kg of caprolactam.

1.4.3.2.2 Nitrogen(II) Oxide Reduction Process

Nitrogen(II) oxide in 80 to 90% yield is produced by the catalytic combustion of ammonia in oxygen in the presence of water vapor on a platinum-rhodium catalyst:

NO reduction process:

1st step: production of NO by combustion of ammonia with pure oxygen

$$2\,NH_3 + 2.5\,O_2 \longrightarrow 2\,NO + 3\,H_2O$$

In the BASF process this is reduced with hydrogen to hydroxylamine on a platinum catalyst on carbon substrates suspended in dilute sulfuric acid. In the Inventa process palladium is used.

2nd step: reduction of NO to hydroxylamine sulfate with hydrogen on a precious metal catalyst suspended in sulfuric acid

$$2\,NO + 3\,H_2 + H_2SO_4 \longrightarrow (NH_3OH)_2SO_4$$

The expected formation of ammonia in a side reaction is largely suppressed by process control measures, e.g. high hydrogen pressure, low hydrogen ion concentration and low temperature, and through a selective poisoning of the catalyst. The yield based on nitrogen(II) oxide is ca. 90%.

Ammonium sulfate byproduct: ca. 0.8 kg/kg caprolactam

The quantity of ammonium sulfate byproduct is this process is ca. 0.8 kg per kg of caprolactam produced. The hydroxylamine content in the solution amounts to ca. 115 g/L.

1.4.3.2.3 Nitrate Reduction Process (DSM/HPO-Stamicarbon)

Nitrate reduction process:

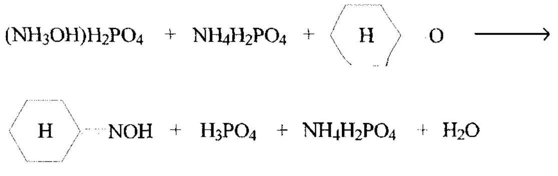
1st step: reduction if an ammonium nitrate-phosphoric acid solution with hydrogen on a suspended metal catalyst to a hydroxylamine phosphate solution

Ammonium nitrate solution is reduced to hydroxylamine phosphate with hydrogen under pressure on a suspended precious metal catalyst (substrate: activated charcoal) in the presence of phosphoric acid (HPO: Hydroxylamine Phosphate Oxime):

$$2\ H_3PO_4 + NH_4NO_3 + 3\ H_2 \longrightarrow (NH_3OH)H_2PO_4 + NH_4H_2PO_4 + 2\ H_2O$$

2nd step: reduction of this solution with cyclohexanone in toluene (two phases) to cyclohexanone oxime and separation of the aqueous phase

After separating off the catalyst, the solution is directly reacted with a solution of cyclohexanone in toluene forming cyclohexanone oxime:



3rd step: regeneration of the aqueous "recycled solution" to ammonium nitrate-phosphoric acid solution by introduction of nitrogen oxides and oxygen

After the separation of residual organic substances, the aqueous phase is reacted with nitrogen oxides and atmospheric oxygen and reused as "recycled solution".

$$2\ H_3PO_4 + 2\ NH_4H_2PO_4 + 2\ NO + 1.5\ O_2 + H_2O \longrightarrow 4\ H_3PO_4 + 2\ NH_4NO_3$$

No ammonium salt byproducts

Ammonium ions formed in the side reactions during the hydrogenation are oxidized with nitrogen oxides to nitrogen in this step. The yield based on the ammonia utilized is ca. 58%. There are no ammonium salt byproducts.

References for Chapter 1.4.3: Hydroxylamine

Reviews:

Ullmann's Encyclopedia of Industrial Chemistry. 1989. 5. Ed., Vol. A 13, 527–532, VCH Verlagsgesellschaft, Weinheim.

Winnacker-Küchler. Chemische Technologie. 1982. 4. Ed., Vol. 2, *Anorganische Technologie I*, Carl Hanser Verlag, München.

Commercial Information:

Caprolactam, *Chemical Economics Handbook*. 1980. 1993. Stanford Research Institute, Menlo Park, California

1.4.4 Nitric Acid

1.4.4.1 Economic Importance

Nitric acid is one of the most important inorganic chemicals. Quantitywise it is one of the top ten industrial chemicals.

The nitric acid production in North America, Japan and Western Europe (as 100% acid) amounted to $27.7 \cdot 10^6$ t in 1992. These regions account for about half of the worldwide production. In the Federal Republic of Germany the $2.5 \cdot 10^6$ t of nitric acid produced in 1982 had decreased to $2 \cdot 10^6$ t by 1992. This decreasing level of production is due to developments in agriculture.

Nitric acid is mostly produced as 50 to 70% HNO_3 (so-called weak acid), the proportion of highly concentrated nitric acid being less than 10%.

The largest plants have capacities of up to 1500 t/d.

HNO_3-capacities in the Western World in 1992 (in 10^3 t/a):

USA	8.4
Canada	1.1
Mexico	0.3
Western Europe	17.3
Japan	0.7

Almost half of the worldwide production of nitric acid is manufactured in these regions

1.4.4.2 Manufacture

1.4.4.2.1 Fundamentals of Nitric Acid Manufacture

Nitric acid is currently almost exclusively produced by the catalytic oxidation of ammonia using the Ostwald process (1902). The reaction of sodium nitrate (Chile niter, the only nitrate occurring naturally in large quantities) with sulfuric acid, operated at the turn of the century, has not been economic since the emergence of the Haber-Bosch ammonia synthesis process shortly before World War I. The

HNO_3 is manufactured in a 3-step process from NH_3:

(1) $NH_3 \rightarrow NO$
(2) $NO \rightarrow NO_2$ (or N_2O_4)
(3) NO_2 (+ H_2O) $\rightarrow HNO_3$

previously developed direct synthesis process from nitrogen(II) oxide produced from nitrogen and oxygen at temperatures >2000°C (arc process, thermal NO-synthesis) is no longer operated industrially.

The process for nitric acid manufacture from ammonia consists of three exothermic reaction steps as shown schematically in Fig. 1.4-5:

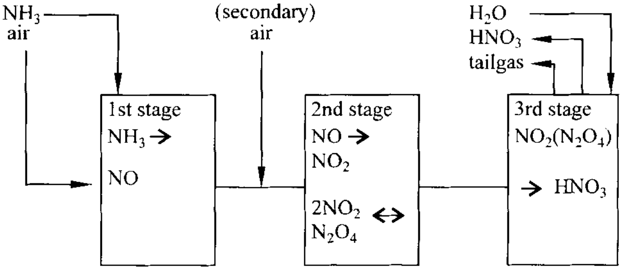


Fig. 1.4-5. Schema of the Ostwald process for the manufacture of nitric acid.

The overall reaction corresponds to:

$$NH_3 + 2\,O_2 \longrightarrow HNO_3 + H_2O \quad \Delta H = -369 \text{ kJ/mol}$$
$$\text{(heat of reaction for 60\% acid)}$$

The three reaction steps are based on very different physical chemical relationships which appreciably influence the operation of the process. The third step is normally followed by tail gas purification, to prevent the emission of nitrous gases.

Catalytic Combustion of Ammonia to Nitrogen(II)oxide:

The oxidation of ammonia (combustion) with (excess) atmospheric oxygen to nitrogen(II) oxide (NO) is carried out in the presence of a catalyst at 820 to 950°C either at atmospheric pressure or at pressures up to 12 bar:

$$4\,NH_3 + 5O_2 \longrightarrow 4\,NO + 6\,H_2O \qquad \Delta H = -904 \text{ kJ/mol}$$

This reaction is one of the most efficient catalytic processes in industrial chemistry, having an extremely short reaction time (10^{-11}s) and a high selectivity. The oxidation of ammonia benefits slightly from pressure reduction, since less nitrogen and dinitrogen(I) oxide (N_2O) is then produced in side reactions:

$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O \quad \Delta H = -1268\ kJ/mol$$

$$4\,NH_3 + 4\,O_2 \longrightarrow 2\,N_2O + 6\,H_2O \quad \Delta H = -1105\ kJ/mol$$

The adverse influence of pressure, necessary in the case of reduced apparatus size (to reduce investment costs), upon yield, can to some extent be compensated by increasing the combustion temperature, but with increased catalyst losses. The yield is generally 94 to 98% (e.g. 97 to 98% at 1 bar, 95 to 96% at 5 bar, 94% at 8 to 10 bar). The combustion mixture contains up to 13% by volume of ammonia, being below the lower explosion limit for ammonia-air mixtures (15.5% by volume at 1 bar). At higher operating pressures the concentration of ammonia in the combustion mixture is lower still (below 11%), since the lower explosion limit decreases with increasing operating pressure.

NO-yield in ammonia combustion is between 94 and 98% depending upon temperature, pressure and flow rate

NH_3/air ratio has to be varied with operating pressure to keep it below the lower explosion limit. NH_3 concentration of 9.5 to 13% are possible depending upon the pressure

The ammonia oxidation catalyst is usually a platinum alloy gauze containing 5 to 10% rhodium, or additionally with 5% palladium, with a diameter of up to 4 m (with 1024 meshes/cm^2 and a wire thickness of 0.06 to 0.076 mm, the latter for higher pressures). The higher the pressures and flow rates the larger the number of gauzes incorporated into the reactor (up to 50 one above another). The ammonia combustion plants operate with bright red glowing platinum gauzes, which leads to precious metal loss e.g. as a result of evaporation of platinum dioxide, which is formed as an intermediate, or by mechanical abrasion (ca. 0.05 to 0.35 g per t of 100% HNO_3). The higher the operating pressures and temperatures in the reactor, the higher these losses. Up to 80% of this precious metal can be recovered by adsorption on marble chips or on palladium-gold gauzes.

Pt catalysts for NH_3 oxidation:

- Pt/Rh 90: 10 or 95: 5
- Pt/Rh/Pd 90:5:5

Contact time ca. 10^{-3} s

During NH_3 oxidation Pt losses occur which increase with increasing pressure. Up to 80% recoverable

Oxidation of Nitrogen(II) Oxide to Nitrogen(IV) Oxide and Dinitrogen(IV) Oxide:

The hot nitrogen(II) oxide-containing gas from the combustion step (e.g. with ca. 10 to 12% NO) is cooled, the heat content being utilized for steam production or waste gas-heating. It is then reacted with additional atmospheric oxygen (secondary air) to nitrogen(IV) oxide (NO_2):

$$2\,NO + O_2 \longrightarrow 2\,NO_2 \qquad \Delta H = -114\ kJ/mol$$

This reaction is favored by low temperatures, the temperature coefficient of the rate constant being negative, and still more strongly by increased pressure due to the volume reduction during the reaction. Dimerization to dinitrogen(IV) oxide is also promoted by low temperatures and high pressures.

$$2\,NO_2 \rightleftharpoons N_2O_4 \qquad \Delta H = -57\ kJ/mol$$

NO oxidation and NO_2 dimerization favored by low temperatures and high pressures

H_2O-content of combustion gases removed by cooling: acid condensate (2 to 50%)

The nitrogen(II) oxide oxidation takes place partly in the waste heat boiler, due to reaction with the excess oxygen present in the combustion gases from the ammonia oxidation, and partly (after addition of secondary air) in the lowest stage of the absorption columns (mostly operated at high pressures) or in an oxidation tower before the absorption column. The higher the pressure in the combustion step the greater the amount of nitrogen(IV) oxide formed during the cooling of the combustion gases. This reacts with the reaction water forming nitric acid, the HNO_3 concentration in these so-called acid condensates being 2 to 50%.

Conversion of Nitrogen(IV) Oxide into Nitric Acid:

The gas mixture obtained by oxidation of nitrogen(II) oxide, containing nitrogen(IV) oxide and dinitrogen(IV) oxide (so-called nitrous gases), is reacted in the third reaction step with water as follows:

$$3\,NO_2 + H_2O \longrightarrow 2\,HNO_3 + NO \qquad \Delta H = -73\ kJ/mol$$
$$N_2O_4 + H_2O \longrightarrow HNO_3 + HNO_2 \qquad \Delta H = -65\ kJ/mol$$

to nitric acid, nitrogen(II) oxide and nitrous acid. The nitrous acid is further oxidized to nitric acid by the (atmospheric) oxygen present, either in the liquid or vapor phase.

The absorption of the nitrous gases in the process water is favored by low temperatures, high pressures and longer contact times. The quantity of process water, of which the acid condensate is a part, is dependent upon the required nitric acid concentration. Higher pressures permit the production of higher nitric acid concentrations (up to 70% HNO_3), since under pressure almost complete absorption of nitrous gases can be attained in a small quantity of process water with low emission of residual gas. Only 45 to 50% nitric acid can be produced at atmospheric pressure.

NO_2/N_2O_4-absorption in water a function of:

- temperature (as low as possible)
- pressure (as high as possible)
- contact time
- mass transfer
- the quantity of water provided

The most important parameter in the absorption is the pressure. At high pressure (up to 15 bar) concentrated acid can be produced and tail gas purification can be dispensed with

1.4.4.2.2 Plant Types

There are basically two types of processes for the manufacture of nitric acid i.e. mono(single)-pressure processes in which ammonia combustion and absorption of nitrogen oxides take place at the same pressure and dual pressure processes in which the pressure in the first stage is lower than that in the second stage. In addition nitric acid plants can be categorized on the basis of operating pressure: low pressure-(L)-, medium pressure-(M)- and high pressure-(H)-plants which operate in the pressure ranges: 1 to 2 bar, 3 to 67 bar and 8 to 12 bar, occasionally up to 15 bar, respectively. The plant type is characterized by the pressure ranges for ammonia combustion and oxidation/absorption.

Modern HNO_3 plants:

- monopressure plants
  - medium pressure 3 to 6 bar
  - high pressure 8 to 15 bar
- dual pressure plants
  combustion at 4 to 6 bar
  oxidation/absorption at 8 to 10 bar

The current tendency in the nitric acid industry is to ever larger plants (capacities up to 1500 t of 100% HNO_3/d) and to ever higher pressures both in the combustion and in the absorption stages to solve emission and other problems. The developments in the USA and in Western Europe are somewhat different: 90% of the plants in the USA being monopressure/high pressure plants (H/H-type), whereas in Western Europe many plants operate in the medium pressure and medium/high pressure ranges (M/M-types and M/H-types respectively).

Plant type selection on the basis of:

- local factors
- raw material and energy costs
- investment costs
- emission regulations

The advantages of H/H-plants are: relatively low plant costs, low space requirements and satisfactory emission values, so that tail gas cleaning is unnecessary. The disadvantages are: high catalyst consumption, high energy consumption (due to compression of gases) and low nitrogen(I) oxide yield. 75 to 80% of the production costs of nitric acid are the cost of ammonia.

Important elements in HNO_3 manufacturing costs:

- ammonia price
- energy costs
- catalyst losses
- amortization of plant

Costs of running the compressors account for almost half of the plant costs

In M/M- and M/H-plants ammonia combustion occurs at comparatively low pressures, the high nitrogen(II) oxide yields are high, the catalyst losses are low and the compression costs are low. Combination with high pressure plants provides a satisfactory solution to absorption and emission problems. Older plants, particularly L/L-type plants, have for environmental reasons been equipped with additional plants to clean up the tail gases.

1.4.4.2.3 Process Description

Air for ammonia combustion has to be carefully prepurified to avoid deactivation of the Pt-catalyst

Utilization of the heat content of the 900°C reaction gases for steam generation reduces the manufacturing costs for nitric acid

Compression energy can be partly recovered by gas expansion driven turbines. Tail gas heating improves energy recovery

The first stage in a nitric acid plant consists of an ammonia evaporator and air compressor whose products are mixed, prewarmed, carefully prepurified with gas filters to remove catalyst poisons and then fed into the combustion chamber in which the gas flows downwards through the platinum gauzes suspended in it. The operating lifetime of catalysts varies from 3 to 18 months depending upon the combustion system. The hot reaction gases with a temperature of ca. 900°C are passed into a heat exchanger (waste heat boiler) in which they are cooled to ca. 150°C [combustion in a L/M-plant type: 10 to 12% NO, 17 to 20% H_2O, 2 to 5% O_2 (by volume) with the remainder being made up of N_2, inert gases and a small amount of NO_2]. The steam generator integrated into the plant produces steam at e.g. 400°C/40 bar which is mostly fed into a local network. This substantially reduces the manufacturing costs of nitric acid. Nitric acid plants with appropriate equipment can supply energy despite the very high energies required for compression, particularly in high pressure plants. Much of the heat liberated in the three exothermic reactions is, however, at such low temperatures (oxidation of nitrogen(II) oxide, absorption of nitrous gases in water) that it cannot be utilized economically.

Compression energy can be partly recovered via gas expansion driven turbines

The acid condensate resulting from the cooling of NO-containing combustion gases is fed into the absorption towers

The nitrogen(II) oxide-containing combustion gas is further cooled in a gas cooler to ca. 20 to 30°C, whereupon most of the water vapor is condensed as a nitric acid-containing acid condensate. This is fed into the absorption towers as part of the process water. The virtually dry gas is oxidized by mixing it with secondary air (blow off air) and also fed into the absorption unit. In dual pressure plants, the reaction gas is compressed to the absorption pressure in an acid resistant nitrous gas compressor and the heat of compression removed by heat exchangers and coolers (heating up the tail gases). Part of the compression energy is recovered by turbines driven by heated tail gases. The nitrous gases are driven up the absorption towers and the process water flowing in countercurrent down the towers absorb the nitrous gases. Here oxidation of the residual nitrogen(II) oxide occurs according to the above equation. The size of the absorption volume is dependent upon this reaction.

Mass transfer systems:

- Raschig rings
- bubble plates
- sieve plates

Most of the large volume absorption towers are constructed of chromium-nickel steel and filled with Raschig rings or with bubble or sieve plates which are sprayed from above with water [which is precooled by supplying the heat for ammonia evaporation (combustion stage)] forming concentrated nitric acid at the bottom of the tower. The acid concentration depends upon the quantity of water fed in at the absorption stage: e.g. ca. 0.20 m^3/t is required for 65% acid and 77.8% nitric acid can be theoretically formed when acid condensate is used as the absorption agent (1.5 mol H_2O is produced per mol NH_3). At higher acid concentrations the emission of nitrogen oxides in the tail gas increases, particularly at low pressures. Absorption at atmospheric pressure or slightly higher pressures is, therefore, only to be found in older plants.

78% acid is theoretically possible if no water is added

At low pressures only weaker acids can be produced, due to too high No_x-values with little process water

Such plants can operate very economically, but may no longer be built due to current legislation concerning nitrous gas emissions.

The residual gas is heated up with the aid of compression heat to ca. 250 to 300°C to improve energy recovery and released into the atmosphere by way of expansion gas driven turbines (with or without precleaning).

In monopressure plants there is no nitrous gas compressor. In plants operating at high pressures e.g. H/H- or M/H-plants, the absorption volume is much smaller: at 10 bar the volume is only one tenth that necessary at 4.6 bar, so only one tower is necessary.

1.4.4.2.4 Manufacture of Highly Concentrated Nitric Acid

Highly concentrated (98 to 99%) nitric acid mainly utilized for nitration

The 50 to 70% nitric acid produced in conventional nitric acid plants is suitable for industrial purposes e.g. the manufacture of fertilizers, the synthesis of ammonium nitrate, for example, requiring 60% acid. However, for nitration reactions in organic synthesis a highly concentrated (ca. 98 to 99%) nitric acid is required. Since nitric acid forms an azeotrope with water at 69.2% nitric acid, concentration of weak acid by distillation is not possible.

Manufacture of highly concentrated nitric acid:

- direct processes (variants of normal HNO_3 synthesis)
- indirect processes (H_2O-removal from weak HNO_3)

Highly concentrated nitric acid can be produced by direct and indirect processes. Direct processes are favored in Western Europe, whereas indirect processes are favored in the USA.

Direct Processes

Direct processes for highly concentrated nitric acid manufacture:

- oxidation of N_2O_4 with pure oxygen in the presence of H_2O under high pressure
- absorption of NO_2/NO in concentrated HNO_3 producing superazeotropic acid, followed by distillation

In the direct highly concentrated nitric acid processes, of which there are many variants, the nitrous gases resulting from the catalytic combustion of ammonia and oxidation of the resulting nitrogen(II) oxide are either separated and the dinitrogen(IV) oxide reacted with oxygen and water forming nitric acid, or dissolved in concentrated nitric acid and the superazeotropic acid distilled. The latter is the more economic process even compared with the indirect processes, because pure oxygen production is not required and the investment costs are lower.

Direct processes for highly concentrated nitric acid manufacture also provide:

- weak acids (in any desired concentration)
- pure N_2O_4

In the Uhde process for manufacturing highly concentrated nitric acid the ammonia combustion is carried out with air at atmospheric pressure and the reaction water is largely separated as acid condensate from the nitrogen(II) oxide upon cooling. The nitrogen(II) oxide is then compressed together with secondary air to e.g. 6 bar. Oxidation takes place in oxidation towers and the residual nitrogen(II) oxide is converted to nitrogen(IV) oxide in a post-oxidative reactor with highly concentrated nitric acid:

$$2\,HNO_3 + NO \longrightarrow 3\,NO_2 + H_2O$$

After cooling and removing residual water, the nitrogen(IV) oxide is physically absorbed in highly concentrated deep frozen nitric acid and is thereby separated from the other components of the gas (nitrogen, residual oxygen). The acid is then distilled producing 98 to 99% nitric acid (sump product), which is partly recycled, and nitrogen(IV) oxide (head product). The latter is liquefied by deep freezing, whereby it almost completely dimerizes to dinitrogen(IV) oxide, which can, if desired, be partly separated off as a byproduct. The liquid dinitrogen(IV) oxide is then stirred with dilute nitric acid and fed back with a high pressure centrifugal pump into the reactor, in which the dinitrogen(IV) oxide/nitric acid/water mixture is oxidized with pure oxygen at a pressure of 50 bar to highly concentrated nitric acid:

$$N_2O_4 + H_2O + 0.5\ O_2 \longrightarrow 2\ HNO_3$$

The gas emerging from the absorption column is scrubbed with acid condensate (ca. 2% nitric acid from the ammonia combustion, see Section 1.4.4.2.1), which reduces the nitrous gas concentration to < 200 ppm, and is then vented. The consumption figures for this process are summarized in the adjoining marginal notes.

In Davy McKee's Sabar process (**S**trong **A**cid **B**y **A**zeotropic **R**ectification) the nitrous gases from the oxidation of nitrogen(II) oxide are absorbed in azeotropic (ca. 68 to 69%) nitric acid in the presence of atmospheric oxygen (at 6 to 13 bar) and superazeotropic acid is formed:

$$2\ NO_2 + 0.5\ O_2 + H_2O \longrightarrow 2\ HNO_3$$

The acid is degassed by blowing out with secondary air and distilled (the head product consisting of highly concentrated acid and the sump product of the azeotropic acid). The azeotropic acid is recycled. The concentration of nitrous gas in the tail gas is <100 ppm. In the Sabar process the manufacture of low or medium concentration acid is possible in addition to highly concentrated acid. These are obtained by adding acid condensate from the combustion of ammonia to the sump of the nitric acid tower.

The Conia process, a pressure process (ca. 5 bar) in small units, produces highly concentrated nitric acid, weak acid in any desired concentration and pure dinitrogen(IV) oxide. In this process most of the combustion water from the ammonia combustion is removed by condensation as 30 to 40% acid condensate. After the oxidation of nitrogen(II) oxide, part of the nitrogen(IV) oxide formed is reacted in countercurrent with acid condensate, additional process water and atmospheric oxygen to medium concentrated nitric acid (50 to 70%) in the usual way. The remaining nitrogen(IV) oxide is processed to highly concentrated nitric acid.

Consumption figures for direct manufacture of highly concentrated nitric acid with O_2-addition per t of 100% HNO_3:

- 0.282 t NH_3
- 125 m^3 O_2
- 285 kWh electrical energy
- 200 m^3 cooling water ($\Delta T = 7°C$)

0.6 t surplus steam

Indirect Extractive Distillation Processes

Highly concentrated nitric acid manufacture by indirect processes:

dehydration of water-containing HNO_3 with concentrated H_2SO_4 or $Mg(NO_3)_2$ solutions

In the USA:
mainly indirect extractive distillation processes:

in Europe:
mainly direct strong nitric processes

Of the various indirect processes for the manufacture of highly concentrated acid only two are industrially important: the sulfuric acid process and the magnesium nitrate process.

In the sulfuric acid process, which poses considerable corrosion problems, medium concentrated nitric acid is first produced using conventional methods (e.g. in a M/M-type unit) as in the magnesium nitrate process. Concentrated sulfuric acid is fed in at the head of the concentrating tower. During the extractive distillation, diluted sulfuric acid accumulates in the sump and 99% nitric acid is driven off. The diluted sulfuric acid is then concentrated by vacuum distillation and recycled.

In the magnesium nitrate process weak acid is distilled with 72% magnesium nitrate solution, whereupon highly concentrated nitric acid is driven off at the head of the dehydration tower. The sump product is then concentrated by vacuum distillation.

1.4.4.2.5 Tail Gases from Nitric Acid Manufacture

Tail gases from HNO_3 plants per t of 100% HNO_3:

- up to 3300 m^3
- NO_x-content: 150 to >2000 ppm

In the manufacture of nitric acid up to 3300 m^3 of the water vapor-saturated tail gases (residual and end gases) are produced per t of 100% nitric acid. They contain up to 97% nitrogen, 1% inert gases, 2 to 4% oxygen (by volume) and, depending upon plant type, 150 to >2000 ppm of nitrogen oxides NO_x (NO, NO_2 and traces of N_2O) calculated on the basis of nitrogen(II) oxide. The nitrogen oxide emission values for low pressure and medium pressure plants are higher. The tail gas quantities can be drastically reduced by carrying out the ammonia combustion and nitrogen(II) oxide oxidation with pure oxygen, but this is uneconomic.

NO_2 content of tail gases (40 to 50% of the NO_x) causes brown coloration (NO is colorless)

Plants for manufacture of highly concentrated nitric acid and modern high pressure absorption plants:

- optimum mass transfer plates
- effective cooling
- sufficiently large reaction volumes

do not have tail gas emission problems (NO_x: 100 to 200 ppm)

Nitric acid plants were in the past identifiable by the yellow-brown color of their tail gas emissions. This color is due to their nitrogen(IV) oxide content (ca. 40 to 50% of the NO_x-content). Modern plants with high pressure absorption steps (ca. 8 to 15 bar, mono or dual pressure processes), optimum mass transfer plates (sieve plate technology), sufficiently large absorption volumes (and hence long contact times) and low cooling water temperatures do not pose any emission problems, because their nitrogen oxide content is <200 ppm. The tail gases are therefore virtually colorless. The increased environmental protection requirements for cleaner air are fulfilled by new plants without the need for additional cleaning steps. The attainment of low NO_x emission values of e.g. 100 to 200 ppm is a considerable advance and could only be achieved by optimizing the absorption step, since subsequent nitrogen oxide removal from the tail gas is very expensive (necessitating the use of sensitive precious metal catalysts, additional fuel and energy and may cause other environmental problems). In modern medium pressure plants (monopressure plants operating at pressures of 5 to 6 bar), however, the nitrogen oxide content in the tail gas is up to 500 ppm and therefore a post-cleaning step is necessary to attain emission values below 200 ppm. The construction of low pressure absorption units in the Federal Republic of Germany has ceased due to emission values $\geq$ 2000 ppm in the absence of a cleaning step. The nitrogen oxide emissions of nitric acid plants currently account for a very small proportion of all NO_x-emissions, which predominantly arise from power stations and motor vehicles.

Removal of NO_x from tail gases is often more difficult than improving the absorption technology

Various processes can be used for cleaning the tail gases of older nitric acid plants or newer medium pressure plants, but often give rise to problems.

Tail gas cleaning of older sub-optimal plants by:
- wet processes
- dry processes (thermal, catalytic, absorptive)

Final emission values of 100 ppm can be achieved by alkali scrubbing e.g. with sodium hydroxide, ammonia or urea solutions, but disposal of the nitrites and nitrates formed is problematic.

Alkali scrubbing is encumbered by disposal of the nitrite and nitrate formed.

NO_x-reduction with hydrocarbons:
- cost intensive
- hydrocarbon emissions

Reductive postcombustion is theoretically possible, in which the tail gases, which still contain a few % of oxygen react thermally at temperatures of 1000°C or catalytically at 170 to 600° with e.g. natural gas, hydrogen, heating oil or carbon monoxide, whereupon the nitrogen oxides are reduced to nitrogen. The precious metal catalyst is, however, rapidly poisoned, the fuel requirements are high, particularly in the case of high residual oxygen concentrations, and the secondary emissions of mainly methane and carbon monoxide pose new problems. The process utilizing selective catalytic reduction with ammonia is favored:

NO_x-reduction with NH_3

$$4\,NH_3 + 6\,NO \longrightarrow 5\,N_2 + 6\,H_2O$$
$$8\,NH_3 + 6\,NO_2 \longrightarrow 7\,N_2 + 12\,H_2O$$

Precious metal or oxide catalysts are used. In the BASF process a vanadium(V) oxide catalyst is utilized and the process operates at a temperature of 230 to 350°C at the pressure of the absorption step, according to the following reactions:

$$NO + NO_2 + 2\,NH_3 \longrightarrow 2\,N_2 + 3\,H_2O$$

and:

$$4\,NO + 4\,NH_3 + O_2 \longrightarrow 4\,N_2 + 6\,H_2O.$$

The residual nitrous gas content in the vented gases is less than 200 ppm and the ammonia content is 10 to 20 ppm. The process is mainly used with monopressure/medium pressure plants (M/M-type) and has made this plant type competitive with the dual pressure plants of the M/H-type. This process is not suitable on energy grounds for use with low pressure plants (< 3 bar). Use of the BASF process slightly reduces the overall yield of ammonia e.g. in the M/M-process from 96 to 95.3%.

A further possibility is the absorption of the nitrogen oxides on molecular sieves (zeolites) at low temperatures. The nitrogen oxides are released at temperatures of 250 to 350°C and are fed back into the nitric acid process.

1.4.4.3 Nitric Acid Applications

HNO_3-consumption spectrum in the USA in 1992 according to use:

total consumption $8.9 \cdot 10^6$ t

• ammonium nitrate	77.6%
• adipic acid	7.9%
• nitrobenzene	4.0%
• toluene diisocyanate	4.2%
• various	6.3%

Most of the nitric acid is utilized in the form of 50 to 70% acid for the manufacture of nitrogen-containing fertilizer, particularly ammonium nitrate. Ammonium nitrate is also used as an explosive e.g. in mining, due to its low explosion temperature (safety explosive). Other industrially important nitrates are sodium nitrate, a speciality fertilizer and oxidizing agent in the glass and enamel industries, and calcium and potassium nitrates, which are also used as fertilizers. Nitric acid is also utilized in the digestion of raw phosphate (Odda process, which is not operated in the USA, see Section 2.1.2.4):

$$Ca_5[(PO_4)_3(F)] + 10\,HNO_3 \longrightarrow 5\,Ca(NO_3)_2 + 3\,H_3PO_4 + HF$$

Worldwide 75 to 85% of the nitric acid production is utilized in the inorganic fertilizer sector and in the USA 60 to 70%. In the USA 15% is used in the blasting agent and explosive sector and up to 15% for adipic acid production (precursor for fibers and plastics). Nitric acid is also used for pickling stainless steel, for other metallurgical purposes and in the nuclear fuel cycle.

References for Chapter 1.4.4: Nitric Acid

Reviews:

Ullmann's Encyclopedia of Industrial Chemistry. 1991. 5. Ed., Vol. A 17, 293 – 339, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1996. 4. Ed., Vol. 17, 80 – 107, John Wiley & Sons, New York.

Winnacker-Küchler. Chemische Technologie. 1982. 4. Aufl., *Anorganische Technologie I*, Bd. 2, Carl Hanser Verlag, München.

Commercial Information:

Chemical Economics Handbook. 1977. *Nitrogen Industry Overview*, Stanford Research Institute, Menlo Park, California

1.5 Phosphorus and its Compounds

1.5.1 Phosphorus and Inorganic Phosphorus Compounds

1.5.1.1 Raw Materials

The most important group of minerals for the manufacturing of phosphorus and phosphorus compounds are the apatites, which have the general formula

Most important raw material for phosphor chemistry: apatite $Ca_5(PO_4)_3(F, OH, Cl)$

$$Ca_5(PO_4)_3\ (F, OH, Cl)$$

The commercially most important of these are the fluoroapatites. The aluminum phosphate deposits in Africa and South America and guano are much less important.

Phosphate ores, especially sedimentary apatites, are widely distributed. There are massive beds particularly in the USA and Africa. The estimated phosphate content of these reserves is many tens of millions of tons, which at the rate of present exploitation is sufficient for over 100 and up to 1000 years. An estimate of the reserves, the exploitation of which, according to current standards, is still not yet economic, is given in Table 1.5-1.

Estimated apatite reserves: $> 100 \cdot 10^9$ t

Table 1.5-1. Reserves of Phosphate Ores in 10^6 t (estimated).

World	USA	Australia	Marocco	Senegal	South Africa	Togo	Tunisia	Other Western Countries	Eastern Europe
131, 000	8500	1900	42,000	200	60	50	280	56,000	22,000

Apatite deposits:
- sedimentary
- magmatic

Sedimentary apatite deposits are in quantity much more important than the magmatic ones.

The magmatic deposits (Kola: Russia, Phalaborwa: South Africa) are extracted in open cast mines or underground mines. They have a high phosphate content and are free of organic impurities. The phosphate ore is extracted together with gangue, which is separated by flotation.

The sedimentary deposits in the USA are exploited by open cast mining and those in North Africa by open cast mining and underground mining. Beds with phosphorus pentoxide contents down to 5% are exploited, wherefrom a marketable material can be obtained by subsequent beneficiation. The individual beneficiation steps are: grinding, washing, sieving, magnetic separation of iron oxides, flotation to remove quartz and calcination to remove organic impurities. A uniform marketable quality is finally obtained by mixing.

Data regarding the phosphorus content in apatites are given either in % P_2O_5 or in $Ca_s(PO_4)_3$ (bone phosphate of lime, BPL). 1% diphosphorus(V) oxide is equivalent to 2.19% BPL. Table 1.5-2 gives a survey of the diphosphorus(V) oxide contents of raw phosphates from different deposits.

Table 1.5-2. P_2O_5-Content of Raw Phosphates in % by weight.

Kola	Phalaborwa	Florida	Idaho	Morocco
39.0	38.4	30.4	31.2	36.8

Marketable raw phosphate contains >30% P_2O_5

Fluorine content of apatite:

between 2.3.and 4.8% by weight. Some apatites contain uranium.

Marketable raw phosphate generally contains more than 30% diphosphorus(V) oxide.

The fluorine content of the raw phosphates mentioned in Table 1.5-2 is between 2.3 and 4.8% by weight. The raw phosphate contains numerous other elements particularly aluminum, iron and magnesium, as well as rare earths and sometimes uranium, all in the form of compounds.

The worldwide capacity and capacities in different regions in 10^6 t/a are given in Table 1.5-3.

Table 1.5-3. Phosphate ore capacities worldwide and in different regions in 1983, 1988 and 1993 in 10^6 t/a (as P_2O_5).

	1983	1988	1993
World	43.4	51	52
Western Europe	0.2	0.2	0.2
Former States of the USSR	10	12	12
USA	19	22	16
South America	2	2	2
Africa	14	14	13

The evolution in raw phosphates imports into the Federal Republic of Germany in the period 1981 to 1993 is shown in Table 1.5-4.

Table 1.5-4. Raw Phosphate Imports into the Federal Republic of Germany in 10^3 t/a.

	1981	1984	1987	1990	1993
phosphate ore	6770	6974	5821	4691	2814
wet-process acid	622	888	1128	755	643

1.5.1.2 Products

1.5.1.2.1 Phosphoric Acid

Economic Importance and Applications

Phosphoric acid is produced both by the digestion of apatite with sulfuric acid (wet-process phosphoric acid) and by combustion of phosphorus ("furnace phosphoric acid"). Most (> 75%) of the mined apatite is utilized in the manufacture of phosphoric acid. The proportion of furnace acid is decreasing in favor of the wet process acid, due to the high energy requirements of phosphoric acid manufactured by phosphorus combustion. The use of furnace acid for fertilizer production, previously usual in the USA, has almost ceased. In those application areas in which high purity phosphoric acid is required (e.g. phosphates for detergents) post-purified wet-process acid is being increasingly used. The phosphoric acid capacities in 1993 are given in Table 1.5-5.

More than 75% of apatite mined is converted into phosphoric acid

In 1993 in the USA and Western Europe together produced ca. 2000 · 10^3 t of phosphoric acid for industrial applications, of which 760 · 10^3 t was used for extraction processes.

Table 1.5-5. Phosphoric Acid Capacities in 1993 in 10^3 t/a.

		1993 Capacity 10^3 t/a
World		34 710
North America:	USA	13 320
	Canada	575
Central America		448
South America		830
Western Europe		1 380
Eastern Europe		2 325
Former States of the USSR		5 870
Africa		5 490
Middle East		1 940
Asia, Australasia:	excl. Japan	2 570
	Japan	410

Applications of phosphoric acid:

- mainly utilized in fertilizer manufacture > 90% of wet-process acid in the USA, ca. 50% in FRG

- production of:
  phosphates for detergents
  industrial cleaning agents
  water treatment agents
  nutrition supplements for animal feedstuffs
  flame retarding agents

Phosphoric acid is directly used for metal treatment

By far the most important product produced from phosphoric acid is fertilizers. More than 90% of the wet-process acid is utilized in the USA in this sector compared with 50% in the Federal Republic of Germany. Other applications are, for example, in:

- phosphates for detergents (declining strongly)
- industrial cleaning agents
- water treatment agents
- nutrition supplements for animal feedstuffs
- flame retarding agents

Phosphoric acid is directly used in the treatment of metals. For applications in the food sector, furnace acid is generally used. Phosphates for washing powders are manufactured from both furnace acid and purified wet-process acid.

Manufacture of Phosphoric Acid

Manufacture of Wet-Process Phosphoric Acid

"Wet-Process Phosphoric Acid":

by reaction of apatite with sulfuric acid and separation of the calcium sulfate formed as its dihydrate or its hemihydrate

Wet Process. The reactions in the digestion of apatite with sulfuric acid are complex. The calcium phosphate portion of apatite reacts with sulfuric acid as follows:

$$Ca_3(PO_4)_2 + 3\,H_2SO_4 \longrightarrow 3\,CaSO_4 + 2\,H_3PO_4$$

whereupon, depending upon the process conditions, the calcium sulfate precipitates either as its dihydrate or as its hemihydrate (see below). The "fluoride part" of the apatite is either removed as gaseous silicon tetrafluoride in the presence of silica and absorbed in scrubbers as aqueous hexafluorosilicic acid, or is largely removed as the sparingly soluble sodium hexafluorosilicate by adding a sodium compound. Part of the fluoride remains in the acid.

Fluoride is mostly removed as gaseous silicon tetrafluoride and recovered in the form of hexafluorosilicic acid

The other components of apatite (iron, aluminum, uranium) partly pass into solution as salts and are partly precipitated with the calcium sulfate. Any carbonate present produces carbon dioxide during digestion. If sedimentary noncalcined apatite is utilized, the phosphoric acid obtained is colored black by the organic impurities.

In principle there are two digestion processes:

- processes in which calcium sulfate dihydrate (gypsum) is formed and is separated off;
- processes in which calcium sulfate hemihydrate occurs as an intermediate of final product.

Digestion processes:

- calcium sulfate dihydrate is formed and is separated off
- processes in which calcium sulfate hemihydrate occurs as an intermediate or final product

Three variants of the hemihydrate process are operated industrially, one or other having more or less importance:

- **variant 1**: calcium sulfate precipitates directly as its hemihydrate and is filtered off;
- **variant 2**: calcium sulfate precipitates initially as its dihydrate and is subsequently recrystallized as its hemihydrate;
- **variant 3**: calcium sulfate precipitates initially as its hemihydrate and is recrystallized as its dihydrate.

Three variants on the hemihydrate process: the calcium sulfate is formed as:

- **variant 1**: hemihydrate and is filtered off
- **variant 2**: dihydrate and is recrystallized as the hemihydrate
- **variant 3**: hemihydrate and is recrystallized as the dihydrate. Recrystallization of variant 3 can be carried out after filtering off the calcium sulfate or in situ

The recrystallization in variant 3 can proceed either after the calcium sulfate hemihydrate had been filtered off or in situ.

Processes yielding anhydrite (anhydrous calcium sulfate) have little industrial importance.

The crucial step in the digestion of apatite is the formation of calcium sulfate. Its properties, in particular, its ability to be filtered, are very important e.g. for throughput optimization. The incorporation of phosphate into the crystal lattice of calcium sulfate reduces the phosphate yield and can render the calcium sulfate unusable in the building industry.

The choice of process depends upon a number of factors such as:

- raw material price
- source of the apatite
- energy costs and energy availability at the plant site

- possibilities regarding the further utilization of the calcium sulfate byproduct.

The most widely used process is the dihydrate process. The process parameters of the different processes are compared in Table 1.5-6.

Table 1.5-6. Apatite Digestion Process, Comparison of Process Variants.

Process	Digestion temperature [°C]	Recrystallization temperature [°C]	Acid concentration [% P2O5]	P2O5-yield [%]	usability of CaSO4 in building industry
Dihydrate	71 to 85	-	28 to 32	93	no
Hemihydrate Variant 1	91 to 99	-	45 to 50	91 to 94	no
Hemihydrate Variant 2	62 to 68	93 to 99	33 to 38	97	yes
Hemihydrate Variant 3	91 to 99	60 to 19	40 to 50	96 to 98	yes

Process developers:

- *Dihydrate*: Prayon, Dorr, St. Gobain/Rhone Progil, Fisons, Kellog-Lopker etc.
- *Hemihydrate, variant 1*: Fisons
- *Hemihydrate, variant 2*: Prayon, Nissan, Mitsubishi, Fisons etc.
- *Hemihydrate, variant 3*: Breyer/Heurty, Dorr, Fisons

The most important requirements for modern plants operating the dihydrate process are:

- reaction temperature of ca. 80°C
- separate feed for ore and sulfuric acid
- vacuum evaporation cooling to ensure a constant reaction temperature (exothermic reaction!)
- monitoring of sulfuric acid (sulfate) concentration and if necessary recycling part of the dihydrate

These measures enable a uniform growth of the dihydrate crystals which is indispensable for efficient filtration.

The phosphoric acid obtained in the dihydrate process has a concentration of 28 to 32% (as P_2O_5). The yield, based on the phosphorus content of the apatite, is ca. 95%. Modern plants have reactors with capacities up to over 1000 t P_2O_5 per day. Fig. 1.5-1 shows a (simplified) flow sheet of a dihydrate plant.

Dihydrate process:

- most widely operated process
- supplies phosphoric acid with 28 to 32% P_2O_5
- gypsum must generally be disposed of

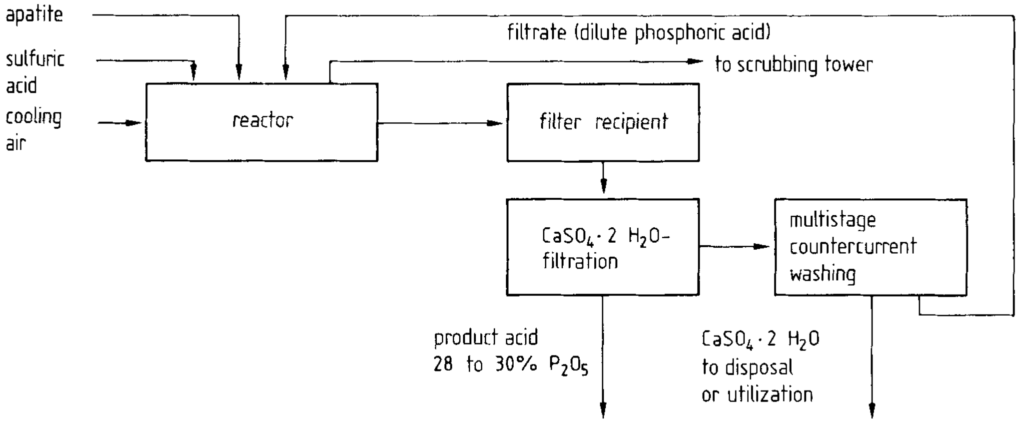


Fig. 1.5-1. Flow Sheet for Phosphoric Acid Manufacture using the Dihydrate Process.

The three industrially operated variants of the hemihydrate process produce different products:

With *variant 1*, in which temperatures of 90 to 100°C are used and in which the hemihydrate is directly filtered off, a relatively concentrated acid (45 to 50% P_2O_5) is obtained, but the yield of diphosphorus(V) oxide is low.

hemihydrate process, variant 1:

- supplies phosphoric acid with 45 to 50% P_2O_5
- P_2O_5-yield is relatively low
- calcium sulfate not marketable

With *variant 2*, in which dihydrate is obtained initially at 60 to 70°C and the filter cake resulting from filtration is recrystallized to the hemihydrate by slurrying in sulfuric acid at temperatures > 90°C, a phosphoric acid with a content of 33 to 38% (as P_2O_5) is obtained and the yield of diphosphorus(V) oxide is very high.

Hemihydrate process, variant 2:

- produces phosphoric acid with 33 to 38% P_2O_5
- P_2O_5-yield very good
- calcium sulfate marketable

With *variant 3*, in which the hemihydrate is formed at 90 to 100°C and changes into the dihydrate upon cooling to 50 to 60°C, the diphosphorus(V) oxide content of the calcium sulfate is less than 0.3% due to the recrystallization and the yield of diphosphorus(V) oxide is higher than that with the dihydrate process. The Nissan process is typical of this process variant.

Hemihydrate process, variant 3:

- produces phosphoric acid with 40 to 50% P_2O_5
- P_2O_5-yield very good
- calcium sulfate marketable

With *variant 3 with recrystallization after filtering off of the hemihydrate*, the acid obtained has a concentration as high as in variant 1 (> 42% P_2O_5). After filtration, the hemihydrate is slurried in dilute acid and recrystallized to the dihydrate. This process calls for very uniformly-shaped hemihydrate crystals and for very complicated recycling of the acid. However, it uses particularly little energy, since the acid produced does not need to be concentrated and the phosphate ore used does not have to be so finely ground as with the dihydrate process. A comparison of the classical dihydrate process with the Fisons hemihydrate process with filtration and conversion of the hemihydrate is given in Table 1.5-7.

Table 1.5-7. Comparison of the Consumption Figures per t of P_2O_5 produced for a Dihydrate Process and a Hemihydrate Process (Variant 3 with filtration of the hemihydrate and conversion to the dihydrate).

Requirements/t P_2O_5 produced	Dihydrate process	Hemihydrate process, variant 3
t phosphate ore	3.45	3.38
t sulfuric acid	2.8	2.74
m^3 cooling water	37.5	23.5
m^3 process water	7.0	7.0
t steam	2.0	0.2
kWh electricity	120	130

Fig. 1.5-2 shows a flow sheet of the Fisons hemihydrate process.

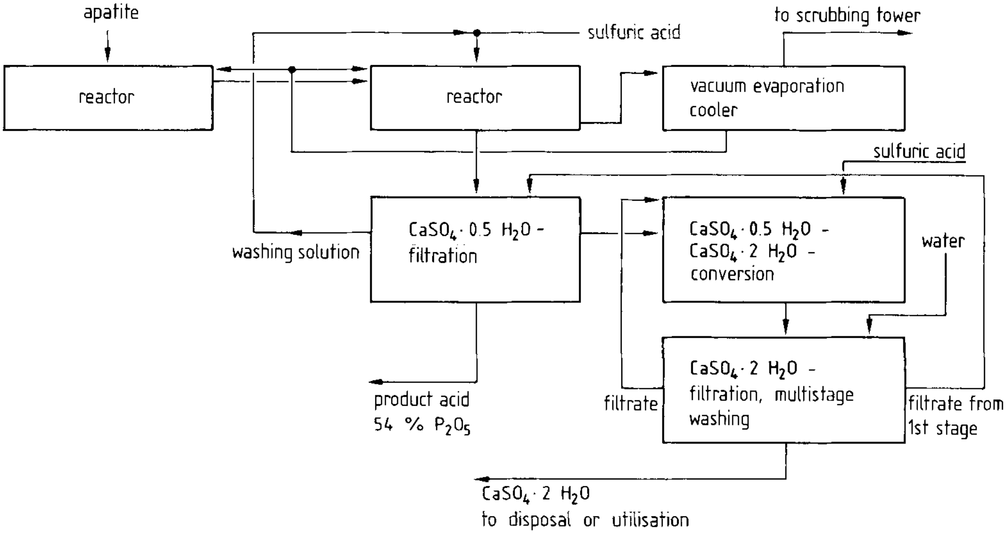


Fig. 1.5-2. Flow Sheet for Phosphoric Acid Manufacture using the Fisons Hemihydrate Process (variant 3).

Concentration of acid: The phosphoric acid produced in several of the above-mentioned processes may, depending upon the application (currently mainly fertilizer manufacture), have to be concentrated. Fertilizer production requires acids containing between 40 and 54% diphosphorus(V) oxide. For transportation purposes further concentration to 52 to 72% diphosphorus(V) oxide is required. The use of certain evaporation processes, e.g. submerged burner, vacuum evaporation etc., to concentrate the phosphoric acid is problematical due to the high corrosiveness of the acid, the formation of precipitates and the release of acid-containing gases (fluorine compounds and phosphoric acid mist). Furthermore, they are very energy intensive.

Dilute acids have to be concentrated:

- to 40 to 54% P_2O_5 for fertilizer manufacture
- to 52 to 72% P_2O_5 for shipping

Purification of wet-process acid: Wet process acid is very impure. During concentration and subsequent standing, wet-process acid deposits a considerable fraction of its insoluble impurities as sediment. These "deslimed" acids are transportable. Table 1.5-8 gives the average composition of such acids.

Table 1.5-8. Average Composition of US Wet-Process Acids after Concentration and Desliming in % by weight.

P_2O_5	Fe_2O_3	Al_2O_3	MgO	SO_4^{2-}	F	organic matter	water insoluble
53.1	1.3	1.6	0.6	3.7	0.9	0.7	2.0

Further concentration to acids with diphosphorus(V) oxide contents of ca. 67 to 72% reduces the fraction of certain impurities even further e.g. the fluoride content is thereby reduced to 0.4%.

Much more extensive purification is possible by:

- precipitation of troublesome ions;
- multistage liquid-liquid countercurrent extraction of the phosphoric acid.

Purification of wet-process acid by:

- concentration and desliming
- precipitation of such troublesome ions as copper, arsenic, sulfate
- liquid-liquid extraction yielding pure phosphoric acid and in some processes a residue of more strongly contaminated acid. Yield of pure phosphoric acid up to 98%

In precipitation purification, heavy metal ions such as copper and arsenic are precipitated as their sulfides and sulfate is precipitated as barium sulfate.

In liquid-liquid extraction three types of extraction agents are used:

- completely water miscible agents, such as methanol or isopropanol;
- partially water miscible agents, such as butanol, isoamyl alcohol, n-heptanol;

- water immiscible agents, such as tri-n-butyl phosphate or di-isopropyl ether.

Upon mixing the impure phosphoric acid with the organic extraction agent two phases are always formed: one consists of a solution of the purer phosphoric acid in the organic extraction agent and the other of an aqueous phosphoric acid solution together with the impurities. Pure acid can be recovered from the organic phase by stripping with water, distilling off the solvent or temperature variation. Depending upon the process used, phosphoric acid yields between 85 and 98% are obtained.

The quality of the acids produced is, depending upon the process used, between industrial and food grades. The strongly contaminated acid remaining after production of pure phosphoric acid can in some processes still be used for fertilizer manufacture.

In 1993 the capacity for extracting purified phosphoric acid in the USA and Western Europe was together $850 \cdot 10^3$ t/a.

It is possible to extract uranium from wet-process phosphoric acid

Processes to extract impurities from phosphoric acid and thereby to purify the acid are currently not operated industrially. However, it is possible to extract uranium from phosphoric acid.

Manufacture of Furnace Phosphoric Acid

"Furnace" phosphoric acid:
- combustion of white phosphorus
- hydration of the diphosphorus(V) oxide formed

Furnace phosphoric acid is obtained by the combustion of white phosphorus in air and the absorption of the resulting diphosphorus(V) oxide in water (in practice dilute phosphoric acid).

$$
\begin{aligned}
4\,P + 5\,O_2 &\longrightarrow P_4O_{10} \\
P_4O_{10} + 6\,H_2O &\longrightarrow 4\,H_3PO_4
\end{aligned}
$$

Two processes are industrially operated: the "IG" and "TVA (Tennessee Valley Authority)" processes. In the TVA-process combustion and absorption take place in separate towers, in the IG-process in a single tower. In this process the walls of the towers are protected from the hot phosphorus flame by pumped phosphoric acid. This pumped phosphoric acid removes the heat of reaction by being circulated through a heat exchanger and provides the water for phosphoric acid formation. The acid produced is extracted from the pumped phosphoric acid. Phosphoric acid mist in the tail gases (6 to 8% of residual oxygen) is removed before venting, for example by venturi scrubbers. The construction materials used have to exhibit very high corrosion resistance.

(Poly)phosphoric acids are thereby produced with diphosphorus(V) oxide contents of 54.5 and 61.5%. (In the USA, polyphosphoric acids with diphosphorus(V) oxide contents of 76 or 84% are often produced to save on transport costs. These are diluted on site before use.) Furnace phosphoric acids are very pure. If necessary, the low arsenic content can be reduced to less than 0.1 ppm by treatment with hydrogen sulfide and filtration of the sulfide formed.

1.5.1.2.2 Phosphoric Acid Salts

The phosphoric acid salts in fertilizers (calcium hydrogen phosphate, ammonium phosphate and mixtures of different phosphoric acid salts) are dealt with in Section 2.1: Fertilizers. Of the phosphates industrially produced for non-fertilizer applications, the following are discussed below:

- sodium mono- and polyphosphates
- ammonium phosphates
- tetrapotassium diphosphate
- calcium phosphates

Phosphoric acid salts used in non-fertilizer applications:

sodium mono- and polyphosphates; ammonium phosphates; tetrapotassium diphosphate; calcium phosphates

Economic Importance and Applications

Sodium Phosphates

Quantitywise, pentasodium triphosphate [sodium tripolyphosphate (STPP)] is the most important sodium phosphate. Table 1.5-9 gives the capacities for pentasodium triphosphate, which is primarily used in detergents and cleaning agents.

Most important sodium phosphate is pentasodium triphosphate, mainly used in detergents and cleaning agents

Table 1.5-9. Production of Pentasodium Triphosphate (STPP) in 10^3 t/a.

	1983	1988	1993
USA	600	500	300
Mexico		100	150
Western Europe	1200	800	600

The reduction in pentasodium triphosphate production in the 1970's, particularly in the USA, was due to the passing on ecological grounds of legislation reducing the maximum permissible pentasodium triphosphate content in household detergents (Table 1.5-10).

The consumption of *all* other sodium phosphates (excluding chloro trisodium phosphate) in the USA in 1993 was $140 \cdot 10^3$ t.

Table 1.5-10. Consumption of Sodium Phosphates in the USA in 10^3 t/a.

1978	1983	1988	1993
630	570	450	260

Applications for mono-, di-, and tri-sodium phosphates:
- metal cleaning
- phosphatizing
- boiler water treatment
- buffer systems
- in the food sector
- in animal nutrition

for disodium dihydrogen phosphate:
- as baking powder

for tetrasodium diphosphate:
- in industrial cleaning agents

for high molecular weight sodium polyphosphates:
- in food manufacture, for stabilization of pigment suspensions and in tanning

Applications: Mono-, di- and trisodium phosphates are used in metal cleaning, for phosphatizing, in boiler water treatment and for buffer systems e.g. in the textile industry. Disodium hydrogen phosphate is used in the food sector and in animal nutrition.

Disodium dihydrogen diphosphate is used as baking powder and tetrasodium diphosphate in industrial cleaning agents.

Higher molecular weight sodium polyphosphates are utilized in the manufacture of processed cheeses, condensed milk and frankfurters and as pigment suspension stabilizers and in the tanning of leather.

Ammonium Phosphates

The ammonium phosphate production for the non-fertilizer sector in the USA in 1993 was $47 \cdot 10^3$ t.

Applications: Their main application is as ammonium phosphates in fertilizers. In addition, they are used in fire protection e.g. as an additive in fire-extinguishing agents for fighting forest fires, as flame retardants in paper, textiles and poly(urethanes), in the prevention of afterglow in matches and as a component of intumescent paints (flame retarding coatings). They are also used in small quantities in animal nutrition, particularly for cattle.

Tetrapotassium Diphosphate

The production of tetrapotasium diphosphate in the USA in 1993 was $22 \cdot 10^3$ t.

Applications: Tetrapotassium diphosphate is used in liquid cleaners due to its high solubility in water.

Calcium Phosphates

The main use of calcium phosphates outside the fertilizer sector is in animal feedstuffs. The different calcium phosphates used are:

- monocalcium phosphate - $Ca(H_2PO_4)_2$ (calcium dihydrogen phosphate) or its hydrate
- dicalcium phosphate - $CaHPO_4$ (calcium hydrogen phosphate) or its hydrate
- defluoridated apatite - $Ca_5(OH)(PO_4)_3$

$620 \cdot 10^3$ t of calcium phosphates (on the basis of P_2O_5) was consumed in the USA in 1993, of which $590 \cdot 10^3$ t was utilized in the manufacture of foodstuffs and the rest in other industrial applications.

Calcium phosphates are mainly used in the foodstuffs sector

In animal nutrition applications calcium phosphates are also used as mixtures with the phosphates of other metals, particularly sodium and magnesium. Calcium phosphates are also utilized as baking powder (monocalcium phosphate) and in toothpastes (dicalcium phosphate dihydrate). Dicalcium diphosphate, which does not react with fluorides, is utilized in fluoride-containing toothpastes.

Other applications:

- as baking powder
- as a cleaning agent in toothpastes

Manufacture of Phosphates

Sodium Phosphates

Sodium monophosphates: Sodium monophosphates are manufactured from furnace and (post-purified) wet-process acid and sodium carbonate or sodium hydroxide.

Sodium monophosphates:
from phosphoric acid and sodium carbonate or sodium hydroxide

$$H_3PO_4 + NaOH \longrightarrow NaH_2PO_4 + H_2O$$
$$H_3PO_4 + 2\,NaOH \longrightarrow Na_2\,HPO_4 + 2\,H_2O$$
$$H_3PO_4 + 3\,NaOH \longrightarrow Na_3\,PO_4 + 3\,H_2O$$

Sodium hydroxide has to be used in the manufacture of trisodium phosphates, since sodium carbonate is not alkaline enough. The salts, which can be anhydrous or hydrated, are produced by conventional techniques. In the dehydration of both hydrogen phosphates particular temperatures must be maintained to avoid condensation to di- or poly-phosphates.

Sodium diphosphates:
from hydrogen monophosphates by thermal dehydration

Sodium di- and poly-phosphates: Diphosphates, disodium dihydrogen diphosphates and tetrasodium diphosphates are industrially produced by heating sodium hydrogen phosphates.

$$2\,NaH_2PO_4 \xrightarrow{245\,°C} Na_2H_2P_2O_7 + H_2O$$

$$2\,Na_2HPO_4 \xrightarrow{300\text{–}900\,°C} Na_4P_2O_7 + H_2O$$

Both reaction time and temperature must be limited during production to prevent further condensation to higher molecular weight phosphates.

Condensation can be carried out in rotary kilns or in spray towers.

Polyphosphates: Pentasodium triphosphate is obtained by the condensation of sodium dihydrogen phosphate and disodium hydrogen phosphate in a 1:2 ratio:

pentanatriumtriphosphate:
$2\,Na_2HPO_4 + NaH_2PO_4 \xrightarrow{300\text{–}550\,°C} Na_5P_3O_{10} + 2\,H_2O$

$$2\,Na_2HPO_4 + NaH_2PO_4 \xrightarrow{300\text{–}550\,°C} Na_5P_3O_{10} + 2\,H_2O$$

Industrially, a phosphoric acid solution is used which is neutralized with the appropriate quantity of sodium hydroxide or sodium carbonate. Condensation of the monophosphate solution is carried out in one or more stages in spray towers or rotary kilns.

The anhydrous pentasodium tripolyphosphate produced has a high and low temperature modification, which react at different rates with water to the hexahydrate. The proportions of the two modifications is dependent upon the temperature at which condensation takes place.

Higher molecular weight polyphosphates: Oligomeric polyphosphates with n = 2 (tetraphosphate) to n = ca. 25 (Graham's salt) can be obtained upon condensation of disodium hydrogen phosphate with sodium dihydrogen phosphate by increasing the proportion of sodium dihydrogen phosphate in the mixture.

The manufacture of these glassy polyphosphates or melt phosphates occurs as follows:

$$2\ Na_2HPO_4 + n\ NaH_2PO_4 \xrightarrow{600\ to\ 800\ °C}$$
$$(n+1)H_2O + (NaO)_2P(O)\text{—}[OP(O)(ONa)]_n\text{—}OP(O)ONa)_2$$
n: 2 to ca. 25

$(NaO)_2P(O)\text{-}[OP(O)(ONa)_2]_n\text{-}OP(O)(ONa)_2$
n: 2 to ca. 25, "glassy polyphosphates"

Sodium dihydrogen phosphate is converted by way of disodium dihydrogen diphosphate (see above) to the high molecular weight Maddrell's salt (n > 1000) upon heating at temperatures above 250°C.

Due to the high corrosivity of melts containing sodium polyphosphate, it is produced in vats lined with zirconium silicate bricks. When the reaction is complete, the melt is quenched on cooling rollers. In a process developed by Hoechst AG (FRG), the polymeric phosphates are obtained by phosphorus combustion with air in the presence of sodium hydroxide in a graphite-lined tower. The total energy for the process is provided by the combustion of the phosphorus.

Ammonium Phosphates

Industrially, three compounds are produced and utilized: ammonium dihydrogen phosphate, diammonium hydrogen phosphate and ammonium polyphosphate. The two hydrogen phosphates are obtained from ammonia and pure phosphoric acid. If the ammonia is added stepwise, wet-process acid can also be used.

Ammonium dihydrogen phosphate and diammonium hydrogen phosphate:

- from ammonia and phosphoric acid

Ammonium polyphosphate $[NH_4PO_3]_n$:

- from phosphoric acid and urea or diammonium phosphate and diphosphorus(V) oxide

$$H_3PO_4 + NH_3 \longrightarrow NH_4H_2PO_4$$
$$H_3PO_4 + 2NH_3 \longrightarrow (NH_4)_2HPO_4$$

Diammonium hydrogen phosphate has a noticeable partial pressure of ammonia at room temperature. The tendency of ammonium hydrogen phosphates to split off ammonia at high temperatures means that higher molecular weight ammonium polyphosphates cannot be produced using the hydrogen monophosphates analogously to sodium polyphosphates. Industrially, they are produced in an ammonia atmosphere from urea and phosphoric acid, or diammonium phosphate and diphosphorus(V) oxide.

$$n\ H_3PO_4 + n\ H_2NCONH_2 \longrightarrow [NH_4PO_3]_n + n\ CO_2 + n\ NH_3$$

Potassium Phosphates

Tetrapotassium diphosphate:

from dipotassium hydrogen phosphate by thermal dehydration

Only tetrapotassium diphosphate is of major industrial importance, due to its high water solubility. It is produced in an analogous way to the sodium compound from dipotassium hydrogen phosphate.

$$2\ K_2HPO_4 \xrightarrow{350\text{–}400\ ^\circ C} K_4P_2O_7 + H_2O$$

Calcium Phosphates

Calcium hydrogen phosphates:

from calcium oxide, or calcium hydroxide, and phosphoric acid

The industrially most widely utilized calcium phosphates are:

- $Ca(H_2PO_4)_2$ - monocalcium phosphate (calcium dihydrogen phosphate) and
- $CaHPO_4$ - dicalcium phosphate (calcium hydrogen phosphate)

are produced by the reaction of calcium oxide, calcium hydroxide or other calcium salts with pure or post-purified phosphoric acid:

$$\begin{array}{ll} CaO + 2\ H_3PO_4 \longrightarrow Ca(H_2PO_4)_2 + H_2O & \text{(idealized} \\ CaO + H_3PO_4 \longrightarrow CaHPO_4 + H_2O & \text{equations)} \end{array}$$

Both compounds are manufactured in anhydrous and hydrated forms.

Defluoridated apatite is obtained by heating apatite in a fluidized bed or rotary kiln at temperatures of ca. 1500°C in the presence of phosphorus or silica and steam.

1.5.1.2.3 Phosphorus

Economic Importance and Applications

The worldwide production of phosphorus in 1995 was $1080 \cdot 10^3$ t, of which $300 \cdot 10^3$ t was produced in the USA. This represents a reduction of 33% in the USA production since 1983 ($400 \cdot 10^3$ t), which is mainly due to increasing energy costs rendering the manufacture of phosphoric acid for fertilizers from elemental phosphorus increasingly uneconomic. In addition there has been a reduction in the utilization of phosphates in household detergents for ecological reasons. In Western Europe there has been a similar trend as can be seen from Table 1.5-11.

Table 1.5-11. Development of the West European Market for Phosphates excluding utilization in Fertilizers (10^3 t/a on P_2O_5 basis).

1986	1993	1997
470	380	320

A survey of the capacities for phosphorus production is given in Table 1.5-12.

Table 1.5-12. Phosphorus Capacities in 1995 in 10^3 t/a.

USA	266
Western Europe	105
Former States of the USSR	360
China	300
India	10

The worldwide phosphorus capacity has decreased from $1350 \cdot 10^3$ t/a to $1080 \cdot 10^3$ t/a in 1995.

Elemental phosphorus:
World capacity in 1995: $1080 \cdot 10^3$ t

Applications

White phosphorus: The estimated use spectra for white phosphorus in the USA and Western Europe in 1994 are given in Table 1.5-13.

White phosphorus is utilized in the production of:

- "furnace" phosphoric acid or phosphates (1977 ca. 85%)
- phosphorus sulfides
- phosphorus oxides
- phosphorus halides
- red phosphorus

Table 1.5-13. Estimated Application Spectrum for White Phosphorus in the USA and Western Europe in 1994 in 10^3 t.

	USA	Western Europe
phosphoric acid	182	40
phosphorus(V) oxide	2	4
phosphorus chlorides	20	28
phosphorus sulfides	11	14
sodium hypophosphite	2	10
total consumption	217	96

Red phosphorus: Red phosphorus is used in the striking surface of matchboxes, for pyrotechnical applications and as a flame retardant e.g. in polyamides.

Red phosphorus utilized:

- for striking surfaces of matchboxes
- for pyrotechnical applications
- as a flame retardant

Manufacture of White Phosphorus

White phosphorus from apatite by electrothermal reduction with coke in the presence of SiO_2

White phosphorus is industrially by far the most important form of elemental phosphorus. It is produced by the electrothermal reduction of apatite with coke in the presence of gravel (silica). The main reactions are represented by the following equations:

$$\begin{array}{lcl} Ca_3(PO_4)_2 + 5\,CO & \xrightarrow{>1400\,^\circ C} & 3\,CaO + 5\,CO_2 + 2\,P \\ 5\,CO_2 + 5\,C & \longrightarrow & 10\,CO \\ \hline Ca_3(PO_4)_2 + 5\,C & \longrightarrow & 3\,CaO + 5\,CO + 2\,P \end{array}$$

Reactions:

- $Ca_3(PO_4)_2 + 5CO \rightarrow 3\,CaO + 5CO_2 + 2P$
- $CO_2 + C \rightarrow 2CO$
- $CaO + SiO_2 \rightarrow CaSiO_3$
- formation of ferrophosphorus (Fe_2P)

Carbon monoxide is regenerated from carbon dioxide and coke. The silica acts as a flux, converting the calcium oxide formed into a low melting slag as follows:

$$CaO + SiO_2 \longrightarrow CaSiO_3$$

This slag also incorporates most of the impurities brought into the process with the ingredients (with the exception of the iron) and part of the fluoride. The iron is converted into ferrophosphorus with the approximate composition Fe_2P.

The apatite must be pregranulated and sintered to ensure sufficient permeability to gases in the furnace

To ensure an adequate permeability to gases in the phosphorus reduction furnace, the raw materials must have a minimum size of 1 to 2 cm. Gravel and coke (smelting coke with preferably <10% ash) can be obtained in this size and the fluoroapatite used is preferably finer and should be agglomerated. This can be accomplished by, for example, pelletization with a pan granulator using the dust from electrostatic filters (see below) as a binder. These pellets then have to be dried and sintered, for which the carbon monoxide-containing flue gases can be used as an energy source.

Modern reduction plants consist of:

- an electrothermal reactor
- a gas purifier
- a phosphorus condenser

Modern reduction plants consist of three units:

- an electrothermal reactor
- a gas purifier
- a phosphorus condenser

Figure 1.5-3 shows a process flow sheet for the electrothermal manufacture of phosphorus. The electrothermal reactor, which is round or triangular with rounded corners, is lined with carbon blocks at the bottom and otherwise with firebricks. The symmetrically positioned carbon electrodes (Soederberg self-baking electrodes or, particularly in the USA, preformed carbon electrodes) have a diameter of 1.3 to 1.5 m in a modern reactor. The electricity consumption is 50 to 70 MW.

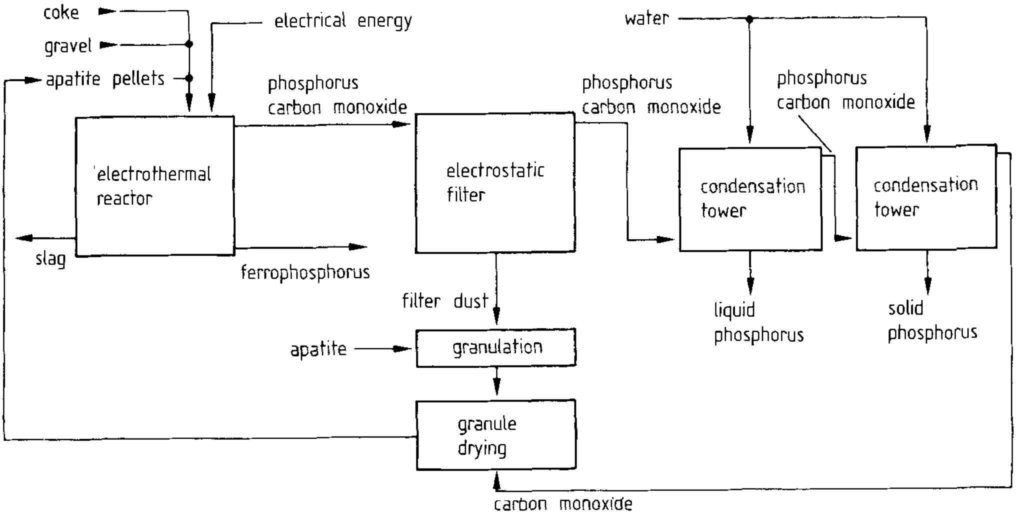


Fig. 1.5-3. Flow Sheet for the Electrothermal Manufacture of Phosphorus.

The feed shutes for the raw materials are positioned symmetrically round the electrodes. The tap-hole for the ferrophosphorus is positioned right at the bottom of the reactor, with the tap-hole for the less dense calcium silicate slag just above it. Carbon monoxide and phosphorus vapor leave by the gas outlet at the top of the reactor.

Gas purification (with hot electrostatic precipitators) has to be carried out at temperatures above 280°C to prevent phosphorus condensation. About 0.04 kg of dust is separated per m^3 of gas.

In modern plants the condensation of phosphorus is carried out in two stages. In a first condensation tower water at 50 to 60°C is sprayed from the top and meets the phosphorus vapor being transported countercurrently from below, whereupon the phosphorus condenses as a liquid. The second condensation tower uses water at 10 to 25°C and solid phosphorus is formed. This is periodically melted and as with the first condensation tower run off into a holding tank. The liquid phosphorus is stored under water, drawn off and transported.

Byproducts:

- carbon monoxide - valuable energy source
- calcium silicate slag - limited use in road building
- ferrophosphorus - usable in metallurgy

The byproducts can, in part, be further utilized: carbon monoxide is a valuable energy source and can, for example, be used in the sintering of the apatite pellets. The calcium silicate slag has, however, only limited marketability e.g. in road building. The ferrophosphorus contains 15 to 28% phosphorus and is, when the silicon content is below 3%, usable in metallurgy. Ferrophosphorus from plants in the Western USA contains 7 to 14% of vanadium (as V_2O_5). This ferrophosphorus is processed to vanadium(V) oxide or vanadium chloride and represents the second most important source of vanadium in the USA. The phosphorus contained in the ferrophosphorus is simultaneously converted into non-utilizable byproducts.

Phosphorus-containing sludge and process water are also produced, which are difficult to dispose of.

Consumed per t of phosphorus produced:

- 12.1 t of raw materials
- ca. $13 \cdot 10^3$ kWh

8 t of byproducts are produced

Production of one ton of phosphorus entails the consumption of:

- 8.0 t Florida phosphate (31% P_2O_5)
- 2.8 t of gravel (97% silicon dioxide)
- 1.25 t of coke (90% carbon)
- 0.05 t Soederberg electrodes
- ca. $13 \cdot 10^3$ kWh of electricity

and the production of the following quantities of *byproducts*:

- 7.7 t silicate slag (90% calcium silicate)
- 0.15 t of ferrophosphorus
- 0.1 t filter dust (20% P_2O_5)
- 2500 m^3 flue gas (85% carbon monoxide)

Reactors with an effective power of 70MW can therefore produce a maximum of 5.4 t of phosphorus per hour.

Manufacture of Red Phosphorus

Red phosphorus:

- worldwide production ca. $6 \cdot 10^3$ t/a
- production by exothermic conversion from white phosphorus in ball mills semi-continuously at 350°C, milling under water, filtering, drying, stabilizing e.g. with magnesium oxide

In terms of quantity produced, red phosphorus is much less important than white phosphorus. The worldwide production is currently about $6 \cdot 10^3$ t/a.

The conversion of white phosphorus to red phosphorus is an exothermic reaction producing red phosphorus as a solid product, making heat removal from the reaction difficult. In a modern process developed by Hoescht A.G. (FRG), the conversion is carried out semi-continuously in a ball mill at 350°C. Mills with a volume of ca. 5m^3 are filled with 3.7 t of iron shot of different diameters. The white phosphorus is fed into the ball mill at a rate such that the reaction temperature is kept constant by the heat of reaction released. The ball mills are at most only half filled. After tempering and cooling, water is added and the red phosphorus ground to a suspension. Heating with sodium hydroxide then removes the residual white phosphorus. The red phosphorus is then filtered off and dried under inert gas. The red phosphorus can be stabilized against autooxidation e.g. by mixing with small quantities of magnesium oxide. Red phosphorus is twice as expensive as white phosphorus.

1.5.1.2.4 Products Manufactures from Phosphorus

Diphosphorus(V) oxide

About 85% of the white phosphorus produced is burnt to diphosphorus(V) oxide.

$$2\,P + 2.5\,O_2 \longrightarrow P_2O_5 \quad \text{or} \quad 4\,P + 5\,O_2 \longrightarrow P_4O_{10}$$

This is mainly directly hydrolyzed to phosphoric acid. Only several thousand tons of diphosphorus(V) oxide are produced annually worldwide. In the USA the capacity for diphosphorus(V) oxide is currently ca. $7 \cdot 10^3$ t/a, which is largely directly utilized.

Diphosphorus(V) oxide is produced using burners similar to those used in the production of phosphoric acid. Here dry gas has to be used, the walls of the combustion chamber being cooled in a so-called "barn", a large settling chamber in which ca. 95% of the diphosphorus(V) oxide formed is condensed. At temperatures between 170 and 200°C a denser and more crystalline product is obtained than when the chamber is water-cooled. The tail gases which contain diphosphorus(V) oxide can, for example, be utilized in a phosphoric acid plant.

Applications: Diphosphorus(V) oxide is used as a drying agent, in dehydration reactions in organic chemistry, for the improvement of the properties of asphalt, and in the manufacture of surface active substances for plastics' and lubricating oil additives.

P_4O_{10}
Manufactured from white phosphorus:
$4P + 5O_2 \rightarrow P_4O_{10}$

Applications:

- mainly in the manufacture of pure phosphoric acid
- as a drying agent
- in dehydration reactions in organic chemistry
- for improving the properties of asphalt
- in the production of additives for plastics and lubricating oils

Phosphorus(V) sulfide

Of the large number of binary phosphorus sulfides, only phosphorus(V) sulfide is commercially important. The USA capacity in 1994 for phosphorus(V) sulfide was $95 \cdot 10^3$ t and that in Western Europe was $90 \cdot 10^3$ t. The consumption of phosphorus(V) sulfide in the USA in 1994 was $70 \cdot 10^3$ t.

It is produced by the exothermic reaction of liquid phosphorus with liquid sulfur at over 300°C:

$$2\,P + 5\,S \longrightarrow P_2S_5 \qquad \text{bzw.}\ \ 4\,P + 10\,S \longrightarrow P_4S_{10}$$

P_4S_{10} manufacture at:
$4P + 10S \xrightarrow{>300°C} P_4S_{10}$
Purification by e.g. distillation

The reaction product can either be directly poured onto cooling rollers or first purified by distillation (b.p. 513 to 515°C). If a non-discolored phosphorus(V) sulfide is required, organic impurity-free phosphorus and very pure sulfur have to be used. The former can be obtained by sulfuric acid extraction and the latter from natural gas purification.

Applications
in the manufacture of:
- insecticides
- lubricating oil additives
- flotation agents

Applications: Phosphorus(V) sulfide is used in the manufacture of insecticides (ca. 40%), lubricating oil additives (ca. 50%) and flotation agents.

Phosphorus Halides

Phosphorus(III) chloride

PCl_3
USA-capacity in 1995: $192 \cdot 10^3$ t/a

The consumption of phosphorus(III) chloride in the USA increased from a low point of $73 \cdot 10^3$ t in 1983 to $142.5 \cdot 10^3$ t in 1994.

The phosphorus(III) chloride capacity in 1995 for both USA and Western Europe was $192 \cdot 10^3$ t and $20 \cdot 10^3$ t in Japan.

Phosphorus(III) chloride is manufactured from white phosphorus and chlorine in an exothermic reaction:

$$2\,P + 3\,Cl_2 \longrightarrow 2\,PCl_3$$

PCl_3 manufacture:
$2\,P + 3\,Cl_2 \longrightarrow 2\,PCl_3$
purification by distillation

This reaction can be carried out in a number of ways. Chlorine can be passed into a suspension of phosphorus in phosphorus(III) chloride. The heat liberated during the reaction is sufficient to evaporate off the phosphorus(III) chloride, which is condensed in reflux condensers and in part returns to the reaction mixture. Part of the distillate is run off and purified by fractional distillation. Direct reaction of stoichiometric quantities of phosphorus and chlorine in a burner is also possible with subsequent working up. Technical phosphorus(III) chloride has a purity of greater than 99.7% and does not contain elemental phosphorus.

Applications: In 1994 about half of the Phosphorus(III) chloride consumed in the USA was utilized in the manufacture of the intermediate phosphorous acid, a further 19.4% to phosphorus(V) oxychloride. Di and trialkylphosphonates, triarylphosphonate, phosphorus(V) sulfochloride and phosphorus(V) chloride are also manufactured directly from phosphorus(III) chloride. Broken down according to the field of application of the end products, the consumption of phosphorus(III) chloride is the USA in 1994: 53.6% was utilized for pesticide production (mainly for glyphosphate), 18% for the manufacture of water treatment chemicals (phosphonic acids) and tensides (acid chlorides of fatty acids and secondary products), 17.1% in the manufacture of polymer additives (flame retardants, stabilizers etc.) as well as small quantities for the production of hydraulic fluids, lubricants and additives for lubricating oils.

Applications:

in the manufacture of:

- phosphorous acid (H_3PO_3)
- phosphorus(V) oxychloride ($POCl_3$)
- di and tri-esters of phosphoric acid
- acid chlorides of fatty acids
- phosphonic acid (H_3PO_3)

Phosphorus(V) chloride

Phosphorus(V) chloride is manufactured continuously in lead-lined towers in which phosphorus(III) chloride is fed in from above and chlorine from below:

PCl_5

Manufacture: $PCl_3 + Cl_2 \rightarrow PCl_5$

$$PCl_3 + Cl_2 \longrightarrow PCl_5$$

The phosphorus(V) chloride formed sinks to the bottom and is removed by a screw conveyor.

Applications: Phosphorus(V) chloride is mainly used as a chlorination agent in organic chemistry.

Application:

as a chlorination agent in organic chemistry

Phosphorus(V) oxychloride

The phosphorus(V) oxychloride consumption in the USA fluctuated in the period 1983 to 1993 between $24.3 \cdot 10^3$ and $29.1 \cdot 10^3$ t. Since the beginning of the 1990's there has

$POCl_3$:

USA-capacity in 1995: $40 \cdot 10^3$ t

been a steady increase in consumption: 1991: 24.7; 1992: 26.0; 1993: 29.1; 1994: 30.7 · 10^3 t. The production capacities in different countries in 1995 were 39.9 · 10^3 t/a in the USA, 100 · 10^3 t/a in Western Europe and 33.6 · 10^3 t/a in Japan.

It is manufactured by reacting pure phosphorus(III) chloride with oxygen with cooling at ca. 50 to 60°C:

$$2\,PCl_3 + O_2 \xrightarrow{50\text{ to }60\,^\circ C} 2\,POCl_3$$

This is a free radical reaction, which is inhibited by small quantities of sulfur, sulfur compounds, iron, copper etc. The reaction product is further purified by fractional distillation.

The extent to which phosphorus(V) oxychloride is still industrially produced from diphosphorus(V) oxide and phosphorus(V) chloride (from phosphorus(III) chloride and chlorine) according to the reaction:

$$P_2O_5 + 3\,PCl_3 + 3\,Cl_2 \longrightarrow 5\,POCl_3$$

is unknown.

Application:
mainly in the manufacture of aliphatic and aromatic esters of phosphoric acid

Applications: Phosphorus(V) oxychloride is mainly used in the manufacture of aliphatic and aromatic esters of phosphoric acid, which are used as flame retardants and plasticizers in plastics, as hydraulic fluids and as extraction agents.

58% of the phosphorus(V) oxychloride consumed in the USA in 1994 was utilized in the manufacture of polymer additives, 14% in the synthesis of hydraulic fluids and lubrication additives.

Phosphorus(V) sulfochloride

Phosphorus(V) sulfochloride can either be manufactured from phosphorus(III) chloride and sulfur at 180°C in an autoclave or by passing phosphorus(III) chloride vapor through molten sulfur:

$$PCl_3 + S \longrightarrow PSCl_3$$

Catalysts such as e.g. aluminum chloride reduce the reaction temperature to such a degree that the reaction can be carried out in phosphorus(V) sulfochloride. Purification is by distillation.

Application of $PSCl_3$:
manufacture of ester chlorides of thiophosphoric acids (precursors for pesticides)

Application; Phosphorus(V) sulfochloride is mainly utilized in the manufacture of ester chlorides of thiophosphoric acids (precursors for pesticides).

Acids and Salts of Phosphorus with $P^{<5+}$

Phosphinic acid and Hypophosphites

The production capacities for sodium hypophosphite in 1995 were $8.6 \cdot 10^3$ t/a in the USA, $4.5 \cdot 10^3$ t/a in Western Europe and $7.8 \cdot 10^3$ t/a in Japan. The estimated production in the USA in 1994 was 5.9 to $6.1 \cdot 10^3$ t.

Hypophosphites, the salts of phosphonic acid, are manufactured by the reaction of white phosphorus with boiling calcium hydroxide, according to the following equation:

$$2\,P_4 + 3\,Ca(OH)_2 + 6\,H_2O \longrightarrow 2\,PH_3 + 3\,Ca(H_2PO_2)_2$$

Hydrogen and calcium phosphite are formed as byproducts. Excess calcium hydroxide is precipitated by passing carbon dioxide through the solution and is filtered off together with the poorly soluble calcium phosphite. Upon addition of sodium carbonate and subsequent filtration a solution of sodium hypophosphite is obtained, which can be converted into phosphinic acid by passing over an ion exchanger.

Applications of hypophosphites:
mainly for electroless plating of nickel

Applications: Hypophosphites are mainly used in electroless nickel plating (e.g. deposition of nickel phosphorus layers with 8 to 10% P in the Kanigan® process).

Phosphorous Acid

In the elegant process developed by Hoechst A.G., phosphorous acid is manufactured by spraying phosphorus(III) chloride and steam (maintained in excess) together, whereupon the heat of reaction of the hydrochloride formed distills off the excess water.

$$PCl_3 + 3\,H_2O \longrightarrow H_3PO_3 + 3\,HCl$$

Phosphorous acid is formed as a byproduct in the chlorination of fatty acids and in the manufacture of phosphinic acid.

Application of phosphorous acid (H_3PO_3): in the manufacture of

- phosphonic acids
- basic lead phosphites

Applications: Phosphorous acid is mainly directly used by the producer for the manufacture of phosphonic acids. For example ca. $41 \cdot 10^3$ t of H_3PO_3, corresponding to 48% of the USA consumption of phosphorus(III) chloride, was utilized in the USA in 1994 for the manufacture of N-phosphonomethyl-glycine (glyphosphate), quantitywise the most produced phosphonic acid. Other phosphonic acids produced from phosphorous acid are utilized as water treatment chemicals. Basic lead phosphite is used as a PVC-stabilizer.

References for Chapter 1.5.1: Phosphorus and Inorganic Phosphorus Compounds

Reviews:

van Wazer, J. R. 1958/1961. *Phosphorus and its Compounds*, Vol. 1 - Chemistry, Vol. 2 - Technology, Biological Functions and Applications, Interscience Publishers, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1991. 5. Ed., Vol. A 19, 465 – 503, *Phosphoric Acid and Phosphates*, 505 – 525, *Phosphorus*, 527 – 543, *Phosphorus Compounds, Inorganic*, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1996. 4. Ed., Vol. 18, 669– 718, *Phosphoric Acids and Phosphates*, 719 – 736, *Phosphorus*, 737 – 798: *Phosphorus Compounds*, John Wiley & Sons, New York.

Winnacker-Küchler. Chemische Technologie. 1982. 4. Aufl., Bd. 2, 204– 267, Anorganische Technologie I, Carl Hanser Verlag, München.

Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry. 1971. Vol. III, Suppl. III, *Phosphorus*, Longman, London.

Commercial Information:

CEH Marketing Research Report. 1995. *Phosphorus and Phosphorus Chemicals*, Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California.

CEH Marketing Research Report. 1995. *Industrial Phosphates*, Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California.

CEH Marketing Research Report. 1994. *Phosphate Industry Overview*, Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California.

1.5.2 Organophosphorus Compounds

The following classes of compounds will be considered:

- esters of phosphoric and thiophosphoric acid and their derivatives
- phosphorous acid esters
- phosphonic acids

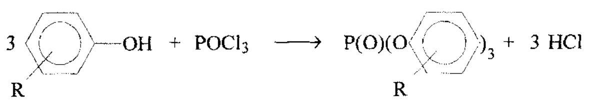
1.5.2.1 Neutral Phosphoric Acid Esters

Triaryl Phosphates

Triphenyl phosphate, diphenyl-cresyl phosphate, tricresyl phosphate and mixed (2-propyl-phenyl)-phenyl phosphates belong to this class of compounds. They are manufactured by reacting phosphorus(V) oxychloride with a slight excess of the appropriate phenols or phenol mixtures in the presence of catalysts (magnesium or potassium salts) at temperatures above 140°C:

Aromatic triesters of phosphoric acid:

triphenylphosphate, diphenylcresylphosphate, tricresylphosphate, mixed isopropylphenyl-phenyl phosphate



R: H, CH_3, $(CH_3)_2CH$

The reaction temperature increases with increasing extent of conversion, the hydrochloride formed escaping as a gas. The excess phenol is distilled off when the reaction is complete. The phosphate esters can be purified by distillation. o-Cresol may not be used in the manufacture of cresyl phosphate on ecological grounds. Isopropyl-phenyl phosphate can, however, be produced using phenol mixtures, which are obtained by the alkylation of phenol with propene.

Manufacture:

by reaction of phosphorus(V) oxychloride with phenols in the presence of catalysts at high temperatures

Diarylalkyl Phosphates

Diphenyl-butyl-, diphenyl-(2-ethylhexyl)- and diphenyl-isodecyl-phosphates are produced industrially. Manufacture is carried out in two stages: first the alcohol is reacted with excess phosphorus(V) oxychloride to the alkyl ester dichloride:

Manufacture of diarylalkyl phosphates:

1st stage: reaction of alcohols with phosphorus(V) oxychloride to the ester dichloride $ROP(O)Cl_2$

2nd stage: reaction of the ester dichloride with an aqueous solution of sodium phenolate

$$ROH + POCl_3 \longrightarrow ROP(O)Cl_2 + HCl$$

R: Butyl, 2-Ethylhexyl, Isodecyl

After distilling off the excess phosphorus(V) oxychloride, the alkyl ester dichloride is reacted with an aqueous solution of sodium phenolate to the triester in a two-phase reaction:

$$ROP(O)Cl_2 + 2NaOC_6H_5 \longrightarrow ROP(O)(OC_6H_5)_2 + 2NaCl$$

Trialkyl Phosphates

Manufacture of trialkyl phosphates: from phosphorus(V) oxychloride and excess alcohol with subsequent neutralization with aqueous alkali

Trialkyl phosphates are manufactured by reacting phosphorus(V) oxychloride with excess alcohol, in particular ethanol, butanol, isobutanol and 2-ethylhexanol:

$$(3 + n)ROH + POCl_3 \longrightarrow P(O)(OR)_3 + (n\ ROH \cdot 3\ HCl)$$

R: Ethyl, Butyl, Isobutyl, 2-Ethylhexyl

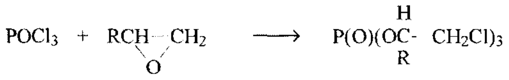
An excess of alcohol is necessary to suppress the hydrochloric acid-induced cleavage of the triester formed. The product is worked up by neutralizing with aqueous alkali and phase separation. (In the case of triethyl phosphate an extraction agent has to be used, due to its solubility in water.) The excess alcohol is distilled off from the organic phase and triethyl- and tributylphosphates are purified by distillation. Dibutyl- and di-(2-ethylhexyl)phosphates, which are formed in small quantities as byproducts, separate from the aqueous phase upon acidification.

Triethylphosphate is also manufactured from diphosphorus(V) oxide and diethylether under pressure (35 bar) at increased temperature (180°C) in the presence of ethylene oxide.

Tris(chloroalkyl)phosphate

Manufacture of tris(choroalkyl)phosphates: from phosphorus(V) oxychloride and alkylene oxides in the presence of catalysts

Chloroalkylesters of phosphoric acid are obtained by reacting alkylene oxides with phosphorus(V) oxychloride in the presence of catalysts (aluminum trichloride, titanium tetrachloride) in an exothermic reaction:



R = H, CH_3, CH_2, CH_2Cl

The esters formed can only be worked up by washing first an acid wash to remove the catalyst and then an alkaline wash, because they readily decompose at high temperatures.

Applications of Neutral Phosphoric Acid Esters

The neutral, halogen-fee phosphoric acids exhibit good flame retarding properties, high stability and low corrosivity. Triaryl- and diarylalkylphosphates are preferred as flame retardants in plastics, whereas trialkylphosphates, dialkylarylphosphates and tris(alkylaryl)phosphates are mainly utilized as heat resistant hydraulic oils. Chloroalkylesters of phosphoric acid are exclusively utilized as flame retardants and then mainly in poly(urethanes).

Applications of neutral phosphoric acid esters:

- as flame retardants [triaryl-, diarylalkyl-, tris(chloroalkyl)esters]
- as hydraulic oils [trialkyl-, dialkylaryl-, tris(alkylaryl)ester]
- as extraction agents (tributylester)

$39.8 \cdot 10^3$ t of phosphoric acid esters were utilized in the USA in 1994 for flame retarding purposes. Of this two thirds ($27.4 \cdot 10^3$ t) was halogen-free and one third ($12.4 \cdot 10^3$ t) contained halogens. The halogen-free flame retardants are made up of triaryl- and alkyldiarylphosphates ($22.3 \cdot 10^3$ t) on the one hand and trialkylphosphates ($5.1 \cdot 10^3$ t), mainly triethylphosphate, on the other.

The consumption of phosphoric acid esters for incombustible special liquids has decreased steadily over the last twenty years. In this sector $22.7 \cdot 10^3$ t was utilized in 1976, $14.2 \cdot 10^3$ t in 1986 and $8.9 \cdot 10^3$ t in 1994. Their partial substitution by water-miscible, glycol-containing systems is now almost complete and therefore the demand will stagnate in the future. In 1994, 55% of the USA consumption of phosphorus-containing special oils was employed as hydraulic liquids in the steel, glass or energy-producing industries (mainly isopropylated and butylated triarylphosphates) and 45% as hydraulic oils in civil aviation (mainly tributyl- and dibutylphenylphosphates).

Tributylphosphate is also utilized as a defoaming agent and as an extraction agent in the extraction of wet-process acid, uranium, lanthanides and other metals.

1.5.2.2 Phosphoric Ester Acids

Manufacture of phosphoric acid esters:

- from mixtures of alcohols and diphosphorus(V) oxide or polyphosphoric acid
- pure dialkylesters as secondary products or byproducts from trialkylester manufacture

The types of phosphoric ester acids available are:

- mixtures of mono-and di-esters by reacting diphosphorus(V) oxide with alcohols:

$$P_2O_5 + 3\,ROH \longrightarrow (RO)_2P(O)OH + ROP(O)(OH)_2$$
$$R: \text{2-Ethylhexyl}, C_8H_{17}\!-\!\!\left[O\text{-}C_2H_4\right]_n \quad n = 4 - 10$$

- mixtures of monoesters with free phosphoric acid by reaction of alcohols with polyphosphoric acid
- pure diesters by alkaline hydrolysis or as a byproduct in the manufacture of trialkylesters.

Applications of Phosphoric Ester Acids

Applications of phosphoric ester acids as:

- tensides
- textile treatment agents
- emulsifiers
- extraction agents

Monoesters of phosphoric acid are used in industrial cleaning agents, often together with phosphoric acid.

Phosphoric acid diesters are utilized as wetting agents and antistatica for textiles and as emulsifiers for cosmetics, cutting fluids, pesticides formulations, in polymerization reactions etc.

The acids are mainly converted into their salts.

In the USA, $31 \cdot 10^3$ t of mono- and diesters of phosphoric acid were manufactured in 1994 for the above applications. This was mainly produced from diphosphorus(V) oxide and ethoxylated long chain alcohols and ethoxylated alkyl phenols.

Pure di(2-ethylhexyl)phosphoric acid is also utilized for the extraction of zinc and other metals.

1.5.2.3 Dithiophosphoric Ester Acids

Manufacture of dithiophosphoric ester acids from alcohols and diphosphorus(V) sulfide

Dithiophosphoric ester acids are obtained by the reaction of diphosphorus(V) oxide with alcohols or phenols:

$$P_2S_5 + 4\,ROH \longrightarrow 2(RO)_2P(S)SH + H_2S$$

R: CH_3, C_2H_5, C_nH_{2n+1} ($n \geq 5$), cresyl

which is exothermic and has to be carried out with cooling.

Dithiophosphoric-O,O-diester with long alkoxy-groups ($>C_5$), optionally with aryloxy-groups, are neutralized in large quantities with zinc oxide to oil-soluble zinc salts and utilized in this form as lubricating oil additives. The zinc dialkyldithiophosphates form a protective layer on metallic materials, which reduces the wear and corrosion of these materials and protects the lubricating oil from oxidation. $96 \cdot 10^3$ t of zinc dialkyldithiophosphate and other lubricating oil additives on the basis of diphosphorus(V) sulfide were utilized in the USA in 1994.

Applications of dithiophosphoric ester acids:

- in the form of zinc salts as lubrication additives
- in the form of their sodium or ammonium salts as flotation aids
- intermediate in the manufacture of insecticides

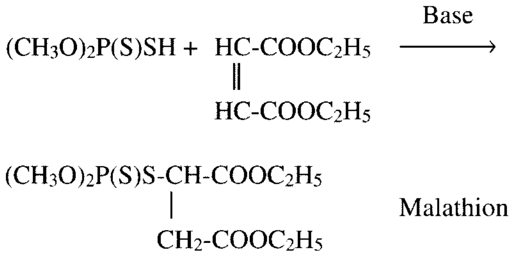
The water soluble sodium and ammonium salts of dithiophosphoric acid-O,O-diesters are used as flotation aids for sulfidic ores.

O,O-dimethyl- and O,O-diethyldithiophosphoric acid is utilized as an intermediate for the synthesis of organophosphorus insecticides (see following Section).

1.5.2.4 Neutral Esters of Thio- and Dithio-Phosphoric Acids

Dithiophosphoric Acid-O,O-triesters

Addition of an acid dithiophosphoric acid-O,O-diester to a -C=C- or C=O double bond results in a neutral O,O,S-triester as, for example in the synthesis of the insecticide Malathion®:



$$(CH_3O)_2P(S)SH + \begin{array}{c} HC\text{-}COOC_2H_5 \\ \| \\ HC\text{-}COOC_2H_5 \end{array} \xrightarrow{\text{Base}}$$

$$\begin{array}{l} (CH_3O)_2P(S)S\text{-}CH\text{-}COOC_2H_5 \\ \qquad\qquad\qquad\quad | \\ \qquad\qquad\qquad CH_2\text{-}COOC_2H_5 \end{array} \qquad \text{Malathion}$$

and in the manufacture of the insecticide Terbufos:

$$(C_2H_5O)_2P(S)SH + HCHO + HS\text{-}C(CH_3)_3 \longrightarrow (C_2H_5O)_2P(S)S\text{-}CH_2\text{-}S\text{-}C(CH_3)_3 + H_2O$$

Terbufos

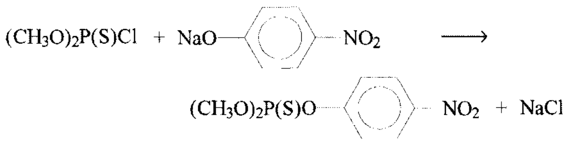
Thiophosphoric Acid-O,O,O-triesters

Chlorination of acidic dithiophosphoric-O,O-dimethyl- or diethylesters results in the splitting off of sulfurdichloride and the formation of the ester chloride of monothiophosphoric acid:

$$2\,(RO)_2P(S)SH + 3\,Cl_2 \longrightarrow 2\,(RO)_2P(S)Cl + S_2Cl_2 + 2\,HCl$$

Alternatively the ester chloride can be produced from phosphorus(V) sulfochloride and an alcohol.

They are then reacted with a compound with a hydroxy group to the neutral O,O,O-triesters of thiophosphoric acid as, for example, in the synthesis of the insecticide Methylparathion:



The diethylarylesters Parathion (E 605®) and Chlorpyrifos are obtained in an analogous process.

Applications of Neutral Thio- and Dithiophosphoric Ester Acids

Applications of neutral thio- and dithiophosphoric ester acids as insecticides

The neutral thio- and dithiophosphoric ester acids with a reactive easily hydrolytically cleavable group, are utilized as insecticides. Their effect is based on in vivo oxidation to the corresponding phosphoric acid ester, which phosphorylates and thereby inhibits the enzyme acetylcholinesterase. The sulfur atoms bonded to the phosphorus produce a delayed effect and make it easier to handle the insecticide. These compounds are, nevertheless, poisonous for humans and animals. Malathion® is less poisonous to humans than many of the other organophosphorus insecticides. An advantage of organophosphorus insecticides is their rapid hydrolytic decomposition in the environment, which largely prevents bio-accumulation.

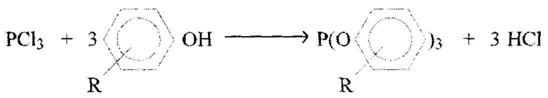
1.5.2.5 Neutral Di- and Triesters of Phosphorous Acid

Triarylphosphites

Triarylphosphites are obtained, analogously to the phosphoric acid esters, by the reaction of phosphorus(V) oxychloride with phenols:

Manufacture of triarylphosphites:

from phosphorus(V) oxychloride and phenols



R is particularly: H, i–C_9H_{19}

Triphenylphosphite is purified by distillation.

Trialkylphosphites

In view of their extreme sensitivity to hydrogen chloride, the synthesis of aliphatic phosphorous acid triesters from phosphorus(V) oxychloride and alcohols can only be carried out in the presence of a molar mixture with inorganic or organic bases:

$$PCl_3 + 3\,ROH + 3\,B \longrightarrow P(OR)_3 + 3B \cdot HCl$$

R is particularly CH_3, C_2H_5

B: ammonia, aniline, trimethylamine etc.

Manufacture of trialkylphosphites:

from phosphorus(V) oxychloride and alcohols in the presence of bases

Cooling is necessary, because the reaction is very exothermic. The operated processes differ in the reaction conditions used (solvent, temperature), the base employed and the working up of the reaction mixture. The ester can be purified by distillation.

Dialkylphosphites

Manufacture of dialkylphosphites:
from phosphorus(III) chloride and alcohols in the absence of bases

Phosphorous acid diesters are obtained by the reaction of alcohols with phosphorus(III) chloride in the absence of bases:

$$PCl_3 + 3\,ROH \longrightarrow (RO)_2P(O)H + RCl + 2\,HCl$$

R particularly CH_3, C_2H_5

This reaction is very exothermic and rapid removal of the hydrogen chloride formed must be provided for, to prevent dealkylation of the ester formed. The phosphorous acid diesters can be purified by distillation.

Applications of Phosphorous Ester Acids

Applications of phosphorous acid diesters:

- as antioxidants in plastics
- as thermal stabilizers in PVC
- as a precursor in the manufacture of:
  - insecticides
  - flame retardants
  - water treatment agents

Triarylphosphites such as tris(nonyl)phosphite or tris(2,4-di-tert.-butylphenyl)phosphite are utilized together with phenols as antioxidants in numerous plastics and rubbers.

Phenyldiisodecylphosphite and diisodecylphosphite are utilized together with liquid calcium-zinc- or barium-zinc-systems as thermal stabilizers for PVC.

The USA consumption of phosphites as antioxidants and thermal stabilizers in 1985 was $11.7 \cdot 10^3$ t, $23.8 \cdot 10^3$ t in 1990 and $24.5 \cdot 10^3$ t in 1994.

The methyl- and ethyl-esters of phosphorous acid are important starting materials for the manufacture of insecticides, veterinary products and flame retardants.

For example, the insecticide Dichlorphos (DDVP) is produced from chloral and trimethylphosphite:

$$(CH_3O)_3P + Cl_3CCHO \longrightarrow CH_3Cl + (CH_3O)_2P(O)O\text{-}CH{=}CCl_2$$

and the insecticide Trichlorfon is obtained from chloral and dimethylphosphite:

$$(CH_3O)_2P(O)H + Cl_3CCHO \longrightarrow (CH_3O)_2P(O)\text{-}CH(OH)\text{-}CCl_3$$

Dimethylphosphite is the starting material for the manufacture of 2-phosphonobutan-1,2,4-tricarboxylic acid, which is used as a calcification inhibitor and corrosion inhibitor in aqueous systems.

1.5.2.6 Phosphonic Acids

Several important phosphonic acids are manufactured by the addition of phosphorous acid to the C=O group of an organic compound.

Hydroxyphosphonoacetic acid is produced in this way from H_3PO_3 and oxoethanoic acid:

Manufacture of hydroxyphosphonic acids: from compounds with C=O groups and phosphorous acid

$$H_3PO_3 + OCH\text{-}COOH \longrightarrow [(HO)_2(O)P]CH(OH)\text{-}COOH$$

and 1-hydroxyethan-1,1-diphosphonic acid from H_3PO_3 and acetic anhydride via intermediates produced by a condensation reaction.

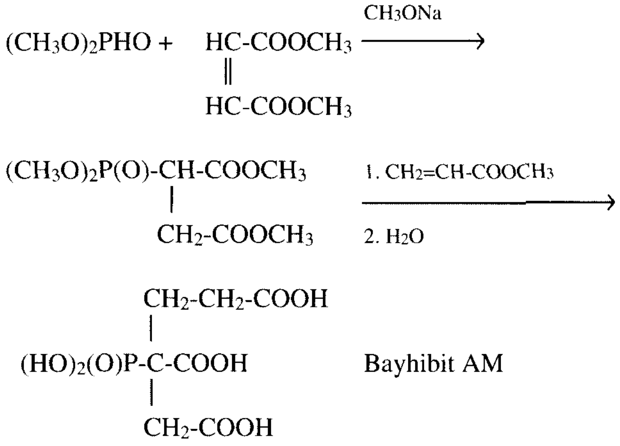
$$2\,H_3PO_3 + (CH_3CO)_2O \longrightarrow CH_3C(OH)[P(O)(OH)_2]_2 + CH_3COOH$$

Phosphorous acid and formaldehyde react with ammonia or a compound with an amino- or imino-group producing an aminomethylenephosphonic acid. Phosphonomethylation occurs in an acid medium and is catalyzed by chloride, which is the reason why hydrolyzed phosphorus(III) chloride is often used as the phosphorus-containing raw material. As a rule all the N-H- hydrogen atoms are replaced by a $CH_2P(O)(OH)_2$- group. Thus with ammonia, amino-tri(methylenephosphonic acid) (AMP) is formed:

Manufacture of aminomethylenphosphonic acid: from N-H-group containing compounds, formaldedyde and phosphorous acid

$$NH_3 + 3\,HCHO + 3\,H_3PO_3 \xrightarrow{HCl} N[CH_2P(O)(OH)_2]_3 + H_2O$$

with diethylenetriamine, diethylentriamin-penta(methylenephosphonic acid) is formed and with imino-diacetic acid, N-(phosphonomethyl)iminodiacetic acid is formed. The latter is an intermediate in the manufacture of 2-phosphono-butane-1,2,4-tricarboxylic acid (Bayhibit®AM from Bayer A.G.).



$$(CH_3O)_2PHO + \begin{array}{l} HC\text{-}COOCH_3 \\ \quad\| \\ HC\text{-}COOCH_3 \end{array} \xrightarrow{CH_3ONa}$$

$$\begin{array}{l} (CH_3O)_2P(O)\text{-}CH\text{-}COOCH_3 \\ \qquad\qquad\quad | \\ \qquad\qquad\quad CH_2\text{-}COOCH_3 \end{array} \xrightarrow[2.\ H_2O]{1.\ CH_2{=}CH\text{-}COOCH_3}$$

$$\begin{array}{l} \qquad\qquad CH_2\text{-}CH_2\text{-}COOH \\ \qquad\qquad | \\ (HO)_2(O)P\text{-}C\text{-}COOH \\ \qquad\qquad | \\ \qquad\qquad CH_2\text{-}COOH \end{array} \qquad \text{Bayhibit AM}$$

Applications of Phosphonic Acids

Applications of phosphonic acids:

- N-(phosphonomethyl)glycine for combatting weeds

The most important phosphonic acid both on the basis of value and quantity is N-(phosphonmethyl)glycine (Glyphosphate), which is utilized in the form of its isopropylammonium salt as a bio-degradable leaf-herbicide for the total and semi-total control of weeds and grasses (Roundup® from Monsanto).

$$H\text{-}N(CH_2COOH)_2 \xrightarrow{HCHO,\ H_3PO_3}$$

$$[(HO)_2(O)P]CH_2\text{-}N(CH_2COOH)_2 \xrightarrow{O_2}$$

$$[(HO)_2(O)P]CH_2\text{-}NH\text{-}CH_2COOH \quad \text{Glyphosate}$$

- other phosphonic acids for the hindering of corrosion and calcification in cooling water and industrial cleaning agents

Hydroxyphosphonoacetic acid is an effective corrosion inhibitor where there is contact between aqueous systems and metals.

2-phosphonbutane-1,2,4-tricarboxylic acid (Bayhibit® AM), 1-hydroxyethane-1,1-diphosphonic acid are used in aqueous systems for the most part as calcification-inhibitors. They hinder even in understoichiometric quantities ("threshold effect") the deposition of poorly soluble salts. Depending on the type of precipitate being inhibited ($CaCO_3$, $CaSO_4$, $BaSO_4$) the degree of supersaturation and other limiting conditions, they are utilized in cooling waters, alkaline cleaning formulations, boiler feed water, crude oil displacement water or detergents.

Neutral phosphonic acid esters are utilized as halogen-free flame retardants in plastics and textile fibers.

- neutral phosphonic acid esters are flame retardants for plastics

References for Chapter 1.5.2: Organophosphorus Compounds

Reviews:

Ullmann's Encyclopedia of Industrial Chemistry. 1991. 5. Ed., Vol. A 19, 545 – 572, *Phosphorus Compounds, Organic,* VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1996. 4. Ed., Vol. 18, 669 – 718, *Phosphorus Compounds,* John Wiley & Sons, New York.

Commercial Information:

CEH Marketing Research Report. May 1995. *Phosphorus and Phosphorus Chemicals*, Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California.

1.6 Sulfur and Sulfur Compounds

1.6.1 Sulfur

1.6.1.1 Occurrence

Sulfur is widely distributed in the Earth's crust. Elemental sulfur is found in sedimentary deposits (domed formations of rock salt, gypsum and limestone, particularly in the Gulf of Mexico, Sicily and Poland) or in deposits of volcanic origin (e.g. in East Asian basins alongside the Philippines and Japan).

It is found in non-elemental form in sulfates (gypsum), in sulfidic ores (e.g. iron pyrites and copper, zinc, lead, nickel and cobalt sulfides) and in fossil fuels. In natural gas and crude oil it occurs bonded to both hydrogen and carbon and

Deposits:

- elemental sulfur in sedimentary or volcanic deposits
- sulfates (gypsum)
- sulfides (inorganic or organic in ores, coal, crude oil and natural gas)
- H_sS in natural gas

in coal as inorganic and organic sulfides. The importance of the sulfur deposits in natural gas and crude oil as sources of sulfur compounds is increasing. The worldwide reserves of sulfur have been estimated to be $25 \cdot 10^9$ t.

1.6.1.2 Economic Importance

1.6.1.2.1 Sulfur from Elemental Sulfur Deposits

Extraction:

- from elemental sulfur deposits: by forcing out with hot water (Frasch process)

Elemental sulfur is extracted from deep sedimentary deposits with particular geological formations, such as salt domes (impermeable layers of anhydrite on salt with sulfur-containing limestone on top) e.g. along the Mexican Gulf, in Canada or Iran, by pumping in superheated water (ca. 165°C) at a pressure of ca. 25 bar and pumping out the molten liquid sulfur (Frasch process). In this process three coaxial tubes are placed in a bore hole sunk down into the anhydrite layer of the dome. The outer tube is provided with a slit at the end and rests on the bottom of the bore hole. The superheated water passes through the slits melts the sulfur in the direct surroundings and pushes it through the bottom slits into the inner tube, the molten sulfur rising up the middle tube. Injection of compressed air (40 bar) into the innermost tube forces the molten sulfur to the surface. The operating range of a bore hole is ca. 50 to 80 m and a single bore hole can produce up to 300 t of sulfur per day.

- mining with subsequent flotation, smelting or distillation

If the sedimentary sulfur deposits lie near the surface, the sulfur ore is mined. The sulfur is then extracted by smelting (Sicily) or by distillation at temperatures above 440°C. A combination of flotation and subsequent smelting is also operated (Poland).

1.6.1.2.2 Sulfur from Hydrogen Sulfide and Sulfur Dioxide

- from H_2S (natural gas, crude oil, coal): by oxidation using the Claus process

Hydrogen sulfide is present in natural gas, refinery gases, synthesis gas and coking oven gases. It has to be removed before the gas can be used or further processed. This is carried out by physical or chemical scrubbing, the hydrogen sulfide being recovered in concentrated form upon regeneration of the absorption liquids.

Conversion of the hydrogen sulfide into elemental sulfur is accomplished using the Claus process, which is exothermic.

A typical Claus plant consists of a combustion chamber, a waste heat boiler and two reactors, which are filled with catalyst. The hydrogen sulfide-containing gas together with a stoichiometric quantity of, for example, oxygen enriched gas and heating gas is passed into the combustion chamber, in which ca. 60 to 70% of the hydrogen sulfide is converted into sulfur according to the following reactions:

Claus process requires:

- a combustion chamber
- a waste heat boiler
- two catalyst-filled reactors

$$2\,H_2S + O_2 \rightleftharpoons S_2 + 2\,H_2O$$
$$2\,H_2S + SO_2 \rightleftharpoons 3/8\,S_8 + 2\,H_2O$$

The process gas from the combustion chamber is cooled in the waste heat boiler to the temperature required for the first reactor of ca. 300°C. In this reactor, filled with a cobalt-molybdenum catalyst (on an aluminum oxide support), the conversion of up to 80 to 85% of the hydrogen sulfide is carried out. After condensing out the sulfur formed at temperatures below 170°C, the temperature of the reaction gases is increased to the reaction temperature of the second reactor (ca. 220°C), which contains a highly active aluminum oxide catalyst with a large surface area (200 to 300 m^2/g) in which the residual hydrogen sulfide and sulfur dioxide react with one another.

The sulfur yield is between 96% (with two catalytic reactors) and 98% (with three catalytic reactors). The tail gases from Claus plants have to be cleaned, for which there are a number of processes. In the so-called Superclaus process a yield of up to 99.5% is obtained by using improved catalysts.

1.6.1.2.3 Sulfur from Pyrites

Heating iron pyrites to ca. 1200°C in the absence of air (Outokumpu process) yields sulfur and liquid iron(II) sulfide.

- from pyrites:
  by heating in the absence of air (Outokumpu process)

1.6.1.3 Economic Importance

Sulfur production in 1993 (10^6 t of S):

• elemental sulfur	
World	34.18
from natural gas	16.80
from crude oil	10.99
from elemental deposits	5.12
other sources	1.27
• sulfur in all forms:	
World	52.66
as elemental sulfur	34.18
as pyrites	7.54
as other forms of sulfur	10.94

$34.18 \cdot 10^6$ t of elemental sulfur was produced worldwide in 1993, of which 80% came from natural gas and crude oil and 15% from elemental sulfur deposits. The importance of extraction from elemental sulfur deposits has decreased considerably. The largest sulfur producers are the USA with $9.49 \cdot 10^6$ t/a and Canada with $7.57 \cdot 10^6$ t/a.

A total of $52.66 \cdot 10^6$ t of sulfur-containing raw materials (on the basis of sulfur content) was produced for further processing in 1993. 65% of this was elemental sulfur, 14% iron pyrites and the rest consists of flue gases from the roasting of non-ferrous metal sulfides, hydrogen sulfide and gypsum.

1.6.1.4 Applications

Applications:

- 85 to 90% for sulfuric acid manufacture
- rest for the production of sulfur dioxide, rubber vulcanization agents, CS_2 and P_2S_5, putty, gunpowder, sulfur dyes, sulfur concrete, paper

Elemental sulfur is mainly used (ca. 85 to 90%) in the manufacture of sulfuric acid. It is also utilized in the production of sulfur dioxide, carbon disulfide, phosphorus(V) sulfide, thiosulfates and sulfur dyes, sulfur-containing putty, gunpowder and fireworks, sulfur concrete, slow release fertilizers and pharmaceuticals and as a rubber vulcanization agent.

1.6.2 Sulfuric Acid

1.6.2.1 Economic Importance

Sulfuric acid production in 1993 (in 10^6 t of 100% H_2SO_4):

World	135.3
USA/Canada	41.3
Asia	33.5
Eastern Europe	19.3
Western Europe	17.0
Africa	16.4
Latin America	6.2
FR Germany	3.5
France	2.5
Spain	2.2

Sulfuric acid is utilized in many processes, it being one of the primary inorganic materials. For a long time it has been a bell-wether for the strength of the chemical industry in a particular country. In recent times a range of large scale processes have been adapted so that they can operate without sulfuric acid. In addition recycling of used acid is playing an increasing rôle. For example, their proportion of Federal German production in 1993 was 15%. Accordingly, the quantities of fresh sulfuric acid produced worldwide has decreased in recent years to $135 \cdot 10^6$ t in 1993, which is still very high.

1.6.2.2 Starting Materials for Sulfuric Acid Manufacture

Sulfuric acid is manufactured by oxidizing sulfur dioxide to sulfur trioxide and then reacting the sulfur trioxide with water:

H_2SO_4 manufactured from:
- SO_2 (fresh acid)
- used sulfuric acid

$$SO_2 + 0.5\ O_2 \longrightarrow SO_3 \xrightarrow[\text{(in } H_2SO_4)]{+ H_2O} H_2SO_4$$

In addition to this fresh acid, sulfuric acid is to an increasing extent produced by recycling waste sulfuric acid.

1.6.2.2.1 Sulfuric Acid from Sulfur Dioxide

In recent years the manufacture of sulfur dioxide and sulfuric acid has been increasing oriented to elemental sulfur as a starting material. Worldwide more than 60% of the fresh sulfuric acid is produced from elemental sulfur and 80% in the USA.

Zinc blende, galena and copper pyrites are important raw material sources in the Federal Republic of Germany. These ores are utilized in the extraction of metals with sulfuric acid being produced as a byproduct, so-called metal acid. As a result of increased efforts in environmental protection, the proportion of recycled sulfuric acid e.g. from nitration reactions or oil refineries, has increased significantly in the last 20 years.

Utilization of pyrites has, on the other hand, strongly decreased in importance in the Federal Republic of Germany for cost and environmental reasons. China, which produced $11.2 \cdot 10^6$ t of sulfuric acid from pyrites in 1993 accounting for 85% of its total sulfuric acid production, is an exception in this regard.

The worldwide production of pyrites, expressed as sulfur, was $7.46 \cdot 10^6$ t in 1993. The largest producer is China with ca. $4 \cdot 10^6$ t/a, Western Europe and the former States of the USSR each produced ca. $1 \cdot 10^6$ t/a.

Manufacture of SO_2 by:
- combustion of S or H_2S
- roasting of metallic sulfides
- cracking of waste sulfuric acid and metal sulfides

Proportion of raw materials in the production of fresh sulfuric acid from sulfur dioxide in the FRG in 1993 (%):

CuS, ZnS, PbS	38
Sulfur	32
used acid and sulfates	15
pyrites	12
other	3

Manufacture of Sulfur Dioxide

SO_2-production by:

- combustion of S:
  liquid S is burnt with air, hot combustion gases are cooled and steam produced

Combustion of sulfur to sulfur dioxide is exothermic and is carried out industrially in a combustion chamber with spray burners for liquid sulfur and dry air as oxidizing agent. Liquid sulfur at 140 to 150°C (liquid sulfur exhibiting a viscosity minimum at this temperature) is sprayed through jets in finely divided droplets into the combustion chamber. There are three plant types: with pressure atomizers, binary burners and rotary atomizers respectively. In the latter hot sulfur at 150°C is passed down the inner wall of a beaker rotating at ca. 4000 to 6000 rpm forming a film. The beaker is surrounded by a ring slit into which high velocity air is forced. The sulfur film is atomized by the air stream entering the chamber and the centrifugal force and is then burnt. The concentration of sulfur dioxide in the exiting gas mixtures is adjusted with air to 9 to 11.5% by volume, the oxygen content of the gas mixture being sufficient for subsequent production of sulfur trioxide. The hot gases are then cooled to ca. 45°C in a waste heat boiler in which steam is produced. A purification step is not necessary.

Sulfur dioxide is also produced by roasting sulfidic ores. Pyrites is, for example, converted into sulfur dioxide and iron(III) oxide (calcine) according to the following equation:

$$2\,FeS_2 + 5.5\,O_2 \xrightarrow{\text{at least 800 °C}} Fe_2O_3 + 4\,SO_2 \qquad \Delta H = -1660\ \text{kJ/mol}$$

- roasting of pyrites:
  - in multiple hearth roasters
  - in rotary tube furnaces
  - in fluidized beds

This reaction is currently preferably carried out in multiple hearth roasters, rotary tube furnaces or fluidized bed furnaces.

In multiple hearth roasters, which have up to 15 hearths, the pulverized material is agitated with a stirrer arm and is transported from one hearth to another, thereby continuously renewing the surface of the ore being calcined. The roasting gases leave the furnace with 9 to 12% by volume of sulfur dioxide at 700 to 750°C. They are cooled over a waste heat boiler, in which steam is produced.

In rotary tube furnaces pyrites and air are intimately mixed in countercurrent. The reaction products are cooled by built-in tubes in which water is evaporated, thereby removing the heat of reaction as usable heat.

In fluidized bed furnaces, consisting of a cylindrical roasting shaft which extends upwards conically to a settling chamber, the sulfidic material is roasted at 650 to 900°C. The air enters via a grill and is uniformly distributed in the shaft and a fluidized layer is produced mainly consisting of iron(III) oxide calcine. The hot gases, containing up to 14% of sulfur dioxide and a little sulfur trioxide, are cooled in a waste hear boiler, 1 ton of pyrites with 45 to 50% sulfur thereby producing about 1.5 tons of steam (40 bar).

Zinc blende is also roasted using fluidized bed technology. Galena, is on the other hand roasted in traveling-grate sinter plants.

- zinc blende is roasted in fluidized bed furnaces
- galena is roasted in traveling-grate sinter plants

Regardless of the roasting process, the hot sulfur dioxide-containing gases have to be purified, so that they can be utilized in the manufacture of sulfur trioxide. The gases exiting from the waste heat boiler are first made dust-free by means of a cyclone and an electrostatic filter at such a high temperature that no sulfuric acid, from the sulfur trioxide in the roasting gas, condenses out. Since the gase still contains all the impurities which are volatile at 350 to 400°C, in particular arsenic trioxide, it must be cooled to ca. 60 to 80°C and scrubbed. This is carried out in acid-resistant venturi scrubbers and coolers. The resulting moist sulfur trioxide-free gases are then dried with sulfuric acid, the resulting gas being a gas at 40°C containing 12 to 14% by weight of sulfur dioxide.

Purification of roasting gases by:

- dust removal in a cyclone and electrostatic filter
- scrubbing with jet scrubbers after cooling

Metal sulfates can be cracked to sulfur dioxide. This is the basis of the Müller-Kühne process, which is operated in several Eastern European countries, the Federal Republic of Germany, Austria and South Africa, but whose importance has strongly diminished of late. In this process calcium sulfate (naturally occurring gypsum or anhydrite or gypsum from the manufacture of phosphoric acid) is reacted with coal in the presence of clay and sand in a rotary tube furnace a temperatures between 700 and 1200°C. Initially calcium sulfide and carbon dioxide are formed, which further react forming calcium oxide and sulfur dioxide:

Cracking of $CaSO_4$:

sulfur dioxide produced from calcium sulfate and coal with Portland cement as a byproduct is only of minor importance

$$\begin{array}{lcl} CaSO_4 + 2\,C & \longrightarrow & 2\,CaS + 2\,CO_2 \\ CaS + 3\,CaSO_4 & \longrightarrow & 4\,CaO + 4\,SO_2 \\ \hline 4\,CaSO_4 + 2\,C & \longrightarrow & 4\,CaO + 4\,SO_2 + 2\,CO_2 \end{array}$$

The gas leaving the furnace contains 7 to 10% by volume of sulfur dioxide.

The calcium oxide is heated with sand and clay at 1200 to 1400°C in a second section of the rotary tube furnace forming Portland cement.

- cracking of other metal sulfates:

sulfur dioxide manufacture from metal sulfates arising from titanium dioxide production, which is a contribution to environmental protection

Metal sulfates are also cracked to sulfur dioxide in the recycling of so-called thin acid arising from the production of titanium dioxide by the sulfate process. The 20 to 25% sulfuric acid produced after digestion and hydrolysis (see Section 5.9.2.2.3) contains 8 to 15% of dissolved metal sulfates, mainly iron sulfate and magnesium sulfate. In the process mainly practiced at present, the thin acid is subjected to multistage vacuum evaporation to 65 to 70% acid. The metal sulfates which precipitate out in this process are mixed with coke and sulfur or pyrites as fuel and cracked in a fluidized bed furnace at ca.1000°C. The oxygen arising from the cracking is removed by employing an excess of fuel, thereby avoiding reoxidation of the sulfur dioxide to the troublesome sulfur trioxide:

$$\begin{array}{lll} 4\,FeSO_4 \cdot H_2O & \longrightarrow & 2\,Fe_2O_3 + 4\,SO_2 + O_2 + 4\,H_2O \\ C + O_2 & \longrightarrow & CO_2 \\ \hline \end{array}$$

$$4\,FeSO_4 \cdot H_2O + C \longrightarrow 2\,Fe_2O_3 + 4\,SO_2 + CO_2 + 4\,H_2O$$

The reaction gases are cooled to 300°C in a waste heat system, resulting in steam production, and purified. The calcine, consisting mainly of iron(III) oxide, can be utilized in the metal or cement industries.

The 65 to 70% sulfuric acid containing a residue of metal sulfates (3 to 5%) is either directly, or after further concentration to 80 to 90%, in admixture with 96% acid or oleum (from a double contact plant fed with sulfur dioxide from metal sulfate cracking) is further utilized in the digestion of titanium ore.

- cracking of waste sulfuric acid

Sulfur dioxide can also be obtained from waste sulfuric acid by cracking. Impure sulfuric acid accrues in many processes, particularly in organic chemistry, the petrochemical industry and the metal industry. The safest way of avoiding waste problems and possible environmental burdens is thermal cracking with the formation of sulfur dioxide:

$$2\,H_2SO_4 \longrightarrow 2\,SO_2 + O_2 + 2\,H_2O$$

with subsequent conversion to sulfuric acid, which can be used again. On economic grounds, a precondition for cracking is that the waste sulfuric acid must contain at least 60% by weight of sulfuric acid. More dilute acids must be concentrated before cracking, which involves further costs, to obtain the minimum concentration of sulfur dioxide necessary for its conversion into sulfur trioxide, because the cracked gas is considerably diluted by direct heating with furnace gases. Depending on the nature of the impurities the thermal cracking can be carried out under reducing or oxidizing conditions, the organic impurities either being reduced to carbon or oxidized to carbon dioxide. The energy necessary for the sulfuric acid cracking process is generally supplied by direct combustion of gaseous or liquid fuels.

Waste sulfuric acid must be at least 60%

thermal cracking of sulfuric acid is carried out by oxidation or reduction, depending upon the nature of the impurities

Acid waste from petrochemical refinery processes is, for example, worked up under reducing conditions. The acidic tar or resin is converted into coke by heating in a reducing atmosphere (furnace gas, ca. 1000°C) in a rotary tube furnace. In a variant of this process the energy is produced by the burning of coke, which is supplied to the rotary tube furnace and burnt together with the coke formed.

reductive cracking by heating on reducing atmospheres

Processes operating via oxidation have the advantage that the organic impurities has already been burnt to carbon dioxide. In addition the cracking energy provider, heating oil or gaseous fuel, is burnt in an excess of air. Cracking is carried out in a brick-lined furnace at ca. 1000°C by finely distributing the waste acid with a centrifugal disc atomizer into the ca. 1800°C furnace gases. The exiting sulfur dioxide-containing gases at ca. 1000°C are cooled in a waste gas boiler, in which steam is produced, and then purified before being fed into the sulfuric acid production.

oxidative cracking by burning the added energy source in an excess of air

The energy requirements for acid cracking are high. Cracking of 70% waste acid at 1000°C under oxidative conditions requires ca. $6.36 \cdot 10^6$ kJ per ton of sulfuric acid (100%). Almost half of this (46%) is required for dehydration of the 70% acid, for the evaporation of the water and sulfuric acid and for the heating of the gases from 20 to 240°C. The actual cracking consumes about 40% of the total energy, the rest being required to heat the reaction products to ca. 1000°C and is generally recoverable.

Sulfur dioxide from waste sulfuric acid: environmentally friendly, but energy intensive and therefore expensive

Conversion of Sulfur Dioxide to Sulfuric Acid

Fresh sulfuric acid:

almost exclusively produced by the contact process, in particular the double contact process

The oxidation of sulfur dioxide to sulfur trioxide and its subsequent conversion to sulfuric acid is currently almost exclusively carried out using the contact process, in particular the double contact process. The lead chamber process is no longer important.

The *contact process* is based on the equilibrium between sulfur dioxide and its oxidation product sulfur trioxide:

$$SO_2 + 0.5\ O_2 \xrightleftharpoons{\text{catalyst}} SO_3 \quad \Delta H = -99.0\ \text{kJ/mol}$$

SO_3-formation favored by:

- lowest temperature possible (lower limit determined by the operating temperature of the catalyst used)
- lowering of the SO_3-concentration
- increased pressure

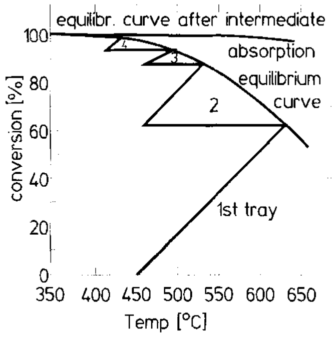
which is only attained sufficiently quickly in the presence of a catalyst. Since this equilibrium shifts in favor of the starting materials with increasing temperature, the process has to be carried out at as low a temperature as possible, this being determined by the operating temperature of the catalyst. A higher sulfur dioxide conversion can be obtained by lowering the concentration of the sulfur trioxide formed (double contact process) or by operating under increased pressure (5 bar) (Ugine-Kuhlmann process).

Catalyst:

divanadium(V) oxide
lowest operating temperature 420 to 440°C

Divanadium(V) oxide catalysts are currently almost exclusively used. They are fused salts, which in a cold state consist essentially of vanadium sulfate and potassium disulfate, applied to a porous support (kieselguhr or diatomaceous earth). The change in valency state between V^{4+}- and V^{5+}-ions is probably a critical step in the catalysis. The lowest operating temperature of this catalyst is generally ca. 420 to 440°C.

Oxidation is carried out on catalyst trays. After passage through the trays, the gas has to be cooled again to ca. 450°C.



Oxidation of sulfur dioxide to sulfur trioxide generally proceeds on classical grid-type catalyst trays. In a contact chamber there are four to five sieve trays, on which the catalyst is spread. Sulfur dioxide-containing gas, whose concentration has been adjusted to 10% with dried air, at 450°C before passing through the first tray, passes from the top to the bottom of the chamber through the catalyst trays. During passage through the first tray the gas is heated to 620°C. Before entering the second tray it must be cooled down to 450°C. In plants operating with sulfur dioxide from roasting processes, in which the purified gas is cold, this cold gas is utilized as a coolant in the heat exchangers, thereby itself being heated to 450°C. In the case of sulfur dioxide-containing gas from sulfur combustion, which is already at 450°C and therefore cannot be utilized as a coolant, water is used in the heat exchangers and steam is produced.

There are two processes for the manufacture of sulfur trioxide from sulfur dioxide on catalyst trays.

In the *conventional contact process* (single contact process) the reaction gases are passed through the four trays without intermediate absorption and the gas is cooled after each tray to 450°C or 430°C for the lowest tray. After passage through the first tray 60 to 63% of the sulfur dioxide has been converted to sulfur trioxide, after the second tray 89 to 90% and after the fourth tray a maximum conversion of 98% is possible, based on sulfur dioxide.

Higher sulfur dioxide conversions (99.6 to 99.7%) can be attained with the *double contact process* developed by Bayer A.G. In this process sulfur dioxide is converted into sulfur trioxide, as in the single contact process, but after the third tray the sulfur trioxide is completely removed from the reaction gas (conversion 90 to 93%, based on sulfur dioxide) by absorption in 98.5 to 99% sulfuric acid. This is achieved by cooling the reaction gas to 180 to 200°C with a gas cooler and then feeding it into the bottom of a Raschig ring-filled absorption tower in which sulfuric acid at 60 to 70°C is fed in at the top in countercurrent to the gas. The acid is thereby heated up to 80 to 85°C and is cooled with air- or water-coolers before it is returned to the absorption tower. The resulting sulfur dioxide-containing gas (ca. 0.6 to 1.1% by volume) is heated up with reaction gas in a heat exchanger and is passed through the fourth and optionally fifth tray, so-called post contact. There it is further converted to sulfur trioxide so that an overall conversion of 99.6 to 99.7% is attained based on sulfur dioxide.

In both contact processes the sulfur trioxide is, after the final passage through the final tray and cooling to 180 to 200°C, absorbed in 98.5 to 99% sulfuric acid. This occurs either in a countercurrent absorber tower or in a jet scrubber in which acid is sprayed from the top in co-current with the reaction gas and is accompanied by conversion of sulfur trioxide into sulfuric acid.

If the gas emerging from the beds is sprayed with oleum in a tower, the absorbed sulfur dioxide does not form sulfuric acid, oleum with a higher sulfur trioxide content is obtained instead.

Cooling:

- in the case of SO_2 from roasting processes by heating cold gas
- in the case of SO_2 from S-combustion by water evaporation

SO_3-manufacture from SO_2 in catalyst trays:

- single contact process:
  - reaction gases are passed through the trays without intermediate absorption
  - maximum conversion, based on SO_2: 98%
  - after 4th tray, absorption of SO_3 with 98.5 to 99% H_2SO_4 or with oleum

- double contact process:
  - after 3rd tray removal of SO_3 by absorption in 98.5 to 99% H_2SO_4

In modern sulfuric acid plants the reaction heat released in the individual process steps is largely utilized for steam production

The production of sulfuric acid from elemental sulfur proceeds exothermically in all reaction steps. Per ton of 100% sulfuric acid a total of ca. 5.4 MJ of heat is produced. Most of this is utilized in the production of steam (1.1 t of high-pressure steam e.g. at 40 bar and 400°C per ton of 100% sulfuric acid).

Purification of tail gases can be dispensed with in the double contact process

Purification processes for the tail gases from the single contact process:

- NH_3-scrubbing
- scrubbing with aqueous $Na_2SO_3/NaHSO_3$ solutions
- absorption on activated charcoal
- oxidation of SO_2 with H_2O_2 or H_2SO_5

With the double contact process it is unnecessary to purify the tail gases to reduce their sulfur dioxide content still further, whereas tail gases from single contact plants have to be purified. This can be realized either by scrubbing with ammonia or with an aqueous solution of sodium sulfite and sodium hydrogen sulfite (Wellman-Lord process), absorption on activated charcoal (sulfacid process from Lurgi) or by oxidative gas purification such as in the peracidox process (oxidation of sulfur dioxide with hydrogen peroxide or peroxomonosulfuric acid).

Double contact process reduces the sulfur dioxide emission by almost a factor of ten

The emission of sulfur dioxide from sulfuric acid plants is strongly reduced with the double contact process. If all the sulfuric acid manufactured in the Federal Republic of Germany were produced by modern plants using the double contact process, the resulting emission of sulfur dioxide would account for only 0.32% of the total emission from human activities.

Gases with a higher sulfur dioxide content than is utilizable in catalyst tray reactors can be processed in a fluidized bed reactor

The catalytic oxidation of sulfur dioxide to sulfur trioxide can also be carried out in a fluidized bed reactor. The gas to be converted is fed in at the bottom of a fluidized bed containing the catalyst in the form of abrasion resistant beads. The whole fluidized bed can be kept at the required temperature by removing the heat of reaction with a pipe cooler. This isothermal mode of operation enables gases with a higher sulfur dioxide content to be processed and more compact plants to be built.

Moist catalysis process for the oxidation of wet SO_2 (from H_2S) to SO_3, produces 75 to 78% sulfuric acid

A variant of the contact process is operated in coking plants, the *moist gas catalysis process*, in which wet sulfur dioxide from the combustion of hydrogen sulfide is converted into sulfuric acid. In this process hydrogen sulfide, from coking plants, is converted to sulfur dioxide and water with an excess of air:

$$2\,H_2S + 3\,O_2 \longrightarrow 2\,SO_2 + 2\,H_2O$$

and the moist sulfur dioxide catalytically oxidized to sulfur trioxide. The high water content of the gas means that only 75 to 78% sulfuric acid can be produced in this process. In coking plants this is generally reacted with the ammonia produced during coking gas purification to form ammonium sulfate. In newer processes the water vapor is largely condensed allowing sulfuric acids with a content of up to 98% to be produced.

Nitrous processes (lead chamber and tower processes) have practically no industrial importance. These processes are wet catalytic processes with nitrosyl hydrogen sulfate as oxidizing agent, which are carried out at temperatures up to 80°C in an aqueous phase and were the main production processes for sulfuric acid up to the 1920's. They have a number of disadvantages over the contact process in particular that only sulfuric acids of up to 78% can be produced. However, the low operating temperature of the nitrous process can be advantageous in particular cases. In a process developed by Ciba-Geigy, sulfuric acid can be produced from gases with low sulfur dioxide contents (0.5 to 3% by volume).

Nitrous process is hardly used any more

1.6.2.2.2 Sulfuric Acid from Waste Sulfuric Acid and Metal Sulfates

Ecological considerations have led to increased processing of waste sulfuric acid and to its recycling in the particular production processes. The later is only possible when the concentration of impurities in the acid after processing is not too high. If the amount of impurities is too high, the only option is thermal cracking.

In the case of low impurity levels, the acid can be concentrated by evaporation and any organic compounds present removed by distillation or oxidation during or after the evaporation to more concentrated sulfuric acid

Regeneration of waste sulfuric acid is very expensive, worked-up acid always being more expensive than fresh acid manufactured from sulfur or pyrites, the cost increasing as the concentration of the acid to be processed decreases. The concentration should therefore be at least 20%. In the case of more dilute acids neutralization with e.g. lime or sodium hydroxide is carried out.

Process used for waste sulfuric acid recovery dependent upon the impurity level:

- high level of impurities: decomposition to SO_2
- low level of impurities: concentration of waste acid and recycling of the H_2SO_4 formed with, if necessary, oxidative removal of organic impurities

Regeneration of waste sulfuric acid is very expensive. Minimum practical concentration for waste acid regeneration is 20%

Concentration of dilute sulfuric acid is energy intensive due to:

- high evaporation enthalpy of water
- heat of dehydration of H_2SO_4 has to be supplied

Concentration is carried out at:

- reduced pressures
- atmospheric pressure

Concentration of waste sulfuric acid is extremely energy intensive due to the high heat of evaporation of water and the necessary supply of the heat of dehydration of sulfuric acid. Concentration processes in which the heat of evaporation is supplied indirectly are mainly carried out under reduced pressure. (The boiling point of 70% sulfuric acid is 160°C at 1 bar and 54°C at 0.01 bar.) Temperatures of 320°C are required at atmospheric pressure to concentrate up to 96% sulfuric acid. The highest concentration attainable by evaporation is 98.3% (azeotropic composition).

Evaporation in two stages:

- stage 1: preconcentration to 60 to 70% acid
- stage 2: superconcentration to over 90% acid

Evaporation is performed in two stages: preconcentration from ca. 20 to 60 to 70% sulfuric acid and superconcentration from 60 to 70% to over 90% acid. Preconcentration is carried out under atmospheric or reduced pressure. The usually operated processes are:

Preconcentration using:

- venturi concentrators:
  utilized for preconcentration of large quantities of dilute H_2SO_4 or for sulfuric acid strongly contaminated with solids

  Utilization of waste heat at low temperatures possible

Venturi concentrator: The to be concentrated sulfuric acid is injected into the radiation scrubber and there brought into contact with a dry gas stream, which takes up and thereby removes the water vapor. The heat of evaporation is either supplied directly via hot gases (furnace gas) or indirectly by heating the acid to be concentrated (e.g. with tail gases from a double contact plant) or by heat exchange with hot sulfuric acid from sulfur trioxide absorption. In this preconcentration process waste heat can be utilized at low temperatures. The venturi concentrator is in particular employed when large quantities of dilute sulfuric acid or sulfuric acid strongly contaminated with solids has to be preconcentrated.

- submerged burner:
  in particular for salt-containing sulfuric acid from titanium dioxide production and metal pickling processes

Submerged burner: Evaporation takes place in an evaporator boiler which is directly heated with combustion gases at 1500°C. This process is in particular used for the preconcentration of salt-containing dilute sulfuric acids, the salts crystallizing out during the evaporation process, and is used e.g. for the treatment of waste sulfuric acid from the production of titanium dioxide and from metal pickling processes.

- forced evaporation evaporator:
  operated at low temperatures under reduced pressure and with indirect heating

Forced evaporation evaporator: This process is generally operated under reduced pressure and with indirect heating at low temperatures and units consist in practice of multistage evaporation systems.

Superconcentration and purification:

In view of the energy and operating cost intensive nature of superconcentration, the starting concentration should be at least 70%. Several superconcentration processes are operated industrially either requiring plants with temperature resistant materials or operating at low pressures:

Plinke process: In this process sulfuric acid is distilled at atmospheric pressure with indirect heating by natural gas and oil combustion (combustion chamber temperature 800 to 1100°C). This process is predominantly used in Europe. The to be concentrated waste acid is fed in at the top of the distillation column into boiling 96% sulfuric acid at atmospheric pressure and 320°C in a cast iron boiler. Water is expelled at the column head leaving a 96% acid. By adding nitric acid, which is mainly reduced to nitrogen, organic impurities can be removed oxidatively.

- Plinke process:
  superconcentration carried out under atmospheric pressure

  oxidative purification by addition of HNO_3

Drum concentrators: Concentrations up to 93% acid are attained by direct contact with furnace gases. The purification effect is less than in the Plinke process. The sulfuric acid to be concentrated flows through a number of brick-lined chambers, which are connected in a cascade, in which furnace gases at 600°C flow in countercurrent to the acid and become saturated with water vapor.

- drum concentrators:
  less purification effect

  direct heating with hot furnace gases

Bayer-Bertrams process: The core of this plant is a quartz falling film evaporator operating at atmospheric pressure and directly heated with furnace gases. A good purification effect can be attained by adding appropriate oxidation agents. Generally the falling film evaporator is operated in tandem with a forced evaporation evaporator to increase the thermal efficiency. Sulfuric acid can be superconcentrated up to 98% with this process.

- Bayer-Bertrams:
  a falling film evaporator operated at atmospheric pressure generally in tandem with a forced circulation evaporator as a first stage, very good purification possible

1.6.2.3 Applications of Sulfuric Acid

Sulfuric acid being a key product in the chemical industry has many applications. Worldwide 65% is utilized in the manufacture of phosphorus and nitrogen fertilizers, whereas in Western Europe only 31% is so utilized. In the Federal Republic of Germany ca. 90% of the sulfuric acid produced is utilized in the chemical industry.

In the petrochemical industry sulfuric acid is utilized, for example, in the alkylation of isoalkanes with alkenes, in the chemical industry in the manufacture inorganic chemicals (e.g. hydrofluoric acid, chromic acid , aluminum sulfate) and organic products (e.g. dyes, explosives, isocyanates, soaps, detergents, fibers and pharmaceuticals). Sulfuric acid is also utilized in the manufacture of titanium oxide pigments, uranium and copper extraction, in steel pickling and in batteries.

Applications of H_2SO_4 in the Federal Republic of Germany and in Western Europe in 1993 (%):

	FRG	Western Europe
chemical industry	90	55
non-chemical industry	3	9
fertilizers	3	31
other	4	5

1.6.3 100% Sulfur Dioxide

100% SO_2 by:

- absorption

A number of processes are used for the manufacture of 100% sulfur dioxide:

Absorption agents are:

- water
- organic amines
- solutions of alkali or alkaline earth hydroxides
- ammonia
- alkali salts of weak inorganic and organic acids

In absorption processes sulfur dioxide is separated with a solvent from SO_2-containing gases. Water at atmospheric pressure or increased pressure (5 bar) is used as an absorption agent for sulfur dioxide, the absorbed sulfur dioxide being subsequently expelled with steam. Strongly alkaline solutions (e.g. alkali and alkaline earth hydroxides), ammonia and to an increasing degree weak alkali salts of inorganic and organic acids (e.g. sodium carbonate or citrates) are used as absorption agents for sulfur dioxide, the sulfur dioxide being subsequently swept out by adding acid. Occasionally aliphatic or aromatic amines are also utilized, the previously used sulfidine process with aqueous solutions of xylidine or toluidine is no longer used. In the USA the DMA-(N,N-dimethylaniline) process is used. In the Wellman-Lord process an aqueous solution of sodium sulfite and sodium hydrogen sulfite is utilized as absorption agent. This process is mainly utilized for desulfurization of furnace gases from power stations and tail gases from Claus plants.

Desulfurization of power station furnace gases is industrially possible using wet and dry purification processes

For flue-gas desulfurization, lime and limestone processes are utilized in which the furnace gas is scrubbed with an aqueous liquid containing the necessary quantity of calcium hydroxide or calcium carbonate for neutralizing the acidic furnace gas components. The end products are calcium sulfite/calcium sulfate sludges or on complete oxidation gypsum:

$$SO_2 + Ca(OH)_2 \longrightarrow CaSO_3 \cdot 0.5\, H_2O + 0.5\, H_2O$$
$$SO_2 + Ca(OH)_2 + 0.5\, O_2 + H_2O \longrightarrow CaSO_4 \cdot 2\, H_2O$$

In addition to this wet scrubbing process, dry purification processes are also utilized for the removal of sulfur dioxide from furnace gases, such as the absorption of sulfur dioxide on activated charcoal (BF-process from Bergbau Forschung).

- condensation by increased pressure and cooling

In the condensation process sulfur dioxide from roasting of sulfur are separated in liquid form by increasing the pressure to ca. 5 bar and cooling with countercurrent coolers, cooled with liquid ammonia.

Sulfur dioxide is formed by reacting sulfur with sulfur trioxide;

- reaction of SO_3 with S

$$2\,SO_3 + S \longrightarrow 3\,SO_2$$

which is freed of sulfur trioxide by treatment with sulfuric acid. In modern processes sulfur trioxide is not utilized as oleum but undiluted in liquid form, as with the sulfur. 25% oleum or liquid sulfur can be used, for example, as a reaction medium.

64.5 · 10^6 t of sulfur dioxide was produced in the Federal Republic of Germany in 1994.

Applications: In 1994 ca. 305 · 10^6 t of liquid sulfur dioxide was consumed just in the USA, of which 40% was utilized in the manufacture of sulfur-containing chemicals such as sulfites, hydrogen sulfites, thiosulfites, dithionites and salts of hydroxyalkane sulfinic acid and alkane sulfonates. It is also utilized in cellulose manufacture, in the chemical dressing of manganese ores, in the removal of sulfur-containing impurities from mineral oils, for disinfection and preservation in the food industry and for the treatment of water.

Applications:
- manufacture of chemicals
- cellulose production
- dressing of ores
- mineral oil processing
- disinfection and preservation agent

1.6.4 100% Sulfur Trioxide

Manufacture: Pure sulfur trioxide is industrially produced from oleum by distillation in stainless steel falling film evaporators or forced circulation evaporators and liquefaction of the vapor, in which a minimum temperature of 27 °C must be respected to prevent solidification of sulfur trioxide. The formation of solid sulfur trioxide modifications during longer transport times is hindered by the removal of water and the addition of stabilizers such as thionyl chloride or oxalyl chloride.

100% SO_3:
- manufacture from oleum by distillation and liquefaction

Applications: 100% sulfur trioxide is utilized for the manufacture of chlorosulfonic acid, thionyl chloride, aminosulfonic acid, dimethyl sulfate and for the sulfonation of organic substances, in particular for the detergent industry. It is superseding chlorosulfonic acid as a sulfonation agent to an ever greater extent, because no corrosive hydrogen chloride is produced.

- applications: various, in particular for sulfonation

1.6.5 Disulfur Dichloride

Disulfur dichloride:

- manufacture from sulfur and chlorine at ca. 240°C

Manufacture: Disulfur dichloride is manufactured in a continuous process by passing chlorine into liquid sulfur at ca. 240°C:

$$Cl_2 + 2\ S \xrightarrow{240\ °C} S_2Cl_2$$

Sulfur dichloride formed as a byproduct is converted to disulfur dichloride by adding excess sulfur.

- applications:

  starting material for the manufacture of thionyl chloride, sulfur dichloride, sulfur tetrafluoride etc. With polyols produces additives for high pressure lubricating oils and cutting oils

Applications: Disulfur dichloride is utilized in the manufacture of sulfur dichloride, thionyl chloride and sulfur tetrafluoride and with polyols for the production of additives for high pressure lubricating oils and cutting oils. In addition it is used as a catalyst in the chlorination of acetic acid. Solutions of sulfur in disulfur dichloride is utilized in the room temperature vulcanization of rubbers.

The worldwide consumption of disulfur dichloride has decreased from $30 \cdot 10^3$ t in 1987 to $15 \cdot 10^3$ t in 1992, due to a strong decrease in the consumption of chlorine-containing lubricants.

1.6.6 Sulfur Dichloride

SCl_2:

- manufacture from S_2Cl_2 and chlorine
- starting material for thionyl chloride
- other applications as for disulfur dichloride

Manufacture: Sulfur dichloride is produced by reacting liquid disulfur dichloride with gaseous chlorine at low temperatures in the presence of catalysts e.g. iodine:

$$S_2Cl_2 + Cl_2 \xrightarrow{I_2} 2\ SCl_2$$

Since it is very unstable, decomposing into its starting materials, it is only produced as an intermediate product.

Applications: Sulfur dichloride is utilized as for disulfur dichloride e.g. for the manufacture of thionyl chloride and in sulfidizing and chlorination reactions.

Ca. $8 \cdot 10^3$ t of sulfur dichloride was consumed worldwide in 1992.

1.6.7 Thionyl chloride

Manufacture: Thionyl chloride is manufactured by reacting sulfur dioxide or sulfur trioxide with sulfur dichloride and chlorine or with disulfur dichloride and chlorine:

1. $SO_2 + SCl_2 + Cl_2 \longrightarrow 2\ SOCl_2$
2. $SO_3 + 2\ SCl_2 + Cl_2 \longrightarrow 3\ SOCl_2$
3. $2\ SO_2 + S_2Cl_2 + 3\ Cl_2 \longrightarrow 4\ SOCl_2$
4. $SO_3 + S_2Cl_2 + 2\ Cl_2 \longrightarrow 3\ SOCl_2$

$SOCl_2$:

- manufacture from SO_2 or SO_3 and Cl_2 with SCl_2 or Cl_2 with S_2Cl_2 on an activated charcoal catalyst

Sulfur dichloride has to be used as a reaction partner for sulfur oxides in all cases.

All the processes operate in the gas phase in continuously operated plants with an activated charcoal catalyst. Unreacted sulfur dioxide, or sulfur dioxide produced as a byproduct, is converted in the gas phase with chlorine to sulfuryl chloride. This is fed back into the thionyl chloride synthesis and there reacts with sulfur dichloride or disulfur dichloride and chlorine to thionyl chloride. Unreacted sulfur dichloride is reacted with sulfur in the presence of a catalyst to disulfur dichloride. Pure thionyl chloride is obtained by fractional distillation.

Applications: $45 \cdot 10^3$ t of thionyl chloride was consumed worldwide in 1992. It is utilized as a chlorination agent e.g. for the manufacture of organic intermediates, pesticides, insecticides, pharmaceuticals, dyes and pigments. It is also utilized for the dehydration of metal chloride hydrates, the chlorination of metal oxides, as a non-aqueous electrolyte and as a cathodic material in particular types of lithium batteries.

- important chlorination agent for the chemical industry
- worldwide consumption in 1992: $45 \cdot 10^3$ t

The byproducts sulfur dioxide and hydrogen chloride, formed upon substitution of the hydroxy-groups of alcohols and carboxylic acids, can be largely absorbed by alkaline scrubbing. The thereby formed sulfite can be oxidized by chlorine to sulfate in alkaline solution.

1.6.8 Sulfuryl Chloride

Manufacture: Industrially sulfuryl chloride is almost exclusively produced by reacting sulfur dioxide with chlorine on an activated charcoal catalyst in a well-cooled tubular converter. Reaction of disulfur dichloride with

SO_2Cl_2:

- manufacture from SO_2 and chlorine on activated charcoal chlorine and oxygen on activated charcoal to sulfuryl chloride is also operated industrially.

- chlorination and sulfochlorination agent

Application: Sulfuryl chloride is used as a chlorination and sulfochlorination agent in the organic chemical industry, in particular for selective chlorination (e.g. for the side chains of aromatic compounds) and in the manufacture of organic intermediates for dyes, pharmaceuticals, pesticides and disinfectants.

1.6.9 Chlorosulfonic Acid

Chlorosulfonic acid ($ClSO_3H$):

- manufactured from SO_3 and HCl

Manufacture: Chlorosulfonic acid is produced by the reaction of liquid sulfur trioxide with hydrogen chloride or by the gas phase reaction of sulfur trioxide, from catalyst tray contact in sulfuric acid plants, with an excess of dry hydrogen chloride at high temperatures.

- applications:
  as a condensation and sulfonation agent, but also utilized for chlorosulfonation and sulfation

Applications: Chlorosulfonic acid is mainly utilized as a dehydrating condensation agent in organic synthesis and in the sulfonation of long chain aliphatic alcohols. $70 \cdot 10^3$ t/a of chlorosulfonic acid is estimated to be currently produced in Western Europe.

1.6.10 Fluorosulfonic Acid

FSO_3H:

- manufactured from SO_3 and HF in fluorosulfonic acid
- application:
  fluorination agent, catalyst, polishing of lead crystal glass

Manufacture: Fluorosulfonic acid is produced by feeding liquid hydrogen fluoride with cooling into a solution of sulfur trioxide in fluorosulfonic acid.

Applications: Fluorosulfonic acid is utilized as a fluorination agent in inorganic and organic chemistry, but also in the manufacture of sulfofluorides or sulfonic acids and as a catalyst for alkylation and polymerization reactions. It is also used in the polishing of lead crystal glass. No statistics are available regarding consumption and production figures.

1.6.11 Sulfurous Acid Salts

Of the salts of sulfurous acid only the sodium salts and calcium hydrogen sulfite are industrially important.

Sodium hydrogen sulfite is manufactured by reacting sulfur dioxide with sodium hydroxide or a sodium sulfite suspension. It is also produced as a byproduct in the synthesis of sodium disulfite.

Sodium hydrogen sulfite ($NaHSO_3$):

- manufactured from SO_2 + NaOH or Na_2SO_3

Sodium disulfite is produced by reacting sulfur dioxide with 50 to 70% sodium hydroxide in saturated sodium hydrogen sulfite solution. Sodium disulfite is isolated from the resulting suspension by centrifugation and dried.
Applications: Sodium disulfite is utilized in the photo-, paper, textile and leather industries and in water treatment.

$Na_2S_2O_5$:

- manufactured from SO_2 + NaOH in saturated solution of $NaHSO_3$
- applications in
  - photographic industry
  - paper industry
  - textile industry
  - leather industry

Sodium sulfite is produced by reacting sulfur dioxide-containing gases with sodium hydroxide in a saturated sodium sulfite solution at 60 to 80°C. The salt is separated by centrifugation and dried in a pneumatic-conveyor drier. It is marketed as its anhydrous salt.
Applications: Sodium sulfite is utilized as a reducing agent, in the manufacture of sodium thiosulfate, as an oxidation-prevention agent for developer solutions in the photographic industry, as an antichlorination agent in the paper and textile industries, for the preservation of food and for the treatment of boiler water.

Na_2SO_3:

- manufacture from SO_2 + NaOH in a saturated Na_2SO_3-solution
- applications in:
  - paper industry
  - photographic industry
  - textile industry
  - food industry

Calcium hydrogen sulfite solutions are produced by the reaction of sulfur dioxide-containing gases with limestone.
Application: These solutions are used in the production of sulfite cellulose.

$Ca(HSO_3)_2$:

- manufacture from SO_2 + $CaCO_3$
- utilized in sulfite cellulose manufacture

1.6.12 Sodium Thiosulfate, Ammonium Thiosulfate

Manufacture: Sodium thiosulfate is produced by reacting sulfur with sodium sulfite suspensions:

Sodium thiosulfate ($Na_2S_2O_3$):

- manufactured from S + Na_2SO_3 or S + $NaHSO_3$

$$Na_2SO_3 + S \longrightarrow Na_2S_2O_3$$

or sodium hydrogen sulfite solutions (sodium hydroxide and sulfur dioxide) and sulfur:

$$2\,NaOH + SO_2 + S \longrightarrow Na_2S_2O_3 + H_2O$$

The addition of sulfur to sodium sulfite is carried out in stirred vessels at 50 to 100°C. After removing excess sulfur, it crystallizes out as its pentahydrate: $Na_2S_2O_5 \cdot 5\,H_2O$.

- applications especially in the photographic industry, but also in bleaching and in paper manufacture

Applications: Ca. 90% of the sodium thiosulfate produced is utilized as a fixing salt in the photographic industry. It is also used as an antichlorination agent in bleaching plants and in paper manufacture. Ca. $30 \cdot 10^3$ t were produced in the USA in 1995.

$(NH_4)_2S_2O_3$:

- manufacture from $(NH_4)_2SO_3 + S$

Ammonium thiosulfate: is produced by reacting sulfur with ammonium sulfite in aqueous alkaline ammonia solution at 80 to 110°C:

$$\begin{aligned} 2\,NH_3 + SO_2 + H_2O &\longrightarrow (NH_4)_2SO_3 \\ (NH_4)_2SO_3 + S &\longrightarrow (NH_4)_2S_2O_3 \end{aligned}$$

Upon cooling the purified solution to ca. 20°C, anhydrous ammonium thiosulfate crystallizes out.

- application as a fixing salt in the photographic industry

Applications: Ammonium thiosulfate is almost exclusively used as a fixing salt in the photographic industry. Compared with sodium thiosulfate it has the advantages of shorter fixing and washing times, ca. 50% higher fixing bath yields and easier silver recovery from the exhausted fixing baths.

1.6.13 Sodium Dithionite and Sodium Hydroxymethanesulfinate

Sodium dithionite has almost completely replaced zinc dithionite for environmental reasons in recent years. Dithionite is manufactured by the reduction of sulfurous acid either in an unbound form or in the form of hydrogen sulfite. The following reducing agents are utilized in the industrial production of dithionite: zinc dust, sodium amalgam, sodium formate and sodium tetrahydroborate. A few years ago an electrochemical process was developed on the basis of sulfur dioxide and sodium hydroxide. Such plants, because of their compact construction, can be advantageously utilized for local production of quantities up to 1000 t/a. The current worldwide demand for sodium dithionite is ca. $300 \cdot 10^3$ t/a. The largest quantities are produced using the zinc dust and zinc formate processes.

$Na_2S_2O_4$:

- manufactured using
  - zinc dust process, ca. 35% of world production

Zinc dust process: Liquid or gaseous sulfur dioxide is reacted with zinc dust in an aqueous suspension at 40°C to zinc dithionite:

$$Zn + 2\,SO_2 \longrightarrow ZnS_2O_4$$

Upon addition of sodium carbonate or sodium hydroxide, zinc precipitates as zinc carbonate or zinc hydroxide:

$$ZnS_2O_4 + 2\,NaOH \longrightarrow Zn(OH)_2 + Na_2S_2O_4$$

After removal of the precipitate and concentration, anhydrous sodium dithionite is precipitated by adding sodium chloride.

Formate process: Sulfur dioxide under pressure (2 to 3 bar) is reacted with a solution of sodium formate in 80% aqueous methanol, the pH being maintained at 4 to 5 by adding sodium hydroxide:

$$HCOONa + 2\,SO_2 + NaOH \longrightarrow Na_2S_2O_4 + CO_2 + H_2O$$

The sodium dithionite formed precipitates out as fine anhydrous crystals.

Amalgam process: Cooled aqueous solutions of sodium hydrogen sulfite are reduced with sodium amalgam (from sodium chloride electrolysis). The sodium dithionite formed is recovered by crystallization.

- amalgam process:
  $NaHSO_3 + NaHg_x$
  ca. 15% of worldwide production

Sodium tetrahydroborate process: Sulfur dioxide is reacted with sodium tetrahydroborate in strongly alkaline aqueous solution forming sodium dithionite:

- $NaBH_4$-process:
  ca. 10% of worldwide production

$$NaBH_4 + 8\,NaOH + 8\,SO_2 \longrightarrow 4\,Na_2S_2O_4 + NaBO_2 + 6\,H_2O$$

Applications: Sodium dithionite is an important reducing agent in the dyeing and printing of textiles. It is also used as a bleaching agent in the textile and paper industries.

Sodium hydroxymethanesulfinate: Dithionites are the starting materials in the manufacture of sodium hydroxymethanesulfonate by the reaction of dithionites with formaldehyde in the presence of sodium hydroxide. In a variant of this process, zinc dithionite, as starting material, reacts with formaldehyde in aqueous solution forming zinc salts of hydroxymethanesulfinic acid and hydroxymethanesulfonic acid. The latter is reduced to zinc hydroxymethanesulfinate with added zinc at 90 °C.

$HOCH_2SO_2Na$:

- manufactured from dithionites, formaldehyde and NaOH
- applications in the textile and paper industries

Subsequent addition of sodium hydroxide or sodium carbonate yields the sodium compound.

- applications:
  direct and discharge printing

Applications: Sodium hydroxymethanesulfinate is used in direct and discharge printing for converting vat dyes into their leuco-forms. The current worldwide demand is ca. 15 to 18 · 10^3 t/a.

1.6.14 Hydrogen Sulfide

H_2S is present in:

- crude oil
- natural gas
- mineral springs

Hydrogen sulfide is present in large quantities in crude oil and especially in natural gas (it is processed to elemental sulfur: see Section 1.6.1.2.2). In addition small quantities are dissolved in mineral springs and it is formed as a byproduct in a large number of chemical reactions.

- manufacture:
  industrially from pure S and pure H_2 at ca. 350°C in the presence of Co/Mo-oxide catalysts

Industrially hydrogen sulfide is mainly manufactured from pure sulfur and pure hydrogen at ca. 350°C in the presence of catalysts, such as cobalt molybdenum oxide on γ-Al_2O_3.

- applications:
  - manufacture of NaHS and Na_2S
  - manufacture of sulfur-containing organic compounds
  - in the production of heavy water

Applications: Hydrogen sulfide is the starting material for the manufacture of sodium hydrogen sulfide, sodium sulfide and organic sulfur compounds, such as thiophenes or thiols. In several plants hydrogen sulfide is utilized for the production of heavy water.

1.6.15 Sodium Sulfide

Currently most sodium sulfide is still manufactured using the classical reduction of sodium sulfate with coal:

$$Na_2SO_4 + 2\,C \longrightarrow Na_2S + 2\,CO_2$$

Na_2S:

- manufactured from:
  - Na_2SO_4 + 2C in
    pot furnaces
    continuous furnaces
    rotary plate furnaces
  - sodium polysulfide + $NaHg_x$

The reaction is carried out in pot furnaces (low brick-lined hearths with lids), continuous furnaces or rotary plate furnaces. The melt produced in the furnace is mashed with water, the undissolved material removed and the solution concentrated to 60 to 62% sodium sulfide by evaporation in cast iron vessels. This concentrated solution solidifies at ca. 90°C.

In addition to the reduction of sodium sulfate, an electrolysis process is operated in which a sodium polysulfide solution (from sodium sulfide solution and sulfur) is reacted with electrolytically produced sodium amalgam. In this reaction sulfur is reduced to sodium sulfide:

$$Na_2S + 3\ S \longrightarrow Na_2S_4$$
$$Na_2S_4 + 6\ NaHg_x \longrightarrow 4\ Na_2S + 6\ Hg_x$$

Sodium sulfide is also formed by the reaction of hydrogen sulfide with sodium hydroxide.

The reduction of sodium sulfate with gaseous reducing agents such as hydrogen (Sulfigran process, formerly operated in Leverkusen), carbon monoxide or hydrocarbons is no longer of industrial importance.

Applications: Sodium sulfide is mainly used in tanning as a hair-removing agent (so-called asher). It is also utilized in ore flotation, dyeing with sulfur dyes in the textile industry and in the chemical industry e.g. for the precipitation of heavy metal ions. Anhydrous sodium sulfide is also utilized in the manufacture of polyphenylenesulfide (PPS), a high temperature-resistant plastic. The current production of sodium sulfide in Western Europe is estimated to be ca. $50 \cdot 10^3$ t/a.

- applications:
  - hair removal agent in the leather industry
  - in ore flotation
  - in the textile industry
  - in the manufacture of polyphenylenesulfide

1.6.16 Sodium Hydrogen Sulfide

Manufacture: Sodium hydrogen sulfide is manufactured by reacting hydrogen sulfide with either sodium sulfide or sodium hydroxide.

Applications: Sodium hydrogen sulfide is mainly used in the paper industry, for ore flotation, in dye chemistry, in the leather industry for hair removal and in the synthesis of organic chemicals. The 1994 USA production of sodium hydrogen sulfide was ca. $100 \cdot 10^3$ t/a.

NaHS:

- manufacture from H_2S + NaOH or H_2S + Na_2S
- application spectrum in the USA in 1994:

paper production	40%
ore flotation	35%
dyes and chemicals	12%
leather industry	9%
other uses	4%

1.6.17 Carbon Disulfide

CS_2:

- manufacture from:
  - carbon and sulfur in retort or electrothermal processes, mainly in countries without methane or natural gases
  - CH_4 or natural gas and sulfur at ca. 650°C

Manufacture: Up to fairly recently carbon disulfide was almost exclusively manufactured by the reaction of carbon, in particular low ash charcoal, with sulfur at high temperatures in brick-lined retorts or in electrical furnaces (electrochemical process). In the USA, Canada, Japan and Europe methane or natural gas is currently largely used as the carbon source and this is reacted with sulfur at ca. 650°C:

$$CH_4 + 2\,S_2 \longrightarrow CS_2 + 2\,H_2S$$

Production of CS_2 in 1991 (10^6 t):

World:	1.287
of which CH_4 + S:	1.052
C + S:	0.235

- application spectrum of CS_2:

- fiber manufacture	65%
- cellophane	10%
- CCl_4	10%
- other uses	15%

Carbon disulfide is purified by distillation. The hydrogen sulfide byproduct is processed to sulfur in Claus plants.

Ca. 1.3 · 10^6 t of carbon disulfide was produced worldwide in 1991, mainly from methane and sulfur.

Applications: Carbon disulfide is mainly used in the viscose industry for fiber production. Smaller quantities are utilized in the manufacture of cellophane from viscose or as a starting material in the production of carbon tetrachloride. In addition carbon disulfide is used in the production of vulcanization accelerators, flotation agents, corrosion inhibitors, pesticides and intermediates for pharmaceuticals.

References for Chapter 1.6: Sulfur and Sulfur Compounds

Schmidt, M., Siebert, W. 1973. *Sulphur*, Comprehensive Inorganic Chemistry, 795 –933, Oxford, Permagon Press.

Stanford Research Institute, Publ. 1996. *Miscellaneous Sulfur Chemicals-United States*; Chemical Economics Handbook, Menlo Park, California, USA.

Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 5, 185 – 195, VCH Verlagsgesellschaft, Weinheim.

Ullmann's Encyclopedia of Industrial Chemistry. 1988. 5. Ed., Vol. A 11, 431 – 434, VCH Verlagsgesellschaft, Weinheim.

Ullmann's Encyclopedia of Industrial Chemistry. 1994. 5. Ed., Vol. A 25, 443 – 486, 507–612, 623–703, VCH Verlagsgesellschaft, Weinheim.

Sulfur:

Borsboom, J., Goar, B. G., Heijkoop, G., Lagas, J. A. 1992, *SUPERCLAUS: Performance World-Wide*, Sulphur **220**, 5–6, 44–47.

Kiyoura, R. 1981. *International Trends in Sulfur and Overview for 1980–1981*. Chemical Economy and Engineering Review **13**, 13—20.

Palm, J. W. 1979. *Sulphur Recovery Plant Operation*, Sulphur **143**, 34—39.

Stanford Research Institute, Publ. 1995. *Sulfur Products*; in Chemical Economics Handbook, Menlo Park, California, USA.

Steudel, R., Mäusle, H.-J. 1980. *Flussiger Schwefel - ein Rohstoff komplizierter Zusammensetzung*. Chemie in unser Zeit **14**, 73 – 81.

Sulfuric Acid:

Bauer, R. A., Vidon, B. P. 1978. *The Ugine Kuhlmann Pressure Process*, Chem. Eng. Prog. **74**, 68 – 69.

Bhattacharya, A. 1976. *Production of Sulphuric Acid and cement from Phosphogypsum Using OSW Process*, Chem. Age India **27**, 1009 – 1014.

Bodenbrenner, K., von Plessen, H., Steiner, R. 1978. *Regeneration von Abfallschwefelsäure*, Chem- Ing.-Tech. **50**, 30 – 36.

The Changing Sulfuric Acid Industry Chem. Week. 2/1982, 40 – 42.

Schulze, J., Ruppert, M. 1980. *Technische-wirtschaftliche Rationalisierung der Schwefelsäure-Produktion - Wege und Ergebnisse*, Chem. Ind. XXXII: *Technische Entwicklung bei den konventionellen Verfahren*, 580 – 586; *Endgasreinigung und Schwefelsäure-Recycling*, 685 –689; *Wirtschaftlichkeitsvergleich - Grundlagen der Vorkalkulation*, 754 –756.

Stanford Research Institute, Publ. 1995. *Sulfuric Acid*; in Chemical Economics Handbook, Menlo Park, California, USA.

Statistisches Bundesamt, Hrsg. 1994. Fachserie 4; Reihe 3.1.

van der Berkhof, B. 1980. *Sulfuric Acid as a By-Product of the European Non-Ferrous Metals Industry*, Sulphur **146**, 24–28.

Sulfur Dioxide:

Statistisches Bundesamt, Hrsg. 1994. *Produktion im produzierenden Gewerbe nach* Waren *und Warengruppen*. Reihe 3.1, Wiesbaden.

1.7 Halogens and Halogen Compounds

1.7.1 Fluorine and Fluorine Compounds

The worldwide consumption of fluorine can be adduced from the consumption of fluorspar, since the contribution from the possible second fluorine source, hexafluorosilicic acid, which is a byproduct in the production of phosphate-containing fertilizers, has been minor up to now. Starting materials for the manufacture of industrial fluorochemicals are:

- fluorspar, CaF_2
- fluorapatite, $3Ca_3(PO_4)_2 \cdot CaF_2$ with 2 to 4% by weight fluorine
- naturally occurring cryolite, Na_3AlF_6, which was extracted in Greenland up to 1963.

The estimated fluorine content in the Earth's crust is ca. 0.09%.

Fluorine sources:

- fluorspar
- fluorapatite
- natural cryolite (minor)

Fluorine content in Earth's crust: 0.09%

1.7.1.1 Fluorspar

The total reserves of economically and marginally economically workable fluorspar is ca. $311 \cdot 10^6$ t. The quantities extracted worldwide were:

- $4.054 \cdot 10^6$ t in 1992
- $4.021 \cdot 10^6$ t in 1993

Applications in the manufacture of:

- raw steel
- aluminum
- fluorochemicals

Table 1.7-1. Fluorspar extraction in 1993 and Reserves in 10^3 t

	World	P.R. China	Mexico	South Africa	France	Italy	Great Britain	Spain	USA	Mongolia	Former States of USSR
Extraction in 1993	4021	2100	370	218	125	75	65	85	60	180	250
Reserves	311,000	27,000	19,000	30,000	10,000	6,000	2,000	6,000	1,100	20,000	62,000

1993 Prices: Mexico/South Africa: 100-112 \$/t, China: 89-97 \$/t, Northern Europe: 105-110 \$/t

Mexico and South Africa have clearly lost market share to China, which has very good quality and inexpensive fluorspar (extraction in Mexico in 1987: 824 · 10^3 t).

1.7.1.1.1 Fluorspar Extraction

Extraction of fluorspar:
- by mining

Beneficiation:
- grinding
- flotation
- drying

Fluorspar is extracted by both open-cast and underground mining and is found together with minor quantities of other minerals such as heavy spar ($BaSO_4$), galena (PbS), quartzite (SiO_2), zinc blende (ZnS) and carbonate and metal(III) oxide. Deep mined fluorspar (calcium fluoride content: 30-80% by weight) has to be concentrated. This beneficiation is carried out by mechanical grinding of ores in crushers or ball mills (particle size <0.1 mm) and subsequent multistage flotation (flotation: separation of mixtures of solids on the basis of the different wettabilities of the components). The ore can be concentrated with a yield of ca. 90% up to a calcium fluoride concentration of 96-98% by weight (so-called acidspar), the residue consisting of ca. 10% by weight beneficiated mixtures with low calcium fluoride contents (met spar), which can, for example, be used in the steel industry. It can be briquetted, if no coarse product is obtained during the process. Remaining impurities are: silicon dioxide (SiO_2), calcium carbonate ($CaCO_3$) and barium sulfate ($BaSO_4$).

1.7.1.1.2 Qualities and Utilization of Fluorspar

Fluorspar is utilized, depending upon quality, in the manufacture of aluminum, bricks, cement, glass, glass fibers, enamel and in the metal working industry (foundries). Other applications consume only small quantities.

The following qualities are marketed:

- metallurgical fluorspar (met grade) as a coarse to lumpy material or briquetted (calcium fluoride content: 60-85%). Utilized as a flux in steel manufacture (lowering of the melting point and viscosity of the slag) and aluminum manufacture. In the latter aluminum fluoride is produced by direct decomposition of aluminum-containing minerals with fluorspar and sulfuric acid:

Metallurgical fluorspar:

- CaF_2-content < 85%
- flux in the manufacture of steel and aluminum

$$3\,CaF_2 + 3\,H_2SO_4 + Al_2O_3 \longrightarrow 3\,CaSO_4 + 2\,AlF_3 + 3\,H_2O$$

65-85 · 10^3 t/a, based on hydrogen fluoride, or 126-165 · 10^3 t/a, based on calcium fluoride, of this quality were consumed in the USA in 1991.

- acidspar (acid grade) with at least 96.5% by weight of calcium fluoride for the manufacture of hydrogen fluoride
- spar for glass/ceramics (ceramic grade, calcium fluoride content: 90 to 95% by weight), also utilized as a flux in welding
- spar for optical purposes (optical grade) with a calcium fluoride content of greater than 99% by weight (e.g. glasses for high energy laser systems)

Acidspar:

- CaF_2-content: 96.5-97.5%
- utilization for manufacture of hydrogen fluoride

Table 1.7-2. Analysis of Ceramic and Acid Grades of Fluorspar in wt%.

	ceramic grade	acid grade
CaF_2	90-95.5	96.5-97.5
SiO_2	1.2-3	1.0
$CaCO_3$	1.58-3.4	1.0-1.5
MgO		0.15
B		0.02
Zn		0.02
Fe_2O_3	0.1	0.1
P_2O_5		0.03
$BaSO_4$		0.2-1.3
sulfide		0.01
Me_2O_3	0.15-0.25	0.1-0.3

Me = trivalent metal such as e.g. Al (III)

Table 1.7-3. US Fluorspar Consumption Spectrum for 1991 (incl. Imports).

fluorspar utilization	
manufacture of hydrogen fluoride	201 · 10^3 t
manufacture of steel	66 · 10^3 t
production of aluminum	127 · 10^3 t
other uses	84 · 10^3 t
total	478 · 10^3 t
comprising imports of	414 · 10^3 t

1.7.1.1.3 Fluorapatite

Byproduct from phosphoric acid manufacture:

Hexafluorosilicic acid, a little used source of fluorine

The hexafluorosilicic acid solutions produced as a byproduct in the production of phosphoric acid by the digestion of apatite [$Ca_3(PO_4)_2 \cdot CaF_2$ with 2-4% fluorine content, byproduct silicon dioxide] with sulfuric acid are important raw materials for the manufacture of fluorochemicals (e.g. manufacture of sodium fluoride NaF). The reserves of available fluorine from fluorapatite are estimated to be $327 \cdot 10^6$ t CaF_2 (of which $32 \cdot 10^6$ t is in the USA), the fluorine quantities available in fluorapatite being therefore considerably greater than the fluorspar reserves. However, the industrial exploitation is still negligible. The reasons therefor are that:

- the aqueous solution of hexafluorosilicic acid produced in addition to phosphoric acid has a concentration of at most 36% by weight, so a large quantity of water has to be transported with it in the event of utilization.
- up to now only the large scale production of fluorides from hexafluorosilicic acid has proved possible, but not of hydrofluoric acid or hydrogen fluoride.
- some of the impurities in hexafluorosilicic acid, in particular phosphorus compounds, make further processing difficult.

Nevertheless, it is expected that this source of fluorine will become more important in the future.

1.7.1.2 Fluorine and Inorganic Fluorides

1.7.1.2.1 Fluorine

Fluorine:

from the electrolysis of molten KF/HF-mixtures at 8 to 12 V with carbon anodes

Fluorine is manufactured electrochemically from a salt melt, which consists of a mixture of potassium fluoride and hydrofluoric acid in a molar ratio of 1:2.0 to 1:2.2. The temperature of the salt melt is ca. 70 to 130°C. Potassium fluoride provides the necessary melt conductivity, the hydrogen fluoride consumed being continuously replenished during the electrolysis.

$$2\,HF \xrightarrow{56.3\ Ah} H_2 + F_2$$

Description of the Electrolysis Cell:

The cathodes and cell are usually made of Monel alloys or steel, the anodes of degraphitized carbon. The cathodic and anodic compartments are not separated by a diaphragm, but by "steel skirts" suspended from the lid into the melt. Fig. 1.7-1 shows a cross-section through an industrial fluorine cell.

Technical data:

Voltage:	8 to 12 V (theoretical separation voltage for fluorine: 2.85 V)
Current density:	1.0-1.5 kA/m^2
Current yield:	90-98%
Energy consumption:	14-17 kWh/kg F_2
Heat removal from the cell:	34.8 MJ/kg F_2

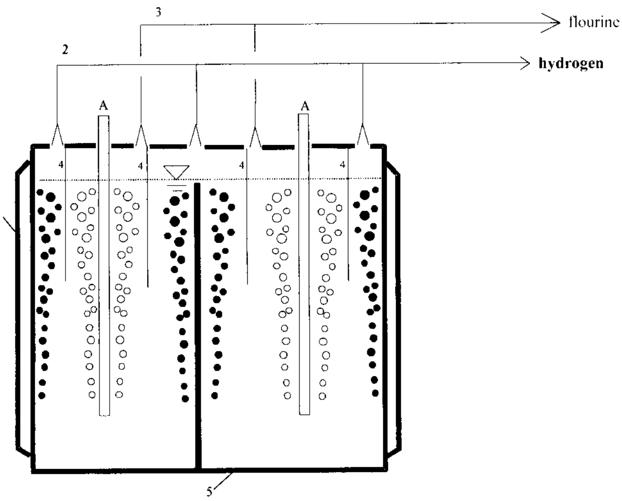


Fig. 1.7-1. Schematic cross-section through an industrial fluorine cell. 1) cooling jacket, 2) hydrogen outlet, 3) fluorine outlet, 4) steel skirt for separating the gas above the melt , 5) vessel at the same potential as the cathode, C = cathode, A = anodes.

The lifetime of the anodes is, for example, 40 to 80 · 10^6 Ah in the type developed by the US Atomic Energy Commission. Since the voltage applied is well above the theoretical value, considerable amounts of heat, ca. 35 MJ/kg fluorine, have to be dissipated. On the other hand, the cooling water temperature must be maintained above the melting point of the electrolyte to prevent its solidification.

The fluorine and hydrogen produced contain ca. 10% by volume of hydrogen fluoride. Cooling below -100°C strongly reduces the hydrogen fluoride content. The residual hydrogen fluoride in the hydrogen is removed by an alkaline scrubber and that in the fluorine further reduced, if necessary, by passing over sodium fluoride.

Further processing of fluorine to:

- uranium hexafluoride
- sulfur hexafluoride

World capacity for fluorine: $> 7.5 \cdot 10^3$ t/a

The fluorine thereby obtained is directly processed further (to uranium hexafluoride, sulfur hexafluoride) or liquefied (b.p. -188°C) and filled into pressure cylinders. Pressure cylinders with mixtures of fluorine and nitrogen, with 10 or 20% by volume of fluorine, are widely marketed (utilized, for example, for the surface fluorination of vehicle fuel tanks). The worldwide fluorine capacity is estimated to be ca. $7.5 \cdot 10^3$ t/a, of which 60% is in the USA, 25% in Europe and 15% in Japan. Ca. 75% of the fluorine manufactured is utilized in the manufacture of uranium hexafluoride, 22.5% in the manufacture of sulfur hexafluoride and 2.5% in the manufacture of tetrafluoromethane. In 1986 ca. 100 t of fluorine was utilized in the manufacture of fluorographite (high conductivity) for use in batteries.

1.7.1.2.2 Hydrogen Fluoride

Economic Importance

World capacity for hydrogen fluoride in 1994: $> 10^6$ t/a

Hydrogen fluoride is a key product in the manufacture of fluorochemicals.

Table 1.7-4. Hydrogen Fluoride Production in 1994 in 10^3 t/a

USA	Japan	Belgium	France	FRG	Greece	Italy	NL	Spain	GB	Mexico
241	124	10	98	90	15	83	12	40	72	55

Manufacture of hydrogen fluoride: from fluorspar and sulfuric acid in externally heated rotary tube furnaces

Industrially hydrogen fluoride is manufactured by the reaction of sulfuric acid with fluorspar (acid grade):

$$CaF_{2(s)} + H_2SO_{4(liq.)} \longrightarrow 2\ HF_{(g)} + CaSO_{4(s)}$$

$$\Delta H_{R,25^\circ C} = +\ 59 kJ \cdot mol^{-1}$$

energy input: 14 MJ/kg hydrogen fluoride

The small quantities of compounds such as carbonates or oxides (e.g. iron oxide) in the fluorspar also react with the sulfuric acid, necessitating a ca. 5-10% excess of sulfuric acid. Silicon dioxide reacts with the already formed hydrogen fluoride to form silicon tetrafluoride, thereby reducing the hydrogen fluoride yield. The above-mentioned impurities in fluorspar produce water and carbon dioxide in addition to silicon tetrafluoride produced from silicon dioxide:

$$SiO_2 + 4\,HF \longrightarrow SiF_4 + 2\,H_2O$$

3.9% CaF_2 and 4.9% H_2SO_4 required/consumed per 1% SiO_2

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + H_2O + CO_2$$

$$M_2O_3 + 3\,H_2SO_4 \longrightarrow M_2(SO_4)_3 + 3\,H_2O$$

1.84% H_2SO_4 per % metal oxide

M = trivalent metal

Since the reaction is endothermic the reaction is generally carried out in an indirectly heated rotary tube furnace (length up to 30 m, diameter up to 3 m) at high temperatures (temperature ca. 200°C). The capacity of such indirectly heated furnaces can be more than 45 t HF per day. 3.8 t of calcium sulfate (anhydrite) is produced per ton of hydrogen fluoride.

The reaction of solid fluorspar with liquid sulfuric acid produces a solid (calcium sulfate) and a gaseous (hydrogen fluoride) product. The reaction passes through a paste-like phase. Many reactor modifications have been developed to attain an optimal reaction in this phase. The aim is thorough mixing of this phase, which is achieved by internal fittings in the rotary tube (e.g. paddles) or by kneading the reaction mixture in a kneader.

Upon leaving the furnace the hydrogen fluoride formed is scrubbed with concentrated sulfuric acid, which is subsequently utilized in the reaction with fluorspar. In this scrubbing the water in the hydrogen fluoride is removed by being bound by added oleum.

The Bayer process is represented as a flow sheet in Fig. 1.7-2.

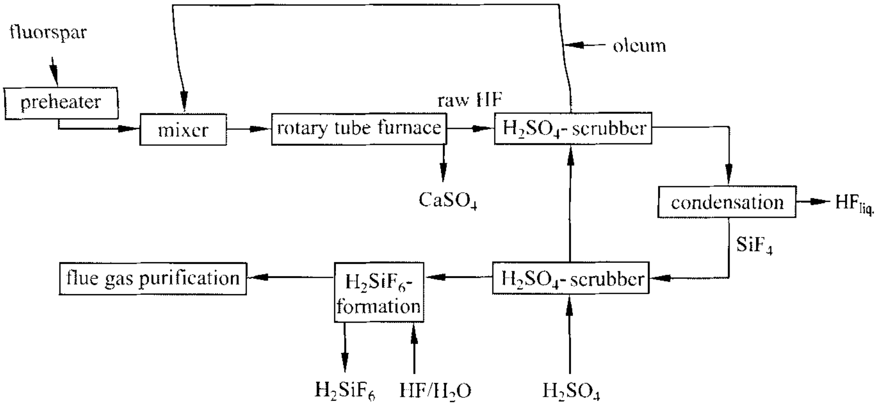


Fig. 1.7-2. Flow sheet of the Bayer process for the manufacture of hydrogen fluoride.

HF manufacture by Bayer A.G.:

- preheating of fluorspar
- high temperature
- high space-time-yield

The necessary process heat is supplied at several points in the process:

- preheating of fluorspar by hot gas
- preheating of sulfuric acid by heat exchange with the raw gaseous hydrogen fluoride
- addition of sulfur trioxide as oleum
- heating of the rotary tube furnace

Fluorspar preheated to 400°C and preheated sulfuric acid are fed into a mixer, in which partial reaction occurs, the reaction being completed in the rotary tube furnace. The raw hydrogen fluoride, which in addition to air, silicon tetrafluoride, hydrogen, sulfur dioxide and carbon dioxide also contains calcium sulfate dust, is scrubbed with sulfuric acid. The scrubbing acid, after addition of oleum to bind the water, is reacted with fluorspar. Pure hydrogen fluoride (b.p. 19.9°C) is obtained by multistage cooling of the raw hydrogen fluoride. If necessary, the hydrogen fluoride can be purified further by post-treatment steps e.g. distillation. The gas remaining after condensation is scrubbed with sulfuric acid to remove residual hydrogen fluoride. Afterwards the gas, which still contains silicon tetrafluoride, is scrubbed with hydrofluoric acid to form hexafluorosilicic acid:

$$SiF_4 + 2\,HF_{(aq.)} \longrightarrow 2\,H_2SiF_{6(aq.)}$$

Upon scrubbing with water, silicon dioxide is produced in addition to hexafluorosilicic acid:

$$3\ SiF_4 + 2\ H_2O \longrightarrow 2\ H_2SiF_6 + SiO_2$$

Byproduct in the production of hydrogen fluoride:

hexafluorosilicic acid

Hexaluorosilicic acid can be widely utilized (manufacture of fluorides and hexafluorosilicates).

Buss has developed a widely operated variant of the fluorspar decomposition in which the pre-reaction is carried out in a continuously operating kneader, which is linked to an indirectly heated rotary tube furnace in which the reaction proceeds to completion. In a further variant (a process developed by DuPont) the necessary heat is supplied by reacting sulfur trioxide with water to sulfuric acid in the reactor (e.g. in a fluidized bed process). The heat of sulfuric acid formation thereby liberated provides much of the energy for the endothermic fluorspar decomposition.

HF-manufacturing process from Buss:

- pre-reaction of CaF_2 and H_2SO_4 in a kneader
- at low temperatures

The calcium sulfate leaving the rotary tube furnace (anhydrite) still contains excess sulfuric acid, which is neutralized with lime. After treatment this anhydrite can be utilized e.g. in the laying of cement floors, for infilling in mines or in the cement industry as a setting regulator.

Byproducts in manufacture of hydrogen fluoride:

calcium sulfate, anhydrite

Application after treatment in:

- building industry
- mining
- cement industry

The pyrolytic cracking of silicon tetrafluoride at high temperatures is a further way of utilizing the hexafluorosilicic acid byproduct:

$$SiF_4 + 2\ H_2O \longrightarrow SiO_2 + 4\ HF$$

This process has a certain importance in the manufacture of FLUOSIL®, a silicon dioxide with a large specific surface area.

Table 1.7-5. Standard quality of technical hydrogen fluoride.

HF	99.95 wt%
non-volatile acids	100 ppm
sulfur dioxide	50 ppm
water	300 ppm
arsenic	25 ppm
hexafluorosilicic acid	100 ppm

Applications

applications of hydrogen fluoride:

- inorganic fluorides

Hydrogen fluoride is mainly utilized:

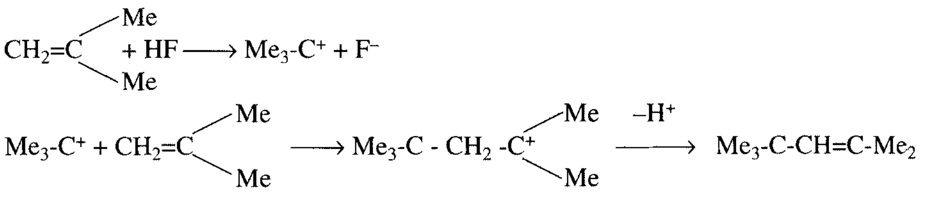
- in the manufacture of inorganic fluorides such as aluminum fluoride, uranium tetrafluoride (HF demand in USA in 1994: 12· 10^3 t including fluorine manufacture), sodium fluoride, boron trifluoride, ammonium hydrogen fluoride and aqueous solutions of hydrogen fluoride

- fluorohydrocarbons
- organofluoro-compound

- in the manufacture of organofluoro-compounds particularly fluorohydrocarbons. Two thirds of the hydrogen fluoride produced is utilized in the manufacture of fluorochlorohydrocarbons. Since the ozone problem surfaced the consumption has decreased, as manufacture of fluorochlorohydrocarbons was only permitted until 31.12.95, while the demand for substitute products, the fluorohydrocarbons, has risen. The consumption of hydrogen fluoride in the manufacture of these substitutes in the USA in 1995/96 was ca. 140 · 10^3 t/a and is still rising as a result of the substitution of fluorochlorohydrocarbons by fluorohydrocarbons. 150 kg of hydrogen fluoride is required to manufacture 1 t of R11 (trichlorofluoromethane), 350 kg of hydrogen fluoride is required for the manufacture of 1 t of R12 (dichlorodifluoromethane) and 540 kg of hydrogen fluoride is required for the manufacture of 1 t of R22 (difluorochloromethane). 551 kg of hydrogen fluoride is required for the manufacture of 1 ton of R134a (tetrafluoroethane, CF_3–CH_2F), one of the substitutes.

- catalysts

- as a catalyst in alkylation reactions e.g. the dimerization of isobutene. This process is increasing in importance due to the rising demand for highly knock-resistant fuels. Manufacture is carried out by utilizing short-chain crude oil fractions:



$$CH_2{=}C(Me)_2 + HF \longrightarrow Me_3\text{-}C^+ + F^-$$

$$Me_3\text{-}C^+ + CH_2{=}C(Me)_2 \longrightarrow Me_3\text{-}C\text{-}CH_2\text{-}C^+(Me)_2 \xrightarrow{-H^+} Me_3\text{-}C\text{-}CH{=}C\text{-}Me_2$$

The hydrogen fluoride is not actually consumed, only compensation for losses due to entraining being required. The entrained hydrogen fluoride is converted into calcium fluoride or potassium fluoride. On average 68 kg of hydrogen fluoride are required per barrel (159.1 L) (current hydrogen fluoride use in the USA: 16 · 10^3 t/a).

Inorganic fluorine products are used in the etching and polishing of glass, pickling of steels and the manufacture of semiconductors. Hydrogen fluoride is marketed as a liquid or as an aqueous solution (in a concentration range of 40 to 75% hydrogen fluoride). Steel containers can be used for hydrogen fluoride contents greater than 70%, plastic or rubber-lined containers being necessary at lower concentrations.

Table 1.7-6. Hydrogen Fluoride Consumption in Western Europe and the USA in 1991 in 10^3 t/a.

	Western Europe	USA
AlF_3	22	**13
F_2	8	
UF_4	6	13
Na_3AlF_6	4	
fluorochlorohydrocarbons/ fluorohydrocarbons	151	152
fluoro-aromatic compounds	12	
steel/etching	12	13
alkylation	6	16
glass	5	
other uses	33	34

** additionally 65-80 · 10^3 t/a of HF from CaF_2 is directly converted to AlF_3.

Table 1.7-7. Hydrogen Fluoride Consumption Spectrum in the USA in %.

	1994	1999 (expected)
Total consumption (10^3 t)	241	251
fluorohydrocarbons	56%	53%
inorganic and organic fluorochemicals	16%	18%
aluminum industry	4%	5%
alkylation	5%	5%
steel/etching	5%	4%
uranium fuels	3%	4%
other uses	11%	11%

1.7.1.2.3 Aluminum Fluoride

Aluminum fluoride:
flux in the aluminum industry

worldwide capacity in 1990:
> 400 · 10^3 t/a

Aluminum fluoride is utilized, in addition to cryolite, as a raw material in the electrolytic manufacture of aluminum (temperature of electrolyte: 950°C, composition: 80-85% Na_3AlF_6, 5-7% AlF_3, 5-7% CaF_2, 2-6% Al_2O_3, 0-7% LiF). No fluorine should actually be consumed in this process, modern plants recovering the fluorine in its entirety. Other uses are: as a flux (in welding, soldering, manufacture of casts), and as a melting point depressant in glass and enamel. The aluminum fluoride capacities in Europe are given in the table below.

Table 1.7-8. Aluminum Fluoride Production in Europe in 1992 in 10^3 t/a.

	France	FRG	Italy	Norway	Spain	Sweden
	50		15	25	14	20
starting material	fluorspar		fluorspar	fluorspar	fluorspar	hexafluorosilicic acid

Most important European manufacturer is PCUK with a capacity of 96 · 10^3 t/a.

Aluminum Fluoride Manufacture from Hydrogen Fluoride

Manufacture of aluminum fluoride:
- from hydrated aluminum oxide
- from hexafluorosilicic acid

In the Lurgi process aluminum hydroxide is first calcined at 300 to 400°C and then reacted with hydrogen fluoride in a fluidized bed reactor at 400 to 600°C (dry process):

$$2\ Al(OH)_3 \xrightarrow{300-400\ ^\circ C} Al_2O_3 + 3\ H_2O$$

$$Al_2O_3 + 6\ HF \xrightarrow{400-600\ ^\circ C} 2\ AlF_3 + 3\ H_2O$$

This process places high demands on the plant materials, alloys such as Inconel or Monel being used.

In the PCUK process calcined hydrated aluminum oxide is reacted with a mixture of hydrogen fluoride and furnace gas. The hydrogen fluoride is produced in situ from fluorspar and sulfuric acid in a directly heated rotary tube furnace. The resulting mixture of hydrogen fluoride and furnace gases is reacted with calcined aluminum hydroxide to aluminum fluoride in a fluidized bed reactor.

Aluminum Fluoride Manufacture from Hydrofluoric Acid

Hydrofluoric acid (15-60% by weight) is reacted in a further process (wet process) with aluminum hydroxide to aluminum fluoride trihydrate ($AlF_3 \cdot 3H_2O$), which is, e.g., calcined in a rotary tube furnace.

Aluminum Fluoride Manufacture from Hexafluorosilicic Acid

Chemie Linz AG Process

In this process a hexafluorosilicic acid solution is reacted with aluminum hydroxide at 100°C. After separating off the silica which precipitates, the aluminum fluoride crystallizes as its trihydrate. Heating above 500°C provides anhydrous aluminum fluoride.

$$2\,Al(OH)_3 + H_2SiF_6 \xrightarrow{100\,^\circ C} 2\,AlF_3 + 4\,H_2O + SiO_2$$

The dehydration of aluminum fluoride trihydrate ($AlF_3 \cdot 3H_2O$) above 300°C results in partial pyrolysis and the formation of aluminum oxide (Al_2O_3) and hydrogen fluoride. This is prevented by first removing 2.5 molecules of water at 200°C and then completing the drying with a short heating at 700°C.

Table 1.7-9. Standard Aluminum Fluoride Quality in % by weight.

AlF_3	Al_2O_3	SiO_2	Fe as Fe_2O_3	S as SO_2
90-92	8-9	0.1	0.1	0..3

This process is operated in Sweden, Rumania, Tunisia and Japan.

UKF Process

In the UKF process hexafluorosilicic acid is reacted with ammonia to ammonium fluoride and silica. After silica removal, the ammonium fluoride solution is reacted with double its molar quantity of aluminum oxide hydrate to a mixture of ammonium aluminum hexafluoride (ammonium cryolite) and aluminum oxide hydrate. After separation, this is converted at 500°C into aluminum fluoride, ammonia and water:

$$H_2SiF_6 + 6\,NH_3 + 2\,H_2O \longrightarrow 6\,NH_4F + SiO_2$$

$$6\,NH_4F + Al_2O_3 \xrightarrow{100^\circ C} [(NH_4)_3AlF_6 + 0.5Al_2O_3] + 3\,NH_3 + 1.5\,H_2O$$

$$2\,[(NH_4)_3AlF_6 + 0.5\,Al_2O_3] \xrightarrow{500^\circ C} 4\,AlF_3 + 6\,NH_3 + 3\,H_2O$$

1.7.1.2.4 Sodium Aluminum Hexafluoride (Cryolite)

Uses of cryolite:

- manufacture of aluminum
- processing of aluminum waste
- as a flux:
  - in steel aluminization
  - in welding technology
- additive in abrasives
- in the remelting of light metals

Cryolite is utilized in the manufacture of aluminum , in the processing of aluminum waste (as a flux in the electrochemical removal of magnesium), as a flux in the aluminization of steel and in welding technology, in the manufacture of glass and enamel, as an additive in the manufacture of abrasives and as an auxiliary product in the remelting of light metals.

Table 1.7-10. Cryolite Production in 1992 in 10^3 t/a.

	France	F.R. Germany	Italy	Spain
quantity	15	42	25	5

The worldwide capacity for cryolite in 1980 was $330 \cdot 10^3$ t/a.

Manufacture of cryolite:

from hydrogen fluoride solutions or, currently more favored , from hexafluorosilicic acid

There are a number of processes for manufacturing cryolite, starting from aqueous hydrogen fluoride solutions of hexafluorosilicic acid. In the latter case hexafluorosilicic acid is first converted into an ammonium fluoride solution, which is then reacted with sodium aluminate.

$$H_2SiF_6 + 6\,NH_3 + 2H_2O \longrightarrow 6\,NH_4F + SiO_2$$

$$6\,NH_4F + 3\,NaOH + Al(OH)_3 \longrightarrow Na_3AlF_6 + 6\,NH_3 + 6\,H_2O$$

In variants of this process, the ammonium fluoride is first reacted with sodium hydroxide to ammonia and sodium fluoride and then with aluminum fluoride to cryolite. After separation, the cryolite is calcined at 500 to 700°C. In the manufacture of cryolite, as in the manufacture of aluminum fluoride, three things particularly need to be taken into consideration:

- the electrolytic manufacture of aluminum demands extreme purity of the ingredients. Phosphate ($< 0.1\%$), silica ($< 0.5\%$) and iron, in particular, interfere and appropriate purification has to be carried out.
- the slight solubility of both aluminum fluoride and cryolite in water. In their production the fluoride concentration in the effluent must be carefully monitored and measures taken to ensure that the maximum permitted emission levels are not exceeded.
- the presence of fluoride residues in the silica byproduct obtained when hexafluorosilicic acid is used as the source of fluorine. The silica must be disposed of appropriately.

1.7.1.2.5 Alkali Fluorides

Sodium fluoride and potassium and ammonium hydrogen fluorides are industrially important (NaF, $KF \cdot HF$, $NH_4F \cdot HF$). They are manufactured by reacting either hydrogen fluoride or hexafluorosilicic acid with the corresponding alkali hydroxides. Ammonium hydrogen fluoride is mainly produced by the reaction of anhydrous ammonia and hydrogen fluoride in the melt. The melt is solidified e.g. by means of cooling rollers. Ammonium hydrogen fluoride can also be obtained by evaporating an ammonium fluoride solution.

Sodium fluoride is utilized in the manufacture of organofluoro-compounds (halogen exchange reaction), as a preservative, and as a source of fluorine for toothpaste additives (sodium monofluorophosphate).

Potassium hydrogen fluoride is used as a frosting agent in the glass industry and as a starting material for the manufacture of elemental fluorine.

Ammonium hydrogen fluoride is used for the dissolution of silicate minerals in the extraction of crude oil, for the pretreatment of aluminum prior to anodization and as a frosting agent in the glass industry.

1.7.1.2.6 Hexafluorosilicates

Sodium and potassium hexafluorosilicate are manufactured by reacting alkali salts (e.g. chlorides) with hexafluorosilicic acid and subsequent separation of the poorly soluble alkali hexafluorosilicates.

Magnesium, zinc and copper hexafluorosilicates, which are very soluble in water, are manufactured from hexafluorosilicic acid and the appropriate oxide and then recovered by evaporating the solution.

Hexafluorosilicates mainly used in:

- wood protection
- water fluoridation

Hexafluorosilicates are mainly used as preservatives in wood protection (particularly magnesium hexafluorosilicate). Sodium hexafluorosilicate is used in water fluoridation.

1.7.1.2.7 Uranium Hexafluoride

Uranium hexafluoride:

see Chapter 6 Nuclear Fuel Cycle

Uranium hexafluoride is the key compound in the separation of the uranium isotopes ^{235}U and ^{238}U. In its manufacture uranium(IV) oxide is first reacted with hydrogen fluoride to uranium tetrafluoride, which is then reacted with elemental fluorine to uranium hexafluoride:

$$UO_2 + 4\,HF \longrightarrow UF_4 + 2\,H_2O$$

$$UF_4 + F_2 \longrightarrow UF_6$$

A detailed description of this process is given in Chapter 6.

1.7.1.2.8 Boron Trifluoride and Tetrafluoroboric Acid

The manufacture of boron trifluoride proceeds either discontinuously by reacting borates with fluorspar and oleum or continuously by reacting, for example, hydrogen fluoride with boric acid in the presence of sulfuric acid, to bind the water formed:

$$Na_2B_4O_7 + 6\,CaF_2 + 7\,SO_3 \xrightarrow{H_2SO_4} 4\,BF_3 + 6\,CaSO_4 + Na_2SO_4$$

$$H_3BO_3 + 3\,HF \xrightarrow{H_2SO_4} BF_3 + H_2O$$

The reaction of boric acid with fluorosulfonic acid also yields boron trifluoride:

$$3\,HSO_3F + H_3BO_3 \longrightarrow BF_3 + 3\,H_2SO_4$$

Pure boron trifluoride is marketed as a compressed gas. It is utilized mainly in the organic industry as a Friedel-Crafts catalyst (Lewis acid) in the form of its complexes or addition compounds with, for example, ether, alcohols, carboxylic acids etc. or as a pure substance.

Boron trifluoride:

application mainly as a Friedel-Crafts catalyst

Tetrafluoroboric acid is industrially important and is manufactured from boric acid and hydrogen fluoride:

$$H_3BO_3 + 4\,HF \longrightarrow HBF_4 + 3\,H_2O$$

Alkali, ammonium and transition metal fluoroborates can be produced from the acid. These fluoroborates are utilized as fluxes in the galvanic deposition of metals, as flame retardants etc.

Fluoroborates:

as fluxes in the galvanic deposition of metals and as flame retardants

1.7.1.2.9 Sulfur Hexafluoride

Sulfur hexafluoride (sublimation temperature -63.9°C) is manufactured from sulfur and elemental fluorine:

$$S + 3\,F_2 \longrightarrow SF_6$$

The reaction is strongly exothermic. Lower sulfur fluorides are formed as byproducts together with the extremely poisonous disulfur decafluoride. Most of the lower sulfur fluorides are easily hydrolyzable, but sulfur decafluoride can only be decomposed by pyrolysis:

$$S_2F_{10} \xrightarrow{400\,^{\circ}C} SF_4 + SF_6$$

After pyrolysis it is scrubbed with aqueous alkali. Oxygen, nitrogen and carbon fluorides (from the fluorine) are removed by distillation under pressure.

Several thousand tons of sulfur hexafluoride are produced worldwide per year.

Worldwide production of sulfur hexafluoride:

several 10^3 t/a

Applications:

- in high voltage switching installations
- in magnesium casting
- heat and noise insulation in insulating glass

Sulfur hexafluoride is utilized as an extinguishing agent in high voltage-power switches, as a protective gas in high voltage installations (due to its high dielectric constant, high electrical breakdown resistance, non-toxicity), for inhibiting the ignition of magnesium melts during casting (added in less than 1% to the air) and in insulating glass, particularly for heat and noise insulation.

1.7.1.3 Organofluoro Compounds by Electrochemical Fluorination

Electrochemical fluorination:

manufacture of perfluoro- compounds with functional groups by electrolysis of the corresponding nonfluorinated compounds in liquid hydrogen fluoride

When no elaborate precautions are taken, reactions of organic compounds with elemental fluorine generally lead to their decomposition and the formation of lower carbon fluorides. The exchange of all the hydrogen atoms of an organic compound by fluorine with retention of any functional groups can be achieved on an industrial scale by electrochemical fluorination, which was discovered by Simons in about 1941. Nickel electrodes are used. The to be fluorinated compound is dissolved in hydrogen fluoride and electrolyzed at voltages between 5 and 10 V, current densities of 100-200 A/m^2 and electrolyte temperatures of 0-20°C. The electrolyte has to be cooled to dissipate the electrical work resulting from the passage of current through the electrolyte. To avoid large entrainment losses of hydrogen fluoride, the hydrogen escaping from the cell, which is saturated with hydrogen fluoride, has to be strongly cooled in a cooler, so that the hydrogen fluoride can be returned to the cell. The perfluorination occurs at the anode, hydrogen being produced at the cathode. The perfluorinated compounds produced are generally insoluble in hydrogen fluoride and have a high density, so that they collect on the bottom of the electrolysis cell. Gaseous perfluorinated compounds (e.g. perfluoromethylsulfonyl fluoride) escape from the cell with the hydrogen produced.

The process was first industrially operated (by 3M) in 1951. The flow chart below shows a electrofluorination plant:

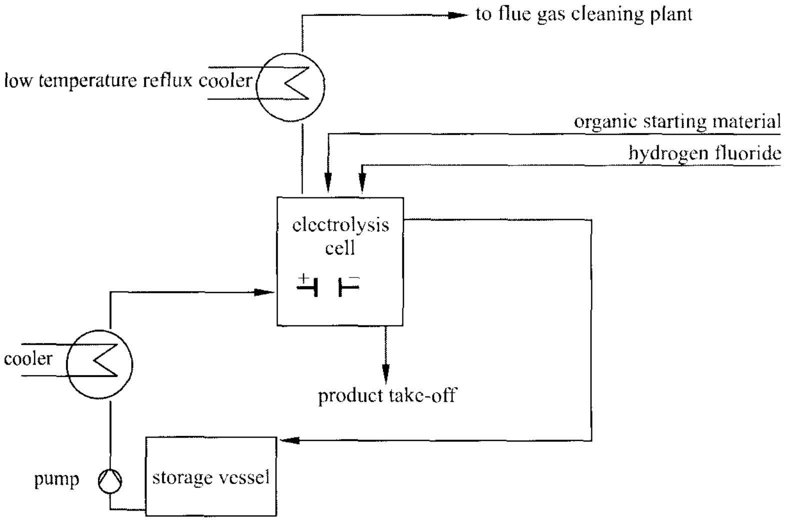


Fig. 1.7-3. Flow Sheet of an Electrofluorination Plant.

Examples of industrially utilized electrofluorination products are e.g. the perfluoroalkylsulfonyl fluorides,

$$C_nH_{(2n+1)}SO_2F + (2n+1)\,HF \xrightarrow{n \cdot 53.6\ \mathrm{Ah}} C_nF_{(2n+1)}SO_2F + (2n+1)H_2$$

which are utilized as starting materials for flame retardants (potassium salt of perfluorobutane sulfonic acid), tensides (potassium salt or tetraethylammonium salt of perfluorooctanoic acid), textile oleophobizing agents, fire extinguishing agents, emulsifiers for the polymerization of tetrafluoroethene and flow improvers for paint systems.

Applications of perfluoro-alkane sulfonic and carboxylic acids and their derivatives:

- flame retardants
- tensides
- textile finishing
- fire extinguishing agents
- emulsifiers
- catalysts
- flow improvers in paints

References for Chapter 1.7.1: Halogens and Halogen Compounds

Kirk-Othmer, Encyclopedia of Chemical Technology. 1994. 4. Ed., Vol. 11, 241pp., *Fluorine Compounds Inorganic*, John Wiley & Sons, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1988. 5. Ed., Vol. A 11, 307 pp., VCH Verlagsgesellschaft, Weinheim.

Chemical Economics Handbook. 1995. Stanford Research Institute, Menlo Park, California, USA.

1.7.2 Chloralkali Electrolysis, Chlorine and Sodium Hydroxide

1.7.2.1 Economic Importance

Chlorine:
indicator for the strength of the chemical industry in a country

About 70% of all chemical products are produced with the involvement of chlorine in one or more synthesis steps. Chlorine production is therefore an indicator of the strength of the chemical industry in a country.

Up to 1985 the growth rate of chlorine production was mostly higher than the chemical industry as a whole and significantly greater than the increase in GNP (Gross National Product).

From 1985 the restrictions on the use of many chlorine-containing products and recycling measures to convert the hydrogen chloride formed in many chlorination reactions into chlorine and chlorine products, such as in dry cleaning, have had an effect.

Products, which due to their persistence or due to their long term effects are harmful to the environment, have been particularly affected, for example several chlorinated pesticides and fluorohydrocarbons. The decline in the use of chlorine in pulp-bleaching should also be mentioned. As a result there was a slight decrease in chlorine production between 1989 and 1992 in the Federal Republic of Germany. Since 1993 the quantity of chlorine produced in the Federal Republic of Germany and worldwide has increased steadily, see Fig. 1.7-4 and Table 1.7-11.

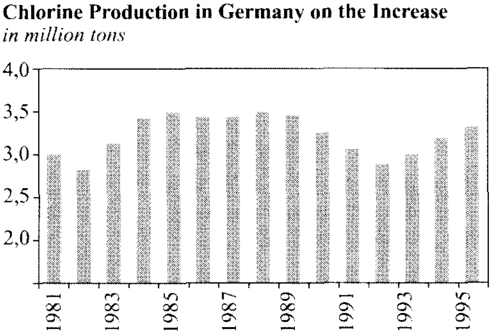


Fig. 1.7-4. Chlorine production in the Federal Republic of Germany (1981 to 1995).

Table 1.7-11. Chlorine Production from 1982 to 1995 in 10^6 t/a.

	Western World	USA	Asia	European Union	FRG
1982	31.5	9.0		7.8	
1987	34.5	10.1		9.5	
1993	37	10.9		8.4	2.9
1995	42	12.0	11.0	9.1	3.3

In 1997 the chlorine production in the European Union was $9.4 \cdot 10^6$ t with the plants operating at 87.8% of capacity.

The capacities of the most important chlorine producers in 1997 were:

Table 1.7-12. Chlorine Capacity from Rock Salt Electrolysis in 1997 (in 10^3 t).

	Europe	USA	Canada	Latin America	Asia	Total
Dow	1300	3600	580	350	0	5830
OxyChem	0	2720	*45	*160	*45	2970
Solvay	1690	0	0	205	*45	1940
PPG	0	1425	100	0	*60	1585
ICI	940	0	335	0	100	1375
Elf Atochem	900	160	0	*135	0	1195
Olin	0	1000	0	0	0	1000
Formosa	0	800	0	0	165	965
Asahi	0	0	0	0	*840	840
Bayer	765	0	0	0	0	765
Trikem	0	0	0	425	0	425

* Joint ventures

Since ca. 97% of the chlorine is produced from the electrolysis of aqueous sodium chloride solution, the linked products sodium hydroxide and hydrogen are produced as byproducts:

$$2\,NaCl + 2\,H_2O \xrightarrow{e^-} 2\,NaOH + Cl_2 + H_2$$

Chlorine production is coupled to the production of:

- sodium hydroxide
- hydrogen

In Table 1.7-13 figures for the production of sodium hydroxide are given for the years 1982, 1987, 1993 and 1995.

The balancing of the marketing of chlorine and sodium hydroxide was and is a difficult problem, in which in the past first one product then the other product was in the forefront.

The marketing of the hydrogen is generally not a problem. If the supply exceeds the demand for chemical synthesis, the excess can be burnt in power stations. Furthermore, the contribution of hydrogen produced by electrolysis only accounts for a few per cent of the total production.

Sodium hydroxide production in 1995:

Western World	45.0 · 10^6 t
FRG	3..5 · 10^6 t

Table 1.7-13. Sodium hydroxide production from 1982 to 1995 in 10^6 t/a.

	Western World	USA	European Union	FRG
1982	34.0	9.7	8.4	
1987	37.3	10.9	10.9	
1993	40.0	11.8	9.1	3.1
1995	45.0	14.0	9.8	3.5

For applications of chlorine and sodium hydroxide see Section 1.7.2.4.

1.7.2.2 Starting Materials

97% of chlorine is produced by the electrolysis of sodium chloride solutions

Almost the whole production of chlorine is produced by the electrolysis of aqueous sodium chloride solutions. Only a small part is obtained by the electrolysis (or oxidation) of hydrochloric acid (or hydrogen chloride) (see Section 1.7.3). Small quantities of chlorine are also produced in the electrochemical manufacture of metals such as sodium.

Availability of NaCl as a raw material is unlimited

Sodium chloride: Sodium chloride is, as a starting material for the electrolytic production of chlorine and sodium hydroxide, available in unlimited quantities. It is either extracted from natural deposits (up to 70%) or from seawater. In the USA, the economically workable deposits of sodium chloride are estimated to be greater than 55 10^{12} t and in the Federal Republic of Germany there is estimated to be 100 · 10^3 km^3 of deposits. Extraction is either carried out by mining or leaching (i.e. dissolution of subterranean salt deposits by injection of freshwater and pumping out the brine).

Extraction of NaCl:

- from natural deposits, either by mining or leaching
- from seawater

While some of the salt produced by mining contains 99% sodium chloride, some contains only 95 to 98%, the rest being clays, anhydrite, quartz, dolomite, fluorspar and mica. In the latter case, the salt is concentrated to 98 to 99% sodium chloride by sieving and gravitational separation. The latter utilizes the differences in specific gravity between sodium chloride and anhydrite and clays in a slurry of magnetite in a saturated sodium chloride solution.

In leaching, the insoluble components are left behind underground.

Evaporated salt can be obtained by evaporating brine. Pretreatment of the brine is necessary to attain sufficient purity. Calcium, magnesium and sulfate ions, in particular, have to be removed:

Purification of the brine by precipitation of impurities in the production of evaporated salt

- Mg^{2+} as $Mg(OH)_2$ by the addition of $Ca(OH)_2$,
- Ca^{2+} as $CaCO_3$ by the addition of sodium carbonate (or CO_2 from furnace gases),
- SO_4^{2-} by evaporating to the point at which sodium sulfate is about to precipitate out.

Evaporated salt:

purity > 99.95%

The evaporation is carried out in multistage plants. Evaporated salt is very pure (> 99.95%, with ca. 100 ppm of Ca^{2+}).

Utilization of evaporated salt is gaining in importance due to the progressive introduction of chloralkali membrane electrolysis technology, which places high demands on the purity of the sodium chlorine-brine utilized.

Extraction of salt from seawater by evaporation of electrodialysis

Extraction of salt from seawater occurs almost exclusively by solar evaporation in salt meadows, except in Japan where it is not possible for climatic reasons. Here electrodialysis is used to concentrate the seawater.

Seawater is evaporated: by concentrating the seawater in the first evaporation pool; transporting to the next evaporation zone, in which calcium sulfate precipitates out; and finally crystallizing sodium chloride in a further evaporation zone. The residual brine is rich in potassium and magnesium salts. The salt obtained is too impure to be used in electrolysis. Washing in special units is sufficient to increase the sodium chloride content to > 99%. 1 m^3 of seawater yields ca. 23 kg of sodium chloride.

Salt purification depends upon electrolysis process to be utilized:

mercury process
diaphragm process
membrane process

Depending upon the electrolysis process utilized: amalgam, diaphragm or membrane, different additional purification steps are required. In the mercury process, solid salt is utilized, which is dissolved in water. If evaporated salt is used, purification can be carried out in a small branch loop. When mined salt is utilized, care has to be taken during dissolution to settle out the impurities. Soluble impurities are removed by precipitating SO_4^{2-} with Ba^{2+}, precipitating Mg^{2+} and Fe^{3+} as hydroxides by the addition of NaOH and precipitating Ca^{2+} as carbonate with sodium carbonate (see the production of evaporated salt).

Purification for the mercury process:

multistage precipitation with Ba^{2+}, NaOH, Na_2CO_3

The membrane process also utilizes solid salt, but with a much higher purity, particularly as regards multivalent ions. Thus the Ca^{2+} content has to be additionally reduced to below 0.1 ppm (compared with 3 ppm for the mercury process) with the aid of ion exchangers such as Lewatit® TP 208 (see Section 1.7.2.3.3).

Purification for the membrane process:

additional purification over ion exchangers

The diaphragm process generally utilizes brine. Multivalent ions such as Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} and silica, which block the diaphragm, are precipitated out by the addition of sodium hydroxide and sodium carbonate.

Purification for the diaphragm process:

precipitation with sodium carbonate

Economic Importance of Sodium Chloride

NaCl-consumption in Western Europe:

- 2/3 as industrial salt, of which > 90% is for electrolysis and sodium carbonate manufacture
- 1/3 as common salt, mainly for salting roads (> 30%) and for food preservation (> 20%)

In Western Europe about two thirds of the sodium chloride is utilized in the chemical industry (industrial salt), of which more than 90% is for electrolysis to chlorine and sodium hydroxide and for sodium carbonate manufacture. For the remainder (common salt) the most important use is for the salting of roads, which is very strongly weather dependent and is declining for ecological reasons. For taxation reasons sodium chloride utilized for the salting of roads is "denatured".

Quantitywise the next most important application is for food conservation in the sectors of meat, dairy products and margarine. Of the numerous other uses the dye, detergent and leather industries and for softening of water (ion exchanger) are worthy of mention.

The worldwide production of sodium chloride in 1993 is given in Table 1.7-14.

Table 1.7-14. Sodium Chloride Production in 1993 in 10^6 t/a.

World	186.2
USA	39.7
China	29.5
F.R. Germany	11.8
Canada	1.2
India	9.5
Australia	9.0
Mexico	7.2
France	6.4
Great Britain	6.3

1.7.2.3 Manufacturing Processes

Three processes are industrially operated in which aqueous solutions of sodium chloride are electrolyzed for the manufacture of chlorine, sodium hydroxide and hydrogen:

- mercury process
- diaphragm process
- membrane process

Manufacture using the membrane process is gaining in importance, since new chlorine capacity exclusively utilizes this technology. In Japan sodium chloride electrolysis is exclusively carried out membrane plants. The percentage contributions of the three processes to chlorine production are given in Table 1.7-15 (Europe) and Table 1.7-16 (worldwide).

Industrially operated electrolysis processes:

- mercury process
- diaphragm process
- membrane process

Table 1.7-15. Contributions of the Chlorine Production Processes in Europe in %.

	Contribution
Mercury process	64
Diaphragm process	24
Membrane process	11

Table 1.7-16. Contributions of the Chlorine Production Processes worldwide in %.

	1980	1990	2010 (estimated)
Mercury process	45	39	15
Diaphragm process	53	45	35
Membrane process	2	16	50

1.7.2.3.1 Mercury Process

Mercury process:

electrolysis of aqueous NaCl-solution on a Hg-cathode and graphite or titanium anode; separate decomposition of the sodium amalgam formed

The amalgam cells consist of slightly inclined steel troughs, over the bottoms of which flow a thin mercury layer, which absorbs the sodium and acts as the cathode. Horizontal anodes adjustable in height at which chlorine is produced are incorporated into the lid of the cells. The chlorine is drawn off upwards through gas extraction slits.

The amalgam emerging from the ends of the cells is converted on graphite into mercury, 50% sodium hydroxide solution and hydrogen in a strongly exothermic reaction (see Fig. 1.7-5, 1.7-6 and 1.7-7).

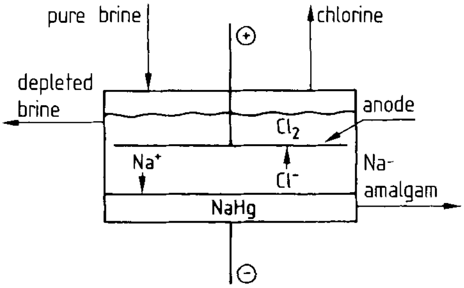


Fig. 1.7-5. Schematic representation of the electrolysis of aqueous Chlorine production in the Federal Republic of Germany (1981 to 1995).

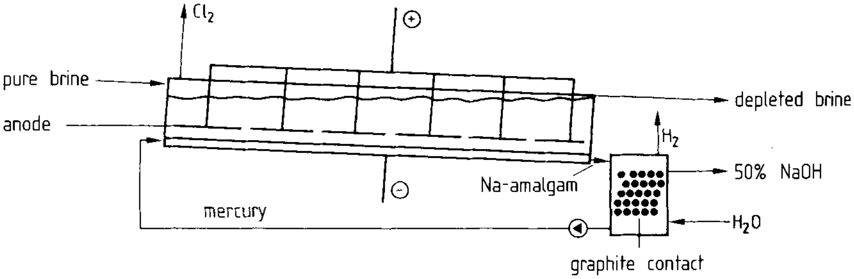


Fig. 1.7-6. Mercury process electrolysis cell.

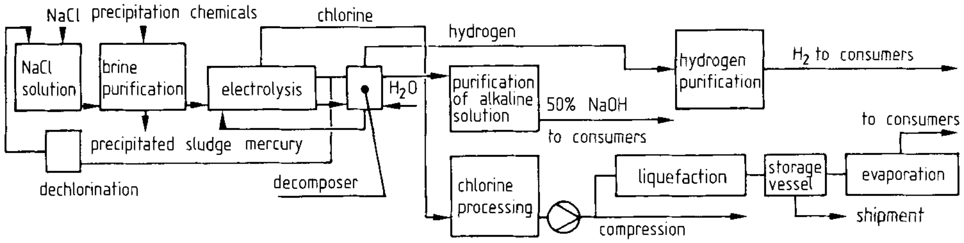


Fig. 1.7-7. Flow sheet of the mercury process.

Description of mercury cells:

- cathode surface area: 10 to 30 m^2
- mercury layer thickness: 3 mm
- sodium concentration in mercury: 0.2 to 0.4% (by weight)
- 50 to 180 individual anodes per cell
- cathode-anode separation: 3 mm
- anode material: graphite or, preferably, titanium coated with a noble metal compound (so-called dimensionally stable anodes DSA®;
- brine throughput per cell: 3 to 20 m^3 /h

A salt solution with a sodium chloride content of ca. 310 g/L is electrolyzed at ca. 80°C, during which the sodium chloride content falls to 260 to 280 g/L. This is then concentrated by adding solid salt and recycled. During electrolysis the following reactions take place:

- reaction at anode:

$$Cl^- \longrightarrow 0.5\ Cl_2 + e^-;\ \text{deposition voltage ca. } 1.24\ \text{V}$$

- reaction at cathode:

$$x\text{Hg} + \text{Na}^+ + e^- \longrightarrow \text{NaHg}_x;\ \text{deposition voltage ca. } -1.66\ \text{V}$$

Typical side-reactions are:

- at the anode:

$$Cl_2 + 2\ NaOH \longrightarrow NaOCl + NaCl + H_2O$$

- at the cathode:

$$Cl_2 + 2e^- \rightarrow 2\,Cl^-$$
$$ClO^- + 2\,H^+ + 2\,e^- \longrightarrow H_2O + Cl^-$$

The electrochemical yield is 94 to 97%, the energy consumption ca. 3300 kWh/t chlorine, the effective cell voltage 4.2 V and the current density 8 to 15 kA/m^2.

The amalgam formed at the cathode is decomposed with water:

$$NaHg_x + H_2O \longrightarrow 0.5\,H_2 + NaOH + xHg$$

The electrical energy stored in the amalgam is thereby converted into heat.

Mercury process:
capacity of industrial plants:
- up to 300 · 10^3 t/a chlorine
- up to 340 · 10^3 t/a sodium hydroxide

Capacities of industrial plants:

- 50 to 300 · 10^3 t/a chlorine
- 56 to 340 · 10^3 t/a sodium hydroxide

In modern units the height of the anodes is computer controlled. Chemical and physical processes are used to reduce the mercury concentration in the effluent, exit gases and products to the ppb level.

1.7.2.3.2 Diaphragm Process

Industrial diaphragm cells consist of a box in which the anode plates are mounted vertically parallel to one another. The cathodes are flat hollow steel mesh structures covered with asbestos fibers, optionally impregnated with fluoroorganic resins, and fit between the anodes (see Fig. 1.7-8, 1.7-9 and 1.7-10).

- monopolar electrode arrangement: anode surfaces of up to 50 m^2 per cell (activated titanium). Cathodes and anodes are all electrically connected with one another
- bipolar electrode arrangement: electrode surface areas of up to ca. 35 m^2. Cathodes and anodes are connected back to back.

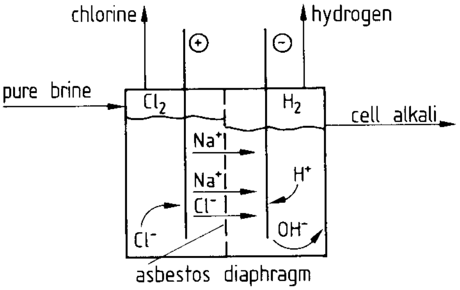


Fig. 1.7-8. Schematic representation of the electrolysis of aqueous salt solutions by the diaphragm process.

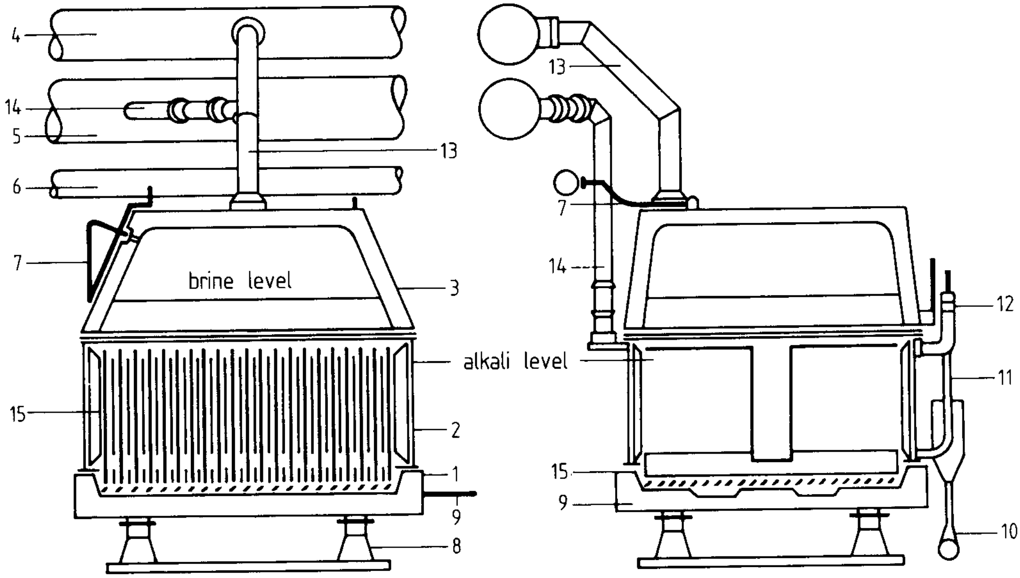


Fig. 1.7-9. Electrolysis cell for the Diaphragm process (Hooker-Cell S 3 from Uhde).

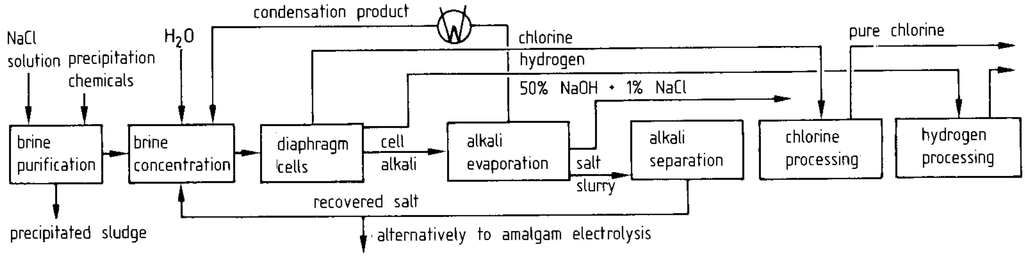


Fig. 1.7-10. Flow sheet of the diaphragm process.

The salt solution fed into the anode chamber passes through the diaphragm into the cathode chamber. The chlorine produced at the anode is drawn off upwards and hydrogen and sodium hydroxide mixed with residual salt are produced at the cathode.

Diaphragm process:

electrolysis of aqueous NaCl-solutions at titanium anodes and steel cathodes. Separation of anode and cathode chambers by an asbestos diaphragm. The anodic solution passes through the diaphragm into the cathode chamber. Dilute NaCl-containing sodium hydroxide is formed.

The asbestos diaphragm has a number of functions:

- it has to hinder the mixing of hydrogen and chlorine. The tangled fiber structure of the asbestos allows liquids to pass through, but not fine gas bubbles (the 4% of chlorine which dissolves in the brine does, however, pass into the cathode chamber where it is reduced thereby reducing the yield).
- it hinders to a large extent the back-diffusion of the cathodically-formed OH^- ions to the anode. The flow rate of the brine into the anode chamber is regulated to limit the back-diffusion and the hydrostatic pressure therein.

Upon electrolysis, the sodium chloride content of an initially saturated solution falls to ca. 170 g/L. The reactions at the anode are the same as in the mercury process. However, hydrogen is produced at the steel cathode:

$$H_2O + e^- \longrightarrow 0.5\,H_2 + OH^-$$

The cell alkali leaving the cathode chamber contains ca. 12% NaOH and 15% NaCl (by weight).

Recovery of sodium hydroxide: The alkali solution is evaporated to 50% by weight of sodium hydroxide, whereupon the salt, except for a residual 1%, precipitates out. This salt is very pure and can be further utilized for concentrating depleted brine or, in the case of combined plants, in the mercury process.

Evaporation is carried out in multi (up to four)-stage forced circulation evaporators. 5 t of water have to be evaporated per t of 50% sodium hydroxide solution. A further purification of this salt-containing sodium hydroxide is possible, but very expensive.

Diaphragm process:

capacity of industrial plants:
up to $360 \cdot 10^3$ t/a chlorine
up to $410 \cdot 10^3$ t/a sodium hydroxide

Capacity of industrial plants:

- $360 \cdot 10^3$ t/a of chlorine corresponding to
- ca. $410 \cdot 10^3$ t/a of sodium hydroxide

at a specific current density of 2.2 to 2.7 kA/m^2.

The electrical energy consumption is ca. 20% less than that in the mercury process.

1.7.2.3.3 Membrane process

In the membrane process the cathode and anode chambers are separated by a water-impermeable ion-conducting membrane (see Fig. 1.7-11).

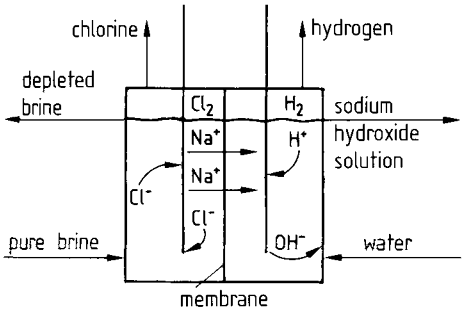


Fig. 1.7-11. Schematic representation of the electrolysis of aqueous salt solutions by the membrane process.

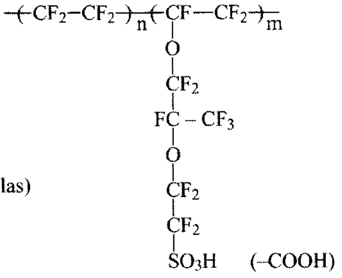
The membrane has to be stable under electrolysis conditions i.e. high salt concentrations, high pH-jump between anode and cathode chambers and to the strong oxidizing agents chlorine and hypochlorite.

These demands are fulfilled by membranes with a perfluorinated polyethene main chain with side-chains with sulfonic acid and/or carboxylic acid groups as produced by DuPont and Asahi Glass.

e.g.

Nafion® (DuPont)

Flemion® (Asahi Glas)



$$-(CF_2-CF_2)_n-(CF(-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H)-CF_2)_m- \quad (-COOH)$$

Multilayer membranes are also used, which have, for example, thin sulfonamide layers on the cathode side.

Membrane process:

cathode and anode chambers are separated by an ion-conducting membrane. Titanium anodes, stainless steel or nickel cathodes used. Na^+ ions travel from anode chamber to cathode chamber. Very pure 20 to 35% NaOH produced.

Operation of membrane cells: The same processes take place on the anodes and cathodes as in diaphragm cells. Activated titanium is used for the anodes and stainless steel or nickel is preferred for the cathodes. No water transport takes place in the absence of current, but upon application of current solvation-water is transported by the current-carrying Na^+ ions as they travel from the anode chamber to the cathode chamber.

The brine has to be much purer than for the mercury process. Ca^{2+} content, for example, must be below 20 ppb, otherwise $Ca(OH)_2$ precipitates in the membrane, rapidly leading to its destruction see Section 1.7.2.2).

The concentration of virtually chloride-free sodium hydroxide in the cathode chamber is between 20 and 35% by weight, depending upon the type of membrane used. With the newest membrane types the current yield with respect to sodium hydroxide is over 97%. This non-quantitative current yield is due to the passage of hydroxide ions into the anode chamber, which causes chlorate formation. Since the brine is recycled, as with the mercury process, appropriate measures have to be taken to limit its chlorate concentration. This can be achieved by feeding in hydrogen chloride, although the pH must not be reduced too much, otherwise the membrane is damaged.

Membrane cells are similar in their construction to a filter press. Mono- and bi-polar cells are available. The cell voltage is ca. 3.15 V and the optimum current density is ca. 4 kA/m^2. The electrode separation is 2 to 5 mm. Electrolysis in membrane cells consumes significantly less electrical energy than mercury cells.

1.7.2.3.4 Evaluation of Mercury, Diaphragm and Membrane Processes

Amalgam Process:

Advantages:

- pure 50% sodium hydroxide solution (without evaporation)
- pure chlorine gas

Disadvantages:

- higher voltage than with the diaphragm process and hence 10 to 15% higher electrical energy consumption

- high costs for brine purification
- high cost of mercury contamination avoidance measures

Diaphragm Process:

Advantages:

- utilization of less pure brines
- lower voltage than in the mercury process

Disadvantages:

- sodium hydroxide produced is both dilute and chloride-contaminated, evaporation required
- chlorine gas contains oxygen
- high cost of asbestos emission avoidance

The economics of the two processes are comparable.

Economics of the mercury and diaphragm processes are similar

Membrane Process:

Advantages:

- pure sodium hydroxide
- lower consumption of electrical energy than for the mercury process
- no utilization of mercury or asbestos

Disadvantages:

- sodium hydroxide content only ca. 35% by weight
- chlorine gas contains oxygen
- very high purity brine required
- high cost and limited lifetime of membranes

The ca. 10% saving in electrical energy over the mercury and diaphragm processes makes this process the most economical one for chlorine manufacture for investment in new plant.

1.7.2.4 Applications of Chlorine and Sodium Hydroxide

1.7.2.4.1 Chlorine

Worldwide, chlorine is mainly utilized in the manufacture of PVC, for pulp and paper bleaching, water treatment and the production of different organic chemicals, in particular propene oxide. However, chlorine utilization in pulp and paper bleaching and the manufacture of chlorohydrocarbons is on the decline.

More than 80% of chlorine is utilized for the manufacture of organic products

A significant increase is expected in chlorine utilization in the manufacture of PVC and phosgenes for isocyanate manufacture.

Table 1.7-17. Quantities of Chlorine Consumed Worldwide for Different Applications in 10^6 t.

	1994	2000 (expected)
PVC	12.5	15.5
C_1,C_2-chlorination	2.1	1.6
pulp bleaching	2.8	1.8
propene oxide	2.5	1.7
water treatment	2.0	2.0
phosgene for isocyanates	2.1	2.4
chlorobenzene	0.8	0.7
alkyl chlorides	0.7	0.8
TiO_2 by chloride process	0.7	0.7

In the Federal Republic of Germany with its highly developed chemical industry, but relatively low PVC-production and virtually no pulp manufacture, utilization of chlorine in the manufacture of organic chemicals dominates. However, most of the end-products do not contain chlorine.

1.7.2.4.2 Sodium Hydroxide

Sodium hydroxide is utilized in a multiplicity of chemical processes, mainly for neutralization and as an alkaline reaction medium. In addition it is used in large quantities in the pulp and paper industries and in the manufacture of aluminum.

The utilization spectrum for the 29.0 · 10^6 t of sodium hydroxide consumed worldwide in 1998 is given in Table 1.7-18.

Table 1.7-18. Utilization Spectrum for Sodium Hydroxide Worldwide in 1998 in 10^6 t/a.

organic chemicals	7.5
inorganic chemicals	7.0
pulp and paper	6.5
aluminum (bauxite)	3.5
textiles	2.5
detergents and cleaning agents	2.0

References for Chapter 1.7.2: Chloralkali-Electrolysis

Commercial Information:

Chemie Report des VCI, 12/96, 1 – 4.

Europa-Chemie 2/97, 8.

Eur. Chem. News 24 – 30, March 1997, 40.

Technical Information:

Varjian, R. D. 1981. *Energy Analysis of the Diaphragm Chlor-Alkali Cell.* Lectures in Electrochemical Engineering, AIChE Symposium Series, 219 - 226.

Thomas, V. H., Penny, R. D. 1981. Review of Mercury cathode Chlorine Technology. Lectures in Electrochemical Engineering, AIChE Symposium Series, 227 – 233.

Simmrock, K. H. et al. 1981. *Einsatz perfluorierter Kationenaustauscher-Membranen in Electrolyseverfahren, insbesondere bei der Chloralkali-Electrolyse*, Chem. Ing. Tech. **53**, 10 –25.

Bergner, D. 1982, *Alkalichlorid-Electrolyse nach dem Membranverfahren,* Chem. Ing. Tech. **54**, 562 – 570.

Stinson, S. C. 1982. *Electrolytic Cell Membrane Development* Surges, Chem. Eng. News, 22 – 25.

Reviews:

Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 6, 399 – 481, VCH Verlagsgesellschaft, Weinheim.

Ullmann's Encyclopedia of Industrial Chemistry. 5. Ed., Vol. A 24, 317 – 339 (*Sodium Chloride*), 345-354 (*Sodium Hydroxide*), VCH Verlagsgesellschaft, Weinheim.

Bergner, D. 1997. *20 Jahre Entwicklung einer bipolaren Membranzelle für die Alkalichlorid-Electrolyse vom Labor zur weltweiten Anwendung*, Chem. Ing. Tech. **69**, 438 – 445.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1991. 4. Ed., Vol. 1, 738 – 1025, John Wiley & Sons, New York.

Minz, F. R. 1978. *Moderne Verfahren der Großchemie: Chlor und* Natronlauge, Chemie in unserer Zeit **12**, 135 – 141.

Purcell, R. W. 1977. *The Chlor-Alkali Industry* and Campell, A. *Chlorine and Chlorination*, in: The Modern Inorganic Chemicals Industry, ed. Thompson, R. The Chemical Society, Burlington House, London, 106 – 133 and 134–148.

Winnacker-Küchler. Chemische Technologie. 1982. 4. Ed., Vol. 2, 379 – 480, Anorganische Technologie I, Carl Hanser Verlag, München.

1.7.3 Hydrochloric Acid – Hydrogen Chloride

1.7.3.1 Manufacture of Hydrogen Chloride

HCl:
from $H_2 + Cl_2$ (high purity possible)

Hydrogen chloride is produced:

- by the reaction of hydrogen with chlorine

$$H_2 + Cl_2 \longrightarrow 2\,HCl \quad (+\,184\,kJ)$$

This process is strongly exothermic (flame temperature > 2000°C) and is especially used when particularly pure hydrogen chloride (hydrochloric acid) is required e.g. in the food sector. It places considerable demands on the construction materials of the plant, particularly that of the burner for which quartz or graphite is preferred. The synthesis furnace and the adjacent cooler can be constructed of steel when dry chlorine and dry hydrogen are used.

HCl:
from $NaCl + H_2SO_4$ (of little importance)

- as a byproduct in the reaction of sodium chloride with sulfuric acid to sodium sulfate:

$$\begin{array}{l} NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl \\ NaHSO_4 + NaCl \longrightarrow Na_2SO_4 + HCl \\ \hline 2\,NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2\,HCl \end{array}$$

The quantities produced are however insignificant (< 2%).

HCl:
byproduct in organic chemistry (ca. 90%)

- mainly as a byproduct in:

chlorination, halogen exchange reactions e.g. in organic chemistry. Typical examples are:
- manufacture of aliphatic and aromatic chlorohydrocarbons
- manufacture of isocyanates by reacting amines with phosgene
- manufacture of pyrogenic silica's by flame hydrolysis of chlorosilanes

1.7.3.2 Economic Importance of Hydrogen Chloride and Hydrochloric Acid

Table 1.7-19. Hydrochloric Acid and Hydrogen Chloride Production between 1987 and 1993 as HCl in 10^3 t.

	USA	F.R. Germany	France	Great Britain	Japan
1987	2996	991	224	175	
1989	3268	958	238	167	
1991	3381	839	216	153	
1992	3610	878	199	148	1786
1993	3492	820	190		

Hydrochloric acid production (as HCl) in 1993:

USA 3492 · 10^3 t
FRG 820 · 10^3 t

Hydrochloric acid is utilized in numerous applications, for example in:

- metal cleaning
- pickling of metals
- manufacture of metal chlorides
- neutralization in inorganic and organic chemistry
- hydrolysis of proteins and carbohydrates
- manufacture of chlorine dioxide for water treatment
- acid treatment of oil wells

Since the amount of hydrogen chloride produced as a byproduct often exceeds demand, part of it has to be converted into chlorine. This is especially necessary where it is a byproduct at sites at which there is no further use for it. This is carried out both by electrolysis (see Section 1.7.3.3) and by a modified Deacon process (Section 1.7.3.4).

Excess HCl is electrolytically converted into $H_2 + Cl_2$

1.7.3.3 Electrolysis of Hydrochloric Acid

The decomposition voltage for the electrolysis of hydrochloric acid is ca. 2 V.

$$2\,HCl \xrightarrow{e^-} Cl_2 + H_2$$

The electrolysis cell used is similar in construction to the membrane cell, with PVC-cloth acting as the diaphragm. The bipolar electrodes are graphite. Small quantities of platinum group compounds may be added to the cathode to

Hydrochloric acid electrolysis:

23% hydrochloric acid is depleted on graphite electrodes forming $H_2 + Cl_2$ to ca. 20%. Anode and cathode chambers are separated with a PVC-cloth diaphragm reduce the overvoltage. Fig. 1.7-12 shows a schema of hydrochloric acid electrolysis.

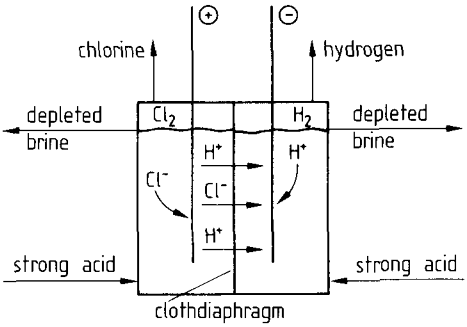


Fig. 1.7-12. Schema of hydrochloric acid electrolysis.

Ca. 23% by weight hydrochloric acid is fed into both the cathode and anode chambers, part of the electrolyte diffusing from the anode chamber to the cathode chamber. The depleted acid leaving the chambers has a concentration of 17 to 20%. Hydrogen chloride from the production of organic chemicals (see above) is adiabatically absorbed in the depleted acid, the resulting heat being used to evaporate part of the water together with steam-distillable organic impurities in the hydrogen chloride. The purity of the hydrochloric acid used is important and post-purification with activated charcoal can be necessary.

Capacity of industrial plants: up to ca. 70 · 10^3 t/a chlorine

The electrode gap is ca. 6 mm. The yield is 97 to 98% at a current density of 4000 A/m^2. Industrial plants produce ca. 70 · 10^3 t/a of chlorine.

Total production: 350 · 10^3 t/a chlorine

In the dual interests of waste disposal and manufacturing economics, this process is currently used to manufacture ca. 350 · 10^3 t/a chlorine.

1.7.3.4 Non-Electrolytic Processes for the Manufacture of Chlorine from Hydrogen Chloride

The non-electrolytic processes for the manufacture of chlorine from hydrogen chloride (Deacon, air oxidation of hydrogen chloride; Weldon, manganese dioxide oxidation of hydrogen chloride) which marked the beginning of industrial chlorine chemistry, are currently of only minor importance.

However, DuPont in Corpus Christi (USA) brought a modified Deacon process on stream in 1975, the Kellog Kel-Chlor® process, in which the hydrogen chloride produced as a byproduct in the manufacture if fluorohydrocarbons is oxidized. Fig. 1.7.13 shows a schema of this process.

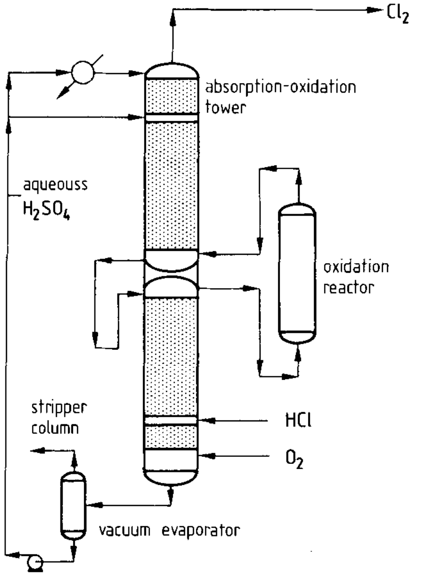


Fig. 1.7-13. Schema of the Kel-Chlor® process.

In principle, hydrogen chloride is oxidized with oxygen under pressure in the presence of catalytically acting nitrogen-oxygen compounds, the water formed being removed with concentrated sulfuric acid. The capacity of the plant is 600 t/d chlorine.

Kel-Chlor® process:
oxidation of HCl with O_2 to Cl_2 with nitrogen-oxygen compounds as catalysts.

References for Chapter 1.7.3: Hydrochloric Acid – Hydrogen Chloride

Commercial Information:
Chemical Economics Handbook. 1994. Stanford Research Institute, Menlo Park, California, USA.

Reviews:
Ullmann's Encyclopedia of Industrial Chemistry. 1989. 5. Ed., Vol. A 13, 283 – 296, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1995. 4. Ed., Vol. 13, 894 – 924, John Wiley & Sons, New York.

1.7.4 Chlorine-Oxygen Compounds

1.7.4.1 Economic Importance

Sodium hypochlorite production in 1994:

USA:	$276 \cdot 10^3$ t/a
Western Europe:	$386 \cdot 10^3$ t/a
Japan:	$141 \cdot 10^3$ t/a

Sodium hypochlorite: Production of sodium hypochlorite in 1994 was $276 \cdot 10^3$ t/a in the USA, $386 \cdot 10^3$ t/a in Western Europe and $141 \cdot 10^3$ t/a in Japan.

Calcium hypochlorite:

consumption in the USA in 1994: $40 \cdot 10^3$ t/a (in chlorine equivalents)

Calcium hypochlorite: Production and consumption of calcium hypochlorite in the most important regions in 1994 are given in Table 1.7-20. The chlorine equivalents are the quantities of chlorine which correspond to the oxidation capacity of the quantities of hypochlorite.

Table 1.7-20. Production and Consumption of Calcium Hypochlorite in 10^3 t chlorine equivalents.

	Production	Imports	Exports	Consumption
USA	55	5	19	40
Western Europe	3	2	2	3
Japan	17	2	13	4

Sodium chlorite production in USA, Japan, France and F.R. Germany

Current production and demand in USA: $10 \cdot 10^3$ t/a

Sodium chlorite: The 1980 capacity of PCUK in France was $50 \cdot 10^3$ t/a. There are other producers in the USA, Japan, France and in the Federal Republic of Germany. Current production and demand in the USA are ca. $10 \cdot 10^3$ t/a.

Sodium chlorate:

World capacity: $> 2 \cdot 10^6$ t/a

Sodium and Potassium Chlorates:

Table 1.7-21. Sodium Chlorate Capacities in 1993 in 10^3 t.

Western Europe	629
USA	1619
Japan	59

The capacity in the USA is still expanding strongly, the annual growth in the period 1987 to 1993 having been greater than 10%.

Ammonium perchlorate:

- most important perchlorate
- capacity in the USA: $30 \cdot 10^3$ t/a

Perchlorates and perchloric acid: The consumption of perchloric acid (70%) is very small, being estimated to be 450 t/a in the USA. The most important perchlorate is ammonium perchlorate, with a capacity in the USA of ca. $30 \cdot 10^3$ t.

Chlorine dioxide: Table 1.7-22 gives information about the growth of chlorine dioxide consumption in the USA.

Table 1.7-22. Chlorine Dioxide Consumption in the USA in 10^3 t.

1983	1987	1990	1993	1998
220	256	385	509	760*

*estimated

1998 Chlorine dioxide consumption in USA:
ca. $760 \cdot 10^3$ t/a

1.7.4.2 Manufacture of Chlorine-Oxygen Compounds

1.7.4.2.1 Hypochlorite

Hypochlorite Solutions:

Hypochlorite:
from bases and chlorine with cooling

Solutions of sodium and calcium hypochlorite as mixtures with sodium and calcium chloride can be easily obtained by reacting aqueous sodium hydroxide or calcium hydroxide slurries with chlorine:

$$2\,NaOH + Cl_2 \longrightarrow NaOCl + NaCl + H_2O$$
$$Ca(OH)_2 + Cl_2 \longrightarrow Ca(OCl)Cl + H_2O$$

The solutions ("bleaching solutions") contain about equimolar quantities of chloride and hypochlorite ions.

Contents given as "available chlorine"

Sodium hypochlorite solutions contain 12 to 15% and calcium hypochlorite 3 to 3.8% of available chlorine. Available chlorine is the quantity of chlorine produced by adding hydrochloric acid, relative to the weight of the product:

$$NaOCl + 2\,HCl \longrightarrow NaCl + Cl_2 + H_2O$$

The reaction of sodium hydroxide with chlorine is strongly exothermic (ΔH = 103 kJ/mol). Production can be carried out discontinuously and is monitored by redox potential measurements. Since hypochlorite is easily converted to chlorate at high temperatures, the reaction temperature must be kept below 40°C, for which coolers constructed of titanium are used. The chlorination is generally carried out in such as way that a slight excess of alkali is retained so as to increase the stability of the solution. The same holds for the manufacture of calcium hypochlorite solutions.

Bleaching solutions are generally used in situ, because they are easily decomposed by light or traces of heavy metals.

Small scale consumers produce hypochlorite solutions directly by electrolysis of sodium chloride solutions in a diaphragmless cell

The above-described manufacture assumes the availability of chlorine. Direct electrolytic manufacture of hypochlorite solutions is appropriate for special applications (cooling of power stations with seawater, effluent treatment etc.), when chlorine is unavailable.

Seawater or brine is electrolyzed in diaphragmless cells. Activated titanium anodes and titanium cathodes are used. The yield based on current consumed is relatively poor, 40 to 60%, due to the hydrogen produced reducing part of the hypochlorite formed. The electrolysis cells are technically uncomplicated and small. The hypochlorite solutions obtained contain several grams of hypochlorite per L.

Solid Hypochlorite:

Bleaching powder:

formerly only transportable form of chlorine, strongly declined in importance

Bleaching powder (chloride of lime) was first used industrially at the beginning of the nineteenth century and for over a century was the only transportable form of chlorine, since chlorine could be made available by acidification with hydrochloric acid. It contains ca. 36% of available chlorine. Since transportation of liquid chlorine became technically feasible at the beginning of the twentieth century, the manufacture of bleaching powder has steadily declined in importance. It is manufactured by reacting moist calcium hydroxide with chlorine, this reaction being fairly slow.

Calcium hypochlorite:

high percentage bleaching powder. Produced e.g. by chlorination of calcium hydroxide suspensions and separation of the calcium hypochlorite formed as its dihydrate.

Calcium hypochlorite: There are a number of processes for the manufacture of calcium hypochlorite ("high percentage bleaching powder"). The oldest is the Griesheim Elektron process ("Perchloron process") in which a calcium hydroxide suspension is chlorinated to such an extent that the calcium chloride formed mostly dissolves, but not the calcium hypochlorite.

$$2\,Ca(OH)_2 + 2\,Cl_2 \longrightarrow Ca(OCl)_2 \cdot 2\,H_2O + CaCl_2$$

The calcium hypochlorite, which precipitates as the dihydrate, is filtered off and dried.

In the Olin process, a calcium hydroxide suspension in a sodium hypochlorite solution is chlorinated and a triple-salt precipitates out upon cooling to -15°C:

$$Ca(OH)_2 + 2\ NaOCl + Cl_2 + 11\ H_2O \longrightarrow Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12\ H_2O$$

This triple-salt reacts with a bleaching powder suspension to form calcium hypochlorite dihydrate which is filtered off and dried.

$$Ca(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12\ H_2O + Ca(OCl)Cl \longrightarrow 2\ Ca(OCl)_2 \cdot 2H_2O + 2\ NaCl + 10\ H_2O$$

The sodium chloride byproduct can be utilized in chloralkali electrolysis.

Other manufacturing processes, such as the ICl, Thann and Pennwalt processes, are variants of this process.

In the PPG-process, chlorine is reacted in a carbon dioxide stream with sodium carbonate to dichlorine monoxide and hypochlorous acid, which is dissolved in water. Reaction with a calcium hydroxide slurry yields calcium hypochlorite:

$$Ca(OH)_2 + 2\ HOCl \longrightarrow Ca(OCl)_2 + 2\ H_2O$$

The content of available chlorine in technical calcium hypochlorite is 70 to 74%. It reacts vigorously with oxidizing agents and decomposes exothermically upon ignition.

Solid sodium hypochlorite is not commercially available, because it is too chemically unstable. "Chlorinated trisodium phosphate", $[Na_3PO_4 \cdot 11H_2O]_4 \cdot NaOCl$, on the other hand, is industrially important in the cleaning agent sector. This has an available chlorine content of 3.65%. It is obtained by reacting a sodium phosphate solution with a sodium hypochlorite solution in the appropriate molar concentrations at 75 to 80°C.

"Chlorinated trisodium phosphate", $[Na_3PO_4 \cdot 11H_2O]_4 \cdot NaOCl$ produced from trisodium phosphate and sodium hypochlorite solutions

In the USA small quantities of lithium hypochlorite are also manufactured ($1.5 \cdot 10^3$ t in 1994).

1.7.4.2.2 Chlorites

Sodium chlorite:

from chlorine dioxide, sodium hydroxide and hydrogen peroxide as a reducing agent

Only sodium chlorite is industrially significant. It is manufactured by reacting chlorine dioxide (Section 1.7.4.2.5) with sodium hydroxide and a reducing agent, usually hydrogen peroxide (other reducing agents have technical disadvantages):

$$2\ ClO_2 + 2\ NaOH + H_2O_2 \longrightarrow 2\ NaClO_2 + 2\ H_2O + O_2$$

An excess of hydrogen peroxide is necessary, since part of it decomposes in the alkaline solution.

Due to its easily initiated self-decomposition, solid sodium chlorite is either supplied as its monohydrate or as mixtures with sodium chloride or sodium nitrate.

1.7.4.2.3 Chlorates

Potassium chlorate:

from sodium chlorate by metathesis

Sodium and potassium chlorate are used industrially. The latter is produced from sodium chlorate by metathesis with potassium chloride:

$$NaClO_3 + KCl \longrightarrow KClO_3 + NaCl$$

Sodium chlorate:

from sodium chloride by electrolysis in diaphragmless cells with anodes of activated titanium and steel cathodes. The electrochemical reaction follows a slow chemical reaction

The formerly operated purely chemical process for the manufacture of sodium chlorate is no longer industrially significant. Sodium chlorate is industrially manufactured electrochemically from brine in diaphragmless cells:

$$NaCl + 3\ H_2O \longrightarrow NaClO_3 + 3\ H_2$$

Steel cathodes are used and anodes of platinum or titanium activated with a mixed oxide of ruthenium oxide and titanium dioxide are used as anodes, supplanting the graphite anodes previously employed. The electrode separation is ca. 3 to 5 mm. Electrolysis is carried out at ca. 80°C, at a voltage of 3.0 to 3.5 and at an energy consumption of 4.95 to 6.05 MWh/t sodium chlorate (at an electricity price of 3.5 USc/kWh electricity costs account for half the manufacturing costs). Since the hydrogen formed at the cathode is contaminated with small quantities of chlorine it has to be appropriately treated, e.g. by scrubbing. Chlorate cells are supplied by a large number of manufacturers.

The chemical and electrochemical processes occurring in the cells are very complex. The current understanding is that the following sequence of reactions takes place:

- chlorine produced at the anode reacts with water to hypochlorous acid which reacts with hydroxide ions produced at the cathode to form hypochlorite ions:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$
$$OH^- + Cl_2 \longrightarrow OCl^- + 2\,HCl$$

- hypochlorous acid and hypochlorite ions react to form chlorate ions:

$$2\,HOCl + ClO^- \longrightarrow ClO_3^- + 2\,HCl$$

Since this reaction is relatively slow, the circuit cycling electrolyte through the electrolysis cell has a large dead volume to allow for the completion of the reaction.

The most important side-reaction is the electrochemical oxidation of hypochlorite ions to chlorate ions at the anode, which can be approximately represented by:

$$6\,ClO^- + 3H_2O \xrightarrow{-6\,e^-} 2\,ClO_3^- + 1.5\,O_2 + 6\,H^+ + 4\,Cl^-$$

As a result of the simultaneous production of oxygen, the utilization efficiency of electrical energy is a third less than with the pure chemical formation of sodium chlorate. The process parameters are therefore selected so as to suppress the electrochemical oxidation of hypochlorite e.g. the concentrations, the temperature (60 to 75°C), the process pH (6.9), the flow conditions and the residence time in the electrolysis cell. Modern plants utilize electricity energy with an efficiency of > 93%.

Another important side-reaction is the reduction of hypochlorite ions at the cathode:

$$ClO^- + H_2O \xrightarrow{+2\,e^-} Cl^- + 2\,OH^-$$

This is, to a large extent, suppressed by the addition of ca. 3g of chromate per L of electrolyte. This coats the cathode with a layer of hydrated chromium oxide, which strongly hinders the diffusion of hypochlorite ions to the cathode.

The sodium chlorate is obtained from the solutions produced during electrolysis, containing 600 g/L of sodium chlorate and 100 g/L of sodium chloride, as crystals by evaporation, the sodium chloride precipitating out first. Technical grade sodium chlorate is 99.5% pure. It decomposes above 265°C forming sodium perchlorate. To an increasing extent, sodium chlorate is being supplied in solution, in some cases without separating off the sodium chloride, to save energy.

In the so-called "Munich process" for the manufacture of chlorine dioxide (see Section 1.7.4.2.5), the chlorate-containing electrolyte is directly reacted with hydrochloric acid.

1.7.4.2.4 Perchlorates and Perchloric Acid

Sodium perchlorate:

manufactured by electrochemical oxidation from sodium chlorate in diaphragmless cells with anodes of lead dioxide or platinum

Potassium and ammonium perchlorate:

from sodium perchlorate by metathesis

The industrially most important perchlorates are sodium, potassium and ammonium perchlorates. Potassium and ammonium perchlorate are manufactured by metathesis from sodium perchlorate, which itself is manufactured electrochemically from sodium chlorate:

$$NaClO_3 + H_2O \longrightarrow NaClO_4 + H_2$$

Oxygen is formed as a byproduct at the anodes. The diaphragmless cells utilized in this process and the cathodes are constructed of steel and the anodes of platinum or β-lead dioxide on graphite. The voltage used is 4.75 V (with a lead dioxide anode) or 6 V (with a platinum anode). The energy consumption is 2.5 to 3 kWh/kg sodium perchlorate. When platinum anodes are used chromate can be added to suppress the cathodic reduction. A small amount of platinum dissolves in the electrolyte, particularly at high temperatures and sodium chlorate contents below 100 g/L. With lead dioxide anodes addition of sodium fluoride brings about an improvement in electrical energy utilization.

The sodium perchlorate formed is worked up by crystallization.

Perchloric acid:

by electrochemical oxidation of chlorine dissolved in perchloric acid

Perchloric acid is manufactured by the Merck process through electrolysis of chlorine dissolved in cold (ca. 0°C) perchloric acid:

$$Cl_2 + 8\ H_2O \longrightarrow 2\ HClO_4 + 7\ H_2$$

Diaphragm cells (with plastic cloth diaphragms) are used with platinum anodes and silver cathodes. A silver cooler is utilized to remove the heat of reaction. The cell voltage is 4.4 V, the yield based on electricity supplied is 60%. Part of the electrolyte is continuously taken off and concentrated to ca. 70% perchloric acid.

1.7.4.2.5 Chlorine Dioxide

Of the chlorine oxides only chlorine dioxide has achieved industrial significance. It is a gas at room temperature. As a result of its explosive properties, it can only utilized in situ and even then has to be diluted with inert gases (nitrogen, carbon dioxide) to 10 to 15% (by volume).

When large quantities are required, it is manufactured from sodium chlorate, for smaller quantities from sodium chlorite.

Sodium chlorate is reacted with hydrochloric acid:

Manufacture of large quantities of chlorine dioxide:

by reaction of sodium chlorate with hydrochloric or sulfuric acid, separation or reduction of the simultaneously formed chlorine

The gaseous, explosive chlorine dioxide has to be immediately diluted with inert gases

$$NaClO_3 + 2\ HCl \longrightarrow ClO_2 + 0.5\ Cl_2 + NaCl + H_2O$$

The most important side-reaction is the augmented formation of chlorine:

$$NaClO_3 + 6\ HCl \longrightarrow 3\ Cl_2 + NaCl + 3\ H_2O$$

Sulfuric acid and sodium chloride can be used instead of hydrochloric acid. With the simultaneous addition of sulfur dioxide chlorine is reduced to chloride, so that the otherwise necessary separation of chlorine from chlorine dioxide, by e.g. stripping with water, is unnecessary (chlorine dioxide is much more soluble in water than chlorine).

In modern plants, 90% of the theoretical yield of chlorine dioxide is obtained.

A number of industrial processes follow the above-described reaction scheme. In the USA and Canada, the ER-process from Erco and the SVP-process from Hooker Chemical Corp. are mainly used. Sodium sulfate disposal problems arise when these processes are operated with sulfuric acid or sulfur dioxide.

These problems do not arise in the Kesting (Munich) process in which the solution produced by the electrolytic manufacture of sodium chlorate is immediately reacted with hydrochloric acid and the chlorinedioxide-chlorine mixture formed blown off from the solution into a column. After separation the chlorine is reacted with hydrogen from the electrolysis to hydrogen chloride, which is fed back into the process. The only starting material in this process is thus chlorine, which is present in the chlorine dioxide obtained and in the hydrochloric acid which is fed back into the process.

Manufacture of small quantities of chlorine dioxide:
reaction of sodium chlorite with chlorine

Sodium chlorite as starting material: Small quantities of chlorine dioxide are produced by reacting sodium chlorite with chlorine:

$$2\,NaClO_2 + Cl_2 \longrightarrow 2\,NaCl + 2\,ClO_2$$

1.7.4.3 Applications of Chlorine-Oxygen Compounds

Applications of
- hypochlorites:
  - for bleaching,
  - disinfection,
  - destruction of poison gases and
  - hydrazine manufacture

Hypochlorites: Sodium hypochlorite (bleaching solution) is utilized for the bleaching and decolorization of pulp and textiles, for disinfection, e.g. in swimming baths, and for the manufacture of hydrazine (Section 1.4.2).

Calcium hypochlorite and bleach are used for disinfection e.g. in swimming baths, in the treatment of cooling water and to render harmless warfare agents of the "2,2'-dichloroethylsulfide-type".

"Chlorinated trisodium phosphate" is a component of household and industrial cleaning agents, particularly in the USA.

- sodium chlorite:
  - small scale manufacture of chlorine dioxide
- sodium chlorate:
  - manufacture of chlorine dioxide and perchlorates,
  - in uranium extraction,
  - as a herbicide
- potassium chlorate:
  - e.g. for matches
- ammonium perchlorate:
  - oxidizing agent in rocket fuel
- chlorine dioxide:
  - pulp bleaching
  - water treatment

Sodium chlorite is utilized primarily for the small scale manufacture of chlorine dioxide.

Chlorate: More than 80% of the sodium chlorate produced is converted into chlorine dioxide for pulp bleaching. In addition it is utilized for the manufacture of perchlorates (in the USA ca. $20 \cdot 10^3$ t/a), for the oxidation of U^{4+} and U^{6+} in the extraction of uranium (16 to $19 \cdot 10^3$ t in the USA in 1979) and as a herbicide. Potassium chlorate is utilized in the manufacture of matches (9 to $10 \cdot 10^3$ t in the USA in 1979) and fireworks.

Perchlorates are mainly used in fireworks and, especially ammonium perchlorate, as an oxidation agent in rocket fuel.

Chlorine dioxide is to an increasing extent replacing elemental chlorine as a bleaching agent for wood pulp, because significantly less chlorinated hydrocarbons are formed. Chlorine dioxide manufactured from sodium chlorate is readily available and is an economical alternative to chlorine. This change-over in bleaching process started in the paper industry in the 1980's and by 1994 accounted for 50% of the bleaching in the North America.

Chlorine dioxide is also utilized in the provision of potable water.

References for Chapter 1.7.4: Chlorine-Oxygen Compounds

Commercial Information:

Chemical Economics Handbook. 1995, 732. Stanford Research Institute, 1000-1002, Menlo Park, California, USA.

Reviews:

Kirk-Othmer, Encyclopedia of Chemical Technology. 1993. 4. Ed., Vol. 5, 932 – 1016, John Wiley & Sons, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 6, 483 – 525, VCH Verlagsgesellschaft, Weinheim.

Chemical Economics Handbook. 3/1995. *Chlorates*, 732, Stanford Research Institute, Menlo Park, California, USA.

Technical Information:

Bleichen mit Natriumhypochlorit. 182. Reiniger + Wäscher, XXXV, Heft 5, 30– 33.

Calcium hypochlorite. Chem. Eng. News, 27.4.1981, 28–29.

Wintzer, P. 1980. *Enticklung und Trend der Chlordioxid-Bleiche mit integrierter Chlorat-Electrolyse für die Zellstoff-Industrie* (Developments and trends in chlorine dioxide-bleaching with an integrated chlorate electrolysis for the wood pulp industry) , Chem. Ing. **52**, Tech. 392–398.

1.7.5 Bromine and Bromine Compounds

1.7.5.1 Natural Deposits and Economic Importance

Bromine occurs in nature mainly as soluble bromides. The concentration of bromine in the Earth's crust is $1.6 \cdot 10^{-4}$ %. It is contained in:

- seawater: 0.065 g/L
- the Dead Sea: 4 g/L
- natural brines: 3 to 4 g/L
- salt deposits: 0.005 to 0.45% (by weight)

Bromine, as bromide ions, occur in:

- seawater
- natural brines
- salt deposits

The most important deposits are in Arkansas (USA) and the Dead Sea (Israel/Jordan).

The waste solutions from the potash industry contain up to 6 g/L of bromide.

The world reserves of bromine are virtually unlimited. The bromine content of the Dead Sea alone is estimated to be 10^9 t.

Bromine reserves virtually unlimited

The worldwide capacity for bromine in 1993 was > 540 · 10^3 t/a. Three companies dominate the production and marketing of bromine and bromine compounds: Ethyl Corp. and Great Lakes Chemical in the USA and Dead Sea Bromine in Israel.

Worldwide production in 1993:
371 · 10^3 t/a

The worldwide production of bromine attained a peak in 1979 and 1989 of greater than 400 · 10^3 t, but has declined since 1990 and was 371 · 10^3 t in 1993. The bromine production figures for the most important countries in 1993 are given in Table 1.7-23:

Table 1.7-23. Bromine Production in 1993 in 10^3 t.

USA	Israel	Great Britain	Former States of USSR	Japan	Other countries
168	135	28	19	15	6

The demand for bromine-containing chemicals for different sectors has strongly shifted in recent years, partly due to environmental considerations. This is demonstrated by the evolution in the application spectrum for bromine consumption in the USA in the period 1980 to 1993 shown in Table 1.7-24.

Table 1.7-24. Application spectrum in the USA in the period 1980 to 1993 in 10^3 t/a.

	Flame retardants	Pesticides	Fuel additive	Drilling fluids	Other
1980	25	15	73		55
1985	48	17	32	18	27
1990	73	23	14	22	43
1993	79	30	11	9	40

1.7.5.2 Manufacture of Bromine and Bromine Compounds

Elemental bromine:
starting material for inorganic and organic bromine-compounds

Almost all bromine compounds are manufactured either directly or indirectly from elemental bromine. Its production is therefore of key importance.

1.7.5.2.1 Bromine

Bromine is manufactured from:

- bromide-enriched starting materials (brines)
- seawater

In both cases bromide ions are oxidized with elemental chlorine:

Bromine manufacture:

from bromides by oxidation with chlorine

$$2\ Br^- + Cl_2 \longrightarrow 2\ Cl^- + Br_2$$

and the bromine formed taken off as a gas.

Manufacture of Bromine from Bromide-Enriched Starting Materials - Brines, Waste Solutions from the Potash Industry ("Hot Debromination")

Bromide-containing brines are heated to ca. 90°C and reacted with chlorine. The elemental bromine is driven out with steam. Ca. 0.5 kg of chlorine and 11 kg of steam are utilized for each kg of bromine.

The mixture of bromine gas and steam is condensed and separated in a separating vessel, the bromine being purified by multistage distillation. The plants are designed to ensure the recycling of bromine- of chlorine-containing aqueous solutions and bromine- and chlorine-containing gases into the reaction tower. The debrominated salt-containing effluent is neutralized before further use. Its heat content is transferred in countercurrent to the incoming bromine-containing brines. More than 95% of the bromine in the starting solution is extracted.

Bromine extraction from brines:

bromine formed is driven out with steam ("hot debromination", the industrially more important process)

Due to the high corrosivity of moist bromine, materials such as glass, tantalum, ceramics and poly(tetrafluoroethene) have to be utilized in the plants.

Most of the bromine produced is extracted by this "hot debromination" process.

Manufacture of Bromine from Seawater ("Cold Debromination")

Before extracting bromine from seawater, the alkaline seawater has to be acidified because bromine disproportionates in alkaline media:

Bromine extraction from seawater:

by acidification and then reaction with chlorine, the bromine formed being driven out with air ("cold debromination"), absorbed in a sodium carbonate solution and finally liberated by acidification

$$3\ Br_2 + 6\ OH^- \longrightarrow 5\ Br^- + BrO_3^- + 3\ H_2O$$

to bromide and bromate.

The seawater is acidified with sulfuric acid to a pH of 3.5, 130 g of 100% sulfuric acid being necessary per t of seawater. The slight excess of chlorine necessary to oxidize the bromide is fed in at the same time as the sulfuric acid. The bromine formed is expelled by air in so-called "blow-out" towers. The bromine (and possibly chlorine or bromine chloride)-containing air is fed into absorption towers in which it is brought into contact with a sodium carbonate solution, whereupon the bromine is disproportionated into bromide and bromate according to the above equation. The bromine in the absorption solution is then converted into elemental bromine with sulfuric acid and expelled with steam:

$$5\ NaBr + NaBrO_3 + 3\ H_2SO_4 \longrightarrow 3\ Br_2 + 3\ Na_2SO_4 + 3\ H_2O$$

This process is operated in plants in Great Britain and Japan. Preconditions for its economic operation are high seawater temperatures and the possibility of disposing of the debrominated solutions so that they do not mix with the to be processed water entering the plant.

1.7.5.2.2 Hydrogen Bromide

Hydrogen bromide:

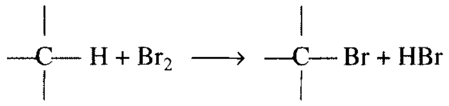
- by reacting hydrogen with bromine
- as a byproduct from the bromination of organic compounds

Hydrogen bromide is manufactured by the combustion of bromine and hydrogen:

$$H_2 + Br_2 \longrightarrow 2\ HBr \qquad \Delta H = -103\ kJ$$

Bromine-free hydrogen bromide can be obtained either by passing the reacted gases over hot activated charcoal or by using an excess of hydrogen.

Hydrogen bromide is a byproduct in the bromination of organic compounds:



$$-\overset{|}{\underset{|}{C}}-H + Br_2 \longrightarrow -\overset{|}{\underset{|}{C}}-Br + HBr$$

Hydrogen bromide dissolves in water forming hydrobromic acid. At 25°C and atmospheric pressure 193 g of hydrogen bromide dissolve in 100g of water.

1.7.5.2.3 Alkali Bromides, Calcium Bromide, Zinc Bromide

Alkali-, alkaline and zinc bromides:

from hydroxides or carbonates and hydrobromic acid

Bromides are produced by reacting the corresponding hydroxide, carbonate etc. with hydrobromic acid:

$$NaOH + HBr \longrightarrow NaBr + H_2O$$

Ammonium bromides is manufactured directly from bromine, whereby ammonia acts as a reducing agent:

$$8\,NH_3 + 3\,Br_2 \longrightarrow 6\,NH_4Br + N_2$$

1.7.5.2.4 Alkali Bromates

Bromates:

mainly by the electrochemical oxidation of bromides

Alkali bromates are mainly manufactured by the electrochemical oxidation of bromide in a process similar to that for the manufacture of sodium chlorate (see Section 1.7.4.2.3):

$$NaBr + 3\,H_2O \longrightarrow NaBrO_3 + 3\,H_2$$

Alternatively they can be manufactured by passing bromine into alkali hydroxide solutions, whereupon disproportionation takes place with the formation of a mixture of bromide and bromate (see Section 1.7.5.2.1), from which the more poorly soluble bromate is separated.

1.7.5.3 Applications for Bromine and Bromine Compounds

Bromine utilized in organic chemistry for the manufacture of:

- fuel additives
- flame retardants
- pesticides
- tear gases
- inhalation anesthetics
- dyes

Typical examples of the utilization of bromine in organic chemical manufacture are:

- *fuel additives*, in particular 1,2-dibromomethane, are utilized in leaded petrol as "lead substitutes" (formation of lead bromide). There was formerly a considerable demand for such products e.g. more than 100 t/a (based on bromine) in the USA in the 1970's, but since the introduction of lead-free petrol this application has become insignificant.
- *flame retardants*, in particular brominated diphenyl ethers, currently account for the largest number of bromine-chemicals. In the context of possible formation of bromo-

dioxins or furans, extensive investigations under realistic fire conditions are presently being carried out under the auspices of the WHO. Although no significant environmental danger has been established, further studies have been recommended to corroborate the results.

- *pesticides* of which bromomethane is the most important. The production of bromomethane has been frozen under the Montreal Protocol, due to its ozone-destroying potential. The production in the USA will not, however, be reduced before the year 2000, due to the lack of alternatives.
- *fire extinguishing agents*: The non-corrosive bromofluoromethane (Halon 1301) and bromochlorodifluoromethane (Halon 1211) may no longer be produced under the Montreal Protocol, due to their ozone layer-destroying potential.
- *tear gases* such as bromoacetophenone and bromoacetone.
- *inhalation* anesthetics such as 2-bromo-2-chloro-1,1,1-trifluoro-ethane.
- *dyes* such as bromo-anthraquinones and dibromoindigo are further examples of bromine – containing organic compounds.

Hydrogen bromide:
for manufacture of bromides

Hydrogen bromide is mainly used for the manufacture of bromides.

Sodium, potassium bromide:
for silver bromide manufacture for use in photography

Sodium and potassium bromide are mainly utilized in the manufacture of silver bromide for photosensitive layers. Utilization as a sedative has declined.

Lithium bromide:
as a drying agent in air conditioning units

Lithium bromide is employed as a drying agent fir air e.g. in air conditioning units.

Calcium bromide:
in crude oil extraction as a packing fluid

Calcium bromide, currently quantitywise the most important inorganic bromide, is utilized in crude oil extraction as a so-called "packing fluid" or "drilling fluid". Packing fluids surround the archimedian screw and equalize the pressure. Depending upon the pressure ratio solutions of sodium chloride, of mixtures of sodium chloride with sodium carbonate or calcium chloride, of calcium chloride, of mixtures of calcium chloride and calcium bromide or of mixtures of calcium bromide and zinc bromide (see below) are utilized. Solutions with 53% by weight of calcium bromides are used, which have a density of ca. 1.7 g/mL.

Up to 150 m^3 of packing fluids per oil well can be used.

Zinc bromide:
as a packing fluid

Zinc bromide is used as a packing fluid in solutions with 55% of zinc bromide and 20% of calcium bromide, which have a density of ca. 1.9 g/mL, for extreme pressure ratios. Such mixtures are, however, very corrosive.

Alkali bromates are sensitive to heat and shock. They are utilized e.g. in the treatment of flour and in hair setting lotions.

Alkali bromates:
for flour treatment

References for Chapter 1.7.5: Bromine and Bromine Compounds

Reviews;
Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 536 – 589, John Wiley & Sons, New York.
Ullmann's Encyclopedia of Industrial Chemistry. 1985. 5. Ed., Vol. A 4, 391–429, VCH Verlagsgesellschaft, Weinheim.
McDonald, R. B. and Merriman, W. R., *The Bromine and Bromine-Chemicals Industry*, in *The Modern Inorganic Chemicals Industry*. 1977. Ed. Thompson, R. The Chemical Society, Burlington House, London, 168-182.

Commercial Information:
Chemical Economics Handbook. 1995, *Bromine*, 719. Stanford Research Institute, 1000-1002, Menlo Park, California, USA.

1.7.6 Iodine and Iodine Compounds

1.7.6.1 Economic Importance

Iodine is extracted from:

- brines, which often accrue in crude oil or natural gas production
- waste solutions from the Chilean niter industry

The extraction of iodine from ashed algae or kelp is currently industrially insignificant.

According to estimated figures from the US Bureau of Mines, the quantities of iodine produced in 1994 were:

Manufacture of iodine from:

- brines
- waste solutions from Chilean niter industry

Table 1.7-25. Estimated Iodine Production in 1994 in 10^3 t/a.

World	Japan	Chile	USA	Other
16.7	7.2	5.6	2.0	1.9

World production in 1994:
16 700 t

Most important producing countries:
Japan, Chile, USA

Only Japan and Chile export iodine on a large scale. The Federal Republic of Germany imported 870 t of iodine in 1979, mainly from Japan and Chile.

World reserves:
$>6 \cdot 10^6$ t

The worldwide reserves of iodine are greater than $6 \cdot 10^6$ t.

Table 1.7-26. World Reserves of Iodine (without Former States of USSR) in 1995 in 10^3 t/a.

World	Japan	Chile	USA	China	Other
>6000	4000	900	550	400	300

1.7.6.2 Manufacture of Iodine and Iodine Compounds

1.7.6.2.1 Iodine

From Brines

Iodine extraction from brines:
oxidation of iodide with chlorine, blown out with air, absorption in hydroiodic acid/sulfuric acid, reduction with sulfur dioxide to hydroiodic acid, part taken of for oxidation with chlorine to iodine

Brines contain between 30 and several hundred ppm of iodine (as iodide). The deposits in the USA are mainly in Michigan and Oklahoma. Extraction is similar to that of bromine. Brines are mixed with hydrochloric or sulfuric acid and oxidized with excess chlorine. The elemental iodine formed is blown out with air and absorbed in a sulfuric acid-hydroiodic acid-water mixture in an absorber. Reduction with sulfur dioxide converts the iodine into hydroiodic acid. Part of this is taken off and the hydroiodic acid oxidized with chlorine to iodine. The iodine is filtered off and dried and any organic impurities oxidized by melting under sulfuric acid.

The following equations give the individual steps:

$$2\ NaI + Cl_2 \longrightarrow I_2\uparrow + 2\ NaCl$$

$$I_2 + SO_2 + 2\ H_2O \xrightarrow{\text{in HI/H}_2\text{SO}_4} 2\ HI + H_2SO_4$$

$$2\ HI + Cl_2 \xrightarrow{\text{in H}_2\text{SO}_4} 2\ HCl + I_2$$

Alternative process:
absorption of iodine as polyiodide on anionic ion exchangers, desorption with alkali, working up to iodine

In Japan another process is used in which the iodine formed by chlorine oxidation is absorbed as polyiodide on an anionic ion exchanger. Desorption with alkali yields concentrated iodide- and iodate-containing solutions which are worked up to elemental iodine.

From Waste Solutions in Niter Production

The Chilean niter deposits contain up to 0.3% iodine in the form of calcium iodate. After dissolution and recrystallization of the niter, the supernatant liquor contains up to 9 g/L of sodium iodate. Iodine is liberated by reduction with sulfur dioxide (in the form of sodium bisulfite), further reduction to iodide being avoided by maintaining stoichiometry:

Iodine extraction from waste solutions from niter production:

reduction of sodium iodate with sodium bisulfate to iodine

$$2\,NaIO_3 + 5\,SO_2 + 4\,H_2O \longrightarrow Na_2SO_4 + 4\,H_2SO_4 + I_2$$

The iodine is filtered off and purified by sublimation. The now iodide-free solution is then neutralized and reutilized for dissolving fresh niter.

1.7.6.2.2 Hydrogen Iodide

Hydrogen iodide is manufactured from iodine and hydrogen on a platinum catalyst at 500°C:

$$H_2 + I_2 \xrightarrow[500\ ^\circ C]{Pt} 2\,HI$$

Hydoiodic acid is also industrially produced by the reaction of hydrazine with iodine:

$$N_2H_4 + 2\,I_2 \longrightarrow 4\,HI + N_2$$

234 g of hydrogen iodide dissolve in 100 g of water at 10°C. Acids with 47% by weight of hydrogen iodide are commercially available.

1.7.6.2.3 Alkali Iodides

Alkali iodides can be manufactured via iron(II) iodide as follows:

$$Fe + I_2 \longrightarrow FeI_2$$

$$FeI_2 + M_2CO_3 + H_2O \longrightarrow Fe(OH)_2\downarrow + CO_2 + 2\ MI$$

M: Na, K

After the iron hydroxide formed has settled, the alkali iodides are separated by concentration and crystallization. Neutralization of hydrogen iodide with alkali hydroxides also provides alkali iodides.

1.7.6.2.4 Alkali Iodates

Alkali iodates are manufactured from the corresponding chlorates by reaction with iodine upon heating in the presence of nitric acid:

$$2\ MClO_3 + I_2 \longrightarrow Cl_2 + 2\ MIO_3$$

M: Na, K

Electrochemical manufacture is also possible.

1.7.6.3 Applications of Iodine and Iodine Compounds

Applications of iodine and iodine compounds:

- as feedstuff additives in particular for cattle and poultry. Ethylenediamine dihydroiodide and calcium iodate are mainly used;
- as catalysts for stereospecific polymerization of butadiene and isoprene; in the Monsanto process for the manufacture of acetic acid;
- for pharmaceutical purposes, e.g. medicines for the treatment of thyroid gland diseases; sodium iodide as an additive in table salt in iodine-deficient areas; potassium iodide as a preventative medication in the event of nuclear accidents; as a contrast agent in diagnostic medicine; radioisotopes for the recognition and treatment of tumors;
- as a stabilizer for polyamide 6.6;
- in the photographic industry (silver iodide);
- for dyes (Bengal Red, erythosine);

- for disinfection, non-ionic organo-iodo complexes being used;
- for induction of rain fall and avoidance of hail damage (silver iodide).

References for Chapter 1.7.6: Iodine and Iodine Compounds

Reviews;

Kirk-Othmer, Encyclopedia of Chemical Technology. 1995. 4. Ed., Vol. 14, 709 – 737, John Wiley & Sons, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1989. 5. Ed., Vol. A 14, 381–391, VCH Verlagsgesellschaft, Weinheim.

Commercial Information:

Chemical Economics Handbook. 1995, *Iodine*, 744. Stanford Research Institute, 1000-1002, Menlo Park, California, USA.

Industrial inorganic Chemistry
Karl Heinz Büchel, Hans-Heinrich Moretto & Peter Woditsch

2 Mineral Fertilizers

The most important mineral fertilizers are those that contain phosphorus, nitrogen and potassium. Only these will be considered in the following sections. Their manufacture is quantitywise the most important chemical production.

2.1 Phosphorus-Containing Fertilizers

2.1.1 Economic Importance

2.1.1.1 General Information

The worldwide consumption of phosphorus in mineral fertilizers for the period between 1980 and 1992 is as follows (Table 2.1-1):

World consumption of mineral phosphate fertilizers in 1992:
$35.42 \cdot 10^6$ t P_2O_5

Table 2.1-1. Worldwide Consumption of Phosphorus in Mineral Fertilizers in 10^6 t/a P_2O_5.

1980	1984	1988	1992
31.20	33.09	36.69	35.42

The consumption is several Western European countries in 1992 is given in Table 2.1-2:

Table 2.1-2. Consumption of Phosphorus in Mineral Fertilizers in several Western European Countries in 1992 in 10^3 t/a P_2O_5.

France	Italy	F.R. Germany	Spain	Great Britain	Benelux	Western Europe
1253	663	519	502	335	136	4136

The production in the Federal Republic of Germany has declined in the period 1989 to 1992, as shown in Table 2.1-3:

Phosphate fertilizer production in FRG in 1992:

250 · 10^3 t/a (P_2O_5-content)

Table 2.1-3. Phosphate Fertilizer Production in F.R. Germany in Period 1989 to 1992 in 10^3 t/a P_2O_5.

1989	1990	1991	1992
639	595	294	250

2.1.1.2 Importance of Superphosphate

Superphosphate: a fertilizer declining strongly in importance (P_2O_5-content only 20%)

In the industrialized countries of the World the production of superphosphate has been declining for some time, because, with a P_2O_5-content of only 19 to 20%, a very high proportion of ballast has to be transported with it. In addition the biological availability of the phosphorus is lower than with other fertilizers. Superphosphate is still important in China and Eastern Europe. The world production by regions in 1994 is given in Table 2.1-4.

Table 2.1-4. Superphosphate Production in 1994 in 10^3 t/a P_2O_5.

World	North America	South America	Western Europe	Eastern Europe	Africa	Asia	Oceania
6301	36	435	155	905	180	4925	525

2.1.1.3 Importance of Triple Superphosphate

Triple superphosphate: importance unchanged (P_2O_5-content ca. 40%)

Estimated worldwide production in 1994: 3.24 · 10^6 t (P_2O_5-content)

The production of triple superphosphate with a P_2O_5-content greater than 40% and biologically more available phosphorus reached a peak in 1984 and has declined 30% since then. The worldwide capacity for triple superphosphate is considerably underutilized. Part of the spare capacity can be utilized for the manufacture of ammonium phosphate. The world production by region in 1990 is given in Table 2.5-5.

Table 2.1-5. Triple Superphosphate Production in 1990 in 10^3 t/a P_2O_5.

World	North America	South America	Western Europe	Eastern Europe	Africa	Asia	Oceania
3236	743	365	231	222	700	975	29

2.1.1.4 Importance of Ammonium Phosphates

Ammonium phosphates are mainly utilized as solid fertilizers, but can also be utilized in solution (for non-fertilizer applications see Section 1.5.1.2.2).

Ammonium phosphates (mono- and di-ammonium phosphates) are particularly important in the USA. Table 2.1-6 gives the world production for ammonium phosphate fertilizers by region.

Ammonium phosphate fertilizers: strongly increasing in importance

World production P_2O_5 (10^6 t):

1980:	15.5
1990:	19.2
1994:	18.3
1999:	21.0 (estimated)

Table 2.1-6. Worldwide Production of Ammonium Phosphate Fertilizer in the Period 1980 to 1994 in 10^3 t/a P_2O_5.

	World	North America	Latin America	Western Europe	Eastern Europe	Africa	Asis	Oceania
1980	15 531	6269	778	1992	4713	228	1479	72
1990	19 155	8032	952	1865	4220	1409	2647	30
1994	18 301	7586	985	2045	2521	1519	3645	0

The most important producer country in Western Europe is Spain with 357 · 10^3 t/a in 1994, only ca. 50 · 10^3 t/a being produced in the Federal Republic of Germany.

2.1.1.5 Importance of Nitrophosphates

The manufacture of this type of phosphorus fertilizer (also known as NPK- or NP-fertilizers) is largely restricted to Europe. The worldwide capacity in 1985 was estimated to be 4.4 · 10^6 t/a P_2O_5, Western Europe accounting for 2 · 10^6 t/a P_2O_5 and Eastern Europe for 1.1 · 10^6 t/a P_2O_5.

Nitrophosphates: mainly in Western Europe (capacity 2 · 10^6 t/a P_2O_5) and Eastern Europe (capacity 1.1 · 10^6 t/a P_2O_5)

2.1.1.6 Importance and Manufacture of Thermal (Sinter, Melt) and Basic Slag (Thomas) Phosphates

These products, which only dissolve very slowly in the soil, are only produced and marketed in limited geographic areas. Their significance is very small in a worldwide context. Their production will be considered below.

Sinter phosphates: "Rhenania phosphates" with a P_2O_5 content of ca. 29% are obtained by sintering apatite, silica and sodium carbonate or sodium hydroxide. Their annual production in the Federal Republic of Germany is over 300 · 10^3 t (corresponding to ca. 90 · 10^3 t/a P_2O_5).

"Rhenania Phosphates":

by sintering apatite, silica and sodium carbonate, P_2O_5 content ca. 29%. Production in the Federal Republic of Germany > 300 · 10^3 t/a

Defluoridized apatites:

world capacity 1.5 · 10^6 t/a (mainly in USA and former States of USSR). P_2O_5 content ca. 42%

Defluoridized apatites are obtained by sintering apatite in the presence of water vapor, silica and other substances. The world capacity (mainly in the USA and former States of the USSR) for this type of product, with a P_2O_5 content of ca. 42% is estimated to be 1.5 · 10^6 t/a. Defluoridized apatite is also used as an animal nutrition supplement.

Melt phosphates:

- by melting apatite with Mg-compounds and silica
- P_2O_5-content ca. 21%
- production mainly in East Asia
- ca. 3% of worldwide phosphate fertilizer production

Melt phosphates: A product with a P_2O_5 content of ca. 21% is obtained by melting apatite with magnesium compounds and silica. These fertilizers are mainly manufactured in Eastern Asia (capacity in Japan and Korea 670 · 10^3 t/a).

Melt and sinter phosphates accounted for ca. 3% of the worldwide production of phosphate fertilizers in 1976, with its share decreasing relative to other types.

Thomas phosphates:

- from the smelting of phosphorus-containing iron ores
- P_2O_5 content between 10 and 18%
- production in the EU: ca. 220 · 10^3 t P_2O_5

Thomas phosphates: The slag resulting from the smelting of phosphorus-containing iron ores contains, in addition to phosphorus, mainly calcium, magnesium, iron and silica. The citrate-soluble P_2O_5 – content of these "Thomas phosphates" varies between 10 and 18%. Ca. 220 · 10^3 t/a P_2O_5 of Thomas phosphates is currently produced in the EU (mainly in Great Britain, the Federal Republic of Germany, France, Benelux). Future production depends mainly on the availability of phosphorus-containing iron ore.

2.1.2 Manufacture of Phosphorus-Containing Fertilizers

2.1.2.1 Superphosphate

Superphosphate (mixture of mono-calcium phosphate and calcium sulfate):

- from apatite and sulfuric acid

The manufacture of superphosphate from apatite and sulfuric acid proceeds according to the idealized overall equation:

$$2\,Ca_5[(PO_4)_3(F)] + 7\,H_2SO_4 \longrightarrow 3\,Ca(H_2PO_4)_2 + 7\,CaSO_4 + 2\,HF$$

Reaction proceeds in two steps:

- fast step: formation of anhydrite and phosphoric acid
- slow step ("curing"): conversion of phosphoric acid to mono-calcium phosphate

This reaction takes place in two steps: anhydrite and phosphoric acid being formed in the fast first step. This phosphoric acid then reacts slowly - over a period of weeks - ("curing") with further apatite producing mono-calcium phosphate hydrate. Part (ca. 10 to 40%) of the fluoride contained in the apatite is expelled in the form of gaseous silicon tetrafluoride, the rest remains in the superphosphate. Any carbonato-apatite and calcium carbonate in the fluoroapatite react forming carbon dioxide.

The manufacture of superphosphate proceeds in five stages:

Manufacture proceeds in five process steps

- grinding of the apatite
- reaction with sulfuric acid
- solidification and crushing of the primary reaction product
- "curing" - completion of the reaction
- comminution and possible granulation of the end product

The grinding of the apatite ($\geq$ 33.5% P_2O_5), if necessary after prior crushing, yields a material with a particle size of, for example, 90% <150 µm. The reaction with the ca. 70% sulfuric acid is currently mainly carried out continuously in mixing units with stirrers or in a stainless steel conical stirrer-less mixing funnel developed by TVA. On average 60 kg sulfuric acid is necessary per 100 kg of apatite.

The initially liquid digestion mixture solidifies within 5 to 20 min and then has to be crushed. A large number of apparatuses have been developed for this primary size reduction e.g. chamber systems in which the material solidifies and is then mechanically removed. In modern continuous plants the reaction mixture is, for example, placed on long rubber conveyor belts upon which it solidifies. During solidification gaseous fluoro-compounds escape and have to be removed and absorbed.

A large number of apparatuses have been developed for crushing the primary reaction product

To complete the after-reaction, the product has to "cure" for several weeks. Then it is crushed and supplied. Since it is dusty and has a tendency to cake, it is often granulated. This can take place both before and after the curing.

In the Federal Republic of Germany superphosphate is marketed with 18% citrate-soluble P_2O_5, whereas in the USA the P_2O_5 content is 20 to 21%.

P_2O_5 content of superphosphate:

- FRG: 18% (citrate-soluble)
- USA: 20 to 21% (citrate-soluble)

2.1.2.2 Triple Superphosphate

The manufacture of triple superphosphate proceeds according to the equation:

$$2\ Ca_5[(PO_4)_3(F)] + 14\ H_3PO_4 \longrightarrow 10\ Ca(H_2PO_4)_2 + 2\ HF$$

Its manufacture is very similar to that for superphosphate. Apatite with a P_2O_5 content $\geq$ 31% is ground to e.g. 70% <

Triple superphosphate (mono-calcium phosphate):

- from apatite and phosphoric acid
- process analogous to superphosphate manufacture
- P_2O_5 content ca. 47% (citrate soluble)
- $CaO:P_2O_5$ molar ratio 0.92 to 0.95

74 µm and wet-process acid with 52 to 54% P_2O_5 are used as starting materials. The molar ratio of CaO to P_2O_5 in the final product should be between 0.92 and 0.95 and the P_2O_5 content should be ca. 47%. The solidification of the reaction mixture occurs faster than in the manufacture of superphosphate.

In the USA, triple superphosphate is often used as a granulate, which can be produced using various methods. In the Dorr-Oliver process, for example, a still liquid digestion mixture is deposited on circulating triple phosphate granules, which are then sieved and dried. The ratio of separated to recirculated granules is 1:12. In general, however, triple superphosphate is first produced and then granulated with water and steam.

2.1.2.3 Ammonium Phosphates

Solid ammonium phosphate fertilizers:

- mono-ammonium phosphate (MAP)
- diammonium phosphate (DAP) and mixtures
- purity ca. 85%

The following ammonium phosphates are used as fertilizers either separately or as mixtures:

monoammonium phosphate $NH_4H_2PO_4$ (MAP)

diammonium phosphate $(NH_4)_2HPO_4$ (DAP)

ammoniumpolyphosphates $[NH_4PO_3]_n$ (APP)

Tri-ammonium phosphate is not a commercial product because of its high ammonia vapor pressure.

Liquid ammonium phosphate fertilizers:

- ammonium polyphosphate (APP)

Properties of APP:

- good water solubility
- sequestration of impurities as water-soluble complexes
- difficult to granulate

Mono- and diammonium phosphate are used as solid fertilizers, whereas ammonium polyphosphate is mainly utilized in solution as a liquid fertilizer, since unlike the orthophosphates, it is very soluble and is more difficult to granulate than the orthophosphates. As a result of its complexing properties, it also keeps impurities (iron, aluminum, magnesium etc.) in solution.

Ammonium phosphate fertilizers are relatively impure (purity ca. 85%), due to their being prepared with nonpurified wet-process acid. Commercial monoammonium phosphate contains 11 to 13% N and 48 to 53% P_2O_5 (theoretically 12.2% N, 61.7% P_2O_5). Commercial diammonium phosphate contains 16 to 18% N and 46 to 48% P_2O_5 (theoretically 21.2% N, 53.7% P_2O_5).

Solid fertilizers: In the manufacture of solid ammonium phosphate fertilizers there are two main problems:

- manufacture of storable, noncaking products
- least possible energy consumption during manufacture

To achieve these aims the manufacturing steps: neutralization of phosphoric acid with ammonia in an exothermic reaction and production of solid materials (e.g. by granulation or prilling) are linked with one another. Several of the many processes for the manufacture of ammonium phosphates will be discussed below.

In the TVA granulation process, slurries of ammonium phosphates, with a deficit or excess of ammonia with respect to mono-ammonium phosphate, are produced by the reaction of ammonia with phosphoric acid. These slurries are granulated by adding the deficient quantities of acid or ammonia necessary for a stoichiometric product and recycling the fine fraction. The granulate is then dried in, for example, rotary dryers, a process which requires considerable energy.

In the TVA tubular reactor process (e.g. pipecross reactors), anhydrous ammonia alone, or diluted with an equal quantity of water, is reacted with phosphoric acid. The reaction product is directly added to recycled particles in an adjacent granulation unit. At this point, further ammonia or acid can be added to the granulating material. The process is designed to utilize most of the heat of neutralization in the drying of the granules.

Non-granular (powdery) mono-ammonium phosphate is obtained in the Swift process by reacting liquid ammonia with phosphoric acid containing 50% P_2O_5 in an impeller-stirred reactor. The reaction products (finely divided mono-ammonium phosphate and steam, temperature ca. 126°C) are fed in at the top of a tower. The steam is driven out by a counter-current of air from below, the solid ammonium phosphate sinking to the bottom. The wet-process acid used in this process does not have to be deslimed beforehand.

The manufacture of ammonium phosphates can be combined with the production of mixed fertilizers e.g. ammonium phosphate with ammonium sulfate (partial substitution of sulfuric acid with phosphoric acid) or ammonium nitrate. The ammonium phosphates can also be converted into mixed fertilizers during granulation by adding potassium salts, urea etc.

Liquid ammonium phosphate fertilizers: Ammonium polyphosphates can be manufactured from phosphoric acids containing either high or low concentrations of polyphosphoric acid, or from orthophosphoric acid solutions.

Manufacture of liquid ammonium phosphate fertilizers (APP):

- by reacting polyphosphoric acid with ammonia
  problems due to scaling of Al- and Mg-phosphates on the tube reactor walls
- by reacting orthophosphoric acid with ammonia at 300°C yielding polyphosphates by water elimination

Initially, polyphosphoric acid was used which was produced by the combustion of white phosphorus (see Section 1.5.1.2.1), solutions with 11% N and 37% P_2O_5 being obtained. These "furnace acids" are currently too expensive for fertilizers, due to increased energy costs, and the polyphosphoric acids now used are manufactured from wet-process acid.

Solutions of liquid fertilizers contain:

- ca. 11% N and 37% P_2O_5
- 60 to 68% polyphosphate

If polyphosphoric acids with a high content of P_2O_5 in the polymer form are used (40 to 50% of total P_2O_5 as polyphosphoric acid), the reaction with ammonia has to be carried out with cooling to avoid hydrolysis to orthophosphates. The energy intensive nature of polyphosphate production has resulted in the current use of acids with about 20 to 30% of P_2O_5 in the polymer form. In a tube reactor developed by TVA, the acid is reacted with gaseous ammonia in an exothermic reaction at 230 to 240°C, whereupon a considerable proportion of the orthophosphate is condensed to polyphosphates with the elimination of water. The resulting melt is dissolved in an aqueous solution of the end product and the required quantities of water and, if necessary, ammonia is added at the same time. Solutions with 11% N and 37% P_2O_5 are generally produced, with 60 to 68% polyphosphate.

In 1985 in the USA, there were more than 135 TVA tube reactor plants operating, each producing 25 t of product per hour. A problem with these reactors is scaling of aluminum and magnesium phosphates on the reactor walls, which results in enforced down time for scale removal.

In a process developed by the company Swift, orthophosphoric acid is used as the starting material. Preheated acid is reacted in a special reactor with gaseous ammonia at high temperatures. At a temperature of 300°C the proportion of polyphosphates in the end product is 60%.

In the USA ammonium phosphate suspensions also marketed as fertilizers

In addition to these soluble fertilizers, suspensions of ammonium phosphate, which may contain other fertilizer substances, are very important, particularly in the USA.

2.1.2.4 Nitrophosphates

In addition to the digestion of apatite with sulfuric acid to phosphoric acid or superphosphate, the digestion of apatite with nitric acid is also of major industrial importance, the digestion with hydrochloric acid on the other hand having no industrial importance. The exothermic reaction with nitric acid proceeds, in principle, as follows:

Manufacture of nitrophosphates:
digestion of apatite with nitric acid and calcium nitrate. The soluble hygroscopic calcium nitrate has to be converted to other compounds or be (partially) removed

$$Ca_5[(PO_4)_3(F)] + 10\ HNO_3 \xrightarrow{45\ \text{to}\ 80^\circ C} 5\ Ca(NO_3)_2 + HF + 3\ H_3PO_4$$

$$\Delta H = -290\ \text{kJ/mol}$$

50 to 60% nitric acid is used up to 20% in excess. The fluoride largely remains in the reaction mixture. Part of the nitric acid is reduced to nitrogen oxides, which have to be removed from the tail gases.

Unlike the digestion with sulfuric acid, calcium is present in a soluble form. Since calcium nitrate is very hygroscopic, it is mostly either converted or separated (and then further utilized). [In a process developed by Lonza AG the calcium nitrate remains in the mixture. The digestion mixture is dehydrated up to the point that only 2 to 3 moles of water are present per mole calcium nitrate. Then the not yet solidified mass is granulated and coated with, for example, basic slag (Thomas meal) or calcium cyanamide etc.]

The conversion can occur:

- either by adding ammonia and carbon dioxide to the reaction mixture, whereupon ammonium nitrate and (only citrate soluble) calcium hydrogen phosphate (dicalcium phosphate) are produced in addition to calcium carbonate (Carbonitric process):

Addition of ammonia and carbon dioxide to the digestion mixture:
formation of calcium hydrogen phosphate, ammonium nitrate and calcium carbonate (Carbonitric process)

$$3\ H_3PO_4 + 5\ Ca(NO_3)_2 + 10\ NH_3 + 2\ CO_2 + 2\ H_2O \longrightarrow 10\ NH_4NO_3 + 2\ CaCO_3 + 3\ CaHPO_4$$

- or by adding sulfate as sulfuric acid, ammonium sulfate or potassium sulfate, whereupon the calcium is converted in an analogous reaction to calcium sulfate. The free phosphoric acid forms calcium hydrogen phosphate upon neutralization (Sulfonitric process).

Addition of sulfate (as sulfuric acid or ammonium or potassium sulfate):
calcium sulfate formed in addition to calcium hydrogen phosphate (Sulfonitric process)

Separation (partial) of the calcium nitrate from the digestion mixture by crystallizing out at low temperatures as its tetrahydrate. The calcium nitrate separated can be converted with ammonia/carbon dioxide to a mixture of calcium carbonate and ammonium nitrate (lime ammonium nitrate) (Odda process)

An example of calcium separation is the Odda process, in which, depending on the temperature reached, a small part or a large part of the calcium nitrate crystallizes out as its tetrahydrate. The calcium-depleted mother liquor is then neutralized with ammonia. The calcium nitrate separated can, for example, be converted into calcium carbonate and ammonium nitrate by reacting with ammonia and carbon dioxide and then after filtering off the calcium carbonate, worked up to ammonium nitrate:

$$Ca(NO_3)_2 \cdot 4\,H_2O + 2\,NH_3 + CO_2 \longrightarrow CaCO_3 + 2\,NH_4NO_3 + 3\,H_2O$$

The calcium carbonate is then generally mixed with a 97% ammonium nitrate melt to lime ammonium nitrate melt to lime ammonium nitrate ("calnitro") (Section 2.2.2.2).

2.2 Nitrogen-Containing Fertilizers

2.2.1 Economic Importance

2.2.1.1 General Information

Consumption of nitrogen fertilizers in 10^6 t N:

- World
  1992: 75.06
- FRG
  1992: 1.72

The consumption of mineral nitrogen-containing fertilizers is given in Tables 2.2-1 to 2.2-3.

Table 2.2-1. Evolution in the World Consumption of Nitrogen Fertilizers in the Period 1980 to 1992 in 10^6 t/a N.

1980	1984	1988	1992
57.22	67.67	75.60	75.06

Table 2.2-2. Consumption of Nitrogen Fertilizers in 1992 by Region in 10^6 t/a N.

World	West Europe	East Europe	Africa	North America	Central America	Asia/ Oceania
75.06	10.01	9.60	2.07	11.58	3.39	38.41

Table 2.2-3. Consumption of Nitrogen Fertilizers in several European Countries in 1992 in 10^6 t/a N.

France	F.R. Germany	Great Britain	Italy	Benelux
2.569	1.720	1.348	0.907	0.552

The demand for nitrogen fertilizers has grown strongly in the last 10 to 15 years, particularly in the Asian-Pacific region. More than half of the worldwide production of nitrogen fertilizers is consumed there.

2.2.1.2 Importance of Ammonium Sulfate

The worldwide production of ammonium sulfate in 1995 is given in Table 2.2-4.

The worldwide consumption of ammonium sulfate in 1995 was estimated to be $3.5 \cdot 10^6$ t N, which corresponds to 70% of capacity and ca. 4% of the total worldwide consumption of nitrogen. In Europe in 1995 the production was $0.7 \cdot 10^6$ t N and the consumption was $0.55 \cdot 10^6$ t N which corresponds to ca. 3% of the nitrogen consumption. Ammonium sulfate is particularly used in less developed countries.

Ammonium sulfate consumption in 1995:

- World: $3.5 \cdot 10^6$ t N (4% of total nitrogen consumption)
- Europe: $0.55 \cdot 10^6$ t N (3% of the total nitrogen consumption)

Table 2.2-4. Ammonium Sulfate Production in 1995 in 10^3 t/a N.

World	North America	Central America	West Europe	Africa	Asia/ Oceania	East Europe
3.473	0.648	0.350	0.705	0.55	1.105	0.610

The future development of ammonium sulfate production depends strongly upon the situation regarding (textile-)fiber production. Ammonium sulfate production is growing more slowly than that of the other nitrogen fertilizers.

Future development of ammonium sulfate production depends upon the development of the textile industry

2.2.1.3 Importance of Ammonium Nitrate

Pure ammonium nitrate, ammonium nitrate-ammonium sulfate mixtures and calcium carbonate-ammonium nitrate mixtures (lime ammonium nitrate, "calnitro", see Section 2.2.2.2) belong to this substance class. The worldwide production of these materials in 1995 was $15.5 \cdot 10^6$ t. In total nitrogen fertilizer production there is a shift to urea, which has a higher nitrogen content and can be inexpensively produced. The total consumption of ammoni-

World production of ammonium nitrate in 1995:

$1.5 \cdot 10^3$ t/a N

USA-consumption in 1996:

$3.17 \cdot 10^6$ t, including $7.13 \cdot 10^3$ t for explosives um nitrate in the USA in 1996 was $3.17 \cdot 10^6$ t N, of which $7.17 \cdot 10^3$ t was utilized in explosives. Table 2.2-5 gives the production of ammonium nitrate in 1995 in selected European countries.

Table 2.2-5. Production of Ammonium Nitrate in selected European Countries in 1995 in 10^3 t N.

Netherlands	France	Great Britain	F.R. Germany	Spain	Italy	Ireland	Belgium
960	670	520	530	339	128	155	350

2.2.1.4 Importance of Urea

Urea is the most important nitrogen fertilizer

World capacity:
1996: $51 \cdot 10^6$ t/a N,
2002: $63 \cdot 10^6$ t/a N (expected)

Urea is the nitrogen compound with the largest production volume worldwide. Its utilization is increasing steadily, it being the preferred nitrogen fertilizer worldwide. Urea is also used in much smaller quantities for the manufacture of industrial products. The following statistics relate to total urea manufacture, since it is mostly impossible to separate the contributions. The worldwide production of urea in 1996 was $51 \cdot 10^6$ t/a N. It is estimated that the worldwide urea capacity in 2002 will be $63 \cdot 10^6$ t/a N. Table 2.2-6 gives the regional production and consumption of urea in 1996.

Table 2.2-6. Worldwide Production and Consumption of Urea in 1996 in 10^6 t N.

	World	North America	Central/ South America	West Europe	East Europe	Africa	Asia/ Oceania
Production	42.9	4.9	2.0	2.1	5.8	1.1	26.9
Consumption	42.9	4.7	2.5	2.4	1.4	1.0	30.5

Urea consumption in the USA in 1996:

total	$3.83 \cdot 10^6$ t N
for fertilizers:	83%
for animal nutrition:	7%
for glues, plastics:	6%

The consumption in the USA in 1996 was $3.83 \cdot 10^6$ t N, of which 83% was used in fertilizers. Half of the consumption in fertilizers was utilized in liquid fertilizers e.g. in urea-ammonium nitrate solutions, the rest being used in solid fertilizers. 7% of urea was utilized for animal nutrition and 6% for urea-formaldehyde resins, glues and melamine. In the period between 1984 and 1996 there was a reduction in urea capacity in Western Europe of 39% to $2.5 \cdot 10^6$ t/a N (Table 2.2-7).

Table 2.2-7. Urea Production in Western Europe in 1984 and 1996 in 10^3 t/a N.

	West Europe	Austria	F.R. Germany	Spain	France	Italy	Ireland	Portugal	Netherlands
1984	4090	140	1140	290	325	780	150	30	140
1996	2515	180	700	170	280	345	175	40	140

2.2.2 Manufacture of Nitrogen-Containing Fertilizers

2.2.2.1 Ammonium Sulfate

Ammonium sulfate is produced is produced as a byproduct in a number of processes both in and outside the chemical industry. In addition it is produced directly in small quantities by the neutralization of sulfuric acid with ammonia, concentrating the solution and crystallization:

Ammonium sulfate from ammonia and sulfuric acid in:

- "saturators"
- reaction towers

$$2\,NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

To obtain the coarse crystals required in agriculture, the reaction is carried out in special plants ("saturators") in which the small crystals have a sufficiently long residence time in which to grow.

70% Sulfuric acid is utilized with gaseous ammonia, the heat of neutralization then being sufficient to evaporate all the water. In a process operated in Japan, sulfuric acid is fed in at the top of a tower and gaseous ammonia at the bottom. The ammonium sulfate can be drawn off from the bottom, which requires no further drying.

In the USA in 1993, 14% of the total production of ammonium sulfate was manufactured from ammonia and sulfuric acid.

Ammonium sulfate is produced as a byproduct in:

- the working up of sulfur dioxide produced by oxidation of sulfide ores;
- the working up of sulfur dioxide from the desulfurization of power station flue gases. The sulfur dioxide is scrubbed from the cooled flue gases with ammonia as ammonium sulfite. The solution is then intensively treated with air to convert most of the sulfite to sulfate and is then sprayed into a 390°C gas stream, whereupon solid ammonium sulfate is produced and any ammonium

Ammonium sulfate as a byproduct in:

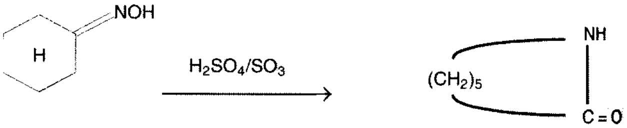
- metal extraction
- desulfurization of furnace gases
- from the ammonia of coking plants
- working up of waste sulfuric acid in organic chemistry
- caprolactam production

sulfite is cracked to ammonia and sulfur dioxide, which is fed back into the process. The ammonium sulfate is finally granulated;

- the working up of ammonia produced as a byproduct in coke production to ammonium sulfate. 11% of the ammonium sulfate produced in the USA in 1993 came from this source;
- the working up of sulfuric acid produced in many organic processes e.g. nitration, alkylation etc. to ammonium sulfate. However, the organic impurities can interfere very strongly in the synthesis process e.g. by foaming or influencing the crystal morphology;
- the manufacture of caprolactam (starting material for polyamide 6) by the Beckmann rearrangement of cyclohexanone oxime in fuming sulfuric acid:

"Classical" caprolactam process:

- 4.4 t ammonium sulfate produced per t lactam



This is the most important source of ammonium sulfate and accounted for 75% of the USA production in 1993. In the "classical" caprolactam process, in which hydroxylamine sulfate produced by the Raschig process and the oxime is rearranged in sulfuric acid, 4.4 t of ammonium sulfate are produced per t caprolactam. In recently developed processes the incidence of byproducts has been significantly reduced or even eliminated.

Recently developed caprolactam processes:

- incidence of byproducts significantly reduced

2.2.2.2 Ammonium Nitrate

Ammonium nitrate:

from nitric acid and gaseous ammonia e.g. in circulation reactors

Ammonium nitrate is manufactured by the neutralization of nitric acid with gaseous ammonia in a strongly exothermic reaction:

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

and is carried out in e.g. in circulation reactors, which ensure a rapid thorough mixing of the reaction components. In some cases these reactions are carried out under pressure to enable the steam formed to be used for preheating the ammonia and the acid. In this way reactor temperatures of up to 180°C can be obtained.

The thermal instability of ammonium nitrate requires:

- small reactor volumes
- pure (chloride-free) nitric acid
- avoidance of an excess of acid

The thermal instability of ammonium nitrate means that the volume of the reactors must be kept as small as possible, the acid used must be as free from impurities as possible and the reaction must be controlled so as to avoid the presence of excess acid.

If nitric acid concentrations above 50% are used, it is possible, with appropriate process design, to evaporate all the water introduced without supplying additional energy.

The ammonium nitrate melt is prilled or granulated

The ammonium nitrate melt leaving the reactor generally has a water content of 3 to 5%, in some plants even as low as 0.5%. The melt is fed into the top of so-called "prilling towers" (up to 60 m high), in which the melt is so dispersed that droplets are formed which, upon cooling with air fed in at the bottom, solidify as they descend. If the melt only contains 0.5% water the resulting prills can be used directly, otherwise they have to be dried further. Granulation can be used instead of prilling.

The (hygroscopic) ammonium nitrate prills have to be posttreated to avoid caking

Posttreatment is necessary, because ammonium nitrate is highly hygroscopic. In view of its strong oxidizing power, only inorganic substances such as attapulgite, kieselguhr or clay can be used.

For safety reasons F.R. Germany only permits ammonium nitrate-mixtures, e.g. with calcium carbonate, to be used as fertilizers

In the Federal Republic of Germany, the use of pure ammonium nitrate as a fertilizer is forbidden on safety grounds. Mixtures, particularly with calcium carbonate, are used instead. Currently mixtures with N-contents of up to 28% are allowed.

(For the manufacture of ammonium nitrate from calcium nitrate see Section 2.1.2.4).

2.2.2.3 Urea

Urea:

from carbon dioxide and ammonia in a two step process:

- 1st step: formation of ammonium carbamate (exothermic, quantitative)
- 2nd step: conversion of ammonium carbamate into urea (endothermic, ca. 70% yield)

Industrially urea is only produced from ammonia and carbon dioxide. Since carbon dioxide is a byproduct in the production of hydrogen for use in the synthesis of ammonia from natural gas or crude oil (in the case of natural gas only in 90% of the required amount), a urea plant is often coupled with an ammonia synthesis plant.

In the first step ammonia and carbon dioxide react forming ammonium carbamate:

$$CO_{2\,\text{gas}} + 2\,NH_{3\,\text{liq.}} \longrightarrow NH_2COONH_{4\,\text{liq.}}$$
$$\Delta H = -117\ \text{kJ/mol}$$

At high pressures this reaction is quantitative. Ammonium carbamate is in equilibrium with urea and water:

$$NH_2COONH_{4\,\text{liq.}} \rightleftharpoons NH_2CONH_{2\,\text{lig.}} + H_2O_{\text{liq.}}$$
$$\Delta H = 15.5\ \text{kJ/mol}$$

Ca. 70% of the carbon dioxide is converted into urea at an ammonia to carbon dioxide molar ratio of 4:1, a temperature of 200°C and a pressure of 250 bar.

Ammonia has to be expelled from the reaction mixture, consisting of an aqueous solution of urea, ammonium carbamate and ammonia, then the ammonium carbamate is thermally decomposed to urea.

The unconverted ammonium carbamate and unreacted ammonia have to be removed from the reaction mixture which consists of an aqueous solution of urea, ammonium carbamate and ammonia. The numerous industrial processes particularly differ in the way in which this separation and the recycling of ammonia and carbon dioxide are carried out, the minimizing of the energy consumption of these large plants (up to 1700 t urea/d) being crucial.

"Once through" processes, in which part of the carbon dioxide is vented, are obsolete

In the first plants, using the "once-through" process, the mixture of carbon dioxide and ammonia resulting from pressure release and thermal decomposition of ammonium carbamate was worked up to ammonium nitrate or sulfate, the carbon dioxide being vented. Modern plants operate with total recycling of carbon dioxide and ammonia achieving yields based on ammonia consumed of 98.6 to 99.5%. Since considerable product loss occurs in the subsequent prilling of the urea, the real yields are even higher.

Current processes comprise:

- solution recycling processes
- stripping processes

Current processes are:

- solution recycling processes
- stripping processes

total recycling of ammonia and carbon dioxide carried out

In the former, the pressure applied to the solution leaving the reactor is reduced stepwise, the carbon dioxide and ammonia released upon each pressure reduction being returned at their respective pressures to the absorber for absorbtion in water or in the urea mother liquor, in countercurrent (Fig. 2.2-1).

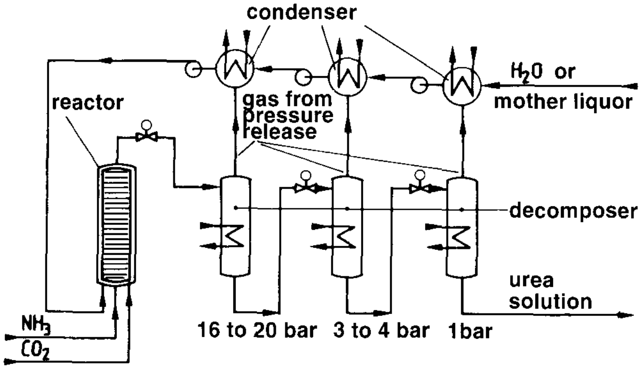


Fig. 2.2-1. Flow sheet of a conventional solution recycling process for urea manufacture. [Taken from Fromm, D. and Lütow, D., "*Modern Processes in the Heavy Chemicals Industry: Urea*", Chemie in unserer Zeit **13**, 78-81 (1979).]

Solution recycling process see Fig. 2.2-1 and 2.2-2.

The pressure on these absorption solutions is increased from step to step, until the synthesis pressure is regained. With this countercurrent absorption a concentrated ammonium carbamate solution is obtained containing little water, which produces equilibrium conditions favorable for urea formation.

Stripping process see Fig. 2.2-3

Recycling processes in which the first decomposition stage is operated at 60 to 80 bar require even less heat (Mitsui-Toatsu, Montedison process) (see Fig. 2.2-2).

In the stripping process, the solution, upon leaving the reactor, is fed into the top of a film evaporator operated at the reaction pressure in which the solution flowing downwards is contacted countercurrently with all the carbon dioxide required in the process (see Fig. 2.2-3). The gases which leave via the head of the film evaporator are partly condensed in the pressurized solution coming from the low pressure decomposer, together with part of the freshly supplied ammonia. This mixture of liquid and gas is fed into the reactor. Since 85% of the carbamate is decomposed in the stripper, a single adjoining low pressure decomposer is sufficient to complete the dissociation. The heat produced in the high pressure condenser is converted into steam, which is used in the operation of the low pressure decomposer (Stamicarbon process).

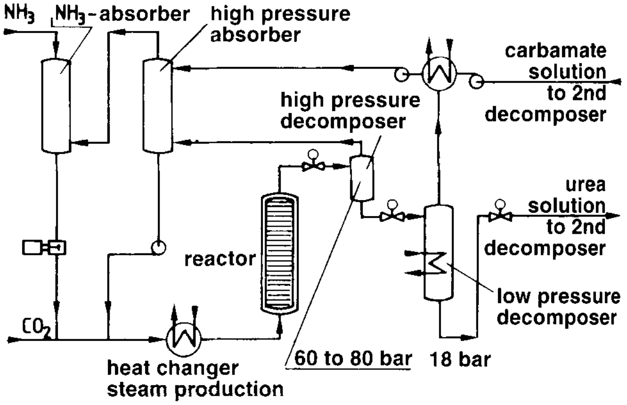


Fig. 2.2-2. Flow sheet for urea manufacture by a solution recycling process with a high pressure depressurization step. [Taken from Fromm, D. and Lütow, D., "*Modern Processes in the Heavy Chemicals Industry: Urea*", Chemie in unserer Zeit 13, 78-81 (1979).]

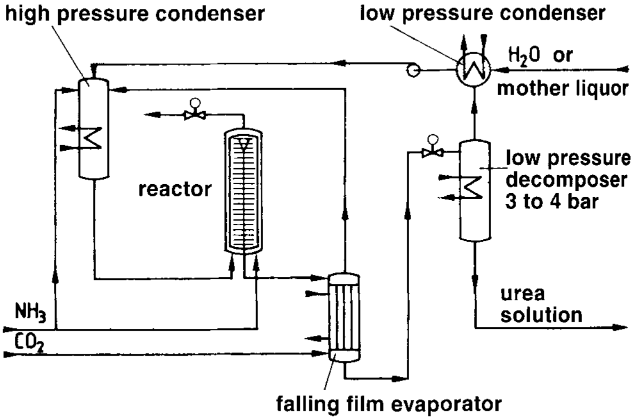


Fig. 2.2-3. Flow sheet for urea manufacture by the stripping process. [Taken from Fromm, D. and Lütow, D., "*Modern Processes in the Heavy Chemicals Industry: Urea*", Chemie in unserer Zeit 13, 78-81 (1979).]

Stripping processes energetically somewhat more favorable than recycling processes

Instead of stripping with carbon dioxide, ammonia can be used (Snam Progetti process). The stripping processes are energetically somewhat more favorable than the recycling processes with high pressure decomposers.

The 72 to 77% urea solutions obtained with these processes are, after prepurification e.g. over activated charcoal to remove oil, either vacuum evaporated until crystallization takes place or evaporated in a falling film evaporator to a urea melt (m.p. 132.7°C). These urea melts or molten crystals are generally prilled (however granulated urea is also produced).

Urea is recovered from the urea solution freed of ammonia and carbamate either by evaporation in a falling film evaporator or by crystallization

Urea cakes fairly easily upon storage. This tendency can be reduced by posttreatment e.g. with kielelguhr or formaldehyde. Sulfur- or polymer-coated urea can be used as a controlled release fertilizer, particularly in the USA ($114 \cdot 10^3$ t/a and $42 \cdot 10^3$ t/a respectively).

Urea for fertilizers is generally prilled, the prills having to be posttreated to avoid caking

Urea forms biuret upon heating:

$$2\,H_2NCONH_2 \longrightarrow H_2NCONHCONH_2 + NH_3$$

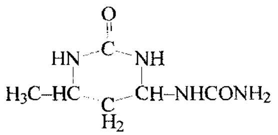
which is harmful to some plants. The biuret concentration must therefore be kept low (technical urea contains 0.3 to 1% biuret).

Important for urea fertilizers: biuret concentration must be low due to possible plant damage

Since urea is relatively quickly metabolized, so-called "controlled release fertilizers" have been developed. Examples are crotonylidene urea (I) (from urea and acetaldehyde) and isobutylidene urea IBDH (II) (from urea and isobutyraldehyde). The most important are, however, the urea-formaldehyde products of which $191 \cdot 10^3$ t were produced in the USA in 1993.

Controlled release fertilizers:

condensation products of urea and aldehydes such as acetaldehyde, isobutyraldehyde and in particular formaldehyde



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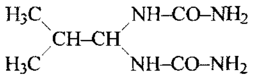


II

2.3 Potassium-Containing Fertilizers

2.3.1 Occurrence of Potassium Salts

Potassium salts are found in numerous deposits in many parts of the world. By far the largest are in Belarus and Canada (Saskatchewan).

Potassium salt deposits in many parts of the world with the largest deposits in Belarus and Canada (Saskatchewan). In Europe deposits in the FR Germany, France, Great Britain, Poland, Spain and Italy

In Europe there are large deposits in the Federal Republic of Germany, France, Poland, Spain, Great Britain and Southern Italy. The two largest deposits in the Federal Republic of Germany are in the Werra-Fulda and Hanover regions.

World reserves of potassium salts: $9.3 \cdot 10^9$ t as K_2O

The available reserves (i.e. deposits which are economically workable) estimated in 1991 are given by region in Table 2.2-8 below:

Table 2.2-8. World Reserves of Potassium Salts in 10^6 t as K_2O.

World	North America	South America	West Europe	East Europe	Asia
9340	4483	60	877	3600	320

FR Germany reserves of potassium salts: $0.8 \cdot 10^9$ t as K_2O

Deposits contain a mixture of salts including sodium chloride, potassium chloride, magnesium salts, calcium sulfate

The potassium salt deposits in the Federal Republic of Germany are estimated to be $790 \cdot 10^6$ t as K_2O.

The salt deposits contain salt mixtures, which mainly consist of the following components:

- sodium chloride (rock salt, halite)
- potassium chloride (sylvine)
- potassium magnesium chloride ($KMgCl_3 \cdot 6H_2O$, carnallite)
- magnesium sulfate ($MgSO_4 \cdot H_2O$, kieserite)
- potassium magnesium chloride sulfate [$(KCl \cdot MgSO_4)_4 \cdot 11H_2O$, kainite]
- calcium sulfate (anhydrite)

In the deposits of the Federal Republic of Germany in the Werra-Fulda region so-called "hard salts" are found (mixtures of potassium chloride, sodium chloride, magnesium sulfate and anhydrite) with carnallite seams, which are also found in the Hanover region. Sylvinite, a mixture of sodium and potassium chloride, is also found there.

2.3.2 Economic Importance of Potassium-Containing Fertilizers

Table 2.2-9 gives the production and consumption statistics for potassium-containing fertilizers by region for 1994:

Production of potassium-containing fertilizers in 1994 in 10^6 t as K_2O:

World:	22.6
Canada:	8.1
FR Germany:	3.3

Table 2.2-9. Production and Consumption of Potassium-Containing Fertilizers by Region in 1994 in 10^6 t as K_2O.

	World	West Europe	East Europe	North America	Central/ South America	Asia/ Oceania	Africa
production	22.6	5.4	5.1	9.5	0.3	2.3	0
consumption	19.1	4.1	2.2	5.1	2.0	5.2	0.5

The production and consumption of potassium-containing fertilizers in the Federal Republic of Germany in 1994 were $3.3 \cdot 10^6$ t as K_2O and $0.65 \cdot 10^6$ t as K_2O respectively. The most important producing country is Canada with $8.1 \cdot 10^6$ t/a as K_2O in 1994.

> 90% of potassium -containing fertilizers is potassium chloride, the rest being potassium sulfate, potassium magnesium sulfate, potassium nitrate

Worldwide more than 90% of the potassium-containing fertilizer used is potassium chloride. Potassium sulfate, potassium magnesium sulfate and potassium nitrate are, however, also used as fertilizers, in particular for plants which have a poor tolerance for chloride ions (e.g. tobacco, spinach, cucumbers etc.) or where magnesium-containing fertilizer is also required.

The worldwide production of potassium sulfate in 1996 was $3.0 \cdot 10^6$ t/a: It is mainly produced in West Europe with $2.4 \cdot 10^6$ t/a.

The worldwide production capacity for potassium nitrate in 1996 was ca. $1.3 \cdot 10^6$ t, of which 75% was for fertilizers and 25% for industrial applications. Table 2.2-10 gives the potassium nitrate consumption by region for 1997.

Table 2.2-10. Potassium Nitrate Consumption in 1997 in several Regions in 10^3 t.

USA	West Europe	Japan
126	260	14

The potassium nitrate production capacities for the main producing countries in 1997 are given in Table 2.2-11.

Table 2.2-11. Potassium Nitrate Production Capacities in the Main Producing Countries in 1997 in 10^3 t.

Chile	Denmark	Israel	USA
470	120	400	300

The Chilean "salt peter" is the only source of potassium nitrate which is not manufactured, but it only contains 20 to 30% KNO_3.

2.3.3 Manufacture of Potassium-Containing Fertilizers

2.3.3.1 Potassium Chloride

Extraction of potassium salts:

- by mining
- by leaching
- from potassium-containing waters

Extraction of potassium salts occurs mainly by mining (in the Federal Republic of Germany currently to a depth of ca. 1200 m), but leaching processes (solution mining, with one plant each in Canada and Utah/USA) and direct extraction from lakes (Dead Sea; Great Salt Lake, Utah; Searles Lake, California; Lake McLoed, Australia) are also utilized.

Four types of separation process, also in combination:

- dissolution processes
- flotation
- electrostatic fractionation
- gravitational separation

The solid salt has to be more or less strongly ground, depending upon the degree of fusion, before it can be further processed. Potassium chloride can be separated from the salt mixtures by:

- dissolution processes;
- flotation;
- electrostatic fractionation;
- gravitational (dense medium) separation.

Dissolution processes exploit the different solubilities of the salts

These processes are also combined with one another. In dissolution processes, the differences in solubility of the various constituents of the raw salt in water are exploited to attain high percentage potassium chloride. The particular process used depends upon the type of salt mixture, but energy consumption, disposal of byproducts etc. are also important.

Flotation process:

50% of the silvinite so processed, coarsely intergrown minerals required

Flotation or a combination of flotation with dissolution processes are currently used for processing 50% of the sylvinite. An important precondition for the use of flotation processes is the availability of coarsely intergrown minerals (predominantly in Canada, USA and the former States of the USSR) is. There is also one plant in the Federal Republic of Germany which uses this process.

Electrostatic process:

- opposite charging of the components
- separation of components using free fall in an electric field
- lower energy consumption
- worldwide ca. $10 \cdot 10^6$ t/a raw salt so processed

In electrostatic fractionation, the fact that the various components of a salt mixture (in particular sylvinite, kieserite and rock salt) become differently charged upon contacting one another under particular conditions. The process consists of the following steps:

- dry grinding of the raw salt
- conditioning
- heating and drying
- (triboelectrical) charging and adjustment of the relative humidity of the air
- (multistage) separation

Grinding reduces the raw salt to a size of < ca. 1 to 2 mm, depending upon the composition. Fines and dust interfere with this process. Conditioning entails the addition of organic compounds, mostly carboxylic acids, in quantities of 50 to 200 g/t raw salt. The salt is then dried e.g. by passing hot air over it. The (triboelectrical) charging takes place in so-called "fluidized bed salt warmers" in which the various salt components become oppositely charged. The residence time of the salt in this unit is less than one minute.

Separation of the charged salt mixture takes place (multistage, with partial recirculation) in so-called "plate separators". In the 2 m high and up to 10 m wide unit, particles fall unimpeded, are deflected sideways by an electric field of 4 to 5 kV/cm and are separated according to the sign of the charge. The electrodes rotate at 10 to 30 rpm against brushes which remove the deposited particles. Energy consumption is low. The throughput of a separation unit is several thousand t per day. $10 \cdot 10^6$ t are currently separated annually using this process.

Dense medium separation: only of minor importance

Dense medium separation can only be carried out with coarsely intergrown minerals. It has found only limited industrial application (Canada). Salt solutions containing ferrosilicon serve as the gravitational liquids.

The potassium chloride produced for use as a fertilizer or in fertilizer mixtures is mostly granulated or compacted.

Disposal of residues:

- deposition in mines
- tips
- in solution: injection under pressure in geological impermeable strata
- discharge in mains drainage

Much of the salt mined together with potassium chloride cannot be industrially utilized. Solid residues can to some extent be disposed of as infill in mines, however, there are limits to this procedure in that the bulk volume of the material being returned is much greater than the volume of salt originally present in the bed. A further possibility is tipping, which is not without its problems due to the solubility of the salt in water. If geological conditions permit, dissolved residues can be injected under pressure into impermeable subterranean strata. Discharge into mains drainage is only possible to a limited extent and has encountered considerable resistance in some cases (salt problems in the rivers Werra, Weser and Rhine in the Federal Republic of Germany for example).

2.3.3.2 Potassium Sulfate

Potassium sulfate production:

- from potassium chloride and sulfuric acid or sulfur dioxide, air and water (Hargreaves process)
- by metathesis of potassium chloride with e.g. magnesium sulfate

Potassium sulfate is manufactured from potassium chloride by reacting sulfuric acid with a mixture of sulfur dioxide, air and water (Hargreaves process):

$$2\ KCl + H_2SO_4 \longrightarrow K_2SO_4 + 2\ HCl$$
$$2\ KCl + SO_2 + 0.5\ O_2 + H_2O \longrightarrow K_2SO_4 + 2\ HCl$$

Potassium sulfate from potassium chloride and sulfuric acid:
worldwide $0.7 \cdot 10^6$ t/a (as K_2O)

Alternatively potassium sulfate is manufactured by metathesis of potassium chloride with the sulfate of another metal, particularly magnesium sulfate. This reaction takes place in two steps:

$$2\ KCl + 2\ MgSO_4 + 6\ H_2O \xrightarrow{H_2O} K_2SO_4 \cdot MgSO_4 \cdot 6\ H_2O + MgCl_2$$

Potassium sulfate from potassium chloride and magnesium sulfate:
worldwide > $1 \cdot 10^6$ t/a (as K_2O)

The double sulfate is separated and reacted with additional potassium chloride:

$$2\ KCl + K_2SO_4 \cdot MgSO_4 \cdot 6\ H_2O \xrightarrow{H_2O} 2\ K_2SO_4 + MgCl_2$$

Worldwide over $1 \cdot 10^6$ t/a of potassium sulfate (as K_2O) is manufactured by this process.

2.3.3.3 Potassium Nitrate

Potassium nitrate:

- from potassium chloride and nitric acid
- from potassium chloride by metathesis e.g. with sodium nitrate

Potassium nitrate is produced by reacting potassium chloride with nitric acid:

$$4\ KCl + 4\ HNO_3 + O_2 \longrightarrow 4\ KNO_3 + 2\ Cl_2 + 2\ H_2O$$

The process is in fact much more complex than this equation indicates.

In analogy with the manufacture of potassium sulfate, potassium nitrate can also be manufactured by metathesis with other nitrates, e.g. with sodium, calcium or ammonium nitrate, as follows:

$$\mathrm{NaNO_3 + KCl \longrightarrow KNO_3 + NaCl}$$

$$\mathrm{Ca(NO_3)_2 + K_2SO_4 + 2H_2O \longrightarrow CaSO_4 \cdot 2\,H_2O + 2\,KNO_3}$$

References for Chapter 2: Mineral Fertilizers

Reviews:

Kirk-Othmer, Encyclopedia of Chemical Technology. 1993. 4. Ed., Vol. 10, 433 – 514, John Wiley & Sons, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1987. 5. Ed., Vol. A 10, 323 – 431, VCH Verlagsgesellschaft, Weinheim.

Chemical Economics Handbook. 11/1997. *World Fertilizer Overview*, Stanford Research Institute, Menlo Park, California, USA.

Phosphorus-Containing Fertilizers:

Commercial Information:

Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California, USA:
- *Normal Superphosphates*, 760.5500A, May 1996.
- *Triple Superphosphates*, 760.5000A, May 1996.
- *Ammonium Phosphates*, 760.6000A, May 1996.

Technical Information:

Chem. Eng. News. 14.9.1981. *Manufacture of Nitrophosphates*, 50-51.

New Industrial Developments. Nov/Dec. 1980. Phosphorus and Potassium **110**, 33-37.

Ullmann's Encyclopedia of Industrial Chemistry. 1991. 5. Ed., Vol. A 19, 421 – 463, VCH Verlagsgesellschaft, Weinheim.

Nitrogen-Containing Fertilizers:

Commercial Information:

Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California, USA:
- *Ammonium Sulfate*, 757.3000A, July 1997.
- *Ammonium Nitrate*, 756.9000A, May 1997.
- *Urea*, 758.8000A, Dec. 1997.

Nitrogen, *Statistical Supplement*, No. 22, Jan./Feb. 1981.

Technical Information:

Ammoniumsulfat aus Rauchgas. 1981. Chemie für Labor und Betrieb **32**, 153 – 154.

Urea. May/June 1980. Nitrogen **125**, 37-40 & 42-43.

Fromm, D. und Lützow, D. 1979. *Moderne Verfahren der Großchemie: Harnstoff*, Chemie in unserer Zeit **13**, 78– 81.

Ullmann's Encyclopedia of Industrial Chemistry. 1985. 5. Ed., Vol. A 2, 243 – 265, VCH Verlagsgesellschaft, Weinheim.

Potassium-Containing Fertilizers:

Commercial Information:

Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California, USA:
- *Potassium chloride*, 764.3001E, Jan. 1998.
- *Potassium sulfate*, 764.3001O, Jan. 1998.
- *Potassium* nitrate, 764.3002D, Jan. 1998.

Technical Information:

Ullmann's Encyclopedia of Industrial Chemistry. 1991. 5. Ed., Vol. A 17, 271 – 277, VCH Verlagsgesellschaft, Weinheim.

Ullmann's Encyclopedia of Industrial Chemistry. 1993. 5. Ed., Vol. A 22, 39 – 103, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1982. 3. Ed., Vol. 18, 920 – 950, John Wiley & Sons, New York.

Bock, R. 1981. *Elektrostatische Trennung der Komponenten von Kali-Rohsalzen*. Chem.-Ing.-Techn. **53**, 916–924.

Singewald, A. Fricke, G. 1983. *Die elektrostatische Aufbereitung von Kali-Rohsalzen*, Chem.-Ing.-Techn. **55**, 39 – 45.

Industrial inorganic Chemistry
Karl Heinz Büchel, Hans-Heinrich Moretto & Peter Woditsch

3 Metals and their Compounds

3.1 Alkali and Alkaline Earth Metals and their Compounds

3.1.1 Alkali Metals and their Compounds

3.1.1.1 General Information

Of the alkali metals: lithium, sodium, potassium, rubidium and cesium, elemental sodium and its compounds are the most important industrially, particularly the mineral and industrial heavy chemicals: sodium chloride, sodium carbonate, sodium hydroxide, sodium sulfate etc. In second place is potassium, which is as its salts (chloride, sulfate, nitrate, phosphate) an important component of mineral fertilizers. Lithium and its compounds have a much lower but steadily increasing importance. Cesium and rubidium are only utilized in very small quantities for special applications.

Commercial importance:

- alkali metals:
  Na >> Li > K > Cs > Rb
- alkali metal compounds:
  Na > K >> Li >> Cs > Rb

3.1.1.2 Lithium and its Compounds

3.1.1.2.1 Natural Deposits and Economic Importance

The most important mineral for the industrial extraction of lithium is spodumene ($LiAlSi_2O_6$), which is found together with lepidolite, petalite and amblygonite (all with Li contents of 4 to 7%) and in salt lakes. The largest known reserves are in Chile (largest known deposit), Australia, USA and Canada. The main producer countries are the USA (North Carolina), Chile, Australia, Russia, Zimbabwe, Brazil and China. The worldwide reserves including the lithium content in salt lakes is estimated to be $7.3 \cdot 10^6$ t (as lithium), of which 60% is in salt lakes.

Lithium content:

• in the Earth's crust	65 ppm
• in seawater	0.17 ppm

Industrially important lithium minerals:

- spodumene $LiAlSi_2O_6$
- lepidolite (lithium mica) $KLi_2Al(F,OH)_2Si_4O_{10}$
- petalite $LiAlSi_4O_{10}$
- amblygonite $LiAl(F,OH)PO_4$

USA is the largest Li producer and consumer

Li-consumption has increased 2.5 fold since 1980

major applications:

Al-electrolysis, batteries, nuclear technology

The extraction of lithium from brines in the USA (Utah, Nevada), Chile, Bolivia and Argentina is becoming increasingly important. In these processes lithium precipitates out as the poorly soluble lithium carbonate, as a byproduct in the production of other salts (borax, potassium salts, sodium chloride and magnesium chloride).

The worldwide production capacity of lithium and lithium compounds in 1995 was $14 \cdot 10^3$ t (as lithium), of which 40% is in the USA. The current capacity in the USA is ca. $8 \cdot 10^3$ t/a and it is still increasing. It supplies 60% of the world market. The capacity in the second largest producer country, Chile, is $3 \cdot 10^3$ t/a and that in the former States of the USSR is $1 \cdot 10^3$ t/a.

3.1.1.2.2 Metallic Lithium

Metallic lithium:

by melt electrolysis of LiCl/KCl-mixture (ca. 1:1)

The proportion of elemental lithium in the total production of lithium and lithium compounds worldwide is ca. 10%. It is exclusively manufactured by melt electrolysis of a mixture of lithium chloride (45 to 55%) and potassium chloride at 400 to 460°C in steel cells with a graphite anode and a steel cathode. The cell voltage is 6.0 to 6.5 V. The metallic lithium formed collects on the surface of the molten salt electrolyte.

Elemental lithium is mainly utilized for the manufacture of lithium hydride and lithium amide and for the synthesis of organo-lithium compounds (e.g. butyl- and phenyllithium), which are used as catalysts in polymerization reactions e.g. in the production of cis-1,4 polyisoprene, as a reducing agent in organic chemistry and in the refining of metal melts in metallurgy. Lithium alloys are also utilized, e.g. Li/Mg-alloys, as extremely light and easy to work construction materials (in aerospace applications). Finally lithium is very important in nuclear technology e.g. nuclear weapons manufacture and increasingly as anodes for batteries with a high energy density and long term stability.

3.1.1.2.3 Lithium Compounds

Most important lithium compounds:

Li_2CO_3, LiOH, LiH, LiCl

Lithium carbonate: Lithium carbonate is industrially the most important lithium compound and the starting material for most of the other lithium salts. It is formed in the processing of lithium minerals and brines. Enriched and calcined lithium ore (spodumene) is digested e.g. with concentrated sulfuric acid at > 250°C, leached with water and finally reacted with sodium carbonate (see Schema in Fig. 3.1-1). Lithium-containing brines are evaporated, the lithium chloride purified and converted with sodium carbonate into lithium carbonate (see Schema in Fig. 3.1-1).

Lithium carbonate is utilized as a starting material for the manufacture of all other lithium compounds and in large quantities in the manufacture of aluminum by melt electrolysis (ca. 25% of the total lithium consumption). Lithium carbonate is also used as a flux in the glass, enamel and ceramic industries, which accounts for a further ca. 25% of lithium consumption. Glasses with high lithium content (on the basis of lithium aluminosilicate) are as a result of their low thermal expansion coefficients virtually fireproof. In psychiatry high purity lithium carbonate is utilized for the treatment of manic-depressive complaints.

Li_2CO_3 applications:

- aluminum manufacture
- glass and ceramic industries
- medicine
- intermediate in the manufacture of other Li salts

Lithium hydroxide: Lithium hydroxide is produced by the reaction of lithium carbonate with calcium hydroxide:

$$Li_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2\,LiOH$$

Lithium hydroxide monohydrate is industrially important in the manufacture of greases e.g. on the basis of lithium stearate. In the USA more than 60% of all greases are produced with the help of lithium soaps (ca. 25% of total lithium consumption).

Lithium hydride: Lithium hydride is manufactured from metallic lithium and hydrogen. It is industrially important as a source of hydrogen and as a reducing agent in organic synthesis, particularly in the form of its derivatives: lithium aluminum hydride and lithium borohydride.

$$2\,Li + H_2 \xrightarrow{700\,^\circ C} 2\,LiH$$

Lithium chloride: Lithium chloride is manufactured by the reaction of lithium carbonate with hydrochloric acid. As a result of its high corrosivity special steels and titanium apparatus are used. The main application of lithium chloride is in melt electrolysis in the manufacture of metallic lithium.

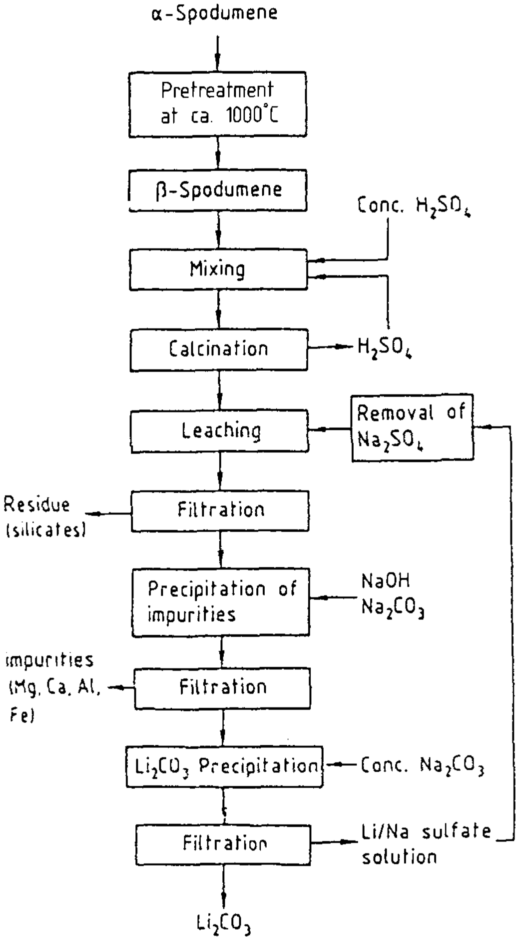


Fig. 3.1-1. Flow schema for the manufacture of lithium carbonate from spodumene.

3.1.1.3 Sodium and its Compounds

3.1.1.3.1 General Information

Industrially important Na compounds:

$NaCl$, $NaOH$, Na_2CO_3, Na_2SO_4, Na-silicates, Na aluminosilicates, Na_2S, Na_2SO_3, NaF etc.

The industrially most important sodium compound is sodium chloride (see Section 1.7.2.2), followed by sodium hydroxide (see Section 1.7.2) and then sodium carbonate. Other sodium salts utilized industrially in large quantities are sodium fluoride (see Section 1.7.1.3.5), sodium-bromine and -iodine compounds (see Sections 1.7.5.2.3 and

1.7.6.2.4), sodium-sulfur compounds (see Section 1.6), sodium-chlorine-oxygen compounds (see Section 1.7.4), sodium silicates and sodium aluminosilicates (see Sections 5.1.2 and 5.1.3), sodium sulfate, sodium hydrogen sulfate and sodium hydrogen carbonate.

3.1.1.3.2 Metallic Sodium

Metallic sodium:
production in the USA declined by 80% since 1970

Economic Importance: The manufacture of elemental sodium is closely coupled to the utilization of lead-containing antiknock agents for Otto motor fuels and is therefore now of only minor importance (due to environment protection legislation). In the USA, by far the most important producer country, the consumption declined 5.4% per year between 1975 and 1996. The worldwide capacity (without Eastern Europe) was $250 \cdot 10^3$ t/a at the end of the 1970's, of which about two thirds was in the USA. The production in the USA in 1996 was only ca. $24 \cdot 10^3$ t, compared with $155 \cdot 10^3$ t in 1970.

USA-production in 1996:
only $24 \cdot 10^3$ t/a

Manufacture of sodium:
by melt electrolysis of NaCl (with added $CaCl_2$ and $BaCl_2$) at ca. 600°C, electricity consumption 10 kWh/kg Na

Manufacture: Metallic sodium is currently almost exclusively produced by the electrolysis of molten specially purified sodium chloride (modified Downs process). Older processes on the basis of thermochemical processes or the electrolysis of molten sodium hydroxide in the Castner Cell are no longer important. In the melt electrolysis of sodium chloride other salts are added (calcium and barium chlorides) to reduce the melting point of sodium chloride of ca. 800°C to ca. 600°C. Graphite anodes are used with steel cathodes and diaphragms of steel wire gauze. The process is very energy intensive, 10 kWh being consumed per kg sodium produced. The cell voltage is ca. 7 V and the yield based on electricity consumed is 85 to 90%. The current capacity per unit is ca. 40 kA. The sodium produced after several purification steps (removal of Ca, CaO, Na_2O) has a purity of 99.95%. The chlorine produced at the same time is purified of salt dust and liquefied.

Applications of sodium:

- for manufacture of
  - NaH, $NaBH_4$,
  - difficult to reduce metals
  - herbicides
  - antiknock agents
- as a coolant in nuclear technology

Applications: The most important application sectors for metallic sodium in the USA are in the production of sodium borohydride (ca. 38%), which is used as a reducing agent, and in the manufacture of herbicides (ca. 25%). A further important sector accounting for 20% of the consumption of sodium, is the production of metals which are difficult to reduce such as uranium, thorium, zirconium, tantalum and titanium. Its utilization in the production of titanium has, however, declined of late. Tetramethyl- and tetraethyl lead produced from lead-sodium alloys with e.g. ethyl chloride has not been produced in the USA since 1991. The manufacture has been moved to Latin America and Asia:

$$4\ \mathrm{PbNa} + 4\ \mathrm{C_2H_5Cl} \longrightarrow (\mathrm{C_2H_5})_4\,\mathrm{Pb} + 3\ \mathrm{Pb} + 4\ \mathrm{NaCl}$$

Sectors consuming smaller quantities of metallic sodium are the manufacture of catalysts, its use as a reducing agent in the manufacture of pharmaceuticals, dyes and other organic chemicals. Sodium is also the starting material for various sodium compounds e.g. sodium peroxide, sodium amide (for organic chemical synthesis), sodium azide (for explosives and in the automobile industry for airbags), sodium hydride (a reducing agent) and organo-sodium compounds (catalysts e.g. for polymerization). Finally sodium is used as a coolant in fast breeder reactors, due to its technically interesting thermal and nuclear properties (see Section 6.4.5).

3.1.1.3.3 Sodium Carbonate

General Information:

Development of industrial sodium carbonate manufacturing processes such as the Leblanc (1790) and Solvay (1865) processes stimulated the development of the inorganic chemical industry

Sodium carbonate (soda) is a heavy chemical product, manufactured and extracted from natural deposits, comparable in importance to sodium hydroxide. The development of processes for the synthetic manufacture of sodium carbonate is closely associated with the history of industrial inorganic chemistry (Leblanc process, Solvay process and the technical developments which resulted from them). The applications of sodium carbonate e.g. in the manufacture of glass and for cleaning purposes have been known since ancient times.

Deposits of Sodium Carbonate Minerals

Very large deposits of sodium carbonate in USA and East Africa

Sodium carbonate occurs, often together with sodium hydrogen carbonate and other minerals, in many deposits. One important mineral is trona ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$). The worldwide natural sodium carbonate deposits are very large (e.g. Wyoming, USA has reserves of ca. $41 \cdot 10^9$ t in depths of e.g. 250 to 450 m). The deposits in salt lakes (USA, Mexico, East Africa, Southern Sahara) are still of major importance.

The reserves in the salt lakes of California are $600 \cdot 10^6$ t, with a further $30 \cdot 10^6$ t in the East African salt lakes (Kenya).

Economic Importance

The world production of sodium carbonate has increased considerably from $12.7 \cdot 10^6$ t in 1960 to $20.6 \cdot 10^6$ t in 1970 to $31.5 \cdot 10^6$ t in 1993, which, except for production in the USA, was almost exclusively synthetic. The capacity in the Federal Republic of Germany is currently $1.9 \cdot 10^6$ t/a. USA production increased from ca. $7.7 \cdot 10^6$ t in 1981, of which 90% was from natural deposits, to $11 \cdot 10^6$ t/a in 1994, which was exclusively from natural deposits. In 1970, sodium carbonate from natural deposits accounted for 15% of the worldwide production. This proportion had increased to 35% by 1994. Further advances in the economics of sodium carbonate production from natural deposits are to be expected upon changing from mining to extraction as an aqueous solution, so-called "solution mining". The high energy costs of sodium carbonate manufacture and stricter environment protection requirements have led to the closure of all the sodium carbonate manufacturing plants in the USA (last plant closed down in 1985). The future production of sodium carbonate is strongly linked to the demand for chlorine, since sodium carbonate and sodium hydroxide are in strong competition in many areas: neutralization processes, synthesis of other sodium compounds etc. If there is a disproportionate increase in chlorine production, the linked product sodium hydroxide will become more competitive and will adversely affect sodium carbonate demand. For specific applications it is often the price of a sodium equivalent which determines whether sodium carbonate or sodium hydroxide is used.

Production of sodium carbonate in 1992 in 10^6 t:

USA	9.4
Former States of USSR	4.0
China	4.0
FR Germany	1.7
Great Britain	1.0
Japan	1.0
France	1.0

Sodium Carbonate Production from Natural Deposits

The most important raw material for the industrial extraction of "natural" sodium carbonate is trona. The sodium carbonate-containing mineral is processed to pure sodium carbonate by two processes. In the *monohydrate process* (see Fig. 3.1-2) the mineral is first calcined, then dissolved in water, then filtered to remove insoluble

Most important sodium carbonate mineral:
trona $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$

Processing to pure sodium carbonate:

- monohydrate process
- sesquihydrate process

constituents and finally evaporated to dryness producing sodium carbonate monohydrate. In the *sesquicarbonate process* trona is first dissolved in water, freed of impurities and then calcined.

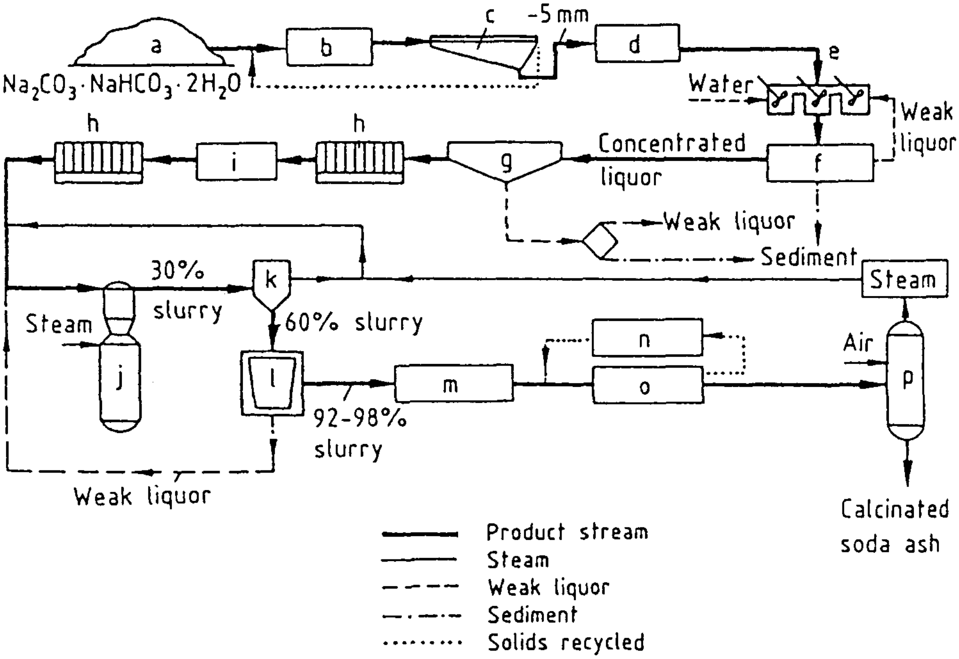


Fig. 3.1-2. Production of calcined sodium carbonate from trona by the monohydrate process.
a) trona storage; b) pulverizer; c) sieve; d) rotary tube furnace; e) dissolution unit; f) classifier; g) concentrator; h) filter press; i) activated charcoal filter; j) vacuum crystallizer; k) cyclone; l) centrifuge; m) dryer; n) cooler; o) classifier; p) product stock

Sodium hydrogen carbonate is extracted from the salt concentrates of the salt lakes. After thermal treatment to remove impurities and crystallization as its monohydrate, it is calcined to pure sodium carbonate.

Synthetic Sodium Carbonate Manufacture

The industrial Solvay process (ammonia-sodium carbonate process) is based on the precipitation of the relatively poorly soluble sodium hydrogen carbonate from an aqueous sodium chloride solution according to:

Solvay process:

- sodium carbonate from NaCl and $CaCO_3$ with ammonia as reaction-aid

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

This reaction is brought about by passing gaseous ammonia into a concentrated sodium chloride solution and then saturating it with carbon dioxide. The precipitated sodium hydrogen carbonate is separated off and then calcined to sodium carbonate e.g. in a rotary tube furnace:

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

Carbon dioxide and the ammonia recovered by treating the ammonium chloride formed with calcium hydroxide are returned to the process cycle. Ammonia is therefore only a reaction-aid. The overall reaction is:

$$CaCO_3 + 2\ NaCl \longrightarrow Na_2CO_3 + CaCl_2$$

with calcium chloride-containing brine as a byproduct, which is difficult to dispose of. A modified Solvay process with reduced energy consumption and improved calcium chloride recovery has been developed by Asahi.

In the Leblanc process introduced at the end of the eighteenth century, sodium chloride is reacted with sulfuric acid, the sodium sulfate formed is reduced with coal to sodium sulfide, which is reacted with calcium carbonate to sodium carbonate. This process has not been industrially important since the 1920's.

Process steps:

- production of a concentrated NaCl-solution
- pyrolysis of $CaCO_3$ into $CaO + CO_2$
- saturation of NaCl-solution with NH_3
- precipitation of $NaHCO_3$ by saturating with CO_2
- separation of $NaHCO_3$
- calcination (CO_2-splitting off) to Na_2CO_3
- production of $Ca(OH)_2$
- NH_3-recovery

Solvay process:

- energy intensive
- waste disposal problem ($CaCl_2$ brine), no longer operated in USA

Leblanc process:

industrially unimportant since the 1920's

Applications

A large part of the sodium carbonate consumed (e.g. 50% in the USA) is utilized in the glass industry, of which ca. 40% is used in the manufacture of bottle glass. Sodium carbonate serves both as a raw material and as a flux for the glass melt to dissolve the sand (see Section 5.1.2.2). A further 19% is utilized in the manufacture of chemicals, of which ca. 10% is for the production of sodium phosphates, mainly pentasodium triphosphate, in addition to silicates (sodium metasilicate pentahydrate and sodium orthosilicate), sodium chromate, sodium dichromate, sodium hydrogen carbonate, sodium nitrate etc. About 13.5% is utilized in the soap and detergent industry and 2.5% in the paper and pulp industry. Small quantities of sodium carbonate are necessary in almost all industry

Applications of Na_2CO_3:

- glass production
- inorganic sodium compounds
- soap and detergent production
- paper and pulp industry
- small quantities utilized in a variety of application areas

sectors (ore dressing, metallurgy, the leather industry, water purification, the food industry, ceramic and enamel manufacture, the textile industry etc.). Sodium carbonate is therefore one of the most widely utilized chemical products.

3.1.1.3.4 Sodium Hydrogen Carbonate

$NaHCO_3$:
very large reserves in the USA (ca. 30 · 10^9 t), which are very little exploited

Mineral Deposits: Sodium hydrogen carbonate occurs naturally e.g. as the mineral nahcolite. Enormous deposits are to be found in the USA (reserves of ca. 30 · 10^9 t in Wyoming, Utah and Colorado), together with oil shale.

Production in 1995 in 10^6 t/a:

World:	0.895
• USA	0.454
• West Europe	0.375
• Japan	0.066

Economic Importance: The production of sodium hydrogen carbonate is much lower than that of sodium carbonate. The production in the USA in 1995 was 0.454 · 10^6 t being only ca. 5% of the sodium carbonate production and corresponding to 50% of the world production of 0.895 · 10^6 t. The capacity in the USA has expanded considerably in recent years and as a result production should increase by 2% per year in coming years. A plant for producing sodium hydrogen carbonate from natural deposits came on stream in the USA in 1991.

$NaHCO_3$ manufacture:
both from synthetic sodium carbonate and sodium carbonate from natural sources; high purity requirements (up to food grade)

Manufacture: In the Solvay process sodium hydrogen carbonate is produced as an intermediate. Due to the high purity requirements of sodium hydrogen carbonate, it cannot, however, be obtained therefrom. It is produced by reacting filtered solutions of calcined sodium carbonate with pure carbon dioxide with cooling:

$$Na_2CO_3 + H_2O + CO_2 \longrightarrow 2\ NaHCO_3$$

Sodium hydrogen carbonate precipitates out, which has to be dried e.g. in a plate dryer, to avoid back reaction. Manufacture of sodium hydrogen carbonate is mostly integrated into the manufacture of synthetic sodium carbonate. In the USA it is also produced from sodium carbonate from natural sources.

Applications: The most important application sector for sodium hydrogen carbonate is the food industry (e.g. production of baking powder), for which in the USA 33% was used in 1995. In addition it is used in the rubber and chemical sectors. Sodium hydrogen carbonate is also utilized in the manufacture of pharmaceuticals, fire extinguisher powder and animal feedstuffs, a strongly increasing application with a 46% share in Western Europe in 1995 and a 25% share in the USA in 1995, and in the textile, paper and leather industries. The remainder is distributed over a number of applications (neutralization agent, manufacture of soaps and detergents etc.). In Japan 27% is surprisingly utilized in bath salts.

3.1.1.3.5 Sodium Sulfate

General Information

Sodium sulfate is an important heavy chemical in the chemical industry and is found in many mineral deposits. The world reserves are so large that with the present rate of consumption they are sufficient for several hundred years. In addition to extraction from natural sources, it is also produced in large quantities as a byproduct e.g. in the production of potassium salts, sodium chloride and borax and in chemical and metal producing processes. Dedicated manufacture e.g. from sodium chloride and sulfuric acid has become less important.

Na_2SO_4-production:
- from natural deposits
- as a byproduct in chemical and metallurgical processes
- from $NaCl + H_2SO_4$

Economic Importance

The worldwide production of anhydrous sodium sulfate or Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) in 1994 was $4.3 \cdot 10^6$ t/a, of which ca. $2.3 \cdot 10^6$ t/a was from natural deposits. It has decreased slightly in recent years due to a stagnation in consumption.

Na_2SO_4 production in 1994 in 10^6 t/a:

World	4.3
• Spain	0.8
• USA	0.65
• Mexico	0.5
• Canada	0.32
• Belgium	0.25
• Iran	0.25
• Japan	0.24

Production from Natural deposits and as a Byproduct

The production of pure sodium sulfate or Glauber's salt from natural minerals, such as thenardite Na_2SO_4 or glauberite $Na_2SO_4 \cdot CaSO_4$, is important in countries such as Spain, Canada, USA and the former States of the USSR, but its importance is decreasing relative to other production processes. More important is production of sodium sulfate from brines from salt lakes (USA, Russia, Canada) or as a byproduct in the production of sodium chloride, sodium carbonate, borax, potassium salts and lithium salts. Sodium sulfate decahydrate is formed during the working up of

Natural Na_2SO_4:
- from minerals (thenardite, glauberite, mirabilite)
- from salt lakes, salt brines, salt deposits (e.g. potassium salt deposits)

potassium salts e.g. in the reaction of kieserite ($MgSO_4 \cdot H_2O$) with sodium chloride. Glauber's salt is converted into anhydrous sodium sulfate by heating in a suspended particle dryer, spray dryer, fluidized bed dryer or evaporator crystallizer.

Sodium sulfate is produced in large quantities as a byproduct in various chemical and metallurgical processes e.g. in the production of sodium dichromate, vitamin C, formic acid, resorcinol and viscose fibers.

Sodium sulfate is also formed as a byproduct in the manufacture of hydrogen chloride by the reaction of sodium chloride with sulfuric acid at high temperatures (Mannheim process, Hargreaves process and the fluidized bed process). At the end of the 1970's the Mannheim process was used to produce about half of the sodium sulfate produced in Europe. However, these processes are hardly operated any more.

Applications

Na_2SO_4 applications:

- paper and pulp industry
- detergent industry
- glass industry
- textile industry
- chemical industry

The main consumers of sodium sulfate are the pulp, detergent and glass industries. In the USA the consumption in all sectors is declining strongly, thus whereas in 1973 $1.8 \cdot 10^6$ t was still consumed this had declined to $0.563 \cdot 10^6$ t by 1995. In the Federal Republic of Germany up to two thirds were utilized in the manufacture of detergents (diluent and suspension agent), but consumption in this sector has declined strongly due to the development of new detergent concentrates. In the USA only 45% is utilized in detergents and 25% in the production of pulp and paper (sulfate pulp from the Kraft process). The remainder is distributed over glass production, textile applications etc.

The demand is however further in decline since e.g. in North America its specific utilization per ton paper has decreased from over 40 kg to in some cases less than 5 kg (due to improved recycling processes). It is used in the digestion of wood in which it is reduced to sodium sulfide, the actual active component. In the manufacture of glass (mainly float glass) sodium sulfate is utilized for clarification and in small amounts can be used instead of sodium carbonate. Smaller quantities of sodium sulfate are utilized in dye manufacture, in dyeing, in electroplating and in the manufacture of animal feedstuffs and chemicals (e.g. sodium sulfide). Glauber's salt can be used as a heat-storage medium.

3.1.1.3.6 Sodium Hydrogen Sulfate

Sodium hydrogen sulfate is manufactured by reacting sodium chloride with sulfuric acid in heated cast iron retorts. The liquid product is solidified in refrigeration units. It can also be manufactured in liquid form directly from sodium sulfate and sulfuric acid and is produced as a byproduct in the manufacture of chromic acid, but this is contaminated with Cr(III)- and Cr(VI)-compounds.

Sodium hydrogen sulfate is used as a cleaning agent, due to its water solubility and the acidity of its aqueous solutions, as a flux, in the textile industry and for the treatment of metal surfaces.

$NaHSO_4$ manufacture:

- $NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$
- $Na_2SO_4 + H_2SO_4 \rightarrow 2NaHSO_4$
- $Na_2Cr_2O_7 + 2H_2SO_4 \rightarrow 2CrO_3 + 2NaHSO_4 + H_2O$

3.1.1.3.7 Sodium Borates

Natural Deposits and Economic Importance

Sodium borate minerals are found in nature mainly as $Na_2B_4O_7 \cdot 10H_2O$ (tincal, raw borax), the most important boron mineral, $Na_2B_4O_7 \cdot 4H_2O$ (kernite, rasorite), $Na_2B_4O_7 \cdot 5H_2O$ (tincalconite) and as sodium calcium borates: $NaCaB_5O_9 \cdot 8H_2O$ (ulexite) and $NaCaB_5O_9 \cdot 5H_2O$ (probertite). The deposits are found in the USA (Boron, California is the largest production site in the World), Turkey, Chile, Argentina, Peru, China and the former States of the USSR. The main producer countries are the USA (38%) and Turkey (38%) in a total extraction of boron minerals in 1995 of ca. $2.89 \cdot 10^6$ t. The most important boron minerals, which are currently extracted in Turkey, are the calcium borates e.g. $Ca_2B_6O_{11} \cdot 5H_2O$, colemanite or borocalcite. Sodium borates are also produced as byproducts in the production of potassium salts from the virtually dried out Searles Salt Lake in California. Seawater also contains a nominal concentration of boron (0.001%), which can be extracted by ion exchangers. The total reserves of boron compounds were estimated in 1996 to be $314 \cdot 10^6$ t, as di-boron trioxide. It was estimated that the largest reserves were in Turkey ($> 200 \cdot 10^6$ t).

Most important boron minerals:

- sodium borates (predominantly $Na_2B_4O_7 \cdot 10H_2O$) also in salt lakes
- sodium calcium borates
- calcium borates

Main producer countries for boron minerals:

USA, Turkey, largest reserves probably in Turkey

World reserves (estimated): $314 \cdot 10^6$ t B_2O_3

Sodium borates are the most important industrial boron compounds. They are mainly utilized as such, but are also used as starting materials (in addition to calcium borates) for the manufacture of industrially interesting boron compounds (boric acid, di-boron trioxide, inorganic borates, refractory boron-derivatives, boron carbide, boron nitride, borides, elemental boron, ferroboron, boron halides, fluoroborates, borohydrides, organo-boron compounds).

Extraction

Manufacture of pure sodium tetraborate ($Na_2B_4O_7 \cdot 5H_2O$ or $Na_2B_4O_7 \cdot 10H_2O$) by working up raw mineral borax or calcium borates

Pure sodium tetraborates are produced from crushed raw sodium borate minerals (tincal, kernite) by dissolution with heating in a weak borax-containing mother liquor, separating off the impurities (clays) and selective crystallization. Either the penta- or deca-hydrate is formed during vacuum crystallization, depending upon the temperature (above or below 60.8°C).

Borax is also manufactured from calcium borates by heating with a sodium carbonate/sodium hydrogen carbonate/sodium hydroxide solution, whereupon the calcium carbonate precipitates out and sodium borate crystallizes out. Anhydrous borax is formed by calcining water-containing sodium borates initially in rotary tube furnaces, then in standing furnaces, it being produced as a liquid which is poured e.g. into molds.

The other sodium borates such as sodium metaborate ($NaBO_2 \cdot 4H_2O$) and disodium octaborate ($Na_2B_8O_{13} \cdot 4H_2O$) are of minor importance.

Applications

In the USA 80% of the boron compound consumption (as B_2O_3) is as sodium borates

The worldwide consumption of boron compounds in 1996 was $1.24 \cdot 10^6$ t (as di-boron trioxide) predominantly (in the USA almost 80%) in the form of sodium borates (as raw ore concentrates, which are often used directly, or in purified or calcined form). The remainder comprises calcium or calcium sodium borates (colemanite, ulexite), which are also often directly utilized e.g. in the manufacture of E-glass fibers and in steel manufacture and other products such as boric acid and di-boron trioxide.

Main application sectors for sodium borates:

- glass, ceramic and enamel industries
- detergents
- fertilizers
- flame retardants
- corrosion protection agents
- metallurgy

Sodium borates are mainly utilized in the glass, ceramic, enamel and porcelain industries (e.g. in borosilicate glasses in which the 12 to 15% di-boron trioxide is used both as a flux and to reduce the thermal expansion coefficient of the glass; glass wool with 5 to 7% di-boron trioxide for insulation purposes; glass fibers with 8 to 9% di-boron trioxide). It is also used for the manufacture of sodium perborate (detergent and cleaning agent), fertilizers [boron is a necessary trace element for plant growth; it is used for combating heart rot in sugar beet] and as a corrosion protection agent in antifreezes. It is also used for metallurgical purposes (flux, welding and solder compounds) and as a flame retardant in cellulose materials. In the USA its utilization for sodium perborate manufacture is lower than that in Europe due to different detergent compositions and washing customs, whereas its utilization in the glass-, glass fiber- and glass wool-sectors is greater than in Europe.

3.1.1.4 Potassium and its Compounds

3.1.1.4.1 General Information

By far the most important potassium compounds are the fertilizer salts (see Section 2.3). Only 5 to 6% of all potassium compounds consumed, as K_2O, are utilized outside the fertilizer industry. In the Earth's crust potassium is the seventh most common element, almost as abundant as sodium. The most important potassium compounds are potassium hydroxide and potassium carbonate (potash).

Potassium:

- indispensable plant nutrient; ca. 95% of the total K_2O production utilized in the fertilizer sector
- seventh most common element in the Earth's crust

Industrially most important potassium compounds:

KOH, K_2CO_3, $KMnO_4$, K phosphates, $KBrO_3$, $KClO_3$, KCN, $KHCO_3$ etc.

3.1.1.4.2 Metallic Potassium

The manufacture of elemental potassium is unimportant with a worldwide production in the early 1990's of less than 500 t/a. It is manufactured by the reaction of molten potassium chloride with sodium at high temperatures, whereupon a potassium/sodium alloy is formed, which is fractionally distilled. Metallic potassium is obtained in a purity of > 99.5%. The formerly operated melt electrolysis of potassium hydroxide or potassium chloride is no longer operated. Potassium is utilized for the manufacture of potassium peroxide K_2O_2 and Na/K-alloys (reducing agent, heat carrier e.g. in the nuclear industry).

Metallic potassium has only minor industrial importance

Manufactured from KCl + Na

3.1.1.4.3 Potassium Hydroxide

Economic Importance: The worldwide production of potassium hydroxide in 1991 was estimated to be $0.78 \cdot 10^6$ t, of which 38% was manufactured in the USA and 42% in Western Europe. In 1980 the USA production was ca. $0.2 \cdot 10^6$ t.

KOH manufacture:

by electrolysis of KCl solutions (mercury and membrane processes)

KOH available in two forms:

- 45 and 50%
- ca. 90% (caustic alkali; by vacuum evaporation)

Manufacture: Potassium hydroxide is almost exclusively manufactured by the electrolysis of potassium chloride, by the mercury, membrane and diaphragm processes. Mercury and membrane processes provide a purer potassium hydroxide, although higher purity demands are made on the potassium chloride used. The technology of potassium chloride electrolysis is similar to that of sodium chloride electrolysis, but with a slightly lower cell voltage. In the case of the mercury process a very pure 40 to 50% potassium hydroxide is produced, whereas in the diaphragm process the dilute potassium hydroxide is concentrated by evaporation. Solid caustic alkali with ca. 90% of potassium hydroxide is mainly produced by vacuum evaporation. Byproducts of the electrolysis are chlorine and hydrogen. The manufacture of potassium hydroxide by the reaction of potassium carbonate with calcium hydroxide is no longer operated industrially.

Application spectrum for KOH in the USA in 1991:

20% K_2CO_3
19% other potassium chemicals
11% K-phosphates ($K_4P_2O_7$ for liquid detergents)
10% liquid fertilizers
10% soaps
30% other products

Applications: Potassium hydroxide is utilized in the manufacture of other potassium compounds (potassium carbonate, potassium phosphates e.g. tetrapotassium pyrophosphate, potassium permanganate, potassium bromate, potassium iodate, potassium cyanide etc.), of dyes, special soaps and battery liquids. It is also used in photographic developers, in glass manufacture and as a drying and absorption agent. In many of these applications its use is declining.

3.1.1.4.4 Potassium Carbonate

K_2CO_3 manufacture:

by carbonation of KOH

The $K_2CO_3 \cdot 1.5H_2O$ produced by carbonation is in part calcined in rotary tube furnaces at 250 to 350°C

Manufacture: Potassium carbonate (potash) was formerly produced by the ashing of wood and other plant raw materials. Since the middle of the nineteenth century, the saline residues from the rock salt industry and salt deposits have been the raw materials for potassium carbonate production. The currently industrially most important process is the carbonation of electrolytically produced potassium hydroxide. 50% potassium hydroxide solution (e.g. from the mercury process) is saturated with carbon dioxide, the solution partially evaporated and the potassium carbonate hydrate $K_2CO_3 \cdot 1.5H_2O$ which precipitates out is separated. After drying, the product is either marketed as potash hydrate or is calcined in a rotary tube furnace at temperatures of 250 to 350°C to anhydrous potassium carbonate. Anhydrous potassium carbonate is also produced in a fluidized bed process in which potassium hydroxide is reacted with carbon dioxide gas in countercurrent in a fluidized bed reactor.

In other processes similar to the Solvay process (see Section 3.1.1.3.3), potassium carbonate is produced directly from potassium chloride with amines such as isopropylamine via a potassium hydrogen carbonate step, but contaminated calcium chloride brine is produced as a byproduct whose disposal poses environmental problems. In the former States of the USSR potassium carbonate is also produced from alkali aluminosilicate deposits (e.g. nepheline) together with aluminum oxide, cement and sodium carbonate.

In the former States of the USSR potassium carbonate is also produced from alkali aluminosilicates e.g. nepheline $KNa_3[AlSiO_4]_4$

Applications: Potassium carbonate is utilized in the glass industry (special glasses, crystal glass, CRT-tubes for televisions), in the manufacture of soap and enamel, in the food industry and in pigment production. It is also utilized as a starting material for other potassium compounds, e.g. potassium hydrogen carbonate (raising agent in the food industry, manufacture of fire extinguisher powder). Potassium carbonate is also used in the production of potassium silicate (detergent) and in many organic chemistry and pharmaceutical syntheses.

Main applications of K_2CO_3:

- glass manufacture
- soaps, detergents
- enamel
- food industry
- for manufacture of other potassium compounds

References for Chapter 3.1.1: Alkali Metals and their Compounds

Technical Information:

Bach, R. O., (Ed.). 1985. *Lithium: Current Applications in Science, Medicine and Technology*, John Wiley & Sons, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1990. 5. Ed., *Lithium and Lithium Compounds*, Vol. A 15, 393 – 414 , VCH Verlagsgesellschaft, Weinheim.

Ullmann's Encyclopedia of Industrial Chemistry. 1993. 5. Ed., *Sodium and Sodium Compounds*, Vol. A 24, 277 - 298, 299 – 316, 317 – 339, and 355 – 368, VCH Verlagsgesellschaft, Weinheim.

Ullmann's Encyclopedia of Industrial Chemistry. 1993. 5. Ed., *Potassium and Potassium Compounds*, Vol. A 22, 31– 38 and 39 - 103VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1995. 4. Ed, *Lithium and Lithium Compounds*,Vol. 15, 434 – 462John Wiley & Sons, New York.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1997. 4. Ed., *Sodium and Sodium Compounds*, Vol. 22, 327 – 353 and 354 – 419, John Wiley & Sons, New York.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1996. 4. Ed., *Potassium and Potassium Compounds*, Vol. 19, 1047 - 1057 and 1004 – 1039, John Wiley & Sons, New York.

Commercial Information:

Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California, June 1995, 746.5000A.

Mineral Yearbook. 1990, Vol. 1, 699, US Department of the Interior, Washington.

Sodium and its Compounds:

Metallic Sodium

Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California, June 1997, 770.1000A.

Sodium Carbonate and Sodium Hydrogen Carbonate

Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California, Sept. 1994, 770.4000A and May 1996, 770.3000A.

Mineral Yearbook. 1990, US Department of the Interior, Washington, 1039.
Mineral Commodity Summaries. 1986. Bureau of Mines, Washington, 144.

Sodium Sulfate and Sodium Hydrogen Sulfate
Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California, June 1996, 771.1000A.
Mineral Yearbook. 1990, US Department of the Interior, Washington, 1061.

Sodium Borates
Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California, Oct. 1996, 717.1000A.

Potassium and its Compounds
Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California, Oct. 1993, 764.3000A.
Mineral Yearbook. 1990, US Department of the Interior, Washington, 881.

3.1.2 Alkaline Earth Metals and their Compounds

3.1.2.1 General Information

Economic importance:

- the alkaline earth metals: Mg >> Ca > Be > Ba > Sr
- the alkaline earth compounds: Ca >> Mg >> Ba >> Sr > Be

By far the industrially most important of the alkaline earth metals, beryllium, magnesium, calcium, strontium and barium, as a metal is magnesium, followed at more than two orders of magnitude remove by calcium. The manufacture of strontium and barium is insignificant, that of beryllium also amounting to no more than a few hundred t/a. Of the alkaline earth compounds the calcium compounds are the most important. This is due to the enormous industrial and economic importance of calcium carbonate (limestone) [not only in the chemical industry but also in the building sector (see Section 5.3.2) and in the metallurgical industry] and other calcium minerals such as calcium phosphate (apatite, see Section 2.1), calcium magnesium carbonate (dolomite), complex calcium silicates (e.g. cement, see Section 5.3.3), calcium sulfate (gypsum, anhydrite, see Section 5.3.4) and calcium fluoride (fluorspar, see Section 1.7.1).

3.1.2.2 Beryllium and its Compounds

Economic Importance: Beryllium is a relatively rare element. The industrially important beryllium-containing minerals are bertrandite $4BeO \cdot 2SiO_2 \cdot H_2O$ and beryl $3BeO \cdot Al_2O_3 \cdot 6SiO_2$. They are mined primarily in the USA, the former States of the USSR, Brazil, Argentina and other countries, and processed to beryllium compounds such as $Be(OH)_2$ or BeO. Since 1969 bertandite is almost exclusively mined for industrial purposes. Up-to-date figures over the worldwide workable reserves of beryllium are not available, but the reserves in the USA are estimated to be $66 \cdot 10^3$ t Be. The worldwide production without China was ca. 245 t Be in 1994, of which 70% was produced in the USA.

Be-content in the Earth's crust:
4-6 ppm

Countries with largest reserves:
USA, former States of the USSR, Brazil, Argentina

Leading Be-producing country:
USA: 70% of world production in 1994

Manufacture: Metallic beryllium is either produced by reduction from beryllium fluoride with magnesium in graphite crucibles at elevated temperatures or, less commonly, by melt electrolysis of beryllium chloride.

Applications: Metallic beryllium is an industrial special metal and belongs together with aluminum and magnesium to the light metals. It is mainly (70 to 80%) utilized in the manufacture of beryllium/copper alloys with 0.5 to 2.5% beryllium (hardenable beryllium bronzes) e.g. for electrical equipment. Its interesting nuclear physical properties results in its use as a moderator- and reflector-material. Beryllium metal and its alloys are also utilized in the aerospace sector, due to their high elasticity-weight ratio and their high tensile stress.

Application spectrum of Be:

70 to 80%:	alloys
10 to 15%:	pure Be and Be-based alloys
6 to 8%:	BeO
rest:	other products

The USA consumption of beryllium was ca. 300 t/a Be in 1986. Of the beryllium compounds beryllium oxide is, as a result of its high melting point and its high chemical resistance, utilized for oxide-ceramic materials.

BeO:
for oxide ceramic

The demand for beryllium is, however, stagnating or declining, mainly due to its toxicity, the recommended maximum concentration being 0.002 to 0.005 mg/m^3 air.

3.1.2.3 Magnesium and its Compounds

3.1.2.3.1 Natural Deposits

Magnesium with a share of 2.1% is the eighth most abundant element in the Earth's crust and the third most abundant metal in seawater, in which it is present as its chloride. Magnesium from seawater is an inexhaustible

Main deposits of Mg:

- seawater
- dolomite
- magnesite rock
- brines and salts deposits

source of raw materials, one km^3 of seawater containing $1.3 \cdot 10^6$ t Mg (0.13%) and there being an estimated 10^{18} km^3 of seawater. The industrially most important magnesium minerals are magnesium carbonate ($MgCO_3$, magnesite), calcium magnesium carbonate ($CaCO_3 \cdot MgCO_3$, dolomite), magnesium chloride, e.g. as a double salt with potassium chloride (carnallite, $KCl \cdot MgCl_2 \cdot 6H_2O$), magnesium sulfate (kieserite, $MgSO_4 \cdot H_2O$) and silicates such as asbestos (see Section 5.2.2) or olivine [$(Mg,Fe)_2SiO_4$].

3.1.2.3.2 Metallic Magnesium

Production of primary magnesium in 1994 in 10^3 t:

USA	135
former States of USSR	4
Norway	30
Canada	24
France	13
China	12

Economic Importance: The worldwide production of primary magnesium in 1994 was $274 \cdot 10^3$ t, the largest producers being the USA and Western Europe (together ca. 74%). In 1970 the worldwide production of magnesium was $220 \cdot 10^3$ t. In recent years ca. 30% of magnesium production has been so-called remelted magnesium (secondary magnesium). The production of magnesium has hardly increased since the beginning of the 1980's. The largest produced is Norsk Hydro with plants in Norway and Canada. Magnesium has not been produced in the Federal Republic of Germany since World War II, the large demand being met by imports.

Magnesium manufactured by two processes:

- melt electrolysis of $MgCl_2$
- silicothermal reduction of dolomite

Similar high energy requirements

Two largest manufacturers of magnesium in the Western World both produce Mg by melt electrolysis (USA, Norway)

Manufacture: Magnesium is manufactured either electrolytically from magnesium chloride (from seawater or salt lakes and salt deposits) or by thermal reduction of ores, such as dolomite, with ferrosilicon. 40% of the magnesium producers in the Western world use electrolysis processes.

In melt electrolysis magnesium is produced at the iron cathodes upon electrolyzing a mixture of anhydrous magnesium chloride with alkali and alkaline earth chlorides (the electrolyte generally contains 8 to 24% $MgCl_2$) at 700 to 800°C and a decomposition voltage of 5 to 7 V. The chlorine produced at the graphite anodes, is generally not marketed, but is used for the production of magnesium chloride. The magnesium deposited collects on the surface of the melt and is sucked off. The yield based on electrical energy consumed is 80 to 90%, due to heat losses and side reactions. The power loading of a single cell is up to 250 kA. In the Dow process a hydrated magnesium chloride, $MgCl_2 \cdot 1.5$ to $2H_2O$, is used instead of anhydrous magnesium chloride.

In the silicothermal production of magnesium, calcined dolomite is reacted with 70 to 85% ferrosilicon at ca. 1200°C under vacuum as follows:

$$2\,(CaO \cdot MgO) + Si(Fe) \longrightarrow 2\,Mg + Ca_2SiO_4 + (Fe)$$

The magnesium vapor initially formed is precipitated in a condensation vessel. In a variant of this process (magnetherm process) aluminum oxide is added to obtain an electrically conducting liquid $CaO\text{-}SiO_2\text{-}Al_2O_3$-slag and the required energy (ca. 18 kWh/kg Mg) supplied by resistive heating (contact with the furnace bottom).

Purification of raw magnesium:

- in salt melts
- by distillation

The crude magnesium obtained from electrolysis or thermal reduction has to be purified (refined) before further processing. This is carried out by mixing salt melts (alkali and alkaline earth chlorides or fluorides) with the liquid metal. The purest magnesium is manufactured by distillation.

Main uses of Mg (ca. 46%):

- Mg-alloys with < 10% Al, Mn, Zn, Si, Be
- Al-alloys with 90% Al and 10% Mg

Mg with a density of 1.74 g/cm^3 is the lightest construction metal

Miscellaneous applications of Mg:

- desulfurization and deoxidification agent in the steel industry
- reducing agent for the manufacture of metals
- for protection of cathodes in galvanic processes
- pyrotechnics

Applications: Ca. 280 · 10^3 t of metallic magnesium was consumed worldwide in 1993, the USA being the largest consumer with ca. 30%. Of the ca. 200 · 10^3 t/a of magnesium produced in the USA, about a third is exported. Most of the magnesium is utilized in the manufacture of alloys, primarily with aluminum. Over 99% of all magnesium alloys contain aluminum. These can be split into extremely light “real” magnesium alloys with magnesium as the main component in admixture with up to 10% of aluminum, manganese, zinc, silicon, beryllium etc. and aluminum alloys with up to 11% magnesium. These can be subdivided on the basis of their properties into casting alloys and wrought alloys. Magnesium is also utilized in the thermal reduction of metal chlorides and other compounds e.g. in the manufacture of titanium, uranium, zirconium, hafnium and beryllium. In the iron and steel industry, magnesium is used in increasing quantities as a desulfurization and deoxidification agent and for the manufacture of cast iron nodules. Magnesium powder is utilized in pyrotechnical applications and magnesium chips in organic synthesis for the preparation of Grignard reagents. Magnesium was also previously utilized in the synthesis of the antiknock agents: tetramethyl- and tetraethyl-lead.

3.1.2.3.3 Magnesium Carbonate

$MgCO_3$:
most important Mg-compound: extraction greatest in Eastern countries with > 50% share

Natural Deposits and Economic Importance: Natural magnesium carbonate (magnesite) is the industrially most important magnesium mineral. It is found in large quantities in both crystalline and amorphous forms in economically workable deposits in China, the former States of the USSR, North Korea, Brazil and Australia. The estimated world reserves are ca. $11 \cdot 10^9$ t to which can be added the very much larger deposits of the double carbonate dolomite, which is also utilized in the manufacture of magnesium and its compounds. $11 \cdot 10^6$ t of magnesite (not including the USA) were extracted in 1990, the main extracting countries being China (18%), the former States of the USSR (15%), North Korea (14%), Austria (11%), Greece (8%) and Turkey (8%).

Synthetic $MgCO_3$:
from Mg-salts and CO_2

Manufacture: Magnesium carbonate is extracted by mining (mainly open-cast) and is processed by gravitational separation, flotation or magnetic separation. Magnesium carbonate-hydrate $MgCO_3 \cdot 3H_2O$ and basic magnesium carbonate ($4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$), hydromagnesite, magnesia alba) are also synthesized in small amounts by precipitation reactions. In such processes magnesium salt solutions (e.g. residual brines from the potash industry) are reacted with ammonium carbonate and hydrogen carbonate, by carbonating precipitated magnesium hydroxide under pressure or by calcining dolomite ($CaO \cdot MgO$ or $CaCO_3 \cdot MgO$) and then reacting with carbon dioxide to soluble magnesium hydrogen carbonate, which upon heating is converted into basic magnesium hydrogen carbonate.

Natural $MgCO_3$:
almost exclusively utilized for MgO manufacture

Applications: Little natural uncalcined magnesite is used directly. It is mainly converted by calcination (above 550°C) into different, mainly refractory, magnesia qualities. This technology is of little importance in the USA, since 90% of the industrially produced magnesium compounds comes from the magnesium content of seawater and brines. Synthetic magnesium carbonate, particularly basic magnesium carbonate, is utilized in the manufacture of thermal insulating materials; as a filler for paper, plastics and rubber; in the paint and printing ink industries; as an additive in table salt (to reduce caking) and in pharmaceuticals.

3.1.2.3.4 Magnesium Oxide

Economic Importance: Magnesium oxide is, after magnesium carbonate, the industrially most important magnesium compound. Worldwide production in 1995 was ca. $5 \cdot 10^6$ t, with an additional $1 \cdot 10^6$ t from seawater and brines.

Manufacture: The raw materials for the production of magnesium oxide are either natural magnesium carbonate (magnesite) which is calcined, or magnesium chloride from seawater and brines (salt deposits). Dolomite can also be utilized as a starting material. In the production of magnesium oxide from seawater, the magnesium hydroxide precipitated by adding calcium oxide or calcium hydroxide or still better dolomite to seawater is calcined after separation. The different magnesia qualities differ depending upon the type and temperature of the process used to calcine the magnesium carbonate or hydroxide. The more reactive caustic magnesia ("chemical magnesia") is calcined at 600 to 1000°C, over-burnt sintered magnesia at 1700 to 2000°C. Fused magnesia is melted at 2800 to 3000°C in an electric arc furnace.

Manufacture of MgO:

from magnesite of dolomite (46%), salt deposits (36%) and seawater (18%)

by calcining:

- $MgCO_3$
- $Mg(OH)_2$ (from $MgCl_2$)

Applications: The most important magnesium oxide product is sintered magnesia (m.p. 2800°C) for the refractory industry (lining of metallurgical furnaces, raw material for refractory bricks). There are three types of refractory brick: (basic) magnesite, magnesite-chrome and chrome-magnesite. Magnesia-containing refractory liners for furnaces are particularly important in steel production (LD-process). Magnesium oxide is also utilized in heat storage materials. Reactive chemical magnesite has gained in importance in recent years. The share of caustic calcined magnesia in the magnesium oxide consumption in the USA grew from 15% in 1975 to 33% in 1980 to 40% in 1984. It is utilized in the manufacture of fertilizer and animal feedstuffs, building materials (Sorel cement, lightweight building panels), chemical and pharmaceutical products.

Fused magnesia is primarily utilized as an insulating material in the electrical heating industry.

MgO qualities mainly dependent upon calcining conditions

MgO types:

- chemical (caustic) magnesia
- sintered magnesia
- fused magnesia

Main application of MgO:

refractory industry and steel furnaces

3.1.2.3.5 Magnesium Chloride

$MgCl_2$ is mainly manufactured by magnesium producers:

in 1996 ca. 520 · 10^3 t/a in the Western World, of which 380 · 10^3 t/a in the USA

Economic Importance: Since the manufacture of magnesium chloride is closely linked with the manufacture of metallic magnesium, it follows developments in this sector. In the mid-1970's ca. 600 · 10^3 t/a of magnesium chloride was produced in the Western World, whereas it was ca. 520 · 10^6 t/a in 1996.

$MgCl_2$ manufacture:

- from seawater
- from salt lakes
- from natural brines
- from residual brines in the potash industry
- from $MgCO_3$, or MgO

Manufacture: Magnesium is found in large quantities in nature. It is produced from different sources: from the residual brines of the potash industry, (mainly as its hexahydrate), seawater, salt lakes, brines, magnesium carbonate (and hydrochloric acid) or magnesium oxide (and chlorine).

In the Dow Chemical process calcium hydroxide is added to seawater, the precipitated hydroxide then being reacted with hydrogen chloride (the calcium precipitating as calcium sulfate due to the simultaneous addition of sulfuric acid) and the magnesium chloride solution is evaporated to dryness at ca. 200°C to produce a product with ca. 1.5 to 2 molecules of water.

Anhydrous magnesium chloride is manufactured by dehydration of the hydrate at > 300°C in a stream of hydrogen chloride.

It can also be manufactured by the direct chlorination of magnesium oxide in the presence of coal at 1000 to 1200°C:

$$2\,MgO + 2\,Cl_2 + C \longrightarrow 2\,MgCl_2 + CO_2\,(\text{or }CO)$$

Applications of $MgCl_2$:

over 60% used in the electrolytic production of magnesium, the rest being mainly used in the building industry

Applications: A large proportion of the magnesium chloride, either anhydrous or from the Dow Chemical process as its sesquihydrate, is used for the electrolytic manufacture of magnesium. The hexahydrate in admixture with magnesium oxide (formation of magnesium oxychlorides) is utilized in the building industry for the manufacture of Sorel cement and lightweight building panels. Magnesium chloride is also used in the granulation of fertilizers, in the oil and sugar industries and as a binder for dust (in mining and in road building).

3.1.2.3.6 Magnesium Sulfate

Economic Importance: The worldwide production of magnesium sulfate products including potassium magnesium sulfate (fertilizer) was 3.4 · 10^6 t/a in the mid-1970's of which 2.3 · 10^6 t was kieserite $MgSO_4 \cdot H_2O$ (a byproduct of the potash industry). The main producer countries are: the USA and the Federal Republic of Germany. The USA consumption in 1996 excluding natural kieserite was 57 · 10^3 t.

$MgSO_4$ products:

- anhydrous $MgSO_4$
- kieserite, $MgSO_4 \cdot H_2O$
- Epsom salt, $MgSO_4 \cdot 7H_2O$
- potassium magnesium sulfate

Manufacture: Magnesium sulfate is widely distributed in nature, e.g. in salt deposits as kieserite, as Epsom salt $MgSO_4 \cdot 7H_2O$, in the form of double salts such as kainite $4KCl \cdot 4MgSO_4 \cdot 11H_2O$ and langbeinite $K_2SO_4 \cdot 2MgSO_4$ and in brines. Large quantities of kieserite, Epsom salt and anhydrous magnesium sulfate are produced in the processing of potassium salts. Magnesium sulfate is also produced by reacting magnesium carbonate or seawater-magnesium hydroxide with sulfuric acid.

$MgSO_4$:
most important byproduct from the potash industry

Applications: Magnesium sulfate is utilized in the potassium chemicals industry for the manufacture of potassium sulfate (from potassium chloride), sodium sulfate and potash magnesia (potassium magnesium sulfate). Magnesium sulfate, particularly as kieserite, is used as a fertilizer (ca. 80% of total consumption). It is also used in the textile industry, in the manufacture of building and refractory materials, in the pulp industry and in the production of animal feedstuffs and motor oil additives.

Main applications of $MgSO_4$ products (kieserite, potassium magnesium sulfate):
fertilizers

3.1.2.4 Calcium and its Compounds

3.1.2.4.1 Natural Deposits

Calcium is the fifth most abundant element in the earth's crust at ca. 4%. The most important calcium minerals are calcium carbonate (limestone, chalk, marble, shell limestone, calcite etc.), calcium magnesium carbonate (dolomite, $CaCO_3 \cdot MgCO_3$), calcium sulfate (gypsum, $CaSO_4 \cdot 2H_2O$, and anhydrite, $CaSO_4$), calcium phosphate [apatite, $Ca_5(PO_4)_3(F)$], calcium fluoride (fluorspar, CaF_2) and calcium aluminum silicates (e.g. anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$). The reserves of limestone are almost unlimited, ca. 7% of the Earth's crust consisting of this mineral. It is the most important starting material for the manufacture of calcium and its compounds.

Limestone and chalk are together with coal, oil, iron ore, sulfur and sodium chloride the most important raw materials of modern industry.

$CaCO_3$-containing minerals are widely distributed, making it an almost inexhaustible raw material source

3.1.2.4.2 Metallic Calcium

Ca-metal is of little industrial importance

Metallic calcium is only manufactured in small quantitiies, currently ca. 1 to 2 · 10^3 t/a worldwide. It is manufactured by the thermal reduction of calcium oxide with aluminum in vacuum at 1200°C:

Manufacture:
by aluminothermal reduction of CaO

$$6\,CaO + 2\,Al \longrightarrow 3\,CaO \cdot Al_2O_3 + 3\,Ca_{gaseous}$$

the resulting calcium vapor being condensed. It is no longer produced by melt electrolysis.

Applications:

- in manufacture of Zr, Th, U and the rare earth metals
- refining agent in metallurgy

Calcium is utilized in the manufacture of special metals such as zirconium, thorium, uranium and the rare earths, as a refining agent in metallurgy (steel, copper, magnesium, tantalum, lead) and in the manufacture of calcium hydride (hydrogen source).

3.1.2.4.3 Calcium Carbonate

Main limestone producers:

- USA with a 32% share
- Western Europe with a 28% share

Economic Importance: The current worldwide extraction of limestone and other calcium carbonate-containing minerals such as dolomite is estimated to be ca. 3 · 10^9 t/a, of which 950 · 10^6 t/a is in the USA. In the rock and earth extraction industry, limestone is in second place, only the mining of sand and gravel being more important. The extraction of limestone in 1995 in Western Europe was 850 · 10^6 t. The 1995 production of synthetic (precipitated) calcium carbonate in the USA was 1.483 · 10^6 t/a.

Production of $CaCO_3$:

- coarse-grained $CaCO_3$
  - by mining
- fine-grained $CaCO_3$
  - by carbonating calcium hydroxide solutions

Mining and Manufacture: calcium carbonate-containing minerals are mainly extracted by open-cast mining. High grade limestone is also extracted in underground workings. A comparatively small quantity of calcium carbonate is produced synthetically e.g. by carbonating calcium hydroxide solutions.

Application spectrum of natural $CaCO_3$ in USA in 1994:

54%	building industry
9%	Portland cement
2%	agriculture
35%	other applications

Applications of fine-grained $CaCO_3$:
as a white filler in paints, in the paper industry etc.

Applications: Natural calcium carbonate is mainly used in the construction industry e.g. in road building and in the cement industry (1 t limestone/1 t cement). It is also utilized in the manufacture of quicklime, as a flux and refining agent (desulfurization agent) and as a sintering aid and slag-former in metallurgy e.g. in the production of pig iron. Significant quantities of limestone are used in agriculture, in glass manufacture, as a desulfurization agent in the purification of flue gases (see Section 5.3.4.6.2) and in a ground form as a filler. Precipitated calcium carbonate is an important filler e.g. in paper manufacture, in which 75% of this calcium carbonate is utilized, in the rubber and plastics industries and in the manufacture of paints.

3.1.2.4.4 Calcium Oxide and Calcium Hydroxide

Economic Importance: Calcium oxide (quicklime) and calcium hydroxide (slaked lime, lime hydrate) are next to calcium carbonate, the most important calcium compounds, being utilized in almost all sectors of industry. The worldwide production (including calcined dolomite) was $130 \cdot 10^6$ t/a in 1994. The leading producer country is China. The most important product is quicklime, which is produced throughout the world partly in very small units, although predominantly in highly industrialized countries.

$CaO/Ca(OH)_2$ production in 1994 in 10^6 t:

China	21.5
USA	19.2
former States of USSR	17.6
Japan	8.5
FR Germany	8.3

Manufacture: Calcium oxide is produced by calcining limestone at ca. 1000 to 1200°C (see Section 5.3.2.3). Various shaft furnaces or rotary tube furnaces [the latter particularly in the USA (e.g. with a capacity of 1000 t/d)] are utilized as calcining units. Calcium hydroxide is produced by the slow addition of water (slaking) to calcium oxide, the process being strongly exothermic.

Manufacture of quicklime in shaft of rotary tube furnaces

Manufacture of CaO is strongly endothermic, that of $Ca(OH)_2$ exothermic

In the so-called dry slaking process just sufficient water is added to yield an easily usable hydrate.

Applications: A large part of the lime, preferably lightly calcined, lime is utilized in metallurgy, e.g. in the iron and steel industry, for the removal of phosphorus and sulfur from the metal melt. Further quantities are used in the chemical industry for the manufacture of calcium compounds (calcium carbide, calcium cyanamide) or of sodium carbonate in the Solvay process and as a neutralizing and precipitating agent. In environment protection technology, lime is used in water and effluent treatment and in increasing quantities for removing sulfur dioxide from flue gases. The sugar industry is another important consumer. Lastly, large quantities of quicklime and lime hydrate are utilized in the construction industry (manufacture of mortar, of building materials e.g. sand-lime bricks, ground consolidation in road building). Calcined lime is also utilized in agriculture and the refractory industry. In the USA its utilization as a building material dominates with 54% and 9% in the manufacture of cement, with similar orders of magnitude of consumption in Western Europe, 34% is consumed in the cement industry.

USA applications spectrum for CaO:

- metallurgy
- chemical industry
- water treatment
- flue gas purification
- sugar industry
- building industry
- agriculture
- refractory industry

3.1.2.4.5 Calcium Chloride

$CaCl_2$ produced in large quantities as a byproduct in chemical processes

Economic Importance: Calcium chloride is produced in large quantities as a byproduct in different chemical processes e.g. in the Solvay process or in the production of propene oxide in the chlorohydrin process, of which only a small part is processed to pure calcium chloride. In 1993 in the USA ca. $0.48 \cdot 10^6$ t (as anhydrous calcium chloride/ was produced mainly from natural sources (mainly subterranean brines and, to a lesser extent, dried out salt lakes in California).

Manufacture: Synthetic hydrated calcium chloride is produced from the calcium chloride containing-residual brines of the Solvay process by evaporation initially in vacuum, then at atmospheric pressure. Calcium chloride is also produced from waste acid by reaction with limestone. Anhydrous calcium chloride is obtained e.g. by evaporation in fluidized bed dryers or spray towers.

Applications of $CaCl_2$ in the USA in 1994:

38%	for salting roads
18%	as a dust-binding agent
20%	for industrial purposes
12%	in concrete manufacture
4%	in crude oil extraction
8%	for other uses

Applications: Calcium chloride is utilized as a drying agent, a dust binder (in road consolidation, in mines) and as a cooling-, defrosting- and antifreeze agent e.g. in the salting of roads at temperatures below those at which sodium chloride is effective. It is also utilized as a concrete additive and in various chemical and metallurgical processes. The addition of calcium chloride to crude drilling-muds (for conditioning drilling mud) increased in importance in the 1970's, but its importance has since waned. In the USA it is mainly used for the salting of roads and for dust binding on unmade roads.

3.1.2.4.6 Calcium Carbide

CaC_2 manufacture only is of minor importance (supplanted by petrochemical feedstocks)

Economic Importance: The production of calcium carbide in Western Europe in 1993 was ca. $500 \cdot 10^3$ t/a, in the USA $220 \cdot 10^3$ t/a, in Eastern Europe including Russia $887 \cdot 10^3$ t/a and in Japan $245 \cdot 10^3$ t/a. The demand for calcium carbide has been almost constant although declining slightly over the last 20 years, due to the decreasing importance of ethyne in organic chemistry (replacement by e.g. ethene) and stagnation in the utilization of calcium cyanamide as a fertilizer. The worldwide production, which in the mid-1960's was still $10 \cdot 10^6$ t/a, had dropped to $6 \cdot 10^6$ t/a by the mid-1970's and is currently about $2 \cdot 10^6$ t/a.

Manufacture: Calcium carbide is manufactured by reacting highly purified calcium oxide with coke in an electrical arc reduction furnace at 2000 to 2200°C:

CaC_2 manufacture is very energy intensive; very pure starting materials are required

$$CaO + 3\ C \longrightarrow CaC_2 + CO,\ \Delta H = 464\ kJ/mol$$

The ca. 80% carbide produced, the rest being mainly calcium oxide, is formed as a liquid and is removed as blocks. Crucial in the economics of calcium carbide production is, in addition to the price of the raw materials, the electricity price, because the process is very energy intensive, 2.8 to 3.1 MWh being required per t. Calcium carbide furnaces with power demands up to 70 MW generally have to be operated with three-phase current and utilize Söderberg hollow carbon electrodes dipped deeply into the reaction mixture.

Applications: Calcium carbide is mainly utilized in the:

Applications of CaC_2:

- manufacture of ethyne
- nitrogenation to calcium cyanamide
- desulfurization of iron in steel manufacture

- production of ethyne:

  $$CaC_2 + 2\ H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

  mainly for welding purposes (autogenous technology), but also in Reppe syntheses and in the manufacture of special carbon blacks. In the USA, for example, 85% is utilized in ethyne production.
- production of calcium cyanamide:

  $$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

  In Western Europe ca. 45% of the consumption of calcium carbide is currently utilized in the manufacture of calcium cyanamide.
- desulfurization in metallurgy: almost 15% of calcium carbide in the USA is utilized for this purpose, with a slightly increasing demand, since it is a cheap desulfurization agent.

Since the advent of petrochemical ethyne-producing processes, carbide-ethyne has hardly been used in organic synthesis. In the USA at the end of the 1970's, only 14% of all ethyne-based chemicals were manufactured using carbide-ethyne.

Importance of carbide-ethyne in industrial chemistry has strongly declined

3.1.2.5 Strontium and its Compounds

Strontium only important in special applications. Applications spectrum in USA in 1993:

• manufacture of special glasses:	67%
• permanent magnets:	13%
• pyrotechnics and pigments:	15%

Strontium mainly occurs in nature as its sulfate (celestine $SrSO_4$) and its carbonate (strontianite, $SrCO_3$). The worldwide extraction of strontium minerals in 1990 was $235 \cdot 10^3$ t/a, mainly in Mexico, Spain, Turkey, China and Iran and to a lesser extent in Algeria, Argentina and Morocco. Metallic strontium itself is of little industrial importance, it being mainly utilized to improve the properties of aluminum alloys. Strontium carbonate is the most important strontium compound. Its worldwide consumption increased from $80 \cdot 10^3$ t/a in 1980 to $198 \cdot 10^3$ t/a in 1993. The four main producing countries for strontium carbonate are Mexico, the Federal Republic of Germany, the USA and South Africa. The most important applications for strontium carbonate are in the manufacture of CRT-screen glass for color televisions (67%), permanent magnets (13%), pyrotechnics and pigments (15%) and other applications (5%).

3.1.2.6 Barium and its Compounds

3.1.2.6.1 Natural Deposits and Economic Importance

Heavy spar (BaSO4) used as a raw material for the manufacture of barium and its compounds

Worldwide extraction in 1995 was $4.4 \cdot 10^6$ t

China	$1.50 \cdot 10^6$ t
India	$0.58 \cdot 10^6$ t
USA	$0.54 \cdot 10^6$ t
East Europe	$0.32 \cdot 10^6$ t
Morocco	$0.27 \cdot 10^6$ t
Turkey	$0.16 \cdot 10^6$ t
FR Germany	$0.15 \cdot 10^6$ t

The most important barium mineral is heavy spar ($BaSO_4$, barite), whose deposits are distributed over the whole world. Worldwide extraction in over 30 countries was $4.4 \cdot 10^6$ t/a in 1995, of which $1.5 \cdot 10^6$ t/a was produced in China, $0.58 \cdot 10^6$ t/a in India and $0.54 \cdot 10^6$ t in the USA. In the Federal Republic of Germany the production of marketable raw heavy spar and the quantity of processed heavy spar were together $0.15 \cdot 10^6$ t/a in 1995. The worldwide production peaked in 1981 at $8.3 \cdot 10^6$ t/a, which is about double the 1995 production of $4.4 \cdot 10^6$ t/a. This decline was mainly due to less exploration and drilling. The worldwide reserves of heavy spar have been estimated to be ca. $1.8 \cdot 10^9$ t, of which $0.17 \cdot 10^9$ t are certain.

Applications of natural $BaSO_4$:

- 90% for crude oil and natural gas extraction
- 5% as a filler and for glass manufacture
- 5% for manufacture of barium chemicals

Industrially important Ba-chemicals:

$BaCO_3$, $BaCl_2$, synthetic $BaSO_4$, BaS, $Ba(OH)_2$

Only a small part of the heavy spar extracted, less than 5%, is processed to barium chemicals (barium carbonate, barium sulfide, synthetic barium sulfate, barium chloride, barium hydroxide etc.). Over 90% is utilized in the extraction of crude oil and natural gas as suspensions in the drilling mud. Ca. 5% is used as a filler in the dye, paint, plastics and rubber industries and in the manufacture of glass.

Metallic barium is little used industrially, its worldwide production being estimated to be a few tons (30 to 40 t). It is utilized in the manufacture of vacuum tubes (television tubes) and as a getter-material for removing undesirable trace gases.

3.1.2.6.2 Barium Carbonate

$BaCO_3$ is after natural $BaSO_4$ the most important barium compound

Economic Importance: After barium sulfate, barium carbonate, which occurs naturally as witherite, is the most important barium compound. The USA production of synthetic barium carbonate, including barium hydroxide, was ca. 25 · 10^3 t in 1996.

$BaCO_3$ manufacture:
$BaSO_4 \rightarrow BaS \rightarrow BaCO_3$

Manufacture: In barium carbonate manufacture from barium sulfate (heavy spar) (see Fig. 3.1-3), the heavy spar is first crushed and pulverized then reduced with coke to barium sulfide at 1000 to 1200°C in a rotary tube furnace. The barium sulfide is then leached from the ground melt with hot water and the solution either reacted with carbon dioxide or sodium carbonate, whereupon barium carbonate precipitates out:

$$\begin{aligned}
&BaSO_4 + 4\,C && \longrightarrow && 4\,BaS + 4\,CO \\
&BaS + CO_2 + H_2O && \longrightarrow && BaCO_3 + H_2S \quad \text{or} \\
&BaS + Na_2CO_3 && \longrightarrow && BaCO_3 + Na_2S
\end{aligned}$$

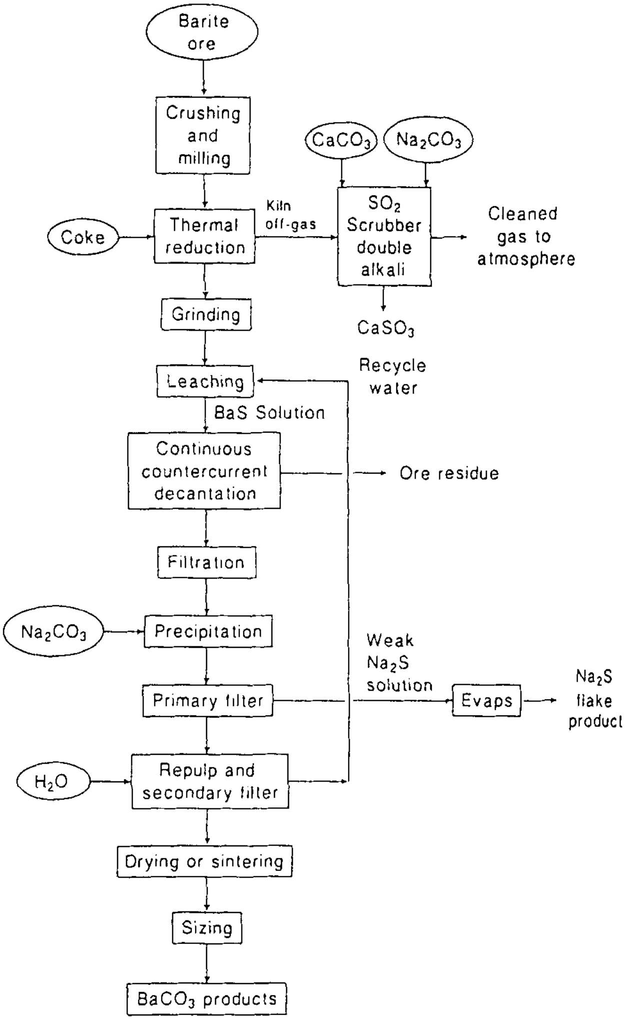


Fig. 3.1-3. Processing of heavy spar to barium carbonate.

Applications for $BaCO_3$:

- tile and ceramic industry
- glass industry
- other barium compounds
- special ceramics (barium ferrite and titanate)
- photographic paper

Applications: The most important utilization sector for barium carbonate is the manufacture of clay tiles and ceramic products, the addition of barium carbonate hindering the bleeding of salts (sodium and calcium sulfate). In the USA 30% of the consumption is devoted to this use. A further 30% is consumed in the glass industry (e.g. for the manufacture of optically special glasses and television screens). About 20% is used in the manufacture of other barium compounds. Other uses are in special ceramics (barium ferrite and titanate), in photographic papers and in various other applications.

3.1.2.6.3 Barium Sulfide

Barium sulfide is the most important intermediate in the manufacture of barium compounds (see Section 3.1.2.6.2). It is also used in the manufacture of lithopone (joint precipitation of ZnS + $BaSO_4$). The importance of Lithopone has declined with the expansion in the use of TiO_2 pigments. USA production of barium sulfide, $112 \cdot 10^3$ t/a in 1965, had declined to $44 \cdot 10^3$ t/a by 1979, since when no further figures have been published.

BaS:
- most important intermediate in the manufacture of barium compounds
- manufacture of H_2S
- manufacture of synthetic barium sulfate

3.1.2.6.4 Barium Sulfate

Synthetic (precipitated) barium sulfate is manufactured by reaction of a barium sulfide solution with sodium sulfate. Synthetic barium carbonate is utilized as a filler and white pigment in the manufacture of paper (blanc fixe) and in the paint, rubber and plastics industries. In medicine it is used as a contrast agent.

Synthetic $BaSO_4$:
manufacture from BaS + Na_2SO_4

Applications of synthetic $BaSO_4$:
- filler and white pigment
- contrast agent in medicine

References for Chapter 3.1.2: Alkaline Earth Metals and their Compounds

Technical Information:
Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. *Beryllium and Beryllium Compounds.* 4. Ed., Vol. 4, 126 – 146 and 147 – 153, John Wiley & Sons, New York.
Kirk-Othmer, Encyclopedia of Chemical Technology. 1995. *Magnesium and Magnesium Alloys/Compounds.* 4. Ed., Vol. 15, 622 – 722, John Wiley & Sons, New York.
Canterford, J. H. 1986. Magnesia - *An Important Industrial Mineral,* Mineral Processing and Extractive Mineral Review, Vol. 2, 57.
Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 1995. *Calcium and Calcium Compounds.* 4. Ed., Vol. 4, 777 – 786 and 787 – 826, and Vol. 15, 319 – 359, John Wiley & Sons, New York.
Kirk-Othmer, Encyclopedia of Chemical Technology. 1997. *Strontium and Strontium Compounds.* 4. Ed., Vol. 22, 947 – 955, John Wiley & Sons, New York.
Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. *Barium and Barium Compounds.* 4. Ed., Vol. 3, 902 – 908 and 909 – 955, John Wiley & Sons, New York.
Ullmann's Encyclopedia of Industrial Chemistry. 1985. *Beryllium and Beryllium Compounds.* 5. Ed., Vol. A 4, 11 – 33, VCH Verlagsgesellschaft, Weinheim.
Ullmann's Encyclopedia of Industrial Chemistry. 1990. *Magnesium and Magnesium Compounds.* 5. Ed., Vol. A 15, 559 – 593 and 595 – 630, VCH Verlagsgesellschaft, Weinheim.
Ullmann's Encyclopedia of Industrial Chemistry. 1985. 1995. *Calcium and Calcium Compounds.* 5. Ed., Vol. A 4, 515 – 518, 533 – 546, 547 – 553 and 555 – 584, and Vol. A 15, 317 – 345, VCH Verlagsgesellschaft, Weinheim.
Ullmann's Encyclopedia of Industrial Chemistry. 1994. *Strontium and Strontium Compounds.* 5. Ed., Vol. A 25, 321, VCH Verlagsgesellschaft, Weinheim.
Ullmann's Encyclopedia of Industrial Chemistry. 1985. *Barium and Barium Compounds.* 5. Ed., Vol. A 3, 325 – 341, VCH Verlagsgesellschaft, Weinheim.

Commercial Information:

Beryllium and its Compounds:.
Chemical Economics Handbook. 10/1995. Stanford Research Institute, Menlo Park, California, 233.3200A.
Minerals Yearbook. 1990.Vol. 1, US Department of the Interior, Washington, 191.

Magnesium, Metallic:
Chemical Economics Handbook. 9/1995. Stanford Research Institute, Menlo Park, California, 233.3900A.

Magnesium Oxide and Other Magnesium Compounds:
Chemical Economics Handbook. 5/1997. Stanford Research Institute, Menlo Park, California, 747.2000A.
Minerals Yearbook. 1990.Vol. 1, US Department of the Interior, Washington, 709.

Calcium and its Compounds:
Minerals Yearbook. 1990.Vol. 1, US Department of the Interior, Washington, 225 and 685.

Calcium Carbonate, Precipitated:
Chemical Economics Handbook. 10/1996. Stanford Research Institute, Menlo Park, California, 724.6000A.

Limestone:
Chemical Economics Handbook. 5/1996. Stanford Research Institute, Menlo Park, California, 214.1000A.

Calcium Chloride:
Chemical Economics Handbook. 10/1995. Stanford Research Institute, Menlo Park, California, 733.5000A.

Calcium Carbide:
Chemical Economics Handbook. 2/1995. Stanford Research Institute, Menlo Park, California, 724.5000A.

Strontium and its Compounds:
CD Römpp Chemie Lexikon. 1995. Version 1.0, Georg Thieme Verlag, Stuttgart/New York.
Minerals Yearbook. 1990.Vol. 1, US Department of the Interior, Washington, 1107.
Mineral Commodity Summaries. 1987. Bureau of Mines, Washington, 1027.

Barium and its Compounds:
Chemical Economics Handbook. 5/1997. Stanford Research Institute, Menlo Park, California, 715.2000A.

Barite:
Chemical Economics Handbook. 3/1997. Stanford Research Institute, Menlo Park, California, 715.1000A.
Minerals Yearbook. 1990.Vol. 1, US Department of the Interior, Washington, 179.
Mineral Commodity Summaries. 1986. Bureau of Mines, Washington, 16.

3.2 Aluminum and its Compounds

3.2.1 General Information

Al is the most important non-ferrous metal both by weight and by volume

Industrially important Al-compounds:
$Al(OH)_2$, Al_2O_3, $Al_2(SO_4)_3$, $AlCl_3$, $NaAlO_2$, Na_3AlF_6

Aluminum is the most important non-ferrous metal, more important than copper, zinc or lead.

The most important compounds apart from aluminum silicate-based ceramics and clay products are aluminum hydroxide and aluminum oxide, since they are raw materials in the manufacture of aluminum. Other industrially important aluminum compounds are aluminum sulfate, aluminum chloride, sodium aluminate, aluminum fluoride and cryolite (see Section 1.7.1).

3.2.2 Natural Deposits

Aluminum is with 8.8% the third most abundant element in the Earth's crust. In nature, it is mainly present as oxides usually in association with the oxides of other elements (Na, Ca, Si) as in feldspars (e.g. lime feldspar, anorthite, $CaO \cdot Al_2O_3 \cdot 2SiO_2$) and their weathering products, i.e. in clay minerals (e.g. kaolinite, $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, and montmorillonite, $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$) or micas (e.g. muscovite).

Al is the third most abundant element in the Earth's crust (after O and Si). It occurs particularly in:

- feldspars
- clays
- micas
- bauxites

The industrially most important minerals for aluminum manufacture are the bauxites (laterite). Bauxite is not a uniform material, but comprises a mixture of different aluminum oxide hydrates and hydroxides [e.g. boehmite, γ-AlO(OH), diaspore, α-AlO(OH)] with aluminum silicates, iron and titanium oxides etc. with between 35 and 70% (mostly 50 to 65%) aluminum oxide.

Most important raw materials for aluminum manufacture are the bauxites:

mixtures of AlO(OH) and $Al(OH)_3$ with SiO_2, Fe_2O_3, TiO_2, etc (Al_2O_3-content generally 50 to 65%)

The most valuable bauxites are those with a high content of easily hydrolyzable hydrargillite (including the laterites from many tropical countries) and low silica-content.

Since bauxites are to be found in many countries of the world, the processing of silicatic aluminum minerals is industrially unimportant. Non-bauxite raw materials (e.g. nepheline and aluminite ores) are processed, to a limited extent, in the former States of the USSR and Poland (accounts for an estimated 16% of the aluminum-plant production in the former States of the USSR).

Over 90% of the bauxite is processed to aluminum oxide. About half of the rest is utilized in the manufacture of refractory materials. As a result of asbestos substitution and more demanding process conditions, the demand for refractory compounds and insulation materials produced from bauxite has increased. The rest is utilized in the manufacture of abrasive aluminum oxide and the manufacture of other aluminum chemicals.

Applications of bauxite:

- Al_2O_3-manufacture (90%)
- manufacture of refractory materials

The worldwide extraction of bauxite increased from ca. $86 \cdot 10^6$ t/a in 1981 to ca. $110 \cdot 10^6$ t/a in 1994, Australia being the leading extracting country. The certain worldwide reserves of bauxite are $36 \cdot 10^9$ t (sufficient for $8 \cdot 10^9$ t of aluminum). The estimated worldwide reserves are 40 to 50 $\cdot 10^9$ t. Over 80% of the reserves are confined to just eight (mainly tropical) countries (e.g. 30% in Guinea and 20% in Australia).

3.2.3 Metallic Aluminum

3.2.3.1 Economic Importance

Al-production (10^6 t/a):

World	(1994)	19.0
USA	(1993)	3.7
former States of USSR	(1992)	3.3
Canada	(1993)	2.3
Australia	(1993)	1.2
Brazil	(1993)	1.2
China	(1992)	1.0
Norway	(1992)	0.8
FR Germany	(1992)	0.6

The worldwide production of metallic aluminum increased from $15.4 \cdot 10^6$ t/a in 1980 to $19 \cdot 10^6$ t/a in 1994, of which $3.7 \cdot 10^6$ t/a was produced in the USA, the leading aluminum-producing country. In addition secondary aluminum is produced by recycling used and waste aluminum e.g. $2.8 \cdot 10^6$ t/a in the USA in 1992. In the future the consumption of aluminum is expected to increase further, due to the opening up of new application sectors. In the transport sector, the second largest consumer in the USA, aluminum consumption increased 11% between 1987 and 1988. In vehicle construction steel and iron are being increasingly replaced by lighter materials such as aluminum. The aluminum content in a car built in North America has increased from 24.5 kg in 1960 to 86.6 kg in 1991.

3.2.3.2 Manufacture

Industrial aluminum manufacture currently almost exclusively by the Hall-Heroult process

The industrial manufacture of aluminum is based on the Hall-Heroult process developed in 1886. In this process aluminum oxide (see Section 3.2.4.2 for the production of aluminum oxide from bauxite) is dissolved in a cryolite (Na_3AlF_6) melt and electrolyzed at 940 to 980°C with direct current. Molten metallic aluminum is deposited at the carbon electrode (cladding of the bottom) and taken off as a liquid. Oxygen is formed at the anode, also of carbon (presintered or Soederberg-electrode), with which it reacts forming carbon dioxide and carbon monoxide.

$$2\,Al_2O_3 \longrightarrow 4\,Al + 3\,O_2$$

$$3\,C + 3\,O_2 \longrightarrow 3\,CO_2\ (\text{or } CO)$$

Electrolyte:

Na_3AlF_6 + 7 to 12% Al_2O_3 + additives (AlF_3, LiF etc.)

LiF-additive:

- improved conductivity
- increased energy yield
- reduced F-emission

The electrolyte essentially consists of sodium hexafluoroaluminate (synthetic cryolite) with added aluminum fluoride and lithium fluoride. The latter is formed in situ from lithium carbonate. These additives make up 2 to 5% of the bath content and result in a reduced melt temperature, an increase in the melt conductivity, an increase in the yield based on electricity consumption and reduced fluorine emission. Over 40% of the aluminum producers in North America already use these additives.

Aluminum oxide is added in an amount of 7 to 12%, dependent upon the bath composition. The eutectic mixture, sodium aluminum hexafluoride/aluminum oxide with 10.5% aluminum oxide, melts at 960°C. The yield with respect to current consumed is 85 to 95%, the cell voltage is 4.5 to 5%, the anode consumption is ca. 0.5 kg/kg aluminum, the power rating of a plant - consisting of many (100 to 200) individual cells connected in series - is in the range 50 to 300 kA.

Aluminum production is very energy intensive, ca. 18 kWh is on average consumed per kg aluminum (in modern plants 14 kWh/kg).

Al production is energy intensive, energy cost making up 25 to 30% of aluminum manufacturing costs in Western industrialized countries

It has been possible in recent years to reduce strongly the fluorine emission and thereby the fluorine consumption e.g. by dry adsorption and dry chemisorption of the hydrogen fluoride-containing gases from the electrolysis furnace with aluminum oxide.

The old problem of the aluminum industry of fluorine emission has to a large extent been solved.

Liquid aluminum (99.5 to 99.9% pure) is produced in the electrolysis furnace by three layer melt electrolysis with the help of fluorine-containing fluxes or by fractional crystallization.

Production processes other than the melt electrolysis of aluminum oxide, such as the energetically more favorable and environmentally more favorable electrolysis of aluminum chloride, have only minor industrial importance.

Al-manufacture from $AlCl_3$ by the Alcoa process is currently unimportant.

3.2.3.3 Applications

The consumption of primary aluminum in Western Europe in 1991 was $4.8 \cdot 10^6$ t/a and that of secondary aluminum was $1.6 \cdot 10^6$ t/a, making $6.4 \cdot 10^6$ t/a overall.

In the Federal Republic of Germany aluminum is mainly utilized in vehicle and aircraft construction with smaller amounts used in machine construction, in the construction industry and as a packaging material. Aluminum is predominantly used in the form of alloys, due to their higher strength than pure aluminum at similar or better corrosion resistance. The most important alloying elements are copper, magnesium, manganese, silicon and zinc, which are generally alloyed with aluminum in quantities of a few per cent [on their own or (mainly) in combination]. There

Al-consumption (10^6 t/a):

USA	(1993)	7.2
Japan	(1991)	3.8
West Europe	(1991)	4.8 primary Al 1.6 secondary Al
FR Germany	(1991)	1.9

Al consumption in the FRG in 1991 in different sectors in 10^3 t:

• transport (vehicle/aircraft)	411
• construction industry	231
• machine construction	105
• packaging	99
• electronics industry	83
• office and household equipment	66

are two types of aluminum alloy: wrought and cast. The first industrially important aluminum alloy was the age-hardenable duralumin (1906) with added copper, magnesium, manganese and silicon.

3.2.4 Aluminum Oxide and Aluminum Hydroxide

3.2.4.1 Economic Importance

Production of hydrated aluminum oxide in 1992 in 10^6 t/a in 1992:

World	41.5
Australia	11.6
USA	5.2
Jamaica	2.9
China	1.9
India	1.7
FR Germany	0.9

The worldwide production of aluminum hydroxide [hydrated aluminum oxide, $Al(OH)_3$], ca. $32.3 \cdot 10^6$ t/a in 1981, increased 4.7% annually in the period 1985 to 1991, but fell 2% to $41.5 \cdot 10^6$ t/a (as Al_2O_3) in 1992. The three leading producing countries in 1992 were Australia (27%), USA (12%) and Jamaica (7%) and currently account for about half of the world production. The production of aluminum oxide (alumina, Al_2O_3), occurring naturally as corundum, was slightly lower, since not all the hydrated aluminum oxide is calcined. The production in the Federal Republic of Germany decreased from $1.51 \cdot 10^6$ t/a in 1982 (before unification) to $0.87 \cdot 10^6$ t/a in 1992 (after unification).

3.2.4.2 Manufacture

$Al(OH)_3$ and Al_2O_3 production is industrially almost exclusively by the Bayer process: digestion of bauxite in sodium hydroxide

The industrial manufacture of aluminum hydroxide and aluminum oxide currently proceeds almost exclusively by the Bayer process i.e. by wet digestion of bauxite. The sinter- and melt-digestion processes with sodium carbonate and/or lime only have minor industrial importance.

Fe-content of bauxite precipitates out as so-called red mud

In the Bayer process, ground bauxite is digested with aqueous sodium hydroxide (200 to 350 g/L sodium hydroxide) at temperatures of 140 to 250°C in autoclaves or in continuous tube reactors, in which the hydrated aluminum hydroxide is dissolved as sodium aluminate. The iron-containing very finely divided so-called red mud is then separated in thickening and filter units and washed. Ca. 1 to 2 t of red mud is produced per t aluminum oxide.

The filtrate, consisting of a solution with a sodium oxide/aluminum oxide molar ratio of 1.5 to 1.8, is cooled with stirring and then seeded with large quantities of aluminum hydroxide, whereupon a large part of the dissolved aluminum hydroxide precipitates out as hydrargillite (see Section 3.2.2):

$$Al(OH)_4^- + H_2O \longrightarrow \gamma\text{-}Al(OH)_3 + OH^-$$

The aluminum hydroxide-depleted alkali is, after separating off the aluminum hydroxide, partially evaporated and then returned to the bauxite digestion. The aluminum hydroxide obtained is processed mainly by calcination in rotating tube furnaces or in, energy-saving (VAW-Lurgi process), fluidized bed furnaces at 1200 to 1300°C to aluminum oxide (α-Al_2O_3). A small quantity of the aluminum hydroxide is carefully dried and used as such.

γ-$Al(OH)_3$ (hydrargillite) is precipitated from the sodium aluminate solution by seeding. It is mainly calcined to α-Al_2O_3.

Active aluminas (various oxides and hydrated oxides) with high specific areas, good absorption characteristics, catalytic properties and high chemical reactivity are either produced by precipitation processes from aluminum salt solutions e.g. via thermal post-treatment of aluminum hydroxide gels, or by the calcination of α-aluminum hydroxide under specific conditions (low temperatures, very rapid heating).

Active aluminas:

- by precipitation reactions from Al-salts
- by careful calcination of (α-Al_2O_3)

Electrocorundum is obtained by reduction melting of the purest possible bauxite or alumina at ca. 2000°C with coke and anthracite in an arc reduction furnace, the impurity oxides in the raw material (iron, titanium, silicon) being thereby reduced and to a large extent removed.

Electrocorundum from:

- pure bauxite
- alumina

by reduction in the melt

3.2.4.3 Applications

Most of the α-aluminum oxide is utilized for aluminum manufacture (ca. 0.5 t aluminum/t Al_2O_3). In the USA over 90% of the aluminum oxide production is utilized in the manufacture of aluminum, the rest being utilized in the manufacture of refractory, grinding, ceramic, glass and enamel products and electrocorundum. It is also used as a filler in polymers (polyesters, epoxides).

Main applications of Al_2O_3:

- in production of Al by melt electrolysis
- ca. 10% utilized in refractory, grinding agent, glass, enamel and plastics industries

Main application of $Al(OH)_3$:

- alumina manufacture

Minor applications of $Al(OH)_3$:

- manufacture of aluminum chemicals
- active aluminas
- flame retardant for polymers

Application of active aluminas:

- absorption agent for water
- absorption agent for gases
- catalyst (carrier)

Applications of electrocorundum:

- grinding and polishing agent
- refractory industry
- hard concretes

α-Aluminum hydroxide is indirectly, via aluminum oxide, also mainly utilized in the manufacture of aluminum. In addition it is utilized in the manufacture of aluminum compounds (aluminum fluoride, synthetic cryolite, sodium aluminate, aluminum sulfate), active aluminas and, particularly in a finely divided form, as a flame retardant and filler in carpets, plastics, foam rubber and wall elements. Active aluminas are mainly used as absorption agents for water (e.g. drying of gases, air and hydrocarbons) and for gases, but are also used as catalysts e.g. in the Claus process (see Section 1.6.1.2.2) and as a filter medium. Electrocorundum, due to its high hardness, is an important grinding and polishing agent and is also used in the refractory industry and in the manufacture of hard concretes.

3.2.5 Aluminum Sulfate

3.2.5.1 Economic Importance

Production of aluminum sulfate (estimated) in 10^3 t/a:

West Europe	(1993)	720
USA	(1993)	600
Japan	(1994)	430

The 1993 production of aluminum sulfate was $600 \cdot 10^3$ t/a in the USA and $720 \cdot 10^3$ t/a in Western Europe, of which $100 \cdot 10^3$ t/a was produced in Sweden, the leading producing country in Western Europe, and $90 \cdot 10^3$ t/a in the Federal Republic of Germany.

3.2.5.2 Manufacture

Manufacture of technical aluminum sulfate [with 57% $Al_2(SO_4)_3$] from $Al(OH)_3$ or bauxite with H_2SO_4

Aluminum sulfate is manufactured by the reaction of aluminum hydroxide or other aluminum raw materials, such as bauxite or kaolin, with sulfuric acid at ca. 170°C in a pressure-resistant agitator vessel. The melt obtained after concentration contains ca. 57% aluminum sulfate (ca. 13 moles of crystallization water). Double salts of aluminum sulfate with potassium, ammonium or sodium sulfate (alums e.g. potassium alum $KAl(SO_4)_2 \cdot 12H_2O$) have been largely supplanted by aluminum sulfate.

3.2.5.3 Applications

Applications of $Al_2(SO_4)_3$:
- paper and pulp industry
- water purification

Aluminum sulfate is largely utilized in three application sectors: in the paper industry, industrial effluent treatment and in municipal and industrial water purification. The consumption of aluminum sulfate is expected to decline due to substitution by non-aluminum sulfate-requiring papers and utilization of other processes and chemicals for water purification. In Western Europe an annual decrease of about 3% was expected in the period 1993 to 1998. Aluminum sulfate is also the starting material for the manufacture of other aluminum compounds e.g. aluminum oxide gel.

3.2.6 Aluminum Chloride

3.2.6.1 Economic Importance

The total production of aluminum chloride in the USA has declined from $72.2 \cdot 10^3$ t/a (as $AlCl_3$) in 1980 to $36.9 \cdot 10^3$ t/a in 1993. These figures include both the production of anhydrous aluminum chloride and aluminum chloride hexahydrate, $AlCl_3 \cdot 6H_2O$, the former having declined in this period from $67 \cdot 10^3$ t/a to $17.6 \cdot 10^3$ t/a and the latter having increased in this period from $5.2 \cdot 10^3$ t/a (as $AlCl_3$) to $19.3 \cdot 10^3$ t/a. In 1993 the production of anhydrous aluminum chloride in Western Europe was $29 \cdot 10^3$ t/a and in Japan was $8 \cdot 10^3$ t/a.

3.2.6.2 Manufacture

Anhydrous $AlCl_3$:
from Al metal and chlorine

$AlCl_3 \cdot 6H_2O$:
from Al $(OH)_3$ and HCl

Anhydrous aluminum chloride is currently mainly manufactured by chlorination of liquid aluminum in ceramic-lined reaction vessels at 600 to 750°C, gaseous aluminum chloride being fed into condensation chambers. The reductive chlorination of aluminum oxide in the presence of coal (e.g. in the Alcoa process, see Section 3.2.3.2) is also operated industrially. Hydrated aluminum chloride is manufactured by reacting aluminum hydroxide with hydrochloric acid or hydrogen chloride.

3.2.6.3 Applications

Main application of $AlCl_3$:

- catalyst in organic chemistry
- application declining strongly due to the utilization of alternative zeolite-based catalyst systems

The main use of anhydrous aluminum chloride is as a catalyst in organic chemistry, particularly in Friedel-Crafts alkylation and acylation (manufacture of ethyl benzene, ethyl chloride, dye and flavoring precursors, detergents and polymers). During the last 20 years the demand for anhydrous aluminum chloride has continuously declined. In essence, the question of environmental compatibility in the disposal of aluminum chloride-containing process residues has led to their substitution by alternative catalysts. In the manufacture of styrene-(ethyl benzene) zeolite-based catalysts have been increasing used. Despite increasing styrene production, the quantity of anhydrous aluminum chloride used in this application is decreasing. As a result of the actual banning and phasing out of lead-containing fuels, the demand for lead tetraethyl is declining. The demand for ethyl chloride for its manufacture is therefore declining strongly as is the demand for the anhydrous aluminum chloride utilized in its manufacture.

Anhydrous aluminum chloride is used as a nucleation agent in the production of TiO_2-pigment by the chloride process.

In the period 1977 to 1981 a pilot plant for aluminum manufacture from aluminum chloride was operated in the USA by Alcoa. In this period most of the anhydrous aluminum chloride produced in the USA was consumed in this plant.

Aqueous aluminum chloride is utilized in the production of pharmaceuticals and chemicals and in the manufacture of special papers.

3.2.7 Sodium Aluminate

$NaAlO_2$:

- intermediate in the digestion of bauxite with NaOH
- from $Al(OH)_3$ and NaOH

Sodium aluminate (theoretical formula $NaAlO_2$) has a certain industrial importance not only as an intermediate in the digestion of bauxite in the Bayer process (see Section 3.2.4.2). USA production of sodium aluminate in 1993 was estimated to be $85 \cdot 10^3$ t/a. Sodium aluminate is produced by dissolving hydrated aluminum oxide in 50% sodium hydroxide. It is utilized in water purification, in the paper industry, for the post-treatment of TiO_2-pigments, for the manufacture of aluminum-containing catalysts, aluminosilicates and zeolites and in the construction industry.

References for Chapter 3.2: Aluminum and its Compounds

Ullmann's Encyclopedia of Industrial Chemistry. 1985. 5. Ed., Vol. A 1, 459 - 494, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 2, 184 – 356, John Wiley & Sons, New York.

Trotmann-Dickenson, A. F. 1973. *Comprehensive Inorganic Chemistry*, 1st Ed., Vol. 1, 993 – 1058, Pergamon Press, Oxford.

Chemical Economics Handbook. 1997. Stanford Research Institute, Menlo Park, California.

Specific Literature:

Aluminum

Pawlek, R. P. 1993. *Recent Developments in the Treatment of Spent Potlining*, JOM, **45** (11), 48 – 52.

Aluminum Oxide

Sleppy, W. C., Pearson, A., Misra, C., Mac Zura, F. 1993. *Non-Metallurgical Use of Alumina and Bauxite*, Light Met. (Warrendale, P.,), 117 – 124.

Chin, I. A. D. 1988. *The State-of-the-Art in BAYER Process technology 1988*. Ibid, 49 – 53.

Hard, R. 1989. *Fire-Retardant Foams*, Cell. Polym., **8** (4), 277 – 295.

Aluminum Chloride.

Sobota, P. 1989. *Inorganic Salts: One of the Controlling Factors of Reaction Mechanism and Complex Formation*, Pure Appl. Chem. **61** (3), 861 – 866.

Aluminum Sulfate.

Hurlbart, R. Z. 1997. *Aluminum Sulfate*, Eng. Chem. Process. Des., Vol. 3, 120 – 130, Editors: McKetta, J. J., Conningham, W. A., Publisher: Dekker, New York.

Strazdins, E. 1989. *Theoretical and Practical Aspects of Aluminum Sulfate Use in Papermaking*, Navd. Pulp. Pap. Res. J., **4** (2), 128 – 134.

3.3 Chromium Compounds and Chromium

3.3.1 Chromium Compounds

3.3.1.1 Economic Importance

The following chromium compounds are economically important:

- chromates and dichromates
- chromium(VI) oxide ("chromic acid")
- basic chromium(III) sulfates (chrome tanning agents)
- chromium(VI) compounds and chromium(IV) oxide,

Chromium compounds:

chromates, dichromates, chromium(VI) oxide, chromium(III) oxide, basic chromium(III) sulfates (chrome tanning agents), chromium pigments which are discussed as pigments in Section 5.9. A flow sheet summarizing the production pathways from chromium ores to the important chromium products is given in Fig. 3.3-1:

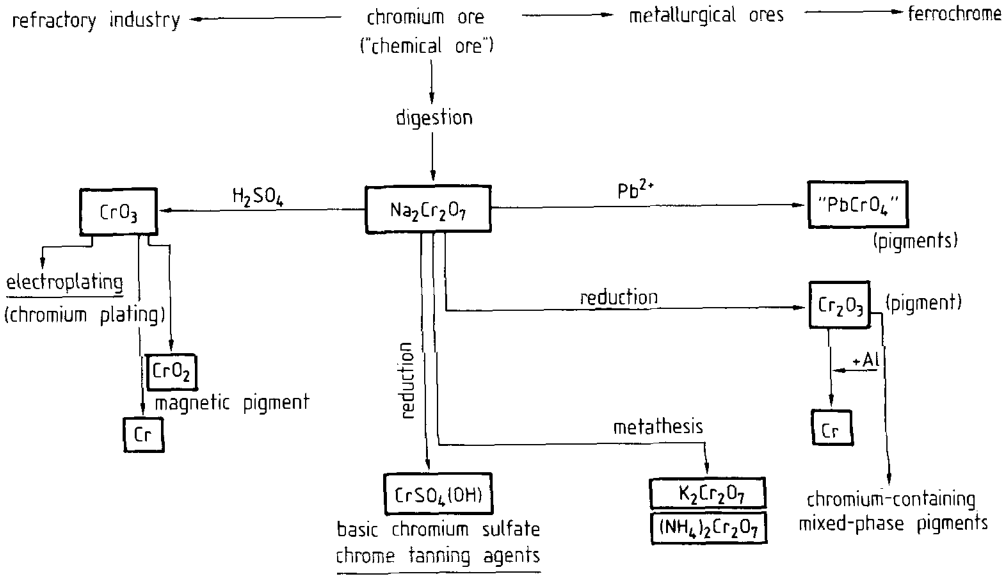


Fig. 3.3-1. Production pathways to the important chromium products.

The most important producers of chromium chemicals are:

- Occidental Chemical, USA
- American Chrome & Chemical, USA
- Nippon Chemical, Japan
- Nippon Denko, Japan
- Bayer, F. R. Germany
- British Chrome & Chemical, UK

There are other production plants in, for example, the former States of the USSR and China.

The sodium dichromate capacity of the US companies in 1996 were:

• Occidental Chemical, USA:	$51 \cdot 10^3$ t/a
• American Chrome & Chemical, USA:	$109 \cdot 10^3$ t/a

The only statistics available over the production of chromium chemicals sites concern the production of sodium dichromate (see Table 3.3-1).

Table 3.3-1. Production of Sodium Dichromate in 1994 (10^3 t).

USA	Western Europe	Japan	China
120	114	44	ca. 50

The sodium dichromate consumption in the USA in 1994 was 110 · 10^3 t/a. In Western Europe in 1994 it was 137 · 10^3 t/a, of which 31% was utilized in the manufacture of tanning agents for leather, a further 31% for the manufacture of chromium(VI) oxide ("chromic acid"), 9% in pigment manufacture and 9% in other applications.

3.3.1.2 Raw Material: Chromite

The raw material for all chromium chemicals is chrome iron ore, so-called chromite, which is a spinel. It contains magnesium and aluminum as minor constituents and has the approximate composition $(Fe, Mg)[Cr,Al,Fe(III)]_2O_4$. Calcium, silicon dioxide and, in some cases, vanadium are also present in small quantities.

The certain reserves of chromite were estimated in 1975 to be 2.8 · 10^9 t, the probable reserves to be 5.4 · 10^9 t. Of the certain reserves 74% are in South Africa and 20% in Zimbabwe. In South Africa the reserves are so large that the mining companies have not bothered to determine them accurately. Exhaustion of the reserves in the near future is not to be expected. Important extracting countries outside Southern Africa are (in alphabetical order): Albania, Brazil, Finland, the former States of the USSR, India, Iran, Madagascar, the Philippines and Turkey. Table 3.3-2 gives the chromite extraction figures for 1992.

Raw material: chromite

main reserves in Southern Africa, reserves very large

Tabel 3.3-2. Chromite Production in 1992 (10^6 t).

Kazakhstan	South Africa	India	Turkey
3.6	3.4	1.0	0.3

Depending upon the minor constituents present, such as magnesium and aluminum, chromite is utilized in:

- the steel industry for the manufacture of ferrochrome, accounting for ca. 75% of the production, for which ores are required with a high chromium to iron ratio (Cr: Fe > 2.5) together with a high magnesium content.

Applications of chromite:

- in the steel industry (75%)
- in the refractory industry (12%)
- in the chemical industry (13%)

- the refractory industry, accounting for ca. 12% of the production, for which a high chromium(III) oxide- and aluminum oxide-content (> 60%) is required with as much magnesium and as little iron as possible.
- the chemical industry, accounting for ca. 13% of the production, for which the chromium(III) oxide- and iron(III) oxide-contents should be as high as possible and those of aluminum, magnesium and silicon dioxide as low as possible. A typical composition (Rustenburg, South Africa) is:

44.5 Cr_2O_3; 26.4 FeO; 3.5 SiO_2; 10.6 MgO; 14.4 Al_2O_3
(in % by weight)

3.3.1.3 Manufacture of Chromium Compounds

3.3.1.3.1 Chromite Digestion to Alkali Chromates

Digestion of chromite:

alkaline oxidative digeation in rotary tube furnaces or annular hearth furnaces. Chromium(III) converted into chromium(VI) and sodium chromate formed leached. Yield of chromium: 75 - 90%

Only alkaline oxidative digestion is suitable for the industrial conversion of chromite to chromium chemicals. This results in alkali (sodium) chromates:

$$4\ FeCr_2O_4 + 8\ Na_2CO_3 + 7\ O_2 \xrightarrow{1000 - 1100^\circ C} 8\ Na_2CrO_4 + 2\ Fe_2O_3 + 8\ CO_2$$

Sodium carbonate can be in part be replaced by sodium hydroxide. The accompanying constituents are converted into sodium aluminate, sodium silicate, sodium vanadate and consume corresponding quantities of alkali.

This digestion separates chromium from the associated elements iron, aluminum, magnesium and silicon in a simple process. Post-purification may be necessary to remove the vanadium.

Prior to digestion, the ore must be finely ground. The chromium ore concentrate enriched by gravitational processes (e.g. spiral classifiers, settling machines etc.) is supplied with a particle size of ca. 0.5 mm. Ball-milling coupled with air classifiers yields a particle size of < 0.1 mm. The sodium carbonate is also ground. Since the sodium chromate formed melts at 792°C, the addition of an inert diluent, which can absorb sodium chromate like a sponge, is necessary to enable air to come into contact with the reaction mixture.

A particularly suitable diluent is the iron oxide residue left after digestion, but calcined pyrites can also be used. A typical digestion mixture consists of:

- 100 parts of ore
- 60 to 75 parts of sodium carbonate
- 50 to 200 parts of diluent

Chromium ore digestion is currently carried out in rotary tube furnaces or annular hearth furnaces. Figure 3.3-2 gives a flow chart of a rotary tube plant with units coupled at either end of it.

The brick-lined slowly rotating tube is inclined at an angle of 2 to 5%. The digestion mixture is fed in countercurrently to the heating gases (heating materials: heavy oil, natural gas, powdered lignite). Since the air employed has to oxidize chromium(III) to chromium(VI), iron(II) to iron(III) and provide the oxygen for the combustion of the heating materials, the air input is so regulated that the flue gases contain 12 to 16% (by volume) of oxygen. The average residence time of the digestion mixture in the furnace is ca. 4 h.

After reaction is complete, the reaction mixture contains up to 30% sodium chromate, up to 45% in annular hearth furnaces. The chromium yield is 75 to 90%.

10% of the reaction mixture is entrained as dust in the flue gases emerging from the head of the furnace. This is removed by, for example, electrostatic gas purification units. The heat content of the gases can be utilized in steam production.

The digested material emerging from the furnace can, for example, be ground in wet tube mills and leached with water. By appropriate adjustment of the conditions only sodium dichromate and part of the sodium vanadate dissolve leaving the iron, aluminum, silicon and magnesium behind as insoluble oxides or hydroxides, which are filtered off with rotary or belt filters. This residue is washed countercurrently in a series of stages. A chromate solution of 500 g/L is thus obtained and the residue contains less than 1/10% by weight of chromium(VI). This residue is either dried and returned as a diluent to the digestion mixture, or treated in the form of a sludge dispersion with reducing agents such as iron(II) sulfate or sulfur dioxide to remove chromium(VI), the water removed and then disposed of in an orderly manner.

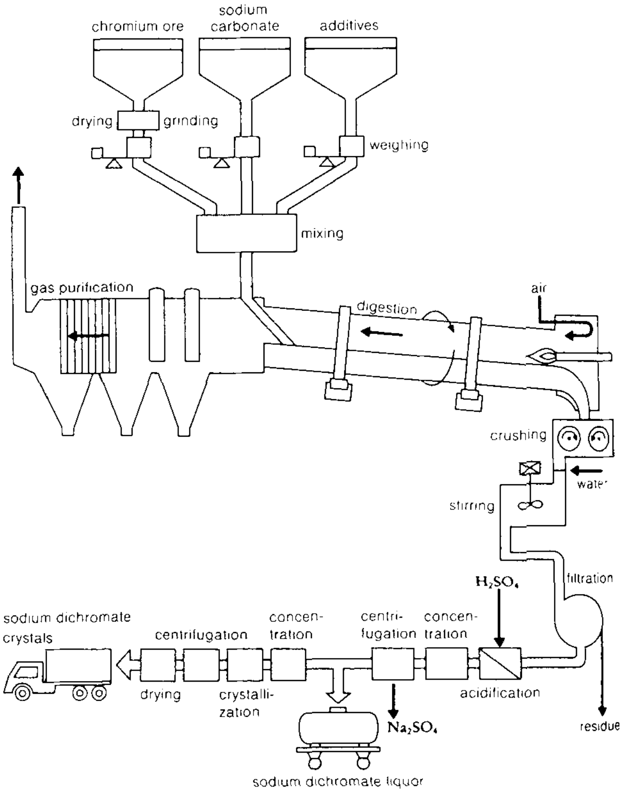


Fig. 3.3-2. Flow chart of a rotary kiln plant for the manufacture of sodium dichromate.

3.3.1.3.2 Alkali Dichromates

The alkali dichromates have a much higher chromium content than "monochromates" and are also easier to produce pure. They are therefore almost exclusively used in practice.

Most important commercial form of chromium(VI):

sodium dichromate dihydrate

Sodium Dichromate Dihydrate

Sodium dichromate dihydrate is obtained from the (mono)chromate by reaction with sulfuric acid or carbon dioxide.

Sodium (mono)chromate is converted to dichromate with:

- sulfuric acid
- carbon dioxide

Sulfuric Acid Process

The reaction between sodium chromate and sulfuric acid proceeds as follows:

$$2\ Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

The discontinuous or continuous addition of sulfuric acid to sodium chromate solution up to a pH of 3 is technically simple. The resulting solution of sodium dichromate dihydrate is then evaporated to 70% by weight, whereupon almost all the sodium sulfate precipitates out and is separated off. The dichromate solution obtained is in part utilized as such. Further evaporation to ca. 1600 g sodium dichromate/L and cooling to 30 to 40°C leads to crystallization of the dichromate. These processes are either carried out stepwise or continuously. Separation is carried out in a skimmer or shear centrifuge.

Conversion of (mono)chromate into dichromate with sulfuric acid:

technically simple process but has dichromate-containing sodium sulfate as a byproduct

The "yellow", i.e. dichromate-colored sodium sulfate byproduct is problematical in that it can not be readily used and the chromium has to be removed in a further process step.

Carbon Dioxide Process

$$2\ Na_2CrO_4 + H_2O + 2\ CO_2 \rightleftharpoons Na_2Cr_2O_7 + 2\ NaHCO_3$$

Conversion of chromate to dichromate with carbon dioxide:

technically complicated process, but no difficulty in utilizing the byproducts

Under normal conditions, the reaction equilibrium lies mainly on the left side of this equation. To promote the formation of dichromate, the reaction has to be carried out under 7 to 15 atmospheres pressure. Sodium hydrogen carbonate thereby precipitates out. It is carried out, if necessary, in a multistage process, in a series of autoclaves, whereby carbon dioxide (added either as a gas or as a liquid) is fed in countercurrent into sodium chromate solution concentrations of 800 to 900 g/L. The reaction is exothermic, cooling being necessary. The sodium hydrogen carbonate precipitate has either to be filtered off rapidly after pressure release to avoid back reaction, or as under pressure.

The chromate-containing sodium hydrogen carbonate is either calcined at 200 to 300°C to sodium carbonate:

$$2\ NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

or converted with sodium hydroxide to sodium carbonate:

$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$

and returned to the digestion. In the latter case, sodium hydroxide can substitute almost all the alkali utilized for the digestion. The further processing of the sodium dichromate solution has already been described in the section: *Sulfuric acid process.*

Potassium and Ammonium Dichromate

Potassium and ammonium dichromate by metathesis of sodium dichromates with potassium or ammonium salts

Potassium and ammonium dichromate are obtained by metathesis of sodium dichromate with potassium or ammonium salts e.g.:

$$Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7 + 2\,NaCl$$

For example, solutions with 400 to 450 g sodium dichromate/L are mixed with ca. 200 g potassium chloride/L while heating to the boiling point of the mixture. The sodium chloride which precipitates is filtered off from the hot solution, which is then cooled whereupon the potassium dichromate precipitates out.

Ammonium dichromate decomposes upon impact or heating above 180°C:

$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4\,H_2O$$

3.3.1.3.3 Chromium(VI) Oxide ("Chromic Acid")

By Reaction of Sodium Dichromate with Sulfuric Acid

Chromium(VI) oxide ("chromic acid"): from sodium chromate and sulfuric acid at ca. 200°

$$Na_2Cr_2O_7{\cdot}2\,H_2O + 2\,H_2SO_4 \longrightarrow 2\,NaHSO_4 + 2\,CrO_3 + 3\,H_2O$$

This reaction can be carried out both in concentrated aqueous solution and, preferably continuously, in the molten state. In the latter case, sodium dichromate is mixed with sulfuric acid in a twin screw and the mixture fed into an externally heated rotary tube furnace. The water first evaporates, then the sodium hydrogen sulfate melts (at 170°C) and finally the chromium(VI) oxide is formed (198°C). Temperature control is critical, since chromium(VI) oxide decomposes at temperatures slightly above this temperature. The reacted mixture then separates in a settling tank. Chromium(VI) oxide is taken off from below and liquid sodium hydrogen sulfate is taken off from above, both being converted into solid material by cooling rollers.

Electrochemical

Since the last edition of this book an electrochemical process for manufacturing chromic acid has been realized industrially. This is carried out in an electrolysis cell with two chambers separated by a cation-exchanger membrane. The anode side is filled with aqueous sodium dichromate solution, the cathode side with sodium hydroxide. Upon applying direct current oxygen is produced at the anode and hydrogen is produced at the cathode. H^+-ions are formed on the anode side and OH^--ions are formed on the cathode side.

Charge exchange between the chambers is only possible by cations from the anode side diffusing through the membrane to the anode side via the cation-exchanging membrane. The blocking function of the cation-exchanging membrane prevents anions from the cathode side diffusing to the anode side. This membrane-behavior causes the anode side to become depleted in sodium ions under the influence of the electric field and chromic acid to be formed. Sodium hydroxide is formed on the cathode side.

Since hydrogen ions can diffuse through the membrane in addition to the sodium ions, the efficiency of the above-described process becomes less favorable with increasing chromic acid concentration and thereby increasing hydrogen ion concentration. Practically achievable are solutions on the anode side in which slightly more than half of the chromium(VI) is present as chromic acid. This chromic acid can be recovered by crystallization. The mother liquor left is returned to the electrolysis process.

The electrolysis is generally carried out continuously in a number of cells linked in series. A block schema of the overall process is shown in Fig. 3.3-3.

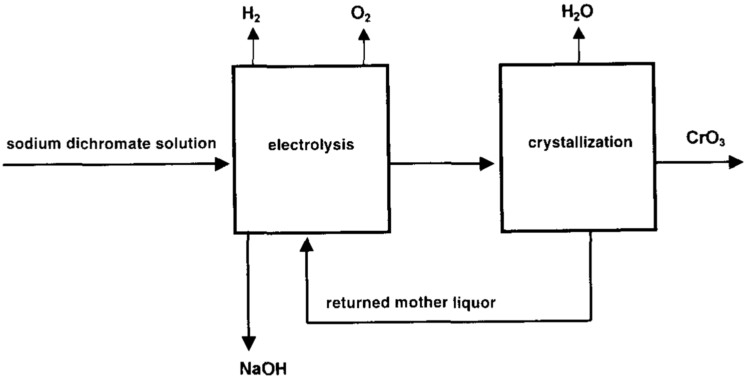


Fig. 3.3-3. Block schema for the electrolysis of sodium dichromate.

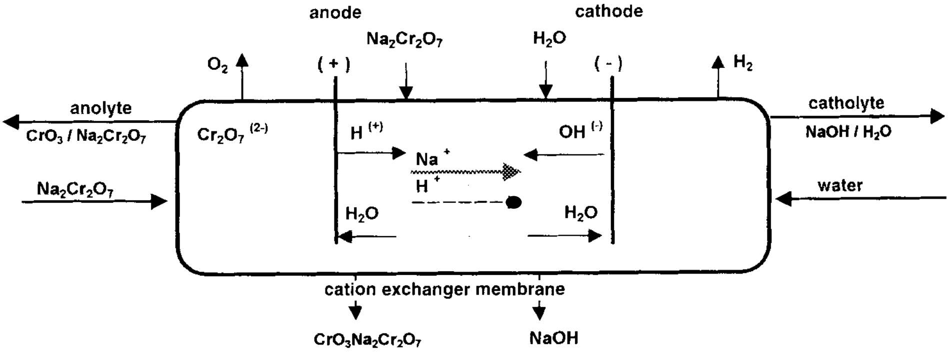


Fig. 3.3-4. Electrolysis of sodium dichromate to chromium(VI) oxide.

3.3.1.3.4 Chromium(III) Oxide

Chromium(III) oxide:

from sodium dichromate by reduction with charcoal, sulfur or ammonium salts.

Chromium(III) oxide is obtained by reducing sodium dichromate with organic materials, charcoal or sulfur in an exothermic reaction:

$$2\ Na_2Cr_2O_7 + 3C \longrightarrow 2\ Cr_2O_3 + 2\ Na_2CO_3 + CO_2$$
$$Na_2Cr_2O_7 + S \longrightarrow Cr_2O_3 + Na_2SO_4$$

These reactions are carried out continuously in furnaces. The reacted mixture is leached with water to remove soluble products, filtered, dried and ground. Very pure chromium(III) oxide (99%) of pigment quality is thereby obtained.

Chromium(III) can also be obtained by reacting sodium dichromate with ammonium salts such as ammonium chloride or sulfate:

$$Na_2Cr_2O_7 + 2\ NH_4Cl \longrightarrow 2\ NaCl + Cr_2O_3 + 4H_2O + N_2$$

Reduction with ammonium salts provides chromium(III) oxide with a particularly low sulfur content

The chromium(III) oxide thus obtained has a low sulfur content, particularly when a substoichiometric amount of ammonium salt is used, and can be used for the aluminothermic manufacture of chromium metal.

3.3.1.3.5 Basic Chromium(III) Salts (Chrome Tanning Agents)

Chrome-tanning is the crosslinking of the collagen carboxyl groups in animal hides with the help of chromium(III) compounds. This results in a material with increased temperature stability and reduced swelling capacity.

Chrome tanning agents:

crosslink the collagen carboxyl groups in animal hides. Basic chromium(III) sulfate or chromium(III) salts of organic acids are used

Basic chromium(III) salts with non-stoichiometric compositions are used in tanning, particularly oligomers of basic chromium(III) sulfate with the approximate composition $Cr(OH)SO_4$. Basic chromium sulfates are marketed as liquids or as a spray-dried powder.

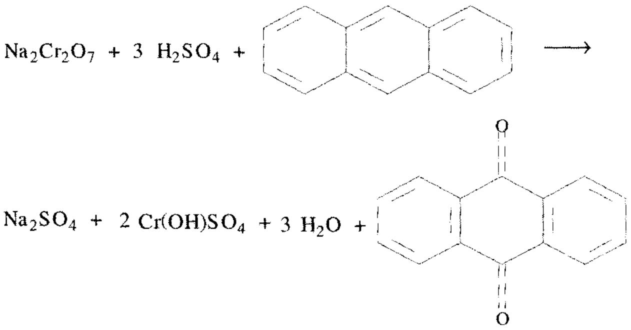
During tanning further buffering is necessary. This is accomplished by adding bases such as sodium carbonate, dolomite or magnesium oxide. If sulfate is partially exchanged for organic anions such as glutarate, the chromium content of the tanning batch is particularly strongly consumed during the tanning process, which is ecologically desirable. Particularly high quality leather is obtained when the formate is used, formate acting by way of complex formation.

Basic chromium sulfates can be manufactured in different ways:

Manufacture of basic chromium sulfates:

- from solutions obtained in the dichrormate oxidation of organic materials such as montan waxes or anthracene

- as a byproduct in the dichromate oxidation of impurities in montan waxes or of anthracene to anthraquinone:



- by the reduction of dichromate by molasses:

- by the reduction of dichromate by molasses

$$8\ Na_2Cr_2O_7 + 24\ H_2SO_4 + C_{12}H_{22}O_{11} \longrightarrow 16\ Cr(OH)SO_4 + 8\ Na_2SO_4 + 12\ CO_2 + 22\ H_2O$$

- by the reduction of dichromate with sulfur dioxide:

- by reduction of dichromate with sulfur dioxide

$$Na_2Cr_2O_7 + 3\ SO_2 + H_2O \longrightarrow Na_2SO_4 + 2\ Cr(OH)SO_4$$

In each case basic chromium sulfates are formed together with sodium sulfate, which is desirable in that it acts as a buffer during the tanning process.

3.3.1.4 Applications for Chromium Compounds

Dichromates: utilized as strong oxidizing agents, particularly in organic chemistry; as starting materials for chromium(VI) oxide, chromium(III) oxide, basic chromium sulfate, as chrome tanning agents, and chromium(III) salts, for wood impregnation, as corrosion inhibitors and as viscosity stabilizers in drilling muds.

Chromium(VI) oxide: utilized for chromium electroplating, as a starting material for chromium dioxide, in wood protection and for the manufacture of chromium-containing catalysts.

Chromium(IV) oxide: utilized in the manufacture of magnetic memory materials.

Chromium(III) oxide: utilized in the manufacture of chromium metal by aluminothermic reduction, as a pigment and as a polishing agent.

Basic chromium sulfate: utilized for the tanning of leather.

3.3.2 Metallic Chromium

3.3.2.1 Economic Importance

Metallic chromium utilized in:

- turbine blades
- iron-free chromium alloys
- cermets

Apart from the utilization of large quantities of ferrochrome (produced by reducing chromite with coal) in the manufacture of alloys containing iron and chromium, smaller quantities of chromium metal are used in, for example, the manufacture of turbine blades, the production of iron-free alloys and cermets (metal ceramics e.g. 23% by weight aluminum oxide, 77% by weight chromium).

Current chromium metal capacities in western industrialized countries:

15 to 20 · 10^3 t/a

In 1994 the USA consumption of metallic chromium was 4 · 10^3 t/a. The current capacity in Western industrialized countries is estimated to be 15 to 20 · 10^3 t/a.

3.3.2.2 Manufacture of Chromium Metal

3.3.2.2.1 Chemical Reduction

In chemical reduction processes chromium(III) oxide is always the starting material, for which it has to be as pure as possible particularly with regard to sulfur content (nickel alloys otherwise form nickel sulfide at grain boundaries). The reduction can be carried out with silicon and, in particular, aluminum and carbon. The reaction:

$$Cr_2O_3 + 2\,Al \longrightarrow Al_2O_3 + 2\,Cr$$

is insufficiently exothermic to be self-sustaining. Strong oxidizing agents such as potassium dichromate, chromium(VI) oxide, potassium perchlorate or barium peroxide are therefore added. The reaction is carried out batchwise in vessels lined with refractory materials. The metal is obtained in ca. 85 to 90% yield with a purity of 97 to 99% (by weight). The main impurities are silicon, aluminum and iron. Operators of this process include Gesellschaft für Elektrometallurgie and Shieldalloy.

Metallic chromium:

- by reduction of chromium(III) oxide with aluminum

Reduction with carbon is achieved by reacting briquettes of chromium(III) oxide and carbon at 1275 to 1400°C in a vacuum of 0.4 mbar in a slow reaction:

- by reduction of chromium(III) oxide with carbon

$$Cr_2O_3 + 3\,C \longrightarrow 2\,Cr + 3\,CO$$

This "Simplex process" is operated by UCC.

3.3.2.2.2 Electrochemical Reduction of Chrome Alum

Electrochemical reduction of chrome alum to chromium metal proceeds as follows:

- dissolution of ferrochrome in sulfuric acid/ammonium sulfate,
- separation of iron as iron(III) alum. Crystallization of chrome alum, $NH_4Cr(SO_4)_2 \cdot 12H_2O$,
- dissolution of chrome alum and electrolytic deposition of metallic chromium.

- by electrolysis of chrome alum solutions (produced from ferrochrome)

Electrolysis is carried out in a diaphragm cell with a stainless steel cathode. A 3 to 6 mm thick layer of chromium is obtained, which is chipped off the cathode at the end of the electrolysis. The energy consumption amounts to 18.5 kWh/kg chromium. After degassing (hydrogen removal), the chromium is 99.3% pure (by weight).

3.3.2.2.3 Electrochemical Reduction of Chromium(VI) Oxide ("Chromic acid")

- by electrolysis of acidic baths containing 300 g/L chromium(VI) oxide with other ingredients (chromium plating)

The electrochemical deposition of chromium upon metals is usually carried out in chromium(VI) oxide-containing baths to which ca. 1% sulfuric acid has been added. The material to be coated is used as the cathode, the anode usually being lead. A diaphragm is not necessary. The baths contain ca. 300 g/L of chromium(VI) oxide, in addition to a number of other components. The yield on the basis of electricity consumed is very poor, due to hydrogen being preferentially produced at the cathode. The energy consumption amounts to ca. 75 kWh/kg chromium. The chromium obtained is relatively pure.

This process is suitable both for the production of metallic chromium and for the coating of objects with thin, decorative or thicker hard chromium layers (chromium electroplating).

References for Chapter 3.3: Chromium Compounds and Chromium

Commercial Information:
American Metal Market. 1992. 1.
American Metal Market. 1995. 6.
Inorganic Chromium Compounds. 1996. Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California.
Chromite/Chromium, 1997. Chemical Economics Handbook, Stanford Research Institute, Menlo Park, California.

Reviews:
Kirk-Othmer, Encyclopedia of Chemical Technology. 1993. 4. Ed., Vol. 6, 228 – 311, John Wiley & Sons, New York.
Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 7, 43 – 97, VCH Verlagsgesellschaft, Weinheim.
Winnacker-Küchler, Chemische Technologie. 1982. *Anorganische Technologie.* Bd. 2, 651 – 677, Carl Hanser Verlag, München.
Winnacker-Küchler, Chemische Technologie. 1986. 4. Aufl. *Metall.* Bd. 4, 201 – 207, Carl Hanser Verlag, München.
Schliebs, R. 1980. Chemie in unser Zeit **14**, 13 – 17.
Stellmach. 1990. *The Commercial Success of Chrome Tanning: A Study and Commemorative,* in J. Am. Leather Chem. Assoc. **85** (11), 407 – 424.

3.4 Silicon and its Inorganic Compounds

3.4.1 Elemental Silicon

3.4.1.1 General Information and Economic Importance

Silicon is, in general, available in three different commercial forms:

- silicon as a component of alloys in the form of ferrosilicon with Si-contents from 8 to 13% (FeSi 10) up to 87 to 95% (FeSi 90)
- metallurgical grade (MG) silicon with purities of 98.5 (Si 98) to 99.7% (Si 99)
- "semiconductor", electronic grade (EG), silicon with a purity, which depending upon the application, has to be > 99.999%

Commercial forms of silicon:

- ferrosilicon
- technical (metallurgical) Si
- ultrapure silicon (semiconductor silicon)

The worldwide production of ferrosilicon in 1997 was ca. $1.8 \cdot 10^6$ t/a, that of technical silicon ca. $0.92 \cdot 10^6$ t/a.

Worldwide production in 1997:
ferrosilicon ca. $1.8 \cdot 10^6$ t/a
technical silicon ca. $0.92 \cdot 10^6$ t/a

The main consumer of ferrosilicon is the steel industry. Technical silicon is mainly utilized in the aluminum industry and the chemical industry.

Main consumer of ferrosilicon:
steel industry

Main consumer of technical silicon:
aluminum industry/chemical industry

The demand for technical silicon in Western industrialized countries increased from $0.49 \cdot 10^6$ t/a in 1985, of which $0.34 \cdot 10^6$ t/a was utilized as an alloy component in the aluminum industry and the rest in the chemical industry for the manufacture of inorganic silicon compounds and ultrapure silicon, to $0.79 \cdot 10^6$ t/a in 1995, of which $0.46 \cdot 10^6$ t/a was utilized in the aluminum industry and $0.33 \cdot 10^6$ t/a in the chemical industry.

Due to the energy intensive nature of silicon production, production plants are to be found at sites with cheap hydroelectric electricity (USA, Canada, Norway, Brazil, the former States of the USSR).

Worldwide consumption increased ca. 5.5% annually in the period 1980 to 1995, the demand in the chemical industry increasing at an annual rate of ca. 8% and ca. 3.5% in the aluminum industry.

The strong growth in demand in the period 1985 to 1995 was mainly covered by increased imports from the former States of the USSR and China and only to a small extent by expansion of the production capacity in Western industrialized countries. In 1995 the former East European

Communist Countries supplied 25% of the demand in Western industrialized countries. Silicon consumption is expected to grow further at ca. 5% annually due to increased consumption in the chemical, electronics and aluminum industries.

The current price of technical silicon is ca. 2.20 to 2.50 DEM/kg, it being considerably influenced by energy costs.

Consumers of ultrapure silicon:

- electronic industry
- photovoltaic applications

Whereas ca. 3000 t of ultrapure silicon ("electronic grade") was produced in 1980 for the manufacture of electronic components markets, the booming electronic industry in the meantime has led to an explosive expansion in production capacity to ca. $20 \cdot 10^3$ t/a, of which 40% is in the USA, 30% is in Japan and ca. 30% is in Europe. Due to the strongly growing electronics market and the emerging photovoltaic market (solar cells on the basis of crystalline silicon), a strongly expanding demand for ultrapure silicon is expected in the future.

Ultrapure silicon is the product of a very expensive multistage purification process (see Section 3.4.1.1.2). The price for this material therefore increases strongly with the degree of refining. 1 kg of polycrystalline ultrapure silicon ("polysilicon") from the pyrolysis of $SiHCl_3$ cost ca. 80 DEM in 1997, silicon single crystals ca. 600 DEM/kg and silicon wafers used in semiconductor technology ca. 1700 DEM/kg.

3.4.1.2 Manufacture

3.4.1.2.1 Ferrosilicon and Metallurgical Grade Silicon

Manufacture of metallurgical grade silicon by reduction of quartzite with coke in an electric-arc furnace

Ferrosilicon and metallurgical silicon are manufactured by reducing quartzites with coke in an electric-arc furnace (carbothermal reduction), see Fig. 3.4-1. The SiO_2-content of the quartzite for the manufacture of ferrosilicon must if possible be above 96%, that for the manufacture of metallurgical grade silicon should be generally as pure as possible and have as high a SiO_2 content as possible (see Table 3.4-1).

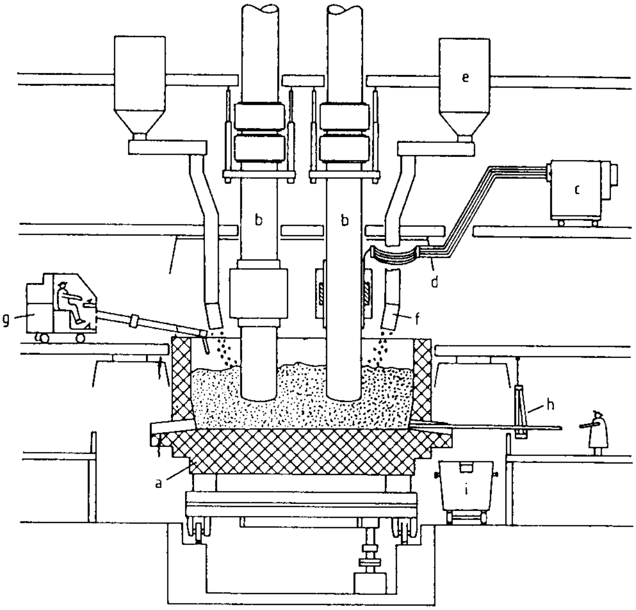


Fig. 3.4-1. Electric-arc furnace for ferrosilicon manufacture.
a) furnace shell with lining (rotatable); b) electrodes; c) transformers; d) secondary energy supply; e) raw material bunker; f) feeding tube; g) raking machine; h) tapping unit; i) receiving pan

Table 3.4-1. Specifications of quartz for the manufacture of metallurgical grade silicon.

Constituent	Content (%)
SiO_2	at least 98
Fe_2O_3	max. 1.5
Al_2O_3	max. 1.0
CaO	max. 0.2
MgO	max. 0.2

Sulfur-, phosphorus- and arsenic- contents are undesirable, since they form poisonous flue gases. High Al_2O_3-contents lead to the formation of sticky slags, which can contaminate the end product.

Manufacture of ferrosilicon:

by addition of iron as iron turnings or shredded iron

In the production of ferrosilicon the Moeller iron in the charge is added in the form of turnings or shredded iron. For silicon-contents above 45%, a shaft electric furnace is used with a power of 8 to 40 MW, whose substructure is lined with carbon bricks. The undesirable formation of SiC is avoided by rotating or oscillating the furnace. It operates with three phase electricity, which in the case of metallurgical grade silicon is introduced by way of graphitized electrodes. Ca. 11 to 14 MWh of electricity energy is consumed in producing 1 t of silicon. The yield based on the silicon-content of the quartz is ca. 80%.

The energy costs are ca. 21% of the raw material costs (quartz and coal) and 28% of the total manufacturing costs.

Overall reaction:

$SiO_2 + 2C \rightarrow Si + 2CO$
proceeds via intermediates (SiO, SiC)

The reduction proceeds in the following steps:

$$\begin{aligned} SiO_2 + C &\longrightarrow SiO + CO \\ SiO + 2\,C &\longrightarrow SiC + CO \\ SiC + SiO &\longrightarrow 2\,Si + CO \end{aligned}$$

Carbothermal reaction requires temperatures in excess of 2000°C. After ca. 1 to 2 h the continuously operating furnace is tapped with an auxiliary electrode. The liquid silicon (m.p. 1413°C) is collected in pans or ingot molds. If necessary, further metallurgical processes such as slag extraction or air blasting with reactive gases can be carried out to rid the silicon melt of included metallic and non-metallic impurities, before the silicon solidifies into brittle blocks.

Latest developments concern the quenching of liquid silicon by feeding a jet of molten silicon into water (water granulation) or casting into cooled ingot molds. The material thus produced exhibits an improved reactivity in the synthesis of methylchlorosilanes (Rochow process).

Metallurgical grade silicon is marketed in a coarsely crushed form or as a finely ground powder in different particle sizes. Powders with increased purity due to acid washing, particularly for the removal of metallic impurities, are specialty products. They are utilized, for example, in the manufacture of silicon nitride powder or reaction-bonded silicon nitride ceramic components and are therefore the starting materials for engineering ceramic specialties.

3.4.1.2.2 Electronic Grade Silicon (Semiconductor Silicon)

Semiconductor silicon:

extremely high purity requirements for p- and n-doped elements

Silicon only exhibits semiconducting properties when ultrapure.

The specific resistance of ultrapure silicon single crystals of up to 150 000 Ω cm decreases upon doping with 1 ppb_a of phosphorus to 100 Ω cm. Therefore the purity requirements are particularly stringent for p- and n-doped elements, boron- and phosphorus-concentrations of 0.1-1 ppb_a may not, for example, be exceeded.

Manufacture of ultrapure silicon by pyrolysis of $SiHCl_3$ or SiH_4

Ultrapure silicon is industrially produced by pyrolysis of very pure $SiHCl_3$ or SiH_4. The process currently used for producing 78% of semiconductor silicon was developed in the period 1953-1956 by Siemens AG (Siemens-C process, see Fig. 3.4-2). The starting material is metallurgical grade silicon, which is reacted in a fluidized bed reactor with hydrogen chloride (HCl) to trichlorosilane ($SiHCl_3$), from which an ultrapure form is obtained by distillation.

$$Si + 3\,HCl \xrightarrow{300\,°C} SiHCl_3 + H_2$$

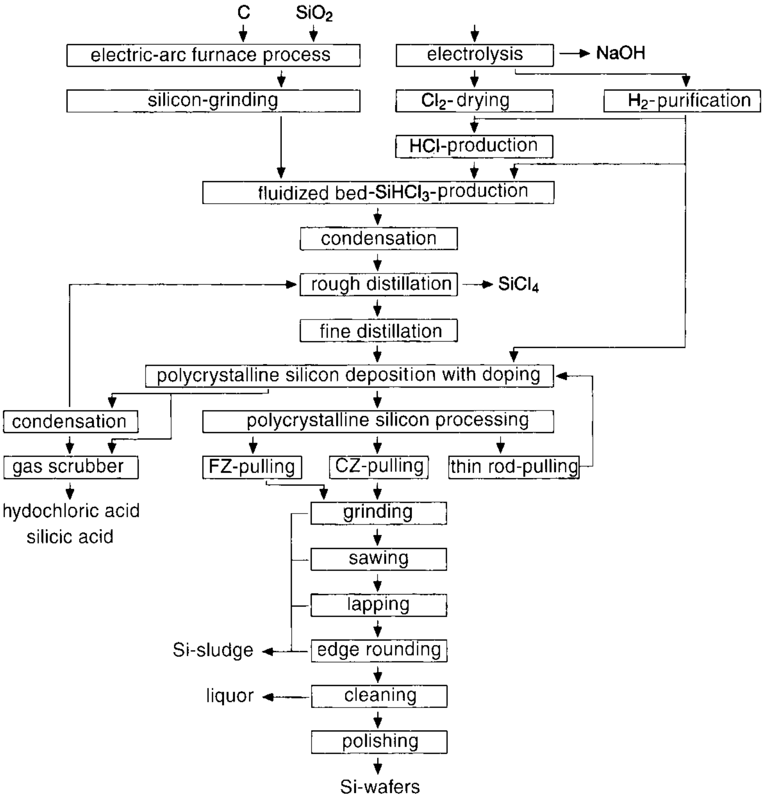


Fig. 3.4-2. Manufacturing process for silicon single crystals from silicon dioxide.

Polycrystalline silicon (polysilicon) is deposited, upon pyrolytic decomposition of $SiHCl_3$ at 1000°C on thin pure Si-rods ("slim rods"). The yield can be improved by carrying out the deposition in a H_2-containing atmosphere:

$$2\ SiHCl_3 \xrightarrow{H_2} Si + SiCl_4 + 2\ HCl$$

The $SiCl_4$ formed as a byproduct is flushed out and further processed to pyrogenic silica and silicic acid esters.

Since the BCl_3, which is always present in trace concentrations in highly purified $SiHCl_3$ through complex formation, is barely depleted under these conditions, a further purification step is necessary. A silicon is obtained from the pyrolysis with ca. 10^{13} boron atoms/mol silicon (ca. 1500 Ω cm, p-type), which is widely used as such.

In recent years the pyrolysis of silane (SiH_4) has been developed and operated industrially as an alternative to the trichlorosilane-pyrolysis process. The silane required as the starting material, is produced by reacting SiF_4 with sodium aluminum hydride:

$$3\ SiF_4 + 2\ Na_3AlH_6 \longrightarrow 3\ SiH_4 + 2\ Na_3AlF_6$$

The Na_3AlF_6 (cryolite) produced as a byproduct in this process is utilized in the aluminum industry and the SiH_4, after ultrapurification, is decomposed in a fluidized bed reactor to hydrogen and ultrapure silicon on nuclei of elemental silicon already present there (see Fig. 3.4-3):

$$SiH_4 \xrightarrow{800\ ^\circ C} Si + 2\ H_2$$

This process supplies ultrapure silicon in the form of ca. 1-3 mm, easily flowing and easily dosable beads. Compared with $SiHCl_3$-pyrolysis, this process is characterized by low process temperatures and non-corrosive byproducts, but, due to the spontaneous inflammability of SiH_4, it requires extensive safety measures. 1500 t of ultrapure silicon was produced by this process in 1997.

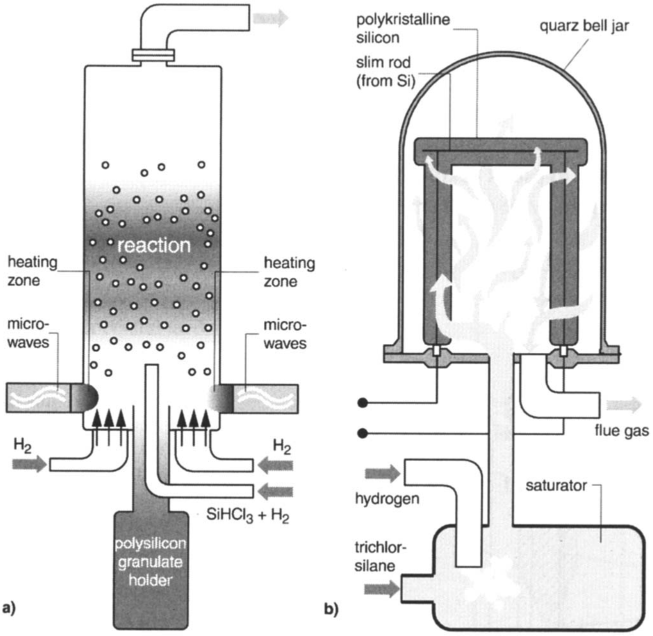


Fig. 3.4-3. Manufacture of ultrapure polysilicon from trichlorosilane and hydrogen.
a) production of silicon granules in the fluidized bed; b) in the deposition process the silicon grows on an electrically heated slim rod in a compact form

An additional industrially utilized alternative is the disproportionation of $SiHCl_3$ to SiH_4:

$$\begin{aligned}
2\,SiHCl_3 &\rightleftharpoons SiH_2Cl_2 + SiCl_4 \\
2\,SiH_2Cl_2 &\rightleftharpoons SiH_3Cl + SiHCl_3 \\
2\,SiH_3Cl &\rightleftharpoons SiH_4 + SiH_2Cl_2
\end{aligned}$$

The $SiCl_4$ formed as a byproduct, is returned to the $SiHCl_3$ synthesis process, thereby closing the cycle:

$$Si + 3\,SiCl_4 + 2\,H_2 \longrightarrow 4\,SiHCl_3$$

Decomposition of trichlorosilane accounts for ca. 78% of the installed capacity for ultrapure silicon production and decomposition of silane for ca. 22%.

The silicon single crystals required for the manufacture of semiconductor components can be obtained in two ways: either by pulling single crystals from the melt using the Czochralski process (CZ-pulling) or by crucible-free zone melting [float zone process (FZ-pulling)]. Cylindrical single crystals with diameters up to 300 mm are produced by CZ-pulling (see Fig. 3.4-4) and FZ-pulling (see Fig. 3.4-5). The ca. 0.4 mm thick silicon wafers utilized in the manufacture of electronic components are then cut from the single crystals using special sawing techniques such as multiple-wire saws or inner-hole saws.

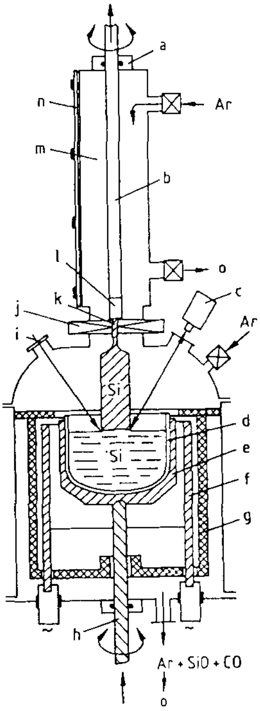


Fig. 3.4-4. Czochralski crystal pulling unit for the manufacture of silicon single crystals.
a) rotary transmission; b) shaft for attaching the crystal seed; c) optical control system; d) quartz crucible; e) graphite crucible; f) graphite heater; g) thermal insulation; h) rotatable shaft for crucible-attachment; i) inspection glass; j) separating disc; k) seed crystal; l) seed-crystal holder; m) receiver for single crystal; n) withdrawal door for single crystal; o) inert gas control valve

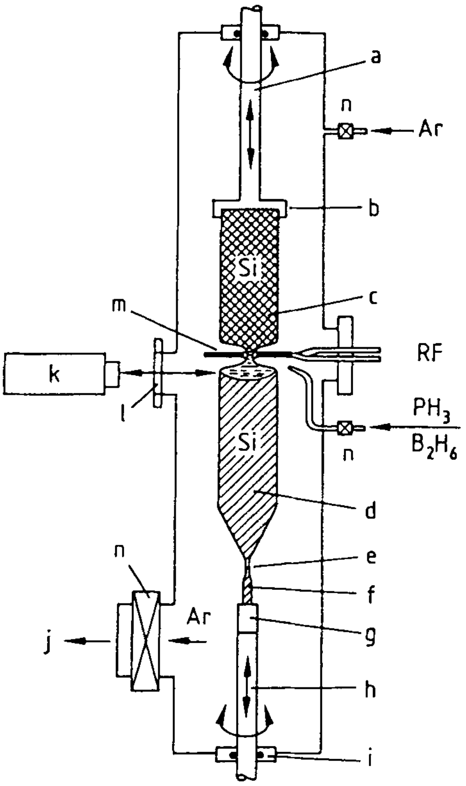


Fig. 3.4-5. Zone melting unit for the manufacture of silicon single crystals.
a) shaft for crystal feed;
b) receiver for the crystal;
c) polycrystalline crystal;
d) single crystal;
e) crystal charge; f) seed crystal; g) seed-crystal receiver; h) shaft for post-guiding the crystal; i) rotary transmission; j) vacuum pump; k) camera for optical control; l) inspection glass; m) induction heating; n) valve. Silicon for electronic components have to be doped with donors (P, As, Sb) or acceptors (B)

Silicon for semiconductor components must be doped with well-defined quantities of electron donors (phosphorus, arsenic or antimony) or electron donors (boron). This can be achieved by addition: before pulling from a crucible, during zone melting (introduction of PH_3) or by conversion of silicon into phosphorus by thermo-neutron bombardment.

Silicon for semiconductor components has to be doped with donors (P, As, Sb) or acceptors (B)

The increasing performance of electronic components has led to increasing density of integrated circuits in microchips for the computer industry. This results in a demand for the most perfect possible crystals and wafers with uniformly higher quality over long production runs, a precondition of which is a high degree of precision in material production, crystal growth, doping and mechanical finishing of the wafer.

Waste from the production and processing of single crystals, i.e. material outside the specification for ultrapure

Silicon for photovoltaic devices:

high purity demands, but not so high as for utilization in electronics silicon production and single crystal growth as well as the silicon residue from CZ-pulling in quartz crucibles, is utilized for the manufacture of polycrystalline silicon for photovoltaic devices. These materials are melted and by directional crystallization (Bridgman process) or casting converted into polycrystalline silicon blocks up to 240 kg in weight. These blocks are then split initially into silicon blocks with a quadratic cross-section, which is then cut by multiple-wire saws into 0.2-0.4 mm thick wafers with a 10 x 10 cm^2 to 15 x 15 cm^2 format. These wafers are ultimately utilized for the manufacture of solar cells. Ca. 10% of the ultrapure silicon produced is utilized for photovoltaic devices.

3.4.1.3 Silicon Applications

Silicon in the form of ferrosilicon is used in large quantities as a deoxidizing agent in steel manufacture. Silicon steel alloys are utilized as dynamo and transformer plates due to their soft magnetic properties, as machine tool steels, as spring steels and as corrosion resistant casting steels for chemical plant.

Applications of metallurgical grade (MG) Si:

- deoxidizing agent in steel production (ferrosilicon)
- constituent of aluminum alloys
- production of chlorosilanes and silicones

Metallurgical grade silicon plays an important rôle as an alloy constituent in aluminum alloys. Addition of 2-25% improve the casting properties of aluminum in the manufacture of castings for example for engine blocks or cylinder heads. The utilization of metallurgical grade silicon in the manufacture of methylchlorosilanes and the silicones produced therewith by direct synthesis (Rochow process) is covered in Chapter 4.

In semiconductor technology ultrapure silicon has largely supplanted germanium because it forms denser etchable protective layers (integrated circuits) and can operate at higher temperatures (150°C)

Ultrapure silicon has largely supplanted germanium in micro- and power-electronics (integrated circuits, microchips, thyristors, transistors, rectifiers etc.). Silicon accounts for more than 90% of the semiconductor market. There are a number of reasons for the dominance of silicon. Silicon forms stable SiO_2-protective layers, which can be removed by simple etch processes. This is the basis on which the etch and doping methods are developed, which permit an extremely high density of electronic components e.g. in microprocessors or memory chips. 64 MB memory chips can be currently produced in this way.

In addition silicon electronic components can be used at higher operating temperatures (ca. 150°C) than germanium components (ca. 75°C).

With solar cells on the basis of ultrapure silicon, sunlight can be directly converted into direct current electricity utilizing the photovoltaic effect. Silicon wafers from single crystal or cheaper directionally crystallized polycrystalline ultrapure silicon are utilized for solar cell manufacture. Solar cell electricity production efficiencies up to 18% are attained with single crystal material and up to 16% with polycrystalline material.

Single and polycrystalline silicon is utilized in solar cells for photovoltaic electricity production.

Solar cells on the basis of crystalline silicon attain electricity production efficiencies up to 18%

Solar cells of crystalline silicon have been used for years due to their proven reliability not only in space applications but also in terrestrial applications such as supplying energy to remote houses and villages, water pumps and electric fencing for fields, meteorological stations as well as for telecommunications and traffic control installations and form the basis of a burgeoning photovoltaic industry. Crystalline silicon solar cells provided more than 80% of the 120 MWp of photovoltaic electricity produced in 1997. The utilization of solar power is currently sensible in places far from an existing energy infrastructure or where, as is often the case in developing countries, a large-scale energy infrastructure does not exist and would require too high an investment to set up. To be able to compete on a wide scale with conventional energy supply in industrialized countries, solar electricity must become a factor of 20 cheaper. Great effort is therefore being devoted to rationalizing all the process steps, to using cheaper silicon sorts ("solar grade") and to developing special processes for the economic manufacture of "solar grade" silicon.

3.4.2 Inorganic Silicon Compounds

The most important industrially utilized silicon compounds include chlorosilanes, methylchlorosilanes, silicones, silicon dioxide and silicic acids in different forms, silicates in the form of glass, water glass, enamel frits, silicate fillers, zeolites, silicon carbide and silicon nitride.

This section will be confined to chlorosilanes and silicic acid esters. The other compounds will be dealt with, in accordance with their application sector, in other sections of this book.

Silicates and Silicate Products: Silicate products are utilized in a multiplicity of applications. They are dealt with under the following product groups:

5.1	Silicate Products
5.1.1	Glass
5.1.2	Alkali Silicates
5.1.3	Zeolites
5.2.3.1	Textile Glass Fibers
5.2.3.2	Mineral Fiber Insulation Materials
5.3.3	Cement
5.3.5	Coarse Ceramic Products for the Construction Industry
5.3.6	Expanded Products
5.5.4	Silicate Ceramic Materials
5.8.4.1	Silicate Fillers

Silicon dioxide and Silicic acids: Manufacture and applications in the filler sector, see Sections 5.8.3.1 and 5.8.4.1.

Silicon carbide: Manufacture and applications in the non-oxide ceramics sector, see Section 5.5.5.4.

Silicon carbide fibers and SiC-coated carbon fibers: see Section 5.2.3.6.

Silicon nitride Si_3N_4: Manufacture and applications in the non-oxide ceramic sector, see Section 5.5.5.4.5.

Metal silicides: Manufacture and applications in the metallic hard materials sector, see Section 5.6.9.

Silicon Halides

The most important industrially utilized silicon halides are silicon tetrachloride ($SiCl_4$) and trichlorosilane ($SiHCl_3$). Both are formed by the reaction of elemental silicon with HCl at temperatures above 300°C, $SiCl_4$ being increasingly favored with increasing reaction temperature:

$$Si + 4\,HCl \longrightarrow SiCl_4 + 2\,H_2$$
$$Si + 3\,HCl \longrightarrow SiHCl_3 + H_2$$

The direct reaction of elemental silicon or ferrosilicon (> 90% Si) with chlorine to $SiCl_4$ is also used industrially.

Since the 1960's processes starting from SiO_2 have been disclosed in the patent literature:

$$SiO_2 + 2\,C + Cl_2 \longrightarrow SiCl_4 + 2\,CO$$

The high temperatures necessary for this reaction are achieved by additionally burning carbon with oxygen or by resistive heating.

Additional heat is also necessary for the manufacture of $SiCl_4$ from SiC:

$$SiC + 2\,Cl_2 \longrightarrow SiCl_4 + C$$

$SiCl_4$ is the starting material for the synthesis of organofunctional silicon compounds and is utilized in the manufacture of highly dispersed SiO_2 (pyrogenic silicic acid) and for the silization of metallic objects.

Tetrafluorosilane (SiF4): see Section 1.7.1.3.2.

Hexafluorosilicic acid (H2SiF6): see Sections 1.7.1.3.2 and 1.7.1.3.3.

Hexafluorosilicates: see Section 1.7.1.3.6.

Silicic Acid Esters

Silicic acid esters, $Si(OR)_4$, are produced by the reaction of $SiCl_4$ with the appropriate alcohols. The most important representative of this group is tetraethoxysilane (tetraethyl orthosilicate) $Si(OC_2H_5)_4$, which is used directly, or after hydrolysis to ethylpolysilicates, as a binder for ceramic pastes, for inorganic zinc dust paints (corrosion protection), for the surface treatment of glass and for the modification of silicates. Silicic acid esters are further used for rendering polymer surfaces scratch-resistant.

Other organic silicon compounds are treated in Chapter 4, "Silicones".

References for Chapter 3.4: Silicon and its Inorganic Compounds

de Linde, J. P. *Future Supply and Demand of Silicon to the Chemical Industry*. in: Øye, H. A., Rong H. M., Nygaard, L., Schüssler, G., Tuset, J. Kr. 1998. Silicon for the Chemical Industry IV, 13 – 21, Trondheim, Norway.

de Linde, J. P. *Silicon Metal: an Era of Growth and Prosperity?* in: Øye, H. A., Rong H. M., Ceccaroly, B., Nygaard, L., Tuset, J. Kr. 1996. Silicon for the Chemical Industry III, 337 – 344, Trondheim, Norway.

de Linde, J. P. *The Outlook for Silicon Metal*, in: Øye, H. A., Rong H. M., Nygaard, L., Schüssler, G., Tuset, J. Kr. 1994. Silicon for the Chemical Industry II, 257 268, Trondheim, Norway.

Boardwine, C. E. *The State of the Silicon Metal Industry*, in: Øye, H. A., Rong H. M. 1992. Silicon for the Chemical Industry, 177 – 180, Trondheim, Norway.

Brenemann, W. C., Rawson, H. J. A. *Comparison of the Trichlorosilane and Silane Routes in the Purification of Metallurgical Grade Silicon to Semiconductor Quality* , in: Øye, H. A., Rong H. M., Nygaard, L., Schüssler, G., Tuset, J. Kr. 1998. Silicon for the Chemical Industry IV, 101 – 112, Trondheim, Norway.

Lobreyer, T., Hesse, K. *polysilicon: Different Processes, Quality Requirements and Market*, in Øye, H. A., Rong H. M., Nygaard, L., Schüssler, G., Tuset, J. Kr. 1998. Silicon for the Chemical Industry IV, 93 – 100. Trondheim, Norway.

Ullmann's Encyclopedia of Industrial Chemistry. 1993. 5. Ed., Vol. A 23, 721 – 748, VCH Verlagsgesellschaft, Weinheim.

Woditsch, P., Häßler, Ch. 1995. *Solarsilicium*. Nachr. Chem. Tech. Lab. **43**, 949 – 954.

Winnacker-Küchler, Chemische Technologie. 1986. Bd. 4, 224 – 229, Carl Hanser Verlag, München.

Brochures of the Firms Elkem and SKW over Ferrosilicon and Metallurgical Grade Silicon.

Brochures of the Firms Wacker-Siltronic and Sivento over Ultrapure Silicon, Trichlorosilane and Silicontetrachloride.

The Economics of Silicon and Ferro-Silicon. 1980. Roskill Information Services Ltd., 3rd Ed.

Rath, G., Wagner, J. 1976. Elektrowärme international, **34**, B81 – B84.

Siemens Zeitschrift, 55. Jahrgang, Jan./Febr. 1981.

CRU International, *Monitor Bulk Ferro Alloys*, Juni 1998.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1997. 4. Ed., Vol. 21, 1084pp, John Wiley & Sons, New York.

3.5 Manganese Compounds and Manganese

3.5.1 Manganese Compounds

3.5.1.1 Economic Importance

Industrially important manganese compounds:

MnO, $MnSO_4$, $MnCl_2$, $MnCO_3$
Mn_3O_4, Mn_2O_3
MnO_2
$KMnO_4$

The following manganese compounds are industrially important:

- manganese(II) salts such as the oxide, sulfate, chloride and carbonate
- manganese(II,III) oxide and manganese(III) oxide
- manganese(IV) oxide
- potassium permanganate ($KMnO_4$)

Statistics over the production capacity for the last 10 years are available for:

Worldwide capacities in 10^3 t/a:

MnO_2:	234.5
$KMnO_4$:	ca. 37

- manganese(IV) oxide:
  The current worldwide production capacity for manganese dioxide from electrochemical manufacture (EMD) is $194.5 \cdot 10^3$ t/a, that for chemical manufacture (CMD) $40 \cdot 10^3$ t/a. 34% of the worldwide EMD-production capacity is in Japan and 21% in the USA. The CMD-production capacities are much more strongly concentrated, 90% of the capacity being in the company Sedema in Belgium.

- Potassium permanganate:
  The current worldwide production is estimated to be $33 \cdot 10^3$ t/a to $41 \cdot 10^3$ t/a, the leading producer countries being the USA with $15 \cdot 10^3$ t/a and China with $7 \cdot 10^3$ t/a to $15 \cdot 10^3$ t/a.

3.5.1.2 Raw Materials

Manganese is the twelfth most abundant element in the Earth's crust. Manganese ores mainly consist of non-stoichiometric manganese(IV) oxides, manganese(II) carbonates and silicates

Manganese in the form of its compounds is widely distributed in nature. It is the twelfth most abundant element in the Earth's crust with ca. 1000 ppm. In soil, rock and sediments its content varies between 200 and 4500 ppm. It is also present in freshwater up to a concentration of several ppm, which has to be taken into account during its treatment.

Manganese ores mainly consist of (impure and non-stoichiometric) manganese(IV) oxides, manganese(II) carbonate and silicate. In addition, manganese is found in considerable quantities in the so-called manganese nodules on the seabed. The total quantity of these nodules is estimated to be 10^{12} t. Harvesting of these nodules would be particularly interesting for the copper, nickel and cobalt present, less so for the manganese content.

Research programs for the exploitation of manganese nodules were agreed by multinational company consortiums in the mid-1980's. Although industrially feasible, the exploitation of manganese nodules is not expected in the next few years.

The most important of the currently accessible manganese ores are:

Pyrolusite:	manganese(IV) oxide
Psilomelane	Ba- or K-containing manganese(IV) oxide hydrate
Cryptomelane	
Manganite:	manganese(III) oxide hydrate
Hausmanite:	manganese(II,III) oxide
Rhodochrosite:	manganese(II) carbonate

The most important deposits are sedimentary. The most important manganese ore-extracting countries with their certain reserves in 10^6 t, based on manganese content, are given in Table 3.5-1.

Most important manganese ore extracting countries:

South Africa
former States of USSR

World reserves: 680 · 10^6 t Mn-content

Table 3.5-1. Leading Manganese Ore Extracting Countries and their Reserves in 1995.

	10^6 t Mn-content	% World share
South Africa	370	54.4
former States of the USSR	142	20.9
Gabon	45	6.6
China	40	5.9
Australia	26	3.8
India	24	3.5
Other	33	4.9
World	680	100

Worldwide extraction of manganese ores in 1995:

7.3 · 10^3 t/a manganese-content

About 94% of the worldwide extracted manganese is used in the iron and steel industry. Parallel to the decline in steel production in the period 1989 to 1992, the worldwide extraction of manganese ores declined from 9.35 · 10^6 t/a (manganese content) in 1989 to 6.57 · 10^6 t/a in 1992 and since then has increased slowly again to 7.3 · 10^6 t/a in 1995. The manganese content of the ores is at least 39%.

3.5.1.3 Manufacture of Manganese Compounds

3.5.1.3.1 Manganese(II) Compounds

Manganese(II) oxide

MnO:

- by reduction of MnO_2 e.g. with carbon or methane

Manganese(II) oxide is manufactured by the reduction of naturally occurring manganese(IV) oxide-containing ores (e.g. pyrolusite) with carbon or methane:

$$MnO_2 + C \longrightarrow MnO + CO$$

at 400 to 1000°C. By appropriate control of the reaction, it is possible to remove some of the oxygen from the manganese(IV) oxide thermally, thereby saving reducing agent. The process is carried out in conventional units such as rotary tube or shaft furnaces. The manganese(II) oxide produced has to be cooled in an inert gas atmosphere to avoid reoxidation.

Manganese(II) sulfate

Manganese(II) sulfate is manufactured by reacting manganese(II) oxide or carbonate with sulfuric acid:

$MnSO_4$:

- from MnO and sulfuric acid, solution purification by precipitation of interfering cations

$$MnO + H_2SO_4 \longrightarrow MnSO_4 \cdot H_2O$$

Removal of interfering cations from the manganese(II) sulfate solution is necessary before the subsequent electrochemical production of manganese(IV) oxide (EMD) or manganese metal. Transition metal ions such as cobalt, nickel or copper and traces of arsenic are precipitated as their sulfides.

Manganese(II) sulfate is formed as a byproduct in the oxidation of organic compounds with manganese(IV) oxide in the presence of sulfuric acid, e.g. in the production of p-anisaldehyde. Aniline oxidation to p-benzoquinone is no longer industrially important in Western industrialized countries, so most $MnSO_4$ is produced from MnO or $MnCO_3$.

Manganese(II) chloride

Manganese(II) chloride is produced by the following processes:

$MnCl_2$:

- from MnO or $MnCO_3$ and hydrochloric acid
- from Mn and chlorine

- reaction of manganese(II) oxide or carbonate with hydrochloric acid:

$$MnO + 2\,HCl \longrightarrow MnCl_2 + H_2O$$

  Heavy metal impurities are precipitated from the resulting solution as carbonates by adding further manganese(II) carbonate.

- reaction of chlorine with manganese or ferromanganese:

$$Mn + Cl_2 \xrightarrow{>700\,^{\circ}C} MnCl_2$$

  The molten iron(III) chloride formed during ferromanganese chlorination can be removed by sublimation leaving manganese(II) chloride.

Manganese(II) carbonate

$MnCO_3$:
- from $MnSO_4$ and alkali (ammonium) carbonate or hydrogen carbonate

Manganese(II) carbonate occurs naturally as the mineral rhodochrosite. It is manufactured from manganese(II) sulfate by precipitation with alkali carbonates, or alkali or ammonium hydrogen carbonate:

$$MnSO_4 + 2\ NH_4HCO_3 \longrightarrow MnCO_3 + (NH_4)_2SO_4 + CO_2 + H_2O$$

After separation and washing, the manganese(II) carbonate obtained has to be dried at 120°C under inert gas to avoid oxidation.

3.5.1.3.2 Manganese(II,III) Oxide (Mn_3O_4) and Manganese(III) Oxide (Mn_2O_3)

Mn_3O_4:
- by heating MnO_2 at 950°C

Manganese(II,III) oxide (mineral: hausmannite) is formed by heating manganese oxides with other valency states in air at 890°C, e.g.:

$$3\ MnO_2 \xrightarrow{950\ °C} Mn_3O_4 + O_2$$

Mn_2O_3:
- by heating MnO_2 at 600 to 800°C

Manganese(III) oxide is formed when manganese(IV) oxide is heated at 600 to 800°C:

$$2\ MnO_2 \xrightarrow{600-800\ °C} Mn_2O_3 + 0.5\ O_2$$

3.5.1.3.3 Manganese(IV) Oxide

Manganese(IV) oxide exists in many modifications. The only modification which approaches a stoichiometric composition is β-MnO_2 (e.g. the mineral pyrolusite) and it is the least reactive. All the other modifications contain additional cations, such as Na^+, K^+, Ca^{2+} and Ba^{2+}, anions, such as OH^-, and water. The average valency state of the manganese is also less than 4 (down to 3.4). The almost amorphous γ-MnO_2 (the mineral nsutite) is particularly reactive.

Manganese(IV) oxide for utilization in dry batteries (γ- and ε-MnO_2) or as the starting material for ferrites (β-MnO_2) can be produced by a number of processes:

- by activation of manganese(IV) oxide minerals (pyrolusite)
- by reaction of manganese(IV) oxide minerals with nitrous gases
- by oxidation of manganese carbonate
- by electrochemical processes starting from manganese(II) salt solutions

Manufacture of manganese(IV) oxide by:

- activation of MnO_2
- reaction of MnO_2 minerals with nitrous gases
- oxidation of $MnCO_3$
- electrochemical oxidation of Mn(II) salts

The products from the second and third processes are known as chemical manganese dioxide (CMD), that from the fourth process as electrolytic manganese dioxide (EMD). Furthermore, a hydrated manganese(IV) oxide with a high alkali ion-concentration (δ-MnO_2) is formed as a byproduct in the oxidation of organic compounds with potassium permanganate, which is also known as manganite. δ-MnO_2 is, for example, a byproduct in the oxidation of o-toluenesulfonamide to o-sulfobenzoic acid imide (saccharin).

Activation of Manganese(IV) oxide Minerals

Manganese(IV) oxide minerals are thermally decomposed to manganese(III) oxide (see Section 3.5.1.3.2), which disproportionates when reacted with hot concentrated sulfuric acid to manganese(II) sulfate and battery active γ-MnO_2:

$$Mn_2O_3 + H_2SO_4 \longrightarrow \gamma\text{-}MnO_2 + MnSO_4 + H_2O$$

Activation of MnO_2 minerals:

1st step: thermal decomposition of manganese(IV) oxide minerals to Mn_2O_3

2nd step: dissolution of Mn_2O_3 in sulfuric acid forming $MnSO_4$ and manganese(IV) oxide, suitable for battery applications

The activated manganese(IV) oxide obtained contains some of the impurities of the manganese(IV) oxide minerals. In France, $2 \cdot 10^3$ t/a of manganese(IV) oxide for batteries are manufactured by this process.

Thermal Decomposition of $Mn(NO_3)_2$ to CMD

Dissolution of suspended mineral manganese(IV) oxide with nitrous gases as $Mn(NO_3)_2$ and precipitation of impurities. Then decomposition of $Mn(NO_3)_2$ to very pure β-MnO_2

Manganese(IV) oxide minerals react with nitrous gases as follows:

$$MnO_2 + N_2O_4 \longrightarrow Mn(NO_3)_2$$

$$Mn(NO_3)_2 \xrightarrow{140\,^{\circ}C} \beta\text{-}MnO_2 + N_2O_4$$

A slurry of finely ground manganese(IV) oxide minerals in water or dilute manganese(II) nitrate solution is treated with nitrous gases in absorption towers. Cu, Zn, Ni and Cd are also dissolved in addition to manganese. These accompanying ions are precipitated as carbonates or hydroxides by adding carbonates (sodium carbonate, manganese(II) carbonate) or calcium oxide. The thus purified manganese(II) nitrate solution is seeded with MnO_2 and decomposed at 140°C. The nitrous gases obtained upon decomposition are further utilized for dissolving manganese(IV) oxide minerals.

The thus obtained CMD with a purity of $\geq 99.5\%$ MnO_2 is currently produced in the USA (Chemetals) in quantities of $4 \cdot 10^3$ t/a for the production of ferrites, thermistors and as a starting material for other very pure manganese oxides.

Oxidation of Manganese(II) carbonate to CMD

Oxidation of $MnCO_3$ with oxygen to Mn(III,IV) oxide, which is further oxidized with sodium chlorate to ε,γ-manganese(IV) oxide

Manganese(II) carbonate is obtained using the process described in Section 3.5.1.3.1. The impurities are mainly precipitated and removed during the neutralization of the manganese(II) sulfate solution.

The oxidation of manganese(II) carbonate proceeds initially with air to a manganese(III,IV) oxide:

$$MnCO_3 \xrightarrow{O_2} MnO_{1.85} + CO_2$$

This is suspended in sulfuric acid and oxidized with sodium chlorate to ε,γ-manganese(IV) oxide:

$$MnO_{1.85} \xrightarrow{H_2SO_4/NaClO_3} MnO_2$$

The oxidation of $MnCO_3$ is the dominant CMD-production process quantitywise. Sedema in Belgium currently produces $20 \cdot 10^3$ t/a of battery-utilizable MnO_2 using this process.

Electrolytic Manganese(IV) oxide (EMD)

The electrochemical processes for manufacturing manganese(IV) oxide are currently the most important, industrially. Ca. $165 \cdot 10^3$ t of EMD was produced in 1986. A purified sulfuric acid manganese(II) sulfate solution is electrolyzed at 90 to 95°C on lead, titanium or graphite anodes at current densities of 0.5 to 1.2 A/dm^2, whereupon manganese(II) is oxidized to manganese(III):

Electrochemical oxidation of $MnSO_4$:

electrochemical oxidation of dissolved $MnSO_4$ to Mn(III), which disproportionates to Mn(IV) and Mn(II), MnO_2 deposits at the anode and is discontinuously removed

$$Mn^{2+} \longrightarrow Mn^{3+} + e^-$$

Hydrogen is produced at the cathode. The Mn(III)-ions formed disproportionate in a non-electrochemical reaction into Mn(IV)- and Mn(II)-ions:

$$2\,Mn^{3+} + 2\,H_2O \longrightarrow \varepsilon\text{-}MnO_2 + Mn^{2+} + 4\,H^+$$

The Mn(IV)-ions formed are deposited on the anode as very disordered ε-MnO_2, which still contains Mn(III)-ions.

The anodes are periodically taken out of the electrolysis unit and the 1 to 3 cm thick layers of ε-MnO_2 formed are mechanically removed, ground, washed and dried producing a product with 92% MnO_2 and 3 to 5% of water. The titanium and graphite anodes can then be reused. In order to maintain the Mn(II)-ion concentration in the electrolyte constant during the electrolysis, fresh electrolyte is added continuously or intermittently and the spent electrolyte taken off and used for manganese(II) oxide dissolution.

3.5.1.3.4 Potassium Permanganate

There are several processes for the manufacture of potassium permanganate. Ferromanganese or manganese(IV) oxide minerals can be used as a starting material.

$KMnO_4$ from ferromanganese:

- by electrochemical oxidation, electrolyte is potassium hydroxide

In the process utilizing ferromanganese as a starting material, the manganese metal is electrochemically oxidized to permanganate:

$$2\ KOH + 2\ Mn + 6\ H_2O \xrightarrow{e^-} 2\ KMnO_4 + 7\ H_2$$

Cast ferromanganese anodes and cooled copper tube cathodes are used with an anodic current density of 23 A/dm^2 at a bath temperature of 20°C. The process is very energy intensive and is currently only operated in small units in the former States of the USSR.

$KMnO_4$ from manganese(IV) oxide minerals:

oxidation of MnO_2 with air via Mn(V) to Mn(VI) (single or two stage), then electrochemical oxidation to Mn(VII)

Processes utilizing manganese(IV) oxide minerals have to pass through the following stages:

$$Mn(IV) \longrightarrow Mn(V) \longrightarrow Mn(VI) \longrightarrow Mn(VII)$$

The first two stages are accomplished with atmospheric oxidation, the third electrochemically.

Oxidation of manganese(IV) oxide minerals to manganese(VI) can be carried out in single- or two-step processes:

- *two-step roasting (melt) processes*:

  In the first step, a slurry of 50% potassium hydroxide solution with finely ground manganese dioxide, in a molar ratio MnO_2:KOH of 1:2.3 to 2.7, is oxidized with air at 390 to 420°C in a fast reaction to manganate(V):

  $$2\ MnO_2 + 6\ KOH + 0.5\ O_2 \longrightarrow 2\ K_3MnO_4 + 3\ H_2O$$

  Rotary tube furnaces or spray towers are used as reactors. In the second step, the manganate(V) formed is oxidized at 180 to 220°C to manganate(VI) after optional grinding:

  $$2\ K_3MnO_4 + H_2O + 0.5\ O_2 \longrightarrow 2\ K_2MnO_4 + 2\ KOH$$

  This reaction proceeds much more slowly than the first step. 3 to 4 h are necessary if intermediate grinding is employed. In the second step a specific partial pressure of water has to be maintained. The types of reactor used are similar to those used for the first step. The yield of manganate(VI) is 85 to 90%.

- *single-step liquid phase processes*:

In this process, a mixture of finely ground MnO_2 minerals and a 70 to 90% potassium hydroxide solution, in a MnO_2: KOH molar ratio of $\geq 1{:}5$, is oxidized with air at 200 to 260°C under a slightly increased pressure. The reaction time is 4 to 6 h. The manganate(VI) formed is crystallized out, the yield being 87 to 94%.

The potassium manganate(VI) produced is then electrochemically oxidized, continuously or discontinuously, to potassium permanganate:

$$K_2MnO_4 + H_2O \xrightarrow{e^-} KMnO_4 + KOH + 0.5\ H_2$$

The manganate(VI) is dissolved in a 12 to 16% potassium hydroxide solution. Depending upon the electrolysis process used, the manganate(VI)-concentration can be 50 to 60 g/L (continuous) or 200 to 220 g/L (discontinuous). Byproducts of manganate(VI)-production (gangue etc.) can be removed by filtration.

The electrochemical oxidation of manganese(VI) to potassium permanganate proceeds continuously or discontinuously on nickel or Monel anodes

Different types of cell are used industrially: mono- and bi-polar, with and without diaphragms. Nickel or Monel anodes and steel cathodes are used. In diaphragmless-processes cathodic reduction of the permanganate formed is suppressed by minimizing the cathode surface area by plastic coating such that the ratio of cathode to anode surface area is 1:150. The anodic current density is 0.5 to 15 A/dm^2 and the temperature is 40 to 60°C. The yield based on the electricity consumed is 60 to 90%. Depending upon the cell type, the permanganate formed crystallizes directly in the cell or in separate crystallizers. Recrystallization may be necessary. Potassium permanganate must be dried below 150°C, because it decomposes exothermically above 200°C.

During electrolysis, per mole of potassium permanganate one mole of potassium hydroxide is produced, which has to be recovered. This can be achieved, for example, by evaporating the mother liquor to 750 g KOH per L, whereupon the dissolved potassium manganate(VI) and calcium hydroxide crystallize out and are removed. The potassium hydroxide can be returned to the dissolution step. Other dissolved impurities from the ores, such as silicates or aluminates, have to be removed from the alkali cycle.

3.5.1.4 Applications of Manganese Compounds

Applications of Mn(II)-compounds:

- as an animal feedstuff and fertilizer additive
- in the ceramic industry
- in metallurgy
- as starting materials for other inorganic Mn-compounds
- in the manufacture of the fungicide "Maneb"

Manganese(II) oxide: is utilized as a starting material for manganese(II) salts, as an additive for fertilizers (in the USA: $20 \cdot 10^3$ t/a), as a nutritional supplement in animal feedstuffs and in the manufacture of oxide ceramic materials.

Manganese(II) sulfate: is utilized in the electrochemical manufacture of metallic manganese and EMD-MnO_2; and as a starting material for the manufacture of the manganese(II) salts of organic acids ("siccative"). It is also utilized in glass manufacture, as an additive in fertilizers and animal feedstuffs and in the production of the fungicide "Maneb" (manganese-ethene-1,2-bis-dithiocarbamate).

Manganese(II) chloride: is utilized in the manufacture of corrosion resistant magnesium alloys, for the coloring of bricks and in dry batteries.

Manganese(II) carbonate: is utilized in the manufacture of other magnesium(II) salts, ferrites and welding rods.

Mn_3O_4 and Mn_2O_3:

- utilized in the manufacture of magnetic materials and semiconductors

Mn_3O_4 and Mn_2O_3: are utilized as starting materials in the aluminothermic production of manganese. The pure oxides are utilized in the manufacture of magnetic materials and semiconductors.

MnO_2:

- mainly utilized in batteries and in the manufacture of ferrites

Manganese(IV) oxide: is utilized as a depolarizer in dry batteries, in the manufacture of ferrites, as an oxidizing agent in organic synthesis, as a crosslinking agent for polysulfide rubbers and as a component of oxidation catalysts.

$KMnO_4$:

- utilized as an oxidizing agent in organic synthesis
- for oxidation of impurities in a multitude of applications

Potassium permanganate: is utilized as an oxidizing agent in organic synthesis, for the removal of trace impurities (e.g. from lower aliphatic alcohols), for effluent and flue-gas purification, in the production of potable water, for the bleaching of inorganic and organic materials and for the purification of zinc sulfate solutions for zinc electrolysis.

3.5.2 Manganese - Electrochemical Manufacture, Importance and Applications

Manganese is mainly utilized as an alloy constituent in the steel industry as ferromanganese and silicomanganese. Pure metallic manganese is required in smaller quantities as an alloy constituent for copper, aluminum and special steels.

The production of a ca. 97% pure manganese metal by reduction of low iron content manganese ores with silicon, which is not dealt with here, is industrially less important than its electrochemical manufacture. The estimated worldwide production capacity for the electrolytic manufacture of manganese in 1988 was 77 · 10^3 t/a.

Production capacity for electrolytic manufacture of manganese:

- in 1988: ca. 77 · 10^3 t/a

$$MnSO_4 + H_2O \xrightarrow{e^-} Mn + H_2SO_4 + 0.5\ O_2$$

A highly purified manganese sulfate solution (see Section 3.5.1.3.1) serves as the electrolyte. The cathodic electrolyte contains 30 to 40 g/L manganese sulfate and 125 to 150 g/L ammonium sulfate and the manganese depleted anodic electrolyte 10 to 20 g/L manganese sulfate, 25 to 40 g/L sulfuric acid and 125 to 150 g/L ammonium sulfate. The anodes consist of lead alloyed with 1% silver, the cathodes of stainless steel or ®Hastelloy, type 316. The cells are operated at 35 to 40°C, a cathodic current density of 2 to 5.5 A/dm^2 and a potential of 5V. The yield based on electricity consumed is 50 to 70%.

Electrochemical manufacture of manganese:

- by electrolysis of highly purified $MnSO_4$ solution. Mn is deposited on the cathode and is discontinuously removed. In addition to oxygen, MnO_2 is formed at the anode in a side reaction

Cathodically, hydrogen ions are discharged as well as manganese ions. Anodically, oxygen is formed together with considerable quantities of manganese(IV) oxide, which precipitate and have to be removed.

When the manganese layers on the cathodes reach a thickness of 1 to 4 mm, the cathodes are removed and the manganese chipped off and dried. It has a purity of over 99.6% with oxygen and sulfur as its main impurities. Most of the other impurities are present in concentrations below 20 ppm.

References for Chapter 3.5: Manganese Compounds and Manganese

General Information:

Ullmann's Encyclopedia of Industrial Chemistry. 1990. 5. Ed., Vol. A 16, 77 – 143, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer. Encyclopedia of Chemical Technology. 1995. 4. Ed., Vol. 15, 963 – 1055, John Wiley & Sons, New York.

Commercial Information:

General

Jones, T. S. 9/1993. *Manganese 1992*, Annual report, U.S. Bureau of Mines, Washington, D. C.

Chemical Economics Handbook. 1997. *Manganese*, Stanford Research Institute, Menlo Park, California, USA.

MnO_2

Chemische Industrie. 1985. XXXVII, 835.

Japan Chemical Week. 1986. **27**, 8.

Chemical Week. Feb. 19, 1986., 42.

$MnSO_4$

Chemical Market Reporter. Feb. 15, 1988, 33.

Chemical Market Reporter, May 4, 1987, 50.

Industrial inorganic Chemistry
Karl Heinz Büchel, Hans-Heinrich Moretto & Peter Woditsch

4 Organo-Silicon Compounds

4.1 Industrially Important Organo-Silicon Compounds, Nomenclature

Industrially produced organo-silicon compounds include monomeric low molecular compounds, almost exclusively belonging to the class of silanes, and oligomers and polymeric compounds including oligomeric silanes, polysilanes, oligomeric silazanes, polysilazanes and particularly oligomeric siloxanes and polysiloxanes (silicones).

Industrially produced silicon compounds:
- low molecular silanes
- oligomer and polymer silanes

Specific IUPAC nomenclature for organo-silicon compounds has not yet been developed. According to general IUPAC rules, the tetravalent compounds should be known as silanes and their ligands should be listed in alphabetical order and hydrogen should not be mentioned.

Nomenclature:
- IUPAC: ligands in alphabetical order

In the technical literature the ligands are listed in the order organo-functional-, non-functional- and silicon-functional-ligands. The term organofunctional ligand means a unit containing a functional group linked to a carbon atom (e.g. -Cl, -NH_2, -C=C-).

- ligands in the industrial literature in the order:
  - organofunctional
  - non-functional
  - silicon-functional

So-called silicon-functional ligands are silicon atom-linked ligands which can be easily substituted (e.g. Si-Cl, Si-OR).

Compounds in which silicon forms part of a ring, are named silacyclo-compounds.

Compounds with several linked silicon atoms, optionally via heteroatoms, are named:

Si - Si	oligo- and poly-silanes
Si - C - Si	carbosilanes
Si - N - Si	silazanes
Si - O - Si	siloxanes

The trivial term silicones is widely used for industrially important siloxanes, their trivial nomenclature being given in Section 4.3.1.

4.2 Industrially Important Silanes

4.2.1 Organohalosilanes

Manufacture of methylchlorosilanes: from Si + CH_3Cl with a copper catalyst

Organohalosilanes are industrially produced by direct synthesis from silicon and alkyl- or aryl-halides in the presence of copper or silver catalysts using a process developed by Rochow and Müller in 1941/42.

$$\mathrm{Si} + 2\,\mathrm{RX} \xrightarrow[300-350\,^{\circ}\mathrm{C}]{\mathrm{Cu}} \mathrm{R_2SiX_2}$$

$$\mathrm{R} = \mathrm{CH_3}, \mathrm{C_6H_5}, \qquad \mathrm{X} = \mathrm{Cl}$$

The methylchlorosilanes are of paramount importance, ca. $1.2 \cdot 10^6$ t being produced worldwide in 1995. They are almost exclusively utilized as starting materials for the production of silicones.

Ethylchlorosilanes and the corresponding ethylsilicones are produced In the former States of the USSR.

Phenylsilanes are also accessible by direct synthesis from silicon and chlorobenzene, but they are currently predominantly produced by other processes.

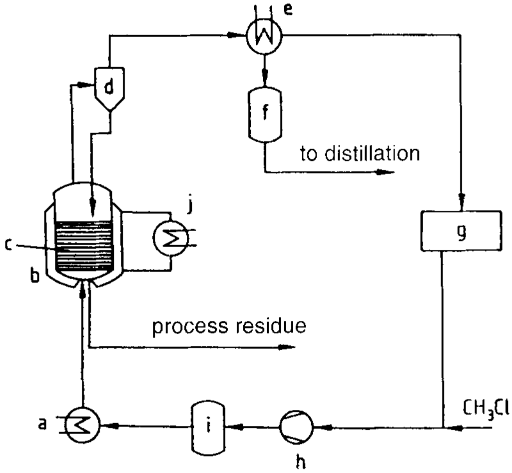


Fig. 4.2-1. Manufacture of methylchlorosilanes.
a) preheater; b) reactor; c) catalyst mixture; d) cyclone; e) heat exchanger; f) raw silane container; g) MeCl purification; h) compressor; i) MeCl container; j) heating/cooling system

The Industrial synthesis of methylchlorosilanes is a heterogeneous gas-solid-synthesis, in which silicon powder is reacted with an excess of chloromethane in the presence of finely divided copper or copper compounds in fluidized bed reactors at temperatures of ca. 350°C.

The rate of reaction and composition of the product mixture are considerably influenced by the purity of the silicon (> 99%) and by the addition of so-called promoters, for example metals, metal compounds, in particular zinc and tin, and non-metals or non-metal compounds, such as phosphorus compounds.

The composition of reaction mixture can be controlled by additives including Zn-, Sn- and P-compounds

The direct synthesis does not proceed exactly according to the reaction equation:

$$\mathrm{Si} + 2\,\mathrm{CH_3Cl} \longrightarrow \mathrm{(CH_3)_2SiCl_2}$$

but produces a product mixture, resulting from partial thermal cracking of chloromethane, consisting of methylchlorosilanes, hydrogen-containing methylchlorosilanes, oligomeric silanes and hydrocarbons.

Hydrogen-containing methylchlorosilanes are formed in addition to dimethyldichlorosilane as the main product

Table 4.2-1. Average Composition of a Raw Silane Mixture from Industrial Direct Synthesis.

$(CH_3)_2SiCl_2$	~ 85 - 90%
CH_3SiCl_3	~ 3 - 5%
$(CH_3)_3SiCl$	~ 3%
CH_3HSiCl_2	~ 1 - 4%
$(CH_3)_2HSiCl$	~ 0.5%
Oligosilanes	~ 3 - 5%
Hydrocarbons	~ 0.1%

After separation of the unreacted chloromethane, which after purification is returned to the synthesis, the raw silane mixture is worked up by distillation. The demands on the purity of the individual silanes are high, since they are almost exclusively used for producing polymeric silicones, whose properties are adversely influenced by impurities, particularly methyltrichlorosilane and dimethyldichlorosilane.

The product spectrum accessible by direct synthesis can be expanded by subsequent rearrangement reactions of the methyl- and chloro-substituents.

The product spectrum accessible by direct synthesis can be expanded by subsequent rearrangement reactions

For example dimethyldichlorosilane is produced from a mixture of trimethylchlorosilane and methyltrichlorosilane under the influence of Friedel-Crafts catalysts, such as e.g. $AlCl_3$.

$$(CH_3)_3SiCl + CH_3SiCl_3 \xrightarrow{\text{catalyst}} 2\,(CH_3)_2SiCl_2$$

Phenyl group-containing chlorosilanes are formed from chlorobenzene and hydrogen-containing silanes

The phenylchlorosilanes and phenylmethylchlorosilanes also required in the manufacture of silicones, currently only produced to a limited extent by direct synthesis, are preferably produced by the reaction of chlorobenzene with hydrogen-containing silanes according to the equations:

$$HSiCl_3 + C_6H_5Cl \xrightarrow{\sim 500\ °C} C_6H_5SiCl_3 + HCl$$

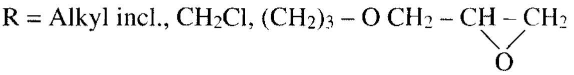
$$CH_3HSiCl_2 + C_6H_5Cl \xrightarrow{\sim 500\ °C} C_6H_5CH_3SiCl_2 + HCl$$

The reactions proceed without a catalyst and $SiCl_4$, CH_3SiCl_3 and benzene are produced as byproducts.

Chlorosilanes with longer alkyl-groups are produced by hydrosilation of alkenes

Chlorosilanes with longer alkyl groups can be obtained by hydrosilation in which an alkene is added to hydrogen-containing chlorosilanes, under the catalytic influence of transition metals (preferably Pt-compounds) e.g. according to the equation:

$$CH_3HSiCl_2 + H_2C{=}CH\text{-}R \xrightarrow{Pt} CH_3(CH_2CH_2R)SiCl_2$$

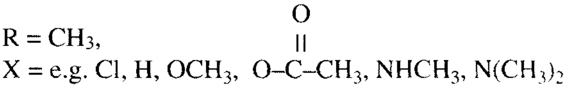


$$R = \text{Alkyl incl.},\ CH_2Cl,\ (CH_2)_3 - O\,CH_2 - \underset{\diagdown O \diagup}{CH - CH_2}$$

4.2.2 Industrially Important Silicon-functional Organo-Silanes

In organo-functional organo-silanes:

$$R_nSiX_{4\text{-}n}$$



$$R = CH_3,$$
$$X = \text{e.g. } Cl,\ H,\ OCH_3,\ O\text{–}\overset{\overset{O}{\|}}{C}\text{–}CH_3,\ NHCH_3,\ N(CH_3)_2$$

X is a group, which is nucleophilically substitutable or solvolytically cleavable by proton-active agents. Such groups include halogens and in particular hydrogen, acyl-, alkoxy-, carboxy-, amino- and amido-groups.

4.2.2.1 Organoalkoxysilanes

Organoalkoxysilanes are utilized in different application sectors, because under application conditions no acidic cleavage products are formed as is the case with organohalosilanes. In addition intentional hydrolysis, e.g. in silicone chemistry, is generally easier to control than in the case of organohalosilanes.

Organoalkoxysilanes can be produced by the stoichiometric reaction of organohalosilanes with alcohols according to the following equation:

Organoalkoxysilanes are formed by reacting organohalosilanes with alcohols with the simultaneous removal of hydrogen chloride

$$R_nSiCl_{4-n} + (4-n)\ R'OH \longrightarrow R_nSi(OR')_{4-n} + (4-n)\ HCl$$

$$R = H, \text{Alkyl, Aryl} \quad R' = \text{incl. } CH_3, C_2H_5$$

A prerequisite for a high degree of reaction is removal of the hydrogen chloride formed either by addition of a base such as tertiary amines or by appropriate control of the reaction.

Industrially this is attained by the utilization of a reaction distillation column, in which a silane-alcohol mixture is fed into the upper one third.

Hydrogen chloride escapes with a small amount of silanes via a condenser during the reaction of chlorosilanes with the rising alcohol vapor in countercurrent forming the heavier volatile alkoxysilanes. The alkoxysilanes produced as a sump product are continually run off. The stoichiometric nature of this process means that the silicon-functional groups such as Si-H and organo-functional groups such as $Si\text{-}CH_2CH_2Cl$ or $Si\text{-}CH_2CH_2CN$ survive intact.

Chloro-alkanes are formed as byproducts due to the reaction of alcohol with hydrogen chloride.

Alkoxysilanes, including tetraalkoxysilanes, are utilized as crosslinking components in silicone rubbers, in the manufacture of silicone resins, as adhesion promoters with special organofunctional groups e.g. glass fiber layers, in the formulation of corrosion-resistant paints and in mold construction.

4.2.2.2 Acyloxysilanes

Acyloxysilanes:

$R_nSi(OCOR')_{4-n}$
R = H, Alkyl, Aryl   R' = e.g. CH_3, $HC{=}CH_2$

have a considerable industrial importance as crosslinking agents in silicone sealants.

The important methyl-, ethyl- and vinyl-triacetoxysilanes are, industrially, exclusively produced by reacting chlorosilanes with acetic anhydride or acetic acid according to the following equations:

Triacyloxysilanes are utilized as crosslinking agents in silicone sealants. Produced by reacting alkyltrichlorosilanes with acetic acid or acetic anhydride

$$RSiCl_3 + 3\ Ac_2O \longrightarrow RSi(OAc)_3 + 3\ AcCl$$

$$RSiCl_3 + 3\ HOAc \longrightarrow RSi(OAc)_3 + 3\ HCl$$

R = CH_3, C_2H_5, $HC{=}CH_2$; Ac = $COCH_3$

Variants with acetic acid are currently preferred, the reaction being carried out analogously to the above-described continuous production of alkoxysilanes.

4.2.2.3 Oximino- and Aminoxy-Silanes

Oximino- and aminoxy-silanes utilized as crosslinking agents in silicone sealants in which acidic reaction products are undesirable

In the crosslinking of silicone sealants with acyloxysilanes, acids are formed as cleavage products. These are often, for different reasons, undesirable in technical applications. Therefore crosslinking agents with neutral cleavage products have acquired increasing importance.

The industrially important methyltributanonoximinosilane is formed by reacting methyltrichlorosilane with 2-butanonoxime:

$$CH_3SiCl_3 + 6\ HOx \xrightarrow{< 60\ ^\circ C} CH_3Si(Ox)_3 + 3\ HOx \cdot HCl$$
Ox = $O{-}N{=}C(CH_3)C_2H_5$

In reactions in solvent, the oxime acts both as a reaction partner and as a base. The oxime-hydrogen chloride-adduct can be isolated as a separate liquid phase. By reacting with bases the oxime can be recovered and returned to the process.

Aminoxysilanes can be obtained by reacting hydroxylamines with chlorosilanes, whereby the hydrogen chloride formed is removed by non-reacting bases.

4.2.2.4 Amidosilanes, Silazanes

Amidosilanes are important as neutral reacting crosslinking agents for silicone sealants (e.g. methyltriacetamidosilane) as well as agents for introducing protective groups in the synthesis of pharmaceuticals (particularly urea-derivatives such as N,N'-bistrimethylsilylurea).

Amidosilanes utilized as neutral reacting crosslinking agents for silicone sealants and as agents for the introduction of protective groups in the synthesis of pharmaceuticals

Amidosilanes can be synthesized with the aid of very strong bases, such as sodium methoxide, from chlorosilanes and organic amides.

N,N'-bistrimethylsilylurea is obtained by reacting hexamethyldisilazane with urea:

N,N'-bistrimethylsilylurea is obtained by reacting hexamethyldisilazane with urea

$$(CH_3)_3NH + H_2NCONH_2 \longrightarrow [(CH_3)_3SiNH]_2CO + NH_3$$

The most important representative of the silazanes is hexamethyldisilazane, which is utilized in large quantities for the introduction of protective groups in the synthesis of pharmaceuticals and for hydrophobizing fillers, in particular silicates. It can be easily produced by reacting trimethylchlorosilane with ammonia:

Hexamethyldisilazane utilized as an agent for introducing protective groups and as a hydrophobizing agent for fillers. Formed by reacting trimethylchlorosilane with ammonia

$$2(CH_3)_3SiCl + 3\ NH_3 \longrightarrow [(CH_3)_3Si]_2NH + 2\ NH_4Cl$$

Transesterification of methyltrichlorosilane, optionally as a mixture with alkyldichlorosilane and ammonia, produces processable intermediates for the manufacture of ceramic fibers and coatings.

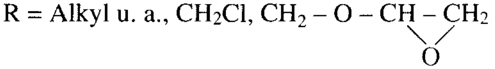
4.2.2.5 Organohydrogensilanes

Organohydrogensilanes are formed as byproducts in the direct synthesis of dimethyldichlorosilane (see Section 4.2.1) and are important in the manufacture of hydrogen-containing siloxanes and organofunctional silanes (see

Organohydrogensilanes utilized as precursors for organofunctional silanes and hydrogen-containing siloxanes

Section 4.2.3) by adding unsaturated compounds in the presence of platinum catalysts, so-called hydrosilation:

$$\text{-Si-H} + H_2C{=}CH\text{-R} \xrightarrow{\text{Pt-compound}} \text{-Si-}CH_2\text{-}CH_2\text{-R}$$



$$R = \text{Alkyl u. a.}, CH_2Cl, CH_2 - O - \underbrace{CH - CH_2}_{O}$$

Trichlorosilane is particularly important as a starting material for organofunctional silanes. It is produced by reacting silicon with hydrogen chloride.

$$Si + 3\ HCl \longrightarrow HSiCl_3 + H_2$$

Trichlorosilane is, furthermore, an important starting material in the manufacture of ultrapure silicon (see Section 3.4.1.2.2).

4.2.3 Organofunctional Silanes

Organofunctional silanes have silicon atoms linked to an organic group with reactive groups

In organofunctional silanes the silicon atom is linked to an organic group with reactive groups. They can be represented by the following general formula:

$X_nR_{3-n}Si\text{-}R'\text{-}Y$
X = silicon functional group
R = Alkyl, R' = Alkenyl
Y = functional group, e.g. Cl, NH_2, CN, SH, $HC{=}CH_2$

4.2.3.1 Alkenylsilanes

Vinylsilanes utilized as crosslinking agent for polymers and as functionalizing agents for silicones

Vinylsilanes are utilized as crosslinking agents for polymers and as functionalizing agents for silicones.

Industrially they are produced in a continuous process by reacting hydrogen-containing silanes with ethyne in the presence of platinum compounds in high boiling point solvents.

$$\mathrm{X_nR_{3-n}\,SiH + HC{\equiv}CH \xrightarrow{\text{Pt-compound}} X_nR_{3-n}\,Si\text{-}CH{=}CH_2}$$
$$\mathrm{X = Cl \qquad R = Alkyl}$$

The addition of a second silane to the vinylsilane formed can be suppressed by using an ethyne excess and removing the vinylsilane from the reaction mixture.

Allylsilanes are also produced in large quantities, for example, by dehydrohalogenation of chloropropylsilanes.

4.2.3.2 Halo-organosilanes

Silanes with organohalo-groups are utilized as precursors in the production of other organofunctional silanes and as a component of different reactive silane products. Manufacture of the most important representative from this product group, chloropropyltrichlorosilane, is carried out continuously by reacting trichlorosilane with chloropropene ("allylchloride") in the presence of platinum catalysts. Alkoxysilanes, which are produced from the chlorosilanes, are often used in practice.

4.2.3.3 Organoaminosilanes

The most important representative of this group is aminopropyltriethoxysilane, which is used as an adhesion promoter and component of silicone products, is manufactured by the addition of acrylonitrile to trichlorosilane producing cyano-ethyltrichlorosilane:

Organoaminosilane utilized as adhesion promoters also in composite materials

$$\mathrm{Cl_3SiH + H_2C{=}CHCN \longrightarrow Cl_3SiCH_2CH_2CN}$$

which is ethoxylated and then reduced to aminopropyltriethoxysilane, according to the following equation:

$$\mathrm{Cl_3SiCH_2CH_2CN \xrightarrow[\text{2) } H_2/Ni]{\text{1) } CH_3CH_2OH} (CH_3CH_2O)_3SiCH_2CH_2CH_2NH_2}$$

Aminopropyltriethoxysilane produced by adding allylamine to trichlorosilane with subsequent ethoxylation and reduction

Alternatively allylamine can be added to triethoxysilane in the presence of rhodium catalysts, according to the following equation:

$$(CH_3CH_2O)_3SiH + CH_2{=}CHCH_2NH_2 \longrightarrow (CH_3CH_2O)_3SiCH_2CH_2CH_2NH_2$$

4.2.3.4 Organomercaptosilanes, Organosulfidosilanes

Silanes with organically linked sulfur are important adhesion promoters and vulcanization additives in the rubber industry

Silanes with organically linked sulfur are very important adhesion promoters and crosslinking agents in the rubber industry and to a lesser extent in the polymer industry. Whereas bis(triethoxysilyl-propyl)sulfide, for example, can be easily produced by reacting chloropropyltriethoxysilane with alkali sulfides:

$$2\ (CH_3CH_2O)_3Si(CH_2)_3Cl + Na_2S \longrightarrow [(CH_3CH_2O)_3Si(CH_2)_3]_2S + 2\ NaCl$$

the mercapto-compounds are best produced by reaction with thiourea.

$$(CH_3CH_2O)_3Si(CH_2)_3Cl + S{=}C(NH_2)_2 \longrightarrow (CH_3CH_2O)_3Si(CH_2)_3S^+C(NH_2)_2Cl^-$$

$$\xrightarrow[-\,(H_2N)_2C\,=\,NH_2^+Cl^-]{+\,NH_3} (CH_3CH_2O)_3Si(CH_2)_3SH$$

4.2.3.5 Other Organofunctional Silanes

Organofunctional silanes with hydroxy-, epoxy-, acryl-, ester- and carboxy-functions are produced industrially. They are in particular utilized as additives for modification of polymers and for functionalizing silicones for different application sectors. Most of these compounds are manufactured by the addition of appropriately functionalized alkenyl-compounds.

References for Chapter 4.1 and 4.2: Organo-Silicon Compounds

Ullmann's Encyclopedia of Industrial Chemistry. 1993. 5. Ed., *Silicon Compounds*,Vol. A 24, 21 – 56, VCH Verlagsgesellschaft, Weinheim.

Patai, S., Pappaport, Z. (Ed.) 1989. The Chemistry of Organic Silicon Compounds, 2 Vols. , Wiley Interscience, Chichester.

Clarke, M. P. 1989. Journal of Organometallic Chemistry, 165 – 222.

Cory, J. Y., Corey, E. R., Gaspar, P. P. (Ed.) 1988. *Silicon Chemistry*, Ellis Horwood, Sussex.

Rochow, E. G. 1987. Silicon and Silicones, Springer Verlag, Berlin.

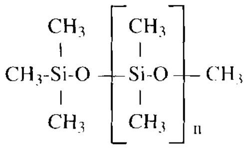
Pawlenko, S. 1986. Organosilicon Chemistry, W. de Gruyter, Berlin.

4.3 Silicones

4.3.1 Structure and Properties, Nomenclature

Silicones are compounds, in which silicon atoms, each linked to one or more organic groups via carbon-silicon bonds, are linked to one another through oxygen atoms to produce straight chain, branched or crosslinked oligomeric or polymeric molecules. The simplest silicones are the α,ω-bis-trimethylsiloxypolydimethylsiloxanes (see formula in the marginal notes).

Silicones = polyorganosiloxanes; e.g.



$$CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-O-\left[\underset{CH_3}{\overset{CH_3}{Si}}-O\right]_n-CH_3$$

n: up to 14 000 known

The name silicones, due to the American chemist Kipping, also extends to formulations of these polymers with other materials.

According to IUPAC Rule D-6.2, the term siloxane is the name for oxygen compounds of the general formula $H_3Si-[O-SiH_2]_n-O-SiH_3$, in which hydrogen can be replaced by organic groups. According to the provisional rules (Pure Appl. Chem. **53**, 2283-2302 (1981) for the designation of organic macromolecules, polydimethylsiloxane should be named catena-poly(dimethyl-silicon)-μ-oxo. The international non-proprietary name for dimethylsiloxanes in cosmetic and pharmaceutical formulations is dimeticon.

Poly(organosiloxanes) are built up of a combination of the units $R_3SiO_{1/2}$ (monofunctional, abbreviated to M), $R_2SiO_{2/2}$ (difunctional, abbreviated to D), $RSiO_{3/2}$ (trifunctional, abbreviated to T) and $SiO_{4/2}$ (tetrafunctional, abbreviated to Q). A combination of these units is chemically possible in the widest sense. In industrial silicone products R is generally a methyl- or a phenyl-group.

Silicone units and silanes from which they are formed:

		silicone unit	
R_3SiCl	⇒	$R_3SiO_{1/2}$	= M
R_2SiCl_2	⇒	$R_2SiO_{2/2}$	= D
$RSiCl_3$	⇒	$RSiO_{3/2}$	= T
$SiCl_4$	⇒	$SiO_{4/2}$	= Q

R is generally methyl or phenyl

The combination of monofunctional units, M, with difunctional units, D, leads to straight chain polyorganosiloxanes terminated by M-units. Combination of only difunctional units produces cyclic polyorgano-siloxanes or open-chain polydiorganosiloxanes with, for example, a hydroxy or alkoxy end group. The incorporation of T- and optionally also Q-units leads to branched polyorganosiloxanes.

Siloxanes with M-, D-, T- and Q-units can be produced from mono-, di- and trichloro-silanes and silicon tetrachloride by hydrolysis or catalytic rearrangement of siloxanes or siloxane-mixtures with the appropriate units.

Combinations of these functional units lead to a multiplicity of products

These diverse polyorganosiloxanes form the basis of industrial silicone products. The product spectrum is vast, manufacturers with a complete product range having in excess of 1000 individual products in their program.

Properties of silicones:

- stable to:
  - high temperatures;
  - oxidation;
  - weather
- hydrophobic
- depending upon structure:
  - foam destabilizing
  - foam stabilizing
- abhesive
- electrically non-conducting
- gas- and vapor-permeable
- physical properties change little with temperature
- physiologically compatible

Silicone products are, as a result of their exceptional properties, widely utilized as raw materials and additives. They are stable at high temperatures and are resistant to oxidation and weathering.

They are also surface active hydrophobic substances which, depending upon their structure, can exhibit either defoaming (as defoaming agents) or foam-stabilizing (as foam stabilizers) properties.

They are abhesive, electrically non-conducting and exhibit high gas and vapor permeability. Their physical properties also vary little with temperature.

4.3.2 Economic Importance

Silicone production in 1995 estimated as similar to production of organochlorosilanes:

World: $1.3 \cdot 10^6$ t/a

Silicones have been produced industrially since the 1940's. In 1995 there were thirteen silicone producers in Western industrialized countries. Silicone production can be estimated on the basis of the production of organochlorosilanes, the starting materials for silicone production, taking into account that ca. 0.5 kg of methylsiloxane is produced from 1 kg of dimethyldichlorosilane. Since silicone products generally contain additives, such as fillers, or are combined with other components, the total quantity of silicone products should be similar to the quantity of (organochloro)silanes produced. This was $1.3 \cdot 10^6$ t in 1995 with a value of ca. $8 \cdot 10^9$ DEM. The largest markets are the USA with a ca. 40% share, followed by the EU and Japan. Virtually the whole worldwide capacity for silicones is to be found in these countries. Notable is the historical and current high rate of growth of the silicone industry.

Most important silicone products:

- silicone oils and associated products
- silicone rubbers (elastomers)
- silicone resins

In Western Europe silicone elastomers dominate with over 40%, followed by silicone oils and associated products with ca. 30% and silicone resins with ca. 10% of the total consumption, whereas in the USA silicone elastomers account for only 25% and silicone oils and their associated products for ca. 65% of the total consumption.

Silicones are relatively independent of crude oil

Since silicones are only partly based on petrochemical products, they are not affected to the same extent as many purely organic products by crude oil shortages and price increases. However, manufacture of the raw material silicon is very energy intensive.

4.3.3 Linear and Cyclic Polyorganosiloxanes

4.3.3.1 Manufacture

Oligomers of linear and cyclic dimethylsiloxanes by hydrolysis or methanolysis of dimethyldichlorosilane

The industrial production of linear and cyclic polyorganosiloxanes is generally carried out by the reaction of organodichlorosilanes with water. The oligomeric siloxanes produced by the hydrolysis are either converted into cyclic siloxanes (e.g. octamethylcyclotetrasiloxane) or to a equilibrium distribution of high molecular weight polysiloxanes by polymerization or polycondensation processes. An exception in the production of oligomeric siloxanes is the synthesis of cyclic and linear oligomeric dimethylsiloxanes from dimethyldichlorosilane using the methanolysis process This has increased in importance in recent years.

By far the most important chlorosilanes, on the basis of quantity (> 90%), utilized in industrial hydrolysis and methanolysis, are the methylchlorosilanes, followed by the chlorosilanes, which contain exclusively, or in combination with methyl groups, the ligands H-, C_6H_5-, CH_2=CH- and CF_3-CH_2-CH_2- linked to a silicon atom.

4.3.3.2 Hydrolysis

The complete hydrolysis of dimethyldichlorosilane leads to an oligomeric mixture, consisting of cyclic dimethylsiloxanes:

$$n\,(CH_3)_2SiCl_2 + n\,H_2O \longrightarrow [(CH_3)_2SiO]_n + 2n\,HCl$$
$$n = 3, 4, 5\,...$$

and dimethylsiloxanes with hydroxyl-end groups:

$$m\,(CH_3)_2SiCl_2 + (m+1)\,H_2O \longrightarrow HO[(CH_3)_2SiO]_mH + 2m\,HCl$$
$$m = 4\,...\, > 100$$

Linear siloxanes with SiCl-end groups produced by hydrolysis of chlorosilanes with a sub-stoichiometric quantity of water

The hydrolysis can, by addition of a deficit of water to the chlorosilanes ("reverse hydrolysis"), also be so carried out that linear dimethylsiloxanes with SiCl-end groups are obtained.

$$(n+2)\,(CH_3)_2SiCl_2 + (n+1)\,H_2O \longrightarrow Cl(CH_3)_2SiO[(CH_3)_2SiO]_nSi(CH_3)_2Cl + 2\,(n+1)\,HCl$$

Industrially: hydrolysis carried out continuously either in the liquid phase or with steam in the gas phase

Complete hydrolysis (excess water) is either carried out continuously in the liquid phase with ca. 25% hydrochloric acid or in the gas phase at temperatures of ca. 100°C. In liquid phase hydrolysis cyclic or linear dimethylsiloxane oligomers are produced in the ratio 1: 1 to 1:2 depending upon process design. Ca. 30% hydrochloric is produced as a byproduct in liquid phase hydrolysis. This can be recycled in the Rochow process by using it to produce chloromethane by reacting it with methanol, thereby recycling the chlorine.

The ratio by weight of cyclic to linear dimethylsiloxanes, as well as the chain length of the linear oligomers, can be varied within wide limits by varying the hydrolysis conditions.

Adjustment of the hydrolysis conditions to favor cyclic or linear dimethylsiloxane oligomers is important in that in silicone production the manufacture of high molecular weight polydimethylsiloxanes occurs both by equilibration polymerization and by polycondensation. In polymerization cyclic oligomers are the main starting materials, whereas in polycondensation oligomers with hydroxy-end groups are the main starting materials. These processes are dealt with in Sections 4.3.3.5 and 4.3.3.6.

Hydrolysis process with appropriate silane mixtures produces organosiloxanes with silicon- and organo-functional groups.

Hydrolysis with a combination of appropriate silane mixtures produces organosiloxanes with both silicon functional groups, such as -SiH, and organo-functional groups, such as vinyl.

The result of hydrolysis can to a limited extent be influenced by the addition of organic solvents. These methods are particularly important in obtaining silanol-group-containing siloxanes, which are particularly important in the chemistry of silicone resins.

In Fig. 4.3-1 a flow schema is shown for the industrial continuous hydrolysis of dimethyldichlorosilane.

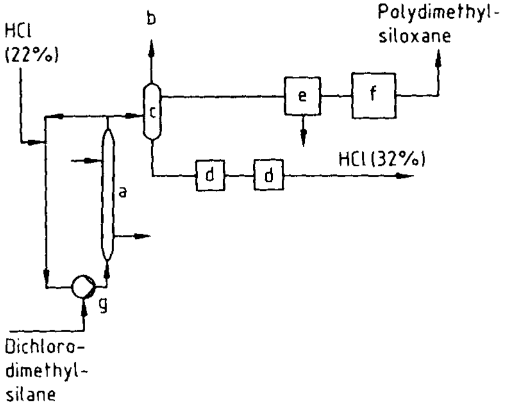


Fig. 4.3-1. Continuous hydrolysis of dimethyldichlorosilane.
a) cooler; b) flue gas; c) phase separation; d) settling vessel; e) water separation; f) neutralization; g) pump.

4.3.3.3 Methanolysis

In recent years an industrial process for siloxane production from dimethyldichlorosilane has been introduced, which is known as "methanolysis" and which enables the recycling of the chlorine contained in the methylchlorosilanes as chloromethane, which is utilized in the direct synthesis process.

Reaction of dimethyldichlorosilane with an excess of methanol leads to siloxane oligomers and chloromethane, which can be utilized in the direct synthesis process (chlorine recycling)

The reaction taking place, depends upon whether the siloxane required is linear with a hydroxy-end group or is cyclic, according to the following equations:

$$n\ (CH_3)_2SiCl_2 + 2n\ CH_3OH \longrightarrow HO\text{-}[(CH_3)_2SiO]_nH \\ 2n\ CH_3Cl + (n\text{-}1)\ H_2O$$

$$n\ (CH_3)_2SiCl_2 + 2n\ CH_3OH \longrightarrow [(CH_3)_2SiO]_n \\ + 2n\ CH_3Cl + n\ H_2O$$

Dimethylether is produced as a byproduct, which depending upon the process variant is removed or converted into chloromethane by reaction with hydrochloric acid in the main reactor.

4.3.3.4 Cyclization

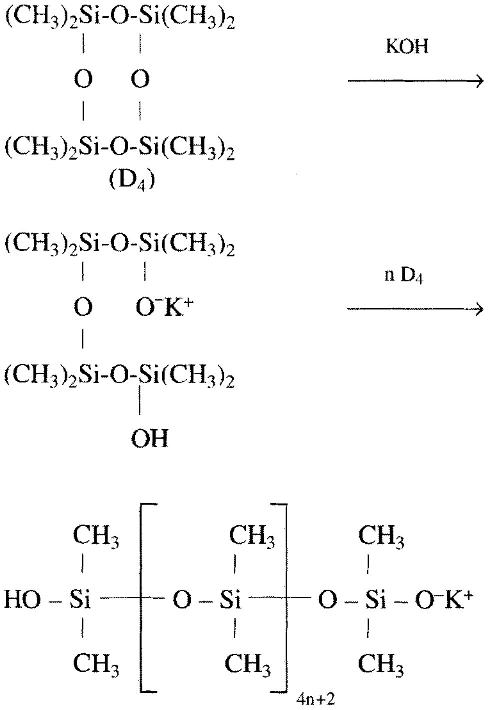
Reaction of siloxane oligomers with potassium hydroxide results in easy to separate and easily purifiable octamethylcyclotetrasiloxane

The manufacture of pure octamethylcyclotetrasiloxane (D_4) and decamethylcyclopentasiloxane (D_5), which are either marketed as such or are used as raw materials in the production of polydimethylsiloxanes by the polymerization process, is carried out by the so-called cyclization process. The hydrolysis or methanolysis product is heated in a suspension of potassium hydroxide and an inert liquid (e.g. mineral oil). This method is chosen to hinder polymerization of the siloxanes to highly viscous liquids. The potassium hydroxide catalyzes an equilibrium reaction in which the Si-O-Si bonds are cleaved and newly made (equilibration). Since in this process the, by comparison with the linear siloxanes, more volatile octamethylcyclotetrasiloxane and decamethylcyclopenta-siloxane are continuously distilled off from the siloxane mixture, the equilibrium is shifted in a direction favoring the desired cyclic siloxane thereby enabling all of the siloxane to be so converted.

4.3.3.5 Polymerization

Polymerization of cyclosiloxane oligomers by equilibration both anionically (with bases) and cationically (acids)

Equilibrium polymerization, which can be anionic or cationic, is utilized to convert cyclic organosiloxanes into polydiorganosiloxane polymer chains. In the chemical industry octamethylcyclotetrasiloxane is preferred as such, or as a mixture with other siloxanes for chain termination and/or production of copolymers for specific applications. Particularly industrially important is anionic polymerization with basic catalysts such as alkali hydroxides, whereby the activity falls off in the order Cs > Rb > K > Na > Li. KOH is most frequently used e.g. as a suspension in octamethylcyclotetrasiloxane at 140°C, the catalyst being active from a concentration of several ppm. According to the assumed mechanism of this catalytic process, potassium siloxanolate is initially formed, which leads to cleavage of the Si-O-Si bonds and chain formation:



In the presence of water, the siloxanolate forms hydroxyl-group terminated polydimethylsiloxane chains with the liberation of KOH, whereupon the molecular weight distribution, depending upon the amount of water added, approximates to a Poisson-distribution. If a mixture of trimethylsiloxy-containing siloxanes (e.g. MD_nM) is added, permethylated polymethylsiloxanes (the so-called M-oils) with different chain lengths are obtained depending upon the amount of added regulator. When the polymerization is complete, the polymer is stabilized by neutralizing the alkaline catalyst.

Cationic polymerization of cyclosiloxanes is carried out with strong protonic or Lewis acids. Industrially important catalysts of this type are perfluoroalkanesulfonic acids and/or sulfuric acid (H_2SO_4).

In another form of acid catalysis, the polymerization of cyclic and linear siloxanes is carried out on acidic solids such as ion exchange resins and acid-activated silicates (heterogeneous catalysis). This process also leads to an equilibrium mixture of linear polysiloxanes with a content of cyclic siloxanes of ca. 15 to 18 % by weight, the latter being separated distillatively and returned to the polymerization process.

4.3.3.6 Polycondensation

Linear short-chain dimethylsiloxanes (oligomers) from hydrolysis or methanolysis processes are utilized as the starting material in the manufacture of polydiorganosiloxanes by polycondensation. If linear siloxane polymers are required, dimethyldichlorosilane with a high purity is necessary, since distillative processing of siloxane diols is not possible due to their tendency to condensation (with cleavage of water).

Treatment of linear siloxane oligomers with OH-end groups with acid catalysts ($PNCl_2$) does not result in equilibrating high molecular weight siloxanes

Polycondensation is carried out discontinuously or continuously in the presence of acid catalysts, preferably phosphonitrile chlorides $(PNCl_2)_x$. The removal of the water liberated in the polycondensation process is achieved by operating the process at high temperatures and optionally under vacuum. Deactivation of the catalyst is carried out with ammonia or amines. The polycondensation process of siloxane diols, which is preferably carried out under vacuum, is very fast (see Fig. 4.3-2, curve a). In a combined polycondensation/polymerization process in the presence of chain length regulating short chain $R(CH_3)_2SiO$-terminated dimethylsiloxanes (R = CH_3, $CHCH_2$, H) the viscosity passes through a clear maximum (see Fig. 4.3-2, curve b), whereas using short chain siloxanols this viscosity maximum is avoided (see Fig. 4.3-2, curve c).

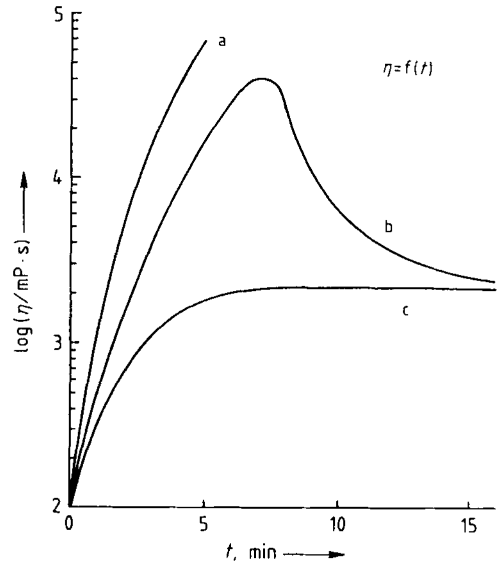


Fig. 4.3-2. Polycondensation - equilibration of siloxane diols.

4.3.3.7 Industrial Realization of Polymerization

For small product quantities, the polymerization of siloxane oligomers is carried out in mixing tanks in which batches of up to 15 t can be easily managed.

The manufacture of larger quantities is realized in continuous plants. The technical requirements of the process steps:

- purification and drying of the starting materials
- dosing of catalyst and regulator
- realization of equilibrium /condensation
- neutralization
- oligomer separation/return of distillate

depend upon the type of polymerization reaction. The different technical requirements for different types of polymerization reaction are summarized in Table 4.3-1.

Table 4.3-1. Characteristics of Polymerization Processes.

starting material	D_4	D_4	$HO[(CHO_3)_2SiO]_nH$
catalyst	KOH	H_2SO_4	$(PNCl_2)_x$
quantity of catalyst, ppm	5 - 20	100 - 1000	5 - 200
polymerization time, min	10 - 90	15 - 30	10 - 20
reaction temperature, °C	140 - 180	20 - 160	40 - 160
non-volatile oligomers, %	13	13	2
modifier	MD_xM	MD_xM	$[R(CH_3)_2Si]_2NH$
neutralization agent	H_3PO_4	ZnO Na_2CO_3	amines

Taking into account the variants, essentially five plant concepts for carrying out the polymerization have prevailed:

- single stage polymerization units
- mixing tank cascade
- screw extruder
- cell reactor (mixing reactor with spiral mixers which approximate to a plug flow)
- solid-(catalyst)-reactor

4.3.4 Manufacture of Branched Polysiloxanes

Manufacture of branched poly(organosiloxanes):

1st step: hydrolysis of a (chloro)organosilane mixture, which contain (trichloro)organosilanes

2nd step: thermal polycondensation

The hydrolysis can be so controlled, that organosiloxanes are produced containing Cl-Si- and RO-Si-groups in addition to HO-Si-groups, which not only react with each other to silicone resins, but also react e.g. with HO-functional poly(ethers)

Branched poly(organosiloxanes) such as those, for example, in silicone resins are manufactured using processes basically similar to those used for linear poly(organosiloxanes), but with the difference that the (organo)chlorosilane mixture contains (organo)trichlorosilane as a branching component. The first reaction step, hydrolysis, can be performed in two ways namely by adding excess chlorosilanes to the water or by addition of water to the chlorosilane mixture. In the latter case the reaction can be so controlled that the hydrolysis is incomplete, forming siloxanes with chlorosiloxy-end groups. Siloxanes with silicon-functional chloro-groups are important starting materials for copolymer compounds, for example with polyethers (see Section 4.4.5), which are utilized, for example, as polyurethane foam-stabilizers.

Direct hydrolysis, which is fundamental to the production of some silicone resins, is mainly used with methyltrichlorsilane, phenyltrichlorosilane and diphenyldichlorosilane and is generally carried out in the presence of a solvent, such as xylene, and higher alcohols, such as n-butanol. The resulting cohydrolysate has silanol and alkoxysilyl-groups and can be converted into the final product by thermal polycondensation. The silicon-functional hydroxy- and alkoxy-groups can, however, also react with hydroxy-functional organic resins, such as polyesters or alkyd resins with the cleavage of water or alcohol to form combination resins. (see Sections 4.4.4 and 4.4.5).

In indirect hydrolysis/alcoholysis the silicone resin synthesis can be so controlled that only alkoxysilyl-end groups are formed. These resins are very stable to yellowing due to further condensation reactions.

In indirect hydrolysis hydrogen chloride is formed which can be further utilized. Direct hydrolysis is generally carried out discontinuously in mixing tanks. Indirect hydrolysis/alcoholysis can be carried out in a continuous process. The industrial plant used is similar to that for the production of alkoxysilanes (see Section 4.2.2.1).

4.4 Industrial Silicone Products

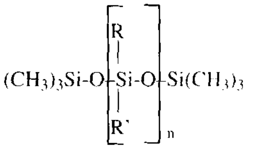
A wide range of silicone products are manufactured using the above-mentioned processes. The most important product groups are described below on the basis of their chemical structure, their properties and their applications.

4.4.1 Silicone Oils

The industrially most important silicone oils are the α,ω-trimethylsilylpoly(dimethylsiloxanes), although these polymers can also contain methylphenylsiloxy- or diphenylsiloxy-groups.

Silicon oils are manufactured in a viscosity range of 5 mPa · s to 1 · 10^6 mPa · s. They exhibit setting points between -60 and -35°C.

Silicone oils:



$$(CH_3)_3Si\text{-}O\left[\begin{array}{c}R\\|\\Si\text{-}O\\|\\R'\end{array}\right]_n Si(CH_3)_3$$

R/R': CH_3/CH_3
CH_3/C_6H_5
C_6H_5/C_6H_5

By comparison with mineral oils, the viscosity of silicone oils changes little with temperature. They are thermally stable, low volatility products (from ca. 50 mPa · s) exhibiting long term stability at 150°C in air and even up

Viscosities: from 1 to 10^6 mPa · s

Properties of silicone oils:

- setting point: -60 to -35°C
- little change in viscosity with
- temperature
- thermal stability
- high specific resistance
- low surface tension
- lack of smell or taste
- physiologically inert

to 200°C in closed systems. Phenyl-group-containing silicone oils exhibit even lower setting points and an even better thermal stability. Silicone oils have good electrical insulating properties, the specific resistance of a polydimethylsiloxane oil being 10^{14} Ωcm and the dielectric breakdown strength being 14 kV/mm. Furthermore, they exhibit low surface tensions: ca. 21 mN/m (for medium viscosity silicone oils). They also lack smell and taste and are virtually physiologically inert, feeding experiments with animals and skin tests not resulting in irritation or pathological symptoms. However, in eyes they cause slight, mainly conjunctival, irritation.

Silicone oils are utilized in many sectors in which they must fulfill different requirements. Their good thermal stability and the weak dependence of their properties upon temperature lead to their utilization as heat transfer media, lubricants, hydraulic oils, brake fluids and dielectric fluids e.g. transformer oils.

Application of silicone oils:

- heat transfer medium
- lubricant
- hydraulic oils
- transformer oils
- brake fluids
- flow improver
- gloss improver
- defoaming agent
- mold release agent
- constituent of skin creams and protective polishes

Their low surface tension results in their utilization in the paint industry as flow, gloss and finish improvers. Silicone oil additives enable effect paints to be formulated such as moire effect paints. Their surface and interfacial activity enables their use as defoaming agents and as foam stabilizers for poly(urethane) foams.

Pure silicone oils are used as defoaming agents in the crude oil industry. In the rubber and plastics industry they are widely used as mold release agents. Their physiological inertness enables their use in cosmetics and pharmaceuticals. Their water repelling (hydrophobic) properties result in skin creams with good protective properties. The hydrophobic properties of silicone oils endow car, furniture and protective polishes with protective and non-aggressive properties.

4.4.2 Products Manufactured from Silicone Oils

Silicone Oil Emulsions

Applications of silicone oil emulsions:

- mold release agent
- deaeration agent
- hydrophobizing and bulking of fabrics
- defoaming agent (silica-containing emulsions)

Aqueous silicone oil emulsions can be produced from silicone oils, as well as polymethylhydrogensiloxanes with trimethylsiloxy-end groups, in the viscosity range around 1000 mPa · s in emulsifying equipment (e.g. baffle-ring pumps), preferably using nonionic emulsifiers. The amounts of silicone oil in these emulsions vary between 3 and 50 % by weight. Silicone emulsions are used as mold release and deaeration agents in the manufacture of tires. Emulsions with H-Si-group-containing silicones are utilized in large quantities in the textile industry for hydrophobizing and bulking fabrics.

If polydimethylsiloxane oils are emulsified together with fine particulate solids, e.g. fumed silicas, very effective defoaming agents are obtained for aqueous media e.g. for the production of aqueous organic polymer dispersions and for dyeing processes in the textile industry.

Silicone Pastes and Greases

Silicone oils can be converted into pastes by incorporating large quantities of highly dispersed silicas or calcium or lithium soaps. These products are utilized as sealants and specialty greases.

Silicone pastes and greases are produced by the incorporation of highly dispersed silica or Ca- or Li-soaps in silicone oils

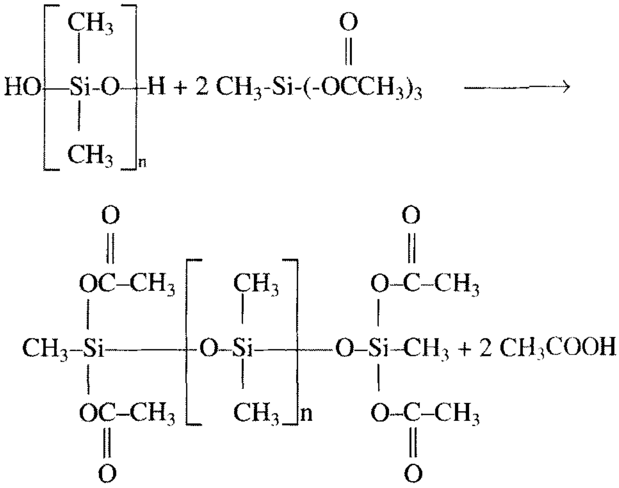
4.4.3 Silicone Rubbers

Among the silicone rubbers there are different product groups which differ in their crosslinking mechanism and application areas.

4.4.3.1 Room Temperature Vulcanizable Single Component Silicone Rubbers

The reaction of a polydimethylsiloxane with hydroxy-groups at either end with an excess of a silane, which contains, as does methyltriacetoxysilane, at least three hydrolyzable silicon-functional groups (a crosslinking agent), results in a silicone polymer with at least four silicon-functional end groups:

Mixing of polydiorganosiloxanes with hydroxy-groups at both ends with crosslinking agents in the presence of fillers and Sn-organic compounds as condensation catalyst leads to room temperature vulcanized silicone rubber



$$HO\left[\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}\text{-}O\right]_n H + 2\,CH_3\text{-}Si(\text{-}O\overset{\displaystyle O}{\overset{\|}{C}}CH_3)_3 \longrightarrow$$

$$CH_3\text{-}\overset{\displaystyle \overset{O}{\overset{\|}{OC}}\text{-}CH_3}{\underset{\displaystyle \underset{\|}{\underset{O}{OC}}\text{-}CH_3}{Si}}\left[\text{-}O\text{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}\right]_n\text{-}O\text{-}\overset{\displaystyle O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3}{\underset{\displaystyle O\text{-}\underset{\|}{\underset{O}{C}}\text{-}CH_3}{Si}}\text{-}CH_3 + 2\,CH_3COOH$$

The resulting silicon-functional polysiloxane is stable during storage in the absence of moisture e.g. after filling in a cartouche.

Such silicone polymers are stable upon storage in the absence of moisture, e.g. filled in a closed cartouche,. Upon contact with moisture, e.g. humidity in the air, hydroxy-groups are formed at either end of the polymer chain with the cleavage of acetic acid, which react, e.g. with one another with the cleavage of water, to form a crosslinked rubber-elastic material. The crosslinking starts at the surface and then spreads into the mass as the moisture diffuses into the polymer.

Hardening takes place with humidity in the air

In industrial single component silicone rubbers, polydimethylsiloxanes with viscosities between 5000 and 100 000 mPa · s and hydroxy-groups at either end are utilized. To improve the mechanical properties of the resulting silicone rubber, strengthening fillers, preferably highly dispersed silicas, have to added in concentrations of 1 to 10 % by weight as well as non-strengthening extender fillers. Up to 30% of a trimethylsiloxy-terminated polydimethylsiloxane and silicone oil are generally incorporated to obtain sufficiently soft silicone rubber after crosslinking. Tin compounds, such as dibutyl-tin dilaurate, are generally incorporated to accelerate the condensation hardening process.

The silane crosslinker contains a wide range of reactive substituents e.g. amino-, carboxy-, carbonamido-, oxime-, carbonyl- and/or alkoxy-groups.

Most of the room temperature crosslinking silicone rubbers are utilized for filling holes in buildings e.g. so-called expanding fillers, in the sanitary sector and for the sealing of windows.

In addition they are used as adhesives for heat-resistant bonds and, for example, formed in place gaskets, particularly in the automobile industry.

Applications of single component room temperature vulcanizable silicone rubbers:

- as a filler in:
  - the building sector
  - the sanitary sector
  - the installation of windows
  - the automobile industry
- as an adhesive for heat-resistant bonds and for gaskets

4.4.3.2 Two Component Room Temperature Vulcanizable Silicone Rubbers

With room temperature vulcanizable two-component silicone rubbers, the polymer and the crosslinking component are mixed immediately before application. Two different crosslinking systems are used, one based on polycondensation and the other on polymer addition.

Room temperature hardenable two-component rubbers are crosslinkable by:

- polycondensation
- polyaddition

In polycondensation systems, a poly(dimethylsiloxane) with hydroxy end-groups at either end and a viscosity of 10^3 to 10^5 mPa · s is crosslinked with tetraalkoxysilanes, e.g. tetraethoxysilane, in the presence of a condensation-accelerating tin compound e.g. dibutyltin dilaurate. Since this hardening, in contrast with single component products, is not dependent upon water diffusion through the hardening mass, thick layers of such rubber systems can be crosslinked quickly and homogeneously.

By polycondensation of crosslinkable systems consisting of:

- poly(dimethylsiloxane) with HO-groups at either end
- tetraalkoxysilanes or their condensation products with as crosslinking agent
- filler
- organo-tin compounds as condensation catalysts

In polyaddition systems the polymer component is a poly(dimethylsiloxane) with methylvinylsiloxy, trimethylsiloxy or vinyldimethylsiloxy end-groups with a similar viscosity to that of the condensation system. These polymers are crosslinked by a hydrosilation reaction with a poly(dimethyl-siloxane), containing on average three methylhydrogensiloxy-groups and having trimethylsiloxy or dimethylhydrogen-siloxy end-groups. Platinum or platinum compounds, such as hexachloroplatinic acid, are used in ppm quantities as the catalyst, the reactions being carried out at room temperature or at temperatures just above room temperature.

By polyaddtion crosslinking systems consisting of:

- vinyl group-containing poly(methylsiloxanes)
- H-Si-group containing poly(methylsiloxanes)
- filler
- Pt-compounds as catalysts

Room temperature hardenable vulcanizable two-component silicone rubbers are usually formulated as flowable materials. They contain reinforcing and extending fillers. Their flowability means that they are able to flow into the finest details of the to be reproduced item. After vulcanization a negative mold is produced, which is complete reproduction of the original in all its detail. This technology is utilized for the restoring and duplication of

Applications of flowable room temperature vulcanizing two-component systems:

- molding compound
- for encapsulating electronic components

external structured concrete components. In the furniture industry replicas of ornamental pieces of furniture are produced and in dentistry precise reproduction of the configuration of teeth is possible using this technology. In the electronic industry their flowability combined with good insulating properties are utilized for encapsulating electronic components and for the manufacture of so-called cable-end pieces.

Filler free material, optionally in solution, for coating paper and plastic foil

Filler-free formulations of two-component silicone rubbers crosslinkable by condensation or addition are utilized, with or without added solvent, for the coating of papers and plastic foil, optionally as an aqueous emulsion, e.g. for strippable paper for self-adhesive labels or packaging foil for bitumen. Vulcanization is carried out at high temperature (100 to 180°C), to attain as short hardening times as possible.

4.4.3.3 Hot Vulcanizable Peroxide Crosslinkable Silicone Rubbers

Hot vulcanizable silicone rubber:

- consists of long-chain, generally vinyl-group-containing poly(methylsiloxanes) and fillers
- crosslinked with organic peroxides
- produced with kneaders, rollers, extruders

Hot vulcanizable silicone rubbers generally consist of very long chain (with viscosities of 10^6 to 10^7 mPa · s), usually vinylmethylsiloxy-group-containing, poly(dimethyl-siloxanes) with trimethylsiloxy- and/or vinyldimethylsiloxy end-groups and highly dispersed fumed silica (10 to 35% by weight). The vinyl-group content, which, in addition to crosslinking over two methyl groups, has a considerable influence on the crosslink density, is very low (< 1% with respect to moles of siloxy-groups). Crosslinking proceeds with organic peroxides, e.g. dicumylperoxide or dichloro-benzoyl-peroxide, at high temperatures, hence the term "hot vulcanizable silicone rubber". The silicone rubber mixtures are produced by the kneaders, rollers and extruders typical of the rubber industry.

4.4.3.4 Hot Vulcanizable Addition Crosslinkable Silicone Rubbers

Hot vulcanizable silicone rubber can also be crosslinked by a hydrosilation reaction. Advantage: no decomposition products of the organic peroxides

Instead of using organic peroxides, the crosslinking of very long (10^6 to 10^7 mPa · s) vinyl-containing high temperature vulcanizable silicone rubber can be realized by a platinum-catalyzed hydrosilation reaction in which a poly(dimethyl-siloxane) has to be added with at least three methyl-hydrogensiloxy-groups. They have the advantage over peroxide systems, that no potentially interfering organic peroxide-decomposition products are formed. They are generally two component systems.

Liquid silicone rubber can be processed in injection molding machines used for plastics

Hot vulcanizable two-component silicone rubber is also available as so-called **l**iquid **s**ilicone **r**ubber (LSR). Such viscosities enable their use in injection molding machines, similar to those used in the plastics industry. Their lower viscosity compared with conventional hot temperature vulcanizable rubbers is realized in part by the use of shorter polymer chain lengths and in part by using highly dispersed reinforcing silica filler whose surface has undergone trimethylsilation e.g. by utilizing hexamethyl-disilazane in the compounder process for LSR-manufacture. In this way the excellent mechanical and thermal properties are retained. A pump and a blender, generally a static blender, are directly linked to the injection molding machine.

Processing of hot vulcanizable silicone rubber by:

- molding to molded articles in presses
- extrusion to tubing and cables in extruders

Hot vulcanizable silicone rubbers can be processed in two different ways: either by extrusion to tubing or cables or by molding to so-called molded articles, such as, for example, crankshaft seals and membranes. High viscosity hot vulcanizable silicone rubber is exclusively used for extrusion articles, extruders typically used in the rubber industry being employed in their processing.

Molded articles, which are conventionally manufactured in presses with high viscosity rubber, have been recently manufactured in automatic injection molding machines using liquid silicone rubber, which enables the mass production of silicone rubber components with short cycle times.

Applications of hot vulcanizable silicone rubbers:

- silicone rubber tubing in medical and food technology
- cables in the electrical industry

Silicone rubber tubes are mainly utilized in medical and food technology e.g. as transfusion tubes, catheters and tubes for drinks. Silicone cables are widely utilized in applications for which thermal stability, weathering resistance and chemical resistance are required e.g. baking ovens, hot lamps and electrical connections for electrical motors and transformers.

- molded articles such as seals e.g. in the automobile industry
- implants in the human body
- contact lenses

Molded silicone rubber articles are generally utilized as seals for equipment running at high temperatures e.g. as crankshaft seals in internal combustion engines or for headlight and gearbox seals.

The physiological inertness of silicone rubber enables its use in the manufacture and packaging of food, as disposable articles for contact with the body e.g. teats for babies and implants in the human body, e.g. artificial heart valves.

Furthermore, optically clear silicone rubber can be used for contact lenses, which are characterized, as are all silicone rubbers, by high oxygen permeability, but whose surfaces have to be hydrophilic.

4.4.3.5 Properties of Silicone Rubber

Properties of silicone rubbers:

- continuously stressable at temperatures between -50 and +180°C
- rubber mechanical properties hardly change between room temperature and 180°C:
  - Shore A hardnesses between 30 and 70
  - tensile strengths up to 12 N/mm^2
  - tear strengths up to 45 N/mm
- good insulation characteristics
- can be made electrically conducting by incorporating carbon black
- can be made difficultly flammable and self-extinguishing by adding platinum compounds

Silicone rubbers exhibit excellent thermal stability. Their elastomeric properties hardly change during several thousand hours in hot air at 180°C. Their elastomeric properties at 180°C are almost as good as those at room temperature. Silicone rubbers thus exhibit markedly better tensile strength at 180 to 200°C than organic rubbers, which exhibit 2 to 3 times the tensile strength of silicone rubbers at room temperature. The best elastomeric properties are achieved with hot vulcanizable silicone rubbers. Shore A hardnesses between 30 and 70 can be realized, tensile strengths up to 12 N/mm^2 and tear strengths (according to ASTM 624B) of up to 45 N/mm.

The hardness of silicone rubbers remains almost unchanged down to ca. -50°C and therefore they are usable in the unusually wide temperature range of -50 to +180°C (for short periods up to 300°C). Silicone rubbers exhibit good stability to chemicals except for strong acids, strong bases and chlorine. Under normal environmental conditions they are stable for decades.

Silicone rubbers are good insulators both at room temperature and at high temperatures and can be made electrically conducting by the incorporation of carbon black. They can be made flame-resistant and self-extinguishing by adding platinum compounds. In the case of fire, hardly any toxic products are formed, except for carbon oxides, non-conducting layers of silicon dioxide being formed with a certain mechanical strength. After burning, silicone rubber cables are still insulating to a certain extent.

4.4.4 Silicone Resins

Silicone resins are branched polysiloxanes. Hardening proceeds by polycondensation at high temperatures

Pure silicone resins are poly(organosiloxanes) with a high proportion of branching, i.e. tri-or tetra-functional siloxy groups together with di- and optionally mono-functional siloxy groups.

Liquid silicone resins or silicone resin solutions are generally fully condensed by several hours heating (curing) at 180 to 250°C to a highly crosslinked solid. The thermally stable coatings formed, particularly if phenyl groups are present, do not lose their transparency, gloss or elasticity even at 200 to 250°C. They are also hydrophobic and extremely weather resistant.

Silicone resin coatings are:

- thermally stable
- resistant to weathering
- hydrophobic

Methyl- and methylphenyl-resins are utilized as raw materials for paints, binders and in building preservation. In the electrical industry they are utilized as electrically insulating lacquers (wire enamel) and for the bonding of glass filaments or mica insulating materials. Special meltable solid resins are flow aids in the injection molding of porcelain matrices.

Applications of silicone resins as:

- paint raw materials and binders for e.g.:
  - electrically insulating lacquers
  - corrosion protection lacquers, pigmented with zinc dust
  - thermally stable stoving enamels for decorative purposes
  - coil coating of metallic plates for facades
  - rendering plastic scratch resistant

Corrosion protection-stoving enamels are produced upon pigmentation with zinc dust. These are utilized for the enameling of components which operate at high temperatures e.g. metal chimneys.

Silicone-polyester combination resins, which belong to the group of silicone polymers, are raw materials for thermally stable stoving enamels. They are utilized for decorative lacquers for cooking and roasting utensils, for heating apparatuses and cookers. Very weather resistant stoving lacquers based on silicone combination resins are also known e.g. for coil coating of metallic plates for facades. Special silicone resins incorporating particles several nanometers in size (e.g. special silicas) are utilized as optically transparent scratch-resistant lacquers. Diluted solutions or emulsions of silicone resins are utilized in the preservation of buildings providing moisture protection and in combination with silicic acid esters as sandstone solidifiers.

- protection of building:
  - for hydrophobizing building materials and house facades
  - sandstone hardening in combination with silicic acid esters

4.4.5 Silicone Copolymers, Block Copolymers and Graft Copolymers

The properties of silicones can be modified by combination with organic polymers. Block copolymers of poly(organosiloxanes) and poly(ethers) as well as thermoplastic-modified silicones are industrially important, in addition to silicone combination resins.

The properties of silicones can be varied by combination with organic polymers

Poly(ethersiloxanes) result from e.g.:

- reaction of branched (chloro)dimethylsiloxy-terminated poly(methylsiloxanes) with poly(ethers) having a hydroxy-group at one end
- addition of poly(ethers) terminated at one end with an unsaturated group to H-Si-containing poly(methylsiloxanes)

Poly(ethersiloxanes) contain a poly(methylsiloxane) polymer, which may be branched, and poly(ether)-blocks. Its structure may be linear or comblike. The blocks are connected by Si-O-C- or Si-C- bridges. Si-O-C- linked products can, for example, be produced by reacting branched dimethyl(chloro)siloxy-terminated poly(methylsiloxanes) (see Section 4.3.3) with monohydroxy-functional poly(ethers.

Si-C- linked polyethersiloxanes can be obtained by adding poly(ethers) with unsaturated end-groups to methylhydrogensiloxy-containing poly(methylsiloxanes).

Poly(ethersiloxanes) are utilized as:

- poly(urethane)-foam stabilizers
- antifoaming agents
- aids in the textile industry

Polyethersiloxanes have surfactant properties. They are utilized in large quantities as foam stabilizers in the manufacture of polyurethane hard and soft foams, the polyether component for this application being a copolymer of ethene oxide and propene oxide. Polyethersiloxanes are, however, also used in antifoaming formulations, as a gloss and deaeration additive in paints and as textile auxiliaries.

Thermoplastic-modified silicones are produced by polymerization of monomers, such as styrene, in the presence of polysiloxanes

Thermoplastic-modified siloxanes are produced by polymerization of monomers such as styrene, methyl methacrylate or vinyl acetate in the presence of e.g. α,ω-dihydroxy-poly(dimethylsiloxane). The reaction can be so controlled that the thermoplastic particles are formed as rods. These, depending upon their type and quantity, determine the mechanical properties of the vulcanized silicone resin obtained via crosslinking of the silicone component. Such products are utilized in the porcelain, electric, electronic and metal industries.

References for Chapters 4.3 and 4.4: Silicones

Ullmann's Encyclopedia of Industrial Chemistry. 1993. 5. Ed., Vol. A 24, 57 – 93, VCH Verlagsgesellschaft, Weinheim.

Noll, W. 1968. *Chemie und Technologie der Silicone*, 2. Aufl., Verlag Chemie, Weinheim.

Ackermann, J., Damrath, V. 1989. Chiuz 86 – 99.

Reuther, H. 1981. *Silicone - Eine Einführung in Eigenschaften, Technologien und Anwendungen*, VEB Deutscher Verlag für Grundstoffind., Leipzig.

Polmanteer, K. E. 1988. *Handbook of Elastomers*, 555 – 615, M. Dekker Inc., New York.

Trego, B. R., Winnan, H. W. 1990. RAPRA Review Rep., Vol. 3, 1 – 31.

Hardman, B. , Torkleson, A. 1989. Encyclopedia Polym. Sci. A Eng, 204 – 308, John Wiley & Sons, New York.

Büchner, W. 1980. *Novel Aspects of Silicone Chemistry*, J. Organomet. Chem. Rev. **9**, 409 – 431.

Industrial inorganic Chemistry
Karl Heinz Büchel, Hans-Heinrich Moretto & Peter Woditsch

5 Inorganic Solids

5.1 Silicate Products

5.1.1 Glass

The art of glass-making is about 5000 years old. The first marked technological improvement was the discovery of the glass-maker's blowing iron, probably in the 2nd Century BC. It is still one of the tools used in the manufacture of special glass products. The mass production of glass dates from the introduction of mechanical glass production and processing at the end of the last century.

5.1.1.1 Economic Importance

The worldwide production of glass in 1995 was $9.9 \cdot 10^6$ t/a, of which about half was produced in Asiatic States, 15% in the USA and ca. 18% in Western Europe.

Worldwide glass production in 1995: ca. $9.9 \cdot 10^6$ t/a, of which 40% is flat glass and 60% is hollow glass

Since 1992 glass production has again increased slightly after the ca. 10% annual fall in production from ca. $15 \cdot 10^6$ t/a in 1986 to ca. $9.1 \cdot 10^6$ t/a in 1992. This was due to the worldwide recession, increased glass recycling and a partial shift from glass to plastic bottles.

Glass production declined at ca. 10% annually between 1986 and 1992 due to recession, increased recycling and substitution

The production of hollow glass (bottles, containers, light bulbs, glass crockery) is about 1.5 times that of flat glass (window glass, mirror glass), although this ratio varies considerably from country to country. Special glasses (e.g. optical glass) are insignificant as regards quantity, but amount to 10% in value.

Special glasses insignificant in quantity, but account for 10% of the value

5.1.1.2 Structure

Glass is a mainly inorganic molten product, which after a strong increase in viscosity upon cooling solidifies without crystallization. Glasses exhibit a diffuse X-ray diffraction pattern, unlike crystals, since the typical long range order of

Glasses are inorganic melt products, which solidify without crystallization. They are three dimensional networks built up without regular, periodic arrangement of the atoms crystals is absent in glasses. The former explanation of the discontinuous changes in the properties of glasses based on the microcrystalline hypothesis typical of crystalline phases, has today been largely supplanted by the network hypothesis drawn up by W. U. Zachariasen in 1933. According to this hypothesis glasses are built up of three dimensional networks without the regular arrangement present in crystals. The arrangement of structural elements of glass with respect to their nearest neighbors, is largely that of atoms in crystalline structures (short range order).

This hypothesis for silicate glasses is supported by the silicon-oxygen-silicon bonding angle distribution in the short range bonding of quartz glass determined in the 1960's and 1970's, which covers a considerably wider range than in crystalline quartz.

The following rules pertaining to the structure of glasses can be derived from the network hypothesis:

- each oxygen atom may not be linked to more than two cations.
- the number of oxygen atoms in the neighborhood of a cation must be ≤ 4.
- the oxygen polyhedrons are only connected with one another at the corners, the lowest number of bonds being 3, to form a three dimensional network.

5.1.1.3 Glass Composition

The preferred conditions for the formation of the glass state are determined by both geometrical and energetic considerations and can be derived from the bonding enthalpies and the melting point, glass formation being probable with higher bonding enthalpies and low system melting points. Examples are B_2O_3 and the system CaO-Al_2O_3.

The oxides, which form the network necessary for glass formation, are known as network-formers and are characterized by bonding enthalpies for cation-oxygen bonding greater than 335 kJ/mol. The ions, which through lower connectivity degrade or change the network are known as network-modifying ions. In addition there are a range of amphoteric cations, which, depending upon the glass type, can be network-forming or network-modifying.

Network formers	Network-modifiers		Amphoteric cations
SiO_2	Li_2O	NaO	Al_2O_3
GeO_2	Na_2O	Ga_2O_3	PbO
B_2O_3	K_2O	In_2O_3	BeO
P_2O_5	Rb_2O	Sc_2O_3	ZnO
As_2O_5	Cs_2O	Y_2O_3	CdO
Sb_2O_5	MgO	La_2O_3	TiO_2
V_2O_5	CaO	SnO_2	ZrO_2
	SrO	PbO_2	ThO_2

The network-modifying cations occupy interstitial spaces in the network. The network expands (e.g. with K^+ ions) or contracts (e.g. with Li^+ ions) depending upon the number and size of these cations.

Almost all industrially manufactured glasses are silicate glasses. Their structural unit is the silicon-oxygen tetrahedron, in which a silicon atom is tetrahedrally surrounded by oxygen atoms. The tetrahedra are connected to one another over common corners i.e. an oxygen atom belongs jointly to two tetrahedra. In pure SiO_2-glass, quartz glass, numerous oxygen atoms are bridging-oxygens. By incorporating other components, e.g. alkali oxide, these bonds are broken and singly bonded non-bridging oxygens are produced.

The industrially important glasses are based on three dimensional SiO_4-tetrahedra linked via common oxygen atoms. The network-modifiers are the holes in the network. Incorporated amphoteric cations can be network-forming or network-modifying

Quartz glass is the only industrially utilized single component glass. It has excellent dielectric and chemical properties, a very low expansion coefficient, a high temperature stability and an exceptionally high transparency to UV-light. It is chemically resistant except to fluoride ions and strong alkali. Quartz is difficult to produce, temperatures above 2000°C being required. Translucent fused quartz (fused silica) can be used where transparency is unimportant. Since in translucent fused quartz the quartz is only sintered together, it contains air bubbles which make it non-transparent.

Quartz glass consists of SiO_2 and is characterized by:

- excellent dielectric properties
- high chemical resistance
- very low thermal expansion coefficient
- high temperature stability
- very high transparency to UV-light

The conventional multi-component glasses contain alkali and alkaline earth ions and frequently also aluminum oxide, boric oxide and other oxide components, depending upon the particular application. They can be remelted and processed at much lower temperatures than quartz. Network-formers also act as a flux, their flux activity increasing with their polarizability. Thus, K_2O is a better flux than Li_2O.

Conventional glasses contain network-modifiers. They are remelted and processed at lower temperatures than quartz glass.

Incorporation of aluminum oxide improves the temperature stability of glasses. Since AlO_2- can be incorporated in the SiO_2-tetrahedron network without the cation necessary for charge compensation, non-bridging sites are produced. Boric oxide acts mainly as a flux and leads to lower melting temperatures. In contrast to alkali oxides, it only slightly increases the thermal expansion coefficient and improves the chemical resistance. Therefore borosilicate glass apparatus is more frequently used in chemical laboratories.

Aluminum oxide improves the temperature stability, boric oxide the chemical resistance as e.g. in Pyrex®: 81.0% SiO_2, 2.0% Al_2O_3, 0.15% Fe_2O_3, 0.05% TiO_2, 0.3% CaO, 0.2% MgO, 4.5% Na_2O, 0.1% K_2O, 11.4% B_2O_3, 0.3% As_2O_3

Flat glass and hollow glass are soda-lime glass with the approximate composition: $Na_2O \cdot CaO \cdot 6SiO_2$, and frequently contain MgO, Al_2O_3, BaO or K_2O

The industrially most important glasses are the so-called soda-lime glasses, which account for over 90% of all the glass produced. Mixtures with alkali and alkaline earth oxides result in much more stable glasses than alkali silicates alone. In addition to Na_2O, CaO and SiO_2, soda-lime glass frequently contains MgO, Al_2O_3, BaO or K_2O in addition to color-giving cations or anions. Magnesium oxide reduces the tendency to crystallization. Aluminum oxide improves its stability still further. Soda-lime glasses are utilized for flat glass and hollow glass products.

Lead glass suitable for fine glass articles (crystal glass), optical glasses and television tubes

Lead oxide acts generally as a network-modifier, in exceptional cases also as a network-former. Its addition leads to easily meltable lead glasses. As a result of their high refractive index, they are suitable for lead crystal glass for handmade fine glass articles and optical glasses. Due to their high absorption of energy-rich radiation, lead glasses are used for the manufacture of television tubes.

Glass ceramics largely consisting of fine crystalline phases formed upon heating at the nucleation temperature and then at a nuclei growth temperature

For special glass compositions, the glass article is subjected after manufacture to controlled crystallization (ceramming), whereupon glass ceramics are produced. These consist of largely crystalline phases with homogeneous fine particulate grains. In the manufacture of glass ceramics the glass article is first heated to the nucleation temperature to induce sufficient crystal nuclei in the glass phase (the nucleation hold). Then the temperature is increased, to promote crystal growth (crystallization hold). The more nuclei produced in the nucleation step, the finer crystalline the glass ceramic. The crystalline content of glass ceramics varies between 50 and 95%. The addition of noble metals, TiO_2, ZrO_2 or sulfides and phosphates, as heterogeneous nuclei, is particularly important industrially. If the crystallites are significantly smaller that the wavelength of light (ca. 50 nm) and the refractive index of the crystals and the glass phase are similar, the glass ceramics are clear and transparent.

Nucleation by heterogeneous nuclei: noble metals, TiO_2, ZrO_2, sulfides, phosphates

Advantages of glass ceramics:

- higher temperature stability
- thermal shock resistance

An advantage of glass ceramic materials is their high temperature stability, compared with glasses with the same composition. In addition they are, unlike ceramic materials, free of pores. The most important glass ceramics are those with extremely high thermal shock resistance based on the very low or even negative thermal expansion coefficients of different crystalline aluminosilicates (cordierite $2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$, β-spodumene $Li_2O \cdot Al_2O_3 \cdot 4SiO_2$, β-eucrypite $Li_2O \cdot Al_2O_3 \cdot 2SiO_2$). Lithium aluminum silicate glass ceramics are therefore utilized for utensils subject to thermal shock and for the hotplates of modern cookers. Other glass ceramic articles are ferroelectric, mechanically workable and photosensitive, selectively etchable glass ceramics. In glass ceramics the creep tendency of materials under mechanical stress can be suppressed, hence, for example, the manufacture of large telescope mirrors from glass ceramics.

Applications of glass ceramics:

- crockery
- cooking surfaces of cookers
- special articles (ferroelectric, mechanically workable, selectively etchable glass ceramics)
- optical mirrors

5.1.1.4 Glass Manufacture

5.1.1.4.1 Glass Raw Materials

The selection criteria for raw materials for glass manufacture are particularly influenced by the purity required for the application, availability, potential for undesirable emissions and cost. Since in the case of the main ingredient in glass production, sand, the transport costs considerably exceed the actual cost, it should generally be available nearby.

Sand, preferably fine particulate, is used as the source of SiO_2 in the manufacture of silicate glasses. Raw materials for the standard network-modifiers are lime, dolomite ($CaCO_3 \cdot MgCO_3$) for the alkaline earth oxides, sodium carbonate for sodium oxide, feldspar (sodium potassium calcium aluminum silicate), or other naturally occurring aluminum silicates, for aluminum oxide. Boron is used in the form of boric acid, borax and other boron minerals, e.g. ulexite ($NaCa[B_5O_6(OH)_6] \cdot 5H_2O$) or colemanite ($Ca[B_3O_4(OH)_3] \cdot H_2O$). Sodium sulfate is used as a fining agent. Other raw materials are necessary in the manufacture of special glasses and are either used as the oxide, carbonate or silicate of the required cations (ZnO, TiO_2, PbO_2, Li_2CO_3, $BaCO_3$, $ZrSiO_4$). Iron, chromium, cobalt, nickel and copper compounds are used as color-giving agents.

Raw materials:

- sand
- lime, dolomite
- sodium carbonate
- feldspars and other aluminum silicates
- boric acid and boron minerals
- cullet from the plant itself

An important raw material is cullet (broken glass), because significantly less heat is necessary for melting it than the usual glass mixture and hence it facilitates the fusing of raw material mixtures (the so-called batch) and reduces dust formation. The proportion of cullet in the batch is between 10 and 50% and depends upon the cullet yield of the plant. In the case of container glass it is 10 to 15%, for flat glass 20 to 30%. On purity grounds, the utilization of cullet from the plant itself is preferred. Since in many countries there is considerable recycling of flat glass (e.g. 78% in the Federal Republic of Germany) and

Recycling share for flat glass in the FR Germany: 78%

Main utilization sectors for recycled glass: container glass, mineral insulation fibers collection according to the color of the glass exists, cullet can be bought in for the production of different glass types. The main utilization sectors for recycled glass are the manufacture of container glass and mineral insulation fibers.

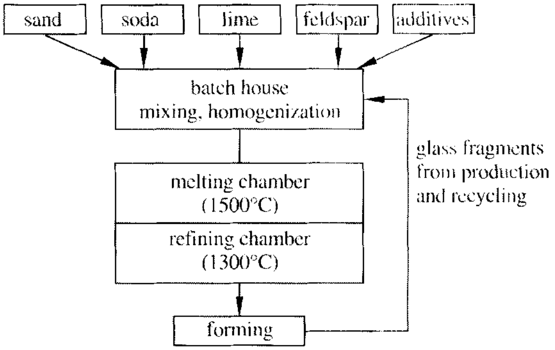


Fig. 5.1-1. Glass manufacture, temperatures relate to soda-lime glasses.

Batch is weighed in so-called batch house and is homogenized in ribbon blenders. Fining and coloring agents are added at this stage.

Quality of glass depends on the efficiency of raw material mixing

The quality of glasses is to a large extent influenced by the accuracy of the weighing and the efficiency of the blending.

3 to 4% of water is frequently added to reduce dust formation during batching, but also to improve homogenization. The same aims apply to briquetting or pelletization of the mixture.

Undesirable coloring through iron-content of the batch. Maximum permissible Fe_2O_3-content for flat glass: 0.10%

Nickel, vanadium, copper, manganese and chromium and in particular iron are contained as impurities in the raw materials. These ions can manifest themselves undesirably in the final product as different colors, depending upon the redox conditions in the glass melt. For high specifications the natural raw materials have to be replaced by appropriately processed starting compounds. The maximum permissible Fe_2O_3-content for a UV-transparent glass is 0.004%, that for spectacle lenses is 0.020% and that for flat glass is 0.10%. Decolorisation of glasses is important to enable the utilization of cheap raw materials with a certain iron content for mass-produced glasses.

- chemical decoloration (by oxidation to Fe^{3+}) for $Fe_2O_3 < 0.1\%$
- physical decoloration (compensation by colored additives) for $Fe_2O_3 > 0.1\%$

Chemical decolorisation is utilized for Fe_2O_3-contents below 0.1%. In this process oxidizing agents which yield oxygen at high temperatures (KNO_3, CeO_2, Sb_2O_3) are added to the glass mixture. These oxidize iron(II) to its trivalent, less color intensive, state. At higher iron oxide contents the yellow-green color of the glass can be physically compensated by colored additives (glassmaker's soap) e.g. by MnO_2.

5.1.1.4.2 Melting Process

Melting process can be divided into:

- fusing
- fining
- homogenization
- temperature adjustment before forming

The melting process can be subdivided into the following phases: fusing, fining (clarification), homogenization and refining (temperature reduction before the subsequent forming). The fusing phase comprises the processes of dissolution, volatilization of low boiling point components e.g. water, decarbonization, desulfatization and different redox reactions.

Components melting at low temperatures, so-called fluxes, react with the high melting point components, liquid phases being formed and solid state reactions occurring e.g. sodium carbonate reacts with the surface of sand from 550°C:

$$Na_2CO_3 + SiO_2 \longrightarrow Na_2SiO_3 + CO_2$$

From 700°C the reaction proceeds further:

$$Na_2SiO_3 + SiO_2 \longrightarrow Na_2Si_2O_5$$

and finally at ca. 780°C the liquid phase of a eutectic composition $3Na_2Si_2O_5 \cdot SiO_2$ is formed. The other carbonates and other high melting components, e.g. feldspars, react in a similar way.

The batch sinters together in this reaction and finally at a temperature between ca. 1200 and 1600°C becomes molten. The melt obtained is, however, not yet homogeneous and it also contains many gas bubbles due to moisture and air included in the batch and to gases formed in the chemical reactions (CO_2, SO_2, O_2).

Fining agents rapidly liberate gas at high temperatures. Sodium sulfate is generally used

The quantity of gases formed is, for a typical soda-lime glass, ca. 10% of the batch. The bubbles are removed by clarifying the glass melt. This entails adding an amount of fining agent, which at the fining temperature rapidly liberates the gas from the melt. The liberated gas rises as bubbles to the surface of the melt, the size of the bubbles increasing as they rise, due to diffusion of gas from the surrounding melt.

Smaller gas bubbles also rise and are taken off. High temperatures accelerate the fining process by reducing the viscosity of the melt and increasing the diffusion rate.

Sodium sulfate, which decomposes forming SO_3, is particularly useful for the fining of glass masses. Sodium nitrate or potassium nitrate, optionally in combination with As_2O_3 (for high melting point glasses, 1450 to 1500°C), is also used.

Inhomogeneities in the batch, melt separation, evaporation and furnace wall corrosion give rise to local fluctuations in the glass composition in the melt. Homogenization is achieved, for example, by blowing additional gases (air, steam) into the bottom of the glass melt or by mechanical mixing.

The glass melt is then cooled to the temperature at which further processing to the end-products takes place.

5.1.1.4.3 Melting Furnaces

Various melting furnaces are used in the glass industry. In the manufacture of flat glass or hollow glass, large continuously operated glass tanks are utilized, which can contain up to 1200 t of melt. Companies which produce a wide range of glass compositions (e.g. for optical glasses), use smaller furnaces e.g. multiple port furnaces or day tank furnaces The unit melters are intermediate in size.

Melting furnaces:

- tank furnace, divided into
  - a melting zone
  - a refining zone

Tank furnaces: Mass-produced glass is manufactured in continuously operated tank furnaces with capacities up to 600 t/d for flat glass and 300 t/d for hollow glass. The melt vessel is an elongated generally rectangular tank (dimensions e.g. 10 m x 40 m, depth 0.5 to 1.5 m). The mixture is constantly introduced at one end of the tank and the glass run off and fed into molds at the other. The temperatures required for remelting and clarifying the glass differ from that of the final melt. This results in the tank being divided into melting and refining zones. The melting, fining and homogenization take place in the melting zone. Refining of the glass is carried out at a lower temperature in the refining zone. For hollow glass manufacture the two parts of the tank are separated by a cooled wall with an opening below the glass surface and there are internal fittings for separating the furnace crown. Flat glass tanks are built without a dividing wall, the lower temperature of the refining zone being achieved by opening the tank cover.

The melting zone can also be divided off by a float made of firebrick.

The furnaces are directly heated by the combustion of oil-air or gas-air mixtures with the flames lapping laterally over the tanks. The hot combustion gases are drawn off from the opposite side and led through prewarming chambers (regenerators) fitted with a grid of refractory bricks. These are used either for preheating the combustion air (in oil heated furnaces) or the combustion air and the gas. The flame direction is reversed at 15 to 30 minute intervals, so that the combustion gases heat up the regenerators on either side of the furnace alternately.

Regenerators are used to utilize the waste gas heat to preheat the burner gas

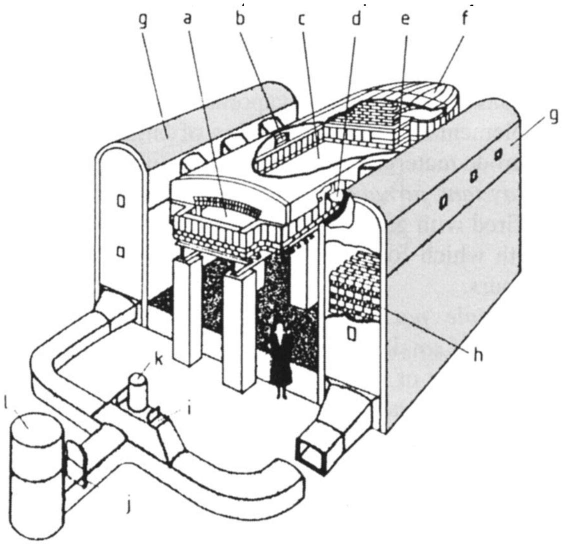


Fig. 5.1-2. Oil-heated, continuously operated Siemens-melter.
a) coating; b) burner with atomizer; c) melting zone; d) burner block; e) outlet; f) refining zone; g) regenerators; h) lining with refractory materials; i) gas reversal mechanism; j) chimney valve; k) air inlet; flue gas chimney

In special tank furnaces, e.g. for the manufacture of textile glass fibers, metal regenerators have been successful for heat recuperation. The regular reversal of the gas direction is then not necessary, simplifying temperature control over that with regenerative heat recuperation.

Tank ovens have been improved further by supplementary electrical heating (electrical boosting) in the melting zone. The glass melt, due to its ionic conductivity, acts as the electrical resistance. Only molybdenum can be used as the

Electrical auxiliary heating (electrical boosting) in the melting zone improves the furnace heating and reduces the evaporation losses electrodes. Electrical supplementary heating reduces the surface temperature and thereby evaporation losses.

Tank furnace parameters:

- specific melting power
- specific heat consumption

Important parameters for tank furnaces are the specific melting power (ca. 2 t/m2d) and the specific heat consumption (ca. 7000 to 10 000 kJ/kg glass). The life span of a tank furnace depends upon the quality of the refractory materials, particularly the tank bricks, and is ca. 6 to 8 years.

Other melters:

- unit melter

Unit melter: For large glass quantities up to a maximum of 100 t in continuous operation, short glass tanks (2 to 3 m wide, 10 to 12 m long) are used, which enable a rapid change from one glass type to another.

- electric melting uints

Electrical melting units: using pure electrical heating are suitable for up to ca. 4 t/d, in exceptional cases up to 240 t/d. These have the advantages of the surface remaining relatively cold and heavy evaporation losses being avoided. Therefore electrical melting units are particularly suitable for glasses with easily evaporatable components. As with supplementary electrical heating of large tank furnaces, the electrode material used is almost exclusively molybdenum.

- day tank furnaces

Day tank furnaces: with melting tanks for 1 to 5 t glass are fired with gas or oil and are named after the work cycle length which for loading, melting, fining and discharge is 24 hours.

- multiple pot furnaces

Multiple pot furnaces: are utilized for discontinuous melting of small quantities of glass at less than ca. 1400°C. They consist of several pots of burnt clay each with ca. 150 to 500 kg of glass mixtures and are heated by direct firing. They are utilized for special glasses, such as crystal glass, colored glass or optical glass.

Large quantities of refractory materials are required for the construction of melting furnaces. The surfaces of the tank furnaces in contact with the glass melt are lined with melt cast or isostatically pressed bricks (e.g. of zirconia) and the cover over the glass tanks is manufactured from mullite or silica materials.

5.1.1.5 Forming

Forming only by hand for complicated special articles and esthetic products, otherwise in large automated plants

Forming is currently carried out in fully automated plants with high throughputs. Manual forming is no longer of any importance, except for complicated special articles and esthetic products. It is carried out at temperatures between 800 and 1400°C depending upon the composition of the glass. Typical processing procedures require viscosities between 10^3 and 10^6 dPa · s. If the temperature difference between these viscosity limits is large, then one refers to a "long" glass and if narrow to a "short" glass. Long glasses are easier to process than short glasses. Floating, drawing, rolling, blowing, pressing and casting are utilized as forming processes.

Flat glass manufacture:

- float-glas process:
  glass melt solidified on a surface of moltentin

Flat glass manufacture: Flat glass is currently almost exclusively manufactured by the Pilkington float-glass process, which has supplanted the formerly operated roller process such as the Fourcault, Pittsburgh and Libbey Owens process. In this process the molten glass flows under a controlled atmosphere from the furnace onto a bed of tin in a several m wide and up to 50 m long tank. A just under 7 cm thick glass layer is produced at ca. 1000°C with surfaces parallel to one another. The glass cools slowly on the tin-bed, so that it can, on leaving the tin-bed, be passed on rollers through a tempering oven.

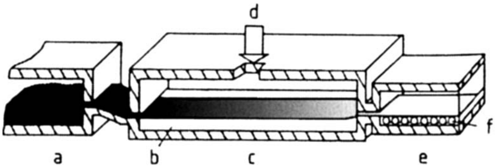


Fig. 5.1-3. Pilkington float-glass process.
a) furnace; b) molten tin; c) float bath; d) controlled atmosphere; e) lehr; f) rollers

Thinner glass qualities down to 2 mm thick are produced by stretching the still workable glass on the tin-bed. The float-glass process supplies flat glass in mirror glass quality, but is restricted to soda-lime glass.

The Corning overflow process is utilized for a wide range of glasses such as chemically hardenable aluminosilicate glasses for automobile and airplane windows and glass for flat panel displays. In this process glass is continuously fed into a slitted trough, from which it flows downwards forming a flat glass sheet.

Hollow glass manufacture:

- press process
- blowing process

Hollow glass manufacture: Pressing and blowing processes are utilized in the automated manufacture of hollow glass. Pressing processes are mainly utilized in the automated manufacture of wide-necked hollow glass objects and consist of placing precise quantities of melt in hot compression molds and molding under pressure. Blowing processes also consist of placing precise quantities of melt in a mold, but then forming it by suction or blowing with compressed air. Glass tubing is produced in a continuous process by constant deposition of molten glass onto a rotating blowing pin, from which the tube is drawn with cooling.

Forming is generally followed by a controlled cooling process in special ovens, with the purpose of reducing the residual stress in the finished glass article to a sufficiently low level. Depending upon the particular glass product, further processing may be necessary such as e.g. grinding, polishing, etching, frosting or application of a reflective coating. Glass objects can be made stronger by subjecting the glass surface to compression strain. This can be realized by thermal hardening in which it is heated up to almost to its softening temperature and then is rapidly quenched in the region near the surface with a blast of air or by submersion in a liquid.

Increasing the strength of glass articles by compression strain in the glass surface (quenching, ion exchange)

Chemical hardening by surface ion-exchange in a salt melt, generally potassium nitrate, is even more effective. In this way sodium ions are exchanged for the larger potassium ions, so that compression strain is realized in the surface.

5.1.1.6 Glass Properties and Applications

Important glass properties influenced by the glass composition:

- viscosity-temperature dependence

The dependence of viscosity upon temperature determines the melting behavior, the forming process, the tempering conditions and the highest application temperature. Near its softening temperature (a viscosity of ca. 10^7 Pa · s), a glass article visibly deforms under its own weight. At room temperature the viscosity of glass is above 10^{20} Pa · s. Forming can be carried out at a viscosity of 10^3 Pa · s.

- thermal expansion coefficient

Most industrial glasses have linear thermal expansion coefficients between $30 \cdot 10^{-7}$/K (thermal shock resistant borosilicate glass) and 80 to $90 \cdot 10^{-7}$/K (window glass). In composite systems, such as used in the electronics industry for fusing (soldering) glasses to metal conductors or casing components, the thermal expansion coefficients of the glass and the metal have to be precisely matched.

- density
- elastic modulus

The density of most industrial glasses is between ca. 2.2 and 2.6 g/cm^3. The density can be considerably increased by incorporating atoms with high atomic weights.

Glasses are purely elastic bodies at room temperature with elastic moduli between ca. 50 and 90 kN/mm^2. The flexural strength and tensile strength values (between 10 and 100 N/mm^2) depend upon the quality of the surface, not upon the glass composition. The compression strength is considerably higher.

Glasses exhibit at room temperature specific resistances between 10^{11} and 10^{12} Ωcm, which decrease significantly with increasing temperature.

- chemical resistance

Glasses are characterized by their high resistance to almost all chemicals and solvents. Hydrofluoric acid, however, rapidly attacks glass, due to the formation of hexafluorosilicic acid. Resistance to aqueous acids and alkalis depends very strongly upon the composition of the glass and the temperature. Borosilicate and aluminosilicate glasses exhibit the best acid resistance. Alkalis attack glass by depolymerizing the silicate network to silicate anions. The reaction rate can be reduced by incorporating CaO, MgO, Al_2O_3 or B_2O_3. Incorporation of ZrO_2 gives the best alkali resistance. Water also attacks glass, which is the basis of the weathering of glass, particularly at high humidities.

Alkali borosilicate glasses are utilized for glass apparatus in chemical technology requiring high chemical resistance and high thermal shock resistance. Glasses with very good alkali resistance, which are also suitable for sodium vapor lamps, contain 10 to 15% ZrO_2.

- transparency to visible light

An extremely important property of most industrially utilized glasses is their transparency to visible light. This holds for the majority of glass products, be they flat glass products, such as window glass, mirrors, or hollow glass products, such as bottles, glass containers, household glasses, light bulbs. It also holds for optical glasses such as spectacles, lenses, prisms etc. In the case of optical glasses, the refractive index and its wavelength dependence (dispersion) are important. Colored glasses are obtained by incorporating coloring transition metal ions or, to a lesser extent, by colloidal precipitation.

References for Chapter 5.1.1: Glass

General Literature:

Ullmann's Encyclopedia of Industrial Chemistry. 1989. 5. Ed., Vol. A 12, 317 – 366, *Glass*, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 12, John Wiley & Sons, New York.

Scholze, H. 1988. *Glas, Natur, Struktur und Eigenschaften*, 3. Aufl., Springer-Verlag, Berlin.

Vogel, W. 1994. *Glaschemie*, Springer-Verlag, Berlin.

Paul, A. 1982. *Chemistry of Glasses*, Chapman & Hall, London.

Rawson, H. 1980. *The Properties and Applications of Glass*, Elsevier, Amsterdam.

Phillips, P. 1981. *The Encyclopedia of Glass*, Crown, New York.

Nölle, G. 1979. *Technik der Glasherstellung*, Harri Deutsch Verlag, Frankfurt.

Duffy, J. I. (Ed.) 1981. *Glass Technology: Developments since 1978*, Chem. Tech. Rev. Ser. No. 184, Noyes, Park Ridge.

Lange, J. 1980. *Rohstoffe der Glasindustrie*, Dtsch. Verlag für Grundstoffindustrie, Leipzig.

McMillan, P. W. 1979. *Glass-Ceramics*, Academic Press, New York.

Economic Information:

Chemical Economics Handbook, Jan. 1996. *Glass products*. 232.1000 E-M. Stanford Research Institute, Menlo Park, California.

5.1.2 Alkali Silicates

5.1.2.1 General and Economic Importance

Alkali silicates are characterized by the weight or molar SiO_2 : alkali oxide ratio

Industrially interesting alkali silicates (sodium and potassium silicates) are characterized either by the SiO_2 : alkali oxide weight ratio or by the SiO_2 : alkali oxide molar ratio. The latter is obtained by multiplication of the weight ratio by 1.032 for sodium silicates and 1.568 for potassium silicates.

Classification of alkali silicates:

- SiO_2/metal oxide 1.5 to 4: water glass in solid or liquid form
- $Na_2O \cdot nSiO_2$: crystalline silicates, e.g. metasilicate for detergents

Alkali silicates can be divided according to their molar SiO_2/metal oxide ratio into two groups:

- sodium and potassium silicates with a molar ratio between 1.5 and 4. These silicates as well as their aqueous solutions are known as water glass. Concentrated water glass solutions are marketed. These are either produced by dissolving solid water glass or by dissolution of sand in strong alkali.
- solid, crystalline sodium silicates, which can contain additional water of crystallization. Commercial products can be described as $Na_2O \cdot nSiO_2$, with n = 0.5, orthosilicate, with n = 1, metasilicate, and with n = 2, disilicate. Their main application sectors are in detergents and cleaning agents.

Production worldwide in 1995, as solid glass: ca. $4 \cdot 10^6$ t/a

The total worldwide production of alkali silicates in 1995 as solids was estimated to be ca. $4 \cdot 10^6$ t/a, to which Western Europe, Japan and the USA each contributed $0.5 \cdot 10^6$ t/a. In Western Europe and the USA ca. 30% thereof is utilized in detergents, ca. 8% for paper, ca. 5% for the treatment of TiO_2 and ca. 3% for water treatment.

5.1.2.2 Manufacture of Alkali Silicates

Manufacture of:

- anhydrous alkali silicates with SiO_2/metal oxide $\geq$ 1.5 from quartz sand and alkali carbonates or hydroxides

Anhydrous alkali silicates with SiO_2/alkali oxide $\geq$ 1.5 (solid glasses) are manufactured by reacting fine particulate quartz sand, which is as pure as possible, is clay-free and has a low iron content, with alkali carbonates or hydroxides at 1300 to 1500°C in tank furnaces lined with refractory bricks or in rotary tube e.g. $Na_2CO_3 + 4\ SiO_2 \longrightarrow Na_2O \cdot 4\ SiO_2 + CO_2$

The alkali silicate melt flows into casting molds in which it solidifies to transparent more or less colored lumps.

Water glass solutions with SiO_2/metal oxides ≥ 2 are produced by dissolving these materials in water under pressure (ca. 5 bar) at ca. 150°C. The colorless, water-clear and alkali-reacting water glass solutions can be adjusted to different viscosities, their viscosity increasing with alkali silicate concentration and, at constant concentration, with increasing SiO_2/alkali oxide ratio. Water glass with low SiO_2/metal oxide ratios can be produced by adding alkali hydroxide during the dissolution process.

- water glass solutions with SiO_2/metal oxide ≥ 2 by
  - solution of solid glass in water at ca. 5 bar and 150°C

Aqueous solutions of alkali silicates can also be produced in an energetically favorable reaction by reacting sand with sodium hydroxide e.g. in autoclaves with stirrers under pressure and high temperatures.

  - reaction of sand with aqueous NaOH under pressure at high temperatures

Of the alkali silicates with $Na_2O \cdot nSiO_2$: only sodium metasilicate, Na_2SiO_3, with n = 1, has industrial and commercial importance. It is either produced by melting sand with sodium carbonate in a 1:1 molar ratio or by reaction of sand with solid sodium carbonate in rotary or drum furnaces.

- sodium metasilicate
  - melting of sand with sodium carbonate
  - reaction of sand with solid sodium carbonate

Alkali silicate powders are produced by spray or drum drying of water glass solutions, which still contain ca. 20% water. They dissolve upon heating with a little water forming water glass solutions.

Metasilicates with crystallization water also have industrial importance, in particular those with 5 and 9 molecules of crystallization water.

They are produced by measured addition of water to anhydrous metasilicate or by spray cooling crystallization of appropriately made up solutions.

- sodium metasilicate with crystallization water
  $Na_2O \cdot SiO_2 \cdot xH_2O$
  x = 5 and 9
  Manufacture by adding water to metasilicate or spray cooling crystallization of solutions

5.1.2.3 Applications

Alkali silicates utilized in:

- detergents and cleaning agents
- silicate fillers
- catalysts
- zeolites
- silicas
- silica gels
- adhesives
- ore flotation
- water treatment
- in the enamel, ceramic and cement industries and in foundries
- chemical consolidation of ground
- deinking in the paper industry
- secondary oil recovery

Potassium water glass utilized:

- for welding electrode-coatings
- as a binder for cathode ray tube luminescent pigments
- for wall impregnation
- as a binder for plasters

Alkali silicates are utilized in large quantities in the manufacture of detergents and cleaning agents and as starting materials in the manufacture of cracking catalysts for the petrochemical industry and of silica fillers for rubbers and plastics. They are also used in the synthesis of zeolites, silica gels and silica sols, in adhesives, as a binder for aqueous paints, in the flotation of ores, in the ceramic and cement industries, in foundries, in water purification for flocculating impurities and in the chemical consolidation of ground.

New applications are the utilization of sodium silicate solutions in deinking (decolorization) processes in the paper industry in paper recycling to increase the efficiency of the bleaching agent H_2O_2 and in secondary oil recovery.

Potassium water glass solutions are mainly utilized in the production of coatings for welding electrodes, as binders for luminescent pigments used in cathode ray tubes, for impregnating walls and as a binder for plasters.

References for Chapter 5.1.2: Alkali Silicates

Ullmann's Encyclopedia of Industrial Chemistry. 1993. 5. Ed., Vol. A 23, 661 – 719, VCH Verlagsgesellschaft, Weinheim.

Dent Glasser, L. S. 1982. *Sodium Silicates*, Chemistry in Britain **18**, 33 – 39.

Schweiker, G. C. *Sodium Silicates and Sodium Aluminosilicates*, J. Am. Oil. Chem. Soc. **55**, 36 – 40.

5.1.3 Zeolites

5.1.3.1 Economic Importance

There is little statistical data regarding the total production of zeolites. Since their market introduction in the 1950's the capacity and consumption of zeolites has steadily increased. This increase has accelerated in recent years due to their utilization in detergents (see Table 5.1-1).

Table 5.1-1. Capacity for the Manufacture of and Consumption of Zeolite A for Detergents in 1995 in 10^3 t/a.

	Western Europe	North America	Far East
consumption	600	317	248
capacity	1077	453	522

Capacity for zeolite A for utilization in detergents in 1995:

$> 2.0 \cdot 10^6$ t/a

5.1.3.2 Zeolite Types

Zeolites are crystalline aluminosilicates, which can be represented by the general formula:

Zeolites are aluminosilicates with Si/Al ratios between 1 and ∞. > 200 types, of which 50 occur naturally

$$[(M^+, M^{2+}{}_{0.5}) AlO_2]_x [SiO_2]_y \cdot [H_2O]_z$$

M^+: e.g. alkali metal cations
M^{2+}: e.g. alkaline earth metal cations

Zeolites (of which there are currently more than 200 types, 50 of which are naturally occurring) are differentiated by the Si/Al ratio in their anionic structure. This varies between 1 (in zeolite A) and ∞ in silicalite, an aluminum-free crystalline silica-modification. The industrially most important synthetic zeolites, apart from zeolite A, are zeolites X and Y with Si/Al ratios of 1 to 3, synthetic mordenite at ca. 5 and ZSM 5 at > 10. The thermal stability and acid resistance of zeolites increase as the Si/Al ratio increases.

Zeolites occur in many different structures. The basic units are always SiO_4- and AlO_4-tetrahedra, linked to one another by common oxygen atoms. Fig. 5.1-5 and 5.1-6 show the structures of zeolite A and zeolite X and Y respectively, as examples of zeolite structures. These zeolites are built up of cubo-octahedra ("β-cages") with SiO_4- and AlO_4-tetrahedra at their corners, as shown in Fig. 5.1-4.

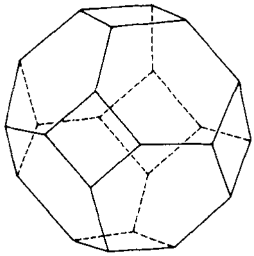


Fig. 5.1-4. Cubo-octahedra – "β-cages".

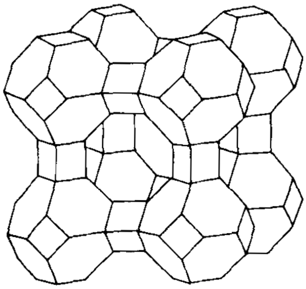


Fig. 5.1-5. Zeolite A structure.

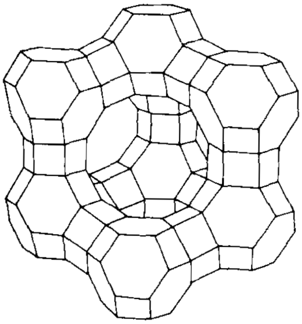


Fig. 5.1-6. Faujasite structure, zeolites X and Y.

The zeolite A structure is produced by linking the β-cages via their quadratic surfaces (over cubes). Linking over the six-corned surfaces with hexagonal prisms leads to zeolite X and Y, which correspond to the mineral faujasite. The cationic sites are not shown in these figures. The complicated structure of ZSM 5 zeolite systems is characterized, see Fig. 5.1-7 by two crossing channel systems: one linear and the other zig-zag.

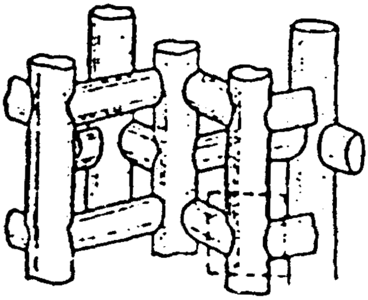


Fig. 5.1-7. ZSM 5 structure. Representation of the pores.

Zeolites are characterized by a system of cavities or channels in the lattice, whose volume and diameter are type specific. These cavities are connected to one another by pores, whose diameter is also type specific. Among zeolites with channels there are types: with channels running parallel to one another, which cross multidimensionally and with multidimensional non-crossing channel systems. In Table 5.1-2, the pore diameters (in 10^{-10} m) and pore volumes (in %) are given for several types.

Table 5.1-2. Pore diameter in 10^{-10} m (Å) and pore volumes (in %) of several Zeolite types.

	A	X	Y	mordenite	ZSM 5
pore diameter	4.1	7.4	7.4	7 x 6.5*	5.6 x 5.3*
pore volume	47	50	48	28	-

*pore opening not circular
inner surface area: 500 to 900 m^2/g (BET)

The values in this table refer to zeolites with sodium cations. The cations are mobile in the lattice and can be exchanged. Upon exchanging sodium cations in zeolite A by potassium ions the pore diameter decreases to 0.3 nm. Cation exchange also affects other properties, such as their adsorption properties and, with appropriate cations, also their catalytic properties.

In addition to the above-described aluminosilicate zeolites, a range of microporous solids have been discovered in recent years. Only the aluminophosphates, the silicoaluminophosphates, the metalaluminophosphates and meso-porous materials will be mentioned here. In this new substance class numerous new structures have been discovered including a range of structures analogous to the zeolites. A further extension of the zeolite family over and above the aluminosilicates are the so-called SiO_2-rich metal silicates with zeolite structures. Particularly worthy of mention is so-called TS-1, a titanium-containing zeolite with ZSM 5 structure, which is suitable for selective oxidation with H_2O_2.

5.1.3.3 Natural Zeolites

Natural zeolites:

result indirectly from volcanic activity. Large deposits in the USA, Japan, the former States of the USSR, South-Eastern Europe. Clinoptilolite is the most widely occurring natural zeolite

Almost 50 zeolite types occur naturally, of which several have attained industrial importance. Natural zeolites result indirectly from volcanic activity. They are formed by hydrothermal transformation of basalts, volcanic ash and pumices and are found e.g. in basalt cavities and in large sedimentary deposits. The industrially most important natural zeolites are:

- clinoptilolite
- mordenite
- chabazite
- erionite

Deposits are mainly found in the USA, Japan, the former States of the USSR, Hungary and Italy. Clinoptilolite is the most widely occurring natural zeolite.

5.1.3.4 Manufacture of Synthetic Zeolites

5.1.3.4.1 From Natural Raw Materials

Synthetic zeolites can be manufactured from:

- natural raw materials such as kaolin
- the synthetic raw materials, sodium aluminate and silica (utilized as water glass, silica fillers, silica sols)

Zeolites, particularly zeolite A, can be manufactured from kaolinitic clays, which as particularly found in Central Europe, Great Britain, Japan, China and USA. To transform kaolin into zeolite, it has to be thermally converted, e.g. by shock heating to > 550°C, to metakaolin. The metakaolin is then suspended in sodium hydroxide solution and converted at 70 to 100°C into zeolite A. Some of the impurities contained in the natural raw material are retained in the final product. If amorphous silica is added, SiO_2-rich zeolites are produced. This process enables the transformation of preformed bodies into zeolite materials.

5.1.3.4.2 From Synthetic Raw Materials

Aluminum for the manufacture of aluminum-rich zeolites is obtained from sodium aluminate solutions, which are obtained by dissolving aluminum oxide hydrate in sodium hydroxide. Silica is used in the form of water glass, fine particulate silica (e.g. silica fillers) or silica sols. The cheaper water glass is preferred, but exhibits the lowest activity of the above-mentioned sources of silica. The reaction has therefore to be carried out in a special way to achieve active gels when SiO_2-rich zeolites are manufactured from water glass. Potassium hydroxide and, especially in the synthesis of the silica-rich ZSM range of zeolites, organic cations, such as tetra-alkylammonium cations or other organic compounds, are utilized as templates in addition to sodium hydroxide.

The manufacture of the industrially important zeolite types A, X and Y is generally carried out by mixing sodium aluminate and sodium silicate solutions, whereupon a sodium aluminosilicate gel is formed. In this gel SiO_2- and Al_2O_3-containing compounds pass into the liquid phase, from which the zeolites are formed by crystallization. As the zeolite growth components are removed from the solution more gel dissolves. The reaction mechanism for zeolite formation is presently not yet fully understood. There is experimental evidence that, depending upon the reaction conditions, different mechanisms are possible.

In zeolite synthesis the desired zeolite end-product is generally metastable with respect to the byproducts associated with it, e.g. the byproduct sodalite is more stable than zeolite A, and the byproduct phillipsite is more stable than zeolites X and Y.

Therefore different variables must be controlled during zeolite syntheses to obtain a material with optimum properties e.g.:

- the stoichiometry of the reaction mixture, which is not the same as that of the zeolite formed
- the respecting of particular concentration ranges
- the respecting of particular temperatures or resulting temperatures
- the respecting of particular pH-values
- the shear energy in stirring (explained by the degradation of oligomeric structures upon stirring)

Industrially important variables in zeolite synthesis are:

- stoichiometry of the reaction mixture
- concentration of the reaction partners
- temperature
- shear energy utilized

The above-mentioned variables do not play a role in all zeolite syntheses. In the manufacture of different zeolites, aging of the gel at temperatures below the crystallization is often useful. In many cases the synthesis can be influenced or accelerated by the addition of small quantities of nuclei.

In the synthesis of zeolite A for utilization in detergents, for which small particles (< 5 μm) and a narrow particle size distribution are necessary, the manufacturing economics have been improved in recent years by optimizing all conditions. Continuous synthesis has not yet been achieved industrially.

At the end of the crystallization, the zeolite formed is filtered off (e.g. with the aid of filter presses or continuous belt filters) and washed. The mother liquor and filtrates from the washings have to be recycled or processed, for ecological and economic reasons.

5.1.3.4.3 Modification of Synthetic Zeolites by Ion Exchange

Synthesized zeolites can be modified by ion exchange. Exchange of sodium by potassium, ammonium, calcium, barium, rare earth and transition metal elements is industrially important

The ability of zeolites to exchange the cation used in the synthesis, mainly sodium or potassium in the case of aluminum-rich zeolites depending upon the zeolite type, with other cations is very important. The exchange equilibrium depends upon the cation and zeolite type. The silver ion, for example, is particularly strongly bound, whereas the Li^+-ion is much more difficult to incorporate. The extent of exchange is determined by the size of cation and also by the structure of the zeolite concerned. Exchange of sodium by potassium and calcium in zeolite A and zeolite X is industrially important. Exchange of sodium by ammonium, rare earth ions and transition metal ions such as nickel, cobalt, platinum, palladium etc. in wide pore and medium-sized pore zeolites which are suitable for catalytic applications such as zeolite Y, zeolite, mordenite, zeolite L or ZSM 5, EU 1, ZSM 22 is also industrially important. Exchange can take place on the zeolite powder as synthesized or on formed articles produced therefrom. Zeolites with a Si/Al-ratio > 1.7 in which cations have been exchanged for ammonium ions can be converted into a stable H-form by heating.

Organic cations incorporated into SiO_2-rich zeolites during synthesis, which due to their size cannot be exchanged by other ions, can only be removed by pyrolysis.

5.1.3.5 Forming of Zeolites

Forming of zeolite powders is, for example, possible by:

- granulation on granulation dishes
- drum granulation
- extrusion
- spray drying

Most applications of zeolites as adsorption agents require molded articles. They can be produced by a number of processes such as bead formation on dish granulators and extrusion of granules and by drum granulators, extrusion or spray drying. Clays are mainly used as binders in the forming process, but SiO_2-containing materials and aluminosilicates are also used. When silica-containing binders are used in the forming process, they can be subsequently converted into zeolite by treatment with sodium aluminate solution at high temperatures. In this way molded articles solely containing zeolite can be obtained. When kaolin is used as a binder subsequent heating of the granules followed by treatment with sodium hydroxide enables binder-free granules to be obtained.

5.1.3.6 Dehydration of Zeolites

Prior to their use as adsorption agents or after industrial utilization for the adsorption of water, zeolites have to be dehydrated. This is carried out at 450 to 650°C e.g. in a rotary tube furnace or a similar unit. Industrially zeolites charged with water or other compounds are regenerated directly by passing hot dry inert gas through the absorber.

Removal of water from zeolites ("activation") by heating to 450 to 650°C

5.1.3.7 Applications for Zeolites

5.1.3.7.1 As Ion Exchangers

In addition to the use of clinoptilolite for the removal of ammonium ions from municipal waste water and cesium 137 from process water, the ability of zeolite A to exchange sodium ions for calcium and, to a lesser extent, magnesium ions from aqueous solutions has acquired considerable industrial importance in the detergent sector. The replacement of ca. 50 to 100% of the tripolyphosphate (see Section 1.5.1.2.2) in detergents by zeolite A considerably reduces phosphate release into mains drainage after passage of municipal waste water through sewage plants. To achieve the same washing power other changes in the composition of the detergent are required in addition to replacement of the phosphate. In recent years the zeolite Na P1 has been increasingly used, due to several technical advantages.

Zeolites as ion exchangers:

- clinoptilolite for the removal of ammonium ions from waste water
- zeolite A and Na P1 in detergents for the removal of calcium and magnesium from washing liquid

5.1.3.7.2 As an Adsorption Agent

Zeolites are capable of strongly binding molecules which are small enough to penetrate their pore systems. This particularly holds for water and for other small polar and polarizable molecules and is the basis of their utilization as

Zeolites as adsorption agents for:

- water removal from gases, air, liquid circuits and in double glazing
- adsorption of carbon dioxide, hydrogen sulfide, mercaptans from gases
- purification of hydrogen

drying- or cleaning-agents for gases such as natural gas, cracked gases, hydrocarbons or air prior to liquefaction. This enables very low dew points to be achieved. Furthermore, they are utilized in closed liquid circuits, e.g. in refrigeration plants and refrigerators, and for preventing condensation and bulging in double-glazed windows by absorbing water and residual solvent in the space between the panes. Utilization of zeolites for heat storage, in which water is absorbed from moist air thereby heating up the zeolite and the air and the zeolite is regenerated (dehydrated) with the help of lower temperature energy, such as waste heat or solar energy, is under discussion and has been practically evaluated.

In addition to the removal of water, zeolites are industrially utilized for removal of trace constituents such as carbon dioxide, sulfur compounds, ammonia etc. from different gas mixtures.

Purification of hydrogen with zeolites (Ca zeolite A) in which carbon monoxide is removed with the help of PSA-technology and ultrapure hydrogen is obtained, is industrially important.

In recent years there have been attempts to utilize SiO_2-rich hydrophobic zeolites, which are obtained by intensive dealuminization (with $SiCl_4$ or ammonium replacement) of zeolite Y, for solvent recovery.

5.1.3.7.3 For Separation Processes

Zeolites for the separation of materials (molecular sieves):

- production of oxygen of oxygen-enriched air
- separation of n- and iso-alkanes
- separation of xylene isomers

Mixtures of n- and iso-alkanes can be separated with the help of calcium-exchanged zeolite A (molecular sieve effect), since only n-alkanes can penetrate into the zeolite cavities (Molex Process).

In the separation of mixtures of aromatic hydrocarbon isomers, the para-isomer is generally preferentially absorbed and can be separated on the basis of kinetic effects. The most well-known example is the recovery of p-xylene (Parex process).

The presence of cations in the cavities of zeolites induce high electrostatic fields. This is utilized in the oxygen enrichment of air. The nitrogen interacts with the cations (calcium exchanged zeolite A or X and lithium exchanged zeolite X) and is thereby more strongly adsorbed than oxygen. By multistage adsorption-desorption cycles under reduced pressure (PSA-technology) it is possible to produce up to 95% oxygen, which has widespread uses.

5.1.3.7.4 As Catalysts

Zeolites as catalysts for:
- catalytic cracking (FCC)
- isomerization
- hydrocracking
- alkylation
- dewaxing
- chemical synthesis

Important processes in which zeolites are utilized as catalysts are:

- catalytic cracking of crude oil distillate for fuel manufacture, so-called FCC-plants (Fluid Catalytic Cracking) utilizing zeolite-containing catalysts and even zeolite Y in a dealuminized or rare earth-exchanged form in a non-zeolite matrix. The catalyst is utilized in fluidized beds. The activity of the catalyst is determined by the zeolite and the matrix. H-ZSM-5 is often added to influence the product mix.
- alkylation of aromatic hydrocarbons, production of ethyl benzene, for which H-ZSM-5 is used.
- isomerization of n-paraffins to iso-paraffins for fuel purposes; noble metal-containing zeolites are utilized, isomerization of xylenes utilizes ZSM 5.
- hydrocracking (conversion of crude oil fractions to petrol in the presence of hydrogen)
- dewaxing, removal or decomposition of long-chain paraffins from crude oil fractions

Worthy of mention are the numerous catalyzed reactions utilizing highly selective zeolite catalysts tailored to the particular process. However, significantly lower quantities of catalyst are utilized compared with those used in petrochemical processes.

Furthermore, there are intense efforts to utilize zeolites for the catalytic purification of combustion gases from combustion engines.

5.1.3.7.5 Miscellaneous Applications

Large quantities of zeolite-containing rock is worked in different countries (including the Federal Republic of Germany in the Eifel region) and is utilized in the manufacture of cements, mortars and lightweight building blocks. In Japan, natural zeolites are used as a filler in paper.

More recent applications of synthetic zeolites are e.g. in the sector of microbiocidal agents (silver zeolites), as deodorants, as nucleation agents for polymers and as antiblocking agents for foils. Utilization in sensory, energy and electrotechnical technologies and in membranes have not yet been realized.

References for Chapter 5.1.3: Zeolites

Reviews:

Ullmann's Encyclopedia of Industrial Chemistry. 1996. 5. Ed., Vol. A 28, 475 – 504, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1995. 4. Ed., Vol. 16, 888 – 925, John Wiley & Sons, New York.

Puppe, L. *Zeolithe, Eigenschaften und Technische Anwendungen.* 1986. Chiuz **20**, 117 – 127.

Szostak, R. *Handbook of Molecular Sieves.* 1992. Van Nostrand, New York.

Zeolites. A Refined Tool for Designing Catalytic Sites. 1995. Proceedings of the International Symposium, Quebec, October 15 – 20, 1995. Ed. Bonneviot, l. and Kaliaguine, S., Studies in Surface Science and catalysis **98**, Elsevier, Amsterdam.

Zeolites and Related Microporous Materials: State of the Art 1994. 1994. Proceedings of the 10th International Zeolite Conference, Garmisch-Partenkirchen July 17 – 22, 1994. Ed. Weitkamp, J., Karge, H. G., Pfeifer, H. and Hölderich, W. Studies in Surface Science and Catalysis **84**, Elsevier, Amsterdam.

Biz, S. and Occelli, M. L. 1998. Catal. Rev. - Sci. Eng., **40** (3), 329.

Molecular Sieves, Science and Technology. 1998. Ed. Karge, H. G. and Weitkamp, J. Vol. 1, Springer-Verlag, Berlin.

Synthesis of High-silica Aluminosilicate Zeolites. 1987. Ed. Jacobs, P. A. and Martens, J. A. Studies in Surface Science and Catalysis **33**, Elsevier, Amsterdam.

Progress in Zeolites and Microporous Materials: 1997. Proceedings of the 11th International Zeolite Conference, Seoul, Korea, August 12 – 17, 1996. Vol. 3, ed. Chon, H., Uh, Y. S. and Ihm, S.K. Studies in Surface Science and Catalysis **105**, Elsevier, Amsterdam.

Technical Information:

Bayer, Baylith®: Product Description – Processes – Product data, 7th Edition, 1993.

Degussa, Schriftenreihe Pigmente Nummer 71, Wessalith® für Waschmittel, 4. Auflage November 1993, *Zeolithe für Waschmittel.*

Ettlinger, M. and Ferch, H. 1979. Seifen – Öle – Fette – Wachse **105**, 131 – 135 and 160 – 161.

Krings, P., Smulders, E., Upadek, H., Verbeek, H. 1984. Information der Henkel-Gruppe, 10 Jahre Phosphatsubstitut Sasil, Düsseldorf.

Chemical Week, January 24, 1996, Phosphates and Zeolites Reach Stalemate.

Zeolites as Catalysts:

Thomas, J. M., Chen, J. and George, A. 1992. Chemistry in Britain, **11**, 991 – 994.

Onaka, M. and Izumi, M. 1992. Advances in Catalysis, **38**, 245 – 282.

Rabo, J. A. and Gajda, G. J. 1989- 90. Catal. Rev.-Sci. Eng. **31**(4), 385 – 430.

Michels, P. and De Herdt, O. C. E. 1987. *Molecular Sieve Catalysts,* EPO Applied Technology Series – Volume 9, Pergamon Infoline Inc., Pergamon Press, Oxford.

Chen, N. Y., Degnan Jr., Th. F., Smith, C. M. 1994. *Molecular Transport and Reaction in Zeolites,* VCH Verlagsgesellschaft, Weinheim.

Hölderich, W., Hesse, M., Naumann, F. 1988. Angew. Chemie **100**, 232.

Occelli, m. L., O'Connor, P. (Ed.). 1997. Fluid Cracking Catalysts, Marcel Dekker, Inc., New York.

Catalysis Today, **19**, 1994.

5.2 Inorganic Fibers

5.2.1 Introduction

5.2.1.1 Definitions, Manufacture and Processing

The term "fibers" includes materials from polymers, metals or ceramics having a cylindrical shape with a length/diameter ratio greater than 10 to 1 and a diameter of less than 250μm, which are generally produced by a particular forming process. Geometrically whiskers represent the lower limit (see Section 5.2.7.4). At larger diameters one has filaments and wires, these being often produced by other processes (e.g. continuous filament process see Section 5.2.6.1). The inorganic fibers are distinguished from organic fibers by their very low hydrogen content, high production temperatures and the wide variation in the choice of elements and compounds which endow many fibers with their thermal stability.

Definitions:

- cylindrical shape
- diameter < 250 μm
- length to diameter > 10 : 1

The fibers are produced continuously (endless fibers, filaments) or discontinuously (short or staple fibers) depending upon the application. Most of the fibers are obtained by extruding a flowable form (melt or solution) of appropriate chemical composition (Section 5.2.3 - 5.2.4). Other processes are based on deposition from the gas phase (Section 5.2.6.2) or thermal transformation (pyrolysis) of organic (Section 5.2.5) or organometallic polymers (Section 5.2.7).

Production processes:
continuous, discontinuous

- extrusion
- deposition from the gas phase
- polymer pyrolysis

The fibers or the yarn or rovings made therefrom can be processed to fleeces or mats (non-oriented semi-finished product) and textiles, lattices or meshes (oriented semi-finished products) and can be utilized as such e.g. for thermal insulation or as filter materials, or in composites with other materials e.g. for fiber-reinforced polymers, metals or ceramics. Fibers are generally marketed after surface treatment (chemical modification, annealing, smoothing) to optimize their application and processing properties.

Processing of semi-finished products:

- fleeces, mats (non-oriented)
- textiles, lattice, mesh (oriented)

Application sectors:

- thermal insulation
- fiber-reinforced composites

Surface modification to optimize properties

5.2.1.2 Economic Importance

Economic importance:

worldwide production in 1993:
organic + inorganic ca. $45 \cdot 10^6$ t/a

synthetic inorganic fibers: $7 \cdot 10^6$ t/a
natural inorganic fibers: $3 \cdot 10^6$ t/a

Worldwide production of fibers was ca. $45 \cdot 10^6$ t/a in 1993, of which ca. 20% was inorganic fibers. Whereas at the turn of the twentieth century the fibers utilized were almost exclusively natural fibers (organic fibers: cotton, sheep's wool and silk; inorganic fibers: asbestos), by 1993 the proportion of synthetic fibers had grown to ca. 50%. This trend appears to parallel the increasing world population and the consumer behavior coupled therewith.

5.2.1.3 Properties

Application fields:

- insulating fibers
- reinforcing fibers
- fillers
- functional fibers

By far the most important application fields for inorganic fibers are the insulation and reinforcing sectors. Fibers are also used as fillers and as filter materials. As with other materials, functional properties such as electrical, optical or magnetic properties are becoming increasingly important for fibers, in addition to mechanical and electrical properties.

Requirements for fibers for thermal insulation:

- non-inflammable
- low thermal conductivity
- ability to be shaped/flexibility

Insulation at high temperatures:

- thermal shock resistance
- maximum application temperature
- high long term use temperature

The fibers utilized for the manufacture of *insulation materials* are characterized their low thermal conductivity, their compactness, their flexibility thereby attaining a high insulation capability using a small amount of material. Utilization at high temperatures additionally requires thermal shock resistance, a high maximum application temperature and a high long term use temperature. The latter is mainly determined by the chemical composition and the mineral stability resulting therefrom (see Section 5.2.4). In this way by, for example, increasing the Al_2O_3-content in the system metal oxide-SiO_2-Al_2O_3 a stability up to ca. 1627°C is attained and with ZrO_2-based fibers stability up to 2027°C is attained (see Section 5.2.7).

Fiber-composites:

combination of reinforcing fibers and a matrix

In the *reinforcement sector* a number of fibers are available, which differ considerably both in price and also in chemical and thermal stability. This has a direct impact on their suitability for the production of fiber composites. Finally there are multiphase materials, in which reinforcing fibers are embedded in the form of short or endless oriented or non-oriented fibers, in a polymeric, metal or ceramic matrix.

Of foremost interest are their mechanical properties, which, together with their low density, have resulted in a class of materials which has enabled the attainment of lightweight structures and hence the partial substitution of classical materials such as metals. The driving force for the development of such materials was the realization of lightweight materials with high rigidity and strength, which could lead to weight saving in vehicles and aerospace craft and hence to reduced fuel consumption or to an increase in payload.

Requirements for reinforcing fibers:

- high tensile strength
- high Young's modulus
- low density

Aim:

lightweight structures
resistance to damage

Although some of the bulk materials corresponding to the fibers are mechanically brittle, the strong reduction in volume faults enables the realization of fibers with an enormous increase in Young's (elasticity) modulus and tensile strain. The mechanical properties of several important reinforcing fibers obtained from tensile-strength tests are summarized in Fig. 5.2-1.

Small diameters of fibers enable their processing to textiles

Mechanical characterization of fibers by tensile-strength tests

$\sigma = \varepsilon \cdot E$

σ: tensile stress
E: Young's (elasticity) modulus
ε: tensile strain

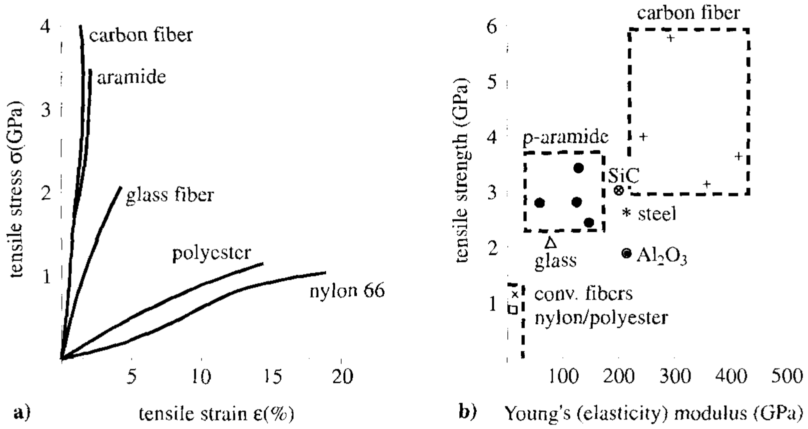


Fig. 5.2-1. Mechanical properties of fibers, T = 27°C.
a) Stress-strain curves; b) Tensile strength and elasticity moduli

The transferability of the mechanical properties of unidirectionally or multidirectionally incorporated reinforcing fibers to the entire composite material is determined by the interface between the fiber and the matrix. At sufficient bonding strengths, the mechanical properties are proportional to the volume fraction of the fibers. Filling levels of 30 to 60 % by volume and in extreme cases up to 80% can be attained, depending upon the location and mutual orientation of the fibers. The theoretical limit for unidirectional fibers is 90.7% by volume (by comparison

Optimization of the properties of composites by:

- increasing the wettability of the fibers by the matrix
- dedicated fiber/matrix bonding
- high volume fraction and position and orientation of the reinforcing fibers
- combination of different fiber types

cubic or hexagonal closest packing of spheres gives a filling factor of ca. 74% by volume).

Special properties (e.g. electrical conductivity) can be varied within wide limits by combining different fiber types (e.g. carbon and glass fibers). Further properties are discussed in the individual sections (and in the references).

5.2.1.4 Classification and Applications

Classification criteria:

- chemical composition
- natural/synthetic fibers
- degree of ordering
- thermal behavior
- mechanical properties

Inorganic fibers can currently be produced from a wide range of element combinations and further fiber-types are in development (see Section 5.2.7), so that a classification according to chemical composition, as favored by preparative chemists, is not reasonable. Other possible classification criteria are e.g. the production process, the source of the fibers (natural or synthetic), their degree of order (amorphous or crystalline), their thermal stability (27 – 2227°C) or physical properties (tensile strength, elasticity modulus). The boundaries between the individual fiber types are, however, often fluid.

- according to application field

In the following sections the fibers are discussed organized according to application field, the order approximating to the order of their industrial importance. A survey of several inorganic fibers together with their most important application fields is given in Table 5.2-1.

5.2.1.5 Physiological Aspects

Fibers with the following dimensions produce lung damage:

- diameters < 3 μm
- lengths greater than 5 μm and less than 100 μm
- ratio of length to diameter > 3 : 1

Code of practice:

- dangerous materials regulations
- MAK value in FRG
- TRK value in FRG:
  asbestos fibers 500 000/m^3

Fibers (length to diameter > 3 : 1) and dust particles (length to diameter < 3 : 1) with a diameter smaller than 3 μm and a length shorter than 100 μm can enter our lungs i.e. they can be breathed into the lungs and there cause damage. To avoid endangering human beings, particular concentration limits in the air should not be exceeded. These hold for their production, processing and use as well as for their disposal. Contact with the fibers is governed by dangerous materials regulations. The maximum permissible work place concentrations (MPC) i.e. the toxicological/work medicinal-based values, are determined for every dangerous material. The industrial reference concentration (Technischen Richtkonzentrationen, TRK value in FRG) reflects the current state of knowledge and provides a guide for the required protective measures. In the case of asbestos fibers and for synthetic mineral fibers the limit is 500 000 fibers per m^3 (= 0.5 fiber/cm^3) and for asbestos dust it is 0.1 mg/m^3.

Table 5.2-1. Important Application Fields for Inorganic Fibers.

Application field	Foremost requirements	Fibers utilized
reinforcement of:		
materials	textile processable high tensile strength high elasticity modulus low density	glass fibers (asbestos)*, carbon fibers, SiC fibers, boron fibers, oxide fibers (Al_2O_3)
seals, frictional linings	compression strength, elastic deformation behavior, thermal stability, abrasion resistance	glass fibers, steel fibers (asbestos)*
tire cord	stability to alternating mechanical stress	steel fibers and very short metal fibers
cement	chemical resistance to cement, mechanical stability	cement-resistant glass fibers, steel fibers, (asbestos)*
insulation:		
heat and cold insulation in buildings	low thermal conductivity, compactness	glass wool rock wool slag wool
fire prevention	high thermal insulation, non-inflammability	aluminum silicate fibers
thermal insulation of high temperature plants	high upper utilization temperature	oxide fibers (Al_2O_3, ZrO_2)
miscellaneous:		
antistatic finish	electrical conductivity	metal fibers
incandescent filaments	high melting point, mechanical stability	tungsten fibers
light-guides	highest purity for virtually loss-free light transmission	special glass fibers
hot gas filtration filtration of liquids (wine and beer production)	chemical stability high specific surface area, high filtration efficiency	oxide fibers (asbestos)*

(Asbestos)* : utilization in some countries strongly restricted or forbidden due to endangering of health (see below) (Federal Republic of Germany: from 1993)

In addition to the geometric dimensions of the fibers, the stability of the fibers in the human body is also a factor in assessing the danger of cancer. A half-life for fibers of less than 30 days is desirable, asbestos fibers having a half-life of more than 100 years. Half-life values for synthetic fibers are in general significantly lower than that for asbestos. The

Biological stability of fibers in the lungs dependent upon:

- chemical composition
- microstructure

stability in the lungs is determined by their chemical composition and by their microstructure.

Possible dangers:

- skin irritation
- allergic reactions
- pneumoconiosis
- lung cancer

Fibers with the above-mentioned geometric dimensions are contained in some commercially available products or occur during their processing, their use or their disposal and can give rise to skin damage (inflammation, allergies) and/or mucous membrane damage. Inhalation of asbestos leads initially to pneumoconiosis, a particular dust-related lung complaint, from which lung cancer can develop after prolonged exposure. Its proven carcinogenic nature has led to severe restrictions on the use of products from asbestos fibers or even their banning (see Section 5.2.2).

Protective measures:

- technical
- personal
- organizational

Alternatives:

- substitute products
- alternative production processes

Safe handling of fibers should be ensured by notices calling attention to the operating instructions in the work place. In general the measures should focus on both technical and organizational details, aiming to reduce the concentration of the dangerous material in the air, e.g. by good ventilation and avoidance of working in the open, and on personal protection to reduce contamination e.g. by use of protective clothing. In addition substitute products and/or alternative production processes are being developed.

5.2.2 Asbestos Fibers

5.2.2.1 General and Economic Importance

Classification of asbestos fibers into serpentine asbestos and amphibole asbestos. Amphiboles differ in their alkali and calcium content

Asbestos, the first inorganic fiber material used, is currently still exclusively produced from natural mineral deposits. It is formed by the hydrothermal conversion of basic and ultrabasic volcanic rock (olivine and pyroxene) to serpentine upon which the actual asbestos formation takes place leading to two asbestos sorts with different structures: serpentine asbestos and amphibole asbestos. Asbestos can be produced synthetically by several hours heating of a polysilicic acid/metal oxide mixture (e.g. Mg, Fe, Co, Ni) in water at 300 to 350°C and 90 to 160 bar. The properties of four important asbestos types are summarized in Table 5.2-2.

Table 5.2-2. Comparative Survey of the Properties of Four Important Asbestos Types.

asbestos type	chrysotile	crocidolite	anthophyllite	actinolite
asbestos class	serpentine	amphibole	amphibole	amphibole
ideal formula	$Mg_3(OH)_4[Si_2O_5]$	$Na_2Fe_5[OH/Si_4O_{11}]_2$	$(Mg,Fe)_7[OH/Si_4O_{11}]_2$	$Ca_2(Mg,Fe)_5[OH/Si_4O_{11}]_2$
fiber diameter (individual fibers), µm	0.015 – 0.4 (hollow fiber)	0.1 – 0.2 (solid fiber)	0.1 – 0.2 (solid fiber)	0.1 – 0.2 (solid fiber)
fiber diameter (fiber bundle), µm	0.75 – 1.5	1.5 – 4	1.5 – 4	1.5 – 4
density, 10^3 kgm^{-3}	2.3 – 2.7	2.8 – 3.6	2.8 – 3.2	3.0 – 3.2
specific surface area, m^2/g	13 – 22 (max. 50)	2.7 – 4.6 (max. 10)	7	–
Mohs hardness	2.5 – 4	4	5.5 – 6	6
tensile strength, GPa	2 – 6	7.5 – 22.5	0.03	0.006
elasticity modulus, GPa	30 – 160	100 – 190	–	–
flexibility	very high	good	low	low
H_2O cleavage temperature, °C	600 – 780	610	950	1040
decomposition temperature, °C	800 – 850	800	950	1040
pH value	9.5 – 10.3	9.1	9.4	9.5
acid resistance	non-existent	good	very good	satisfactory
stability in lungs	good – satisfactory	good	good	good
zeta potential	positive	negative	negative	negative

The different chemical composition and structures of chrysotile and amphibole asbestos have a considerable influence on their physical properties.

Serpentine asbestos and amphibole asbestos have very different physical properties

The macroscopic individual fibers of chrysotile asbestos consist of more or less parallelly oriented fibrils, which have a diameter of 15 to 40 nm and according to electron microscopic investigations are composed of carpet roll-like hollow fibers. The wall partitions of these small rolls consist of double layers of the composition $Mg_3(OH)_4Si_2O_5$, in which one brucite $Mg(OH)_2$- and one Si_2O_5- layer are condensed with one another. These crystal lattices not fitting precisely with one another leads to curvature and hence a hollow fiber. Chrysotile asbestos is, as a result, easily fragmented into very fine fibers, which are soft and flexible and hence, of all the asbestos types, they lend themselves most easily to spinning. Industrially, however, chrysotile is always present as fiber bundles.

Chrysotile asbestos fibers consist of bundles of hollow micro-fibers (fibrils) of 15 to 40 nm in diameter

Due to this structure chrysotile is easily broken into very fine spinnable fibers

In contrast amphibole asbestos consists of Si_4O_{11}-bands as the supporting entities. These are condensed with metal hydroxide bands to double bands, which are held together

Amphibole asbestos fibers are solid crystalline needles by cations. Amphibole asbestoses cannot therefore be fragmented into such fine fibers and the fragments are more like hard crystalline needles.

The tensile strength of asbestos fibers increases with increasing temperature in contrast to glass fibers

The tensile strength of asbestos fibers is 2 to 10 GPa, a maximum value of 22.5GPa being attainable due to its single crystalline structure. In some application fields it is important that the tensile strength of asbestos fibers increases by 10% up to 400°C, whereas glass fibers at this temperature only possess a fraction of their strength at room temperature (see Table 5.2-3).

Table **5.2-3.** Average values for Density, Tensile Strength and Elasticity Modulus of Fibers.

Fiber type	density, Mgm^{-3}	elasticity modulus at 23°C, GPa	tensile strength at 23°C, GPa	tensile strength at 400°C, GPa
chrysotile asbestos	2.3 – 2.7	up to 160	2 – 6 (max. 20) depending on fiber length	–
crocidolite asbestos	2.8 – 3.6	up to 190	7.5 – 22.5 depending on fiber length	5 - 15
glass fibers	2.4 – 2.5	73 – 77	ca. 2	0.6 – 0.9

Zeta potentials:

- chrysotile asbestos: positive
- amphibole asbestos: negative

Behavior with acids:

- chrysotile asbestos unstable
- amphibole asbestos fairly stable

TRK value of asbestos from 1988:
0.5 fibers/cm^3

Use banned in FR Germany from 1993

The different structure types lead to very different properties. Unlike amphibole, chrysotile fibers exhibit a positive zeta potential, which is important for its utilization as a filtration and clarifying agent in the food and drink industries as well as for the separation of viruses and pyrogens from pharmaceutical solutions. Due to the accessibility of its hollow fibers, chrysotile asbestos is unstable to acids unlike amphibole.

Since the toxic properties of fibers which enter the lung (see Section 5.2.1.5) and also those of the fine dust which occurs upon processing asbestos and asbestos-containing materials have become known (occurrence of asbestosis, lung cancer and mesothelioma, particularly with smokers), the regulations pertaining to safety provisions have been considerably tightened. In the MPC-list asbestos is classified in the group of carcinogenic materials without a MPC value. The TRK value is 0.025 mg/m^3 and 0.5 fibers/cm^3. Since 1993 the utilization of asbestos and asbestos-containing products have been banned in the Federal Republic of Germany, which has led to much substitution (e.g. with glass, PAN, and aramide fibers; wollastonite, ceramic fibers).

The worldwide production of asbestos attained a maximum of $4.85 \cdot 10^6$ t/a in 1979. Due to the health risks attached to its use, there has been a significant decline in production since then (see Table 5.2-4). In 1997 the worldwide production was only $2 \cdot 10^6$ t/a. In the meantime amphibole asbestos has been banned in most countries. In the Federal Republic of Germany first the application of sprayed asbestos was banned in 1979, then with the entry into force of the dangerous materials ordinance in 1989 the ban was considerably extended and since 1993 a general ban has been in force for the production and new use of asbestos. A corresponding ordinance also exists in the USA, a general ban of all asbestos sorts was, however, lifted in 1991. The situation is possibly also mitigated by the reserves (see Section 5.2.2.2) being only barely adequate. The strong decrease in the Western Industrialized Countries is compensated by an increase in developing countries.

Worldwide production:

1960	$2.15 \cdot 10^6$ t/a
1979	$4.85 \cdot 10^6$ t/a
1997	$2.00 \cdot 10^6$ t/a

Consumption of asbestos currently stagnating

The different qualities (see Table 5.2-2) are reflected in asbestos fiber prices. In 1993 the longest fibers cost ca. 3800 DM/t compared with 4427 DM/t in 1979, whereas short fibers of Group 7 cost only 290 DM/t compared with 220 to 420 DM/t in 1979.

In the USA in 1993 ca. $13.7 \cdot 10^3$ t of asbestos fibers were produced corresponding to a turnover of 11.5 million US$. The number of mines has decreased from fourteen in 1960 to only two in 1993.

5.2.2.2 Occurrence and Extraction

Ca. 98% of the worldwide production of asbestos ($3.1 \cdot 10^6$ t/a in 1993, see Table 5.2-4) is chrysotile. The most important deposits are in Canada and the former States of the USSR with the largest amphibole asbestos deposit being in South Africa. The worldwide reserves have been estimated to be 100 to $150 \cdot 10^6$ t/a and should at current consumption levels ($2 \cdot 10^6$ t/a in 1997) last for 50 to 75 years. The asbestos content of the stone from economically workable deposits is ca. 4 to 10% (Quebec, Urals), the minimum level for economic workability being ca. 3%.

Asbestos deposits:
- 98% chrysotile asbestos
- 2% amphibole asbestos

Deposits of chrysotile asbestos sufficient for 50 to 75 years

Table 5.2-4. Worldwide production of Asbestos in 10^3 t/a.

Country	1960	1979	1993
Russia/former States of the USSR	600	2020	1700
South Africa	170	250	120
Zimbabwe	ca. 50	260	140
Canada	1120	1430	580
USA	45	93	15
China	30	250	240
Brazil	ca. 50	140	230
Others	85	407	85
Total	2150	4850	3110

Industrial extraction of asbestos:

- using the dry process:
  - crushing the rock
  - shredding
  - air classification
  - sorting

The industrial extraction of asbestos fibers by the dry process starts with crushing and loosening of batches of asbestos-containing rock with jaw crushers and double-roll mills. The asbestos fibers are liberated from the dried raw product by repeated breaking up, crushing in pan mills and shredding in drums equipped with knifelike projections. The fibers are separated from the gangue by sieving and air classification and sorted into different fiber lengths with grading drums.

- using the wet process:
  - separation of asbestos fibers using hydrocyclones
  - sorting with a rotary sieve

The wet process enables a narrower fiber length distribution to be obtained for amphibole asbestos. In this process the asbestos fibers are separated from the rock in the crushed mixture by using a hydrocyclone and the longer and shorter fibers separated with a rotary sieve.

Asbestos properties dependent upon:

- asbestos type
- deposit
- chemical composition
- fiber length
- degree of decomposition

The classification of asbestos fibers is carried out on the basis of type and deposits, important classification criteria are also, however, fiber length, degree of decomposition and fiber texture. This leads to a grouping according to industrial application (Table 5.2-5).

5.2.2.3 Applications of Asbestos Fibers

Table 5.2-5. Trade Classification of Chrysotile Asbestos

Group number	Description and typical application fields
A Crude asbestos	hand selected, unshredded
1	contains staple fibers > 1.90 cm and longer
2	contains staple fibers 0.95 to 1.90 cm in length
B mill fibers	ground
3	spinning fibers for asbestos fabric, clothing, asbestos cement pressure pipes
4	slate fibers for asbestos cement pipes
5	long board fibers for asbestos board and packaging, seals, floor tiles, roofing
6	board fibers for asbestos cement boards, roofing
7	short fibers for floor covering, asbestos paper, frictional linings, asbestos cement plates, roofing

Asbestos due to its unique combination of many desirable properties such as e.g. thermal stability, non-inflammability, resistance to rotting, resistance to chemicals, spinnable fibers, good thermal insulation, mechanical strength and good wettability by organic and inorganic binders is utilizable in a broad range of applications in almost all industrial sectors. For example asbestos is used in asbestos cement plates and pipes, brake and clutch linings, asbestos textiles, floor coverings, plastic molding compositions, high pressure sealing plates, asbestos boards, asbestos papers, as filter materials, in molding compounds, as an insulation material, as a diaphragm material and in many other application fields (see Table 5.2.6).

By far the largest quantity of asbestos is utilized in asbestos composites for reinforcing inorganic (cement) and organic (PVC, rubber, duromers) binders. Whereas the consumption in Western industrialized countries has declined steeply (95% in the USA; banned in FRG since 1993), more than $2 \cdot 10^6$ t of asbestos was processed worldwide in 1997 mainly to building materials made from asbestos cement, which were utilized in Asian and Eastern European countries and in developing countries.

Application-related properties of asbestos fibers:

- non-inflammability
- thermal stability
- resistance to rotting
- resistance to chemicals
- spinnable
- mechanical strength
- thermal insulation properties
- good wettability
- very high specific surface areas

Main application fields for asbestos composites for reinforcing of:

- cement
- PVC
- rubber
- duromers

Consumption of asbestos fibers in 10^3 t/a:

	FRG	USA
1975	162	552
1985	75	156
1993	0	32

Table 5.2-6. Consumption of Asbestos in the USA according to Application Field, 10^3 t/a.

application field		1975	1985	1993
roofing		42	26.0	16.0
floor covering		123	7.0	0
asbestos cement	boards	40	7.0	0
	pipes	139	28.0	1.0
frictional coatings		60	34.0	10.0
reinforced plastics		14	0.7	0.1
seals		15	6.0	3.0
other		119	47.0	1.5
all fields		552	156.0	31.6

Substitution of asbestos by:

- glass fibers
- steel fibers
- mineral wool
- carbon fibers
- organic fibers

Since asbestos fibers have been classified as carcinogenic materials, considerable efforts have been made to replace asbestos by other fiber materials, such as, for example, glass fibers (in roofing), steel fibers (in frictional linings), mineral wool (in furnace construction) and organic fibers (in packing materials). These efforts have been made more difficult by the higher price of competing fibers and in some cases by their poorer properties.

Thousands of millions of dollars are expended annually on the disposal of existing asbestos-containing products.

Composites

Asbestos cement has been utilized in the building industry since 1900:

asbestos cement: Portland cement reinforced with 10 to 20% (chrysotile-) asbestos

The most important fiber-reinforced inorganic-based product is asbestos cement, which has been used in the building industry since 1900. Asbestos fibers (normally chrysotile) are bonded by Portland cement and the mixture sets to a fiber-reinforced material with 10 to 20% asbestos, which has excellent properties (Eternit®, Fulgurit® etc.)

Manufacture of asbestos cements:

slurry of cement with asbestos fibers is filtered, pressed into molds (20 MPa) and left to set for 24 to 48 h

In classical asbestos cement processes, a slurry of asbestos fibers and cement is produced and deposited as a fibrous fleece in continuously operating cylindrical sieves. This fleece is then compressed under 200 bar pressure and allowed to set in molds for 24 to 48 h. This process can be accelerated by steam hardening.

Consumer products from asbestos cement:

- boards and shingles
- pipes and molded products

This or similar processes are used for manufacturing boards and shingles for roofs and other industrially molded components, including high pressure tubes suitable for use at pressures up to 40 bar.

Asbestos cement materials are widely used due to their good mechanical properties, low thermal conductivity and resistance to weathering, frost and rotting. The slurry of asbestos and cement can also be processed directly using a spray process, as so-called asbestos spray for fire-retarding layers as well as for thermal (hot and cold) and sound insulation.

Asbestos cement products exhibit:

- good mechanical properties
- low thermal conductivity
- weathering resistant
- rot resistance

The high frictional coefficient (0.4 to 0.5 compared with < 0.1 for glass fibers) of asbestos fibers is crucial to its utilization in the frictional lining sector. In the manufacture of brake and clutch linings 20 to 60% asbestos is incorporated together with fillers, metal chips and preferably phenol resins and rubber into a composite material, which has to satisfy many requirements. Currently there are asbestos-free so-called "semimetallic" brake linings, which consist of mixtures of metal fibers, metal powders, cellulose fibers, aluminum silicate fibers and mineral wool bonded with synthetic resins.

Frictional linings are composites from:

- 20 to 60% asbestos
- phenol resins
- rubbers
- fillers
- metal chips

Asbestos-reinforced organic binders (thermoplastics, duroplasts and elastomers) are widely utilized e.g. hardenable molding materials on the basis of asbestos-reinforced phenol or melamine resins for the manufacture of insulating components for combustion engines, components for electrical installations, cogwheels etc. Possible fiber substitutes are glass fibers, carbon fibers and other synthetic fibers (e.g. aramide fibers) and non-fiber fillers such as calcium carbonate, clay or talcum.

Hardenable molding materials on the basis of phenol or melamine resins with asbestos are used in the manufacture of:

- insulating components in combustion engines
- components for electrical installations
- cogwheels

Asbestos is incorporated in thermoplastics in the manufacture of poly(vinylchloride) tiles and floor coverings, although this is being increasingly replaced by glass fibers. Asbestos-reinforced rubber is utilized as a sealant and is used in the manufacture of It-sheets ("It" is an abbreviation of "Gummi-Asbest"), which is known under different trade names e.g. Klingerit®. Amphibole asbestos is preferred over the usually used chrysotile asbestos for acid-resistant seals. Other fibers e.g. graphite or poly(tetrafluoroethene) fibers are also being used more and more in these applications.

Asbestos-reinforced PVC for:

- tiles
- floor coverings

Asbestos-reinforced rubber for:

- sealing materials ("It"-sheets)
- rotary seals

Woven, flocculated or twisted asbestos textiles are frequently the basis of sealing components such as packing for rotary seals and gaskets. Asbestos paper and asbestos board, produced by the filtration and compression of an asbestos fiber slurry in analogy to paper production, are utilized for cylinder-head gaskets for water-cooled combustion engines.

Manufacture of asbestos paper and board by filtration and compression of an asbestos fiber slurry

Textiles and Filter Materials

Manufacture of asbestos textiles from chrysotile and varying amounts of "carrier fibers" (cotton or organic fibers)

Chrysotile is the asbestos-type most suitable for asbestos textiles. Only about 0.8% of the raw material is spinnable. In the manufacture of asbestos textile products, so-called carrier fibers (cotton or synthetic fibers) have to be added to achieve the required strength. These reduce the maximum operating temperature of the textiles from the ca. 480°C of yarn consisting of 99 to 100% asbestos, the temperature reduction being a function of the carrier fiber-content. Asbestos-free mineral fiber textiles are generally used in the high temperature sector.

Asbestos used as a filter material for:

- clarification of food and beverages
- separation of germs, viruses and pyrogens

The utilization of chrysotile asbestos as a filtration material ranges from the clarifying filtration of foods and beverages (ca. $1.3 \cdot 10^{10}$ L of wine is filtered annually through asbestos in the EU) to degermination to the separation of viruses and pyrogens from highly sensitive pharmaceutical solutions. The high specific surface area, positive zeta potential and ion exchange properties of chrysotile asbestos are a particularly favorable combination and make it difficult to find an asbestos-free substitute.

5.2.3 Textile Glass Fibers

5.2.3.1 General and Economic Importance

Since it became known in the USA in the 1940's that plastics could be reinforced by glass fibers, they have developed into an important product group. These are known as textile glass fibers to distinguish them from insulating glass fibers.

Tensile strength and elasticity modulus of glass fibers depend upon their diameter

Tensile strength and elasticity modulus increase with decreasing fiber diameter, reflecting the decrease in the probability of volume defects per unit length (see Table 5.2-7).

Table 5.2-7. Tensile Strength $\sigma_{tensile}$ of Textile Glass Fibers as a Function of Fiber Diameter $\varnothing_{fiber}$.

$\varnothing_{fiber}$	19	10.2	5.1	2.5	[µm]
$\sigma_{tensile}$	0.7	1.3	2.8	6.0	[GPa]

Thus despite the high brittleness of glass, glass fibers are due to their small diameter flexible, pliable products, which can de processed like textiles. Their diameter is generally between 10 and 25 µm but well below 10 µm for some applications. It is important that glass fibers behave completely elastically under load (i.e. during manufacture and textile processing). Their elongation at fracture is ca. 3%.

Textile glass fibers with diameters with diameters from less than 10 to ca. 25 µm exhibit high strength and stability. They are manufactured in different compositions. By far the most important of these is E-glass, an alkali-deficient Ca/Al/B-silicate, used for the reinforcement of plastics

Differently constituted glass fibers are utilized in the different application fields:

- E-glass, an alkali-poor calcium-aluminum-boron-silicate-glass, for polymer reinforcement and for applications in the electrical sector
- A-glass, a soda-lime glass, for less demanding applications
- C-glass, an alkali-calcium-boron-silicate-glass, with particularly high chemical resistance
- D-glass, for high dielectric requirements
- R-glass, S-glass, special glasses for particularly high mechanical demands also at high temperatures
- AR-glass (AR = alkali-resistant), ZrO_2-containing special glass with improved resistance to alkalis

Chemical composition:

55 – 75%	SiO_2
< 13%	alkali ions
< 21%	MgO, CaO
< 25%	B_2O_3, Al_2O_3

further components: Fe, Ba, Ti, Zr

The composition of the different types of textile glass fibers are given in Table 5.2-8. E-glass fiber is by far the most important textile glass fiber.

Table 5.2-8. Chemical Compositions of Important Textile Glass Sorts (% by weight).

Glass type	A	C	D	E	R	S	AR
SiO_2	72.5	65.0	74.0	54.5	60.0	65.0	71.0
Al_2O_3	0 – 1.5	0 – 4	–	14.5	25.0	25.0	1.0
Fe_2O_3	1.5 – 0	4 – 0	0.2	0.5	0.3	–	–
B_2O_3	–	5.0	22.5	7.5	–	–	–
CaO	9.0	14.0	0.5	17.0	9.0	–	–
MgO	3.5	3.0	0.2	4.5	6.0	10.0	–
BaO	–	1.0	–	–	–	–	–
ZrO_2	–	–	–	–	–	–	16.0
TiO_2	–	–	–	0.1	0.2	–	–
Li_2O	–	–	–	–	–	–	1.0
K_2O	–	8.0	1.5	0 – 0.8	0.1	–	–
Na_2O	13.0	0.5	1.3	0.8 – 0	0.4	–	11.0

Production of textile glass fibers in 1993 in 10^3 t/a:

World	2075
USA	794
Western Europe	483
Japan	312
Others	486

Current market volumes for glass fiber reinforced composites with polymer matrix in 10^3 t/a:

Western Europe	1300
FR Germany	196

The worldwide production of textile glass fibers was ca. $2 \cdot 10^6$ t/a in 1993. An increase to $3 \cdot 10^6$ t/a is expected by the end of the twentieth century. The USA, Western Europe and Japan together produce about 75% thereof, with an increasing share being produced in Eastern Europe and in Asia. The USA production in 1993 was $794 \cdot 10^3$ t/a with a value of 2.523 million US$. The current European market for glass-reinforced polymers is $1.3 \cdot 10^6$ t/a, with $196 \cdot 10^3$ t/a being produced in the Federal Republic of Germany.

5.2.3.2 Manufacture

All industrially important glass fibers are manufactured from silicate melts. They retain their glassy X-ray amorphous structure in the solid state.

Textile glass fibers are produced from silicate melts with sufficient fiber drawing potential. The viscosity increase upon cooling ensures that the molten filament cools to a fiber

Silicate melts suitable for fiber production have to fulfill many requirements: first a sufficient fiber drawing potential, which is dependent upon the ratio of surface tension to viscosity. Fixing of the molten filament in the form of a fiber is a consequence of the increase in viscosity with decreasing temperature. Good fiber formation requires a viscosity-temperature dependence which is relatively flat. The glass must also not exhibit a tendency to crystallization.

The manufacture of textile glass fibers is illustrated below by that for E-fibers.

Raw materials for the manufacture of E-glass fibers:

kaolin, quartz sand, colemanite (calcium borate), boric acid, limestone, dolomite and fluorite

The raw material mixture is melted at ca. 1350°C in tank furnaces lined with chromium oxide and zirconia bricks

The preferred raw materials for the manufacture of E-glass fibers are kaolin (aluminum silicate), quartz sand, colemanite (calcium borate, $Ca[B_3O_4(OH)_3]H_2O$), boric acid, limestone, dolomite and fluorite, which have undergone careful quality control regarding impurity elements and particle fineness. The well-mixed raw materials are melted in flat elongated tank furnaces, which are gas- or oil-heated. Stringent requirements have to be met by the brick-lining of the furnace, due to the high melt temperatures of ca. 1350°C and the corrosiveness of the melt. Chromium oxide bricks are utilized for the sidewalls and zirconia bricks for the bottom of the tanks.

Uninterrupted spinning of the melt requires that it be very homogeneous and free from nonmolten raw materials and gas bubbles

The melt remains in the furnace for several days. A satisfactory yield during the subsequent drawing process requires that the fining of the glass melt be as good as possible i.e. very homogeneous and free from nonmolten raw materials and gas bubbles. This is achieved by air injection through one or more rows of platinum tubes at the bottom of the tank into the glass melt and by adding fining agents.

The hot combustion gases are utilized indirectly using heat exchangers, mainly reversible exchangers made of steel, for preheating the air for the oil or gas burners.

The fined glass melts can be converted into fibers by three processes: by direct melting, marble melting and rod drawing.

Conversion of glass melts into fibers is achieved using the direct melt, marble melt and rod drawing processes with the direct melt process dominating.

The industrially most important process is the direct melt process in which the glass melt passes through a forehearth before being spun. This zone consists of a brick-lined channel in which the melt is cooled to the ca. 1250°C necessary for satisfactory spinning with spinning jets mounted on its side arms.

- Direct melt process:
  the molten glass is led though spinning jets by way of brick-lined (cooling channels)

In the older marble melt process glass marbles manufactured separately are melted in the spinning jets. The marble melt process is only used when very fine fiber diameters are required or when special glass compositions are being used. The rod drawing process is less important. In this process glass rods are fed at a constant speed into the melting zone and fibers are drawn continuously onto a spool.

- Marble melt process:
  separately manufactured glass marble melted in the spinning jets

- Rod drawing process:
  glass rods drawn to fibers in the melting zone

In the direct melt and marble melt processes, the glass melt or glass marbles are fed into platinum-rhodium alloy spinning jets (bushings) which are maintained at ca. 1250°C by resistive heating. The individual bushings have multiples of 200 orifices in particular 400, 800, 1000 or 2000 orifices with diameters of 1 to 2 mm. Upon emerging from a jet the glass melt forms filaments which combine into a spinning strand below the bushings, so that each spinning strand consists of as many individual filaments as there are orifices in the jet. Sometimes several strands are manufactured from the filaments from a single jet ("spin dividing"). The spun filaments are wound at speeds of up to ca. 200 km/h on winding machines thereby producing "spinning cakes". The diameter of the glass fiber at constant drawing speed is determined by the quantity of glass per unit time emerging from each spinning orifice. The quantity of glass emerging is, for a given orifice geometry and a constant glass composition, only dependent upon the temperature of the glass.

The spinning jets (bushings) each with 400, 800, 1000 or 2000 orifices 1 to 2 mm in diameter are made of a Pt-Rh alloy and are maintained at the spinning temperature by direct resistive heating

The filaments are combined are combined into one ore more spinning strands ("spin dividing") below the spinning jet

The spinning strands are wound at speeds of up to 200 km/h on winding machines producing "spinning cakes", immediately quenched below the bushings with a water spray and finally coated with size

Sizes are aqueous dispersions with the following ingredients:

- film-formers
- adhesives
- lubricants
- antistatic agents
- various aids such as emulsifiers, plasticizers, wetting agents

On their way to the winding machine the filaments are immediately quenched after formation with a water spray and are led past a sizing roller, where they are coated with so-called size. This is an aqueous dispersion which contains film-forming and adhesion promoting substances together with lubricants, antistatic agents, plasticizers, emulsifiers and wetting agents.

Functions of the sizes:

- protection of the glass surface
- guarantee processability
- bonding of the glass fiber to the organic matrix

The function of sizes is to protect the vulnerable glass fiber surface, guarantee good fiber processability and provide a good bond between the glass fibers and the plastic being reinforced. Almost every organic matrix and every manufacturing process for glass fiber reinforced plastic components requires a size with a different composition.

Film formers: organic polymers

Adhesion promoters: organofuctional alkoxy-silanes or Cr- and Ti-complexes

Antistatica: inorganic and organic salts

The film formers used are organic polymers such as poly(vinyl acetate), poly(esters), epoxides, poly(urethanes), poly(acrylates), poly(alkenes). These protect the fiber during processing and bond the individual filaments together into spinning strands. The adhesion promoters used include chromium and titanium complexes, but organofunctional trialkoxy-silanes are mainly used e.g. vinyltrimethoxysilanes or those with the general formula $(RO)_3Si-(CH_2)_3-X$, such as γ-aminopropyltriethoxysilane, where X is chlorine or a mercapto-, methacryloxy-, or glycidyl-group and R is an alkyl or hydroxyalkyl group. These adhesion promoters improve the mechanical properties of glass fiber-reinforced polymers, due to their having functional groups which react with the surface hydroxy groups of the glass fibers and others which form chemical bonds with the polymer matrix. For glass fibers not destined for the reinforcement of plastics e.g. yarns and twists, adhesion promoter-free sizes are used. Lubricants such as fatty acid esters, fatty acid amides, paraffins and poly(alkenes) reduce the frictional damage of fibers and make their processing easier. Inorganic and organic salts are added to prevent electrostatic charging. The size amounts to 0.2 to 2% by weight of the dry fibers.

After drying, the spinning cake is converted into glass fiber end-products:

- so-called “rovings” formed by combining multiple spinning strands into glass fiber hanks
- cut glass: cut spinning strands
- milled glass fibers
- textile glass mats

The spinning cake obtained after coating with size is dried in forced air drying kilns and then converted into glass-fiber end-products. In the manufacture of so-called “rovings” many spinning cakes are combined in parallel glass fiber hanks and are wound on precision winding machines. Cut glass is produced by cutting the spinning strands from the spinning cake to the desired length (e.g. 3 to 6 mm) with rapidly turning cutting rollers. Milled glass fibers are produced by grinding precrushed spinning cakes.

In the manufacture of textile glass mats spinning strands, either cut or uncut, are deposited completely randomly and stiffened with a binder.

Glass fiber yarns and twists are obtained by twisting glass filaments or glass staple fibers, which are short glass fibers mainly manufactured by the so-called jet blowing process in which the glass filaments emerging from the jet orifices are tangled together by uniform very fast gas jets. Glass fiber textiles are woven from rovings or yarn in specialized mills.

- glass fiber yarns and twists
- glass fiber textiles

New developments have led to the elimination of the spinning cake stage for glass fiber products, the rovings being wound directly ("direct roving"). Cut glass can also be directly produced by the cutting of spinning strands ("direct chops").

New developments avoid the necessity of producing the spinning cake as an intermediate product

5.2.3.3 Applications

The main application of glass fibers (ca. 80%) is in the reinforcement of plastics. By embedding glass fibers in plastics important properties such as tensile strength, compression strength, flexural strength, elasticity modulus, impact resistance, thermal expansion, maximum use temperature and creep tendency can be improved. Thus a new class of materials has arisen, which due to its easier processability, lower density and good corrosion resistance can compete in the building industry, the electrical industry, mechanical engineering, vehicle construction, and boat building against traditional materials such as wood and metal. The usual matrix materials are viscous processable resins, which harden to duroplasts e.g. phenolic resins (crosslinking by condensation), epoxide resins (crosslinking by reaction) or polyesters (crosslinking by polymerization). Thermoplastics such as polycarbonate, polyamides, polysulfone and polyetherketone are also utilized. Polyimide resins are used for high temperature applications (> 200°C).

Ca. 80% of glass fiber production utilized for reinforcing plastics with resulting improvement in the following properties:

- tensile, compression and flexural strengths
- elasticity modulus
- impact resistance
- thermal resistance
- maximum use temperature
- creep tendency

Application spectrum for glass fiber-reinforced plastics in FR Germany in 1996:

	10^3 t/a	%
• vehicle construction	59	30.0
• electrical industry	51	25.7
• industry & agriculture	40	20.3
• building industry	28	14.2
• sport & leisure activities	6	3.1
• consumer products	7	3.6
• other	6	3.1
• total	197	100

90% of glass fiber-reinforced polymers are duroplasts, generally unsaturated polyester resins

Other application sectors:

- glass fiber mats and textiles for bituminous roofing felt and for carpet backing
- glass fiber textiles for printed circuit boards and grinding disks
- noncombustible textiles e.g. fireproof curtain fabrics

Glass fiber mats and textiles are utilized in the manufacture of bituminous roofing felt and for carpet backing. Glass fiber textiles are also used in the manufacture of printed circuit boards and in the manufacture of grinding disks. Since they are non-inflammable, glass fibers are incorporated into noncombustible textiles such as fireproof curtain fabrics.

Glass fiber filters are utilized in dust removal technology. Alkali resistant AR-glass fibers are utilized in the reinforcement of cement for nonloadbearing applications, because E-glass fibers are destroyed by the alkalinity of the bonding cement.

5.2.4 Optical Fibers

Optical fibers consist of a:

- Core glass with a high refractive index
- Cladding glass with a lower refractive index

Step-index and graded-index fibers differ in their (radial) refractive index profiles.

Optical fibers consist of thin flexible glass strands with a core of optical quality high refractive index glass (GeO_2- or P_2O_5-doped quartz glass) and a cladding of lower refractive index boro- or fluorosilicate glass or in some cases special plastics like silicone resins or fluoropolymers. There are two types: step-index fibers (with a constant refractive index in the fiber core) and graded-index fibers (with continuously decreasing refractive index from the fiber core to the outside of the fiber). The latter exhibit particularly low transmission losses and dispersion (variation in signal transmission time) of the light pulse fed into the ends of the fibers.

Step-index fibers are manufactured using the rod/tube or the double crucible process, in which the core and cladding glasses are melted separately from ultrapure powders and transferred into two crucibles with concentric orifices at the bottom and drawn into a fiber. To obtain a semi graded refractive index profile, a diffusion process can be applied in a curing furnace. Step index fibers with a transmission loss of < 10 dB/km at a wavelength of 0.85 μm can be obtained.

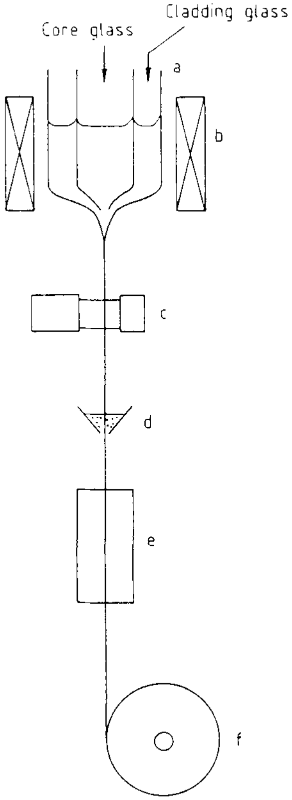


Figure 5.2-2. Schematic of the double-crucible method for producing multicomponent glass fibers.
a) Double crucible; b) Furnace; c) Furnace -diameter monitor; d) Coating applicator; e) Curing furnace; f) Take-up drum.

Graded-index fibers are manufactured from preforms in a drawing tower at temperatures between 2000 and 2300 °C. The preforms are prepared using various vapor phase techniques. The Modified Chemical Vapor Deposition (MCVD) process, developed by Bell laboratories, achieves deposition of glass forming materials by passing vapors of e.g. $SiCl_4$, $GeCl_4$, BCl_3 $POCl_3$ through a rotating heated silica tube. The composition is gradually changed to obtain the desired variation of the refractive index. The tube collapses at a temperature of 2000 °C into solid preforms. In the Vapor Phase Axial Deposition (VAD) process, developed by Japanese companies and the Outside Vapor Deposition (OVD, Corning Glass Works) fine glass particles (soot) are produced by flame hydrolysis of the mentioned gaseous compounds in a H_2-O_2-burner and deposited on a rotating seed rod. The soot preforms are dehydrated in chlorine gas and sintered to a preform from which graded glass fiber can be drawn.

Manufactured by:

step-index fibers:

- Rod/tube process
- Double crucible process

graded-index fibers:

- Vapor phase techniques (with $SiCl_4$, $GeCl_4$, BCl_3 $POCl_3$ as starting materials) for graded-index fibers.

Since the gaseous compounds can be purified very effectively the resulting fibers are very pure with transmission losses of < 5 db at a wavelength of 0,85 µm.

The bandwidth of graded index fiber is much higher (> 1000 MHz · km) than of step index fibers (50 – 100 MHz · km).

Immediately after the drawing process the fiber is coated (e.g. with a silicone resin, PVC, urethane-acrylate resins) to prevent microcracking and thus significantly increase its tensile strength, so that it can withstand the tension in the manufacture and installation of cables.

Optical glass fibers are mainly used for telecommunication systems. They are becoming increasingly economical compared with conventional systems because of their long repeater spacing and high transmission capacity.

By 1997 30 x 10^6 km of optical fiber cables had been installed worldwide and it is expected that this figure will grow to 45 · 10^6 km until 2000.

5.2.5 Mineral Fiber Insulating Materials

5.2.5.1 General Information and Economic Importance

Main constituents of mineral insulating fibers:

- Si, Al, Zr, O
- Ca, Mg, Na, K
- B, Fe, Ti, Mn

The mineral fiber insulating materials dealt with in this chapter, are generally amorphous and consist mainly of SiO_2 and Al_2O_3 with different contents of metal oxides. The most important properties of mineral fiber insulating materials are their thermal conductivity (in the range of 0.03 to 0.04 W/mK), their low bulk densities (between 10 and 200 kg/m^3), their porosity, their elasticity, their temperature stability and their flammability.

Important properties of mineral fiber insulating materials:

- thermal conductivity
- bulk density
- porosity
- springing power
- temperature stability
- flammability

Temperature limits for utilization:

• glass wool	347 - 397°C
• rock/slag wool	697 - 747°C
• refractory ceramic fibers	ca. 1447°C
• Al_2O_3 fibers	ca. 1647°C
• ZrO_2 fibers	ca. 2027°C

The thermal insulation properties depend upon the structure and the bulk density, which can be influenced during processing by varying the thickness, length and arrangement of the fibers in the mat, the proportion of non-fibrous material and the degree of compression of the fibers. For the same bulk density the thermal conductivity increases with increasing fiber thickness, due to a less even distribution of included air. The thermal conductivity also increases with increasing temperature. The temperature stability of fibers increases with increasing aluminum content. The temperature limits for utilization of mineral fibers have to be taken into account and the product selected on the basis of temperatures to which they are to be subjected. The temperature limit for glass wool is a maximum of 347 to 397°C, for rock and slag wool, 697 to 747°C, and for refractory ceramic fibers, ca. 1247 to 1447°C. Pure Al_2O_3-fibers are crystalline and can be utilized for thermal insulation at temperatures up to 1647°C and ZrO_2-fibers are stable up to ca. 2027°C.

Mineral fibers for the production of insulating materials are named after their starting materials as glass or rock fibers and as refractory ceramic fibers. The names mineral, glass or rock wool are usually used, since they, in contrast to textile glass fibers, are produced as short, randomly oriented fibers. The end products are therefore known as mineral wool insulation materials.

The economic importance of mineral wool is considerable. In 1995 the worldwide production was just under $5 \cdot 10^6$ t/a, shared equally by the USA, Western Europe and the rest of the World. The share of refractory ceramic fibers is small and in 1995 accounted with $190 \cdot 10^3$ t/a for ca. 1 - 2% of the total production of synthetic mineral fibers.

Economic importance:

Worldwide production in 1995: $5 \cdot 10^6$ t/a

1/3	Western Europe
1/3	USA
1/3	Rest of World

Of the $1.37 \cdot 10^6$ t of mineral wool produced in the USA in 1992 with a value of 3,061 million US$, 85% was used for building insulation, 12.5% for the insulation of industrial plant and 2.5% for the insulation of pipelines.

$390 \cdot 10^3$ t of mineral wool was produced in the Federal Republic of Germany in 1995 with a value of 511 million DM, of which half by weight was rock wool and half was glass wool. Depending upon the form in which it is used (fiber, paper, mats, textiles etc.) and the application temperature, the prices charged vary between 5-40 DM/kg (up to 1200°C), to 5-70 DM/kg (up to 1400°C), to 100-120 DM/kg (up to 1600°C).

Production in FR Germany in 1995:

- $390 \cdot 10^3$ t mineral wool (rock wool : glass wool ≈ 1:1)
- 10 500t refractory of ceramic fibers

5.2.5.2 Manufacture

General Information

Mineral fibers are manufactured from silicate melts of appropriate composition. These melts are converted into fibers with considerably more efficient use of time and space than in the manufacture of textile glass fibers, since the melts are spun at much lower melt viscosities. After solidification the fibers consist of amorphous glasses (according to X-ray diffraction measurements) with

Mineral fibers are manufactured from silicate melts:

- fiber diameter: 0.5 to 30 μm
- fiber length: 1 cm to several dm

diameters between 0.5 and 30 µm and lengths between 1 cm and several dm depending upon the manufacturing process used.

Raw Materials

Raw materials for glass wool:

sand, lime, dolomite, feldspar, kaolin, alumina-containing igneous rock, sodium carbonate, sodium sulfate, potassium carbonate, boron minerals

In the manufacture of *glass wool*, the raw materials are those usually used in the glass industry i.e. sand, lime, dolomite, feldspar, kaolin, alumina-containing volcanic rocks, sodium carbonate, sodium sulfate, potassium carbonate and boron minerals. The purity requirements particularly as regards iron content are not particularly high.

Raw materials for rock wool:

sedimentary or magmatic rock e.g. clay, marl, basalt, particularly diabase, and additives e.g. lime, dolomite

Rock wool is manufactured from sedimentary or magmatic rocks (e.g. clay, marl, basalt and in particular diabase) with small quantities of additives e.g. lime and dolomite. *Slag fibers*, produced from slags from metallurgical processes, e.g. blast furnace slags, with added mineral raw materials such as lime, dolomite, quartz or clay, are only of minor commercial importance.

Raw materials for refractory ceramic fibers: kaolin and cyanite in addition to alumina, quartz, zircon

The suitability of a raw material composition for fiber formation is determined by the ratio of the viscosity increasing components SiO_2 and Al_2O_3 to the viscosity decreasing ones such as alkali, alkaline earth, iron, manganese and titanium oxides. Pure ceramic raw materials are utilized in the manufacture of low flux *refractory ceramic fibers*, particularly kaolin and cyanite (Al_2SiO_5) together with alumina, quartz and zircon.

Typical compositions of mineral fibers are given in Table 5.2-9.

Table 5.2-9. Composition of Mineral Fibers (in % by weight)

	Glass fibers	Rock fibers	Slag fibers	Refractory ceramic fibers
SiO_2	48.2	45.5	40.6	52.9
Al_2O_3	9.3	13.4	12.5	45.1
B_2O_3	–	–	–	0.08
Fe_2O_3	1.5	8.2	–	–
FeO	0.4	5.8	1.0	–
CaO	28.2	10.8	37.5	–
MgO	3.8	10.0	5.0	–
TiO_2	0.2	2.0	0.4	1.7
MnO	0.05	0.2	0.3	–
P_2O_5	0.06	0.06	0.2	–
CaS	–	–	1.0	–
S	–	–	0.5	–
K_2O	3.6	1.4	0.3	–
Na_2O	4.4	2.5	1.5	0.2

Manufacture of Melts

The raw materials are melted at temperatures of 1200 to 1600°C in tank, cupola, electric arc or electrical melting units. Tank furnaces similar to those used for the manufacture of glass are used for the production of glass wool. The melt vessel is a large rectangular tank with the mixture added at one end and the melt taken off at the other.

Water-cooled cupola furnaces several meters high and with shafts up to 1 m wide are used for the manufacture of rock and slag fibers. The raw materials are added alternately with coke. Metallic iron is formed from the iron-containing raw material and has to be regularly drawn off.

Electric arc resistance heated furnaces and electrical melting units are mainly used for refractory ceramic fibers, due to the high melting temperatures of the raw materials. In ovens with resistance heating the melt itself acts as the electrical resistance, since silicate melts generally become sufficiently conductive with increasing temperature to transport sufficient current, due to ionic conduction.

The raw materials for the different mineral fibers are melted in different furnaces:

- glass wool: tank furnaces with gas or oil heating
- rock and slag wools: cupola furnaces
- refractory ceramic fibers: electric arc and electrical melting units

Manufacture of Fibers

The manufacturing processes can be divided into pulling, centrifugal and blowing processes. These one step processes can be combined with a second blowing step. The pulling process is currently less important than the centrifugal, blowing and two stage centrifugal-blowing processes.

Fiber formation by:

- centrifugal processes
- jet processes
- pulling processes
- two-stage centrifugal-jet processes

Centrifugal process: In the drum centrifugal process the melt flows into a rapidly rotating drum with orifices in the casing, through which is it thrown due to centrifugal forces. In the Hager-Rosengarth centrifugal process the melt flows onto a rotating gas-heated centrifugal ceramic disc. The melt is flung off by way of axial guiding grooves producing fibers 12 to 30 µm in diameter and 100 to 600 mm in length.

Centrifugal processes:
fibers formed from melts with the aid of centrifugal forces

Thin fibers 2 to 10 µm in diameter and with an average length of ca. 15 mm are obtained by the *cascade centrifugal process*, widely used for the production of rock and slag wools. In this process the melt flows onto one of three to four rotors with horizontal axes. From there the melt is transferred with increasing speed to the casing

Cascade centrifugal process used for manufacture of rock and slag fibers surface of the next rotors. The melt droplets flung from the rotors are twisted into fibers and separated in a stream of air from the solidified melt droplets.

Blowing process:

melt is drawn into fibers with high speed gas jets

Blowing process: Blowing processes also supply thin fibers 3 to 12 μm in diameter and several cm in length.

In the blow shreeding Process the melt jet falls into the path of a horizontal high velocity jet of steam or air which draws it into fibers. In the jet-blowing process a fine melt stream flows out of the base plate of a platinum tank. These are drawn into fibers by the action of high speed acute-angled gas jets from slit jets or a multitude of single jets.

Drum centrifugal blowing process (TEL process) mainly used for glass wool production

Two-step centrifugal jet process: the drum centrifugal blowing process (TEL process) is mainly used in the manufacture of glass wool. The melt is thrown out of orifices in the casing of a metal drum rotating and the melt strands further shredded by high velocity hot combustion gases from a concentric combustion chamber at right angles. Fibers with diameters between 5 to 10 μm and lengths of 20 to 400 mm are thereby produced.

Processing of Fibers into Insulating Materials

Production of insulating materials by deposition of fibers as a fleece

Lubricating oils hinder fiber breakage

Binder-free insulating materials:
- loose wools
- stitched onto carrier materials to mats

The fibers from the fiber-shredding units fall into a fleece shaft with a perforated conveyor belt at the bottom. The fibers are deposited as a thick fleece due to the application of a slight vacuum. A lubricating oil emulsion (e.g. vegetable oil) is added to the fleece shaft to reduce the frictional forces and hence the chafing of fibers. In the absence of binders the fibers can be used as loose wool or stitched or nailed onto a support, such as wire gauze, crepe paper or corrugated paper, into mats.

Bonded insulating materials, e.g. sheets or rolls, are manufactured by spraying a binder resin, generally phenol/formaldehyde, onto the fibers and hardening under compaction in a tunnel kiln

In the manufacture of bonded insulating materials, the fibers in the fleece shaft or on the conveyor belt are sprayed with an aqueous binder, generally a phenol-formaldehyde resin. The binder content in the bonded insulating material is 3 to 4%. Compaction to the desired density and hardening of the resin binder occurs in a tunnel kiln, through which the fibers are continuously transported on a conveyor belt. The compaction is achieved with a second belt which exerts the required pressure on the upper surface of the continuous sheet. This is often followed by laminating the sheet with e.g. paper, aluminum or plastic foil. Finally the product is rolled up or cut into sheets.

5.2.5.3 Applications

Main application sector for mineral fiber is as insulating materials:

thermal and sound insulation and fire protection in the construction industry

Mineral fiber insulating materials are mainly utilized in the construction industry for thermal and sound insulation and fire protection. Products based on glass wool, rock wool and slag wool are used. The thermal conductivity of glass wool is more favorable than that of rock wool, as a result of glass fiber-based materials having a lower bulk density than those based on rock fibers. Mineral wool products are used for the insulation of refrigeration plants, cold storage chambers etc., where hard foam insulating materials e.g. expanded poly(styrene) or poly(urethane) cannot be used due to more strict fire protection requirements. For this application the mineral fibers have to be protected against moisture e.g. condensed water.

Insulation of refrigeration plants requires mineral fiber insulating fibers protected against condensed water

In the industrial sector loose wool and molded components, e.g. cup-shaped pieces, are used for the insulation of industrial plant in addition to sheets and rolls. Preformed insulating tubes are utilized for insulating pipelines, but mineral wool mats stitched onto wire gauze are often also used.

Insulation of industrial plants with loose wool, sheets and rolls, as well as preformed molded components

Thermal insulation at very high temperatures (e.g. in furnaces for the metal and ceramic industries) consists mainly of several mineral fiber types on top of one another: refractory ceramic fibers being arranged on the hot side, with in the case of very stringent thermal stability requirements aluminum or zirconium oxide fibers (see Section 5.2.7.2) being used, and rock wool insulation on the cold side. This considerably reduces the consumption of expensive ceramic fibers without loss of efficiency. The utilization of high temperature-resistant fibers in furnace construction often enables linings of refractory brick to be dispensed with. This enables the construction of lighter and more rapidly heated and cooled furnaces resulting in substantial savings in fuel.

For thermal insulation at very high temperatures ceramic fibers are combined with rock wool for economic reasons.

5.2.6 Carbon Fibers

5.2.6.1 General Information and Economic Importance

Manufacture of carbon fibers:

- by inert thermal degradation of nonmeltable polymer fibers

The industrial manufacture of carbon fibers (C-fibers) is based on the thermal degradation of nonmelting organic polymers, or organic polymers which have been rendered nonmelting, to carbon in the absence of oxygen. The

Classification of C-fibers in two types:

- isotropic structure
- anisotropic structure

quality and composition of the fiber starting material and the manufacturing technology used are therefore decisive in determining the ultimate properties attained by the C-fibers. Particularly important for applications in composites, are the mechanical properties of the C-fibers, which are determined by their microstructure and degree of crystallinity. Industrially utilized C-fibers can be classified into two fundamentally different types: isotropic and anisotropic. Their different mechanical properties can be explained in terms of their different fiber structures (see Table 5.2-10).

Table 5.2-10. Starting Materials and Properties of different types of Carbon Fibers.

starting material	cellulose fibers, cotton wool, animal fibers	poly(acrylonitrile) fibers			Fibers from mesophase pitch
microstructure	amorphous	crystalline	crystalline	crystalline	crystalline
fiber structure	isotropic	anisotropic	anisotropic	anisotropic	anisotropic
fiber type	–	HT	IM/HMS	HM	HM
density, Mg/m^3	1.5 – 1.6	1.75 – 1.80	1.75 – 1.80	1.8 – 1.9	1.8 – 2.2
tensile strength, GPa	0.9 – 1.1	3.5 – 6.5	4.5 – 5.5	3.9 – 4.5	2.0 – 2.2
elasticity modulus, GPa	40 – 60	230 – 300	300 – 450	450 – 600	500 – 880
strain, %	1.8 – 2.0	1.5 – 2.2	1.0 – 1.5	0.7 – 1.2	0.3 – 0.4

Isotropic carbon fibers:

amorphous glassy carbon, poor mechanical properties

Isotropic carbon fibers, whose degree of crystalline order is exceptionally low and whose structure is similar to glassy carbon, have the poorest mechanical properties. Their strength is, however, sufficient for their utilization as insulting fibers, filter media and for catalyst support.

Anisotropic carbon fibers:

mechanical properties dependent upon the degree of orientation of the graphite strands in the direction of the fiber axis

Anisotropic fibers, on the other hand, consist of intertwined graphite strands. Their extreme anisotropic properties are known from measurements on graphite single crystals. Graphite exhibits high bonding strength and a very high elasticity in the layer plane, whereas these values are 1 to 2 orders of magnitude lower perpendicular to the plane. The mechanical properties of anisotropic C-fibers (particularly the elasticity modulus) are therefore dependent upon the extent to which the graphite strands are ordered in the direction of the fiber axis.

In *high modulus Type HM*, also known as graphite fibers, the layer planes of the graphite fibrils are predominantly oriented parallel to the fiber axis with high long range order. In the case of *high rigidity C-fibers of Type HT* the layer planes are also oriented along the fiber axis, but with poorer long range order. *C-fibers of Type HMS* were developed in the middle of the 1980's and exhibit both high strength and a high elasticity modulus.

There are three types:

HM: **H**igh **M**odulus
HT: **H**igh **T**enacity
HMS: **H**igh **M**odulus and High **S**trength

The ca. 6 nm wide and over 100 nm long strand-like graphite crystals formed by degradation of the organic polymer material are arranged into microfibrils which are intertwined and have grown together. This is the basis of the strength of this fiber type. They represent the building blocks of all the anisotropic carbon fibers.

The worldwide consumption of carbon fibers has increased strongly in recent years. After their development at the end of the 1960's, a consumption of 1000 t/a was first achieved in the USA in 1982. The worldwide consumption has increased from 3160 t/a in 1985 to 8700 t/a in 1995, of which 40% was consumed in the USA, the rest being equally divided between Japan, the European Union and the rest of the World. A worldwide consumption of 12000 t/a is predicted for the year 2000.

Worldwide consumption of reinforcing carbon fibers:

1979	560 t
1985	3160 t
1995	8705 t

according to country in 1995:

USA	3660 t
Japan	1875 t
EU	1465 t
Others	1705 t

The economic importance of the different C-fibers is reflected in their production capacities. Therefore in the USA the capacity for PAN-based C-fibers (6200 t/a) is a factor of 25 higher than that for pitch-based C-fibers (250 t/a) and a factor of 80 higher than that for rayon-based C-fibers (ca. 100 t/a).

Production capacity in the USA in 1995:

PAN-based	6200 t/a
Pitch-based	250 t/a
Rayon-based	ca. 100 t/a

In the USA in 1994 PAN-based fibers commanded a price of 26 to 44 DM/kg (elasticity modulus = 220 to 230 GPa), 77 to 143 DM/kg (elasticity modulus = 280 to 300 GPa), 165 to 275 DM/kg (elasticity modulus = 350 GPa) and 650 to 1200 DM/kg (elasticity modulus > 450 GPa). In the long term prices of 25 to 35 DM/kg for a minimum order of 1000 kg of C-fibers of the HT-Type are expected.

Rayon-based reinforcing fibers, as a result of their high price of > 800 DM/kg, are only of minor importance. A comparison of the production figures for high performance C-fibers and standard C-fibers shows that the importance of the high performance HT- and HM-C-fibers has steadily increased (see Table 5.2-11).

Table 5.2-11. Production Volumes of Standard and High Performance C-Fibers in the USA in the Period 1979 to 1995.

Year	production (t)	
	high performance C-fibers	standard C-fibers
1979	175	150
1985	1440	285
1990	3390	380
1995	3660	50

5.2.6.2 Manufacture and Applications

Process:

- fiber-shaped starting materials and spinning to organic polymeric fibers
- stabilization of fiber-shape
- carbonization
- graphitization

The manufacture of C-fibers generally occurs by the thermal degradation of suitable organic polymers at temperatures between 900 to 3000°C (see Table 5.2-12). The weight loss accompanying the scission of gaseous molecules (e.g. CH_4, CO, N_2) should be as low as possible.

Table 5.2-12. Pretreatment, maximum temperatures and yield of carbon upon the pyrolysis of different starting materials.

starting materials	stabilization treatment	calcining temperature (°C)	carbon yield in %
poly(vinyl alcohol)	atmospheric oxidation at 200°C	up to 2500	ca. 20
phenolic resins	–	up to 900	ca. 65
rayon	HCl; O_2	up to 1300	30
		up to 2900	25
poly(acrylonitrile)	oxidation at 220 to 250°C	1600/3000	55 - 60
mesophase pitch	atmospheric oxidation below the softening point	1500/3000	80

Requirements for the starting materials for C-fibers:

- non-meltability
- high yield of carbon

The polymeric starting materials must satisfy the following requirements:

- the fiber shape of the organic polymer fiber must be retained, i.e. the polymer must not melt during the thermal degradation process. Any meltable polymers utilized have therefore to be hardened by stabilization treatment (intermolecular crosslinking) i.e. rendered nonmeltable.
- the yield of carbon after thermal degradation should be as high as possible.

Isotropic structure:
carbon felt, carbon wool and woven carbon by pyrolysis of organic precursors:
1st phase: precoking at 300°C
2nd phase: carbonization at ca. 1000°C

Carbon felt, carbon wool and woven carbon, which due to their isotropic structure only exhibit low mechanical strengths and low elasticity moduli, are manufactured by the pyrolysis of organic textiles. Depending on the form of the starting material utilized e.g. as woven textiles or felt, woven carbon or carbon felt is produced after carbonization.

Raw materials:
organic textiles

The manufacturing process proceeds in two stages, the first comprising the decomposition of the organic material at ca. 300°C (precoking). In the second stage the precoked material is degraded at ca. 1000'C to elemental carbon in the absence of air.

Applications of carbon felts, carbon wool and woven carbon:

- high temperature heat insulation
- packing materials
- filter material
- catalyst support

Carbon felts are mainly utilized for thermal insulation at high temperatures e.g. in resistive or induction furnaces. Carbon wool is manufactured by decomposing cotton wool or similar materials and is mainly utilized as a packing material for high temperature heat insulation. Its resistance to chemical corrosion makes it suitable as a filter material for corrosive media, as a support for catalysts and for corrosion-resistant linings in chemical plant.

Manufacture of isotropic C-fibers from pitch:
1st step: melt spinning
2nd step: render nonmeltable
3rd step: inert carbonization

Raw materials for C-fibers from pitch:

- thermally degraded PVC
- coal extracts
- tar pitch
- bitumen

Applications:

- electrically conductive materials
- reinforcement
- frictional lining

Carbon fibers manufactured from pitch are also isotropic, if neither the pitch nor the woven fiber has undergone special treatment. Pitch or coal extract is melt spun at temperatures between 250 and 400°C and the fibers crosslinked and thus rendered nonmelting by treatment with oxidizing agents such as atmospheric oxygen. Subsequent heating in inert atmospheres at temperatures above 1000°C carbonizes the fibers. Suitable raw materials are thermally degraded poly(vinylchloride), crude oil bitumen, hard coal pitch or coal extracts, which are dissolved in high boiling point highly aromatic oils. These fibers are utilized in electrically conductive composites (coatings, thermoplastics, duroplasts), the reinforcement of concrete and frictional linings.

Anisotropic structure:
HT- and HM-fibers

PAN-fibers are currently mainly utilized for the industrial manufacture of anisotropic reinforcing fibers of the HT- and HM-types. The production process is shown in the flow chart below (Fig. 5.2-3).

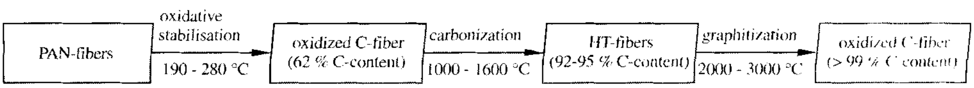


Fig. 5.2-3. Process steps in the manufacture of C-fibers from poly(acrylonitrile) (PAN).

Reinforcing carbon fibers from poly(acrylonitrile) (PAN)-fibers:

1st step: stabilizing oxidation under tension at 300°C;
2nd step: inert carbonization at 1600°C
3rd step: graphitization at 3000°C

PAN-fibers [poly(acrylonitrile) content > 95%] utilized as starting materials are initially subjected to oxidative pretreatment at temperatures below 300°C with the fibers clamped to prevent shrinkage and to produce preorientation in the direction of the fiber axis in the subsequently formed graphite crystals. In the second stage (carbonization stage), high strength carbon fibers of the HT-type are formed at ca. 1600°C, which are converted in a third stage by graphitization at temperatures up to 3000°C into high modulus carbon fibers (HM-type).

High modulus C-fibers from special pitch:
1st step: polymerization > 300°C to mesophase pitch
2nd step: melt spinning
3rd step: oxidative crosslinking
4th step: inert carbonization at 1500 to 3000°C

A process developed by Union Carbide utilizes special pitches to produce high modulus C-fibers. Bitumen or coal tar is first treated at temperatures above 300°C, whereupon a high viscosity phase ("mesophase") is formed which contains a significant proportion of anisotropic graphite precursors ("liquid crystals"). This mesophase pitch is then melt spun, oxidatively crosslinked and carbonized at 1500 to 3000°C. The advantage of this process is a higher yield of carbon (80%) compared to other processes (see Table 5.2.4-3) and inexpensive polymeric starting materials. Furthermore, preorientation occurs upon spinning the pitch to fibers, so that an expensive drawing process can be dispensed with. The tensile strength is lower than for PAN-based fibers, but very high elasticity moduli are attained.

Reinforcing carbon fibers from reconstituted cellulose (rayon):

graphitization with stretching above 2600°C to high modulus C-fibers

In rayon-based C-fibers, historically the first C-fibers, oxidative crosslinking is followed by carbonization at 1000 to 1300°C and a high temperature step at 2000 to 3000°C with simultaneous stretching. The fibers are drawn by tensioning at temperatures above 2600°C. This increases the degree of anisotropy and thereby the elasticity modulus. The high weight loss during pyrolysis and the expensive stretching process at high temperatures account for the high prices of these fibers, so it is only utilized for a few applications. These fibers are used, for example, in the extreme conditions pertaining in space (heat shields, rocket jets).

Marketed form:

bundles of endless fibers with 1000 to 160 000 individual filaments

Processed to:

yarn, textiles, felts and staple fibers

Carbon fibers are commercially available as endless fiber-hanks with 1000 to 160 000 individual filaments. Carbon fibers are flexible and can be treated as textile fibers, due to the small fiber diameter of the individual fibers (ca. 8 μm). Therefore two-dimensional woven articles, knitted articles and felts are available in addition to yarn and thread. Staple fibers are formed by cutting or grinding endless fibers and are available in different lengths (0.5 to 50 mm).

Carbon in the form of endless fibers is a relatively young industrial field, which has developed explosively since its introduction in the 1970's. Whereas in the beginning it was predominantly utilized in the field of military aviation, its utilization in the fields of sports articles and civil aviation has since grown apace. The utilization of C-fibers in civil aviation increased on the 1980's (1 t C-fibers per Boeing 767). At the beginning of the 1990's there was a decline in their use in military aviation, which was more than compensated by increases in the sports article field. In 1995 1200 t of C-fibers was utilized just for the shafts of golf-clubs. Table 5.2-13 shows the evolution in consumption of C-fibers in the different sectors for the period 1979 to 1995.

Application spectrum of C-fibers in %:

	1986	1996
sports articles	45	46
aerospace	40	18
industrial applications	15	36

Table 5.2-13. Consumption of C-fibers according to Application Sector in t/a.

	1979	1990	1995
sports articles in the skiing, golf, tennis, archery, angling, and boat-building sectors	285	2705	3975
aerospace for secondary and primary structures	165	1980	1555
industrial applications, mechanical engineering, automobile manufacture, medical technology	110	1455	3170

Their consumption spectrum changed considerably in the period 1986 to 1996, the aerospace share decreasing from 40% to 18%, the sports article sector share barely changing from 45% to 46% and the industrial applications increasing strongly from 15% to 36%. Annual increases of 5 to 10% are expected.

Composites with:

- polymer matrix
- carbon matrix

Advantages:

- weight reduction
- high strength and stiffness
- corrosion resistant
- noise reduction
- reduced acceleration forces
- low expansion coefficient
- integrated construction

Most of the C-fiber reinforced composites have a polymer matrix. This enables significantly lighter materials (ca. 10 to 25% weight saving compared with aluminum) than metals to be produced with comparable strength and stiffness. Advantages in aviation are lower fuel consumption, a higher payload or a greater range. Whereas in the beginning such materials were only used for secondary structures (wing flaps, rudders, paneling), further development of the materials has enabled their use in primary structures such as rudder assemblies, elevator units, load-bearing surfaces and fuselage components. In automobile construction and mechanical engineering composites are particularly important for heavily loaded, rotating or oscillating components. In addition to weight saving they are also utilized for noise reduction, reduction of acceleration forces and precise control of small weights.

Applications at high temperatures:

200 to 600°C:	carbon fiber/carbon matrix composites
> 600°C:	only in inert atmospheres

Carbon matrices are more suitable than polymers ones for applications at temperatures of 250 to 600°C. Above 600°C they are, however, (as are the C-fibers as such) only utilizable in inert atmospheres. C-fiber reinforced carbon matrix composites are particularly used in aircraft brakes, in fusion reactors and as a substitute for monolithic graphite. In addition they are utilized in the medical sector (implants), in furnace construction (heaters) and in energy conversion (heat exchangers). The market for carbon fiber/carbon matrix composites in 1993 was estimated to be ca. 250 t.

5.2.7 Metal Fibers

Fibers of:

- steel, tungsten, nickel, aluminum, different alloys and boron

Metal fibers of steel, nickel, tungsten and various alloys constitute, based on their diameters, the transition between fibers and wires. They are generally polycrystalline and are mainly produced by physical working processes.

Boron fibers are produced by chemical vapor deposition (CVD) onto a substrate filament (e.g. tungsten or carbon) and thereby consist of two components. They exhibit both metallic and nonmetallic properties, which is to be expected for pure boron due to its position in the periodic table.

Metal-coated fibers are also marketed.

5.2.7.1 Steel and Tungsten Fibers

Properties:

- electrical and thermal conductivity
- high density, high melting point
- high tensile strength, high elasticity modulus

Metal fibers exhibit a range of valuable properties e.g. electrical and thermal conductivity, high tensile strength, high elasticity modulus and high melting points (see Table 5.2-14).

Table 5.2-14. Properties of Metal Fibers.

fiber	melting point, °C	density, Mg/m^3	tensile strength, GPa	elasticity modulus, GPa	diameter, µm
steel (tire cord)	1400	7.8	2.5	205	150
martensitically hardened steel (Taylor wires)	1400	8	3.8	210	7
tungsten	3400	19.3	3 – 4	350 – 420	12

Since the densities of metal fibers are relatively high, they are only suitable as reinforcing material when no extreme demands are made regarding weight saving, in particular the concrete and rubber sectors. Demand for polymer matrices with embedded metal fibers has parallelled the growth of the electronics industry. These composites are utilized for protection against electromagnetic effects. The prices for metal fibers vary strongly with diameter and application. Thus the prices of steel fibers are between 1.80 and 3.30 DM/kg for use in concrete or frictional linings and between 8.30 and 11.20 DM/kg for antistatic or screening applications. The price for tungsten fibers is between 500 and 1500 DM/kg, depending upon fiber diameter and quality (purity, alloy).

Manufacture:

- metal cutting processes
- foil cutting processes
- extrusion processes
- metalization of fibers
- dissolution of wires

Metal fibers can be produced by metal-cutting processes, by foil cutting processes, powder metallurgically by the sintering of metal powders which can be extruded with the help of organic binders to fibers, by metallization of non-metalic fibers and also by the controlled chemical dissolution of wires to the required fiber thickness. Thin metal wires and thick metal fibers can in principle be produced by the same methods.

and particularly for the manufacture of thin filaments:

- continuous filament process
- melt spinning processes
- Taylor process

In addition to these process, special processes are known, particularly for the manufacture of thin metal fibers: the continuous filament process, melt spinning processes and the Taylor process.

Continuous filament process:

multiple pulling of wires through ever narrower dies with intermediate annealing. The process is used for the manufacture of steel fibers for tire cord (ca. 150 µm)

In *continuous filament processes* rolled or predrawn wire is pulled on drawing banks in a multistage process through orifices, die stones or die rings with decreasing cross-sections. The resulting increased brittleness of the material is eliminated by intermediate annealing. Manufacturing costs increase strongly with decreasing diameter, due to the increased probability of fiber fracture. Fibers with diameters > 150 µm can be produced fairly cheaply. The steel fibers important for the tire industry are produced using this method. The brass-coated fibers have diameters of ca. 150 µm.

Bundle pulling process:

continuous filament process with a wire bundle embedded in a matrix (copper): fiber diameters down to 0.5 µm

Much thinner metal fibers are manufactured by the so-called *bundle pulling process*, in which wires are embedded in a ductile matrix (e.g. copper) and are jointly subjected to a continuous filament process. The fibers remaining, after removal of the matrix, have diameters down to 12 µm, but diameters down to 0.5 µm can be obtained with this process.

Melting spinning process:
quenching a jet of molten metal before disintegration into droplets

In *melt spinning processes* a metal melt is forced through dies as a thin jet into a liquid medium so quickly that the solidification rate is faster than the rate of disintegration of the jet into droplets.

Melt extraction is industrially more widely operated, in which a metal fiber is extracted by contact dipping a cooled rotating disc into a metal melt or a metal droplet. Fibers with diameters down to 40 μm and lengths up to several cm can be thereby produced.

Taylor process:
melting and drawing

The so-called *Taylor process* is a variant of the melt spinning process, in which a glass tube filled with metal or an alloy, as powder or as wire, is run through a heating apparatus, melted and drawn to thin metal-filled filaments. Very thin wires down to 1 μm can be produced as monofilaments (Taylor wires). Depending upon the application, the glass skin has to be removed or it can be retained as an insulating coating.

Applications:

- seals
- sound attenuation
- filter material
- in composites with polymers for electromagnetic protection
- light bulb filaments
- electrodes

Stainless steel fibers, produced by the bundle drawing process, are used for seals, for sound attenuation, for antistatic finishes or as filter materials.

An important application field for stainless steel fibers is the textile sector, in which 0.5 to 6% of these fibers are incorporated to endow carpets, protective clothing etc. with an antistatic finish. A further application is protection against electromagnetic pulses, interference and charging. Tungsten fibers with a diameter of 12 μm are used for boron or SiC deposition and as light bulb filaments. Furthermore, metal fibers are used in the filtration of polymer melts and corrosive liquids, as well as for electrodes with high surface areas.

5.2.7.2 Boron Fibers

Properties:
tensile strength 3 - 4 GPa
elasticity modulus ca. 400 GPa

WAK (27 - 327°C): $4.9 \cdot 10^{-6}$/K

Boron fibers possess good mechanical properties at low densities, which accounts for their use in composites for lightweight structures. Commercially obtainable boron fibers exhibit an elasticity modulus at room temperature of 400 Gpa, a tensile strength of 3 - 4 GPa and a thermal expansion coefficient from room temperature to 327°C of $4.9 \cdot 10^{-6}$/K. The maximum use temperature is 367°C, the elasticity modulus having dropped to 240 GPa at 627°C.

Boron fibers exhibit good chemical compatibility with polymer matrices, hence their utilization in composites therewith. At the production temperature of 577 – 677°C, boron reacts with the surface of metal matrices to form borides, particularly in the cases of aluminum and magnesium alloys. Boron fibers coated with 2 to 6 µm thick BN-, SiC- or B_4C-layers to increase their oxidation resistance and act as a diffusion barrier are also marketed. These coatings suppress undesirable metal boride formation in metal matrices.

Boron fibers have at their core a tungsten (ca. 12 to 15 µm in diameter) or carbon fiber, which serves as a substrate during manufacture. Due to the high density of tungsten (19.3 Mg/m^3), a fiber thickness of 100 to 200 µm is necessary to achieve a low overall density for the fiber (ca. 2.6 Mg/m^3). Therefore, latterly deposition on carbon fibers (density: 1.8 Mg/m^3, diameter 8 to 10 µm) has been favored. This development has been driven by their commercial availability of carbon fibers. In addition to their low density (ca. 2.0 to 2.3 Mg/m^3) these fibers exhibit a low surface roughness and low internal stress.

Boron fibers contain a core of tungsten or carbon:

diameter: 100 – 200 µm
density (Mg/m^3): 2 – 2.3 for B/C-fibers
2.6 for B/W-fibers

Whereas other high performance fibers have exhibited annual growth rates of 15 – 25% per year in the period 1987 to 1992, boron fibers have not yet achieved major economic importance. The worldwide production decreased from 40 t in 1987 to ca. 20 t in 1996. The price of 1 kg boron prepreg has increased from 1300 DM/kg in 1979 to 3200 DM in 1995. The worldwide capacity is estimated to be less than 50 t/a.

Economic importance:
low

Attempts to produce boron fibers in a pure state have been frustrated by the brittleness of the material, which has hindered the manufacture of continuous filaments. Currently boron fibers are produced by chemical vapor deposition (CVD) in which boron is deposited by reducing BCl_3 in a hydrogen-containing atmosphere at 1127 to 1177°C, according to the overall reaction:

$$BCl_3 + 1.5\ H_2 \longrightarrow B + 3\ HCl$$

on a heated substrate fiber.

Manufacture:
by gas phase deposition of boron on carbon or tungsten fibers at 1127 to 1177°C according to:

$BCl_3 + 1.5\ H_2 \rightarrow B + 3\ HCl$

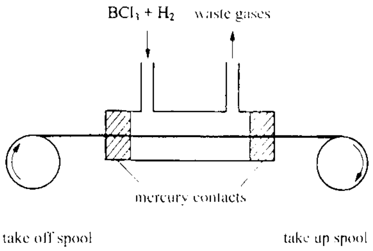


Fig. 5.2-4. Schematic representation of the deposition chamber for the continuous manufacture of boron fibers

In the USA in 1996 ca. 1/3 of the BCl_3 production (70 t) was utilized for the production of boron fibers. Tungsten and carbon fibers are utilized as substrates and can be heated to the reaction temperature by direct resistive heating using mercury contacts. The reaction tubes, which are ca. 2 m high and often arranged in a row, allow the substrate fibers to pass individually through them.

Boron fibers can be utilized for the reinforcing of polymers or, due to their thermal and chemical resistance,

Applications:
reinforcing of polymers and metals for aerospace components and the sports sector

of metals. The resulting composites are utilized in aerospace components and in the sports sector. Boron fibers for light composites are utilized in the form of reinforcing strands in which the fibers are arranged parallel to one another in a partially polymerized epoxy resin so-called prepregs or embedded in an aluminum alloy foil. Three dimensional components, e.g. pressure resistant cylinders, are produced by winding or lamination.

5.2.8 Ceramic Reinforcing Fibers

5.2.8.1 General information and Economic Importance

Economic importance:
minor, but increasing

The market for high performance fibers from ceramics is an up and coming industrial field. Al_2O_3-SiO_2- and SiC-fibers are commercially available, others are in evaluation or in the process of market introduction. Quantitywise the amounts manufactured vary between 0.1 and 100 t/a, but due to their high price (several 100 to several 1000 DM/kg) the turnover in 1995 was ca. 10 to 100 million DM.

Ceramic reinforcing fibers are mainly utilized for the manufacture of composites with:

- polymer matrices, PMC
- metal matrices, MMC
- ceramic matrices, CMC

Both continuously and discontinuously reinforcing fibers are utilized

Ceramic reinforcing fibers are utilized both in a continuous form (endless fibers) and in a discontinuous form (e.g. whiskers, short fibers). Most of the continuous fibers are utilized in the manufacture of composites with polymer matrices (PMC), where they are in competition with other high performance fibers (boron, carbon fibers), mainly for military or aerospace applications. Discontinuous fibers are generally used for the manufacture of metal matrix (MMC) and ceramic matrix (CMC) composites.

In Table 5.2-15, the important properties of four fiber types are compared:

- CVD-SiC-monofilaments
- polymer-derived SiC-fibers
- Al_2O_3-fibers
- SiC-fibers

Application sectors:

- high temperature thermal insulation
- metallic and ceramic composites

Lightweight constructions with improved mechanical properties versus classical metallic materials

These fibers are, due to their high thermal stability, particularly suitable for applications in high temperature thermal insulation and for the manufacture of metal matrix and ceramic matrix composites. They are clearly superior to metal materials due to their lower weight, particularly in the lightweight construction of accelerated structure elements for which the basic material should represent an improvement as regards both strength and toughness. This has already been shown in the cases of glass and carbon fibers (see Sections 5.2.3 and 5.2.6) for polymer matrices. The manufacture of metal and ceramic matrix composites is currently at the end of development and beginning of market testing.

Table 5.2-15. Comparison of the Properties of Typical Reinforcing Fibers.

	SiC-monofilament	SiC-fibers	SiC-whiskers	Al_2O_3-fibers
type	SCS-6	Tyranno	Tokawhisker	Nextel 610
manufacturer	Textron Inc.	UPE Industries	Tokai Carbon	3M Company
density, Mg/m^3	2.5 – 3.0	2.55	3.20	3.88
diameter, µm	140	8 – 12	0.5	10 – 12
tensile strength, GPa	3.6	2.5 – 3.0	14.0	2.9
Elasticity modulus, GPa	400	200	450	375
Maximum application temperature, °C	1400	1200	1400	1100

5.2.8.2 Oxide Fibers

In the reinforcing sector, α-Al_2O_3-fibers are the furthest in development. Low diameter fibers are obtained by the sol-gel process, the spinning of solutions or suspensions and from melts.

Manufacture of Al_2O_3-fibers by spinning of:

- sol-gel-starting materials
- solutions or suspensions

and drawing from melts

The starting point for the *suspension process* is a finely divided aluminum oxide powder suspended in water. An additive provides the necessary viscosity. Spinning of this finely divided suspension with the help of additives provides raw aluminum oxide fibers, which by calcining and treatment at high temperature is converted into non-porous sintered α-aluminum oxide fibers.

Suspension process:

1st step: production of a suspension of finely divided Al_2O_3 in water with spinning additives
2nd step: melt or dry spinning of the suspension
3rd step: calcining at 300 – 800°C
4th step: high temperature treatment at 1800°C (sintering)
5th step: SiO_2-coating

The fibers are manufactured in bundles of several 100 filaments and exhibit tensile strengths of 1.4 to 2.3 GPa and elasticity moduli of 320 to 380 GPa. Disadvantages of the fibers formerly manufactured by DuPont (types: FP and PRD-166, are no longer manufactured) are their high density (3.6 to 4.2 Mg/m^3) and the brittleness of the ca. 20 µm in diameter fibers (see Table 5.2-16). Fibers from Mitsui Mining (type: ALMAX) with a diameter of 10 µm are commercially available at a price of 1900 DM/kg. They are mainly utilized in the reinforcing of aluminum and magnesium.

Table 5.2-16. Properties of Aluminum Oxide-based Fibers.

process	composition, structure	type, company	diameter, µm	density, Mg/m^3	tensile strength, GPa	elasticity modulus, GPa
blowing process	Al_2O_3-SiO_2	Saffil,	1 – 5	3.4	1.5 – 2.0	300
	glassy	ICI Americas				
suspension process	Al_2O_3	ALMAX	10	3.6	1.8	320
		Mitui Mining				
	Al_2O_3-ZrO_2	FP,	20	3.9	1.4	380
	polycrystalline	PRD 166	20	4.2	2.3	380
		DuPont				
sol-gel	Al_2O_3-B_2O_3	Nextel 312	10	3.4	1.7	150
	Al_2O_3-SiO_2	Nextel 720,	12	3.9	2.1	260
	Al_2O_3	Nextel 610	14	3.6	2.8	380
	glassy	3M Company				
edge-defined film growth	Al_2O_3	Saphikon	125	4.0	3.5	470
	single crystal	Saphikon				

Sol-Gel process:

1st step: partial hydrolysis of metal alkoxides and gel formation
2nd step: dry spinning of gel to green fibers
3rd step: calcining at 1000 – 1400°C

The *sol-gel process* starts from a polymeric precursor, which is produced by the partial hydrolysis of aluminum alkoxides. Spun green fibers thereof are pyrolyzed at 1000 to 1400°C. The 3M Company markets different types of fibers produced using this process under the name NEXTEL®. These endless fibers contain 100% Al_2O_3 (Nextel® 610), 85% Al_2O_3 (rest SiO_2; Nextel® 720) and 62% Al_2O_3 (rest boron; Nextel® 312). The addition of oxides generally reduces the tensile strength and the creep resistance. Nextel®312 cost ca. 320 DM/kg in 1993.

Process for growing single crystals:

similar to the Czochralski process, seed crystals being pulled from a Al_2O_3-melt producing monofilaments 25 µm in diameter

- very good properties
- extremely high price

Single crystalline endless fibers can be pulled from the melt in an analogous process to the Czochralski process, seed crystals being placed in the melt and pulled slowly from the melt to produce monofilaments ca. 25 µm in diameter. The advantages of this process, e.g. high purity, no grain boundaries and better mechanical properties, have to weighed against the very high price of these fibers which in the coming years is unlikely to fall below 10 000 to 20 000 DM/kg.

Another type of aluminum oxide-fiber is the Saffil®-fiber from ICI Americas. The raw fibers are produced in the form of short fibers up to several cm in length by a blowing process (see Section 5.2.5.2) from an aqueous medium. The spinnable or blowable solution is obtained from different aluminum salts by adding small quantities high molecular weight spinning aids [e.g. poly(etheneoxide)]. The raw fibers produced by blowing, then have to be decomposed by heating at high temperatures, whereupon the individual fibers are consolidated by sintering. These Saffil®-fibers are mainly utilized for thermal insulation applications at high temperatures up to a maximum of 1650°C (see Section 5.2.5). In addition they are utilized in hot gas filtration and in the manufacture of metal matrix composites (MMC). Its consumption in 1996 was ca. 300 t at a price of 70 to 140 DM/kg.

Blowing process:
1st step: blowing a spinnable aqueous Al-salt solution
2nd step: sintering the fibers

Applications in following sectors:

- thermal insulation
- hot filtration
- composites

Several oxide fibers on the basis of ZrO_2, $Pb(Zr,Ti)O_3$ (PZT), $Y_3Al_5O_{12}$ (YAG) and $YBa_2Cu_3O_x$, which exhibit e.g. catalytic, magnetic, dielectric or superconducting properties, are currently under development or in evaluation for special applications.

Special fibers with:

- catalytic properties
- magnetic properties
- dielectric properties
- superconducting properties

under development or in evaluation

5.2.8.3 Non-oxide Fibers

SiC-fibers stand out among the non-oxide fibers. They possess high structural stability even at high temperatures. This is reflected in their very good resistance to corrosive media, which is also found for monolithic silicon carbide ceramics, making the fibers very suitable for the manufacture of fiber reinforced composites for high temperature applications. There are two basic types: substrate-based fibers, with usually a core of tungsten or carbon and filament thicknesses between 100 and 250 µm; and polymer derived fibers, which are produced by a melt-spinning process with subsequent thermal treatment and have diameters between 10 and 30 µm.

Manufacture of SiC-fibers by:

- polymer pyrolysis
- gas phase deposition
- sintering processes
- chemical conversion

Silicon carbide fibers can be manufactured using the same process as boron fibers (see Section 5.2.7.2), if methyltrichlorosilane is used as the starting material. Deposition from the gas phase proceeds according to the following equation:

Gas phase deposition of SiC on W- or C-fibers at 1200°C (CVD process):
$CH_3SiCl_3 \rightarrow SiC + 3\,HCl$

$$CH_3SiCl_3 \xrightarrow{1200\ ^\circ C} SiC + 3\,HCl$$

Advantages compared with C- and B-fibers:

- higher thermal stability
- low corrosion tendency
- few contact reactions

Reinforcing of:

- metals
- ceramics

Disadvantage: large fiber diameter limits textile processing in the manufacture of composites

can be performed on tungsten fiber or carbon fiber substrates. To obtain stoichiometric SiC, a reactive gas (hydrogen) and a carrier gas (e.g. helium) have to be used. Compared with boron fibers, SiC-fibers have the advantages of higher stability to chemicals and higher oxidation stability at a similar strength. Unlike the deposition of boron, no reaction takes place during the deposition of SiC on carbon fibers, which makes them especially suitable as substrates. Carbon fiber supports are also preferred for economic reasons and for the resulting reduction in overall fiber density. Commercial SiC-fibers exhibit monofilament tensile strengths of 2 to 4 GPa and elasticity moduli of ca. 400 GPa. They are suitable for the reinforcing of plastics, metals and other matrices. Their large diameter (100 to 200 µm) is a disadvantage, making these fibers difficult to process as textile fibers. Some important properties are summarized in Table 5.2-17.

Process steps in polymer pyrolysis:

1st step: polymerization of molecular precursors.
2nd step: spinning of highly viscous polymers.
3rd step: fixing of the fiber shape by intermolecular crosslinking reactions
4th step: pyrolytic decomposition in an inert gas atmosphere
5th step: high temperature treatment

The manufacture of silicon-containing fibers via polymer pyrolysis is characterized by strongly chemically oriented processing. Non-stoichiometric silicon carbide is frequently obtained in which other elements are present e.g. B, N, O, Ti, Zr, Al, etc. Molecular precursors are first polymerized to highly viscous compounds. In the case of poly(carbo)silanes, for example, chlorosilanes are reacted with alkali metals and in the case of polysilazanes chlorosilanes are reacted with ammonia or amines. These are then spun in solution or in the melt and the resulting polymer fibers rendered nonmeltable by physical or chemical hardening. In the pyrolytic decomposition step the hydrogen present is cleaved as CH_4, NH_3 or hydrogen and nitrogen and CO are also split off. At temperatures of 800 to 1400°C a predominantly amorphous structure is produced, in which nano- and microcrystalline deposits are present. The final ceramic fibers have a diameter of 8 to 15 µm and their tensile strengths and elasticity moduli are generally lower those for CVD-SiC-fibers (see Table 5.2-17).

Table 5.2-17. Properties of Silicon-based Fibers.

process	composition, structure	type, company	diameter, µm	density, Mg/m^3	tensile strength, GPa	elasticity modulus, GPa
chemical vapor deposition (CVD)	β-SiC on W polycrystalline	Sigma, BP	100	3.4	3.5	410
	β-SiC on C polycrystalline	SCS-6, Textron	142	3.0	4.0	390
polymer pyrolysis	$Si_{44}C_{25}N_3Ti_{11}O_{12}$ nanocrystalline	Tyranno, UBE	10	2.40	3.0	190
	$Si_{57}C_{31}O_{12}$ nanocrystalline	Nicalon, Nippon Carbon	14	2.55	3.0	200
	$Si_{64}C_{36}O_{<0.5}$ nanocrystalline	HI-Nicalon, Nippon Carbon	14	2.74	2.8	270
	$Si_{67}C_{28}B_2Ti_2O_1$ microcrystalline	SYLRAMIC, Dow Corning	10	3.0	3.4	390
	$Si_{17}B_{17}C_{17}N_{48}O_1$ amorphous	SiBN(C), Bayer AG	12 - 15	1.85	2 - 4	180 - 350
sintering	β-SiC polycrystalline	[CAR], Carborundum	30	3.1	1.5	420
chemical conversion	β-SiC polycrystalline	[MER] MER	5	4.6	2.4	340 - 410

Melt-spinning of SiC-suspensions and the chemical conversion of C-fibers have minor commercial importance

There are two further processes for the manufacture of SiC-fibers: sintering of melt-spun SiC-suspensions; and the chemical conversion of C-fibers by reaction with gaseous SiO. These processes have not yet achieved major commercial importance.

C-fibers and ceramic reinforcing fibers can be coated with SiC by CVD for purposes of reinforcing reactive matrices and for the adjustment of the interface between the matrix and the fiber

Fibers manufactured by the deposition of SiC on carbon yarn, consisting of up to 10 000 individual fibers ca. 10 µm in diameter, also belongs to the SiC-coated substrates. In this case the SiC-skin produced by the thermal decomposition of methyltrichlorosilane above 1000°C only has a thickness of 500 nm. All the monofilaments can be uniformly coated by a suitable choice of deposition conditions. Other coating systems are currently under development. Since the SiC-layers serve as a reaction and diffusion barrier, SiC-coated carbon fibers are suitable for reinforcing reactive matrices such as magnesium or aluminum. The formation of carbides is thereby prevented, making such composites utilizable up to a temperature of 400°C. The CVD-coating of ceramic reinforcing fibers serves mainly to adjust the interfacial characteristics between matrix and fibers, to minimalize contact reactions during manufacture and application and to increase the tolerance to damage of the composites.

Composites with metal and ceramic matrices are in development or evaluation. The high fiber prices and the expensive manufacturing process are hindrances. Fibers for the temperature range of 1300 to 1600°C are being developed.

The prices of SiC-based fibers vary between 1000 and more than 10 000 DM/kg. The manufacturing processes for fiber-reinforced metals and ceramics are expensive, so that these composites have not achieved major industrial importance. Current developments aim to reduce the oxygen concentration of fibers, increase thermal stability and evaluate cheaper manufacturing processes. The composites aimed for would be utilized in the sectors of energy conversion, e.g. in the turbines of aircraft (bearing components) and incinerators (lining, hot gas filter) and would achieve a marketing breakthrough at the beginning of the twenty-first century.

5.2.8.4 Whiskers

Whiskers:

diameter:	0.1 to 1 μm
length:	10 to 200 μm

maximum mechanical properties

Whiskers are single crystalline fibers with a diameter of several tenths of a μm and lengths of 10 to 200 μm. They are characterized by maximum achievable mechanical properties. Thus, for example, tensile strengths of over 10 GPa have been measured with SiC-whiskers.

Production in 1996:

silicon carbide	< 100 t
potassium titanate	ca. 5000 t

More than 100 different materials have to date been produced as whiskers and characterized. However, only SiC- (50 to 100 t, 1996) and potassium titanate whiskers (ca. 5000 t) have achieved commercial importance. Important properties of whiskers are summarized in Table 5.2-18.

Table 5.2-18. Properties of Whiskers.

	tensile strength, GPa	elasticity modulus, GPa	density, Mg/m^3	fiber diameter, μm	fiber length, μm
silicon carbide	14.0	450	3.2	0.5	10 – 15
potassium titanate	4.8 – 5.5	200 – 240	3.3	2 – 5	10 – 20

Whiskers are generally produced from the gas phase at high temperatures

Silicon carbide whiskers are generally manufactured by a metal-catalyzed process, in which carbon and silicon are condensed from the gas phase. Another process utilizes rice husks decomposed at 500°C. At temperatures of 1800°C the carbon/SiO_2-mixture formed is converted into α-SiC. Potassium titanate whiskers are synthesized from potassium molybdate, potassium carbonate and titanium dioxide at temperatures above 1200°C.

Whiskers can be easily mixed with powders and processed as such. Composites are formed with metal (utilization in automobile construction e.g. pistons of whisker-reinforced aluminum), ceramic or polymer matrices for frictional applications (e.g. brake and clutch linings). Small quantities command prices of 1500 to 2000 DM/kg. For larger quantities prices of 100 to 150 DM/kg are expected.

Processing to composites is similar to known processes in monolithic materials

References for Section 5.2: Inorganic Fibers

5.2.1 Introduction

Ullmann's Encyclopedia of Industrial Chemistry. 1985-1986. 5. Ed., VCH Verlagsgesellschaft, Weinheim.

Römpp Chemielexikon. 1996. Hrsg. Falbe, J. et al., 10 Aufl.

Chemical Economics Handbook. April 1995. Stanford Research Institute.

Gefahrstoffverordnung. Technische Regln Gefahrstoffe.

Umgang mit Keramikfaserprodukten, Handanleitung. 1993. Hrsg. Von der Deutschen Keramik-Faser-Gesellschaft unter Mitarbeit der Berufsgenossenschaft, Düsseldorf.

5.2.2 Asbestos Fibers

Liebau, F. 1985. *Structural Chemistry of Silicates*, Springer, Berlin.

Chemical Economics Handbook. 3/1995. Stanford Research Institute, *Asbestos* 712.000A-W and 542.000U-X: *Asbestos Replacement.*

Ullmann's Encyclopedia of Industrial Chemistry. 1985. 5. Ed., *Asbestos*. Vol. A 3, VCH Verlagsgesellschaft, Weinheim.

Clarke, G. 3/1982. Industrial Minerals, 19 - 37.

Alleman, J. E., Mossmann, B. T. 1997. *Asbest: Aufstieg und Fall eines Wunderwerkstoffs*, Spektrum der Wissenschaft, 86.

ECFIA/DKFG: Keramikfasern (RCF) Hintergrund-informationen.

5.2.3 Textile Glass Fibers

Ullmann's Encyclopedia of Industrial Chemistry. 1989 and 1988. 5. Ed., *Asbestos*. Vol. A 12 and Vol. A 11, Section 2, *Glass Fibers*, VCH Verlagsgesellschaft, Weinheim.

Chemical Economics Handbook. 3/1995 and 1/1996. Stanford Research Institute, *Textile Glass Fibers USA* 542.8000A-R and *Glass*, 232.1000O-T.

Arbeitsbemeinschaft Verstärke Kunststoffe e.V., GFK-Marktentwicklung 1991 – 1996.

Loewenstein, K. L. 1993. *The Manufacturing Technology of Continuous Glass Fibers*, 3. Ed., Elsevier, Amsterdam.

Mohr, J. G., Rowe, W. P. 1978. *Fiber Glass*, Van Nostrand Reinhold Comp., New York.

v. Falkai, B. 1981. *Synthesefasern, Grundlagen, Technologie, Verarbeitung*, 248, Verlag Chemie, Weinheim.

Tagungshandbuch 242. 191. Intern. AVK-Tagung, Berlin, *GFK ohne Grenzen.*

Brehm, B. , Sprenger, K.-H. 1985. *Moderne Faserverbundstoffe*. Sprechsaal, Vol. 118, 253.

5.2.4 Mineral Fiber Insulating Materials

Ullmann's Encyclopedia of Industrial Chemistry. 1988. 5. Ed., *Fibers*, Vol. A 5, *Synthetic Inorganic*, Section 3, *Refractory Fibers*, VCH Verlagsgesellschaft, Weinheim.

Chemical Economics Handbook. 2/1997. Stanford Research Institute, 542.6001D-O.

Produktinformationen der Firmen Deutsche Rockwool Mineralwolle GmbH. Gladbeck, und RATH-Fasertechnik-Vertriebs GmbH, Düsseldorf.

Schupp, M. E. 1990. *A Global of the Refractory Ceramic Fiber Market*, Ceramic Bulletin, Vol. 69, 63.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1991. 4. Ed., John Wiley & Sons, New York.

v. Falkai, B. 1981. *Synthesefasern, Grundlagen, Technologie, Verarbeitung*, 248, Verlag Chemie, Weinheim.

Zander, H. P. 1989. *Keramische Faserstoffe: Eigenschaften – Konstruktionen – Risiken und Grenzen*, Sprechsaal, Vol. 122, 126, 347, 574.

Technische Maßnahmen zur Verminderung der Risiken durch künstliche Mineralfasern (KMF) sowie Anforderungen an mögliche Alternativen, Bundesanstalt für Arbeitsschutz und Umweltbundesamt. 1997. Berlin.

5.2.5 Carbon Fibers

Ullmann's Encyclopedia of Industrial Chemistry. 1988. 5. Ed, Vol. A 11, *Fibers*, 5. Fibers Synthetic Inorganic, Section 5, *Carbon Fibers*, VCH Verlagsgesellschaft, Weinheim.

Chemical Economics Handbook. 2/1997. Stanford Research Institute, *Carbon Fibers*, 542.4000B-Z, 542.4001A-Z, 542.4002A-L.

Donnet, J.-B. et al. (Ed.). 1998. Carbon Fibers, 3. Ed., Marcel Dekker, New York.

Blumberg, H. 1997. *Fibers for Composites – Status Quo and Trends*, Chemical Fibers International, **47**, 36.

Dietrich, W. 1995. *Vow Ski zur Tragfläche*, Physik in unserer Zeit, **26**, 35.

Produktinformationen der Firmen Tory, Frankfurt/M., SGL, Meitingen und Tenax, Wuppertal.

Segal, C. L. 1996. *21st Century Market – Opportunities for Advanced Fibers and Composites*, SAMPE, **32**, 12.

5.2.6 Metal Fibers

Ullmann's Encyclopedia of Industrial Chemistry. 1988. 5. Ed., Vol. A 11, *Fibers.5. Synthetic Inorganic*, Section 4, *Metal Fibers*, VCH Verlagsgesellschaft, Weinheim.

Chemical Economics Handbook. 2/1997. Stanford Research Institute, *Specialty Inorganic Fibers*, 542.6002B-M and *Specialty Inorganic Fibers*, 542.6000F-K.

Carlson, J.-O. 1986. *Boron Fibers*, Encyclopedia of Material Science and Engineering, Ed. Bever, M. B., Vol. 1, Pergamon Press, 402.

5.2.7 Ceramic Reinforcing Fibers

Chemical Economics Handbook. 2/1997. Stanford Research Institute, *ceramic Reinforcing Fibers*, 542.6000K – Z and 542.6002A – Z and 542.6002A – C; *Silica Fibers*, 542.6001P – Z and 542.6002A – U.

Product information from the companies: UBE Industries and Nippon Carbide, Japan, and 3M Company, Minnesota, USA.

Kriegesmann, J. (Hrsg.). 1993. Technische Keramische Werkstoffe, Köln, Kap. 4.4.0.0 *Faser- und whiskerverstärkte Werkstoffe.*

Bowman, K. J. et al. (Ed.) 1995. *Handbook on Continuous Fiber-Reinforced Ceramic Matrix Composites*, Am. Ceram. Soc., Westerville, Ohio.

Lehmann, R. L. et al. (Ed.) 1995. *Handbook on Discontinuously Reinforced Ceramic Matrix Composites*, Am. Ceram. Soc., Westerville, Ohio.

Cooke, T. F. 1991. *Inorganic Fibers – A Literature Review*, J. Am. Ceram. Soc. **74**, 2959.

Segal, C. L. 1996. *21st Century Market – Opportunities for Advanced Fibers and Composites*, SAMPE, **32**, 12.

Kostikov, V. I. (ED.). 1995. *Fibre Science and Technology*, Chapman & Hall, London.

Baldus, J.-P., Jansen, M. 1997. *Moderne Hochleistungskeramiken – amorphe anorganische Netzwerke aus molekularen Vorläufern*, Angew. Chem. **109**, 338.

5.3 Construction Materials

5.3.1 General Introduction

Many inorganic substances are used in the construction industry:

Bonding agents:

inorganic substances which harden in the presence of water or air which bond pieces of stone

- hydraulic bonding agents: harden in air and in water (e.g. cement)
- air bonding agents: harden only in air (e.g. calcined gypsum)

Bonding agents in the construction industry are inorganic substances which can bond pieces of stone together. They are processed with water and harden through chemical or physical reactions to a stone-like mass. There are hydraulic binding agents and air-bonding agents. Hydraulic bonding agents harden both in air and water and when hard are water resistant. The different silicate cements (see Section 5.3.3) and hydraulic hardening limes (see Section 5.3.2.3) fall into this category. Air bonding agents only harden in air and are not water-resistant (see Section 5.3.2.4).

Calcined gypsum, anhydrite (see Section 5.3.4), magnesia cement (see Section 5.3.3.8) and silicate-free limes (see Section 5.3.2) belong to this category. Mixtures of bonding agents with sand are known as *mortar*, mixtures of hydraulic bonding agents with coarse admixtures such as gravel, rubble or expanded materials (see Section 5.3.6) are known as *concrete*. *Plasters* are mixtures of lime and sand or lime, sand and gypsum.

Mortar:
mixture of bonding agents with sand

Concrete:
mixture of gravel, rubble or expanded materials with hydraulic bonding agents

Natural stone or artificial *stones* such as bricks (see Section 5.3.5), sand-lime bricks, aerated concrete bricks (see Section 5.3.2.5) and expanded-clay blocks (see Section 5.3.6.2.3) are used for building walls.

Building of walls with stones, bricks, sand-lime bricks, aerated concrete bricks

Tiles (see Section 5.3.5), concrete roofing tiles, asbestos cement tiles (see Section 5.3.3.7), porous gypsum boards (plasterboard) and metallic materials are used as roofing materials.

Roofing materials:
tiles, concrete roofing tiles, asbestos cement tiles, metals

Other inorganic materials are also used, which are considered in other sections of this book: glass (see Section 5.1.1) and sound and thermal insulation materials (see Section 5.2.3).

Glass, sound and thermal insulation materials

5.3.2 Lime

5.3.2.1 Economic Importance

The term lime normally covers both limestone ($CaCO_3$) and "quicklime" (CaO), which is produced from it by calcination. "Slaked lime" [$Ca(OH)_2$] is formed by reacting quicklime with water.

"Limestone": $CaCO_3$
"Quicklime": CaO
"Slaked lime" or "lime hydrate": $Ca(OH)_2$

Table 5.3-1. Lime and Dolomite Consumption in the Federal Republic of Germany in 1994, estimated from Chemical Economics Handbook 1996.

consumer sector	share (%)	quantity in 10^6 t/a
industry	39	3.224
building materials	29	2.397
environmental protection	13	1.075
various incl. export	9	0.744
building trade	8	0.661
agriculture	2	0.165
total	100	8.267

Lime consumption in 1994:

- FRG: $8.27 \cdot 10^6$ t/a
- World: $130 \cdot 10^6$ t/a

Table 5.3-2. Worldwide Production and Production in Leading Producing Countries of Lime (in 10^6 t) according to Chemical Economics Handbook-SRI International 1996

year	1991	1992	1993	1994
World	145.5	140.0	137.8	130.0
USA	17.3	17.8	18.5	19.2
China	20.4	20.9	21.5	21.5
Japan	9.9	8.9	8.9	8.5
Mexico	7.2	7.2	7.2	7.2
Former States of USSR	28.7	25.3	22.0	17.6
FR Germany	8.3	8.3	8.2	8.3

5.3.2.2 Raw Materials

Deposits of calcium carbonate:

- as calcite, aragonite and vaterite
- with $MgCO_3$ in the form of $CaMg(CO_3)_2$

The starting material calcium carbonate occurs naturally as calcite and more rarely as aragonite and vaterite. In natural deposits calcium carbonate is often found as mixtures with magnesium carbonate. The mineral $CaMg(CO_3)_2$ is known as dolomite.

- in mixtures with clays as marl
- further deposits as marble, travertine, shell limestone and chalk

Mixtures of limestone with clays are so-called marl. Other deposits of limestone are marble, travertine, shell limestone and chalk whose properties depend upon their origin.

5.3.2.3 Quicklime

"Lime burning" is the thermal decomposition of $CaCO_3$:

"Lime burning":

$CaCO_3 \rightarrow CaO + CO_2$

$$CaCO_3 \xrightarrow{>900\ ^\circ C} CaO + CO_2$$

Industrial decomposition of:

- $CaCO_3$ at 900 to 1100°C
- $MgCO_3$ at 650 to 750°C

The decomposition temperature of $CaCO_3$ is ca. 900°C, that of $MgCO_3$ between 400 and 480°C. Industrially the decomposition of $CaCO_3$ is carried out at 900 to 1100°C.

Hydraulic limes:

by decomposition of marl

With dolomite rock, which can contain up to 50% dolomite, the decomposition proceeds in two stages: first the magnesium carbonate is decomposed at 650 to 750°C and then the calcium carbonate is decomposed above 900°C. When the limestone is contaminated with clays (marl) compounds such as $2CaO{\cdot}SiO_2$, $3CaO{\cdot}Al_2O_3$, $2CaO{\cdot}Fe_2O_3$ and $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ are formed on calcination. These compounds are also constituents of Portland cement clinkers (see Section 5.3.3.3.2) and harden upon reaction with water (hydraulic limes or highly hydrated limes), but not upon reaction with carbon dioxide. The quality of the quicklime is affected by the source and composition of the limestone and also by the nature of the fuel used.

Industrial lime burning:

- in shaft kilns

Lime burning formerly took place in holes in the ground and kilns with wood, coal or peat as fuel, in which the limestone covered the fuel. These developed into the so-called "shaft kilns". Limestone is ground into coarse particles (ø = ca. 60 to 120 mm) and loaded layer-wise with coal in the shaft kiln. The burning of the mixed-in coal produces a temperature of 900 to 1100°C, whereupon carbon dioxide is liberated.

- in modified shaft kilns

Since with this oven type only coarse particles are burnt, the quality of the burnt lime is not particularly uniform (it containing insufficiently burnt or overburnt lime). This led to the development of improved continuously operated shaft kiln types, which basically comprise a preheating zone, a calcining zone and a cooling zone. Coal, coke (lower ash content) or gas and oil are generally used as fuels. There are different kiln types such as crossflow kilns, doubly inclined kilns, cocurrent/countercurrent/regener-ative kilns, double shaft/regenerative kilns and ring shaft kilns. These new developments all achieve a more uniform temperature distribution and thus a better product quality and more effective energy utilization. In addition the processing of more finely ground limestone (ø = ca. 20 to 70 mm) is possible.

- in rotary kilns

In addition to the different shaft kiln types, rotary kilns are often used for lime burning. This enables good quality quicklime to be obtained with cheap fuels. Smaller limestone particles (10 to 60 mm) are utilized.

- in calcimatic furnaces (rotary grate kilns)

Calcimatic furnaces (rotary grate kilns) consist of a circulating grate on which the product to be burnt is fed as a thin layer through a stationary heating zone. Since the product is not moved during the calcining, very fine limestones can be burnt in these kilns.

- in fluidized bed kilns

Dorr-Olivier have developed a unit in which the burning proceeds in a fluidized bed.

- in floating gas furnaces

In floating gas furnaces, the reaction is carried out in cyclones connected in series. This produces very reactive quicklime.

Currently shaft kilns with the most modern technology and rotary kilns with preheaters are mainly used, depending upon the required product properties.

5.3.2.4 Slaked Lime

Hardening reaction of slaked lime:
$CaO + CO_2 \rightarrow CaCO_3 + H_2O$

The mode of action of lime as a bonding agent is based on the reaction of calcium hydroxide with carbon dioxide in the air:

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$$

Quicklime must therefore be first converted into slaked lime:

$$CaO + H_2O \longrightarrow Ca(OH)_2 + 65.5\ \text{kJ/mol}$$

Table 5.3-3. Capacity in t/d and heat consumption in kJ/kg of different furnace types for the burning of lime.

furnace	capacity	heat consumption
shaft kiln	80 to 400	3500 to 4500
double inclined kilns	140	3900
cocurrent/regenerative kilns	300	3770
rotary kilns	up to 1000	5020 to 8370
calcimatic kiln	max. 300	5000 to 5700
fluidized bed kilns	100 to 200	4900

Strength of hardened lime is based on intergrowth of $CaCO_3$ crystals

This strongly exothermic process is technically known as "slaking" and is carried out in different processes, which are described in the following sections. The strength of the hardened lime is based on the intergrowth and matting together of the calcium carbonate crystals formed.

5.3.2.4.1 Wet Slaking of Quicklime

"Wet slaking":
leads to a wet lime hydrate slurry ("milk of lime")

"Wet slaking" leads to a wet lime hydrate slurry (so-called "milk of lime"). This process was formerly carried out at the construction site itself by scattering quicklime into a controlled excess of water, thereby achieving a lime hydrate slurry with a high plasticity.

Today "wet slaking" is industrially carried out only by large consumers such as mortar manufacturers. In addition to batch processes continuous processes can also be used, which generally operate at 90°C.

5.3.2.4.2 Dry Slaking of Quicklime

Dry slaking: yield dry $Ca(OH)_2$

In dry slaking calcium hydroxide is obtained as a dry powder. Use is made of the fact that so much heat is produced by the reaction of calcium oxide with water that the amount of water bound is approximately equal to that which can be evaporated. The so-called reactivity of the quicklime influences the product quality. Highly reactive lime leads, upon slaking, to a granular material, which has to be ground again.

Reaction carried out in:

- overflow tanks

Industrially, a continuously operating overflow tank is generally used. About twice the stoichiometric quantity of water is added to the calcium oxide in a premixer and the mixture transported to the reaction tank, in which the heat from the exothermic reaction heats up the reaction mixture to 100° C. The evaporating excess water entrains the very small lime hydrate particles and carries them upwards, where they are separated by an overflow from the coarse particles. The hydration process is then completed. The calcium hydroxide obtained contains less than 1% water.

- in autoclaves in the case of difficult to slake and MgO-containing limes (Corson process)

In the case of difficult to slake lime, i.e. particularly highly calcined limes and limes with a high magnesium oxide-content, complete hydration can only be achieved under pressure. During the reaction a pressure of 2 to 8 bar is attained under which even the poorly soluble components are hydrated. The steam is separated from the dry calcium hydrate by rapid pressure release (Corson process).

5.3.2.4.3 Lime Hydrate from Calcium Carbide

"Acetylene lime": from calcium carbide

Very cheap "acetylene lime" was formerly produced as a byproduct of the manufacture of ethyne from calcium carbide:

$$CaC_2 + 2\,H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

Since most ethyne is now manufactured directly from crude oil or natural gas, this process is now only of minor importance.

5.3.2.5 Steam-Hardened Construction Materials

Sand-lime bricks and aerated concrete blocks:

from lime and silicate raw materials

Large-quantities of quicklime are used in the manufacture of sand-lime bricks and aerated concrete blocks. These are construction materials which are manufactured from lime-containing and silicate-containing raw materials and whose strength is due to the hydrothermal reaction of the raw materials to calcium silicates.

Hardening by hydrothermal reaction and formation of calcium and magnesium silicates

Sand-lime bricks are manufactured by mixing lime, sand and water in a ratio of ca. 1:13:0.7, forming and then hardening in autoclaves at 180°C and 7 to 9 bar.

Aerated concrete:

- by foaming of the reaction mixture of lime, sand and optionally cement
- by gas-forming reactions: e.g. formation of hydrogen from aluminum powder, water and $Ca(OH)_2$

Aerated concrete bricks are widely used as light building materials. They are obtained by mixing gas-forming additives into a moist mixture of lime, sand and optionally cement. Industrially, the following reaction is generally used:

$$2\,Al + 3\,Ca(OH)_2 + 6\,H_2O \longrightarrow 3\,CaO \cdot Al_2O_3 \cdot 6\,H_2O + 3\,H_2$$

The well-known Ytong® building materials are manufactured using this process. Aluminum can be used instead of zinc or magnesium. Other gas-forming additives e.g. hydrochloric acid/limestone or hydrogen peroxide/chlorinated lime have been described, but have hardly been used industrially.

$$2\,HCl + CaCO_3 \longrightarrow CaCl_2 + H_2O + CO_2$$

$$H_2O_2 + CaCl(OCl) \longrightarrow CaCl_2 + O_2 + H_2O$$

5.3.2.6 Applications of Lime

Applications of limestone:

- raw material for the manufacture of quicklime
- as cut and hewn stone
- as rubble for roads or railway track
- as an additive for mortar or concrete
- as a filler (see Section 5.8)
- in the metallurgical industry as a sintering aid for fine ore pellets, as a slag-former, as a desulfurization agent
- in the chemical industry in the manufacture of sodium carbonate and fertilizers [lime ammonium nitrate

NH_4NO_3 + $CaCO_3$, calcium nitrate $Ca(NO_3)_2$] (see Sections 2.2 and 3.1)
- in the glass industry (see Section 5.1.1)
- in cement manufacture (see Section 5.3.3.3.3)
- as a fertilizer (see Chapter 2)

Applications of quicklime:

- in the iron and steel industry for removing sulfur and phosphorus
- for the treatment of effluent
- in the chemical industry for the manufacture of calcium compounds (calcium carbide, calcium cyanamide) and as a cheap base (see Section 3.1)
- as a fertilizer
- in the sugar industry for the removal of oxalic and citric acids from cane juice
- in the construction industry (with different specifications under DIN 1060)

Applications of lime hydrate:

- for the manufacture of whitewash (paint)
- for the manufacture of caustic soda
- for flue gas desulfurization (see Section 5.3.4.6.2)
- for the manufacture of wollastonite (see Fillers: Section 5.8)
- in the construction industry (with different specifications under DIN 1060)
- as a fertilizer (see Chapter 2)

5.3.3 Cement

5.3.3.1 Economic Importance

Table 5.3-4. Cement production worldwide (in 10^6 t) according to figures from the World Statistical Review No. 17, Cement Production, Trade, Consumption Data, Cembureau, 1996 .

	1992	1993	1994
World	1246	1292	1363
America	165	175	188
Asia	660	734	800
Europe	252	241	251

Cement production in 1994:
World: 1363 · 10^6 t/a

Europe: 211.4 · 10^6 t/a
(most important producers)

Table 5.3-5. Cement Production in Europe (in 10^6 t/a).

	1992	1993	1994
Italy	41.4	34.7	33.2
F.R. Germany	33.2	32.5	36.1
Turkey	30.2	32.7	31.9
Spain	25.0	23.9	26.7
France	22.6	20.5	21.1
Poland	12.8	13.0	14.9
Greece	13.6	13.9	14.3
Great Britain	11.0	11.1	12.2
Belgium	8.1	7.6	8.4
Portugal	7.6	7.6	8.0
Austria	5.0	4.8	4.6

5.3.3.2 Composition of Cements

The composition ranges of particular cement types and cement additives in the three component system $CaO-SiO_2-Al_2O_3$ are given in Fig. 5.3-1.

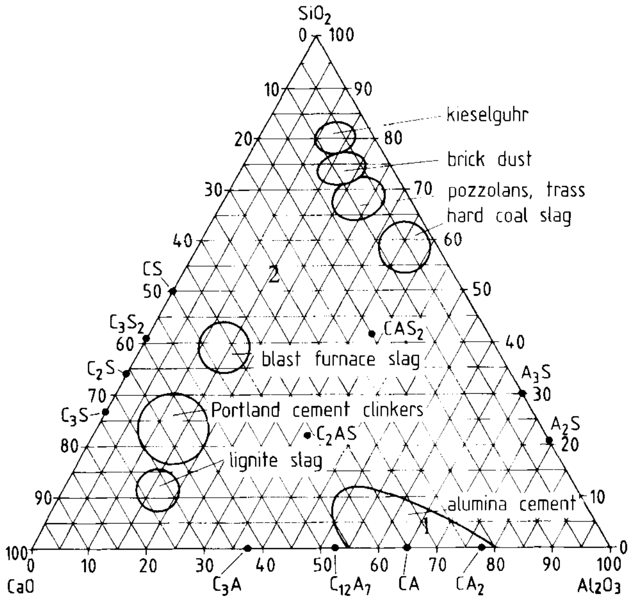


Fig. 5.3-1. Three component system $CaO-SiO_2-Al_2O_3$ with composition ranges for the hydraulic bonding agents.
(1) strongly fire-resistant alumina cement; (2) acidic blast-furnace slag

5.3.3.3 Portland Cement

5.3.3.3.1 Raw Materials

The cement type manufactured in the largest quantities and used most is "Portland cement". It consists of so-called Portland cement clinkers admixed with gypsum or anhydrite.

Portland cement:

consists of Portland cement clinkers and gypsum

Lime- and clay-containing raw materials such as limestone, lime, clay, marl, lime marl, or clay marl (marls are naturally occurring mixtures of limestone and clay) are utilized as raw materials in the manufacture of Portland cement clinkers.

Raw materials for Portland cement clinkers:

limestone or lime, clay, marl

5.3.3.3.2 Composition of Portland Cement Clinkers

For the composition of Portland cement clinkers also see Fig. 5.3-1 and Table 5.3-8.

Table 5.3-6. The Important Clinker Phases and their Properties.

name	formula	abbreviation*	technical properties of cement
tricalcium silicate (alite)	$3CaO \cdot SiO_2$	C_3S	rapid hardening, high heat of hydration, high strength
dicalcium silicate (belite)	$2CaO \cdot SiO_2$	C_2S (a-,a'-,b-mod.)	slow, steady hardening, low heat of hydration, high strength
tricalcium aluminate	$3CaO \cdot Al_2O_3$	C_3A	in larger quantities, rapid solidification, high heat of hydration, contraction tendency, sensitivity to sulfate water
calcium aluminum ferrite	$2CaO(Al_2O_3,Fe_2O_3)$	$C_2(A,F)$	slow hardening, resistant to sulfate water
free lime	CaO	C	in small quantities unproblematical, in large quantities induces bursting and too rapid hardening
free magnesia	MgO	M	in larger quantities induces magnesia bursting

* The following abbreviations are usual in cement chemistry: C = CaO; S = SiO_2; A = Al_2O_3; M = MgO; N = Na_2O; K = K_2O; C = CO_2; H = H_2O

5.3.3.3.3 Manufacture of Portland Cement

Since tricalcium silicate endows Portland cement with its desirable properties such as rapid hardening and high

Main constituent of Portland cement clinkers: tricalcium silicate strength, it is important to ensure that as much tricalcium silicate as possible is obtained in the manufacture of Portland cement clinkers, by using appropriate mixing ratios of the raw materials and sintering in the existence range of tricalcium silicate (between 1250 and 2070°C).

Important in the manufacture of Portland cement clinkers:

- accurate adjustment of the lime content (free lime in the clinkers causes "lime bursting")

It is important to adjust the lime content as accurately as possible. According to H. Kühl, the maximum lime content which can be bonded by the components SiO_2, Al_2O_3 and Fe_2O_3, can be calculated using the formula:

$$CaO_{max} = 2.8\ SiO_2 + 1.1\ Al_2O_3 + 0.7\ Fe_2O_3$$

At higher lime contents, free lime is present in the clinkers. The $Ca(OH)_2$ or $Mg(OH)_2$ formed upon hydrating free lime (CaO or MgO) takes up more space than the original oxide. Therefore, CaO (or MgO) in coarse crystalline lumps gives rise to so-called "lime bursting" (or "magnesia bursting"), since the reaction with water is very slow and continues after the cement is hard.

- lime saturation factor $LSF = CaO/CaO_{max}$

The quantity of lime added is always, therefore, kept below the calculated limit (the so-called *lime saturation factor*, $LSF = CaO/CaO_{max}$).

- silicate modulus: $SiO_2/(Al_2O_3 + Fe_2O_3)$

A further factor in defining the raw mixture is the *silicate modulus*, which is the ratio of SiO_2 to the sum of Al_2O_3 and Fe_2O_3. If the silicate modulus is too high, the cement sets slowly.

- alumina modulus: Al_2O_3/Fe_2O_3

The *alumina modulus* is the ratio of alumina to iron oxide. If the alumina modulus is 0.637 or less, no tricalcium silicate in formed in the melt phase.

The *hydraulic modulus*, which is the ratio of CaO to the sum of SiO_2, Al_2O_3 and Fe_2O_3, was often used previously. For good cement quality, it should be between 1.7 and 2.3.

- finest possible grinding of the raw materials, to ensure a quantitative reaction

In the preparation of the reaction mixture, the raw materials also have to be ground as finely as possible to ensure as complete a reaction as possible during burning.

There are several processes for the manufacture of the clinkers:

Preparation processes:

- in the wet process the raw materials are ground wet to a raw slurry, which is then formed and burnt

- in the *wet process* the starting materials are ground wet to a "wet slurry", which is then dried in a rotary kiln and burnt. The wet process ensures a simple and accurate dosing of the components and requires little energy during grinding. The subsequent burning process is, however, very energy intensive, due to the quantity of water which has to be evaporated. This process is only

Table 5.3-7. Comparison of processes for cement manufacture and the furnace types used therefor.

	wet processes	half wet processes half dry processes		dry processeses		
furnace type used	long wet rotary kiln	short rotary kiln	shaft kiln	long dry rotary kiln	floating gas heat exchanger kiln	floating gas heat exchanger kiln with precalcination
equipment for heat exchange	chains, crosses, chamber preheater	hearth preheater		chains, crosses, lifters, chamber packing	cyclone or chamber preheater	cyclone or chamber preheater
feed material	raw slurry	blocks from filter-pressed raw slurry	pellets and fine coal or coke particles	dry raw powder, granules	dry raw powder	dry raw powder
H_2O content in %	30 to 40	10 to 20	up to 10	0.5 to 1	0.5 to 1	0.5 to 1
kiln dimensions diameter in m	3 to 7.6	2.5 to 6	2 to 3	3 to 7	3 to 6	6
length in m	80 to 230	30 to 100	8 to 10	70 to 230	40 to 110	100
heat consumption in GJ/t clinker	5 to 6	3 to 3.8	3.1 to 4.2	3.6 to 4	3 to 3.8	ca. 3.3
throughput in t/d	300 to 3800	300 to 3300	up to 300	300 to 3000	300 to 5400	up to 8500

economic where the starting materials have high water contents (> 20%) or when wet treatment is unavoidable e.g. with "slurries" or chalk.

- in the half-wet process the wet ground raw slurry is dewatered mechanically before sintering

- in the *half-wet process* the wet-prepared raw slurry is dewatered in filter presses and then pressed in paste molds to pellets, which are burnt in rotary kilns.

- in the half-dry process the dry-ground raw mixture is moistened and granulated prior to sintering

- the *half dry process* differs from the half-wet process in that the raw mixture is produced by dry grinding and mixing of the starting materials and the homogenized raw powder is granulated to pellets with water on granulating tables.

- in the dry process the raw materials are processed dry

- in the *dry process* the starting materials are also dry ground and mixed to "raw powder". During grinding the product is dried with the hot flue gases of the firing kiln to a residual moisture content below 1%, in which state it is fed into the firing kiln.

Burning temperature for Portland cement clinkers: ca. 1450°C

The burning of the raw materials in all the described processes is carried out at ca. 1450°C, mainly in rotary kilns. Table 5.3-7 summarizes the individual processes and the kiln types used for them.

Heat recovery in rotary kilns: with grate preheaters or cyclone preheaters

In rotary kilns the raw powder is preheated by the hot flue gases. The use of special preheaters (grate preheaters, cyclone preheaters) can make heat recovery even more efficient.

Table 5.3-8. Typical chemical compositions of a Portland cement clinker.

SiO_2	16 – 26 %	CaO	58 – 67 %
Al_2O_3	4 – 8 %	MgO	1 – 5 %
Fe_2O_3	2 – 5 %	$K_2O + Na_2O$	0 – 1 %
Mn_2O_3	0 – 3 %	SO_3	0.1 – 2.5 %
TiO_2	0 – 0.5 %	P_2O_5	0 – 1.5 %

The largest rotary kilns with grate preheaters (Lepol furnaces) have a capacity of up to 3000 t clinker per day and those with cyclone preheaters up to 5000 t per day. In the latest developments the calcining is partly carried out in a preliminary step, in so-called precalciners, which are between the preheater and the rotary tube, to reduce the thermal loading of the rotary tube. The required clinker throughput can then be achieved with smaller rotary tubes or existing plants can increase their capacities. The largest plants with cyclone preheaters produce up to 8000 t/day.

Shaft kilns are only economic for very small plants ($\leq$ 300t/day) and their number has declined sharply since 1974.

The heat consumption of the wet processes is significantly higher than that of dry processes. Thus few wet furnaces are still in operation.

Wet process hardly operated due to higher energy consumption

After the rotating tube furnace, the burnt clinkers are immediately transferred to a cooler, to ensure rapid cooling. Slow cooling leads to a reduction in the tricalcium silicate content and to crystallization of the melt. Grate, tube and planetary coolers are used. The cooling air is then utilized in the calcination process.

Rapid cooling of the clinkers to obtain a high content of the tricalcium silicate phase

The burnt clinkers are then ground. Before grinding, up to 6.5% of gypsum ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$) is added to delay solidification together with other hydraulic materials such as blast-furnace slag or trass, as required.

Ready-to-use Portland cement:
by grinding the clinkers with added gypsum

5.3.3.3.4 Applications of Portland Cement

Portland cement is widely used in the construction industry for the manufacture of concrete with admixtures such as gravel, sand and expanded materials, with steel reinforcement as reinforced concrete and as a binder between bricks and other building blocks.

Uses of Portland cement:

- as a binder in concrete
- to bond together bricks and other building blocks

5.3.3.4 Slag Cement

Lime is added during the manufacture of raw iron in blast furnaces to separate off the iron ore gangue, mainly consisting of clays. At the reaction temperatures of ca. 1600°C, easily melting slags are formed, similar in composition to Portland cement (see Fig. 5.3-1). Upon addition of an appropriate "activator" (such as lime hydrate) the rapidly cooled glassy solidified blast-furnace slag possesses hydraulic properties. It is therefore described as "latent hydraulic". Blast-furnace slags and melts are, therefore, rapidly cooled with water upon being vented from the blast furnace producing a glassy "foundry sand" as sand-like grains (it is important that the glassy content is as high as possible). Mixtures of Portland cement clinkers with less than 35% foundry sand are known as iron Portland cement, mixtures with higher slag contents, as blast-furnace slag cement. The Portland cement clinker is

"Foundry sand" (blast-furnace slag):
formed upon addition of lime during iron ore gangue separation in blast furnaces

Iron Portland cement:
mixtures of Portland cement clinkers with < 30% foundry sand

Blast-furnace slag cement:
mixtures of Portland cement clinkers with > 30% foundry sand

here used as an activator for the blast-furnace slag (clinker activation).

Supersulfated cement:
by activation of the latent hydraulic properties of foundry sand with gypsum

Activation of the latent hydraulic properties of foundry sand can also be achieved with gypsum (sulfate activation). Mixtures of foundry sand with a high aluminum oxide and lime content with ca. 15% calcium sulfate (as raw gypsum or natural anhydrite) are known as supersulfated cement.

Properties of blast-furnace slag cements:

- lower heats of hydration
- higher chemical resistance

Blast-furnace slag cements with high slag contents have lower heats of hydration than pure Portland cement, which is advantageous for large scale concrete structures (e.g. dams). The lower calcium hydroxide content results in their being somewhat more chemically stable than Portland cement. Blast-furnace slag cements are used in similar applications to Portland cement.

5.3.3.5 Pozzolan Cements

Pozzolans:
natural or synthetic silica-containing materials, which react with the $Ca(OH)_2$ formed during cement hardening

Lime hydrate is formed during the hardening of Portland cement (see Section 5.3.3.9), which makes only a small contribution to the strength of the hardened cement paste. Pozzolans are silica-containing natural or synthetic materials, which can form calcium *silicate* hydrates with lime and water even at low temperatures. Their addition to Portland cement clinkers can therefore improve the strength of the cement, but their slower hardening is a drawback. The pozzolans are ground together with cement clinkers and gypsum to form pozzolan cement.

Natural pozzolans:
trass, santorin earth

Synthetic pozzolan:
fly ash

Naturally occurring pozzolans are trass (a volcanic tufaceous rock found in the Rhineland, Bavaria and Austria), santorin earth (Greece) and the Italian pozzolans (Pozzuoli near Naples). A synthetic material with similar properties is fly ash, which is produced in hard coal- and lignite-fired power stations.

Properties of pozzolan elements:
good chemical resistance

Pozzolan cements exhibit good chemical resistance.

The composition range of the pozzolans is shown in Fig. 5.3-1.

5.3.3.6 Alumina Cement

Alumina cement consists of calcium oxide and aluminum oxide compounds (see Fig. 5.3-1), mainly CA, CA_2 and $C_{12}A_7$ (the abbreviations are explained under Table 5.3-6).

It is manufactured from limestone ($CaCO_3$) and bauxite (mainly Al_2O_3). The melting point of mixtures of limestone and bauxite is in the range ca. 1500 to 1600°C and the sintering interval for rendering the batch liquid is limited to a very narrow temperature range.

Industrially, alumina cement is produced either in rotary or shaft kilns by fusing the raw material mixture (melt cement) or using electric arc furnaces (electro-melt cement). Alumina cement exhibits a very high initial strength, which, however, particularly at high temperatures, decreases strongly with time. It is therefore forbidden in the Federal Republic of Germany for load-bearing structures made of reinforced concrete. Alumina cement is less stable to alkali due to the possibility of freely soluble alkali aluminates being formed.

Alumina cement is used in refractory pastes at temperatures up to 1700°C. "Rapid setting cement" consists of mixtures of alumina cement and Portland cement (used e.g. in sealing water leaks).

Alumina cement:
- consists of CaO/Al_2O_3 compounds
- manufactured from limestone and bauxite

Melt cement:
by fusing of the raw material mixture in rotary kilns

Electro-melt cement:
by fusing in an electric arc furnace

Properties of alumina cement:
- high initial strength, which decreases strongly over time
- applications: in refractory pastes and in rapid setting cement

5.3.3.7 Asbestos Cement

Asbestos cement is regarded as an application rather than a cement type. The aqueous slurry of cement and asbestos is mechanically dewatered and sets to a very rugged material, from which pipes, containers, roofing-tiles etc. can be manufactured (Eternit®, Fulgurit®). For further information see Section 5.2.2.3.

Asbestos cement:
by setting of an asbestos-reinforced cement slurry

5.3.3.8 Miscellaneous Cement Types

"Expanding cement" (shrinkage-compensated cement) do not shrink upon hardening. Addition of 10 to 15% of calcium sulfate or aluminate even effects an expansion ("managed gypsum bursting").

"White cement" is a Portland cement manufactured from particularly pure raw materials with very low iron oxide contents.

Expanding cement:
mixture of Portland cement and calcium sulfate or aluminate

White cement:
low iron oxide Portland cement

Sorel cement:
mixture of MgO and magnesium salts

So-called *"sorel cement"* is not a cement in the true sense of the word. Mixtures of caustic burnt magnesite (reactive MgO, produced by heating magnesium carbonate just above its decomposition temperature) and magnesium salts harden into a stone-like mass. "Sorel cement" is obtained by reacting magnesium oxide with concentrated magnesium chloride solution:

$$3\ MgO + MgCl_2 \xrightarrow{H_2O} 3\ MgO \cdot MgCl_2 \cdot 11\ H_2O$$

$3MgO \cdot MgCl_2 \cdot 11H_2O$ is formed in fine needle-shaped crystals and develops its strength, as with Portland cement or gypsum, by matting of the needles. The material is not water resistant and is used for flooring plasters and industrial flooring. With added sawdust it is known as woodstone or xylolith.

Woodstone or xylolith:
sorel cement with added sawdust

Magnesia cement exhibits, even when dry, a considerable electrical conductivity. As a result flooring produced from it does not exhibit static charging.

Heraklith®:
stone-like mass from MgO and magnesium sulfate

Magnesium sulfate also forms a stone-like mass with magnesium oxide, which is used for the manufacture of lightweight boarding (Heraklith®).

5.3.3.9 Processes in the Solidification of Cement

After mixing the cement:
- C_3A and gypsum react to ettringite

Upon mixing cement powder with water, part of the tricalcium aluminate C_3A and gypsum dissolve and react together forming ettringite:

$$3\ CaO \cdot Al_2O_3 + 3\ CaSO_4 + 32\ H_2O \longrightarrow \underbrace{3\ CaO \cdot Al_2O_3 \cdot 3\ CaSO_4 \cdot 32\ H_2O}_{\text{ettringite}}$$

- delayed setting of Portland cement by deposition of ettringite on cement particles

The ettringite crystals on the surface of the cement particles are so fine that they cannot bridge the gap between the cement particles and therefore do not form a solid structure. This is the basis of the delay in solidification upon adding gypsum to cement. Without gypsum the tricalcium aluminate immediately reacts with water to calcium aluminate hydrate, which fills the space between the cement particles with its large crystals and leads to very rapid solidification of the cement slurry.

Portland cement (containing gypsum) solidifies after 1 to 3 hours. The needle-shaped ettringite crystals recrystallize forming larger needles which bond the cement particles together and solidify the crust.

- solidification of Portland cement: after 1 to 2 hours by recrystallization of small ettringite crystals to larger crystals

The hydration of tricalcium silicate C_3S and dicalcium silicate C_2S (for abbreviations see below Table 5.3-6) are responsible for the further solidification of Portland cement. This reaction only begins in earnest after ca. 4 hours. Initially long needles of calcium silicate hydrate are formed, which bond the cement particles together. Later, smaller needles of calcium silicate hydrate fill the gaps left. The more reactive tricalcium silicate hydrolyzes much faster than dicalcium silicate.

Solidification of Portland cement:

- hydration of tricalcium silicate and dicalcium silicate to a tobermorite-like phase $3CaO \cdot 2SiO_2 \cdot 2H_2O$

Table 5.3-9. Reaction Products of the Components of Portland Cement Clinkers with Water.

clinker components		reaction products	
name	formula	formula	description
tricalcium *silicate* (alite)	$3CaO \cdot SiO_2$	$3CaO \cdot SiO_2 \cdot nH_2O$	tobermorite-like phase
dicalcium *silicate* (belite)	$2CaO \cdot SiO_2$	$3CaO \cdot 2SiO_2 \cdot nH_2O$	
in the absence of sulfate			
tricalcium aluminate	$3CaO \cdot Al_2O_3$	$4CaO \cdot Al_2O_3 \cdot 19H_2O$ $4CaO \cdot Al_2O_3 \cdot 13H_2O$	tetracalcium aluminate hydrate
calcium aluminum ferrite	$CaO(Al_2O_3, Fe_2O_3)$	ditto, Al partly replaced by Fe	
in the presence of sulfate			
tricalcium aluminate	$3CaO \cdot Al_2O_3$	$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ and $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$	ettringite "monosulfate"
calcium aluminum ferrite	$CaO(Al_2O_3, Fe_2O_3)$	ditto, Al partly replaced by Fe	

$$2(3\,CaO \cdot SiO_2) + 6\,H_2O \longrightarrow 3\,CaO \cdot 2\,SiO_2 \cdot H_2O + 3\,Ca(OH)_2$$

$$2(2\,CaO \cdot SiO_2) + 4\,H_2O \longrightarrow 3\,CaO \cdot 2\,SiO_2 \cdot H_2O + Ca(OH)_2$$

The calcium aluminate still present reacts with the calcium hydroxide formed to tetracalcium aluminate hydrate. Calcium aluminum ferrite forms the analogous hydration product, which reacts more slowly. Part of the aluminum is replaced by iron:

Subsequent reactions:

tricalcium aluminate reacts with $Ca(OH)_2$ to tetracalcium aluminate hydrate

$$3\,CaO \cdot Al_2O_3 + Ca(OH)_2 + 12\,H_2O \longrightarrow 4\,CaO \cdot Al_2O_3 \cdot 13\,H_2O$$

$$4\,CaO \cdot Al_2O_3 \cdot Fe_2O_3 + 4\,Ca(OH)_2 + 22\,H_2O \longrightarrow 4\,CaO \cdot Al_2O_3 \cdot 13\,H_2O + 4\,CaO \cdot Fe_2O_3 \cdot 13\,H_2O$$

Final phase in the solidification:

ettringite reacts with tricalcium aluminate forming "monosulfate"

The initially formed ettringite reacts with the tricalcium aluminate present and with the calcium hydroxide produced in the meantime to form "monosulfate":

$$2\,(3\,CaO \cdot Al_2O_3) + 3\,CaO \cdot Al_2O_3 \cdot 3\,CaSO_4 \cdot 32\,H_2O + 4\,H_2O \longrightarrow \underset{\text{„monosulfate"}}{3\,(3\,CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12\,H_2O)}$$

The temporal changes in the proportions of the phases occurring during the solidification of Portland cement are schematically shown in Fig. 5.3-2.

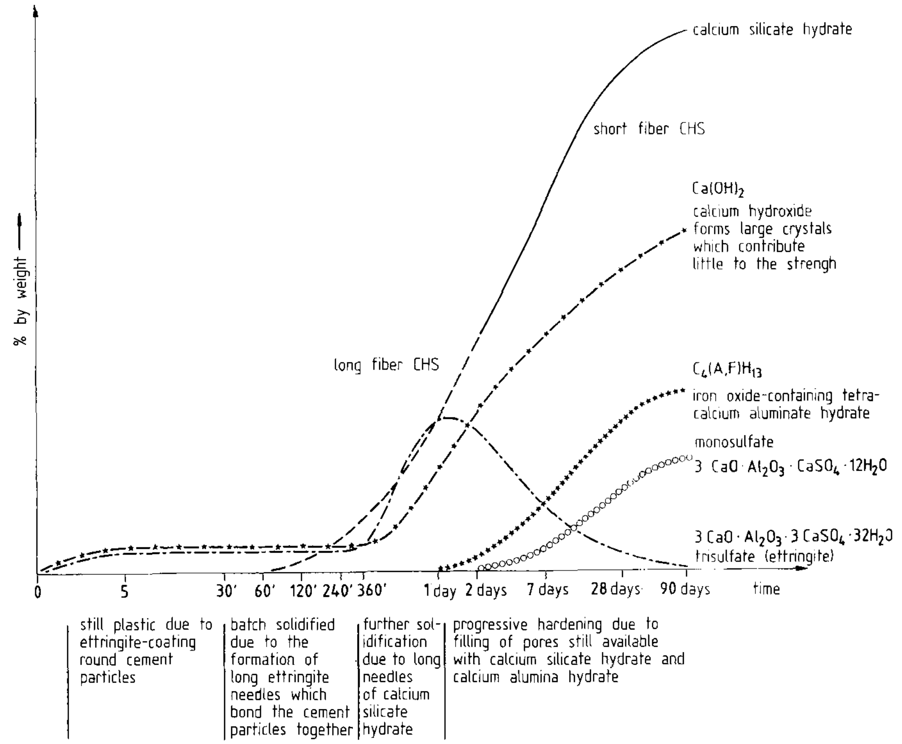


Fig. 5.3-2. Processes in the setting of cement. [according to F. W. Locher in Zementtaschenbuch (Cement Handbook) 1984, p. 67, Bauverlag, Wiesbaden (1984)]

5.3.4 Gypsum

5.3.4.1 Economic Importance

The leading gypsum producer and gypsum consumer is the USA. Most is consumed in the construction industry for the manufacture of gypsum plasterboard and in the cement industry.

In the Federal Republic of Germany in 1994 the consumption of gypsum was $6.2 \cdot 10^6$ t/a, of which 60% was provided by natural gypsum and 40% by REA-gypsum (gypsum from flue gas desulfurization). The proportion of REA-gypsum should increase by the year 2000 to 55% corresponding to $5.6 \cdot 10^6$ t/a.

Natural gypsum production in 1994 in 10^6 t:

World:	95.2
USA:	17.3
FRG:	2.3

The gypsum from phosphoric acid production (phosphogypsum) is largely dumped on land or in the sea, only 3 to 4% being further utilized, particularly in countries without their own gypsum deposits. In the Federal Republic of Germany this gypsum has disappeared from the market as a secondary raw material because of its impurities and concomitant purification costs. The production of phosphogypsum in the wet acid process worldwide is estimated to be $140 \cdot 10^6$ t/a. The worldwide consumption of phosphogypsum in 1995, however, only amounted to 93 t/a.

Phosphogypsum:
worldwide $> 140 \cdot 10^6$ t/a

Table 5.3-10. Worldwide production of natural gypsum in 10^6 t/a, World Mineral Statistics 1991 – 1995, British Geological Survey 1996.

	1993	1994
World	92.4	95.2
USA	15.8	17.2
China	10.6	11.0
Canada	7.7	9.0
Thailand	7.4	8.1
Iran	7.8	7.9
Spain	7.3	7.4
FR Germany	2.1	2.3

In the Federal Republic of Germany ca. 0.5 to $1 \cdot 10^6$ t/a of natural gypsum is utilized annually in the cement industry and 0.4 to $0.5 \cdot 10^6$ t/a in the mining industry. Ca. $0.35 \cdot 10^6$ t of anhydrite is produced annually in the manufacture of hydrofluoric acid (fluoroanhydrite), of which ca. $35 \cdot 10^3$ t is utilized in the cement industry and

Natural anhydrite: 0.5 to $1 \cdot 10^6$ t/a

Production of fluoroanhydrite:

World (1996)	$2.1 \cdot 10^6$ t/a
Europe (1996)	$0.7 \cdot 10^6$ t/a
FR Germany	$0.35 \cdot 10^6$ t/a

the rest in the construction industry. It is estimated that ca. $0.7 \cdot 10^6$ t of fluoroanhydrite was produced in 1996 in Europe and ca. $2.1 \cdot 10^6$ t worldwide.

Technologies for flue gas desulfurization have been developed

Production of flue gas desulfurized (REA) gypsum:

Europe :	$6 \cdot 10^6$ t/a (in near future)
Japan:	$3 \cdot 10^6$ t/a
FR Germany:	$3 \cdot 10^6$ t/a

More than $62 \cdot 10^6$ t of sulfur dioxide is produced worldwide in the combustion of coal, crude oil and natural gas. Technologies have been developed to remove the sulfur dioxide contained in flue gas, industrially utilizable gypsum being produced. In Japan the $3 \cdot 10^6$ t of gypsum produced by flue gas desulfurization is completely utilized industrially. After equipping the large coal-powered power stations in the Federal Republic of Germany with desulfurization units, ca. $3 \cdot 10^6$ t of ultrapure REA-gypsum was produced in 1994, which is utilized as a secondary raw material in the construction and cement industries. In Europe ca. $6 \cdot 10^6$ t/a of such gypsum is expected to be produced in the near future.

5.3.4.2 Modifications of Calcium Sulfate

Deposits:

- as gypsum $CaSO_4 \cdot 2H_2O$
- as anhydrite $CaSO_4$
- as bassanite $CaSO_4 \cdot 0.5H_2O$

The following modifications of calcium sulfate are known:

$CaSO_4 \cdot 2\,H_2O$:	natural gypsum, dihydrate
$CaSO_4 \cdot 0.5\,H_2O$:	bassanite, hemihydrate
$CaSO_4$:	anhydrite

Calcium sulfate α- and β-hemihydrates have different crystal habits and specific surface areas

Calcium sulfate occurs naturally as its dihydrate, (natural gypsum) as anhydrous anhydrite and rarely as its hemihydrate in the form of the mineral bassanite. Only the deposits of natural gypsum and anhydrite are of economic interest. For applications in the construction industry only the hardenable modifications, calcium sulfate hemihydrate (α- and β-form) and anhydrite, which are manufactured by dehydrating the dihydrate, are important. The properties and formation conditions of the different calcium sulfate modifications are given in Table 5.3-11.

Table 5.3-11. Formation Conditions and Properties of the Calcium Sulfate Modification.

formula	name	forms of occurrence	crystal form	stability range [°C]	in laboratory [°C]	industrially [°C]	properties	applications
$CaSO_4 \cdot 2H_2O$	gypsum dihydrate	–	mono-clinic	< 40 only stable phase under normal conditions	< 40	< 40	"hardened gypsum", by needle-shaped intergrown crystals, high strength. Acts to accelerate hardening in mixtures with hemihydrate or anhydrite	
$CaSO_4 \cdot 0.5H_2O$	bassanite hemihydrate	α-hydrate	rhombo-hedral	metastable	< 45 in aqueous medium	80 to 800	very high strength, rapid and slow hardening	molding plaster, industrial and dental plaster
		β-form	rhombo-hedral	metastable	45 to 200 in dry air	120 to 180	medium strength, medium hardening rate	stucco and mortar; in mixtures with anhydrite as (multiphase) plaster
$CaSO_4$	anhydrite III, "soluble A"	α-anhydrite III β-anhydrite III β-anhydrite III'	hexa-gonal	metastable	50 vacuum 100 air	290	reacts very rapidly with water to the hemihydrate, low strength	siccative
$CaSO_4$	anhydrite II, "insoluble A" (natural A)	AII poorly soluble AII insoluble AII flooring plaster	rhombo-hedral	40 to 1180		< 500 500 – 700 > 700	slow to very slow reaction with water (hence use of activators), high strength	filler, Keene's cement, flooring plaster, in mixtures with β-hemihydrate as gypsum plaster
$CaSO_4$	anhydrite I	–	cubic	> 1180	> 1180	–		industrially uninteresting since only exists at > 1180°C

The monohydrate is formed by "zeolithic" take up of water by calcium sulfate hemihydrate

The α- and β-forms of the hemihydrate do not differ in their crystal form. Their different solubilities and reaction behaviors are due to different crystal habits and specific surface areas. α-Hemihydrate crystallizes in well-formed large crystals, whereas β-hemihydrate crystallites are extremely small. α- and β-Hemihydrates are regarded as being two extreme forms of the same phase. They possess the ability to take up further water "zeolithically" forming the "monohydrate" described in the literature.

Anhydrite III is formed upon dehydration of calcium sulfate hemihydrate

The "soluble" anhydrite III occurs in three variants, which are important in the industrial manufacture of plaster.

Anhydrite II: identical to naturally occurring anhydrite; rehydration behavior dependent upon manufacturing temperature

"Flooring plaster" contains ca. 10% CaO

Anhydrite II is formed at higher temperatures from anhydrite III or calcium sulfate hemihydrate and is identical to naturally occurring anhydrite. It occurs in three different intermediate forms. The rehydration rates of these intermediate forms depend upon temperature. The flooring plaster (*Estrichgips*) obtained above 700°C partly consists of CaO, since decomposition of anhydrite begins above 600°C:

$$CaSO_4 \longrightarrow CaO + SO_3$$

The individual modifications are formed from the dihydrate at increasing temperatures in the following order:

$$\text{dihydrate} \longrightarrow \text{hemihydrate} \longrightarrow \text{anhydrite III} \longrightarrow \text{anhydrite II} \ (\longrightarrow \text{anhydrite I})$$

5.3.4.3 Natural Gypsum

Raw material treatment:

- extraction
- grinding
- thermal dehydration

Natural gypsum is either extracted in open cast or underground mines. It is ground, homogenized and then thermally dehydrated, the process depending upon the required properties of the final product.

Dry dehydration yields calcium sulfate β-hemihydrate and/or anhydrite

Industrial realization:

- mainly in kettles and rotary furnaces
- sporadically in grinding-pyrolysis, carrier gas combustion or Hofolite combustion processes

In the manufacture of calcium sulfate β-hemihydrate, anhydrite and multiphase plaster the dehydration is carried out in the dry state. At temperatures of 120 to 180°C the β-hemihydrate is obtained, at higher temperatures anhydrite or multiphase plasters. Industrially directly or indirectly heated rotary tubes or so-called kettles, which are mostly indirectly heated, are used. Here and there other processes are used e.g. the grinding-pyrolysis process in which dehydration takes place in the pulverizer during the grinding. A carrier gas combustion process and a dehydration process in a heated auger (Holoflite combustion process) have also been described.

Continuous grate furnaces (Knauf) have been successfully used in the manufacture of overburnt plaster at high temperature in addition to conventional rotary kilns. In this process the material to be pyrolyzed is placed on a continuously moving belt which is transported under a burner hood. The hot combustion gases are sucked through the layer of material being burnt with the help of fans. Since the material being burnt does not move, very little dust is produced in this process.

- in continuous grate furnaces: especially for the manufacture of overburnt plaster

Modern rotary kiln plants have capacities of up to ca. 500 t/d, continuous grate furnaces up to 1000 t/d. The residence times are less than 1 hour. In kettles throughputs up to 150 t/d with residence times of several hours are aimed for. Box shaft kilns are no longer viable due to the lengthy (several day) calcination times.

Capacities:

- 500 t/d for rotary kilns
- 1000 t/d for continuous grate kilns

Calcium sulfate α-hemihydrate can only be manufactured using wet processes in autoclaves at temperatures of 120 to 150°C. Processes described in the literature which operate at atmospheric pressure in acids or aqueous salt solutions, have not yet been industrially applied.

Calcium sulfate α-hemihydrate produced by wet dehydration in autoclaves

Since the product properties depend upon the plant used, most modern plaster factories use several dehydration processes. Multiphase plasters are then produced by mixing. By observing precisely defined conditions these can also be obtained in a single process step (see Table 5.3.12).

Manufacture of multiphase plasters:

- by mixing different plasters
- by observing precisely defined reaction conditions during dehydration

Table 5.3-12. Phase Compositions in % of the Different Plaster Types.

	production	production	$CaSO_4 \cdot H_2O$	$CaSO_4 \cdot 0.5H_2O$		$CaSO_4$		residue
plaster types	unit	temperature [°C]		α-form	β-form	anhydrite II	anhydrite III	
molding plaster	autoclave	130 to 135	0.1	94	2	–	1.9	2
plaster of Paris	kettle	180	2	2	73	10	1	10
	rotary tube	120 to 180	2	2	71	19	5	–
wall (multphase) plaster*	–	–	2	26	14	58	–	–
overburnt plaster	continuous grate	200 to 900	2	–	–	18	74	–
flooring plaster	rotary tube	800 to 1000	–	–	–	–	90	10

* mixed from plaster of Paris and overburnt plaster.

5.3.4.4 Natural Anhydrite

Working up of natural anhydrite:
- fine grinding
- addition of activators

Natural anhydrite is extracted by open cast or underground mining. A hardenable product is obtained by fine grinding to < 0.2 mm particles and the addition of "activators" (ca. 2% heavy metal or alkali sulfates, or calcium hydroxide) to natural anhydrite.

5.3.4.5 Fluoroanhydrite

Fluoroanhydrite from hydrofluoric acid manufacture at 200°C:

$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF$

Calcium sulfate is formed as a byproduct in the industrial manufacture of hydrofluoric acid by reacting fluorspar (CaF_2) with concentrated sulfuric acid in rotary kilns at ca. 200°C (see Section 1.7.1):

$$CaF_2 + H_2SO_4 \xrightarrow{200\ °C} CaSO_4 + 2\ HF$$

Neutralization of residual H_2SO_4 by reaction with CaO

as anhydrite II (fluoroanhydrite). This contains unreacted fluorspar and small amounts of free sulfuric acid (0.5 to 10%) as undesirable impurities. The latter is immediately removed from the fluoroanhydrite emerging from the rotary kiln by neutralization with added calcium oxide in a mixing screw.

$$CaO + H_2SO_4 \xrightarrow{200\ °C} CaSO_4 + H_2O$$

Hardenable product by:
- fine grinding
- addition of activators

After a final grinding (fine grinding) to the required product fineness, the fluoroanhydrite is suitable for final processing. Should activators be required, these may still be added (see Section 5.3.4.4).

5.3.4.6 Byproduct Gypsum

5.3.4.6.1 Byproduct Gypsum from the Manufacture and Purification of Organic Acids

Byproduct gypsum from the manufacture or purification or organic acids via their Ca-salts

Small quantities of calcium sulfate dihydrate are formed in the production or purification of organic acids such as citric, oxalic or tartaric acids by way of their calcium salts:

$$CaC_2O_4 + 2\ H_2O + H_2SO_4 \longrightarrow CaSO_4 \cdot 2\ H_2O + H_2C_2O_4$$

5.3.4.6.2 Byproduct Gypsum from Flue Gas Desulfurization

Stricter environmental protection legislation has led to the equipping of power stations with desulfurization units especially in Japan and Western Europe, including the Federal Republic of Germany, and also in the USA.

Increasingly strict environmental protection legislation has led to increased use of desulfurization plants

In so-called wet processes (used in most units) flue gas from which any dust has been removed is sprayed in a scrubber with a limestone suspension [plants also operate with $Ca(OH)_2$], whereupon the SO_2 reacts with the $CaCO_3$ to form insoluble $CaSO_3 \cdot 0.5H_2O$ as a sludge. This is converted into soluble $Ca(HSO_3)_2$ by reducing the pH and then is completely oxidized with oxygen from the air. The sulfuric acid thereby formed reacts with excess limestone forming further gypsum. Purification and separation is carried out with hydrocyclones and filters or centrifuges. Very pure $CaSO_4 \cdot 2H_2O$ is formed with ca. 10% moisture, so-called REA-gypsum, which can be directly utilized in the construction and cement industries. 5.4 t gypsum are produced per ton of sulfur-content in coal.

REA-gypsum from flue gas desulfurization by reaction of SO_2 with $CaCO_3$- or $Ca(OH)_2$-suspensions and subsequent oxidation to $CaSO_4 \cdot 2H_2O$

5.4 t of gypsum is formed per t of sulfur in fuels in flue gas desulfurization

$$SO_2 + CaCO_3 + 0.5\ H_2O \xrightarrow[\text{pH 7-8}]{} CaSO_3 \cdot 0.5\ H_2O + CO_2$$

$$2\ CaSO_3 \cdot 0.5\ H_2O + 2\ SO_3 + H_2O \xrightarrow[\text{pH 5}]{} 2\ Ca(HSO_3)_2$$

$$Ca(HSO_3)_2 + 2\ H_2O + O_2 \longrightarrow CaSO_4 \cdot 2\ H_2O + H_2SO_4$$

So-called "dry processes" are also utilized here and there, in which finely ground lime dust ($CaCO_3$, $Ca(OH)_2$ or CaO) are jetted directly into the hot flue gas or are mixed with the fuel in the burner. Separation is performed with a fabric filter.

5.3.4.6.3 Phosphogypsum

The largest quantity of byproduct gypsum arises in the production of phosphoric acid (so-called "phosphogypsum") by the reaction of natural phosphates with sulfuric acid (see Section 1.5.1):

$$Ca_5(PO_4)_3F + 5\ H_2SO_4 + 10\ H_2O \longrightarrow 3\ H_3PO_4 + 5\ CaSO_4 \cdot 2\ H_2O + HF$$

1.7 t gypsum/t raw phosphate produced in production of wet process phosphoric acid

Direct use in the construction industry hindered by impurities such as organic or inorganic admixtures or substances incorporated into the gypsum crystal lattice

The 1.7 t gypsum/t raw phosphate produced is so impure that it is unsuitable for direct use in the construction industry. These impurities are either admixtures of organic substances: soluble alkali and magnesium salts; poorly soluble salts (e.g. Na_2SiF_6); or phosphates and fluorides incorporated isomorphously in the gypsum crystal lattice.

Two-stage phosphoric acid manufacturing processes producing phosphogypsum with lower impurity levels:

- Central-Prayon process
- Nissan process

The impurity content can be affected by the way in which the phosphoric acid manufacturing process is carried out: single stage processes, or newer processes, which lead to the hemihydrate, have a higher impurity level, so that further purification steps are necessary. Two step processes, which either lead via the dihydrate to the hemihydrate (*Central-Prayon process*) or via the memihydrate to the dihydrate (*Nissan process*), provide products, which can be utilized without further purification steps. Should further purification of the phosphogypsum be necessary, two types of process are possible:

- Type I: “dry processes” which lead to calcium sulfate β-hemihydrate and multiphase plaster, and
- Type II: “wet processes” which yield calcium sulfate α-hemihydrate.

Dry Processes

Dry purification processes lead to calcium sulfate β-hemihydrate and multiphase plasters

Dry processes always consist of two stages: washing to remove the soluble impurities with, if necessary, organic impurity removal by flotation, and dry calcination.

Industrial realization using the following processes:

- Rhône-Poulenc

- Knauf

- CdF-Chimie/Air Industries

The following processes differ only in the way they are technically carried out:

Rhône-Poulenc process: washing in a hydrocyclone, drying and calcination either separately or in a single step.

Knauf process in different variants: after washing and flotation, drying is carried out with partial dehydration. The resulting mixture of dihydrate and hemihydrate is recrystallized with the addition of lime hydrate and stoichiometric quantities of water, then pelletized and calcined

CdF-Chimie/Air Industries process: washing is carried out in a hydrocyclone. The subsequent thermal treatment is carried out in three steps: drying, dehydration to calcium sulfate β-hemihydrate and anhydrite III and rehydration of the anhydrite III to calcium sulfate β-hemihydrate.

CERPHOS process (Centre d'Etudes et de recherche des Phosphates Mineraux): in the washing step the fine fraction, containing a particularly high impurity concentration, is separated in a hydrocyclone. Drying and calcining is carried out as in conventional calcium sulfate production.

- CERPHOS

Wet Processes

The wet processes also consist of a washing step (if necessary with flotation) and a dehydration step, which is carried out in the aqueous phase in continuously operating autoclaves. The only industrially operated process is the Guilini process. This process can be carried out with all types of phophogypsum. Wet processing is particularly economic when further direct treatment of the gypsum, e.g. to gypsum plasterboard, is possible, i.e. when no drying of the material is necessary.

Wet purification process:

industrial realization in the Guilini process in autoclaves

5.3.4.7 Processes in the Setting of Plaster

"Plaster setting" is the reaction of calcium sulfate hemihydrate, anhydrite II or anhydrite III with water i.e. the opposite reaction to the manufacture of plaster:

"Setting" is the rehydration of calcium sulfate hemihydrate or anhydrite

plaster production by dehydration		hardenable modifications	hardening by rehydration	
		$CaSO_4 \cdot 0.5H_2O$		
$CaSO_4 \cdot 2H_2O$	$\xrightarrow{-H_2O}$	$CaSO_4 \cdot$ A II	$\xrightarrow{+H_2O}$	$CaSO_4 \cdot 2H_2O$
		$CaSO_4 \cdot$ A III		

The plaster powder should be suspended as homogeneously as possible when making a slurry of plaster in water to avoid settling. This ensures thorough wetting of the individual plaster particles and the dissolution of the outermost layers of the hydrated hemihydrate (or anhydrite) particles.

Slurrying with water to a homogeneous suspension

After this so-called "induction period", dihydrate crystals from the supersaturated solution start to nucleate round the particles. Further growth of the needle-shaped dihydrate crystals follows which, for the correct ratio of water to plaster, mat to a close-grained structure in which not yet

After the "induction period" (initial solution of hemihydrate or anhydrite), nucleation of dihydrate occurs. Further crystal growth leads to a close-grained structure of dihydrate crystals which accounts for the rigidity of plaster

Excess water is removed by drying

hydrated components and mixing water are embedded. After the solid structure is formed, the solid mass of plaster still has to dry. The transition of hemihydrate and anhydrite II to dihydrate occurs directly without intermediates, but anhydrite III is converted to the dihydrate by way of the hemihydrate. The hardening properties of plaster depend upon many factors e.g. composition, manufacturing process, particle shape, particle size distribution and additives (accelerators or decelerators).

5.3.5 Coarse Ceramic Products for the Construction Industry

Coarse ceramic products are tiles and hard bricks

manufacturing process similar in some ways to that for fine ceramic products

The clay products used in the construction industry are so-called coarse ceramic products. They include bricks, roofing tiles, clinkers (hard bricks), drainpipes and protection covers for cables. The manufacture of such products hardly differs from that described in Section 5.5.3 for the general manufacture of ceramic products.

Loam, marl, tile clay, clay stone and shaly clay are used as raw materials in the manufacture of tiles. The chemical composition of the raw materials is similar to that for the manufacture of fine ceramic products (see Section 5.5). The quantities of impurities can, however, be higher.

Light tiles are obtained by:

- incorporating light additives, such as perlite, vermiculite, kieselguhr
- introducing pores and cavities by pyrolysis of organic additives
- incorporating foaming additives

Light construction materials are of particular interest in the construction industry. The manufacture of light tiles can be achieved using different processes:

- incorporation of light additives, such as vermiculite, perlite or diatomaceous earth (kieselguhr), enabling a reduction in the raw density of the ceramic from 1.9 Mg/m^2 to 0.8 Mg/m^2.
- incorporation of suitable organic materials, such as wood (sawdust), carbon black, peat etc. These additives decompose upon firing leaving pores and cavities behind. Particularly suitable organic materials are expanded polystyrene beads or synthetic resin beads (Poroton® process).
- incorporation of gas-forming materials. If, for example, aluminum powder is added to the moist batch the material foams. Hardening can also be carried out in pressure vessels, such as used in the manufacture of sand-lime bricks (see Section 5.3.2.5).

Light bricks are manufactured almost exclusively by the incorporation of expanded polystyrene beads and/or sawdust.

5.3.6 Expanded Products

5.3.6.1 General Information

Inorganic expanded products are materials with closed pore structures and low densities, which exhibit very good insulation properties. They are manufactured using certain clays, shales, glasses and blast furnace slags.

Expanded products are materials with closed pore structures and low densities

Manufactured from clays, shales, glasses and blast furnace slags

It has long been known that clays can swell upon rapid heating. The industrial application of these bloating properties was described by Stephen John Hayde in 1912 (US Patent 1,255,878). These expanded clay granules were marketed under the name Haydite. In Europe, the first attempts to produce expanded clay were in Denmark. This product was marketed under the name LECA (*L*ight *E*xpanded *C*lay *A*ggregates). A similar process was developed in the former States of the USSR and was widely used under the name Keramzit. Expanded clay has been produced in the federal Republic of Germany by the LECHA process sinse 1955. The capacity for expanded clay and shale manufacture in the Federal Republic of Germany is ca. 1.5 to 2 · 10^6 m^3/a.

Expansion of clays by rapid heating

Expanded product capacity in FR Germany:
1.5 to 2 · 10^6 m^3/a

5.3.6.2 Expanded Products from Clays and Shales

5.3.6.2.1 Raw Materials

Materials suitable for the manufacture of expanded clays or shales are those which form a glass-like ("pyroplastic") phase at high temperatures (ca. 1100 to 1200°C), whose viscosity is so high that gas produced in the product cannot escape and therefore bloats the material. The volume change of a clay granulate as a function of temperature is shown in Fig. 5.3-3.

Expandable raw materials form a glass-like "pyroplastic") phase at 1100 to 1200°C and are expanded by the gases formed at these temperatures

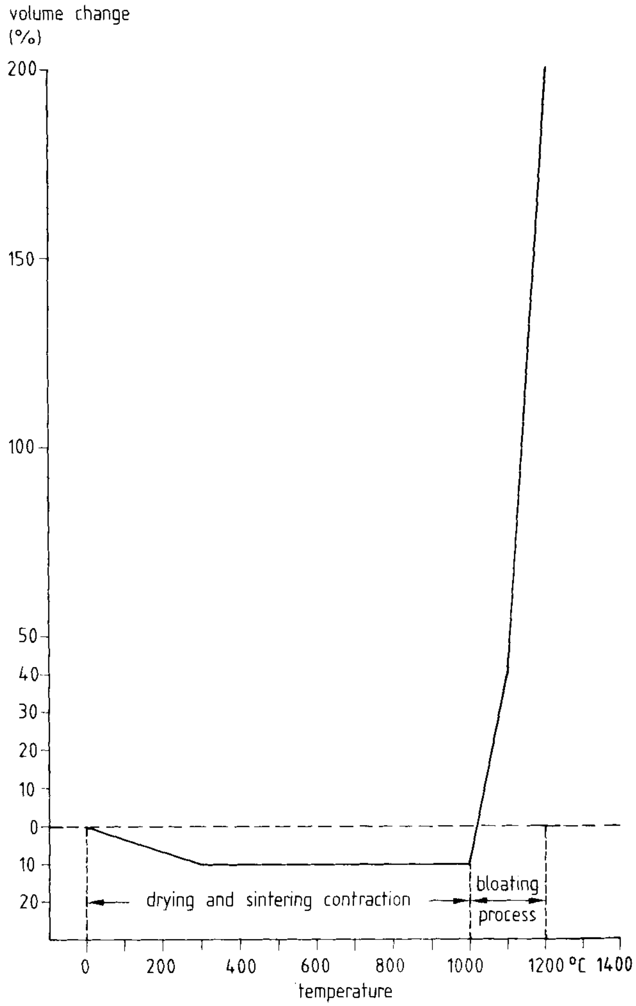


Fig. 5.3-3. Volume change in expanded-clay manufacture as a function of temperature (schematic).

The bloating of clays depends upon:

- plasticity
- fine particle content
- Fe_2O_3-content
- organic C-content
- lime content
- mineral composition
- sulfur content
- sintering and melting points
- softening and bloating ranges

The bloating of clays is favored by:

- high plasticity
- large fine particle content
- Fe_2O_3-content of at least 3 to 6%
- organic impurities (their content can be 0.6 to 2.5% or higher). Particularly favorable is a ratio of organic C-content to Fe_2O_3 content of 0.04 to 0.2
- low lime content (< 5%)

- high proportion of clays of the illite and mica group; low kaolinite content (see Fig. 5.3-4)
- sulfur-containing admixtures
- small temperature difference between sintering and melting point, which should be at ca. 1200°C
- small difference between the softening temperature and the temperature at which the maximum amount of gas is produced
- expanding process temperature range of at least 50 to 100°C

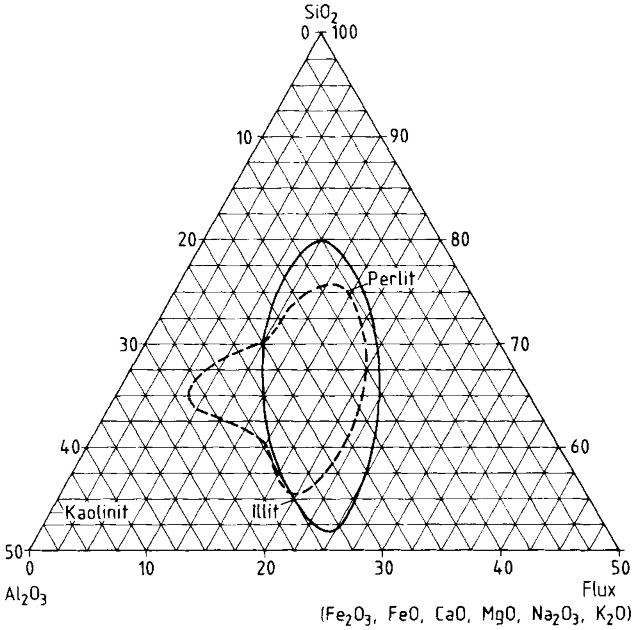


Fig. 5.3-4. Chemical composition of expandable clays.
——— according to C. M. Riley, - - - - - according to H. Wilson

If a natural clay does not possess the required bloating properties, it can be made bloatable by incorporating so-called bloating aids. Suitable additives are: organic materials such as bitumen, heavy oil or lignin sulfate, carbon, iron oxide, iron hydroxide and gypsum. The addition of SiO_2 or Al_2O_3 is advisable at high flux contents.

Additives for increasing bloatability:
e.g. organic materials, iron oxide, gypsum

5.3.6.2.2 Gas-forming Reactions in the Manufacture of Expanded Products

Bloating gases are: CO_2, CO, O_2, SO_2, H_2

The most common expanding gases are CO_2, CO, O_2, SO_2 and H_2. They are formed in the:

Gas-forming reactions are the decomposition of:

- organic materials
- sulfur-containing compounds
- carbonates
- iron oxides

- decomposition of organic impurities at high temperatures:

$$C_{org} + O_2 \longrightarrow CO_2$$

- decomposition of sulfur-containing compounds:

$$2\ CaSO_4 \longrightarrow 2\ CaO + 2\ SO_2 + O_2$$

$$FeS_2 \longrightarrow FeS + S_{gaseous}$$

$$S_{gaseous} + O_2 \longrightarrow SO_2$$

- decomposition of carbonates:

$$CaCO_3 \longrightarrow CaO + CO_2$$

- decomposition of iron oxides:

$$6\ Fe_2O_3 \longrightarrow 4\ Fe_3O_4 + O_2$$

According to C. M. Riley this is the most important gas-forming reaction.

At temperatures above 1100°C, the following reaction scheme has been proposed:

$$\begin{array}{lcl} Fe_2O_3 + C & \longrightarrow & 2\ FeO + CO \\ Fe_2O_3 + CO & \longrightarrow & 2\ FeO + CO_2 \\ 4\ FeO + 4\ Al_2O_3 & \longrightarrow & 4\ FeAl_2O_4 \\ 2\ Fe_2O_3 + C + 4Al_2O_3 & \longrightarrow & 4\ FeAl_2O_4 + CO_2 \end{array}$$

Spinel formation can be confirmed by X-ray diffraction.

5.3.6.2.3 Manufacture of Expanded Products

The processing of the raw materials is different for plastic clays and lumpy shale. Plastic clays are crushed, ground, mixed, partially dehydrated and then formed into pellets of different sizes on a granulation table or similar apparatus before being thermally treated (half-wet process). Lumpy raw materials, such as shale, are only ground and, if necessary, classified (dry process) before thermal treatment. Adjustment of the bulk density of the final product to the required value is carried out during the subsequent thermal treatment.

Processing of raw materials:
- crushing
- grinding
- forming

A prerequisite for the manufacture of products with low bulk densities is a rapid temperature increase in the range from 600°C to the bloating temperature (1100 to 1200°C). The gas production reactions then occur at the same time as the glass phase is formed and the total amount of gas produced can be used for bloating the granulate. Products with higher densities arise when the heating process is carried out more slowly, because gas production has started before the glass phase is formed and hence some gas escapes before the particle surface is sintered.

Expanding process occurs at ca. 1100 to 1200°C

The thermal treatment is carried out using different processes:

Technical realization:

a) *LECA process*: in this process the thermal treatment is carried out with (preferably directly heated) rotary kilns. Rotary kilns with grate preheaters (MIAG) or shaft preheaters (Krupp) are employed for predrying the materials. Upon leaving the kilns the product still has a temperature of ca. 900 to 1000°C. A cooling drum is coupled to the rotary kiln, which ensures uniform cooling of the product. Cooling down to about 400°C should not be too fast, since otherwise hairline cracks (cooling cracks) and stress occurs in the granulate, which considerably reduces the compressive strength of the granules.

- LECA process with rotary kilns

b) *Sintering process*: in this process the granulated raw material is mixed with a solid fuel (mostly coal) and conveyed on a traveling grate under a firing hood (gas-fired). The combustion gases are led through the product. The advantage of this process is that the material is very rapidly heated to the expansion temperature. As a result very little of the expansion gas escapes before the bloating process begins and poorly bloatable products can also be economically processed (e.g. in Lurgi plants).

- sintering by mixing fuel with the raw material

c) *Circulation flow processes*: the dried material is fed into a swirl chamber in which hot combustion gases are fed

- circulation flow process

in from below with such a high velocity that they entrain the falling granulate particles. The intensity of the gas jets decreases as they go upwards so that the granulate can fall again, whereupon the circulation starts again. The expansion only takes ca. 40 s.

- manufacture of expanded-clay blocks by ceramic bonding

d) *Manufacture of large blocks from expanded clay granulate*: the manufacture of larger blocks from expanded clay granulate is carried out by sintering expanded clay granulate, e.g. from rotary kilns, while still hot, in heated molds (so-called "ceramic bonding").

5.3.6.3 Expanded Products from Glasses (Foam Glass)

Both naturally occurring and industrial glasses, preferably waste glass, are suitable for the manufacture of bloated products from glasses.

Perlite: expands at ca. 1000°C upon evaporation of entrapped water

Perlite is a glassy volcanic rock with water trapped in its fine pores. The rock is pulverized and then heated to ca. 1000°C, whereupon the material melts and the entrapped water evaporates bloating the molten glass to many times its initial volume.

"Foam glass": waste glass finely ground with powdered coal or $CaCO_3$

Bloating due to $CaCO_3$ decomposition

Synthetic glasses can also be processed to so-called "foam glass". Waste glass is ground with powdered coal or calcium carbonate and/or magnesium carbonate to a very fine powder. After optional addition of a binder, this is granulated and then sintered at ca. 700°C. Decomposition of calcium or magnesium carbonate begins at this temperature, the carbon dioxide formed foaming the material. At the same time the glass becomes more difficult to melt due to the incorporation of calcium or magnesium carbonate.

No cooling is required due to the sintering of the material.

5.3.6.4 Applications of Expanded Products

Advantages of expanded products: low weight, good insulation properties

Expanded products have the dual advantages of low weight and good insulation properties. They are therefore utilized in the following application fields:

Applications in:
- lightweight concrete

- additive in lightweight concrete for prefabricated units, cavity blocks and construction concrete (e.g. in skyscrapers) (Fresh concrete density 0.5 to 1.0 Mg/m^3 versus 2.3 to 2.4 Mg/m^3 for normal concrete with sand and gravel as additives).

- as an additive in insulation concrete with light cement bonding
- loosely packed for floor and roofing insulation
- in the manufacture of so-called UP-lightweight concrete using expanded clay or expanded shale granules with organic binders. Legupren® lightweight concrete consists of foamed unsaturated polyesterresins with light additives and is used in prefabricated units
- as an insulation layer in road building
- for keeping of plants in hydroculture. Here expanded clay granules are used as substrates, which are as free as possible from sulfur and which can take up large quantities of water.

- insulation concrete
- loosely packed state for insulation
- UP-lightweight concrete
- road building
- hydroculture

References for Chapter 5.3: Construction Materials

Commercial Information:

Lime:

Chemical Economics Handbook 1996, Stanford research Institute, Menlo Park, California, 7245000A and 2141000A.

Cement:

World Statistical Review No. 17 1996. Cement: Production, Trade, Consumption Data, Cembureau.

Gypsum:

World Mineral Statistics 1991 – 1995. British Geological Survey.

General Information:

Lime:

Oates, T. *Lime and Limestone*, Ullmann's Encyclopedia of Industrial Chemistry. 1990. 5. Ed., Vol. A 15, 317 – 345, VCH Verlagsgesellschaft, Weinheim.

Oates, T. 1998. *Lime and Limestone*, WILEY-VCH, Weinheim.

Boynton, R. S. *Lime and Limestone*, Kirk-Othmer, Encyclopedia of Chemical Technology. 1995. 4. Ed., Vol. 15, 319 – 359, John Wiley & Sons, New York.

Boynton, R. S. 1980. *Chemistry and Technology of Lime and Limestone*, John Wiley & Sons, New York.

Kalk-Taschenbuch. 61. Auflage, Bundesverband der Deutschen Kalkindustrie e.V.

Grundlach, H. 1973. *Dampfgehartete Baustoffe*, Bauverlag, Wiesbaden.

Cement:

Locher, F. W., Kropp, J. *Cement and Concrete*, Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 5, 489 – 544, VCH Verlagsgesellschaft, Weinheim.

Helmuth, R. A., Miller F. M., Greening, N. R., Hognestad, E., Kosmalka, St. H., Lang, D. *Cement*, Kirk-Othmer, Encyclopedia of Chemical Technology. 1993. 4. Ed., Vol. 5, 564 – 598, John Wiley & Sons, New York.

Duda, W. H. Cement Data Book Bd. 1 1985, Bd. 2 1984, Bd. 3, 1988, Bauverlag GmbH, Wiesbaden.

Kühl, H. 1956 – 1961. Zementchemie (3 Bände), VEB Verlag Technik, Berlin.

Czernin, W. 1977. *Zementchemie für Bauingenieure*, Bauverlag, Wiesbaden.

Gypsum:

Wirsching, F. *Calcium Sulfate*, Ullmann's Encyclopedia of Industrial Chemistry. 1985. 5. Ed., Vol. A 4, 555 – 584, VCH Verlagsgesellschaft, Weinheim.

Petersen, D. J., Kaleta, N. W., Kingston, L. W. *Calcium Compounds (Calcium Sulfate)*, Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 812 – 826, John Wiley & Sons, New York.

Schütz, M. 1997. Stand der Rauchgasentschwefelungstechnik, VGB Kraftwerkstech. **77**, 943 – 945.

Clay Products:

Hauck, D., Hilker, E., Hesse, E. *Construction Ceramics*, Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 7, 425 – 460, VCH Verlagsgesellschaft, Weinheim.

Piltz, G., Schmidt, H. 1973. *Ziegeleierzeugnisse*, Handbuch der Keramik, Gruppe II G, Verlag Schmid GmbH, Freiburg.

Expanded Products:
Kromer, H., Potschigmann, W. 1977. *Blähton*, Handbuch der Keramik, Gruppe II M, Verlag Schmid GmbH, Freiburg.
Riley, C. M. 1951. *Relation of Chemical Properties to the Bloating of Clays*, J. Amer. Ceram. Soc. **34**, 121.
Hill, R. D. 1960. *Some Causes of Bloating in Expanded Clay and Shale Aggregates*, Austr. J. Appl. Sc. **11**, 374.

5.4 Enamel

5.4.1 General Information

The principle of enameling is very old. The first artistic enamel work originates from the Aegean region (ca. 1600 to 1200 BC). Enameling on an industrial scale for industrial and household use as we know it today, is on the other hand fairly recent, dating from the beginning of the nineteenth century. It has experienced a boom since World War II.

According to RAL 529 A2, "enamel is a preferably glassy solidified mass produced by melting or fritting an inorganic mainly oxide composition, which is melted in one or more layers, optionally with additives, on objects of metal or glass".

Enamels are mainly applied to (alloyed) steel, but cast iron and aluminum are also enameled

Industrially, enameling is currently mainly carried out on steel (and steel alloys). The applied layers in steel-enameling adhere very firmly to the substrate as a result of chemical reactions which take place between the glowing metal and the molten frits, leading to a composite material. The sheet steel-enamel bond can withstand a tensile stress of 1000 kp/cm^2. In addition to steel (ca. 90%) cast iron (ca. 6%) and aluminum (ca. 4%) are also enameled. Annually ca. 450 · 10^3 t/a of enamel is applied to a total surface of ca. 750 · 10^6 m^2. Ca. 30% is used in Europe and 20% in the USA. In the Federal Republic of Germany there are ca. 50 enameling plants with an annual enamel consumption of ca. 13 · 10^3 t.

Worldwide enamel production:
ca. 450 · 10^3 t/a

5.4.2 Classification of Enamels

There are different classifications for enamel, according to application or chemical composition. These are partly overlapping. In this section an introduction is given based on two classifications:

- layer arrangement classification;
- color and opacifying system classification.

Layer Arrangement

In principle, enamels can be applied as a single layer or in multiple (two) layers The layers can be stoved separately or together. The classic processes operate with ground coat and cover coat enamels and one stoving per layer.

Enamels can be applied in single or multiple layers. In multilayer application:

- ground coat enamel (1st stoving)
- cover coat enamel (2nd stoving)

The ground coat enamel should provide adhesion (the enamel adhesion) to the metal. In the case of the enameling of sheet steel the ground coat enamel should largely dissolve the iron oxide formed during stoving, so that this does not reach the cover coat enamel layer and there give rise to visible defects. The stoved ground coat consists of fine ca. 10 to 40 µm bubbles thereby attaining sufficient elasticity to resist the mechanical stresses occurring during the use of the enameled object. In general at least two different ground coat enamels are used together ("hard" and "soft" frits). This increases the stoving interval and ensures multipurpose utilization.

Typical ground coat enamel compositions are given in Table 5.4-1.

Table 5.4-1. Oxide Composition of a hard and soft Ground Coat Enamel for Steel- plate (in % by weight).

	SiO_2	B_2O_3	*Me_2O	CaO	Al_2O_3	P_2O_5	CoO NiO	BaO	F
"hard"	45 – 55	8 – 14	15 – 18	5 – 10	3 – 5	0 – 2	1 – 2	–	1 – 2
"soft"	35 – 45	14 – 20	16 – 22	5 – 10	0 – 5	0 – 2	1 – 3	1 – 5	1 – 5

* Me = Na, K, Li.

Cobalt and nickel oxides are necessary for a good adhesion between steel and enamel. These adhesion-promoting oxides are indispensable, particularly in the case of non-pickled objects which have only been degreased.

Ground coat enamel contains cobalt and nickel oxides as adhesion-promoting oxides (good adhesion to the substrate)

After stoving the ground coat enamel layer, the cover coat is applied and stoved. The purpose of the cover coat enamel layer is to endow the enameled object with its typical properties and those properties desired for the application:

- chemical resistance (e.g. to corrosion)
- color and color stability
- smooth, glossy or matte surfaces
- scratch resistance

Ground coat and cover coat enamel can also be fired together (two-layer-single stoving processes)

In modern two-layer-single-stoving processes the ground coat and cover coat enamels are stoved simultaneously thereby saving a transit through the furnace. The enamels have the same function as in the classic processes. However, due to their simultaneous firing the ground coat and cover coat enamels have to be adapted to each other. This can be achieved by ensuring that the ground coat melts earlier than the cover coat and has a ca. 40 mN/cm higher surface tension. This avoids undesirable mixing of the ground coat and the cover coat enamels.

A number of variants are possible in two-layer-single stoving coatings, depending on whether the layers are applied wet or dry via electrostatic application of powder (see Section 5.4.5.2).

Table 5.4-2. Two Layer Single Stoving Processes

	powder/powder	powder/wet	wet/wet (Combismalt)
ground coat enamel	dry	wet	wet
cover coat enamel	dry	dry	wet

Single layer enameling combines the functions of ground coat and cover coat enamel. Bright colors are only realizable for pickled and nickel-plated steels; dark colors do not need this pretreatment

A further enameling process is single-layer enameling. In direct enameling, enamel may be applied to acid-pickled and optionally nickel-plated steels or to steels which have only been degreased.

Direct enameling has to combine the functions of ground coat and cover coat enamels, i.e. provide adhesion to steel and the properties for the particular application.

Since direct enamel cannot be obtained for bright colors (most difficult for white) due to the dark intrinsic color of the adhesion-promoting oxide, direct white and direct color enameling is only successful for pickled and nickel-plated steels. In general a nickel layer of 2 g/m^2 sheet steel is necessary. Higher demands are also placed on the steel than in the case of two layer enameling (low carbon steels, stronger pickling).

Degreased sheet steel is increasingly used for direct enameling with dark colors such as black, brown, blue or dark gray, rather than pickled sheet steel. Suitable frits combine good adhesion with good surface quality and excellent chemical resistance.

Coloring and Opacifying Systems

White enamels:

opacification occurs during stoving by crystallization of titanium dioxide

White enamels are currently obtained by so-called "recrystallization opacity":

The opacifying agent (preferably titanium dioxide or alternatively zirconium dioxide) is dissolved in the glass during the smelting of the frit and due to the rapid quenching of the smelt is unable to crystallize, despite the glass being supersaturated with it at low temperatures. Nucleation and precipitation of the opacifying agent take place during enamel stoving at ca. 820°C, whereupon particles are formed with the optimum size for the pigments. Boron-titanium enamel, in particular, has a very high covering power, so that layer thicknesses of 100 μm are sufficient to cover the dark background. A typical ingredient mixture for a boron-titanium enamel is given in Table 5.4-3.

Table 5.4-3. Typical Raw Material Mixture for a Boron-Titanium Enamel (% by weight).

	% by weight
SiO_2	41.3
B_2O_3	19.7
K_2SiF_6	8.5
Na_2SiF_6	1.2
TiO_2	17.6
$NaNO_3$	5.7
$NaH_2PO_4 \cdot 2H_2O$	6.0

Opacifying agents can also be added ("directly to the mill") while grinding the frit.

Colored enamels:

coloration by dissolving oxides in the glass or by adding colorants during grinding of the frit

Two different processes are used for the coloration of transparent and semi-opaque enamels:

- coloration in the melt, the glass itself being colored;
- addition of colorant during grinding, which preferably should nor dissolve in the glass during stoving.

Both methods are to a limited extent (only for bright colors) also suitable for recrystallizing titanium enamels.

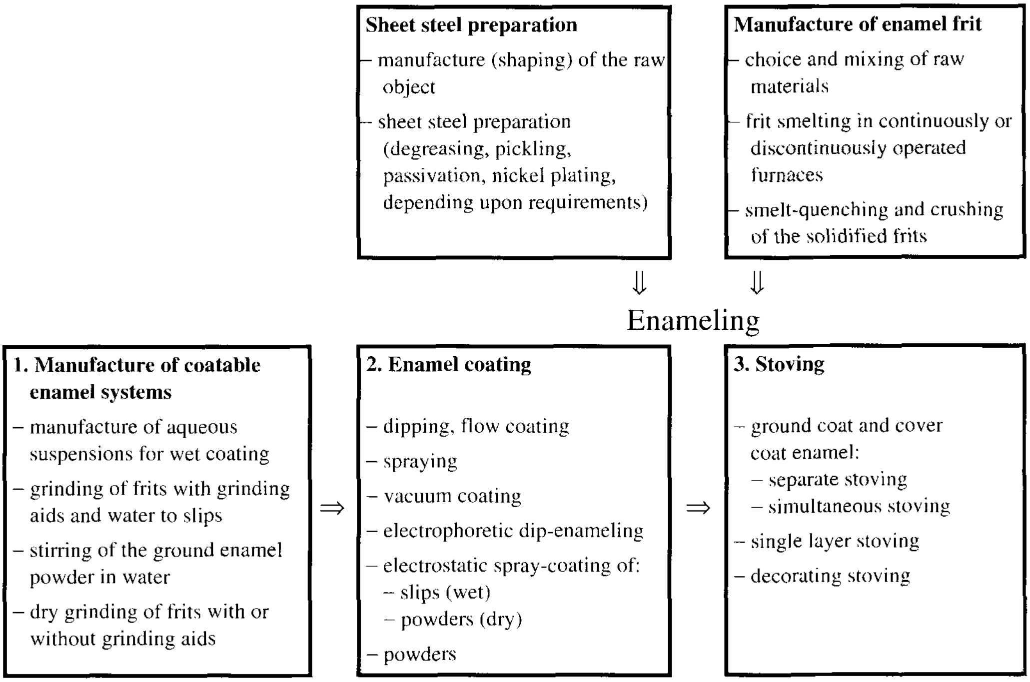
Cobalt, copper, chromium and manganese oxides are mainly used for melt coloration. The colorants used are, in the main, those used in the ceramic industry e.g. oxides such as chromium(III) or iron(III) oxides; spinels such as $CoAl_2O_4$; rutile, zirconium and tin colorants.

Formulas must be adjusted to take into account any interaction between the colorants and the glass during stoving.

The enameling of objects is a complex process comprising many steps. A flow sheet of sheet steel enameling is given in Schema 5.4-1.

Process of sheet steel enameling comprises several steps:

- sheet steel preparation
- manufacture of enamel frit
- manufacture of coatable enamel systems
- enamel coating
- enamel stoving



Schema 5.4-1. Flow Sheet of Sheet Steel Enameling

The manufacture of enamel frits and the actual enameling are dealt with in greater detail in Sections 5.4.4 and 5.4.5 respectively.

5.4.3 Enamel Frit Manufacture

5.4.3.1 Raw Materials

Oxides, carbonates, fluorides and nitrates of the following elements are usually utilized:

- lithium, sodium, potassium (potassium also as potassium feldspar),
- magnesium, calcium, barium,
- boron, aluminum (boron also as borax),
- silicon, titanium, zirconium (zirconium as zirconium silicate),
- phosphorus, antimony, vanadium (phosphorus as alkali phosphate),
- cobalt, nickel, zinc,
- manganese, iron, copper.

Fluorine can be incorporated as fluorspar, cryolite or alkali hexafluorosilicate.

Raw materials for enamel frit manufacture:

Oxides, carbonates, nitrates and fluorides of:

- alkali, alkaline earth metals
- Al
- Si, Ti, Zr
- Sb, V
- Co, Ni, Zn
- Mn, Fe, Cu

5.4.3.2 Smelting of Frits

In frit manufacture the raw materials of the particular frit recipe are intimately mixed, fed into the furnace and smelted. Various furnace types can be used:

- rotary drum kilns with direct flame heating (batch operation, small quantities),
- continuously operating tank furnaces, flame or electrically-heated furnaces (in the case of high throughput the high temperature electrical conductivity of the glasses is utilized in electrical heating).

Most enamels melt at ca. 1250°C. Only a few difficult to melt frits require temperatures of ca. 1350°C. The raw materials are smelted, but not, as in glass manufacture, refined. Fig. 5.4-1 schematically shows the construction of drum and flame-heated tank furnaces.

Enamel frit manufacture:

- discontinuous smelting in drum furnaces. Quenching of smelt in water

- continuous melting in tank furnaces. Quenching of smelt over cooled rollers

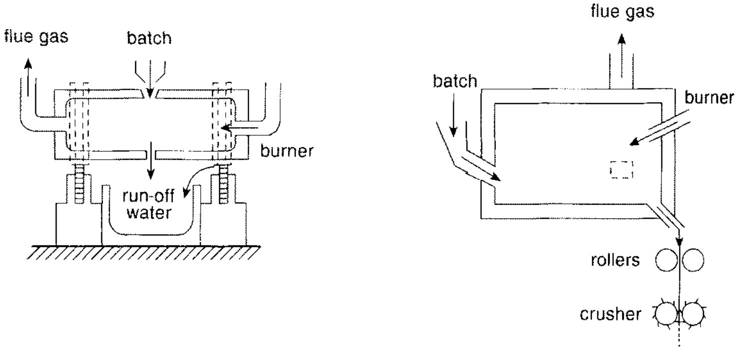


Fig. 5.4-1. Drum and tank furnaces.

In drum furnaces molten frits upon emerging from the outlet are quenched in water forming granules. The smelt from continuous furnaces flows over water-cooled rollers to a crusher, forming flakes.

Flue gas purification is necessary

Part of the raw material mixture evaporates during smelting: fluoride (as hydrogen fluoride, silicon and boron fluorides) and nitrogen oxides are formed in addition to water and carbon dioxide. Effective scrubbing of the flue gases is therefore necessary, which is easier with an electrically heated furnace than with a gas-heated one.

5.4.4 Enameling

5.4.4.1 Production of Coatable Systems

For wet coating, enamel frits are converted into aqueous suspensions (slips) by grinding together with:

- water
- clays
- regulating salts
- optionally inert materials and coloring agents and opacifying agents

In wet coating processes, which are still more widely used, aqueous suspensions, so-called slips, are used (see Section 5.4.3.4.1). Slips are produced by grinding granules or flakes in lined ball mills. The frits are ground together with grinding aids, the mill admixtures. Mill admixtures are (with respect to the frit weight):

- water, 40 to 60%;
- enamel clay, 4 to 10%
- regulating salts, 0.2 to 1%
- inert materials (quartz, Al_2O_3, $ZrSiO_4$), 5 to 30%
- coloring and opacifying agents, 0 to 8%

The milling time depends upon the frit type, the degree of filling of the mill and the degree of grinding required. Grinding times of ca. 4 hours are generally aimed for.

The amount of water is adjusted so as to give a slip density between 1.6 and 1.8 g/mL, deionized water being generally used.

The type and amounts of clay and regulating salts (potassium, sodium, magnesium salts and borax) influence the consistency of slips and depend upon the chosen coating process. Their addition should bring about a easily flowing, slightly thixotropic slip, which does not readily settle on standing.

For some time finished enamels have been utilized for wet application, which have to be premilled dry with mill admixtures. The necessary quantities then only have to be stirred with water to a utilizable suspension.

Dry premilled enamel frits and mill admixtures can be introduced in water into the slip

In dry coating processes the frit is ground dry with or without additives to the required fineness. For powder coating no further additives are necessary. Powders for electrostatic coating have to be hydrophobized to adjust the specific resistivity of the powder surface to 10^{13} to 10^{16} Ω-cm. This is achieved by adding charging agents to the mill. Special silicones are especially suitable therefor.

Powders for electrostatic coating are brought to a specific resistivity of at least 10^{13} Ω-cm by coating with silicone oils

5.4.4.2 Coating Processes

A number of coating processes are used industrially:

- wet application by:
  dip coating, flow coating, vacuum coating, spraying, electrophoretic and electrostatic processes;
- dry application by:
  electrostatic powder coating, dredging (for cast iron).

5.4.4.2.1 Wet Application Processes

In dip coating, the article to be enameled is dipped into the slip and taken out again, the excess slip running off. This process is mainly used for castings produced in small production runs. In flow coating, the slip runs over the articles. This process is mainly used in the utensil sector for enameling pots. The enamel is applied in large automated units. Application to the inner walls of hollow objects, e.g. hot water tanks, can be achieved by sucking in the slip under vacuum and then allowing it to drain off.

Wet application processes:

- dip coating, flow coating
- spraying
- vacuum coating
- electrostatic spray coating
- electrophoretic dip coating

For the above processes the slips are made very thick and with a high density to ensure a uniform run off and a sufficient layer thickness.

In spraying processes the slip is mainly applied by robots from spraying pistols. Spray application is particularly used for large objects such as baths and flat-ware. The slips are more watery and have a lower density than those for dip coating and flow coating.

Spray application can also be carried out electrostatically by applying electrical voltage differences of the order of 100kV between the pistol and the object, which significantly reduces the slip losses, since the number of suspension droplets which reach the object is higher.

In the electrophoretic dipping process, the sheet steel acts as the anode. The negatively charged enamel particles in the aqueous slip, migrate in the electrical field at current densities of 3 to 6 A/dm^2 to the object being enameled, which is preferably flat, because otherwise additional electrodes are necessary. Deposition of enamel mainly takes place in field-favored regions (addition of special additives), which become increasingly insulating as the coating proceeds. This retards deposition in these regions, whereupon deposition occurs in less favored regions (reversal). At the same time, the deposited layer becomes dehydrated by electroosmosis. The slip density must be kept constant.

All wet coated components must be dried before stoving. This is carried out with infrared radiation or in air convection driers.

5.4.4.2.2 Dry Application Processes

Dry application processes:
- for cast iron:
  strewing of enamel powder onto the glowing object or by dipping the glowing object into the enamel powder
- for sheet steel:
  electrostatic deposition of charged enamel powder onto the earthed object

The classical dry application of ground enamel to cast iron objects is operated in addition to wet application. The cast iron enamel is dredged through a sieve onto the glowing object. The enamel powder melts and is subsequently melted smooth in a furnace. Multiple application yields thicker layers.

For smaller cast iron objects, a dipping powder process can also be used, in which the glowing object is repeatedly dipped into the enamel powder.

In sheet steel enameling (particularly for flat-ware), the powder electrostatic coating has become the preferred process. The electric voltage difference between the pistol and the object is with 60 to 90 kV slightly weaker than that in wet electrostatic processes. Frit particles are charged by adsorbed ions. The required oxygen ions are corona charged with the outlet of the powder gun acting as a corona electrode. The charged frit particles are deposited as a cloud on the earthed object through electrical forces acting along the field lines and by mechanical forces (compressed air) (see Fig. 5.4-2).

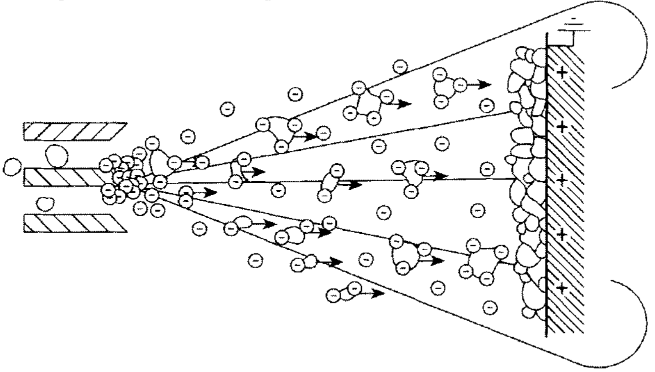


Fig. 5.4-2. Electrostatic deposition of charged frit particles from a pistol nozzle onto an earthed object.

Nondeposited enamel powder is recovered and reused, so that there are practically no losses of frit powder.

5.4.4.3 Stoving of Enamels

Enamels are stoved in circulating or continuous furnaces, which are indirectly heated either electrically or by a fuel-heated radiating tube

A large number of furnace types have been developed for stoving enamels, which are heated electrically or indirectly by a fuel-heated radiating tube. The most widely used types are continuous and circulating furnaces. In these furnaces, the object being enameled is transported continuously through the furnace hanging on chains or lying on racks. In circulating furnaces the exiting hot object gives up its heat to the object entering the furnace.

During travel through the oven the object passes through preheating, stoving and cooling zones. For objects of thin sheet metal (e.g. cooker trays) a stoving temperature of 820°C is sufficient, whereas for objects of thicker sheet (e.g. hot water heaters) temperatures up to 860°C may be necessary. The operation of the furnace is controlled by the temperature and the chain speed. The resulting furnace curve is adapted to the enamel being applied and the process being used (single layer or two-layer-one stoving-enameling).

5.4.5 Applications of Enamel

Enameled articles are used in a multitude of household and industrial applications

Enameled articles are used both in the home and in industry. Typical household applications are:

- kitchen utensils (pots, pans, frying utensils),
- heating and cooking apparatus (standing oven, cast iron fires, gas furnaces, cooker ovens, microwave ovens, grills, barbecues),
- hot water heaters, continuous flow water heaters,
- housing of washing machines,
- baths, shower floors, sanitary equipment,
- chimney entry pipes, oven vents,
- desks

and industrial applications are:

- vessels in chemical plants (stirring tanks, reactors),
- silos,
- petrol pumps, signs, drinking troughs for animals,
- internal and external architecture (panels),
- flat heating elements,
- heat exchangers in the flue gas desulfurization plants of power stations.

References for Chapter 5.4: Enamel

General Information:

Andrews, A. I. 1961. *Porcelain Enamels,* The Garrand Press, Champaign, Illinois, USA.

Kyri, H. 1973. *Handbuch für Bayer* Email, Bayer Rickmann GmbH, Köln.

Emons, H. H. et al. 1983. *Grundlagen der technischen anorganischen Chemie,* 383 - 389, VEB Deutscher Verlag für Grunndstoffindustrie, Leipzig, bzw. Otto Salle Verlag, Frankfurt/Main und Verlag Sauerländer, Aarau.

Dietzel, A. H. 1981. *Emaillierung,* Springer-Verlag, Berlin.

Petzold, A., Pöschmann, H. 1992. *Email und Emailliertechnik,* 2. Auflage, Deutscher Verlag für Grundstoffindustrie, Leipzig.

Commercial Information:

Deutscher Email-Verband e.V., Zehlendorfer Str. 24, D-58097 Hagen.

New Developments:

Hoffmann, H., Zybell, P. *Entwicklungen in der Emaillierung, Einflüsse neuer Basismaterialien, Technologien und Anlagesysteme,* Met Oberfläche (7), 274 – 278 (1986).

Hoffmann, H. *Die Entwicklungsgeschichte der Anlagen für die Elektro-Tauch-Emaillierung (ETE),* Met. Oberfläche **41(4)**, 175 - 178 (1987).

Münstedt, R. *Mehrschichtemaillierungen in einem Brand,* Mitteilungen des Vereins Deutscher Emailfachleute e. V., **37**.

Münstedt, R. *EDV-Einsatz bei der Entwicklung und Auswahl von Emails,* Mitteilungen des Vereins Deutscher Emailfachleute e. V., **40** (10).

5.5 Ceramics

5.5.1 General Information

Ceramics are predominantly crystalline solids of non-metallic inorganic compounds

The term "ceramics" is a collective term for products consisting of nonmetallic compounds produced by sintering in a high temperature process.

With the development of cermets (ceramic-metallic composites materials) and glassy ceramics, the borderlines between ceramics and metals and ceramics and glasses have become somewhat blurred. Modern ceramics include both materials and products, which range from single crystals and dense polycrystalline materials by way of glass-bonded composites to foams and glassy substances.

The properties of ceramic products are determined by their chemical and mineralogical composition and by their microstructure

The properties of ceramic materials are influenced not only by their chemical and mineralogical compositions, but also critically by their manufacture-dependent microstructure. Under the terms microstructure or structure is meant the spatial distribution of the individual phases as well as the shape, size and orientation of the particles, pores and glassy phases.

Continuous demands for ever higher quality ceramic products and the emergence of new fields of application (e.g. fuel rods for nuclear reactors, ceramic gas turbines and components for engines, refractory furnace linings for coal gasification plants) increasingly require the development of new materials and technologies, although knowledge over the manufacture of ceramics originates in antiquity.

5.5.2 Classification of Ceramic Products

Classification of ceramic products:

- clay ceramic (clay content > 20%)
- specialty ceramics (clay content < 20%)

Ceramic products are frequently classified into two groups on the basis of their chemical composition (Fig. 5.5-1):

- clay ceramic materials with more than 20% by weight of clay minerals in the raw mixture;
- specialty ceramic materials which have a lower clay mineral content or are clay mineral free.

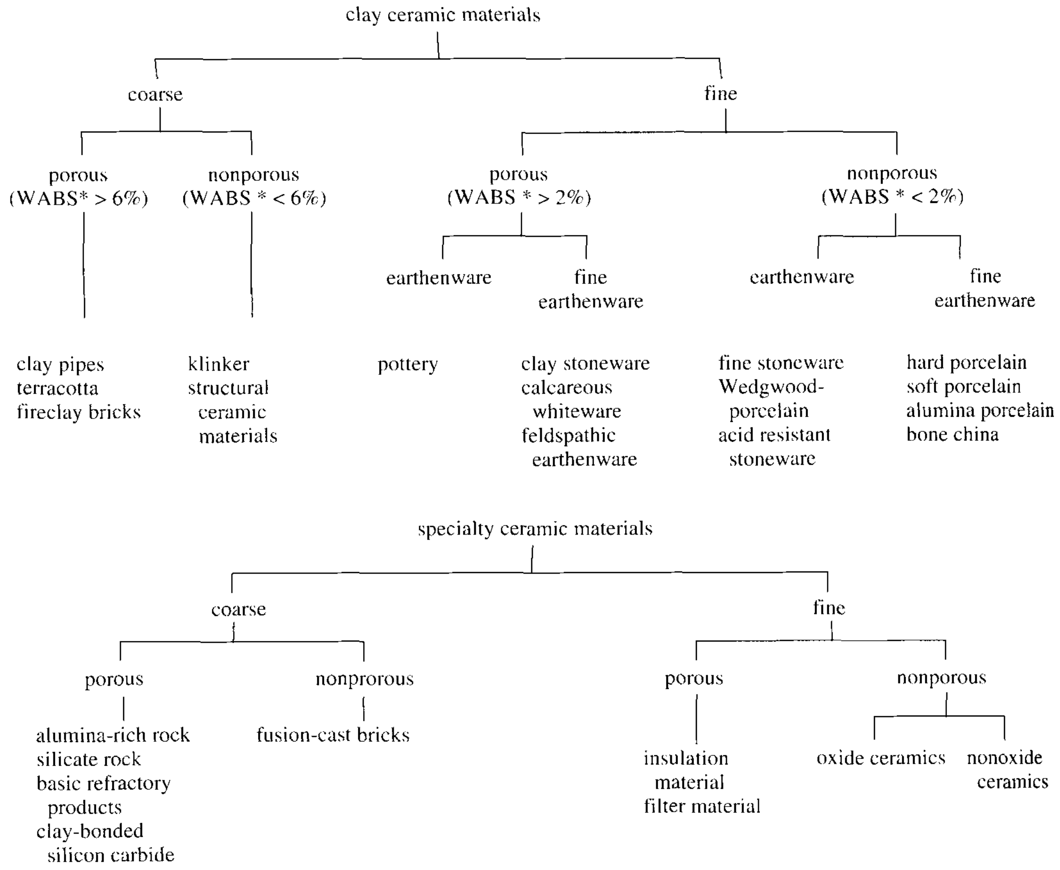
Quantitywise clay ceramic products are the industrially more important.

- fine ceramics
- coarse ceramics

Within both groups the bulk homogeneity is an important distinguishing characteristic, "fine ceramic products" have grains less than 0.2 mm in size, whereas coarse ceramics have larger pores and crystal sizes.

- porous
- nonporous

Ceramic products can be further classified on the basis of their porosity (porous to nonporous).



* WABS = ability to take up water

Fig. 5.5-1. Classification of Ceramic Materials.

5.5.3 General Process Steps in the Manufacture of Ceramics

The manufacture of ceramic products generally proceeds via the following process steps:

- preparation of the raw materials (grinding, classification, mixing),

- forming (pressing, punching, slip or spray casting),
- drying or prefiring (removal of water or organic binders),
- ceramic firing or sintering
- posttreatment and finishing (mechanical processing, glazing).

These process steps are illustrated below in the context of the manufacturing processes of industrially important clay ceramic products.

Manufacture of ceramics:

- preparation of the raw materials
- forming
- drying
- sintering
- posttreatment

5.5.4 Clay Ceramic Products

5.5.4.1 Composition and Raw Materials

The properties of the different clay ceramic products is critically influenced by the relative concentrations of the three main components in their pastes, these being clay (kaolin), quartz and feldspar. Fig. 5.5-2 shows a three component diagram of these ingredients for typical batches of clay ceramic pastes for the manufacture of a number of industrially important products.

Clay ceramic pastes are essentially mixtures of:

- clay (kaolin)
- quartz
- feldspar

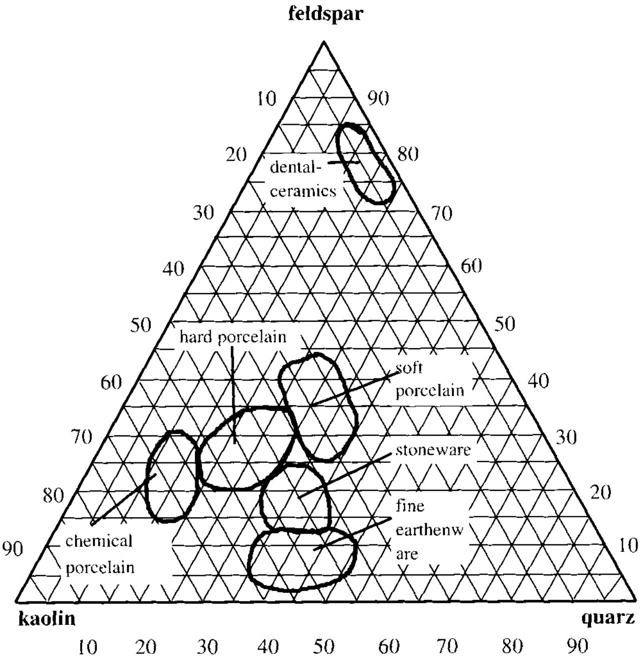


Fig. 5.5-2. Typical Compositions of Clay Ceramic Pastes.

Clay materials impart to moist clay ceramic raw material batches the plasticity important for their processing. Quartz is used as a "lean clay" and reduces the shrinkage upon firing. The feldspar acts as a flux due to its alkali content.

The main kaolin mineral is kaolinite. The content of coloring ingredients should be low

Kaolins (kaolinitic clays) are formed as weathering products of fluorspars or fluorspar-containing rocks (granite, porphyrite, gneiss etc.). Their main mineral is kaolinite occurring as fine platelet crystals with the composition $Al_2(OH)_4Si_2O_5$. The kaolins, particularly from primary deposits, always contain feldspars and quartz in varying quantities. Those used in porcelain manufacture have a low content of coloring impurities such as iron oxides.

Illitic clays contain the mineral illite as their main constituent, which is produced by hydrolytic degradation of potasium mica and has approximately the following composition:

$$(K,H_3O)_yAl_2(OH)_2(Si_{4-y}Al_yO_{10}) \text{ with } y = 0.7 \text{ to } 0.9$$

They are widely used as a raw material in the manufacture of clay ceramic products.

Kaolin and clay minerals are layer silicates

Kaolin and clay minerals belong to the large group of layer silicates. Their ability to form plastic pastes with water, endows the batches of clay ceramic products with the plasticity important for their processing.

Important European kaolin and clay deposits are found in the Federal Republic of Germany (Oberpfalz, Westerwald, Saxony), England (Cornwall, Devon), in the Czech Republic (Bohemia) and in Spain (Galicia).

Finely divided iron- and clay-free quartz is needed as a lean clay in porcelain, fine earthenware or stoneware pastes. This is obtained by grinding pure quartz sand or quartz gangue (quartz powder).

Feldspars are produced from pegmatic or arcose deposits or as a byproduct in the washing of kaolin

Feldspars are found in nature as constituents of coarse crystalline late magmatic deposits (pegmatite) or in feldspar-rich sands (arcose). It is often found together with kaolins and is produced as a byproduct in kaolin processing (see Section 5.5.4.2). Clay ceramic pastes with high feldspar contents fire to products with glassy finishes (porcelain, dental ceramics). In porcelain batches potash feldspar $KAlSi_3O_8$ (orthoclase) is preferred to soda feldspar $NaAlSi_3O_8$ (albite) due to its more favorable melting behavior.

Other raw materials such as aluminum oxide (calcined alumina), calcium-containing fluxes (marble, calcite, limestone, chalk) or lithium-containing fluxes (eucryptite, spodumene) are also added in small quantities.

5.5.4.2 Extraction and Treatment of Raw Kaolin

Raw kaolin is mainly extracted by open cast mining. Secondary deposits can be exploited using excavators, whereas primary deposits of kaolin are often washed out of the rock with a high pressure water jet.

Separation of kaolin and other clay minerals from the accompanying quartz and feldspar by elutriation and particle size classification in hydrocyclones

To obtain a uniform mineralogical composition with a high alumina content (Al_2O_3 content > 37%), the raw kaolin is elutriated and simultaneously classified in hydrocyclones, whereupon kaolinite and the other layer silicates are separated from the accompanying quartz and feldspar on the basis of their different particle size distributions.

The kaolin suspension (kaolin, milk) is partially dewatered by sedimentation and filtration

After leaving the hydrocyclone, the water content of the fine product, so-called kaolin milk, is reduced to 25 to 30% in settling tanks and filter presses. The filter cake is often only dried to a water-content of 10 to 15%.

Different feldspar qualities and particle size-classified quartz sands are obtained as byproducts of the kaolin elutriation.

5.5.4.3 Manufacture of Clay Ceramic Batches

The particle size distribution of the raw materials influence the properties of the ceramic products

The properties of the clay ceramic products vary with the particle size distribution of the raw materials.

Whereas finely ground raw materials are required for fine ceramic products, mixtures of raw materials with different particle sizes are utilized for coarse ceramic products.

Paste production proceeds by:

- wet grinding of dressed raw materials
- mixing of components in suspension
- magnetic separation of iron impurities

Coarse grinding of the raw materials with crushers, pan grinders, hammer mills or cross beater mills is often carried out by the raw material suppliers. Thus in ceramic manufacture only fine grinding is required, for which wet grinding in ball mills, in which greater communition effects are realized than in dry mills, is satisfactory.

The clay constituents of the ceramic pastes are produced during raw material processing in sufficient fineness < 40 µm so that they can be immediately made into a slip by adding water in stirring tubs. This is mixed with the suspension of feldspar and quartz from wet mills and filtered over a sieve to remove any coarse particles still present. Magnetic separators are used to remove iron-containing impurities which have entered the paste during milling and processing and which would otherwise introduce undesirable coloration into the ceramic product.

- adjustment of the forming process-dependent water content

The preparation of pastes is determined by the intended forming process. Castable pastes with a water content of 30 to 35% are stabilized by adding flocculants. Clay-containing slips also contain 0.2 to 0.4% by weight of water glass and other sodium silicates or calcined sodium carbonate, as additives.

For the manufacture of turning pastes, the paste slip is dewatered with filter presses to water contents of 20 to 25% by weight, comminuted in a sieve kneader and formed in vacuum extruders into suitably sized slugs.

Drying of pastes to flowing powders by spray drying

Complete drying of the paste is generally carried out by spray drying. The spray-dried granules produced can be utilized both in dry pressing processes and with added water for casting and turning pastes.

Dry processing of ceramic pastes is much less energy intensive than wet processing. Removal of iron impurities poses severe problems

As a result of increasing energy costs, interest in dry processing technology, which avoids the expensive evaporation of water, has increased Mixing of the appropriate fine preground raw materials is carried out in intensive mixers (edge-runner mixers, Eirich mixers) and then just sufficient water is added to the homogenized mixture for the intended forming process. In these dry processes the removal of iron impurities is extremely difficult.

Storage in moist atmospheres produces more plastic clay ceramic pastes

One aspect of the processing of clay-rich batches for quality products is so-called “draining” or “maturing” storage in damp atmospheres for several weeks or months (in China some of the clay for porcelain manufacture has been drained for several hundred years!) During storage, water probably seeps between the crystal platelets of the clay minerals with the aid of bacteria and a homogeneously moistened paste with improved plasticity is formed.

5.5.4.4 Forming Processes

Choice of forming process is dependent upon:

- shape of the end-product
- required properties
- size of production run

The choice of a particular forming process depends upon the geometric shape of the component being manufactured. The required end product properties such as density and the batch size are also important.

The individual forming processes require pastes with different water contents (see Table 5.5-1).

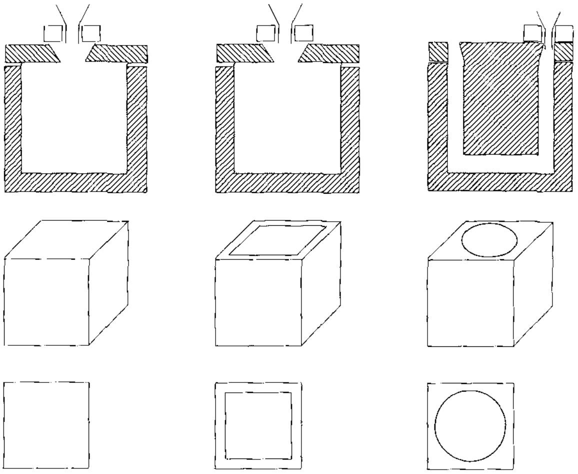
Table 5.5-1. Water Content of Porcelain Batches for Different Forming Processes.

paste type	water content in % by weight
casting pastes	33 to 36 (+ deflocculant)
turning and roller pastes	22 to 24
extruded pastes	22 to 24
leather-hard pastes	15 to 18
moist molding pastes	8 to 12 (+ plastification)
dry molding pastes	1 to 4

5.5.4.4.1 Casting Processes

Casting processes require the highest water contents. Such processes are particularly used for the manufacture of nonrotation symmetrical and complicated components. Casting processes can be divided into hollow casting, cored casting and solid casting (see Fig. 5.5-3).

Casting processes require high water contents. Can be classified into:



solid casting

hollow casting (inner shape corresponds to outer shape)

cored casting (inner shape corresponds to the core)

Fig. 5.5-3. Casting Processes for Ceramic Formed Articles.

- hollow casting
- cored casting, solid casting

The casting processes are based on the ability of plaster of Paris molds to extract water from the casting paste by capillary forces. In time a thick solid layer is formed at the plaster surface. In hollow casting the residual casting paste is poured off once the solid layer adhering to the plaster surface has reached the required thickness. In core casting and solid casting the paste is topped up until the whole cavity is filled. On standing, water is abstracted and solidification and shrinkage occurs, which aid the release of the molded article from the mold.

Despite widespread development work, plaster of Paris molds are still utilized today due to their excellent absorptive capacity even taking into account the limited reuse of the molds: a maximum of 100 castings being possible.

Prerequisite for the casting process:

control of the rheological properties of the casting slip

A particular prerequisite for the success of the casting process is precise control of particular rheological properties of the casting paste, which is achieved by controlling the water content and adding dispersing agents and deflocculants (such as alkali silicates, alkali phosphates, humic acid or tannic acid).

5.5.4.4.2 Plastic Forming

Turning on a potter's wheel is the oldest forming process

Plastic forming is based on the plasticity of water-containing clay ceramic pastes and, in the form of the potter's wheel, is the oldest known sort of forming. This turning of ceramic products can be automated on a large scale using the roller process.

In the large scale roller process the two variants are:

- jiggering of flat articles
- roller turning of hollow articles

In jiggering, the ceramic paste is mounted on a rotating mold, which forms the inside of the molded article, and the outer surface is formed by a profiling tool rotating in the same direction but at a higher speed. Jiggering is suitable for the manufacture of flat articles such as plates. Hollow articles (cups, bowls) are formed by roll turning in which the mold forms the outside of the article and the roller head forms the inner contours. Since the molds are made of plaster, the water is abstracted as with the casting process and the article shrinks away from the mold.

Extrusion molding used to make differently shaped slugs and tubes, so-called preforms

In extrusion molding so-called "slugs" are produced from the paste as preforms. These are subsequently formed into their final shape. In the manufacture of insulators the piston is dried to a "leathery hardness", which does not undergo any further shrinkage. These preforms are further processed with profiling tools.

A new plastic forming process has been developed, injection casting, in which clay ceramic pastes are injected into the mold and further compressed by closing the slightly opened tool. This process can also be used for manufacturing nonrotationally symmetric articles.

Injection casting enables the manufacture of nonrotationally symmetric articles

5.5.4.4.3 Forming by Powder Pressing

Dry pressing techniques can be used for simple geometric shapes and high numbers of articles. Dry or moderately moistened powder is compressed under pressure, during which the strength required for further processing is attained. Certain requirements have to be met by the powder, regarding flow and compaction properties. Granulate from spray driers, which also contains binder, is particularly suitable.

Dry pressing process utilizable for simple geometric forms and long production runs. Stringent demands placed on the powder properties

The primary particle size distribution of the powder, as well as the granule shape, has an influence upon the attainable density and strength of the molded article. The static friction between the individual particles and the compression mold can be reduced by lubricating additives, which largely suppress the development of structural stress.

The molded article should have as high density and strength as possible

Molded articles with low structural stress are obtained with presses working from two sides

Compression pressures of up to 2 kbar are used depending of the composition of the powder and the required "green density" of the unsintered molded article.

Highly mechanized plants can produce up to 300 unsintered articles/min/press. The achievable dimensional precision of the molded article is very high with tolerances down to several tens of microns in thickness and ca. 1% in weight. Greater tolerances are allowable for large format refractory products.

Throughput of dry presses is high. Dimensional precision of the greenware (unfired molded article) is good

Isostatic pressing is a special type of dry pressing process. In this process the paste is poured into suitable preformed rubber matrices, which are placed in a perforated metal holder. The powder compression takes place in a pressure chamber with oil or hydrostatic pressures of 2 to 4 kbar. New processes exploit the compressibility of plastic pastes, to enable a dry isostatic compression. Such pressure application on all sides produces a very uniformly compressed molded article, but one usually requiring further mechanical working due to the resilience of the rubber matrices not being completely geometrically constant. Insulators for sparking plugs (see Section 5.5.5.1.2) are among the ceramic products manufactured on a large scale using this process.

Isostatic pressing processes produce molded articles with a very uniform density distribution

In the manufacture of high grade components from engineering materials such as SiC or Si_3N_4, isostatic pressure is assuming increasing importance e.g. in the manufacture of valves for automobiles, bearings in the form of balls, rollers and bushings.

5.5.4.5 Drying Processes

Drying of unsintered formed articles is accompanied by shrinkage due to water loss

In a further process step the moisture or pressing aids, which have been added to improve processing, have to be removed from the unsintered molded articles. The drying process is accompanied by shrinkage of the article, which in the event of uneven shrinkage can result in cracking. Clay-rich pastes with high shrinkage must therefore be dried particularly carefully. Organic aids are removed by heating.

Particularly favored are moist air processes in which the article is thoroughly heated at high relative humidity and the temperature then slowly increased with decreasing humidity. Shrinkage ends at water contents of ca. 8 to 10%, at which point the temperature can be more strongly increased.

Drying is carried out in rocking, box and tunnel driers often utilizing the combustion heat from kilns. Rapid drying (ca. 10 min) with IR irradiation has recently been introduced for thin-walled articles (crockery). This compares with drying times for large format articles of up to 24 h and more (e.g. sanitary ware).

5.5.4.6 Firing of Ceramics

5.5.4.6.1 Physical-Chemical Processes

Ceramic products are rendered durable by their thermal treatment: firing

An important step in the manufacture of ceramic products is their thermal treatment at relatively high temperatures: > 800°C. This step, known as "firing", leads to strengthening of the unsintered molded articles into durable final products with the required form. The processes which take place are collectively known by the technical term "sintering".

During the firing of clay ceramic products the following physicochemical processes take place:

During the firing of clay ceramic pastes a number of physicochemical processes take place, which are important for the mechanical and thermal properties of the final article:

- the kaolinite OH-groups are split off at 400 to 600°C forming metakaolinite, which is stable up to 950°C. At temperatures ≥ 1150°C cristobalite and mullite ($3Al_2O_3 \cdot 2SiO_2$) are formed in the form of flakes (so-called primary mullite) via a spinel-type intermediate phase:

- formation of mullite flakes and cristobalite

$$Al_2(OH)_4(Si_2O_5) \longrightarrow \underset{\text{(metakaolinite)}}{Al_2O_3 \cdot 2SiO_2} + 2H_2O$$

$$Al_2O_3 \cdot 2SiO_2 \longrightarrow \gamma\text{-}Al_2O_3 + 2SiO_2$$

$$3Al_2O_3 + 6SiO_2 \longrightarrow \underset{\text{(mullite)}}{3Al_2O_3 \cdot 2SiO_2} + \underset{\text{(cristobalite)}}{4SiO_2}$$

- the feldspar components melt at or below 985°C, upon attaining the melting point of the potash feldspar-silica eutectic. This melting point can be reduced to 920 to 950°C by impurities. The feldspar-melt dissolves the SiO_2 present in the starting mixture and also that formed by the thermal decomposition of metakaolinite. This results in an increase in melt viscosity which compensates the normally observed decrease in viscosity with increasing temperature. For this reason porcelains exhibit good dimensional stability in a wide firing-temperature range.
- needle-shaped secondary mullite is then formed in a further chemical process during the thermal treatment. This makes a major contribution to the strength of the final article. The precipitation of secondary mullite from the feldspar melt occurs on sites with slight alkali deficiency.

- melting of feldspar
- dissolution of SiO_2
- precipitation of needle-shaped mullite

The rates of these reactions, which represent only part of the very complex chemical processes involved, are diffusion limited. By varying the firing temperature and firing time, articles can be obtained either with very high transparency due to almost complete dissolution of the crystalline phases or with high mechanical strength with high quartz contents.

Diffusion processes determine the rate constants of the physicochemical processes

5.5.4.6.2 Firing Conditions

Firing of mass-produced articles carried out in continuously operating tunnel kilns

Continuously operating tunnel kilns heated with gas, oil or electricity, in which the articles travel through a well-defined temperature-time profile, are currently almost exclusively used for the manufacture of the mass-produced articles of the brick, refractory and crockery porcelain industries. Such kilns are 20 to 150 m long and have transit times between 1 and >72 h. Muffle kilns, which operate discontinuously, are still important for small production runs and specialty products.

Discoloring iron impurities are Fe_2O_3 and Fe_3O_4 in oxidizing atmospheres and FeO in reducing atmospheres during firing

The firing atmosphere is particularly important in the case of white articles. In oxidizing atmospheres traces of iron in the starting materials oxidize to Fe_2O_3 and Fe_3O_4, depending upon the firing temperature, coloring articles brown to blackish blue. Even quantities of Fe_2O_3 below 0.35% by weight are troublesome. Upon firing in a reducing atmosphere, achieved with an air-deficient combustion mixture, FeO is formed, which dissolves in the melt phase giving a gray, greenish or bluish coloration. Under such conditions a white color is obtainable with iron(II) oxide contents of up to 0.6% by weight.

For glazed article the firing takes place in two steps:

- biscuit firing
- glost firing:
  during the glost firing the unsintered molded articles are supported by kiln furniture

Glazed porcelain and fine earthenware articles are mostly fired twice. In the first (biscuit) firing at 900 to 1000°C, the article attains the strength required for the application of glaze. No sintering of the article takes place and the articles can be stacked one on top of another. After the "biscuit" firing the articles are coated with glazing slip and the "glost" firing carried out at product-dependent temperature between 1100 and 1500°C. During this firing the articles must not touch one another. This is achieved by using so-called kiln furniture, consisting of racks made of clay- or directly-bonded silicon carbide or cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), mounted on the tunnel kiln trolley. Hollow articles may require supports made of shaped porcelain (so-called cases) to prevent deformation under their own weight.

5.5.4.6.3 Glazes

The rough surfaces of fine ceramic products are smoothed with flux-rich glazes consisting of the same raw materials used for the product together with added low melting point oxides (alkali oxides, alkaline earth oxides, lead oxide and boron oxide). The glazing mixture is applied by dip-coating or spraying onto the raw or precalcined articles. So-called glazing slips i.e. aqueous suspensions of the glazing mixture are required for both processes. In the production of slips, water-soluble substances have first to be converted into insoluble compounds by a short fusion process (frit glazes).

Glazing mixtures mostly produce a homogeneous melt upon firing which solidifies on cooling to a glassy finish

Glazing mixtures can be rendered insoluble by fritting

Salt glazes (thin layer glazes) are obtained by blowing rock salt into the firing chamber. The sodium chloride reacts with the water vapor in the furnace atmosphere forming HCl and Na_2O, which form low melting point sodium aluminum silicates on the surface of the article being fired.

5.5.4.7 Properties and Applications of Clay Ceramic Products

A survey of the fine ceramic clay-containing products will be given in this section, the coarse ceramic products having been for the most part dealt with in the sections concerned with construction materials (see Section 5.3.5) and refractory products (see Section 5.5.5.3).

5.5.4.7.1 Fine Earthenware

Porous clay ceramic products can absorb more than 2% of their weight of water. This group of products includes colored earthenware (pottery) and the, generally white, fine earthenware (see Table 5.5-2). Due to its liquid and gas permeability, fine earthenware can be utilized in the manufacture of ceramic filters and diaphragms. Glazing renders it impermeable and suitable for the manufacture of household utensils, sanitary ware, wall panels and tiles (majolica, faience).

Fine earthenware articles are porous and white or ivory in color

Feldspathic earthenware (hard earthenware) or calcareous whiteware (soft earthenware) are produced depending upon the flux used.

Table 5.5-2. Earthenware Products and their Properties.

Products	composition of the batch in % by weight				firing conditions	advantages	disadvantages
	clay minerals	quartz	feldspar	calcium carbonate			
calcareous whiteware (soft earthenware)	40 to 45	up to 40	–	15 to 25	biscuit 1150°C glost 1000 to 1060°C	cheap, low density	brittle, poor thermal shock resistance
mixed earthenware	45 to 50	48 to 42	1 to 3	5 to 7.5	biscuit 1180°C glost 1000 to 1100°C	harder, less brittle than calcareous earthenware	
feldspathic earthenware (hard earthenware)	40 to 55	55 to 42	5 to 3	–	biscuit 1240°C glost 1000 to 1100°C	hard and denser than calcareous & mixed earthenware	more expensive and heavier

5.5.4.7.2 Stoneware

Stoneware articles are impervious to water, lightly glazed and fracture conchoidally

The term stoneware includes a range of different ceramic products, whose pastes mainly consist of presintered, generally illitic, clay and are fired to a nonporous product.

Fine stoneware for household utensils (real stoneware) is manufactured by casting and is gray, yellow or red. A well-known example of such fine stoneware is "Wedgwood porcelain".

Industrial fine stoneware (for laboratory apparatus, insulators) is manufactured from low quartz clays which fire to a light color, producing a porcelain-like article.

Acid and alkali resistance of stoneware can be improved by additives

Acid-resistant stoneware is given a salt glaze and is resistant to all acids except hydrofluoric acid. The acid resistance can be increased by adding zirconium oxide or phosphates, the alkali resistance by adding barium oxide, magnesium oxide or chromium oxide.

5.5.4.7.3 Porcelain

Porcelain articles when thin-walled are translucent and fracture conchoidally

Due to the high flux content in the batch and the resulting high proportion of melt phase in the ceramic firing, porcelain is dense, white and glassy, thin walls being translucent and transparent.

Porcelains are classified according to their chemical composition as well as on the basis of their firing temperatures. The hard porcelain, favored in Mid-Europe for the manufacture of utensils and technical articles, is produced from classical mixtures consisting of 50% kaolin, 25% feldspar and 25% quartz and are fired at 1380 to 1460°C. The thermal shock resistance, particularly required for chemical apparatus porcelains and cooking utensils, can be increased by reducing the quartz content, but at the expense of transparency.

Hard porcelain consists of 50% kaolin, 25% quartz and 255% feldspar. Firing temperature: 1380 to 1460°C

By partial or complete replacement of quartz by alumina, alumina porcelain is obtained with a very high strength. The processing of pastes is made more difficult by the abrasive action of alumina.

If the feldspar and quartz content is increased over that in hard porcelain, soft porcelain is obtained which is fired at 100 to 150°C lower temperatures. Highly plastic clay (ball clay) is added to obtain plastic and easy to work pastes, despite the lower kaolin content. Sanitary porcelains for the manufacture of bathroom articles are soft porcelain articles.

Soft porcelains have higher feldspar and quartz contents. The firing temperatures are 100 to 150°C lower

A particular type of soft porcelain, widely manufactured in English-speaking countries, is vitreous china, which produces nonporous, but nontransparent articles.

A special soft porcelain is vitreous china, which is used for sanitary articles

Bone china is used, particularly in Great Britain, for crockery and ornamental objects and exhibits particularly high transparency and high whiteness. Its firing mixture consists of 40 to 50% bone ash, 20 to 30% feldspar and 20 to 30% kaolin. The phosphates introduced by the bone ash or apatite possess strong glass-forming properties. The firing temperature has to be reduced to 1200 to 1280°C to prevent too much softening during firing.

Bone china is a high quality product, whose ingredient mixture contains phosphate (40 to 50% bone ash). Used for crockery and ornamental objects

So-called dental porcelains produced with particularly feldspar-rich mixtures (70 to 90% feldspar, 15 to 25% quartz, 2 to 8% calcite or kaolin) are not really clay ceramic products. Due to the high flux content, a glossy surface is formed upon firing and no glazing is necessary.

Dental ceramics (dental porcelain) consist almost entirely of feldspar

5.5.4.7.4 Rapidly Fired Porcelain

Conventional porcelain types require tunnel kiln transit times of 24 to 72 h. Firing times of 1 to 3 h are attainable with the recently developed rapidly fired porcelains. With such short firing times the furnace throughput can be kept high even when the articles are mounted as a single layer

Newly developed rapidly fired porcelains only require fire times of ca. 3 h on the kiln trolley. Thus the kiln furniture can be largely dispensed with and the inert mass of the firing kiln reduced. The object of this development was a reduction in energy consumption.

The batches for rapidly fired porcelains must be adapted to the short firing times

The batches for rapidly fired porcelains have to be adapted to the short firing times to obtain product properties comparable with those of conventionally fired porcelains, despite the diffusion-controlled slow chemical reactions. Suitable mixtures contain lower concentrations of quartz and fluxes and contain prefired raw materials such as calcined kaolin (fireclay). Satisfactory transparency can be obtained by using very fine particulate quartz sorts, which dissolve sufficiently rapidly in the glass phase.

5.5.4.8 Economic Importance of Clay Ceramic Products

Table 5.5-3. Production Statistics for Clay Ceramic Products in the Period 1991 to 1994.

	1991	1992	1993	1994
Fine ceramic products (in 10^3 t)				
household and ornamental articles				
of porcelain (also vitreous china)	107	93	85	72
of fine earthenware and stoneware			22	19
ceramic sanitary ware			73	77
insulators and insulation components	35	35	33	34
technical products			23	26
wall and floor tiles$^{1)}$	47 344	45 816	45 417	41 698
Stone and earth (in 10^3 t)				
inner, facing & hard bricks$^{2)}$	10 460	11 534	12 551	15 950
roofing tiles	556	633	671	746
formed refractory products	1 247	1 182	1 128	1 153

1) in 1000 m^2; 2) in 1000 m^3

5.5.5 Specialty Ceramic Products

5.5.5.1 Oxide Ceramics

5.5.5.1.1 General Information

Oxide ceramics are very dense fine ceramic products from single phase metal oxides

In contrast with clay ceramic products, oxide ceramics consist essentially of a single crystalline phase of a pure high melting point metal oxide. Oxide ceramics are generally nonporous fired fine ceramic products. They contain little or no low melting point silicate phase.

The manufacture of such materials proceeds according to the process steps described in Section 5.5.3. However, in comparison with clay ceramic products a few characteristic chemically determined process modifications have to be taken into consideration:

- high demands are placed on the purity of oxide ceramic raw materials. As a result natural products have to be chemically processed.
- oxide ceramic pastes do not have the clay mineral-induced plasticity of clay ceramic pastes. The rheological properties of pastes necessary for particular forming processes have, therefore, to be obtained with organic additives and water. In practice binders with partial plasticizing effects such as starches, celluloses, dextrin, molasses, gelatines, lignins, bitumen, natural or synthetic resins or waxes are preferred.
- in injection molding processes, oxide powder, mixed with thermoplastics or waxes, is hot pressed into forms and the molded articles removed from the form, after cooling. In the subsequent firing the organic residue is pyrolyzed leaving no residue.
- sintering of oxide ceramic products occurs without a melt phase at temperatures generally 200 to 300°C below the melting point of the oxides. For very finely divided highly reactive powders with sintering aids, which increase the rate of diffusion of anions and cations in oxide lattices via a defect mechanism, sintering to a nonporous material can be achieved at even lower temperatures.
- sintering of objects is associated with shrinkage due to the decreasing porosity. This shrinkage leads to certain dimensional variation in the finished ceramic component, which is too large for many applications e.g. mechanical engineering. This can be remedied by finishing via grinding, lapping and polishing with diamond or boron carbide tools.

Raw materials for oxide ceramics have to be very pure

Oxide ceramic pastes are not plastic

Oxide ceramic pastes are plasticized with binders and plastifying additives

Solidification obtained by sintering (200 to 300°C below the melting point). Sintering temperature influenced by the particle size of oxide particles

Shrinkage during firing must be taken into account in the manufacture of greenware

5.5.5.1.2 Aluminum Oxide

The industrially most important oxide-ceramic material is sintered aluminum oxide. The raw materials used are so-called calcined alumina and melted corundum.

Raw materials for aluminum oxide ceramics are:

- calcined alumina (fine particulate)
- melted corundum (coarse crystals)
- sintered corundum (coarse crystals)

Calcined alumina (α-Al_2O_3) is obtained by heating the aluminum hydroxide $Al(OH)_3$, which is produced in the bauxite digestion using the Bayer process, at temperatures above 800°C. Depending upon the process parameters, the aluminum oxide consists of 0.3 to 0.5 µm primary particles, which are generally agglomerated into 10 to 100 µm particles. Coarser crystals are obtained by the fusion of bauxite or precalcined raw materials with carbon in electric furnaces. The impurities are reduced to metal and can be separated from the oxide melt. Purer products are obtained by the fusion of Bayer alumina. Upon quenching the melt, mm-sized aluminum oxide particles, so-called melted or electro-corundum, are formed. The alumina can also be sintered at temperatures of ca. 2000°C into 0.01 to 1 mm-sized platelet-shaped crystals.

Manufacture of denser molded articles requires precisely adjusted particle size distributions

The manufacture of molded articles is usually carried out with mixtures of aluminum oxides with different particle size distributions. This is particularly important when pore-free end-products are required, because this enables a higher volume concentration of aluminum oxide to be obtained than the 74% of ideally cubic close packed spheres by filling the gaps with smaller particles. The particle size distributions used in practice are usually determined using empirically determined approximate formulae (Andreasen or Fuller distribution curves) which take into account the morphology of the individual particles.

Sintering of aluminum oxide ceramics is carried out at temperatures between 1500 and 1800°C. The sintering rate is increased and undesirable particle growth prevented by adding MgO, Y_2O_3, TiO_2, Cu_2O or MnO in quantities of 0.1 to 5% by weight.

Important properties of aluminum oxide ceramics:

- high temperature resistance
- good thermal conductivity
- high electrical resistivity
- chemical resistance

drawback:

- mediocre thermal shock resistance

The important properties of aluminum oxide ceramics are their high temperature stability (melting point of Al_2O_3: 2050°C), their good thermal conductivity, their high electrical resistivity and their high chemical resistance. Their mediocre thermal shock resistance is a disadvantage. All these properties are dependent upon the chemical purity and particle size distribution of the oxide powder and the density, structure and pore size distribution of the ceramic.

The choice of manufacturing process is closely linked with the intended application of the particular article.

The various possible applications of aluminum oxide ceramics corresponding to specific properties are listed in Table 5.5-4.

Table 5.5-4. Application Fields for Aluminum oxide Ceramics.

required property	application fields
wear resistance	drawing dies for wire, thread guide
hardness, toughness	abrasive particles, cutting ceramics
corrosion resistance	components for acid or alkali pumps, crucibles, grinding balls, lamp tubes for sodium vapor lamps
high temperature stability	melting crucibles, protective tubes for thermocouples
high electrical resistivity	insulators (sparking plugs), thin disc substrates for minaturized integrated circuits
compatibility with living tissue	material for artificial limbs (e.g. for hips and teeth)

5.5.5.1.3 Zirconium Oxide

The mineral baddeleyite (ZrO_2) is found in nature only in small quantities. The main raw material for zirconium oxide ceramics is thus zircon ($ZrSiO_4$), from which pure ZrO_2 is produced by fusing with lime and coke to reduce the SiO_2 and the impurities.

The natural raw material for zirconium oxide ceramics is the mineral zircon ($ZrSiO_4$)

Zirconium(IV) oxide exists in three modifications: monoclinic, tetragonal and a cubic fluorite structure. The monoclinic form is converted into the tetragonal form with volume reduction upon heating at 1100 to 1200°C. The corresponding increase in volume upon cooling results in the fracture of pure sintered molded ZrO_2 articles. Addition of 10 to 15% by weight of CaO or MgO stabilizes the cubic high temperature modification.

Zirconium(IV) oxide exists in monoclinic, tetragonal and cubic modifications

Sintering of such stabilized ceramics is carried out at temperatures of ca. 1800°C in air.

Stabilized zirconium oxide can be used up to 2600°C. Important application fields are:

- furnace construction
- resistive heating elements
- solid electrolyte
- neutron reflectors in nuclear reactors

Due to its high melting point (melting point of pure ZrO_2: 2700°C) stabilized zirconium(IV) oxide ceramics are utilized in furnace construction, for the manufacture of melting crucibles and in the steel industry for continuous casting nozzles. Other important application fields are resistive heating elements and solid electrolytes in fuel cells. The latter utilizes the unusually high conductivity of zirconium oxide ceramic materials, particularly that of Y_2O_3-stabilized ZrO_2 (Nernst mass).

In nuclear reactor technology hafnium-free zirconium(IV) oxide is used as a neutron reflector, due to its low neutron capture cross-section.

5.5.5.1.4 Beryllium Oxide

Beryllium oxide ceramics have technically valuable properties. Their application is limited due to their high price and poisonousness

Beryllium oxide ceramics exhibit the highest thermal conductivity of all the ceramic products and are the best electrical insulators at high temperatures. Despite these exceptional properties, beryllium oxide ceramics have only found limited application due to their high cost and poisonousness. They are manufactured by sintering dry or plastically pressed fine particulate beryllium oxide at 1400 to 1450°C in a hydrogen atmosphere.

Typical application fields are: casting molds for molded vanadium components, crucibles for high frequency induction furnaces and substrates for integrated circuits. In nuclear reactor technology beryllium oxide is mixed with nuclear fuel as a moderator for fast neutrons.

5.5.5.1.5 Uranium Oxide and Thorium Oxide

Large quantities of UO_2-ceramics are needed in nuclear reactors

The fuel rods in light water reactors preferably contain UO_2-pellets

UO_2-pellets are manufactured using the dry pressing process

The increasing use of nuclear energy has led to the manufacture of uranium(IV) oxide ceramics becoming an important branch of the ceramics industry. Fuel rods for light water reactors, the most common reactor type, preferably consist of sintered uranium(IV) oxide pellets ca. 6 mm in diameter with a length to diameter ratio of 0.9 to 1.2. The total fuel load for a light water reactor is 15 million of such pellets. The estimated total demand of uranium(IV) oxide has hardly increased in recent years and part of it has been replaced by UO_2/PuO_2-mixed oxides from reprocessing plants.

Pellets of U-235 enriched uranium(IV) oxide powder are manufactured using the usual dry pressing process at pressures of 2800 to 4200 bar. Subsequent sintering at 1650°C in a nitrogen/hydrogen atmosphere produces sintered bodies with 96% of the theoretical density and a grain size of 10 µm.

"Sol-gel" process enables the remote-controlled manufacture of spherical particles of $(U,Pu)O_2$

Interest in the so-called "sol-gel process" for the remote-controlled manufacture of plutonium-containing fuel rods is increasing due to its high safety. In this process a filter cake of freshly precipitated uranium(IV) oxide is converted ultrasonically into a UO_2-gel, which after drying is fired at 1150°C. The resulting microspheres, 40 to 60 µm in diameter, are then poured into casing tubes using vibratory techniques.

Coated ThO_2 or UO_2 fuel balls are utilized in high temperature reactors

Coated spherical ThO_2- or UO_2-particles are increasingly utilized in the fuel of gas-cooled high temperature reactors. Their 50 to 1500 µm core of uranium(IV) oxide is manufactured using conventional sintering techniques. This is then pyrolytically coated with many layers of carbon and silicon carbide (see Section 5.7.5.1).

The uranium-thorium mixed oxide for fast breeder reactors can be processed in a similar way.

Thorium oxide ceramics are only slightly radioactive

Thorium oxide ceramic materials have a limited importance in conventional applications. Thorium oxide crucibles, for example, exploit its extremely high melting point of ca. 3300°C and its good corrosion resistance.

5.5.5.1.6 Other Oxide Ceramics

Pure sintered magnesium oxide ceramics have little importance compared with magnesium oxide-containing refractory products. They are used as high temperature materials.

Nonporous spinel oxide ceramics of $MgAl_2O_4$ are notable for their very good high temperature corrosion resistance to alkaline media. Sintered yttrium oxide exhibits still better corrosion resistance at high temperatures (Y_2O_3 melting point: ca. 2400°C), but its utilization possibilities are limited by its high price.

In recent years sintered titanium(IV) oxide has been utilized in addition to aluminum oxide in the textile industry in which it is utilized as an abrasion-resistant material for thread guides.

A new oxide ceramic solid electrolyte is so-called β-aluminum oxide, a compound of Al_2O_3 with 5 to 10% Na_2O. Materials of this type are currently being evaluated in sodium-sulfur batteries.

5.5.5.2 Electro- and Magneto-Ceramics

5.5.5.2.1 Titanates

Most important electroceramic material: sintered $BaTiO_3$

$BaTiO_3$, which has a perovskite crystal lattice, is a ferroelectric material i.e. a material in which the change in polarization P with varying applied electric field E traces a dielectric hysteresis loop analogous to the hysteresis loop exhibited by ferromagnetic materials.

Technically useful properties of such perovskite ceramics are their high permittivities (relative dielectric constants), the semiconductor properties of certain chemical compositions and their piezoelectric properties.

Large scale manufacture of $BaTiO_3$ from barium carbonate and titanium oxide

Barium titanate is manufactured by a solid-state reaction at 1000°C according to the following equation:

$$BaCO_3 + TiO_2 \longrightarrow BaTiO_3 + CO_2$$

Very pure barium titanate is obtained by coprecipitation of barium and titanium compounds (e.g. as oxalates or citrates) followed by calcination. In the manufacture of electroceramics, this is followed by the usual ceramic processes: grinding, molding and a sintering at 1300°C.

Ceramic dielectric exhibit extremely high permittivities

The permittivity of these ceramic dielectrics varies between 1000 and 12 000 depending upon the particle size of the $BaTiO_3$-powder and its chemical composition. These also affect the temperature dependence of its permittivity.

The physical properties of barium titanate are influenced by partial substitution with other ions

Barium can be partly substituted by strontium or lead and the titanium by zirconium or tin.

Applications of $BaTiO_3$-ceramics:

- dielectrics for condensers
- cold conductors
- piezoelectrics

For its application as a cold conductor, small amounts of barium or titanium are substituted by higher valency state ions such as antimony, niobium or the rare earths together with traces of copper, iron or manganese. Such cold conductors exhibit a strong increase in specific resistance (10 to 100 Ω-cm) with temperature e.g. an increase of a factor of 10^3 to 10^6 between 50 and 100°C.

Piezoceramics are currently no longer manufactured from $BaTiO_3$, but from lead titanate zirconate, $Pb(Ti,Zr)O_3$, which also crystallizes in a perovskite lattice. Ceramic capacitors to a value of $4.1 \cdot 10^9$ DM were produced in 1995, ca. 50% of the turnover for functional ceramics, in which the three region USA, Japan and Europe have equal shares.

5.5.5.2.2 Ferrites

General Information

The term "ferrites" has become established as a general term describing all magnetoceramic materials.

Ferrites are classified according to their crystal structure into two types:

1. "Cubic" ferrites crystallizing in the spinel ($MgAl_2O_4$) structure with the general chemical composition $M^{2+}Fe_2{}^{3+}O_4$;
2. "Hexagonal" ferrites crystallizing in the magnetoplumbite ($PbFe_{12}{}^{3+}O_{19}$) structure with the general chemical composition $M^{2+}Fe_{12}{}^{3+}O_{19}$.

The magnetic properties of these compounds and hence their applications are closely coupled to their crystal structure. This is the basis of their classification into ferrites with "soft" magnetic properties (cubic) and "hard" magnetic properties (hexagonal).

Ferrites are magnetoceramic materials. There are two types:

- cubic ferrites (soft ferrites) $M^{2+}Fe_2{}^{3+}O_4$
- hexagonal ferrites (hard ferrites) $M^{2+}Fe_{12}{}^{3+}O_{19}$

Soft Ferrites

The magnetic properties required for coil- and transformer core are: the highest possible permeability and the lowest possible coercive force so that a high induction is produced with low magnetic fields and demagnetization in an AC field occurs easily and with low losses (soft ferrites). These requirements are met by ferrimagnetic compounds with high saturation magnetization at low crystal anisotropy.

Soft (cubic) ferrites with high permeabilities are used as coil- and transformer-cores

As Table 5.5-5 shows, several ferrites with the spinel structure possess the required properties. Mixed crystal formation of these compounds with each other or with other spinels produces a range of materials with different magnetic properties, giving the possibility of finding materials for special applications. Thus, for example, MnZn- and NiZn-ferrites are preferred for high frequency applications. Compounds in the system $MnO\text{-}MgO\text{-}Fe_2O_3$ with an iron deficiency exhibit an almost rectangular hysteresis loop (rectangular ferrites).

Ferrites with the spinel structure form mixed crystals over the whole concentration range

Rectangular ferrites are utilized in core memory systems in computers

The manufacture of high quality ferrites mainly requires chemically processed raw materials, particularly metal oxides. These are first ground and mixed in a wet mill. The actual starting materials are formed during subsequent annealing.

Manufacture of ferrite powder by:

- annealing oxide mixtures

- annealing of coprecipitated hydroxides, carbonates, oxalates

In the case of ferrites with very complex compositions, annealing of the oxide raw materials often produces insufficiently homogeneous compounds. In such cases a homogeneous mixture of thermally decomposable compounds (metal hydroxides, carbonates or oxalates) is produced wet chemically by coprecipitation. This preliminary product is then spray dried and presintered.

Finally the usual process steps in oxide ceramic technology are carried out: wet grinding, molding and sintering to the ceramic article.

Soft ferrites with low porosity are obtained by hot pressure processes

Since a low porosity is desirable for soft ferrites to optimize their permeability, hot pressing is used for molding high quality products. This process combines dry pressing and sintering in a single step. The pressure used is ca. 150 to 2000 bar and the temperature is about half the melting point temperature of the lowest melting eutectic. The compression molds are made of graphite, Al_2O_3- or SiC-ceramics or of refractory metals such as molydenum, tungsten, niobium or tantalum.

* conversion of technical units into SI-units:

1 Gauß = 10^{-4} Tesla (T)

$$1\ \text{Oersted (Oe)} = \frac{10^3}{4\pi}\frac{\text{Ampere}}{\text{Meter}}\left(\frac{A}{m}\right)$$

$$1\ \text{Gauß} \cdot \text{Oersted} = \frac{10^{-1}}{4\pi}\frac{\text{Joule}}{\text{Meter}^3}\left(\frac{J}{m^3}\right)$$

Table 5.5-5. Magnetic Properties of Simple Ferrites with Spinel Structure.

compound	saturation magnetization M_s at 20°C in Gauss*	Crystal anisotropy constant at 20°C in J/m^3	Curie temperature in K
$MnFe_2O_4$	400	$-2.8 \cdot 10^3$	573
$FeFe_2O_4$	480	$-1.1 \cdot 10^3$	858
$CoFe_2O_4$	425	$+2.0 \cdot 10^3$	793
$NiFe_2O_4$	270	$-6.2 \cdot 10^3$	858
$CuFe_2O_4$	135	$-6.0 \cdot 10^3$	728
$MgFe_2O_4$	120	$-2.5 \cdot 10^3$	713

Other applications for cubic ferrites:

- recording and erasure heads for tape recorders
- ferrite antennae
- high frequency components

The most important application of cubic ferrites, quantitywise, is the manufacture of coil- and transformer-cores. In terms of numbers, recording and erasure heads for tape recorders, ferrite antennae for the frequency range 0.5 to 1.5 MHz and other components for high frequency technology are also important.

Hard Ferrites

Hard ferrites are permanent magnetic materials

For permanent magnets, materials with the highest possible remanence and coercive force are required, so that they cannot be easily demagnetized by external magnetic fields.

These requirements are fulfilled by the hexagonal ferrites (hexaferrites) $BaFe_{12}O_{19}$ and $SrFe_{12}O_{19}$.

The theoretical maximum coercive force with such materials is 17 000 Oe. However in practice, with the optimum particle size of 1 µm only values of 3000 to 4000 have been attained. This is due to lattice defects and the formation of coarse particles during sintering.

Magnetic properties of ceramic permanent magnets are strongly influenced by the particle size distribution

A special feature of hexaferrites is their pronounced magnetic anisotropy. The preferred direction for magnetization is perpendicular to the plane of the platelet-shaped hexagonal crystals. By parallelly orienting the platelets in the finished ceramic (anisotropic ferrite) the required remanence of > 4000 G and virtually rectangular hysteresis loops can be obtained.

Hexaferrites are magnetically anisotropic

A guide to the quality of hard ferrites can be obtained from the maximum energy product $(B \cdot H)_{max}$, which can be determined from the hysteresis loop. This is proportional to the available energy per unit volume permanent magnet. For anisotropic ferrites the technically attainable value for $(B \cdot H)_{max}$ is 4 MG·Oe. Isotropic ferrites without crystal orientation with $(B \cdot H)_{max}$ values of 1 MG·Oe are used for cheap mass-produced articles.

A quality guide for permanent magnets is the maximum energy product $(B \cdot H)_{max}$

Isotropic hexaferrites are manufactured in a similar way to soft ferrites, using natural or waste iron oxide as a raw material.

The process for manufacturing anisotropic hexaferrites differs only in the molding process. The hexaferrite powder obtained by firing the oxide mixture at 1100 to 1300°C is wetted with ca. 40% water and wet ground. The suspension is pumped into compression molds, whose molding plug contains a filter and run off pipes for the water. The crystal platelets are oriented by applying a magnetic field during the compression step. Subsequent sintering at 1150 to 1250°C requires exact maintenance of a well-defined temperature profile due to the anisotropic shrinkage.

Molding of anisotropic ferrite ceramics takes place in the presence of an external magnetic field

Hexaferrites are mainly utilized in the manufacture of DC-motors, alternators, magneto-igniters, magnetic couplings, dynamic loudspeakers and magnetic adhesion systems. The estimated worldwide production in 1995 was $150 \cdot 10^3$ t/a with a value of > 500 million DM and exceeded the production of metallic permanent magnets.

Hexaferrite permanent magnets have many applications:

- DC-motors
- alternators
- magneto-igniters
- magnetic couplings
- dynamic loudspeakers
- magnetic adhesion systems

Worldwide production in 1995:

$150 \cdot 10^3$ t/a (exceeds metallic permanent magnets)

5.5.5.3 Refractory Ceramics

5.5.5.3.1 Definition and Classification

Refractory behavior of ceramic materials is determined by the Seger cone test

Ceramic materials are termed refractory, when they exhibit a cone-fusion point of at least SK 17 (average cone-fusion point 1500°C) in the Seger cone test according to DIN 51 063. Highly refractory materials have a cone-fusion point of at least SK 37 (1830°C).

Softening behavior of ceramic materials is compared using the Seger cone test

A characteristic property of highly refractory materials is their softening behavior under pressure (pressure softening, pressure flow)

The so-called Seger cone values (SK) correspond to different ceramic bodies, which soften and deform at particular temperatures. The cone-fusion point is that temperature at which the point of the cone reaches the level of the cone feet. The different Seger cones are sequentially numbered with increasing cone-fusion point. The softening of a ceramic paste is characterized by the number of the Seger cone which has the same cone-fusion point. For many of the current refractory materials the cone-fusion point is too high to be measured according to DIN 51 053 which measures the softening at high temperatures under pressure (pressure deformation or pressure flow).

Oxide products have achieved industrial prominence as refractory materials mainly because they can be cheaply manufactured from natural raw materials (see Table 5.5-6).

Choice of suitable refractory materials dependent upon:

- thermal stability
- thermal expansion coefficient
- thermal shock resistance
- chemical resistance
- thermal conductivity
- abrasion resistance

Apart from their thermal stability a number of other factors are important in the choice of refractory materials e.g. thermal expansion coefficient, thermal shock resistance, chemical resistance, thermal conductivity and abrasion resistance. These properties depend upon both the microstructure and composition of the ceramic material.

Table 5.5-6. Melting and Decomposition Temperatures of Important Constituents of Refractory Products.

name	formula	melting point in °C	name	formula	melting point in °C
cristobalite	SiO_2	1723	mullite	$3Al_2O_3 \cdot 2SiO_2$	1850
corundum	Al_2O_3	2050	cyanite	$Al_2O_3 \cdot SiO_2$	1325[2]
chromium(III) oxide (eskolait)	Cr_2O_3	2435	analusite	$Al_2O_3 \cdot SiO_2$	1350[2]
periclase	MgO	2825	sillimanite	$Al_2O_3 \cdot SiO_2$	1530[2]
calcium oxide	CaO	2572	wollastonite	$CaO \cdot SiO_2$	1540
zirconium oxide (stabilized)	ZrO_2	2690	forsterite	$2MgO \cdot SiO_2$	1890
rutile	TiO_2	1830	chromite	$FeO \cdot Cr_2O_3$	2180
silicon carbide	SiC	2760[1]	picrochromite	$MgO \cdot Cr_2O_3$	2330
silicon nitride	Si_3N_4	1900[1]	spinel	$MgO \cdot Al_2O_3$	2135

[1] decomposition temperature; [2] decomposition to mullite and cristobalite

Refractory products are classified according to their chemical composition (see Table 5.5-7).

In addition they are characterized according to their temperature treatment:

- "unfired products", in which bonding with inorganic or organic binders proceeds at temperatures below 150°C;
- "heat-treated products", in which bonding with inorganic or organic binders proceeds at temperatures between 150 and 800°C;
- "fired or melted products", in which the mainly ceramic bonding takes place at temperatures above 800°C.

Furthermore, they are also classified according to their form. Molded products include all shapes of brick and fusion-cast products. Nonmolded products include mixtures for monolithic constructions (pressing compounds, plastic compounds) in which the ceramic bonding occurs during the use of the material.

Refractory products are also characterized on the basis of their temperature treatment:

- unfired
- heated treated
- fired or melted

and their form:

- molded
- nonmolded

Table 5.5-7. Classification of Refractory Products.

category	main ingredient		Other major
	% by weight	formula	ingredient
silica products	> 93	SiO_2	–
fireclay products:			
• acidic	67 to 76	SiO_2	Al_2O_3
• half acidic	22 to 30	Al_2O_3	SiO_2
• basic	30 to 45	Al_2O_3	SiO_2
alumina-containing products:			
• alumina-enriched products	50 to 55	Al_2O_3	SiO_2
• cyanite bricks	55 to 65	Al_2O_3	SiO_2
• sillimanite bricks	60 to 70	Al_2O_3	SiO_2
• mullite bricks	72 to 75	Al_2O_3	SiO_2
• bauxite bricks	75 to 85	Al_2O_3	SiO_2
• corundum bricks	60 to 99.5	Al_2O_3	SiO_2
neutral bricks:			
• zirconium silicate bricks	< 67	ZrO_2	SiO_2
• forsterite bricks	< 550	MgO	SiO_2, FeO
• chromium ore bricks	30 to 45	Cr_2O_3	MgO, FeO, Al_2O_3
basic products:			
• magnesia bricks	> 80	MgO	–
• magnesia/chromite bricks	10 to 40	chrome ore	MgO
• chromite/magnesia bricks	40 to 80	chrome ore	MgO

5.5.5.3.2 Alumina-Rich Products

Raw materials for alumina-rich refractory products:

- aluminum silicates
- bauxite
- bauxite + kaolin
- corundum

In contrast with pure aluminum oxide ceramics, the raw materials used in the manufacture of alumina-rich refractory products are, for economic reasons, natural products. The choice of aluminum silicates: cyanite, andalusite or sillimanite (chemical composition: $Al_2O_3{\cdot}SiO_2$) or low iron bauxite with an Al_2O_3-content > 85% and a SiO_2-content < 10%, depends upon the aluminum oxide content required. Natural mixtures of alumina hydrates (bauxite) and kaolin with Al_2O_3-contents of 48 to 70% are fired to so-called mullite chamottes. To obtain still higher Al_2O_3-contents, industrially produced corundum has to be added.

In presintering above 1500°C the starting materials change as follows:

$$\text{bauxite + kaolin} \longrightarrow \text{mullite chamotte}$$

$$\text{aluminum silicate} \longrightarrow \underbrace{\text{mullite + cristobalite}}$$

$$\text{calc. alumina + kaolin} \longrightarrow \text{sintered mullite}$$

$$\text{bauxite} \longrightarrow \underbrace{\text{mullite+corundum+glass}}_{\text{sintered bauxite}}$$

Manufactured by:

- addition of binders
- molding
- firing at 1200 to 1800°C

The manufacture of refractory bricks is carried out by hand ramming or mechanical pressing of mixtures of granular raw materials and binders (sulfite waste liquor, ball clay) and then firing at temperatures between ca. 1200 and 1800°C.

Applications:

- steel industry
- cement industry
- glass industry

Alumina-containing refractory linings are widely utilized in the steel industry. Bricks with high alumina contents are, due to their resistance to alkali slags, also used in the cement and glass industries.

5.5.5.3.3 Fireclay Products

According to their chemical composition, fireclay products belong to the clay ceramic materials. However, their preferred utilization for refractory furnace linings makes it more reasonable to discuss them with the other refractory products.

Fireclay products are cheap refractory construction materials

Although the range of refractory products is continuously expanding, fireclay products are still the most important quantitywise. This is due to their possessing in a single product: a relatively high melting point, chemical resistance and the low thermal expansion coefficient with the plastic properties of the paste so important for molding.

Fireclay produced by firing clay minerals

In fireclay products, mullite and SiO_2 are bonded together by a glass phase

The clay minerals manufactured as described in Section 5.5.4.2 are used as raw materials in the manufacture of fireclay products. Direct firing of the molded article is disadvantageous due to the large shrinkage during firing. The so-called "chamotte" is therefore first produced in a precalcining process. This is then crushed, classified and mixed with plastic ball clay. The molding can be carried out by any of the above-mentioned processes for clay ceramic products. The main firing at 1250 to 1500°C results in fire bricks with 25 to 30% mullite, 25 to 60% glassy phase and up to 30% of cristobalite and quartz.

Applications:

- blast furnace linings
- casting ladle linings
- tank furnace linings

The bricks are used in blast furnaces, for the lining of casting ladles and the refractory linings of tank furnaces for the glass industry.

5.5.5.3.4 Silicate Products

Refractory silica products are manufactured from quartzites

The raw materials for the manufacture of silica-rich refractory construction materials are quartzites from different sources with different compositions fulfilling the following specification:

$$SiO_2 > 95\%,\ Al_2O_3 + TiO_2 < 2.5\%$$
$$Fe_2O_3 < 1.5\%,\ Na_2O + K_2O < 0.1\%$$

Phase transition of quartz makes firing of silicate products more difficult

In the manufacture of silicate bricks, quartzites are crushed, ground, classified and mixed according to their grading curves. 1.5 to 2% lime is added to improve their sintering behavior. The firing of silicate bricks must be carried out very carefully to ensure the conversion of quartz into its high temperature modification. The required highest possible conversion of quartz into cristobalite and tridymite requires firing times of up to 14 days at 1450°C.

Applications:

- tank furnaces for glass manufacture
- coking ovens

Silicate bricks have almost completely lost their former importance in the steel manufacturing sector and are mainly utilized in tank furnaces for glass manufacture and in coking ovens.

5.5.5.3.5 Basic Products

Basic products contain varying quantities of magnesium oxide. Naturally occurring magnesite ($MgCO_3$) is used as the raw material and upon firing is converted into sintered magnesia:

$$MgCO_3 \xrightarrow{800\text{ bis }900\text{ °C}} MgO\text{ (caustic)} + CO_2$$

$$\downarrow \xrightarrow[1900\text{ °C}]{1600\text{ bis}} \underset{\text{(sintered magnesia)}}{MgO}$$

"Seawater magnesia" produced by precipitation of magnesium hydroxide from seawater

The known magnesite deposits are no longer sufficient to supply completely the increasing demand for magnesium oxide. This has led to the increasing utilization of so-called seawater magnesia. The oceans contain, on average, 5% of dissolved magnesium salts ($MgSO_4$, $MgCl_2$), which by metathesis with lime or calcined dolomite (CaO, MgO) can be converted into insoluble magnesium hydroxide. The hydroxide is separated, washed, dried and subsequently fired, as is magnesite, to caustic magnesia or sintered magnesia.

Manufacture of magnesia bricks:

- dry compression process
- sintered at 1550 to 1800°C

Magnesia bricks are generally formed with added sulfite waste liquor and magnesium sulfate using the dry pressing process and are sintered in box or tunnel kilns at 1550 to 1800°C under a slightly reducing atmosphere. Low iron magnesia bricks are high grade refractory products. They are mainly used to line steel-producing furnaces and in the crowns and covers of tank furnaces for the glass industry.

Magnesium oxide seldom used in pure form. Addition of chromium ore improves its properties. Applications:

- open hearth furnaces
- rotary kilns for the cement industry
- furnaces for the nonferrous metals industry

The thermal shock resistance of magnesia bricks can be improved by adding chrome ore. Sintering at 1750°C leads to so-called direct bonding upon formation of the spinels $MgO{\cdot}Cr_2O_3$ and $MgO{\cdot}Fe_2O_3$. Such bricks are utilized in open hearth furnaces, in the rotary kilns of the cement industry and in the furnaces of the nonferrous metals industry.

Other industrially important basic products are forsterite and dolomite bricks. Forsterite bricks are manufactured by firing naturally occurring low iron olivine, a mixed crystal of $2MgO{\cdot}SiO_2$ (forsterite) and $2FeO{\cdot}SiO_2$ (fayalite).

Dolomite bricks are a cheap refractory construction material with limited application possibilities

The starting material for refractory dolomite bricks is calcined dolomite, which is produced from dolomite by deacidification at temperatures of ca. 1000°C and then firing at 1500 to 1800°C. They are very much cheaper than magnesite products, but are also less slag-resistant. To prevent hydration, dolomite bricks have to be impregnated with tar.

5.5.5.3.6 Specialty Refractory Products

The industrially most important refractory products are supplemented by specialty products for particular applications. The most important of these is zirconia bricks. They are produced from natural zircon ($ZrSiO_4$) with optional addition of quartz or alumina using standard ceramic techniques. They are used in tank furnaces in the glass industry, aluminum melting furnaces and high temperature furnaces.

Zirconia bricks are the most important specialty refractory products

Chromium oxide-corundum bricks (mixed crystals of Al_2O_3 with 5 to 10% Cr_2O_3) exhibit very good resistance to alkaline slags. They are utilized in parts of blast furnaces (Fig. 5.5-4) and demand for them is expected to increase in the future.

Importance of chromium oxide-corundum bricks is steadily increasing

Pure chromium oxide bricks with 95% Cr_2O_3 are manufactured from synthetic Cr_2O_3 and are utilized in the refractory linings of tank furnaces for the production of E-glass fibers.

Pure chromium(III) oxide bricks are, due to their high price, only utilized for special applications

5.5.5.3.7 Economic Importance

Refractory products are of considerable economic importance. Estimated worldwide production for the period 1995 to 2000 is ca. $8 \cdot 10^6$ t/a. In 1995 $1.4 \cdot 10^6$ t/a was produced in the Federal Republic of Germany, $3.3 \cdot 10^6$ t/a in the USA and $0.8 \cdot 10^6$ t/a in Japan. Table 5.5-8 gives the consumption spectra of refractory construction materials in the USA, Japan and the Federal Republic of Germany:

Refractories industry is very important producing ca. $8 \cdot 10^6$ t/a worldwide, which has stabilized at this high level

Table 5.5-8. Consumption Spectra for Refractory Construction Materials in %.

Industry sector	USA	Japan	FR Germany
iron and steel	51.5	70.8	58.6
nonferrous metals	6.8	2.0	2.8
glass	5.5	1.7	5.3
cement and lime	4.0	4.4	4.7
chemical	3.0	0.8	1.5
energy	2.0	0.5	1.8
ceramic	8.2	3.7	6.8
various	19.0	16.1	18.5

The iron and steel industry is by far the most important consumer of refractory products. The use of refractory con-

The development of the steel industry determines the consumption of refractory products struction materials in the steel industry therefore largely determines the quality standards, the raw material requirements, the qualities produced and the technology of the refractories industry.

Market for nonmolded refractory products increasing

In recent years there has been a significant decline in demand for formed products and an increase in nonformed products capable of manufacture with low energy input. In addition the proportion of high quality products has increased considerably at the expense of silicate bricks and fire bricks.

The recent fundamental changes in the field of refractory linings in the steel industry, which are not yet at an end, are illustrated in Fig. 5.5-4 in which classic and modern blast furnaces are compared with one another.

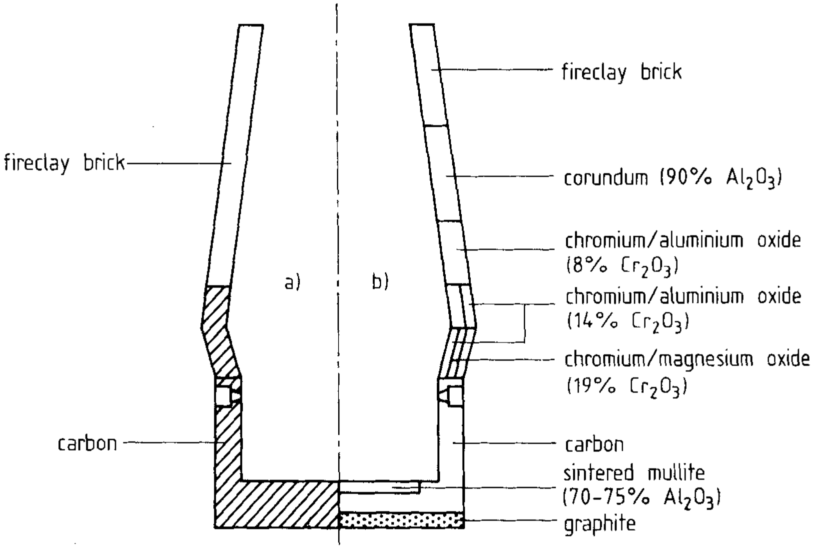


Fig. 5.5-4. Comparison of Classic and Modern Blast Furnace Lining.
a) classic blast furnace lining common in the early 1960's; b) example of a modern blast furnace lining for a furnace with a 14 m crucible diameter.

5.5.5.4 Nonoxide Ceramics

SiC, Si_3N_4, B_4C and BN are the most important nonoxide ceramics

Included in the term "nonoxide ceramics" are all non-electrically conducting materials in the boron-carbon-silicon-aluminum system. The industrially most important representatives, apart from carbon (see Section 5.7.4), are silicon carbide (SiC), silicon nitride (Si_3N_4), boron carbide (B_4C), boron nitride (BN) and aluminum nitride (AlN).

In contrast with the oxide ceramics, the nonoxide ceramics are not thermodynamically stable in oxidizing environments, although their stability in other chemical media is excellent. Materials of silicon-containing compounds can nevertheless be used under oxidizing conditions up to ca. 1600°C, because a passivation layer of SiO_2 is formed at the surface which strongly hinders further oxidation.

Nonoxide ceramics are very stable at high temperatures to all chemical media except oxygen

Nonoxide ceramics are utilized in applications requiring mechanical properties (high strength and hardness) and thermal shock resistance, particularly above 1000°C, superior to those of oxide ceramics and metals.

Utilized in applications requiring good mechanical properties at high temperatures

5.5.5.4.1 Economic Importance

Silicon carbide is the only nonoxide ceramic product of major industrial importance, apart from carbon. The worldwide production of unworked SiC was $450 \cdot 10^3$ t/a in 1995, corresponding to 90% capacity utilization. The USA and Canada accounted for $85 \cdot 10^3$ t/a of this, Western Europe for $195 \cdot 10^3$ t/a, Japan and China for $110 \cdot 10^3$ t/a and other regions for $90 \cdot 10^3$ t/a. The previously predicted strong growth in worldwide production has not materialized. The largest European production plants are in Norway and the Netherlands.

Silicon carbide is an industrially important product with a current worldwide production of $450 \cdot 10^3$ t/a

Ca. 25% of the worldwide SiC-production for metallurgical purposes is utilized for metallurgical purposes, 25% is processed to grinding and polishing agents and 50% for other applications, mainly ceramics.

5.5.5.4.2 Manufacturing Processes for Silicon Carbide

Silicon carbide is manufactured industrially by the electrochemical reaction of high purity quartz sand with carbon in an electric resistance furnace (Acheson process):

Industrial manufacture of SiC is carried out using the Acheson process by reacting SiO_2 with carbon in an electric furnace

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

Preferred carbons are petroleum coke (pitch coke) and anthracite. Addition of sodium chloride ensures the removal of troublesome impurities as volatile chlorides. The presence of sawdust increases the porosity of the reaction mixture and eases outgassing.

Acheson process requires temperatures above 2000°C

The electric furnaces, in which this reaction is carried out, are ca. 15 · 3 · 3 m^3 in size and are lined with refractory material. Electrodes at opposite ends are connected to a graphite core. The furnace is filled round this core with the reaction mixture and electrically heated to 2200 to 2400°C. The heating up time is ca. 18 h and the reaction time a further ca. 18 h. After cooling, the sides of the furnaces are removed and the unreacted material on the edges removed. The silicon carbide, which has formed round the graphite core, is broken up and separated into different qualities.

The different qualities of SiC can be distinguished by their color

SiC-manufacture is energy intensive (6 to 12 kWh/kg SiC)

The purest SiC is bright green (99.8% SiC), the color changing with decreasing SiC-content from dark green (99.5% SiC) to black (99% SiC) to gray (90% SiC). 70 t of raw mixture yields 8 to 14 t of high grade SiC and 6 to 12 kWh of energy are required to produce 1 kg of raw silicon carbide.

The raw silicon carbide is processed by crushing in jaw crushers or hammer mills and subsequent fine grinding in ball mills. Very pure SiC qualities are obtained by chemical treatment with sulfuric acid, sodium hydroxide or hydrofluoric acid.

Silicon carbide occurs in a large number of different crystal structures

Silicon carbide is remarkable for its unusually large variety of different morphologies, which differ in their stacking sequences of hexagonal and rhombohedral layers. All hexagonal and rhombohedral forms are often simply described as α-SiC. The commercially available SiC produced by the Acheson process is α-SiC.

The Acheson process produces α-SiC

Cubic β-SiC is produced by gas phase processes (CVD process)

The manufacture of cubic β-SiC, which is favored at temperatures below 2000°C, or mixtures of α- and β-SiC is carried out by deposition from the gas phase (Chemical **V**apor **D**eposition). β-SiC powder with good sintering properties and small crystallite size is e.g. obtained by the thermal decomposition of alkyl silanes or alkyl dichlorosilanes in plasmas or flow reactors at temperatures above 1000°C:

$$CH_3SiCl_3 \longrightarrow SiC + 3HCl$$

Gas phase process produces high quality, but expensive, products

In another process metallic silicon is evaporated in an electrical arc and reacts with methane to silicon carbide. A disadvantage of all gas phase processes is their high cost compared with the Acheson process.

5.5.5.4.3 Refractory Silicon Carbide Products

Properties of SiC ceramics:

- high thermal conductivity
- high hardness
- mechanical strength

Despite its comparatively high price, silicon carbide is a significant refractory product due to its exceptional properties, such as its high thermal conductivity, high hardness and mechanical strength. It is used in zinc distillation kilns and in the manufacture of muffles, capsules and kiln furniture for the clay ceramic industry (see Section 5.5.4.7.2). In recent years silicon carbide has also been used in the refractory linings of blast furnaces and utilization in other sectors of the steel producing industry is in evaluation.

Coarse SiC products are bonded with clay minerals or silicon nitride

A temperature resistant binder is necessary to bond SiC-bricks (carborundum bricks). Clays or other silicates are usually used, the particles being bonded by a glass phase. The bricks must be fired at ca. 1500°C in an oxidizing atmosphere to reduce the reduction of bonding clay to silicon and thereby prevent the bricks becoming brittle. The resulting oxidation of silicon carbide is limited by the formation of a passivation layer of SiO_2 on the SiC particles.

Clay-bonded bricks have a SiC-content of 40 to 90%. Bricks without a glassy binder are obtained by bonding with silicon nitride. Since these SiC-rich bricks exhibit thermal shock resistance, Si_3N_4-bonding is of increasing importance.

5.5.5.4.4 Fine Ceramic Silicon Carbide Products

Development of fine ceramic SiC-products open up new application possibilities:

- high temperature heat exchangers
- sealing and slip rings
- pump components

The utilization of silicon carbide ceramics for high temperature resistant components in mechanical engineering and apparatus construction (e.g. in high temperature heat exchangers) is steadily increasing. Since silicon carbide ceramic components can be operated at temperatures up to 1400°C without cooling and are ca. 60% lighter than high temperature alloys, ever more applications are being explored.

Dense SiC ceramics are manufactured by hot pressing:

350 bar at 1900 to 2000°C

Only highly dense ceramics with high thermal shock resistance can be utilized for such strongly mechanically and thermally stressed components. These demands are met by hot-pressed silicon carbide produced at pressures of 350 bar and sintering temperatures of 1900 to 2000°C. The necessary, but very expensive, mechanical finishing is disadvantageous for industrial manufacture of hot-pressed silicon carbide.

Pressureless sintering of SiC is only possible with extremely fine powders

It is technically easier to manufacture a molded component from SiC-powder by slip casting or dry pressing, working it mechanically and then sintering pressureless at 1950 to 2000°C. Due to the low sintering activity of silicon carbides, such processes have only been recently successfully carried out with the advent of fine particulate SiC-powders (specific surface area > 5 m^2/g) with low oxygen-contents ($< 0.2\%$). Boron or aluminum and free carbon or boron carbide are added as sintering aids.

Reaction sintering by reacting liquid silicon sucked into pores with graphite

Reaction sintered SiC contains excess silicon

So-called "reaction sintered" silicon carbide is manufactured by a new process. The forming of a mixture of SiC-powder, graphite and a plastification agent is carried out by conventional techniques. Then the plastification agent is burnt off by presintering leaving a still porous component into which liquid silicon is sucked. This reacts with the graphite powder forming SiC. An excess of silicon (typically 2 to 12%) fills the remaining pores. The maximum utilization temperature of reaction sintered SiC depends upon the silicon content but is limited to a maximum of 1300°C.

5.5.5.4.5 Fine Silicon Nitride Ceramic Products

Silicon nitride (SN) ceramics possess similar properties to silicon carbide ceramics and can be utilized in the same application sectors.

$$3Si + 2N_2 \longrightarrow Si_3N_4$$

Four processes are possible for the manufacture of Si_3N_4-powders:

1. Direct nitriding of silicon at 1200 to 1400°C;
2. Reaction of SiO_2-C-mixtures at temperatures of up to 1500°C in a nitrogen atmosphere;
3a. Reaction of $SiCl_4$ with ammonia in the liquid phase (e.g. in an organic solvent);
3b. Reaction of $SiCl_4$ with ammonia at temperatures up to 1500°C.

2) $3\ SiO_2 + 6C + 2N_2 \longrightarrow Si_3N_4 + 6CO$

3a) $3\ SiCl_4 + 16NH_3 \longrightarrow Si_3N_4 + 12NH_4Cl$

3b) $3\ SiCl_4 + 4NH_3 \longrightarrow Si_3N_4 + 12HCl$

All these processes produce mixtures of α- and β-Si_3N_4 in varying proportions.

Of these processes direct nitriding and the reaction of $SiCl_4$ with NH_3 are currently industrially operated.

A very pure reaction product is obtained by the reaction of $SiCl_4$ with NH_3, which initially consists of air- and moisture-sensitive silicon diimide. High purity SN-powder with a particle size < 1 μm, which exhibits high sintering activity, is obtained by crystallization after dechlorination. Upon subsequent surface oxidation of the individual particles, an oxygen-content of less than 2%, an isoelectric point of 2 can be attained and the processing range in aqueous media can be extended to pH's greater than 3.

During the reaction of $SiCl_4$ with NH_3 in solvents, 5 t of ammonium chloride is produced per t of silicon nitride. This can be reduced to less than 1 t in the high temperature reaction.

Current high grade SN-powders have impurity levels of less than 100 ppm and contain adjustable oxygen contents, preferably mainly on the surface. The specific surface area is ca. $12m^2/g$, which corresponds to a primary particle size of less than 1 μm.

Compression and sintering of powder to finished ceramic can be carried out by hot pressing at 140 bar and 1650 to 1750°C. Addition of MgO, Y_2O_3, Al_2O_3, ZrO_2 or $SiBeN_2$ brings about an improvement in densification during sintering. Production of SN-ceramics with 99% of the theoretical density has in recent years been attained by pure sintering processes with dry pressed powders.

Ceramic components of Si_3N_4 are manufactured by:

- hot pressing
- pressureless sintering
- reaction sintering

Additive and sinter regime selection enables needle-formed structures with different properties to be made to order

The manufacture of reaction-bonded Si_3N_4 begins with a preform of silicon. This preform is nitrided in an atmosphere of pure nitrogen or of nitrogen/hydrogen. The reaction proceeds without volume change, but the products have a minimum porosity of 10%. 98% of the theoretical density can be achieved by postsintering.

Incorporation of Al_2O_3 or BeO in Si_3N_4 produces new ceramic materials such as SiAlON and SiBeON

Incorporation of metal oxides in the α- and β-Si_3N_4 lattice produces new ceramic materials. The development of this class of materials began with the incorporation of Al_2O_3 (SiAlON), but oxides such as MgO, BeO (SiBeON), Y_2O_3, ZrO_2 etc. can also be incorporated.

The practical utilization of silicon carbide and silicon nitride ceramics or of SiAlON in the above-mentioned application sectors has steadily increased in recent years. Ca. 400 t/a of SN-powder is currently consumed in the manufacture of SN-components. The main applications are for cutting tools, roller bearings, dosing and deliver pipes for aluminum processing, as well as a multiplicity of other components which enjoy the advantages of SN-ceramics.

The strengths of SN-ceramics are their low weight, their high abrasiveness and their temperature, chemical and corrosion resistance. New technical solutions for systems are thereby possible, which are not achievable with traditional materials.

5.5.5.4.6 Manufacture and Properties of Boron Carbide

Coarse particulate boron carbide is produced by reacting boron/oxygen compounds with carbon. Its worldwide production in 1995 was 600 t/a

In the industrial manufacture of boron carbides, boron(III) oxide(1) or boric acid (2) are reacted with carbon in resistively heated furnaces at 2400°C (as in SiC-manufacture):

$$(1)\quad 2B_2O_3 + 7C \longrightarrow B_4C + 6CO$$

$$(2)\quad 4H_3BO_3 + 7C \longrightarrow B_4C + 6CO + 6H_2O$$

The tetraboron carbide produced by these processes consists of coarse hard particles suitable for grinding applications (ca. 360 t/a) or as starting materials for the manufacture of metallic borides (see Section 5.6.8).

Fine particulate tetraboron carbide is produced by the reduction of boron(III) oxide with magnesium or aluminum in the presence of carbon:

$$2B_2O_3 + 6\,Mg\,(4Al) + C \longrightarrow B_4C + 6MgO$$

Finely divided boron carbide can be processed to ceramics. Applications:

- armored plate
- protective material in nuclear reactors

Fine particulate powder with particle sizes below 5 µm can be compressed by hot pressing at 2100 to 2200°C to dense ceramic products. These are used in the manufacture of armored plating or in nuclear reactors as a protective material against neutrons (high neutron capture cross-section of boron).

The main markets are in the highly industrialized countries: North America (40%), Europe (30%) and Japan (30%).

5.5.5.4.7 Manufacture and Properties of Boron Nitride

Boron nitride (BN) exists in a hexagonal modification with a graphite-like crystal structure and a cubic high temperature/high pressure modification with a diamond-like structure.

Boron(III) nitride crystallizes in a hexagonal and a cubic modification

The most widely used industrial process for the manufacture of hexagonal boron(III) nitride is the reaction of boron(III) oxide with ammonia at 800 to 1200°C in a calcium phosphate matrix:

Hexagonal boron(III) nitride is produced by reacting boron(III) oxide with ammonia (1) or nitrogen and carbon (2)

$$(1)\quad B_2O_3 + 2NH_3 \longrightarrow 2BN + 3H_2O$$

After the reaction the matrix is dissolved in cold hydrochloric acid and unreacted boron(III) oxide washed out with hot alcohol. A raw product with 80 to 90% purity is thereby obtained. Postreaction in nitrogen at 1800°C or in ammonia at above 1200°C increases the BN-content still further.

A very pure crystalline boron(III) nitride is obtained by reacting boron(III) oxide with carbon and nitrogen at 1800 to 1900°C:

$$(2)\quad B_2O_3 + 3C + N_2 \longrightarrow 2BN + 3CO$$

Hexagonal boron(III) nitride is not yet used in large quantities. Interest in this material is increasing, due to its wide application possibilities.

BN-powder is, due to its graphite-like properties, predestined for utilization as a high temperature lubricant or as a mold lubricant in metal casting. Formed articles of boron(III) nitride are used as melting crucibles for high purity metals or semiconductor alloys and as refractory linings for plasma burners, rocket jets and combustion chambers. 200 t/a of hexagonal BN were produced in 1995.

Hexagonal boron nitride has graphite-like properties.

Applications:

- high temperature lubricant
- mold lubricant
- melting crucible for metals
- refractory lining for combustion chambers

Cubic boron nitride (barazon) is manufactured from hexagonal-BN in a high temperature/high pressure synthesis.

Application:

- diamond substitute in the grinding agent sector

Cubic boron(III) nitride is manufactured from hexagonal BN in a high pressure synthesis at 50 to 90 kbar and 1500 to 2200°C in the presence of alkali or alkaline earth metals as catalysts. Cubic boron(III) nitride is, after diamond, the hardest known material. It is utilized in the grinding agent sector instead of diamond, due to its better chemical resistance at high temperatures.

The market for cubic boron(III) nitride was ca. 200 t in 1995.

5.5.5.4.8 Manufacture and Properties of Aluminum Nitride

Aluminum nitride (AlN) is manufactured by direct nitriding or reductive nitriding of a homogeneous mixture of aluminum oxide or aluminum hydroxide and finely divided carbon, or a compound which releases carbon upon thermal cracking under a nitrogen atmosphere.

$$2\,Al + N_2 \longrightarrow 2\,AlN$$
$$Al_2O_3 + 3C + N_2 \longrightarrow 2\,AlN + 3CO$$

Other processes via the gas phase have not yet got beyond the development phase.

The aluminum nitride produced by these processes has to be further processed by grinding under moisture-free conditions, without introducing impurities.

Further advantage: similar thermal expansion coefficient to silicon

The main application sector for aluminum nitride is as substrates for the electronic industry, where aluminum nitride is replacing aluminum oxide to an increasing extent in highly integrated systems due to its significantly higher thermal conductivity. Other application fields are evaporation boats, metallization supports and in aluminum processing technology.

150 t/a were produced worldwide in 1995 by 7 companies. Demand is only growing slowly. Only a small part of its worldwide manufacturing capacity is utilized.

References for Chapter 5.5: Ceramics

Ceramics, General Information:

Kingery, W. D., Bowen, H. K. and Uhlmann, D. R., *Introduction to Ceramics*. 2nd Ed., John Wiley & Sons, Inc., New York 1976.

Salmang, H. und Scholze, H. *Die physikalischen und chemischen Grundlagen der Keramik*. 5. Ed. Springer-Verlag, Berlin-Heidelberg-New York, 1986.

Kienow, S., *"Keramik"*, in Winnacker, K. und Küchler, L. (Eds.), Chemische Technologie. 4. Ed., Vol. 3, 159-214, Carl Hanser Verlag, München, 1983.

Phelps, G. and Wachtmann, I., *Ceramic, General Survey*, Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 6, 1 – 42, VCH Verlagsgesellschaft, Weinheim.

Cannon, R., *Ceramics, Standard Products*, Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 6, 43 – 53, VCH Verlagsgesellschaft, Weinheim.

Greenhut, V. and Haber, R., *Ceramics*, Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 6, 55 – 78, VCH Verlagsgesellschaft, Weinheim.

Blühm, J., *Ceramics, Electronic*. Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 6, 79 – 92, VCH Verlagsgesellschaft, Weinheim.

Ceramics, Classification:

Hennicke, H. W., Ber. Dt. Keram. Ges., **44**, 209-211 (1967).

Ceramics, Raw Materials and Preparation:

Lochmann, R., *"Ceramics (Overview)"* in Kirk-Othmer, Encyclopedia of Chemical Technology. 1983. 4. Ed., Vol. 5, 594-602, John Wiley & Sons, New York.

Trawinski, H., *"Die Aufbereitung von Kaolin"* in Handbuch der Keramik. Gruppe I B 1, Verlag Schmid GmbH, Freiburg 1967 und 1973.

Tawinski, H., Ber. Dt. Keram. Ges. Bd. **53**, 117 – 121, (1976).

Ceramics, Forming:

Ceramics Fabrication Processes, in Treatise Mater. Sci. Technol. **9** (1976).

Mostetzky, H., *"Formgebung in der Keramik"*, in Handbuch der Keramik, Gruppe I D 1, Verlag Schmid GmbH, Freiburg, 1978.

Ewsuk, K. G., *"Ceramics (Processing)"*, in Kirk-Othmer, Encyclopedia of Chemical Technology. 1983. 4. Ed., Vol. 5, 603-633, John Wiley & Sons, New York.

Kienow, S. and Hennicke, H. W., Ber. Dt. Keram. Ges., **57**, 267 – 272 (1980).

Seilsdorfer, H. and Moser, G., Metall **34**, 925 – 929 (1980).

Ceramics, Firing of Ceramics:

Hare, Th. M., *"Ceramics (Thermal Treatment)"*, in Kirk-Othmer, Encyclopedia of Chemical Technology. 1979. 3. Ed., Vol. 5, 260 – 266, John Wiley & Sons, New York.

Gardeik, H. O. und Scholz, R., *"Brennen in der Keramik"*, in Handbuch der Keramik, Gruppe I E 3, Verlag Schmid GmbH, Freiburg, 1978.

Johnson, D. L., Mater. Sci. Res. **11**, 137 – 149 (1973).

Clay Ceramic Products:

Schüller, K. H., *"Porzellan"*, Ullmanns Encyklopädie der technischen Chemie. 1980. 4. Ed., Vol. 19, 391 – 410, Verlag Chemie, Weinheim-Deerfield Beach (Florida)-Basel.

Schüller, K. H., *"Porzellan"*, in Handbuch der Keramik, Gruppe II A, Verlag Schmid GmbH, Freiburg, 1978.

Hufnagel, O. und Stern, H., *"Steingut und Fayence"*, in Handbuch der Keramik, Gruppe II B, Verlag Schmid GmbH, Freiburg, 1978.

Fischer, P., *"Kanalisations-Steinzeug"*, Handbuch der Keramik, Gruppe II D 1, Verlag Schmid GmbH, Freiburg, 1972.

Vogel, H., *"Chemische-technisches Steinzeug"*, Handbuch der Keramik, Gruppe II D 2, Verlag Schmid GmbH, Freiburg, 1977.

Hahn, Ch. und Rothemund, D., *"Dentalkeramik"*, Handbuch der Keramik, Gruppe II L, Verlag Schmid GmbH, Freiburg, 1977.

Mörtel, H., Ber. dt. keram. Ges. **55**, 59 – 61 (1978).

Commercial Information:

Statistisches Bundesamt: *Produktion im Produzierenden Gewerbe nach Waren und Warengruppen*. 3. Quartal 1980, Verlag Kohlhammer GmbH, Stuttgart, Mainz, 1981.

Specialty Ceramics:

Phelps, G. W., Wachtmann, J. B., *"Ceramic, General Survey"* in Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A6, 1-42, VCH Verlagsgesellschaft, Weinheim.

Unruh, H. G., *"Ferroelectrics"* in Ullmann's Encyclopedia of Industrial Chemistry. 1987. 5. Ed., Vol. A10, 309-321, VCH Verlagsgesellschaft, Weinheim.

Ervens, W., Wilmesmeier, H., *"Magnetic Materials"* in Ullmann's Encyclopedia of Industrial Chemistry. 1990. 5. Ed., Vol. A16, 1-51, VCH Verlagsgesellschaft, Weinheim.

Ainger, F. W., *"Ferroelectric Ceramic Oxides"*, in Cockayne, B and Jones, D. W., Modern Oxide Materials. Academic Press, London-New York, 1972.

Kampcyk, W. und Röß, Ferritkerne – Grundlagen, Dimensionerung, Anwendung in der Nachrichtentechnik. 1. Ed., Siemens A.G., Berlin-München, 1978.

Brockmann, F. G. *"Magnetic Ceramics - a Review"*, Amer. Ceram. Soc. Bull. **47**, 186 – 194 (1968).

van den Broek, C. A. M and Stuijts, A. L., *"Ferroxdure"*, Philips Technical Review **37**, Nr. 7 (1977/78).

Roberts, J. T. A., *"Ceramic Utilization in the Nuclear Industry"*, *Part I*, Powder Metall. Int. **11**, 24 – 29 (1979).

Roberts, J. T. A., *"Ceramic Utilization in the Nuclear Industry"*, *Part II*, Powder Metall. Int. **11**, 72 – 80 (1979).

Chester, J. H., Refractories, Production and Properties, The Iron and Steel Institute, London, 1973.
Granitzki, K.-E., Ambs, H., Krönert, W., Müller, E. und Schweinsberg, H., Feuerfeste Stoffe im Gießbetrieb, Gießerei Verlag GmbH, Düsseldorf, 1979.
Harders, F. und Kienow, S., Feuerfestkunde. Springer-Verlag, Berlin-Göttingen-Heidelberg, 1960.
Ambs, H., Bens, F., Breuer, G. und Schäfer, H., *"Feuerfeste Erzeugnisse"* in Ullmanns Encyklopädie der technischen Chemie. 1976. 4. Ed., Vol. 11, 549 – 565, Verlag Chemie, Weinheim-Deerfield Beach (Florida)-Basel.
Koltermann, M., Radex Rundschau Heft **4**, 1121 – 1127 (1979).
Granitzki, K.-E., Gießerei **67**, 122 – 127 (1980).

Nonoxide Ceramics:
Smoak, R. H., Korzekwa, T. M., Kunz, S. M. and Howell, E. D., *"Carbides (Silicon Carbide)"*, in Kirk-Othmer, Encyclopedia of Chemical Technology. 1978. 3. Ed., Vol. 4, 520 – 535, John Wiley & Sons, New York.
Gugel, E., *"Nichtoxidkeramik"*, in Handbuch der Keramik, Gruppe II K 2, Verlag Schmid GmbH, Freiburg, 1975 und 1977.
Gugel, E., *"Net-Shape Processing of Nonoxide Ceramics"*, Annawerk Keramische Betriebe GmbH, Mitteilung Nr. 311, Rödental.
Nitzsche, H.-G. und Fickel, A., *"Über Technologie und Eigenschaften von CERANOX-Werkstoffe"*, Annawerk Keramische Betriebe GmbH, Mitteilung Nr. 163, Rödental.
Bunk, W. und Böhmer, M. (Hrsg.), *Keramische Komponenten für Fahrzeug-Gasturbinen.* Statusseminar im Auftrag des BMFT, Springer-Verlag, Berlin-Heidelberg-New York, 1978.
Nathan, K. R., Science **208**, 841 – 847 (1980).
Dickson, T., Industrial Minerals, Dec. 1980, 65 – 71.
Fitzer, E. and Hegen, D., Angew. Chem. **91**, 316 – 325 (1979).

5.6 Metallic Hard Materials

5.6.1 General Information

Hard materials are divided into metallic and nonmetallic hard materials

The industrially important hard materials can be divided into two groups, metallic and nonmetallic:

- metallic hard materials include the carbides, borides and silicides of the elements in subgroups IV to VI of the periodic table together with thorium and uranium carbide;
- nonmetallic hard materials include diamond (see Section 5.7.2), corundum and other hard minerals together with

silicon carbide (see Sections 5.5.5.4.2 to 5.5.5.4.4) and boron carbide (see Section 5.5.5.4.6).

The hardness of metallic hard materials is almost without exception between those of corundum and diamond

As the metallic hard materials, particularly the carbides, alloy easily with iron group metals, they are important in the production of cemented carbides (see Section 5.6.5.4). Apart from their great hardness, which is in the range 9 to 10 on the Mohs scale, they exhibit comparable electrical and thermal conductivities to metals, very high melting points and high chemical resistance.

The metallic carbides and nitrides are for the most part interstitial compounds and form mixed crystals with one another

In crystal structure the metallic carbides and nitrides are almost all interstitial compounds in which the carbon or nitrogen atoms are found in the octahedral interstices of the metal lattice. The borides and silicides as well as a few carbides (e.g. Cr_3C_2) possess more complex structures.

Only tungsten and titanium carbide are produced in large quantities

The most important metallic hard materials, as regards quantity, are tungsten carbide, WC, and titanium carbide, TiC with a production worldwide in 1995 of $20 \cdot 10^3$ t/a and $3.5 \cdot 10^3$ t/a respectively. Also worthy of mention is the $1.5 \cdot 10^3$ t/a of titanium carbonitride, Ti(C,N), produced in 1995, which is used as the hardening component in the cermet sector. Other metallic hard materials are produced in quantities below that of titanium carbide. In individual cases they can be very important as components of alloys in the realization of particular material properties.

5.6.2 General Manufacturing Processes and Properties of Metal Carbides

Carbides generally manufactured by reacting metals or metal oxides with carbon (lamp black) at high temperatures (1200 to 2300°C). The processes utilized are:

- carburization in the solid phase
- carburization in metal melts (menstruum process)

Carbides are produced by reacting elemental carbon, or gases which yield carbon, with metals or metal compounds at sufficiently high temperatures (1200 to 2300°C). This carburization is preferably carried out in a protective gas atmosphere or in a vacuum. The commonly used processes are:

- carburization of loose or compressed powders of metal or metal oxide (occasionally metal hydrides) with reactive carbon in a protective gas atmosphere;
- manufacture in carbon-containing metal baths, preferably in molten iron alloys, molten nickel or molten aluminum with subsequent separation from the regulus (mentstruum process);

- carburization with gases
- gas phase deposition (Chemical Vapor Deposition)

- carburization of metals or metal oxides with carbon-yielding gases (e.g. methane);
- deposition from gas phase reactions of metal halide-hydrogen-carbon mixtures (CVD process).

By far the most important process is carburization in the solid phase

By far the most widely used manufacturing process for metal carbides is the first process. The finest possible metal or metal oxide powder and carbon are either dry mixed or ground together in a suitable organic liquid. Low ash and low alkali carbon blacks are used, since the purity of the starting materials strongly influences the purity of the carbide formed. Contamination of the products with nitrogen or oxygen compounds is avoided by carburizing under a protective gas atmosphere.

The following furnace types are utilized for carburization reactions:

The material to be mixed or ground is optionally compressed and, depending upon the required reaction temperature and reaction atmosphere, reacted in one of the following furnace types:

- gas-heated furnace
- continuous carbon-tube furnace
- high frequency induction furnace

- gas-heated, lined furnace into which the reaction mixture is placed in a graphite or fire brick crucible. The combustion gas also serves as the protective gas atmosphere;
- electrically-heated resistive furnaces, mainly so-called continuous carbon-tube furnaces in which the graphite tube serves as the electrical resistance and in which the reaction mixture is continuously transported in boats through the furnace. Hydrogen is used as the protective gas atmosphere;
- high frequency induction furnaces in which the graphite reaction crucible in sealed in containers under high vacuum is inductively heated with an induction coil coupled to a high frequency source. Temperatures up to 2800°C can be attained.

Technical carbide grades do not, in the main, have stoichiometric compositions and often contain free carbon

The proportions of raw materials in the batches are empirically adjusted to give carbon contents in the carbides as close as possible to the stoichiometric quantities, while keeping the quantity of free carbon as low as possible.

The most important properties of the metal carbides are summarized in Table 5.6-1.

Table 5.6-1. Properties of the Metal Carbides.

compound	theoretical carbon content in % by weight	actual carbon content in % by weight	density in g/cm^3	melting point[1] in °C	Vickers microhardness HV 0.05
TiC	20.05	19 to 19.5	4.93	2940 to 3070	3000
ZrC	11.64	11.4	6.46	3420	2700
HfC	6.30	6.3	12.30	3820 to 3930	2600
VC	19.08	18.5 to 18.9	5.36	2650 to 2684	2900
NbC	11.45	up to 11.3[2]	7.78	3613	2000
TaC	6.23	6.1 to 6.3	14.48	3825 to 3985	1800
Cr_3C_2	13.33	13 to 13.3	6.68	1810	1350
β-Mo_2C	5.89	up to 5.8	9.18	2485 to 2520	1500
WC	6.13	up to 6.1	15.7	2720 to 2775	1200 to 2500[3]
ThC	4.92		10.64	2652	850
ThC_2	9.37		8.65	2655	600
UC	4.80		13.50	2560	920
UC_2	9.16		11.86	2500	620

[1] melting range given when literature data inconsistent
[2] after two carburizations
[3] different crystal surfaces have different hardnesses (hardness anisotropy)

5.6.3 Carbides of the Subgroup of the IVth Group

5.6.3.1 Titanium Carbide

After tungsten carbide, titanium carbide, TiC, is the most important metallic hard material. It is manufactured from pure TiO_2 and carbon black in induction furnaces at 2000 to 2200°C:

$$TiO_2 + 3C \longrightarrow TiC + 2CO$$

Manufacture of TiC in induction furnace at 2000 to 2200°C:

$TiO_2 + 3C \longrightarrow TiC + 2CO$

TiC is also produced in small quantities from titanium scrap in nickel and iron baths using the menstruum process (see Section 5.6.2).

Titanium carbide has the highest hardness of all metal carbides (see Table 5.6-1), but is rarely used on its own in cemented carbide technology, since the high oxygen content of the titanium carbide makes the hard metal too brittle. It is thus mainly utilized in the manufacture of

Titanium carbide has the highest hardness of all metal monocarbides mixed crystals such as (Ti,W)C, (Ti,Ta,W)C and (Ti,Ta,Nb,W)C for hard metals.

Thin layers of TiC on cemented carbides increase the abrasion resistance (application as a cutting material)

One possibility of exploiting the hardness of pure TiC is by coating cemented carbides. Thin layers (5 to 8 μm) of TiC of Ti(C,N) can be deposited using the CVD process by thermal decomposition of titanium tetrachloride in a methane/hydrogen atmosphere.

5.6.3.2 Zirconium Carbide and Hafnium Carbide

Zirconium and hafnium carbide are only of minor importance

Zirconium carbide, ZrC, and hafnium carbide, HfC, can be manufactured in a similar way to titanium carbide. They are not very important in cemented carbide technology. The recent strong reduction in the price of HfC has enabled its application as a substitute for the dearer tantalum carbide.

5.6.4 Carbides of the Subgroup of the Vth Group

5.6.4.1 Vanadium Carbide

Vanadium carbide only used in small quantities as a particle growth inhibitor in WC-Co alloys

Vanadium carbide is manufactured by the carburization of pure vanadium pentoxide (mostly produced from ammonium vanadate) in vacuum at 1700°C. Vanadium carbide exhibits a high hardness, but its brittleness prevents its wide utilization in cemented carbides. In WC-Co alloys, it is added in quantities of < 1% by weight as a particle growth inhibitor.

5.6.4.2 Niobium Carbide and Tantalum Carbide

Niobium carbide, NbC, and tantalum carbide, TaC, are obtained by the reaction of their pentoxides with low ash carbon black at 1600 to 1800°C in a hydrogen atmosphere. A higher carbon content can be obtained by postcarburization at 1600°C.

Niobium-containing tantalum carbide manufactured with the menstruum process is industrially important

Cheap niobium-containing tantalum carbide can be obtained from tantalum scrap, tantalum slag or ferrotantalum in an iron melt using the menstruum process. The carbide is separated chemically from the melt cake by dissolving the iron in warm hydrochloric acid.

Pure TaC is the only carbide utilized in cemented carbides in which it acts in a similar way to VC as a particle growth inhibitor. NbC-TaC mixed crystals are preferred for economic reasons and will replace TiC in cutting materials of the WC-TiC-Co-type (see Section 5.6.5.4) and improve scaling resistance.

5.6.5 Carbides of the Subgroup of the VIth Group

5.6.5.1 Chromium Carbide

Cr_3C_2 is a common component of corrosion and scaling resistant cemented carbides with a nickel bonding phases

Chromium carbides are not interstitial compounds

The chromium-carbon phase diagram shows the existence of three carbide phases: $Cr_{23}C_6$, Cr_7C_3 and Cr_3C_2. Only Cr_3C_2 has industrial importance and it is manufactured by the carburization of chromium(III) oxide under a hydrogen atmosphere.

Chromium carbides are mainly utilized in cemented carbide alloys with a nickel bonding phase. These alloys are notable for their good corrosion and scaling resistance combined with abrasion resistance and are therefore utilized in high temperature applications.

5.6.5.2 Molybdenum Carbide

Application of Mo_2C in TiC-Mo_2C-Ni cutting materials

Of the different molybdenum-carbon phases only dimolybdenum carbide β-Mo_2C has any industrial importance. It is manufactured by reacting molybdenum(VI) oxide or metallic molybdenum with carbon black at 1350 to 1800°C in carbon tube short circuit furnaces under hydrogen atmospheres. Due to its low hardness the use of Mo_2C is virtually limited to TiC-Mo_2C-Ni cutting materials.

5.6.5.3 Tungsten Carbide

WC is industrially the most important metal carbide

Two tungsten-carbon compounds exist in the tungsten-carbon system: W_2C and WC as well as low melting point eutectica in the systems W/W_2C and W_2C/WC. Monotungsten carbide is by far the most important metal carbide in cemented carbide metallurgy (see Section 5.6.5.4).

Tungsten carbide is produced by the carburization of high purity metallic tungsten

WC is manufactured by first reducing tungstic acid, H_2WO_4, tungsten(VI) oxide, WO_3, or ammonium paratungstate, $5NH_3 \cdot 12WO_3 \cdot 5H_2O$ with hydrogen at 700 to 900°C to high purity (> 99.9% W) tungsten powder. Carburization is performed at 1500°C either in vacuum in induction furnaces or under hydrogen in electrical resistance furnaces. The total carbon content of the WC produced is between 6.05 to 6.20% by weight compared with the stoichiometric value of 6.13%, the over-stoichiometric carbon content being present in a free state.

Properties of WC influenced by:

- raw material particle size
- raw material reduction conditions

The powder properties of WC are influenced by the particle form and particle size of the raw material, the reduction conditions and the carburization conditions.

Ultrafine tungsten carbide is manufactured in a plasma at 3000°C:

$WO_3 + (CO \text{ or } CH_4) \longrightarrow WC$

There is increasing interest in the hard metal properties of ultrafine tungsten carbide particles < 100 nm in diameter (see Section 5.6.5.4), which are manufactured by reacting very finely divided tungsten(VI) oxide with CO or CH_4 at temperatures of ca. 3000°C in a plasma. However, these ultrafine carbide particles contain a relatively high concentration of oxygen, which limits their range of applications.

5.6.5.4 Cemented Carbides Based on Tungsten Carbide

Cemented carbides are sintered alloys with one or more hard material phases

Cemented carbides are sintered materials consisting of very hard and high melting point metal carbides in a matrix of low melting point bonding metals of the iron group, particularly cobalt.

Cobalt is the preferred binder for the hard material phase in which WC or other hard materials are embedded

The most important property of tungsten carbide in its utilization in cemented carbides is its ability to dissolve partially in compressed powder mixtures of WC and ferrous metals, particularly cobalt, at 1300 to 1500°C. In the case of sintering with a liquid phase, WC partly crystallizes out of the binder phase of the WC-Co-alloy upon cooling. It becomes embedded in the tough but hard (not brittle) binder phase.

Powder metallurgical processes similar to ceramic processes

Cemented carbides are manufactured by powder metallurgical processes, which in many respects are similar to ceramic processes. A mixture of the carbides with the metallic bonding phase is first subjected to wet grinding, producing a finely dispersed distribution of the components. Removal of the grinding liquid is followed by vacuum drying and, in the case of high grade products, reductive annealing at moderate temperatures to remove traces of oxygen. Subsequent forming is by dry pressing, extrusion molding or hot pressing. After presintering at 900 to 1150°C and finishing, sintering is carried out at 1400 to 1700°C in vacuum or under hydrogen. In the manufacture of pore-free materials, postcompression with hot isostatic presses may follow.

The chemical composition and applications of the different qualities of tungsten carbide-containing cemented carbides are summarized in Table 5.6-2.

In the manufacture of cemented carbide the oxygen content should be minimized.
Manufactured by:

- intimate mixing by wet grinding
- forming
- presintering at 900 to 1150°C
- finishing
- sintering at 1400 to 1700°C
- optional postcompression with hot isostatic presses

Table 5.6-2. Chemical Composition and Applications of Tungsten Carbide-Containing Cemented Carbides.

cemented carbide quality	chemical composition	WC content in % by weight	application
K-quality	WC-Co	88 to 96	cutting tools for short-chip materials, drilling plates for impact stress applications
P-quality	(W, Ti, Ta, Nb)C-Co	65 to 85	cutting tools for long-chip materials
M-quality	(W, Ta, Nb)C-Co	70 to 80	wide range of uses
G-quality	WC-Co	75 to 96	chip-less forming

WC-Co materials from ultrafine tungsten carbide are specialty products with increased abrasion resistance and therefore higher cutting efficiency.

5.6.6 Thorium Carbide and Uranium Carbide

Thorium carbides (ThC, ThC_2) and uranium carbides (UC, UC_2) exhibit metallic properties, but in other properties differ significantly from the carbides of the subgroups of the IVth, Vth and VIth groups of the periodic table. Their hardnesses are substantially lower (see Table 5.6-1), they are pyrophoric and are easily hydrolyzed in water or weak acids. Their only economic importance is as carbidic fuels in nuclear technology, particularly for high temperature and breeder reactors which are currently in the evaluation phase.

Carbide powder is manufactured by carburization of the metal, metal oxide or metal hydride with nuclear-pure graphite at ca. 2000°C. Carbide powder pellets (see Section 5.5.5.1.5) or beads up to 0.6 mm in diameter are formed and sintered using ceramic process technology. Reaction sintering is commonly used for the manufacture of uranium carbide fuel beads, in which uranium oxide and carbon are first mixed then annealed to form the carbide and then are sintered to 90 to 95% of the theoretical density. An

Uranium and thorium carbides are not typical hard materials

The importance of uranium carbide increases as high temperature nuclear reactors are introduced

Carbidic nuclear fuels utilized in the form of pellets or graphite- or SiC-coated beads additional coating of the beads with multiple layers of graphite and silicon carbide deposited by pyrolysis keeps the fission products in the nuclear fuel.

5.6.7 Metal Nitrides

Metallic nitrides have similar properties to the corresponding carbides. They are of minor industrial importance

The metal nitrides of the transition metals of the subgroups of the IVth, Vth and VIth groups are very similar to the corresponding carbides in their structures (interstitial compounds of the MN type) and their properties such as hardness, melting point and electrical conductivity (see Table 5.6-3). Tungsten and molybdenum nitrides are exceptions with different structures and decompose with nitrogen loss above 800°C.

The following processes are used in the manufacture of metal nitrides:

- nitriding of metal oxides under nitrogen or ammonia in the presence of carbon;
- nitriding of metals or metal hydrides under nitrogen or ammonia;
- reaction of metal chlorides or metal oxychlorides with ammonia;
- reaction of metal chlorides with nitrogen or ammonia in a hydrogen plasma with gas phase deposition (CVD-process).

Table 5.6-3. Properties of Metal Nitrides.

compound	melting point in °C	Vickers hardness HV 0.05
TiN	2950	2100
ZrN	2985	1600
HfN	3390	1700
VN	2180	1560
NbN	2205	1400
TaN	3095	1150
CrN	1085, 1500?	1100
Cr_2N	1590	1580
Mo_2N	decomposition	not determined
W_2N	decomposition	not determined

By comparison with the metal carbides, the industrial demand for the nitrides is very small. This is in part due to the poor wettability of the nitrides by ferrous metals, which makes the manufacture of hard metal alloys more difficult.

TiN-coatings are industrially important, increasing the abrasion resistance of cemented carbides and producing a decorative golden yellow coloration on articles of jewelry.

Titanium nitride coatings utilized as abrasion resistant layers on cemented carbides and as decorative layers (golden yellow) on articles of jewelry

Crucibles of titanium nitride and zirconium nitride are utilized for the melting of lanthanum alloys. ZrN, HfN and TaN are also used as electrodes in electronic valves. Niobium and zirconium nitrides could be used as superconductors due to their relatively high superconductor transition temperatures of 16.8 and 10 K respectively.

Niobium and zirconium nitrides have relatively high superconductor transition temperatures

5.6.8 Metal Borides

Metal borides are notable for their high melting points, high hardness, good electrical conductivity and chemical resistance (see Table 5.6-4). They are manufactured by the following processes:

Metal borides possess excellent hard material properties, but are difficult to work

- melting of metal-boron mixtures in arc furnaces;
- reaction sintering of compressed metal-boron mixtures;
- reduction of mixtures of metal oxides and boric oxide with aluminum, silicon or magnesium with simultaneous boride formation;
- reaction of metal oxides with boron carbide to generally carbon-containing borides;
- deposition from the gas phase reaction of volatile boron and metal compounds.

Table 5.6-4. Properties of Metal Borides.

compound	melting point in °C	Vickers hardness HV 0.05
TiB_2	2850	3400
ZrB_2	3040	2250
HfB_2	3200	2900
VB_2	2450	2100
NbB_2	3000	2600
TaB_2	3150	2500
CrB	2050	2140

Table 5.6-4. Properties of Metal Borides (continued)

CrB_2	2150	2100
MoB	2350	2500
MoB_2	2100	2350
WB	2400	3750
W_2B_5	2300	2600

Borides cannot be processed with bonding metals to hard metal alloys

Despite their interesting properties wide application of borides is not possible, because they cannot be processed with bonding metals to hard metal alloys and the more expensive hot press process must be used. Furthermore, borides form low melting point eutectics with ferrous metals.

Titanium diboride and the chromium borides are virtually the only borides utilized industrially:

- TiB_2 as an electrode and crucible material
- CrB, CrB_2 for abrasion resistant layers

The high resistance of titanium diboride, TiB_2, to many metal melts, particularly aluminum, has led to its use as an electrode and crucible material for electrometallurgical processes.

In addition to the titanium borides, the chromium borides, CrB and CrB_2, are utilized in abrasion resistant layers on the basis of Ni-Cr-B-Si and in scaling-resistant composite materials.

5.6.9 Metal Silicides

The silicides of the metals of the subgroups of the IVth, Vth and VIth groups are, in principle, manufactured using the same processes as those utilized for the corresponding borides.

Silicides are unsuitable for use in hard metal alloys

The silicides exhibit the lowest melting points and hardness values of the metallic hard materials (see Table 5.6-5). Their brittleness makes them unsuitable for utilization in hard metal alloys. Silicides have only been utilized industrially in metallurgical fields in which their scaling resistance and chemical resistance are important. They are also deposited using the CVD process e.g. as protective layers on high melting metallic surfaces.

Molybdenum disilicide is utilized for the manufacture of electrical heating elements, which can be operated in air at temperatures up to 1600°C

Molybdenum disilicide stands out and is utilized in electrical heating elements, which can be operated at temperatures of up to 1600°C in air due to the formation of SiO_2 layers on surface.

Table 5.6-5. Properties of Metal Silicides.

compound	melting point in °C	Vickers hardness HV 0.05
$TiSi_2$	1545	950
$ZrSi_2$	1550	1025
$HfSi_2$	1545	975
VSi_2	1680	1090
$NbSi_2$	1950	1050
$TaSi_2$	2300	1230
$CrSi_2$	1520	1150
$MoSi_2$	2030	1290
W_2Si_5	2165	1200

References for Chapter 5.6: Metallic Hard Materials

Kiefer, R. and Benesovsky, F., Hartmetalle, Springer-Verlag, Vienna, 1965.

Stoll, W. M. and Santhanam, A. T., *"Industrial Hard Carbides"*, in Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 861 – 878, John Wiley & Sons, New York.

Santhanam, A. T., *"Cemented Carbides"*, in Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 848 – 860, John Wiley & Sons, New York.

Haag, H. and Tulhoff, H. *"Carbide und andere pulvermetallurgische Vorstoffe"*, in Winnacker, K. and Küchler, L. (Htsg.): Chemische Technologie. 1973. 3. Ed., Vol. 6, 498 – 518, Carl Hanser Verlag, München.

Holleck, H. *Binäre und Ternäre Carbid- und Nitridsysteme der Übergangsmetalle,* Materialkundlich-Technische Reihe 6, Gebr. Bonträger, Berlin-Stuttgart, 1984.

Benesovsky, F., *Pulvermetallurgie und Sinterwerkstoffe,* Druchschrift der Metallwerk Plansee AG & Co. KG, Reutte, 1980.

Grewe, H., *"Hartstoffe"*, in Handbuch der Keramik, Gruppe II K 3, Verlag Schmid GmbH, Freiburg, 1976.

Grewe, H. and Kolaska, J., Metall **33**, 23 – 27 (1979).

Schedler, W., Hartmetalle für den Praktiker, VDI-Verlag, Düsseldorf, 1988.

Eschnauer, H. and Kny, E., *"Hard Materials"* in Ullmann's Encyclopedia of Industrial Chemistry. 1989. 5. Ed., Vol. A 12, 603 – 615, VCH Verlagsgesellschaft, Weinheim.

5.7 Carbon Modifications

5.7.1 Introduction

Allotropic forms of carbon:

- graphite
- diamond

Graphite modifications:

- hexagonal graphite
- rhombohedral graphite

Diamond modifications:

- cubic diamond
- hexagonal diamond

Carbon exists in two allotropic forms: graphite and diamond. Under normal conditions graphite is the thermodynamically more stable form. Two modifications of graphite are known: a hexagonal and a rhombohedral form.

These modifications obviously represent ideal structures and a number of deviations in the arrangement of the carbon layers is observed. In this chapter industrially manufactured forms of carbon, e.g. carbon black or activated carbon, are dealt with as carbon modifications since their structures are in principle based upon those of diamond and graphite.

5.7.2 Diamond

Classification of diamonds according to origin:

- natural diamonds
- synthetic diamonds

Classification of diamonds according to application:

- gem diamonds
- industrial diamonds

The systematic search for natural diamond deposits and their commercial mining started at the end of the nineteenth century with the discovery of seams in South Africa. Synthetic diamonds were first reproducibly produced in 1953 in Stockholm in a laboratory by a team of scientists.

Only very pure almost colorless perfectly crystalline stones with certain minimum dimensions can be worked to cut diamonds. Diamonds that do not fulfill these requirements are known as industrial diamonds and are exclusively used as industrial materials.

5.7.2.1 Economic Importance

The worldwide production of synthetic and natural diamonds in 1990 was 350 Mct (350 megacarats = 70 t).

The mining of natural raw diamonds currently accounts for 29% of diamond production quantitywise, but this small quantity accounts for 92% of the value of raw diamonds (see Table 5.7-1).

Table 5.7-1. Worldwide Production in 1990 of Natural and Synthetic Raw Diamonds (1 carat = 0.2 g).

	quantity in 10^6 carat (ton)	value in 10^6 US$
natural diamonds	100 (20)	5500
synthetic diamonds	250 (50)	500

Of the natural raw diamonds produced in 1990, 45% were further processed to industrial diamonds and 55% to gem diamonds. This 55% of gem diamonds accounts for 98% of the total value of natural diamonds, whereas industrial diamonds only account for 2%.

In 1990 the South African company De Beers mined 23% of the natural diamonds, quantitywise, and 45% valuewise. In the same year, a subsidiary of De Beers, the Central Selling Organization (CSO), marketed 77% of the natural diamonds produced, quantitywise, and 70% valuewise.

The main producers of synthetic diamonds are De Beers and General Electric.

Not included in the production figures in Table 5.7-1, is the production of in-situ produced diamond coatings by gas phase pyrolysis (chemical vapor deposition, CVD), which are acquiring increasing industrial importance. The worldwide market for diamond-like- and CBN-coatings (CBN =cubic boron nitride) had a volume in 1993 of 40 million US$, with an annual growth rate to 1998 of 30 to 40%.

5.7.2.2 Mining of Natural Diamonds

The primary source of diamonds is rock of volcanic origin, which is called kimberlite after the first important deposit discovered in South Africa. These deposits are strongly worn away by weathering and erosion and therefore most of the diamonds are to be found in the surrounding areas in old water courses, alluvial deposits and sometimes under water on seabeds.

Diamond deposits:

- primary: kimberlite rock
- secondary: deposits (alluvial) formed by erosion, weathering and washing out from kimberlite veins

Standard underground and open cast mining techniques are used for extraction on land. Underwater mining is practised off the coast of Namibia. There diamond-containing clays are sucked up from the seabed and immediately concentrated on site.

The gangue is separated by mechanical methods and the diamonds concentrated by processes which permit separation on the basis of their high density (3.51 g/cm^3). The high density minerals separated together with the diamonds are removed by utilizing the nonwettability of diamonds by water. Diamonds adhere to greasy surfaces and in the skin flotation process they float on the surface, whereas the wetted heavy minerals sink. Ferromagnetic minerals can also be removed by magnetic separation. A widely used extraction process uses X-ray excited luminescence. Upon detecting a diamond, sluicing occurs automatically e.g. deflection with an air jet perpendicular to the stream of diamonds solely directed to the particular diamond. In the extraction of very small diamonds, separation processes on the basis of electrostatic charging have been found useful. Hand sorting and hand classification are indispensable, particularly for gem diamonds. The choice of separation process depends strongly upon the type of deposit.

Without the high regard, that gem diamonds enjoy in our society, the extraction of natural diamonds would be completely uneconomic. Even in the rich Kimberley seams in South Africa, only 2.5 carats (0.5 g) of diamonds are obtained per t of processed rock, only 0.4 carats of diamond being obtained in 1985 in the Premier Mine (also in South Africa).

The alluvial deposits on the cost of Namibia together with the adjacent Namaqualand to the South is the richest gem diamond source in the World.

5.7.2.3 Manufacture of Synthetic Diamonds

Diamond is metastable under normal conditions and only becomes the more stable form of carbon at pressures above 16 kbar. The synthesis of diamonds from graphite therefore requires high pressures and, to increase the rate of reaction, high temperatures. The processes used are either diffusion-controlled (so-called catalytic process) or diffusion-less.

More than 90% of all synthetic diamonds are manufactured catalytically from graphite using such catalysts as:

- iron,
- cobalt,
- nickel,
- manganese,
- chromium,

- alloys and carbides of these and other transition metals.

Graphite is utilized as the starting material and is introduced with the catalysts into the generally metallic reaction vessel. This is electrically heated and is embedded in a series of holders designed to maintain the temperature and pressure. The pressure is produced hydraulically and exerted on the reaction vessel by a plunger made of a very hard material (e.g. tungsten carbide), which are differently geometrically arranged depending upon the apparatus. Upon heating under pressure, the catalyst metal melts dissolving the graphite and carbon precipitates as diamond from the supersaturated solution. At the end of this "recrystallization", which only lasts a few minutes, the diamonds are present as a mass of agglomerated single crystals. The catalyst metal is then removed mechanically and chemically and the diamonds sorted on the basis of size and shape. The average size of the diamonds is 0.05 to 0.5 mm. This synthesis is reproducible making it possible to produce large quantities of diamonds of uniform quality. If diamond seed-crystals are used with growth times of up to a week, larger single crystalline diamonds, up to 5 mm in size, can be obtained in the laboratory. This process is not economical for the synthesis of gem diamonds, due to the high mechanical and thermal stress of the pressure apparatus used.

Catalysts for the diffusion-controlled synthesis of diamonds:

transition metals, their alloys and their carbides

Reaction conditions for the diffusion-controlled phase change:

- temperature: ca. 1500 to 2500°C
- pressure: 50 to 100 kbar

Processes without catalysts are only of minor industrial importance, since they provide only gray graphite-contaminated diamond powder with a maximum crystal size of ca. 50 µm and require significantly higher pressures of 120 to 300 kbar. In the dynamic process operated by DuPont the pressure and temperature are produced for a few microseconds in a shock wave apparatus. The starting material is also graphite, which should be as crystalline as possible. Static high pressure synthesis processes without catalysts are industrially unimportant.

Conditions for diffusionless phase change:

- pressure: 120 to 300 kbar

Polycrystalline diamond coatings can be produced by gas phase pyrolysis (chemical vapor deposition, CVD). Coating is carried out in a reaction chamber, which contains a carbon- and hydrogen-containing gas mixture at low pressure (e.g. 10 mbar), a local heat source for producing reactive carbon and hydrogen species and the article being coated at a temperature of 600 to 1000°C. Under these special conditions diamond and hydrogen are favored over methane. A rough polycrystalline diamond layer grows on the article at a rate of 100 µm/h. Tools, membranes and optical and electronic components can be usefully coated with this process (see Section 5.7.2.1). At higher pyrolysis temperatures graphite is predominantly formed (see Section 5.7.5.1).

5.7.2.4 Properties and Applications

Exceptional properties of diamonds:

- hardness of 10 on the Mohs scale,
- highest thermal conductivity,
- high refractive index and dispersion.

The exceptionally high hardness of diamond, the easy cleavage along the three main lattice planes of the crystal, its high refractive index and its optical dispersion makes diamonds a valuable raw material for brilliants. The gem diamonds utilized are still exclusively natural diamonds.

Applications of diamonds as a hard material for drilling, cutting, grinding, polishing etc.

Due to their hardness, their thermal and chemical resistance and the highest thermal conductivity of any solid, almost all synthetic diamonds and a large proportion of the natural diamonds are utilized for drilling, cutting, grinding and polishing for which they are embedded in a resin or metal matrix. Recently, tool blanks have been obtainable, in which sintered polycrystalline diamond is applied to a tungsten carbide support. In the sintered diamond layer, the single crystals are randomly oriented and linked to one another by C-C-bonds. Sintered diamond has a much higher tensile strength than diamond single crystals, because the cleaving of a single crystal can generally not extend to spatially differently oriented neighboring crystals. Diamonds are used to work diamond itself, glass, ceramics, tungsten carbide, rocks, metals, alloys and plastics.

Special utilization fields:

- coatings for high grade optical components
- semiconducting diamonds in thermistors

Due to its transparency to UV-radiation, IR-radiation and visible light, diamond can be utilized as a coating material for optical components. Semiconducting diamonds (doped with boron, beryllium or aluminum) are utilized in special thermistors for the temperature range -200 to +500°C.

5.7.3 Natural Graphite

5.7.3.1 Economic Importance

The worldwide production of naturally occurring graphite increased from $392 \cdot 10^3$ t/a in 1970 to $596.7 \cdot 10^3$ t/a in 1980 and in the period 1980 to 1993 remained almost constant at an average of $597 \cdot 10^3$ t/a. Since 1980 China has been the leading producer, accounting for 25% of worldwide production and 25% of the economically workable world reserves (see Tables 5.7-2 and 5.7-3). Natural graphite has not been mined in the USA since 1990, but there has been a considerable expansion in graphite production in Canada since 1988.

Table 5.7-2. Production of Natural Graphite in 1990.

	10^3 t/a	%
China	140.0	23.4
South Korea	99.7	16.7
Former States of the USSR	80.0	13.4
India	61.0	10.2
North Korea	35.0	5.8
Mexico	24.9	4.2
Canada	10.2	1.7
Others	147.5	24.6
World	598.3	100.0

Table 5.7-3. Estimated Reserves of Natural Graphite in 1993.

	10^3 t	%
China	5500	26.2
South Korea	3150	15.0
Mexico	3100	14.8
Canada	1500	7.1
Madagaskar	980	4.7
India	735	3.5
Brazil	500	2.4
Others	5535	26.3
World	21000	100.0

Natural graphite is interesting for special applications, due to its high crystallinity. Demand, particularly for high grade types, has therefore increased. Synthetic graphite is, however, predominantly used in the processing industry.

5.7.3.2 Natural Deposits and Mining

The crystalline size of natural graphite is between 0.1 µm and several mm

Carbon content of raw graphite ores ca. 20 to 100% by weight depending upon the deposit

Natural graphite occurs in the form of flakes (scales) and pieces (coarse lumps) as well as in a very finely divided form. The latter is called amorphous graphite, which is a misnomer because even in its finest form it consists of crystals, however small. It is predominantly found in its hexagonal modification, although the rhombohedral form is also found. The degree of crystallinity and carbon content vary from deposit to deposit.

Graphite deposits are found in or at the edges of stratified rock

Flake graphite is found in beds in metamorphic rock, such as gneiss or marble and is formed from carbon-rich sediments (e.g. at Passau from algae colonies). Lump graphite is found where magma has solidified in stratified rock formations (limestone, slate). Coal in the veins and cavities at the edge of stratified rock formations is possibly converted into graphite under the influence of the high temperatures (Sri Lanka). Finely crystalline (and microcrystalline) graphite is also formed from carbon-containing sediments in metamorphic stratified rock. Seams of graphite originating from coal seams are also found (Mexico).

Graphite ore is extracted by underground and open cast mining. Beneficiation takes place by sorting according to carbon content, crushing and enrichment.

Concentration of the graphite is often unnecessary

The lump graphite found in Sri Lankan deposits is the purest natural graphite known, with a carbon content of up to 100%. Such high purity is not required for many applications. Thus enrichment of graphites with low carbon-content can often be dispensed with or, if needed, only needs to be carried out to the particular purity level required. This assumes that the impurities do not have undesirable properties as regards its intended application e.g. abrasive impurities in graphite destined for solid lubricant applications.

A typical enrichment process is flotation which is used, for example, in the Graphitwerk Kropfmühl (near Passau, Federal Republic of Germany) to produce flake graphite types with carbon contents between 70 and 97% as follows: the raw ore is coarse ground in crushers, ground with water in a rod mill, freed from most of the gangue in a rake classifier and then subjected to multistep flotation separation interspersed with wet grinding steps. In the flotation cells graphite flakes surrounded by air bubbles float to the surface, forming a graphite scum which is sucked off, centrifuged and dried. Purer graphite types with carbon contents > 99.5% require additional chemical refining, e.g. sodium carbonate digestion or hydrofluoric acid leaching. The combined use of sieving, grinding and classification enables marketable types to be obtained with well-defined particle sizes down to < 5 µm, while retaining the flake shape.

Concentration generally carried out using flotation techniques

Highly purified graphite types (> 99.5% C) only obtainable by additional chemical refining:

- sodium carbonate digestion
- hydrofluoric acid leaching

Cryptocrystalline natural graphite is also beneficiated using flotation, but this is complicated by its small particle size and the resulting more homogeneous distribution of the accompanying minerals. Oils are preferred as flotation media.

5.7.3.3 Properties and Applications

The foremost properties of graphite are:

- high temperature resistance, particularly thermal shock resistance,
- chemical resistance (corrosion resistance),
- very high thermal conductivity,
- high electrical conductivity,
- softness,
- low density,
- ease of delamination.

It exhibits anisotropic physical properties as a result of its crystallographic structure of well-separated parallel sheets of carbon atoms. Thus graphite single crystals exhibit far higher electrical and thermal conductivity parallel to the layers of carbon atoms than perpendicular to them. Macroscopically, however, this anisotropy is seldom observable due to the random orientation of the individual particles.

The properties of graphite are strongly anisotropic, the electrical conductivity varying with direction by a factor of 10^4

Ca. 80% of natural graphite production is utilized in applications in which high temperature stability is required.

Thus natural graphite is present in refractory bricks, casting molds, crucibles and retorts as well as brake linings and lubricants as a temperature-resistant, thermally conductive constituent. Graphite-containing refractory bricks are utilized in the lining of smelting furnaces and converters. In metal foundries high grade casting molds, channels and crucibles are utilized which contain up to 50% by weight of graphite. In steel production the surfaces of ingot molds and channels are impregnated with graphite to prevent penetration of molten steel (applied as so-called founder's black). Graphite is also utilized for covering melts, for carburization and as a deoxidant.

- brake and clutch linings

In brake and clutch linings graphite has largely supplanted the toxicologically suspect asbestos.

- lubricants
- lead pencil "leads"

The softness of natural graphite is exploited in lubricants and self-lubricating seals. The particularly pure graphite from Sri Lanka is preferred for such applications, since no solid abrasive impurities are present. For the same reason, graphite is used as the "lead" in lead pencils.

Special applications:

- batteries
- rendering plastics antistatic

Minor applications of natural graphite, quantitywise, exploit its electrical conductivity. Natural graphite, or to an increasing degree mixtures with special conductive carbon black and manganese(IV) oxide (pyrolusite) to increase the electrical conductivity, is utilized in dry cells. It is also utilized in brushes for motors or generators, contact rods, conductive paints and for rendering plastics antistatic.

Table 5.7-4 gives the consumption spectrum for natural graphite in the USA in 1992.

Table 5.7-4. Consumption Spectrum of Natural Graphite in the USA in 1992.

	10^3 t	%
refractory bricks	13.0	31.1
brake linings	7.4	17.7
lubricants	7.0	16.7
steel manufacture, foundries	4.3	10.3
pencil leads	2.9	6.9
other	7.2	17.3
total	41.8	100.0

5.7.4 Large Scale Production of Synthetic Carbon and Synthetic Graphite

5.7.4.1 Economic Importance

The most important application of synthetic graphite is in electrode material for steel manufacture in electric arc furnaces. For each ton of electric furnace steel produced, on average, 5 to 8 kg of graphite are utilized. The production figures for synthetic graphite and electric furnace steel are therefore largely correlatable with one another. Graphite anodes were used up to 1980's in the electrolysis of aqueous hydrochloric acid, but have been largely replaced by platinized titanium(IV) oxide. This is reflected in the production figures for synthetic graphite (see Table 5.7-5).

Table 5.7-5. Production of Synthetic Graphite in the USA in the period 1981 to 1991 (in 10^3 t/a).

	1981	1986	1991
anodes	17.1	4.5	4.4
electrodes	234.0	126.9	154.4
powder	33.5	22.7	58.8
other	52.3	35.3	9.4
total	336.9	189.4	227.0

5.7.4.2 General Information about Manufacture

Carbon and graphite can be manufactured by many processes. The industrially operated processes are generally purely thermal and utilize solid, liquid or gaseous carbonizable or graphitizable materials. Synthetic carbon is produced in the first process step and is converted into graphite in a second step.

In large scale production only solid and liquid, preferably meltable, starting materials are important. The raw materials used are almost all more or less graphitizable. Nongraphitizable carbon is, as special carbon, of minor industrial importance. It is also produced by gas phase pyrolysis of special carbon and graphite types and is dealt with in Section 5.7.5. Carbon fibers have already been dealt with in Section 5.2.3.3.

Industrial manufacture of carbon:

by pure thermal decomposition of carbon-rich raw materials in inert atmospheres.

Industrial production of graphite:

by heating graphitizable carbon in an inert atmosphere generally in the absence of catalysts

Basic processes involved:

- mixing of raw materials
- forming
- carbonization
- graphitization

Since, under economically acceptable conditions, carbon neither melts nor is sintered, production has to be carried out in such a way that a molded article is formed suitable for its intended application, which only needs further mechanical working. The raw materials, solids and binders are thus mixed, molded into the required form, fired to the carbon article and, if required, finally graphitized.

5.7.4.3 Manufacture of Synthetic Carbon

5.7.4.3.1 Raw Materials

Raw materials:

- solid materials:
  - petroleum coke,
  - pitch coke,
  - furnace coke,
  - anthracite,
  - carbon black,
  - natural graphite
- binders: different sorts of pitch

The raw materials utilized in the manufacture of carbon and graphite products can be divided into solids and binders.

The following solids are generally used:

- petroleum coke from residues or intermediates of crude oil refining,
- pitch coke from coal tar pitch,
- furnace coke from coal,
- anthracite,
- carbon black,
- natural graphite.

Most important solid is petroleum coke

Cokes are formed from the appropriate materials by liquid phase pyrolysis. More or less structured cokes are formed depending upon the pyrolysis conditions and the composition of the starting materials. The ease of graphitization increases with increasing crystallinity and with increasing crystallite size of the coke. Petroleum cokes are the preferred raw materials with well-ordered strongly anisotropic needle coke, a type of petroleum coke, being one of the most valuable raw materials. For some applications, however, isotropic cokes are used. Important quality criteria for the solids, other than crystallinity, are:

- low sulfur content,
- low content of volatile components,
- low ash content (metallic impurities, silicon),
- low coefficient of thermal expansion,
- high density.

Most important binder is coal tar pitch

Addition of carbon black, anthracite and natural graphite improves certain properties. Anthracite is also used in the manufacture of carbon electrodes for economic reasons.

Various pitch sorts are used as binders for the solids. They have to endow the mixture with favorable forming characteristics, have a high carbon content and fire to an, if possible, graphitizable coke which binds the solids permanently together. The most important binding agent is coal tar pitch.

5.7.4.3.2 Processing

The volatile components in green petroleum coke can be reduced to less than 0.5% and the density increased by calcining at 1300 to 1400°C

The so-called "green" petroleum coke produced by delayed coking still contains volatile components, which escape at high temperatures, leading to excessive porosity and cracking. In addition form stability cannot be ensured. To avoid this it is first subjected to calcination in gas fired rotary kilns or rotary hearth kilns at 1300 to 1400°C. This is also necessary with anthracite, which can be calcined at even higher temperatures.

The comminuted solids are mixed with ground or molten binder at high temperatures

The cokes (or other solids) are then comminuted and classified according to particle size. To obtain a formed article with the highest possible filled volume, a precisely determined mixture of a number of fractions with different particle sizes is used rather than a uniform particle size. These are intimately mixed with the binder generally using double arm kneaders, vortex mixers and mixing screws. Additives can also be introduced at this stage such as oils which aid forming, or iron oxide which retard sulfur outbursts during graphitization.

The proportion of binder should be kept as low as possible

The ratio of binder to solids is dependent on the one hand upon the particle composition of the solid, since all the particles have to be coated as homogeneously as possible, and on the forming process, to ensure a certain plasticity in the bulk. On the other hand the probability of firing faults increases with increasing binder content and thus a compromise has to be sought.

5.7.4.3.3 Densification and Forming

The so-called green mixture is heated to a temperature just above the softening point of the binder and introduced into the form in which it is later to be fired. In almost all forming processes it is simultaneously densified to obtain dimensional accuracy, avoid cavities and prevent cracking during firing. During densification orientation of the anisotropic coke particles occurs in the direction of the resulting applied force, so that the unsintered formed articles generally exhibit anisotropic properties. The degree of anisotropy can be varied within certain limits by the type of forming process used.

Unsintered formed articles are produced under pressure at temperatures just above the softening temperature of the binder

Forming is carried out with the following apparatuses:

- ram extruders,
- screw extruders,
- cavity presses,
- isostatic presses,
- vibrating compressors,
- ram molds.

Extruders are generally used, although the number of vibrating compressors has increased in recent years, not least because unsintered molded articles with lower binder contents are easier to fire. Isostatic pressing is suitable for quasi-isotropic unsintered formed articles.

5.7.4.3.4 Carbonization

Carbonization of the binder in inert atmospheres at 800 to 1300°C

Firing of the unsintered formed article to carbon articles is carried out at temperatures between ca. 800 and 1300°C, utilizing gas or oil heating:

- ring furnaces (highest energy efficiency),
- single chamber kilns,
- rotary hearth kilns.

Complete firing can take several weeks. Pyrolysis gases make up ca. 30% by weight of the binder

The formed article is generally protected from air by coke, which both supports the unsintered formed article as the binder softens during heating and covers it and is partly burnt.

At low temperatures it is heated up as slowly as possible, to ensure a high degree of carbonization and to give the gaseous pyrolysis products (ca. 30% by weight of the binder) time to escape through the fairly impermeable mass. In addition this avoids cracking due to high temperature differences between the surface and the interior of the unsintered formed articles.

5.7.4.4 Graphitization of Synthetic Carbon

5.7.4.4.1 General Information

Graphitization processes are carried out at 2600 to 3000°C in inert atmospheres in direct or indirect processes. In direct processes (e.g. Acheson and Castner processes) the carbon articles between the electrodes are heated, either directly or indirectly with resistive materials in between, and the required temperature for graphite formation attained by resistive heating. In indirect processes there is no physical contact between the energy source and the carbon article.

During graphitization the carbon articles are heated in inert atmospheres at 2600 to a maximum of 3000°C

Graphitization processes are either:

- direct processes (Acheson and Castner processes), or
- indirect processes

The high temperatures effect an increase in ordering in the crystalline regions. The randomly oriented layer planes in the carbon article become ordered and large regions attain an almost ideal graphite lattice. In addition defects inside the crystallites are annealed. The attainable degree of structural perfection is limited by the degree of orientation in the starting material (coke or carbon article).

Upon graphitization the carbon article attains a graphite-like microstructure. The degree of graphitization depends upon the final temperatures (not the firing time) and the degree of orientation of the starting material

The heating rate during graphitization must also be chosen to avoid high temperature gradients in the carbon articles. The heating times are shorter than for carbonization, but the whole process still takes 1 to 3 weeks. The heating rate is also limited by the sudden escape of sulfur (puffing) at ca. 1600°C during which the article undergoes an expansion in volume. This effect can be reduced by using inhibitors.

5.7.4.4.2 Acheson Process

The Acheson process is the oldest and still most important graphitization process. The carbon articles are placed with their long axes perpendicular to the direction of the electrical current in the furnace bed and are surrounded with a resistive bed of granular coke in which most of the Joule heat is produced. A constant furnace resistance is essential for uniform product quality (avoidance of local temperature peaks). The way in which the furnace is loaded is therefore critical.

Acheson process, most important graphitization process:

heating up of the carbon article by a resistive bed of coke

In Acheson furnaces articles with very different shapes can be graphitized, making the process very versatile. The capacities of currently operated furnaces range up to net loads of 100 t or more. A typical Acheson furnace is 12 to 15 m long and 3 to 3.5 m wide and is loaded with 35 to 55 t of carbon articles. After a heating time of 3 days final

Advantages of Acheson furnaces:

- robust construction,
- virtually trouble-free operation,
- suitable for almost any type of carbon article.

temperatures of 2800 to 3000°C are attained. A further 8 to 10 days are required for cooling the furnace, so that a production cycle takes about 2 weeks.

Most important disadvantages of the Acheson furnaces:

- low energy efficiency,
- poor time and space utilization.

In the Acheson process only ca. 30% of the energy of ca. 3 to 10 kWh/kg supplied is utilized for graphitization. Other disadvantages are the high cost of loading, the poor time and space utilization yield and the high emission of noxious gases (mainly SO_2), whose controlled disposal is exceptionally difficult due to the size of the older furnaces and the high operating temperatures. New plants have thus been designed to operate continuously or semicontinuously (transportable individual furnaces between stationary mounted electrodes, the electrodes being run down from above in coupled U-shaped units which move in unison). This results in more rational production and easier disposal of noxious gases.

5.7.4.4.3 Castner Process

Castner process:

direct heating of the carbon articles without intermediate resistive materials

The Castner process operates without intermediate resistive materials. The heat is thus exclusively produced in the carbon articles themselves, which are directly spanned between two electrodes at least one of which is movable to allow for changes in dimensions.

Castner furnaces are smaller than Acheson furnaces. Heating up and cooling down phases are significantly shorter than in the Acheson process. Also here there is a switch to continuous operation.

The Castner process is characterized by more efficient energy utilization and by more uniform graphitization compared with the Acheson process. Disadvantageous is the more complex furnace construction and restrictions concerning the dimensions of the carbon articles.

5.7.4.4.4 Other Graphitization Processes

The other graphitization processes transfer the heat indirectly to the carbon articles, which makes continuous operation easier.

Heat transfer by indirect processes:

- by induction,
- by radiation

Heating can be carried out by induction in which the furnace is surrounded by an induction coil and the dimensions of the article and the coil have to be precisely correlated with one another. Alternatively heating takes place by radiation, which is more flexible.

Both processes are limited to smaller carbon articles and are utilized for the production of specialty products.

5.7.4.4.5 Purification Graphitization

Very pure graphite sorts are attainable by modifying the above-described processes. Purification can be achieved purely thermally or thermochemically. The purely thermal processes entail increasing the firing temperatures to ca. 3000°C and firing times and using carbon black to absorb the escaping volatile impurities. In thermochemical processes impurities are converted into volatile halogen compounds by reaction with:

- elemental chlorine or fluorine,
- halocarbon compounds,
- solid halides.

Purification graphitization:

- purely thermal,
- thermochemical.

5.7.4.5 Impregnation and Processing of Carbon and Graphite Articles

The carbon and graphite articles obtained using the above-described processes contain up to 20 to 25% by volume of open pores formed by the escape of gaseous pyrolysis products upon binder carbonization. For many applications it is essential to fill up at least some of the pores by posttreatment or to seal the surface to gases and liquids. This is accomplished with:

- pitch,
- synthetic resins,
- pyrolytic carbon,
- metals and alloys by the formation of surface layers of carbides, silicides, borides and nitrides,

which may require further heat treatment at high temperatures. Impregnation can also improve certain properties e.g. density, strength and corrosion resistance.

Formed articles may have to be pretreated to enable effective impregnation to be carried out. Carbon articles have to be worked with diamond or cemented carbide tools due to their hardness, whereas graphite articles are predictably much softer and therefore easier to work.

20 to 25% of the volume of carbon and graphite articles are open pores

Reduction of porosity and improvement of certain properties by:

- impregnation.

Graphite articles can be much more easily and more precisely worked than carbon articles

5.7.4.6 Properties and Applications

Properties of formed synthetic carbon articles:

- hardness similar to ceramics,
- strength similar to ceramics,
- brittleness similar to ceramics,
- low electrical conductivity,
- chemical resistance.

Properties of formed synthetic graphite articles:

- high thermal and electrical conductivity,
- other properties increasingly resemble those of natural graphite as the degree of crystallinity increases

Formed carbon articles are comparable in their hardness, strength and brittleness to ceramic articles. They exhibit a certain electrical and thermal conductivity and a very high chemical resistance. Formed graphite articles on the other hand exhibit significantly higher electrical and thermal conductivities. Their tensile strength and elastic modulus at room temperature are, however, lower, but increase strongly with increasing temperature. The other properties of synthetic graphite increasingly resemble those of natural graphite as the degrees of crystallinity and order increase. Synthetic graphite is more expensive, significantly purer and less crystalline than natural graphite.

Application fields for industrially produced carbon and graphite:

- electrode manufacture,
- refractory linings for blast furnaces,
- manufacture of casting molds, sintering molds and crucibles,
- chemical plant construction,
- mechanical engineering,
- nuclear technology,
- electrical industry,
- welding technology.

Most of the synthetic carbon and graphite is utilized in electrodes in electric arc furnaces, its use in the production of electric furnace steel by the melting of scrap being particularly important. In electric arc smelting furnaces with open arcs, the more expensive graphite electrodes are preferred, whereas in the electric arc reduction furnaces with immersed arcs carbon electrodes are preferred. Carbon electrodes for high temperature applications are often produced in situ from a plastic raw mass (Söderberg electrodes). Synthetically produced carbon and graphite are utilized:

- as graphite electrodes for open electric arc furnaces (electric furnace steel production),
- as carbon electrodes for closed electric arc furnaces (phosphorus, silicon or calcium carbide production by electrothermal reduction),
- as carbon electrodes for the electrolytic manufacture of aluminum,
- as graphite anodes in the fusion electrolysis of metal chlorides,
- as carbon anodes in the electrolysis of KF/HF,
- as blocks, bricks, plates and tamping compounds for the lining of furnaces, tanks and ingot molds,
- in casting molds, sintering molds, ingot molds and crucibles for foundries, metallurgical processes, glass production, glass working, the ceramic industry and in semiconductor technology (zone melting, single crystal growth etc.),
- in chemical plant construction: e.g. in heat exchangers, columns, containers, pumps, piping, rupture disks for pressure relief etc.,

- as a material for bearings, seals etc. in mechanical engineering,
- as high purity graphite for nuclear technology for moderators, reflectors and fuel elements (particularly for high temperature reactors) and as a construction material in reactors and reprocessing plants,
- as carbon or graphite brushes, sliding contacts and sliding rings in electrical machines or for electrical conduction,
- as small electrodes in the spark erosion machining of metals, as welding electrodes, arc lamp electrodes, and spectral carbonization (in analytical techniques).

5.7.5 Special Types of Carbon and Graphite

The types of carbon and graphite described in this section have been developed over the last 50 years. Their manufacture is in some cases much more complicated than mass-produced types and as a result their industrial importance is correspondingly low. Their specific properties are, however, so exceptional that a bright future is forecast for special applications.

New carbon modifications, which consist of discrete polyhedral molecules, have been intensively investigated since the early 1990's. The structures of these fullerenes range from the highly symmetrical buckminsterfullerenes, C_{60}, to the chiral fullerenes, C_{76}, to larger tubular or carbon particles built up of onionscale-shaped molecules. Possible applications, such as the manufacture of superconducting alkali metal-doped fullerenes or their utilization as a support for catalysts, are being developed, but are not yet market ripe.

5.7.5.1 Pyrolytic Carbon and Pyrolytic Graphite

Pyrolytic carbon and pyrolytic graphite produced by thermal decomposition of gaseous or vaporized carbon-containing compounds

Pyrolytic carbon and pyrolytic graphite are deposited on substrates by gas phase pyrolysis (chemical vapor deposition, CVD) of:

- methane,
- ethane,
- propene,
- benzene,
- carbon tetrachloride etc.

The pyrolysis reactions take place at temperatures between 800 and 3000°C, both in the gas phase and on the substrate surface. Their property mix can be varied within wide limits by appropriate choice of process parameters. The production of an isotropic structure is just as possible as the obtaining of spiral, columnar or extremely anisotropic laminar structures. Graphite whiskers can also be produced.

Utilization fields for pyrolytic carbon and pyrolytic graphite:

- nuclear technology,
- medicine,
- aerospace applications

Pyrolytic carbon is utilized for impregnating porous synthetic graphite by first filling the pores (low deposition temperature, low partial pressure or forced flow of the gases through the graphite article) and then sealing the surface gas- and liquid-tight at high temperatures. Such high-grade graphite components are utilized for applications in which the highest resistance to erosion and oxidation is required e.g. guiding tubes for fuel rods in nuclear reactors. Nuclear fuel components are first rendered isotropic in a fluidized bed (thermal and mechanical stress relaxation and absorption of gaseous decomposition products) then lamellarly or granularly encapsulated with pyrolytic carbon to give coated particles (gas tightness, strength). As a result of their excellent biocompatibility, isotropic pyrolytic carbon articles are being increasingly used in medicine as heart flaps and valves and in prosthetic devices. Alloys with silicon carbide are also used. Pyrolytic carbon can also be utilized as the matrix material in one, two or three dimensional carbon fiber-reinforced carbon/carbon-composite materials, which are also used in medicine e.g. for bone plates. Still further applications for these materials are as temperature resistant highly abrasion resistant brakes and clutch plates with residual slip properties for aircraft, as ablation shields and as cladding for rockets. Carbon fibers can even be strengthened by coating with pyrolytic carbon.

Pure anisotropic pyrolytic graphite was formerly used on rocket noses, rocket jets, the leading edges of the wings of supersonic aircraft etc. for the directional dissipation of thermal energy, due to its high thermal conductivity in the carbon layer plane. However, its anisotropic thermal expansion perpendicular to the layer planes results in very rapid scaling off of this insulation which has led to its discontinued use. Extremely anisotropic pyrolytic graphite articles, obtained by additional heat treatment at 3000°C under pressure applied perpendicularly to the layer plane, are used for monochromatizing X-rays and neutron radiation and as a starting material in the manufacture of intercalated compounds (see Section 5.7.5.3).

5.7.5.2 Glassy Carbon and Foamed Carbon

Glassy carbon and foamed carbon are also formed by the pyrolysis of carbon-rich materials, but in this case solid state pyrolysis at up to ca. 1000°C, rather than liquid or gas phase pyrolysis.

Glassy carbon and foamed carbon from solid state pyrolysis

Thermosetting plastics, i.e. nonmelting unfoamed or foamed organic polymers or polymers rendered nonmeltable by dehydration, crosslinking, cyclization or aromatization, are used as starting materials, mainly:

- phenol formaldehyde resins,
- polyfurfuryl alcohols,
- poly(acenaphthalene) rendered nonmelting by treatment with sulfur,
- poly(acrylonitrile) foam rendered nonmelting by oxidation,
- phenol resin-impregnated poly(urethane) foam.

Starting materials for glassy carbon and foamed carbon:

- thermosetting polymers,
- polymers rendered nonmelting by chemical treatment

The principle is the same as that used in the manufacture of carbon fibers (see Section 5.2.3.3), only here formed solid polymer articles are used instead of carbon fibers. The formed articles for glassy carbon are solid, should not be too large and preferably should have wall thicknesses no greater than 5 mm. Otherwise even at extremely slow heating rates uniform escape of the gaseous pyrolysis products cannot be guaranteed and cracks are formed. The formed articles for foamed carbon, on the other hand, consist of foamed polymers and can, unlike glassy carbon, be manufactured with larger dimensions. Foamed carbon blocks and plates can be easily produced.

Glassy carbon is a nongraphitizable modification of carbon with extremely small crystallites (max. 10 nm) with a ribbon structure. The strong intertwining of the carbon ribbons is reminiscent of a polymer coil. Heating under the usual graphitizing conditions leads to parallel ordering. Glassy carbon is therefore isotropic and is also extremely hard and brittle. The slit-shaped micropores appear to close with increasing temperature making tempered glassy carbon almost impermeable to gases and very resistant to oxidation.

Glassy carbon is nongraphitizable

Glassy carbon can only be machined with diamond tools or with ultrasonic techniques. The shape must therefore be defined as exactly as possible during the forming of the polymer

Application fields for glassy carbon:

- laboratories,
- analysis,
- metallurgy,
- semiconductor industry,
- medicine,
- aerospace

Small glassy carbon articles such as crucibles, boats or tubes are utilized under conditions in which high purity and temperature stability are required. Glassy carbon can be used, as with pyrolytic carbon, in prosthetic devices in human medicine. Furthermore the matrix in "all carbon composites" can consist of glassy carbon rather than pyrolytic graphite. The application fields are the same as those mentioned in Section 5.7.5.1.

Foamed carbon is nongraphitizable

Formed articles of foamed carbon can be produced after carbonization by machining plates or blocks

Foamed carbon is also nongraphitizable. The cell structure of the polymer foam remains intact upon careful carbonization and densities lower than 0.1 g/cm^3 are obtainable. The thermal conductivity is just above that of plastic foams, but foamed carbon can be used at much higher temperatures. Its relatively low compressive strength can be increased by impregnation with pyrolytic carbon, although the thermal conductivity increases at the same time. By comparison with glassy carbon, foamed carbon is easy to work, so that the shape does not have to be established at the start of the process. Foamed carbon is corrosion resistant, as are all carbon modifications.

Application fields for foamed carbon:

- metallurgy,
- foundry technology,
- fire protection,
- catalyst production,
- laboratories.

Foamed carbon has 600 times the thermal insulation capacity of the same weight of firebrick and is therefore used as a self-supporting thermal insulation material in furnaces or in fire-retarding sandwich-constructions. Foamed carbon cores are used in foundry technology, because they are easily produced and can be easily removed by combustion from inaccessible cavities. Furthermore foamed carbon is utilized as a filter material for the filtration of corrosive materials, as sintered plugs in gas inlets, as an electrode material and as a catalyst support.

5.7.5.3 Graphite Foils and Membranes

Process steps in the production of graphite foil:

- oxidation of flake graphite or pyrolytic graphite to graphitic oxide,
- thermal decomposition of the graphitic oxide,
- pressing the bloated graphite to a foil.

Graphite foil is manufactured from high purity natural flake graphite or strongly anisotropic pyrolytic graphite, as starting materials. In this process they are oxidized with fuming sulfuric acid or a mixture of sulfuric acid and nitric acid, hydrolyzed to graphitic oxide, which is washed, dried and then decomposed to bloated graphite by rapid heating to ca. 1000°C and is then pressed without added binder into a foil.

Graphite membranes are obtained by drying a graphitic oxide gel on a polished surface, reducing with hydrogen at temperatures above 500°C and graphitizing the carbon membrane formed at temperatures above 2500°C.

Graphite foils and graphite membranes are flexible, impervious to gases and liquids, even at high temperatures, exhibit high anisotropy and are more chemically resistant than most of the synthetic graphite types. Graphite foils are preferably used in the manufacture of crimpable flat seals, self-lubricating sealing rings and packing seals. They are also utilized for lining pipes and containers in which corrosive substances are handled, for lining press and casting molds to obtain smooth surfaces and as efficient heat-reflecting shields in high temperature furnaces. Flat thermal conductors and rupture disks for pressure relief are also manufactured from graphite foil. Graphite membranes are utilized as dialysis membranes in seawater desalination.

Process steps in the manufacture of graphite membranes:

- reduction of a graphitic oxide film with hydrogen,
- graphitization.

Application fields for graphite foil and graphite membranes:

- machine tool manufacture,
- chemical plant construction,
- metallurgy,
- foundry technology,
- electrical industry,
- seawater desalination.

5.7.6 Carbon Black

Carbon black is the oldest synthetic carbon modification and is in fact one of the oldest chemical products. Carbon black was even used in the cave paintings of the Old Stone Age as a black dye. Its manufacture in the form of lamp black was, according to very early documents, known to the Ancient Egyptian and Ancient Chinese cultures.

Carbon black has been produced for several thousand years and is one of the oldest chemical products

Depending upon the manufacturing process the 5 to 500 nm primary carbon black particles consist of more or less strongly deformed or twisted graphite layers, which are spherically oriented round a growth center. The extent of the individual layers varies strongly but particularly near the surface can amount to several thousand nanometers in both spatial directions. The layers can also extend from one growth center to another, often giving the aggregates formed a chain or coil structure. Within small regions the fragments of several graphite layers may lie parallel and at the same distance to one another. These separations are somewhat larger than in the case of single crystal graphite and the layer sequence is completely random.

Structure of spherical primary carbon black particles:

shell-shaped oriented individual graphite layers of different sizes, which in small regions are oriented parallel to one another and thus constitute quasi-crystallites. Carbon black is therefore not amorphous!

5.7.6.1 Economic Importance

Carbon black production capacity in 1995:
worldwide: $7.3 \cdot 10^6$ t/a
worldwide (excl. East Europe): $6.0 \cdot 10^6$ t/a

The worldwide production capacity for carbon black in 1995 was estimated to be $7.3 \cdot 10^6$ t/a. Table 5.7-6 gives a survey of the carbon black production capacities in 1995 for different regions and countries. The value for Eastern Europe are uncertain.

Table 5.7-6. Production Capacities for Carbon Black (all types) in 1995.

	production capacity in 10^3 t/a	production capacity in % of worldwide capacity
USA	1650	22
Eastern Europe	ca. 1300	ca. 18
Western Europe	1268	17
Asia (excluding Japan)	1223	17
Japan	785	11
South America	435	6
Canada	181	2
Mexico	95	1
Other	400	5

Three companies, Cabot, Degussa and Columbian Chemicals, account for 40 to 50% of the worldwide carbon black production capacity.

Ca. 90% of the carbon black produced is utilized as an additive in the rubber industry, ca. 70% being utilized in vehicle tires, ca. 20% in other rubber products and ca. 10% in plastics, printing ink and paint manufacture.

5.7.6.2 Manufacture

5.7.6.2.1 General Information

Carbon black manufacture from carbon-rich raw materials by:

- pyrolysis in the presence of oxygen,
- pyrolysis in the absence of oxygen.

Carbon blacks are manufactured by the pyrolysis of gaseous raw materials (or materials converted into a gaseous state) or liquid (or molten) raw materials from the natural gas, crude oil or coal industries. There are two groups of processes: those in which part of the required thermal process energy is obtained by burning part of the raw material by intentional combustion in air, the so-called "incomplete combustion processes"; and those in which the required energy is completely supplied externally, the so-called "thermal decomposition processes".

The reaction conditions in the latter group of processes resemble those for the manufacture of pyrolytic carbon and pyrolytic graphite (see Section 5.7.5.1), but carbon black formation takes place at much higher partial pressures of the substance being pyrolyzed.

5.7.6.2.2 Pyrolysis Processes in the Presence of Oxygen

Furnace Black Process

Furnace black processes currently account for more than 95% of the carbon black manufactured. A great advantage of such processes is their flexibility in producing different carbon black types, types with primary particle sizes between 10 and 80 nm being producible.

Furnace black processes now the most flexible and important processes, 95% of carbon black manufactured using these processes

The first process of this type utilized gases as raw materials and produced carbon blacks for rubber with only moderate reinforcement properties at a maximum yield of 30%. The changeover to liquid and melting raw materials increased the yield of carbon black for rubber to 40 to 70% and enabled a much broader range of raw of products to be produced, so that this type of raw material is now almost exclusively used e.g. aromatic compound-rich viscous residues from oil refineries, coking plants, catalytic crackers and steam crackers for the production of ethene and from the catalytic synthesis of petrol.

Main raw material for furnace black processes:

- in the USA: residue from the catalytic synthesis of petrol
- rest of the world: residue from ethene production, coal tar oil

The required high carbon/hydrogen ratio in the feedstock is obtained by the highest possible proportion of condensed aromatic compounds conducive to their being pumpable at high temperatures. Furthermore, the content of asphalt (very high molecular weight polyaromatics) should not exceed a certain maximum, otherwise nonreinforcing microcarbon is formed. The sulfur content should also be low, since ever stronger emission regulations mean that sulfur emission must be severely restricted. The residual ash content should also be as low as possible to prevent the formation of hard abrasive and possibly catalytically active particles. Finally the alkali metal content should also be low, since it hinders the formation of structured i.e. aggregated carbon black. Conversely the degree of aggregation can be controlled by dosing with small amounts of alkali metals.

Quality criteria for carbon black raw materials:

- high C/H-ratio,
- pour point,
- viscosity,
- density,
- low asphalt content,
- low sulfur content,
- very low alkali metal content.

Carbon black properties can be influenced by:

- temperature,
- residence time,
- quantity of additives (particularly KOH, KCl),
- type of feedstock atomization,
- turbulence in the mixing zone.

The preheated feedstock is atomized radially to the smallest possible droplets in a tubular reactor, the so-called "carbon black furnace". There is a zone of high turbulence immediately in front of the injector in which the atomized feedstock is intimately mixed with hot gases from the combustion of the fuel (preferably natural gas, but also coking gas or liquid gas) in an excess of preheated air. The air excess is so adjusted that up to ca. 50% by weight of the carbon black-feedstock is consumed. The temperature obtained in the pyrolysis zone is 1200 to ca. 1800°C. Carbon black formation is weakly endothermic.

High pyrolysis temperatures and short residence times in very finely divided carbon black with large specific surface areas

The reaction mixture is quenched with water spraying to 800 to 500°C and then passed through heat exchangers which cool it further to 350 to 250°C. High pyrolysis temperatures, which can be controlled by the quantity and temperature of the combustion air, and short residence times, which can be achieved by adjusting the gas speed and the quenching position, lead to very finely divided carbon blacks with high specific surface areas. In modern plants the carbon black is separated in agglomeration cyclones with bag filters. The so-called tail gas has a finite heat content due to its carbon monoxide, hydrogen and hydrocarbon contents and can be utilized for energy production.

Compaction of fresh carbon black powder by:

- "degassing",
- dry pearling,
- wet pearling.

The first two processes are mainly used for carbon blacks for coloring

After deposition, the small proportion of coarse particles is separated by grinding and sieving and the impurities are removed. The very light carbon black powder is then compacted by "degassing" in which it is passed over rollers with a gas-permeable coating and a partial vacuum inside. Alternatively it is granulated dry without granulation aids in drums. This is only possible with very fine carbon blacks. Most of the carbon black produced is granulated wet with granulation aids in special pearling machines. The bulk density can thereby be increased to 500 g/L, which is about 10 times the bulk density of the noncompacted carbon black powder.

The production capacity of a modern large reactor is up to 2000 kg carbon black/h

Plants operating the furnace black process can produce up to $16 \cdot 10^3$ t/a in a single reactor. The reactor lifetime is almost two years despite the high thermal and mechanical stress.

Channel Black Process

The channel black process is the oldest process for the manufacture of fine particulate carbon black and was operated in the USA from the end of the nineteenth century to 1976. The fine particulate channel black first made possible the production of long-lived car tires with a mileage of several tens of thousands of miles.

In the channel black process natural gas is burnt in many small glowing flames in contact with water-cooled iron rails, so-called "channels". It is no longer operated due to the minimal utilization of raw material (3 to 6%), incomplete carbon black deposition and the resulting environmental problems.

The channel black process was formerly utilized for manufacturing fine particulate carbon black

Gas Black Process

The gas black process was developed in the 1930's by Degussa AG as an alternative to the channel black process, because natural gas was not available in sufficient quantities in Germany.

High boiling point aromatic compound-rich oils, preferably coal tar products, are used as the feedstock. This is evaporated at ca. 350°C and is transported by a combustible carrier gas, such as hydrogen, coking gas or methane, to the burners. Whereas in the channel black process a whole battery of flames make contact with a cooled surface, in this process the cooled surface is a slowly rotating cylinder. The thus produced gas black is characterized by a very small particle size (10 to 30 nm) and a high proportion of oxygen-containing surface groups, which account for its acid reaction in aqueous suspensions.

Most gas blacks are oxidatively posttreated to increase the concentration of acid groups on the surface even further (see Section 5.7.6.2.4). Due to their good dispersion properties, gas black is mainly used as pigment black in the paint and printing ink industries.

Main feedstocks in the gas black process:

- raw naphthalene,
- anthracene oil,
- anthracene oil residue

Advantages compared with the channel black process:

- less expensive feedstocks,
- higher carbon black yield.

Lamp Black Process

The lamp black process is simply an industrialized version of the old lamp black production techniques. Oil in flat cast iron pans up to 2 m in diameter is burnt under an extraction hood with a nonstoichiometric quantity of air. The carbon

Feedstock for the lamp black process:

- aromatic compound-rich oils

black is separated from the combustion gases in cyclones and filters. The yield is ca. 50%.

The lamp black process produces particularly coarse particulate carbon black with a high density ("heavy black"). Due to the broad particle size distribution of 60 to 200 nm, it has not been possible to replace lamp black with furnace black in some applications.

5.7.6.2.3 Pyrolysis Processes in the Absence of Oxygen

Thermal Black Process

Thermal black production:
proceeds discontinuously by endothermic pyrolysis of natural gas

The thermal black process operates discontinuously and generally utilizes natural gas as a feedstock. A production unit consists of two cylindrical furnaces connected to one another, in which refractory bricks are piled one on top of another for heat storage with a large cavity in between. The two furnaces are operated alternately: while the first furnace is being heated to the reaction temperature (ca. 1300 to 1500°C) with a stoichiometric mixture of air and combustible gas (mainly natural gas), natural gas is fed into the second already heated furnace and is thermally pyrolyzed. Since the reaction is endothermic, the furnace cools and the gas flows are switched when a critical minimum temperature is reached and the first furnace utilized, while the second is heated up again. The cycle time is about 5 minutes.

Thermal blacks are particularly coarse

The reaction products are quenched by water sprays in a cooling zone and the carbon black separated in filter units. The yield is ca. 35% of the carbon content of the feedstock and combusted gas. The residual gas consists almost entirely of hydrogen and can be mixed with natural gas for heating the furnace or for diluting the gas to be pyrolyzed. Coarser carbon black is produced than in the lamp black process, with primary particle sizes of 120 to 200 nm or 300 to 500 nm being attained depending upon whether the natural gas is diluted with inert gas or not.

Acetylene Black Process

Acetylene black process:
operates continuously by exothermic pyrolysis of acetylene

In the acetylene black process the tubular reactor only has to be heated once to 800°C by the combustion of an acetylene/air mixture. The pyrolysis reaction is then carried out with pure acetylene, which proceeds strongly exothermically and is therefore self-sustaining. The reactor has in fact to be cooled to maintain a constant temperature. The carbon black yield is 95 to 99%!

Acetylene blacks are chemically very pure. Their particles significantly deviate from the other carbon blacks in being significantly nonspherical. They are utilized in dry cells, due to their higher electrical conductivity and their good absorptive capacity.

Electric Arc Process

Arc black is produced as a byproduct in the production of acetylene by the Hüls electric arc process

In the Chemische Werke Hüls electric arc process, acetylene is produced by pyrolyzing hydrocarbons with boiling points up to 200°C in an electric arc. Fine particulate carbon black is produced as a byproduct in such quantities that working up is worthwhile.

Arc black consists of platelet-shaped primary particles as with acetylene black.

5.7.6.2.4 Posttreatment

Species on the carbon black surface:

- physically adsorbed organic substances

The chemical nature of the surface of carbon black is crucial to its applications-related behavior and in the first instance is a function of the manufacturing process. In addition to physically adsorbed organic substances, chemically combined surface oxygen is present on the surface, which is formed upon pyrolysis in the presence of sufficient oxygen and accounts for the acidity of gas blacks. Furnace blacks produced in oxygen-poor conditions with feedstocks with low sulfur contents have an excess of basic metal oxides on their surfaces and have neutral to alkaline properties. The content of physically and chemically bonded species is known as the volatile content, since it can be removed by heating to 950°C in the absence of air.

Oxidative posttreatment can increase the surface-content of acid groups and thereby make the carbon black more hydrophilic

In many cases it is desirable to augment the content of volatile components. This is accomplished by oxidative posttreatment in which acidic surface groups are formed. This oxidation can be carried out at high temperatures both in the liquid phase and in the gas phase with e.g.:

- air,
- NO_2/air-mixtures,
- ozone,
- nitric acid,

- sodium hypochlorite.

This posttreatment is mainly carried out on gas blacks for pigment manufacture. Strongly oxidized gas blacks can contain more than 20% by weight of volatile components.

As the surface concentration of oxygen-containing groups increases the initially hydrophobic carbon black surface becomes increasingly hydrophilic. Such posttreated carbon blacks are preferred for use in aqueous and polar organic media.

5.7.6.3 Properties and Applications

Physical properties important for the utilization of carbon blacks:

- primary particle size,
- structure (aggregate size and shape),
- specific surface area,
- adsorption capacity,
- light absorption capacity.

The following characteristics are of primary importance for carbon black applications:

- primary particle size, manufacturing process controlled,
- carbon black structure, being the degrees of chain formation and branching,
- specific surface of area, variable within wide limits,
- adsorption capacity for water, solvents, binders and polymers,
- light absorption capacity for visible, IR and UV light.

These and other properties are quantified by a multitude of standardized measurement procedures and collated in the form of characteristic values. Table 5.7-7 gives a survey of the physical and chemical characteristics of different carbon black types produced by different processes.

Table 5.7-7. Relationship between Manufacturing Processes and Chemical and Physical Characteristics of different Carbon Black Types (arranged according to increasing particle size).

characteristic	gas black	acetylene black	furnace black	lamp black	thermal black
average particle size (nm)	10 to 30	32 to 42	10 to 80	110 to 120	120 to 500
specific (nitrogen) surface area (m^2/g)[1]	90 to 500	ca. 65	15 to 450	16 to 24	6 to 15
DBP-absorption (ml/100g)[2]	n.a.	150 to 200	40 to 200	100 to 120	37 to 43
oil absorption (g/100g)	220 to 1100	400 to 500	200 to 500	250 to 400	65 to 90
color strength	90 to 130	n.a.	60 to 130	25 to 35	ca. 20
volatile content (%)	4 to 24	0.5 to 2	0.5 to 6	1 to 2.5	0.5 to 1
pH-value	4 to 6	5 to 8	6 to 10	6 to 9	7 to 9

[1] including pores; [2] DPB = dibutyl phthalate

Carbon blacks can be classified according to application sector as rubber blacks, dye or pigment blacks and special blacks. The most important and largest consumer of carbon blacks is the rubber and plastics industry (see Section 5.7.6.1) in which carbon black has been used as a filler, particularly as a reinforcing filler, since the chance discovery in 1912 that carbon black-filled rubber articles exhibit higher abrasion resistance than the then current zinc oxide-filled rubbers.

Main application of carbon blocks:

- filler in the plastics and rubber industry

Important physical characteristics for rubber blacks are, in addition to the average particle size, the DPB (dibutyl phthalate) absorption, which increases with increasing structure (agglomeration of primary particles), and the specific (nitrogen) surface area, which increases with decreasing particle size and increasing porosity of the primary particles. (see Table 5.7-7).

These characteristics correlate to a certain extent with application-related properties. Thus the reinforcing effect of rubber blacks increases with decreasing particle size, increasing nitrogen surface area and increasing DBP-absorption (i.e. with increasing structure). Highly reinforcing carbon blacks are also termed active carbon blacks. They are mainly used in tire treads and conveyor belts, since here high abrasion resistance is required. Semi-active carbon blacks are principally used in tire body mixtures, tire side-walls or inner tubes, where little heat is generated under the mechanical stress. The coarse inactive carbon blacks permit a higher degree of filling and are utilized in mechanically less stressed articles such as gloves, cable insulation or seals. A detailed classification of rubber blacks not only takes the reinforcing properties in finished rubbers into account, but also the vulcanization rate of rubber mixtures and the particle size. Thus rubber blacks are classified according to the ASTM standard with a large letter N for normal curing or S for slow curing, together with a three figure number where the first figure is related to the particle size and the last two figures are randomly assigned numbers. Table 5.7-8 gives a summary of the classification of rubber blacks.

Table 5.7-8. Classification of Rubber Blacks.

classification according to reinforcing effect	figure n according to ASTM classification D 1765	average particle size in nm
active carbon black	1	11-19
	2	20-35
	3	26-30
semi-active carbon black	4	31-39
	5	40-48
	6	49-60
	7	61-100
inactive carbon black	8	101-200
	9	210-500

Further application fields for carbon blacks:

- paint industry,
- manufacture of printing inks,
- plastics industry,
- fiber industry,
- paper industry,
- building industry,
- electrical industry,
- manufacture of hard materials,
- refractory industry.

Pigment blacks (also known as color blacks) are mainly used in the printing ink, paint, plastics, paper and building industries.

The optical properties of pigment blacks are considerably influenced by average particle size, the smaller the particles the higher the color depth and strength. The color strengths in Table 5.7-7 give the fraction of titanium(IV) oxide (white pigment) necessary to endow the carbon black sort with a particular gray tone. The oil absorption is important in dye manufacture and gives a rough estimate of the binder requirement.

In the paint sector fine particulate, oxidatively treated carbon blacks are utilized for deep black paints and coarser particulate carbon blacks for gray or colored paints.

Carbon blacks for black printing inks not only perform as black pigments, but also regulate the viscosity. Posttreatment adapts pigment blacks to particular binder systems (see Section 5.7.6.2.4).

Pigment blacks are needed in the plastics sector, particularly for UV-stabilization of polyolefins.

An application-oriented classification of pigment blacks distinguishes between High Color (HC), Medium Color (MC), Regular Color (RC) and Low Color (LC) pigment blacks. A third capital letter relates to the manufacturing process: furnace black process (F) or gas black process (C, from the historically similar channel black process).

A posttreatment is represented by a further (o), representing "oxidized".

The application-related groups can be correlated with particle size ranges (see Table 5.7-9).

Table 5.7-9. Classification of Pigment Blacks.

designation		average particle size in nm
gas black	furnace black	
HCC	HCF	10 – 15
MCC	MCF	16 – 24
RCC	RCF	25 – 35
	LCF	> 36
gas black, oxidized		
HCC(o)		10 – 17
MCC(o)		18 – 24
RCC(o)		> 25

5.7.7 Activated Carbon

5.7.7.1 Economic Importance

Table 5.7-10 summarizes capacity, production and apparent consumption of activated carbon in 1990 in important industrial regions.

Activated carbon production in 1990 in Western Europe, USA and Japan:
$286 \cdot 10^3$ t/a

Table 5.7-10. Capacities, Production and Apparent Consumption of Activated Carbon in 1990 (in 10^3 t).

	capacity	production	apparent consumption
USA	131	117	116
Western Europe	99	88	83
Japan[1]	76	81	88
total	306	286	287

[1] including Japan foreign participations and activated carbon regenerated by the producer

As a result of stricter environmental measures a 2 to 5% increase in production is expected in the next 5 years.

5.7.7.2 Manufacture

5.7.7.2.1 General Information

Feedstocks for the manufacture of activated carbon:

- uncarbonized, e.g. wood, sawdust, peat, nut shells,
- carbonized, e.g. coal, low temperature lignite coke

A wide range of organic products is suitable as feedstocks for the manufacture of activated carbon. Wood, sawdust, peat, coconut shells and even olive stones are the preferred uncarbonized feedstocks. Of the (already) carbonized feedstocks coal, low temperature lignite coke, charcoal and coke from acid sludges (e.g. from the manufacture of lubricants) are utilized. The properties of activated carbon are very much influenced by the type of feedstock utilized.

Activation processes:

- "chemical activation", particularly for uncarbonized feedstocks,
- "gas activation", particularly for carbonized feedstocks

There are two fundamentally different processes for converting these feedstocks into activated carbon:

- chemical activation,
- gas activation.

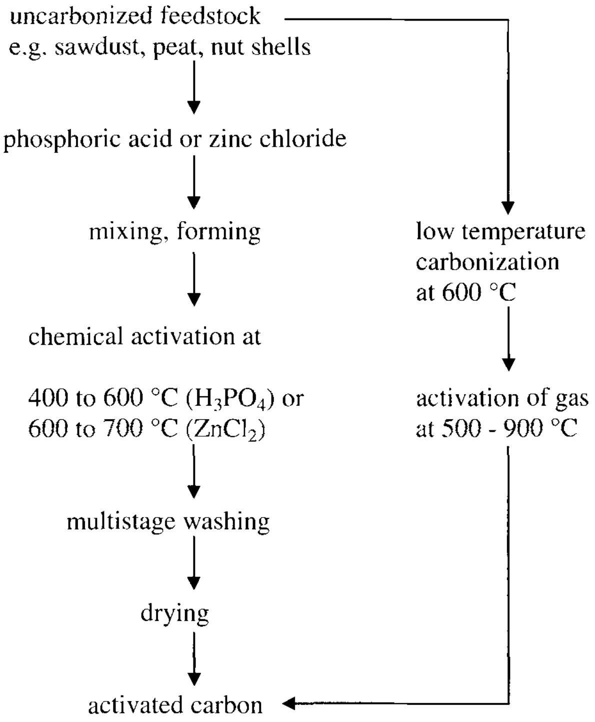


Fig. 5.7-1. Flow Chart for the Manufacture of Activated Carbon from uncarbonized feedstocks by Chemical and Gas-phase Activation

Chemical activation is generally carried out with uncarbonized feedstocks, gas activation generally with carbonized feedstocks. The aim of both processes is to convert the particular feedstock into a material with a high specific surface area (BET values between 400 and 2500 m^2/g) and the optimum pore size distribution for the required application. There are three types of pores:

- micropores with diameters of 0.4 to 2 nm,
- mesopores with diamters of 2 to 50 nm,
- macropores with diameters greater than 50nm.

5.7.7.2.2 Activated Carbon by "Chemical Activation"

The preferred feedstock for "chemical activation" (see Fig. 5.7-1) is wood, in the form of sawdust. These processes are based on the dehydration of the feedstock by reaction with dehydration agents and are particularly effective with cellulose-containing materials. Chemicals such as phosphoric acid or zinc chloride are utilized. Sawdust is mixed with phosphoric acid or zinc chloride, optionally formed, and then heated to 400 to 600°C when phosphoric acid is utilized or to 600 to 700°C when zinc chloride is utilized.

Chemical activation:

dehydration of the feedstock by reaction with phosphoric acid or zinc chloride at 400 to 700°C with subsequent removal of the activation agent by repeated washing

Processing of materials activated using this process is relatively difficult and complex, since on economic and ecological grounds most of the chemicals have to be recovered. They have to be repeatedly washed to obtain an activated carbon which is largely free of activation agent.

Powdered activated carbon is usually produced using these processes, but it is also possible to produce formed carbon by forming (granulating) mixtures of sawdust or peat and activation agent.

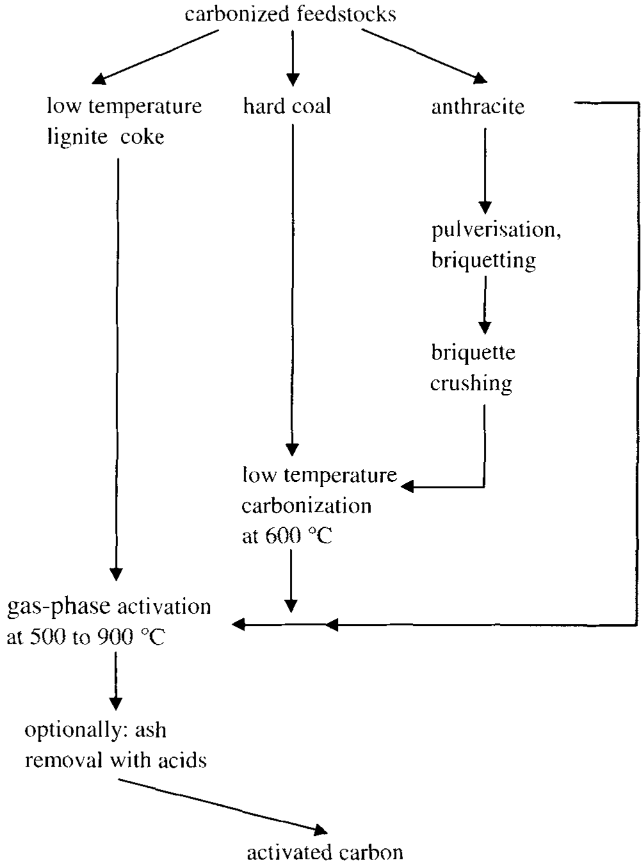


Fig. 5.7-2. Flow Chart of the Manufacture of Activated Carbon from Carbonized Feedstocks by Gas-Phase Activation

5.7.7.2.3 Activated Carbon by "Gas Activation"

Production of pores in a carbon matrix

Gas activation:

production of pores in a carbon matrix by reaction of the carbon with:

- steam,
- carbon dioxide,

or their mixtures at 500 to 900°C

"Gas activation" (see Figs 5.7-1 and 5.7-2) means the formation of pores in a carbon matrix by the removal of carbon by oxidation with steam or carbon dioxide or their mixtures. Whereas oxidation with oxygen proceeds too rapidly, reaction with steam or carbon dioxide proceed at a moderate rate. Since these reactions are significantly endothermic, oxygen is added to the H_2O/CO_2-mixtures, to ensure by exothermic combustion of hydrogen and CO that the reaction temperature does not drop below 800°C.

1) $C + H_2O \longrightarrow CO + H_2$ $\Delta H = 117\ kJ$
2) $C + 2H_2O \longrightarrow 2H_2 + CO_2$ $\Delta H = 57\ kJ$
3) $C + CO_2 \longrightarrow 2CO$ $\Delta H = 159\ kJ$

Activation with steam and carbon dioxide proceeds at 800 to 1000°C.

In the gas activation of uncarbonized feedstocks, a low temperature carbonization process, leading to carbonization, has to be carried out before activation. This low temperature carbonization process has a considerable influence on the pore distribution in the final product.

Coal, which contains a high fraction of volatile components, has to be preoxidized and then carbonized at low temperatures, whereas anthracite can in principle be activated directly. In practice, however, pulverization, briquetting with the aid of a binder, briquette communition and low temperature carbonization are generally carried out. This makes subsequent activation much easier. Lignite low temperature coke can be directly activated.

Coal has generally to be preoxidized and carbonized at low temperatures before gas activation

If formed carbon is manufactured from low temperature lignite coke, a low temperature carbonization of the binder (pitch, organic resin), which consolidates the ground coke, has to be carried out. In this way the binder is also carbonized (see Section 5.7-3).

The ash content of materials such as coal or lignite can, for example, be reduced by acid treatment (with hydrochloric acid, nitric acid) either before or after activation.

Ash removal by acid treatment before or after activation

The methods used by different companies for the manufacture of activated carbon are generally regarded as company know-how, so that nothing is known of the actual units utilized for the manufacture of particular activated carbon types. In practice, units typically used for high temperature reactions, such as rotary kilns, multiple hearth furnaces, fluidized bed reactors, shaft furnaces etc., are used. Activation gas and feedstock can be fed in in cocurrent or countercurrent. Heating can proceed directly or indirectly. In direct heating, the gas formed upon activation (hydrogen, carbon monoxide) is immediately burnt in the reactor. There is also a process in which the gas formed is utilized for the indirect heating of a fluidized bed reactor.

The following units are utilized for gas activation:

- rotary kilns,
- multiple hearth furnaces,
- fluidized bed reactors,
- shaft furnaces.

low temperature linite coke
↓
grinding
↓
bonding, forming
↓
low temperature carbonization at ca. 600 °C
↓
activation at 500–900 °C
↓
formed carbon

Fig. 5.7-3. Flow Chart of The Manufacture of Formed Carbon from Low Temperature Lignite Coke

The residence time in the reactors depends upon the particular process conditions used and has a considerable influence upon yield, pore size distribution and BET-surface area of the activated carbon produced.

5.7.7.3 Reactivation and Regeneration of Used Activated Carbon

Reactivation of used activated carbon (especially granular and formed carbon) mainly accomplished by steam treatment analogously to activation

Reactivation is effected using the methods of gas activation, generally using steam as the activating gas. Depending upon the quantity, reactivation is carried out by the manufacturer or by the user. The reactivation of formed and granulated carbon is currently the most important. The reactivation of powdered activated carbon has latterly become more widely practised despite its greater technical difficulty. The gaseous, in some cases toxic, byproducts liberated upon reactivation have to be rendered harmless by subsequent combustion.

Solvent vapor-saturated gas purification activated carbon is regenerated with steam

Activated carbon utilized for gas purification, e.g. for the adsorption of solvent vapor, can be regenerated by desorption with steam at 120 to 140°C. The activated carbon then has to be dried. In special cases other types of regeneration are possible.

5.7.7.4 Applications of Activated Carbon

Activated carbon is generally used as granules or as a powder, the use of granular activated carbon slightly exceeding that of the powdered material. In Western

Europe increasing quantities of extruded activated carbon cylinders are being produced, 2 to 12 mm in length and 0.8 to 5 mm thick. Japanese manufacturers supply thin activated carbon fibers in small quantities (< 1000 t/a).

Pulverized activated carbon is mainly utilized in the liquid phase in the purification of foods, pharmaceuticals and chemicals, the activated carbon being separated by filtration. The used powdered carbon is not, as a rule, regenerated. The high adsorption effect of powdered material, the flexibility of batch operation and the low investment costs for filtration compensates these disadvantages.

Granulated activated carbon is thus preferred, if a high volume stream continuous purification operation makes it necessary. Thus gas purification is almost exclusively carried out in fixed-bed adsorbers with granulated carbon. Potable water in Western Europe and Japan is preferably freed of organic impurities by percolation over granulated activated carbon.

Table 5.7-11 gives economic data over the different application fields for activated carbon.

Table 5.7-11. Applications of Activated Carbon (all types) in Different Industrial Regions in 1990 (in 10^3 t).

	USA	Japan	Western Europe
applications in the liquid phase:			
water purification:	43.2	31.1	19.1
potable water	20.9		
effluent	18.2		
food:	19.8	8.8	26.5
saccharides	15.0	3.12	
drinks		3.35	
chemicals and pharmaceuticals	10.7	11.8	19.9
other	12.9	2.9	
applications in the gas phase:			
gas purification:	22.1	20.7	17.4
cigarette filters	0.8	8.0	
solvent recovery	5.0	1.9	

Applications of activated carbon:

in the liquid phase:

- potable water and effluent processing,
- decolorizing of natural products such as sugars, drinks, salad oils,
- purification of chemicals,
- gold production

in the gas phase:

- solvent recovery,
- petrol tank venting in cars,
- ambient air and exhaust air purification,
- in cigarette and gas-mask filters,
- as catalysts or catalyst supports.

The main application in the liquid phase is in potable water processing. In the USA large quantities of beet sugar are decolorized with activated carbon (in Europe sulfite is generally used). Other applications in the food sector are the purification of glucose and other saccharides, the purification of glutamic acid, treatment of salad oil and many drinks. In gold production (carbon-in-pulp process), activated carbon is utilized for the adsorption and concentration of gold-cyanide complexes.

In purifying mixtures of gas-forming substances, activated carbon is utilized in cigarette filters (mainly in Japan), in gas-mask filters, in venting filters for car petrol tanks (mainly in the USA and Japan) and in air conditioning units for the purification of ambient air. Industry also utilizes activated carbon for the recovery of a multiplicity of volatile solvents from the ambient air, for adsorption of poisonous or noxious gases (e.g. hydrogen sulfide) and as catalysts or catalyst supports.

References for Chapter 5.7: Carbon Modifications

Diamond

Reviews:

Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 1074 – 1096, John Wiley & Sons, New York.

Römpp Chemie Lexikon, 9. Aufl., Bd. 2, S. 926 – 930, Georg Thieme Verlag, Stuttgart (1990).

Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 5, 96 – 98, VCH Verlagsgesellschaft, Weinheim, New York.

Commercial Information:

Mining Journal, 100 – 101, Feb. 8, 1991.

Diamond & Structural Carbon News, June 1994.

Natural Graphite

Reviews:

Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 1097 – 1117, John Wiley & Sons, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 5, 99 – 110, VCH Verlagsgesellschaft, Weinheim, New York.

Commercial Information:

Chemical Economics Handbook, SRI International, Menlo Park, California, 731.5000, (1994).

Synthetic Carbon and Synthetic Graphite

Reviews:

Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 953 – 1011, John Wiley & Sons, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 5, 103 – 120, VCH Verlagsgesellschaft, Weinheim, New York.

Commercial Information:

Chemical Economics Handbook, SRI International, Menlo Park, California, 731.5000, (1994).

Special Carbon and Graphite Types

Reviews:

Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 1012 – 1015, John Wiley & Sons, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 5, 120 – 124, VCH Verlagsgesellschaft, Weinheim, New York.

Carbon Black

Reviews:

Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 1037 – 1074, John Wiley & Sons, New York.

Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 5, 140 – 158, VCH Verlagsgesellschaft, Weinheim, New York.

Was ist Ruß?", Degussa-Company brochure.

Commercial Information:
Chemical Economics Handbook, SRI International, Menlo Park, California, 731.3000, (1995).

Activated Carbon
Reviews:
Kirk-Othmer, Encyclopedia of Chemical Technology. 1992. 4. Ed., Vol. 4, 1015 – 1037, John Wiley & Sons, New York.
Ullmann's Encyclopedia of Industrial Chemistry. 1986. 5. Ed., Vol. A 5, 124 – 140, VCH Verlagsgesellschaft, Weinheim, New York.

Commercial Information:
Chemical Economics Handbook, SRI International, Menlo Park, California, 731.2000, (1992).

Activated Carbon Fibers
Suzuki, M., Carbon **32**, 577 – 586 (1994).

Fullerenes
Krätschmer, Synthetic Metals **70**, 1309 – 1312 (1995).
Krätschmer, *Vom Fuller bis zu Fullerenen, Beispiele einer interdisziplinären Forschung*, Vieweg, Braunschweig, (1996).

5.8 Fillers

5.8.1 General Information

Inorganic fillers are fine particulate solids, which differ from inorganic pigments in their refractive indices: fillers generally have refractive indices < 1.7 (vs. vacuum) and pigments have higher refractive indices. An additional distinguishing characteristic is given by the term filler itself implying that these materials should fill and hence be a major component. Pigments on the other hand are mainly utilized in small quantities. Both distinguishing characteristics are unsatisfactory in as much as a filler with n < 1.7 in a suitably chosen matrix can exhibit a certain covering power thus exhibiting a pigment-specific property, which is in fact used industrially. On the other hand certain fillers are only used in small quantities. The borderline is thus fluid.

Distinguishing characteristics of inorganic fillers for inorganic pigments:

- refractive indices < 1.7 (vs. vacuum),
- generally a major component of the particular formulation.

Fillers have two functions: to make the product less expensive (classic definition) and to improve an existing property or add a property compared with the unfilled product. The two functions cannot always be combined. Furthermore, the utilization of a filler often makes the manufacture of the product easier.

Fillers should:

- make a product less expensive,
- improve the product's properties.

Fillers often make the manufacture of the product easier.

Inorganic fillers can be divided into natural and synthetic fillers. The former are obtained by the mechanical or chemical processing of naturally occurring minerals and the latter by chemical synthesis involving not only inorganic but also organic raw materials.

Classification of inorganic fillers into:

- natural fillers,
- synthetic fillers.

In this chapter, the most important inorganic fillers will be dealt with, with the exception of fibers (see Section 5.2) and carbon blacks (see Section 5.7.6).

5.8.2 Economic Importance

In the filler sector there are hardly any reliable market surveys, which is at least partly due to the variety of types and the large number of manufacturers.

Quantitywise, natural fillers dominate with ca. 70 to 80% by weight of the total consumption, calcium carbonate accounting for the largest share.

The high growth rates in the past, particularly in the plastics and rubber sectors (see Table 5.8-1), will not continue. After stabilization in 1991, an annual growth rate of ca. 5% is expected in the future.

Table 5.8-1. Estimated Consumption of Fillers for Plastics (excluding fibers) in the USA in 10^3 t (Business Communications Co., Stamford/Conn.).

	1976	1980	1985	1990
carbonates	770	1093	1776	2886
SiO_2 (quartz, cristobalite)	29	39	74	140
silicates: talc	43	113	181	293
kaolin (clays)	59	76	99	130
mica	0.4	0.5	0.5	0.6
others	5	8	13	21
glass (flakes, solid and hollow balls)	5	7	15	31
aluminum hydroxide	77	150	210	294
other mineral fillers	11	11	13	15

5.8.3 Natural Fillers

5.8.3.1 Silicon-Based Fillers

Silicon-based natural fillers classified into:

- hydrated silicas and silicon dioxide: "silicas",
- "silicates".

Natural silicon-based fillers are divided into hydrated silicas and silicon dioxide (silicas) on the one hand, and silicates, on the other. There is no sharp dividing line between these two groups, since the former do not always occur in a pure form and may contain silicates together with other impurities. Since their main component is SiO_2, this classification will be used here.

Natural fillers with silicon dioxide as main component:

- quartz,
- cristobalite,
- tripolite,
- novaculite,
- kieselguhr (diatomaceous or infusorial earths),
- siliceous earth,

Silicon dioxide occurs naturally mainly as quartz, partly in very large deposits (quartz gravel, quartz sand). Cristobalite is seldom found, but is produced synthetically (see Section 5.8.4.1.5). Tripolite, a special quartz type resulting from the weathering of sandstone, and novaculite, a lamellar-shaped microcrystalline quartz found in Arizona (USA), are of little importance. Novaculite has a large number of silanol groups on the surface and functions as an active reinforcing filler. The kieselguhrs, also known as diatomaceous or infusorial earths, contain between 70 and 90% by weight of amorphous silicon dioxide and are formed from kiesel algae found in both freshwater and seawater. Aluminum silicate is mostly present in kieselguhr as a minor constituent. The kieselguhrs should not be confused with siliceous earth, a mineral of purely inorganic origin which contains 70 to 75% by weight of quartz and up to 25 to 30% by weight of kaolinite (see below) only found in the neighborhood of Neuberg on the river Danube (Neuburg siliceous earth).

Natural silicate fillers:

- talc,
- pyrophyllite,
- kaolin (china clay),
- mica,
- muscovite,
- phlogopite,
- vermiculite,

Of the naturally occurring silicates, talc is a very important and versatile filler. Talc is a magnesium silicate with a lamellar structure and when pure has the composition $3MgO \cdot 4SiO_2 \cdot H_2O$. In Europe large deposits are found in the Fichtel Mountains, on the fringes of the Eastern and Southern Alps and in Scandinavia. Pyrophyllite is also a lamellar silicate, but with aluminum as the cation: $Al_2O_3 \cdot 4SiO_2 \cdot H_2O$. It is similar in properties to talc and is used for similar applications. Another aluminum silicate with a lamellar structure, kaolinite $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, is the main constituent of kaolin, which in the English Speaking World is mostly known an "china clay" due to its original use in the manufacture of porcelain (see Section 5.5.4.1). Kaolin is mainly formed by the weathering or hydrothermal decomposition of feldspars. It is the second most important filler in the rubber industry, after carbon black. Kaolin is also utilized in calcined form in polymers. The two largest deposits are in Cornwall (Great Britain) and Georgia (USA). Minerals in which aluminum is substituted on part of the silicon sites of the anion layer (aluminosilicates), such as micas and particularly muscovite (with potassium as the compensating ion), phlogopite (potassium and magnesium) and vermiculite (magnesium), are also used as fillers. Apart from these laminate-structured silicates one silicate with a band

- wollastonite,
- perlite.

structure is used as a filler: wollastonite $CaSiO_3$. The last natural silicate filler worthy of mention is perlite, which is manufactured from volcanic glassy stone by thermal expansion (see Section 5.3.6.3) and is utilized both in unground and ground form.

5.8.3.2 Other Natural Fillers

Natural carbonate fillers:

- calcite,
- dolomite,
- chalks.

The most important natural fillers are calcium and magnesium carbonates. Of the numerous deposits, those suitable for processing are well-crystallized calcite ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$) as well as chalks ($CaCO_3$), which are formed from the shells of maritime microorganisms and possessing a loose earthy structure.

Natural sulfate fillers:

- heavy spar,
- light spar.

Of the naturally occurring metal sulfates only heavy spar ($BaSO_4$) is important for filler manufacture. Smaller quantities of gypsum ($CaSO_4 \cdot 2H_2O$, light spar) are also processed to fillers.

- micaceous iron oxide.

Lamellar-shaped crystalline haematite (α-Fe_2O_3) can also be used as a filler. Due to its morphological relationship to micas, it is known as micaceous iron oxide.

5.8.3.3 Beneficiation of Natural Fillers

Beneficiation:

- washing,
- coarse crushing,
- coarse to medium crushing,
- classification,
- grinding
- filtration,
- drying,
- sieving.

The route from mineral to filler is similar for all the above-mentioned materials. The important beneficiation operations after mining from deposits are: washing, coarse crushing, coarse to medium crushing, classification, wet or dry grinding, filtering, drying and sieving. They may not be performed in this order and several of the steps may in fact be repeated. In the case of microcrystalline, loose raw materials such as siliceous earth, talc, kaolin or chalk, elutriation and flotation processes are used in beneficiation (see Section 5.5.4.2, kaolin). In the grinding of mica, care must be taken to avoid destroying its lamellar structure. In some cases colored impurities are converted into colorless compounds with the help of additives or washed out (bleaching). Sometimes a calcination step is used. Natural fillers posttreated with organic compounds are increasingly becoming available.

5.8.4 Synthetic Fillers

Some fillers have to be synthesized, because they do not occur naturally. Some fillers are synthesized, despite the fact that they occur naturally in sufficient quantities and with sufficient purity, because even with the most careful processing it has not proved possible to realize all the potentially available properties.

Reasons for the synthetic manufacture of fillers:

- no naturally available deposits,
- realization of better properties than those of the natural fillers.

5.8.4.1 Silicas and Silicates

This group of fillers include pyrogenic, i.e. thermally produced, or wet chemically produced silicas, wet chemically produced silicates, glasses and cristobalite.

5.8.4.1.1 Pyrogenic Silicas

The most important process for the manufacture of pyrogenic silicas is flame hydrolysis in which tetrachlorosilane is decomposed in an oxyhydrogen flame:

Pyrogenic silicas (Aerosils®) are manufactured by three processes:

- flame hydrolysis,
- electric arc process (currently unimportant),
- plasma process (not yet operated industrially).

$$\begin{array}{lcl} 2\,H_2 + O_2 & \longrightarrow & 2\,H_2O \\ SiCl_4 + 2\,H_2O & \longrightarrow & SiO_2 + 4\,HCl \\ \hline 2\,H_2 + O_2 + SiCl_4 & \xrightarrow{\text{ca. } 1000\,^{\circ}\text{C}} & SiO_2 + 4\,HCl \end{array}$$

The silica formed is, like all synthetic silicas, amorphous according to X-ray diffraction spectra. Their most important properties are given in Table 5.8-2.

The oldest, but in the meantime least significant process for the production of fine particulate silica, is the oxidation of gaseous silicon monoxide with air. Quartz sand and fine particulate coke can, for example, be used as starting materials and are reacted with one another in an electric arc as follows:

$$\begin{array}{l} SiO_2 + C \longrightarrow SiO + CO \\ SiO + CO + O_2 \longrightarrow SiO_2 + CO_2 \end{array}$$

Variants in which a plasma is used as the energy source instead of the electric arc, are not yet operated industrially.

5.8.4.1.2 Wet Chemically Manufactured Silicas and Silicates

Silicas and silicates are wet chemically manufactured using:

- precipitation processes,
- gel processes,
- hydrothermal processes.

The wet chemical manufacturing processes can be divided into precipitation processes, gel processes and hydrothermal processes, of which the precipitation processes are the most important.

Precipitation processes:
water glass + acid

In precipitation processes acid is added to a water-glass solution and acid, generally H_2SO_4, simultaneously with water in a large agitator vessel.

$$Na_2SiO_3 + H_2SO_4 \longrightarrow SiO_2 + Na_2SO_4 + H_2O$$

Silica properties can be influenced:

- speed of acid addition,
- intensity of stirring,
- working up procedure.

Colloidal primary particles are thereby formed which agglomerate as the reaction proceeds and finally coalesce to aggregates. Metallic ions (Ca, Mg) are added to accelerate the often delayed precipitation. These ions are subsequently extracted with acid. The process can be very precisely controlled with respect to the properties of the required product. Further control can be achieved during the working up (filtration, washing, drying and grinding). Table 5.8-2 gives the important properties of silicas manufactured by precipitation.

If the water-glass solution is reacted with alkaline earth or aluminum salts, silicates are obtained instead of silicas.

Gel processes:
acid + water glass (generally)

Silica gels dried under supercritical conditions are called aerogels

In contrast to the precipitation processes, the formation of flocculant precipitates is avoided in gel processes. Normally the sequence of addition is simply reversed, the water-glass solution being added to the acid with the pH of the solution remaining acidic. Initially an unstable hydrosol is formed, which after a time becomes a hydrogel. This hydrogel is carefully washed, then dried and finally ground. A special drying process using dewatering under supercritical conditions leads to so-called aerogels. Aerogels are characterized by high nanoporosity. The properties of silica gels and aerogels are given in Table 5.8-2.

Table 5.8-2. Properties of differently manufactured Silicas. [from H. Ferch, Progr. Org. Coat. **9**, 139 (1981)]

	Primary particle size[1] (in nm)	Specific surface area[2] (in m^2/g)	Tap volumes[3] (in mL/100g)	porosity
Aerosils® (by flame hydrolysis)	5 to 50	50 to 600	1000 to 2000	nonporous
precipitated silicas	5 to 100	30 to 800	200 to 2000	low
silica gels	3 to 20	250 to 1000	100 to 200	very high
aerogels	3 to 20	250 to 400	800 to 2000	high

[1] determined by electron microscope
[2] BET values
[3] DIN 53194

In the hydrothermal process, aqueous suspensions of quartz sand and chalk are heated under pressure:

$$CaO + SiO_2 \xrightarrow{H_2O} CaSiO_3\ aq$$

The proportions can be varied within wide limits. The calcium can be largely washed out with acid. Working up proceeds in the usual above-described manner.

Hydrothermal process: fairly insignificant

5.8.4.1.3 Posttreatment of Silicas

The purely thermal posttreatment of dried silicas, which depending upon the temperature leads to more or less strong splitting off of water, is only of major importance for silica gels and is termed "activation".

Physical posttreatment of silicas: heating

Chemical posttreatment is already widely utilized and will probably be even more widely utilized in the future. It renders hydrophilic silica organophilic or hydrophobic by treating preferably pyrogenic silica, but also precipitated silicas, with organic or element-organic compounds, which react with the silanol groups forming chemical bonds:

$$\equiv Si\text{-}OH + Cl\text{-}SiR_3 \longrightarrow \equiv Si\text{-}OSiR_3 + HCl$$

$$R = Me, Et\ etc.$$

or are strongly adsorbed on the surface. Hexamethyldisilazane, alkoxyalkylsilanes and polydimethylsiloxanes are industrially utilized in addition to chloroalkylsilanes.

Chemical posttreatment of silicas with:
- chlorosilanes,
- aminosilanes,
- silicones,
- alcohols,
- amines and quaternary ammonium compounds,
- isocyanates,
- waxes,

and other compounds.

It is possible to endow the surface of silicas with functional groups e.g. by treatment with silane adhesion promoters $X_3Si{-}R{-}Y$, where Y is the functional group

5.8.4.1.4 Glasses

Glass as a filler in the form of:
- solid beads,
- hollow beads,
- flakes.

Whereas finely ground glass is only of interest for special applications, a market for precisely manufactured glass beads has developed fairly quickly. This is due to their geometric shape i.e. their surface to volume ratio, the absence of the sharp edges of other fillers and in the case of hollow beads their low density (0.3 to 0.6 g/cm^3). Glass beads lead to a filled product with a strongly isotropic property spectrum. They are, in the meantime, deliverable with diameters from 1 µm upwards (preferred diameters: 4 to 44 µm). In addition glass in the form of small flakes can also be utilized as a filler. They are usually posttreated with adhesion promoters to increase interaction between the glassy filler and the matrix (see Section 5.8.4.1.3).

5.8.4.1.5 Cristobalite

Cristobalite from quartz by heating in the presence of catalysts

Cristobalite (see Section 5.8.3.1) is produced in large quantities by thermal treatment of quartz sand. The transition temperature, generally ca. 1100°C, can be reduced by adding catalysts. The most important advantage of cristobalite, in comparison with quartz, its much higher whiteness.

5.8.4.2 Aluminum Hydroxide

Primary raw material for aluminum hydroxide manufacture is bauxite

The raw material for the manufacture of aluminum hydroxide is bauxite, a mineral with ca. 45 to 60% Al_2O_3 in the form of hydrargillite (gibbsite), böhmite and diaspore with iron oxides or hydroxides, silica (as kaolinite) and titanium dioxide as minor constituents. The largest deposits are to be found in Africa and Australia.

Continuous digestion of bauxite with sodium hydroxide in autoclaves or tubular reactors at 140 to 250°C under pressure using the Bayer process

Bauxite is digested with sodium hydroxide under pressure and at high temperature using the Bayer process, whereupon soluble sodium aluminate is formed:

$$Al(OH)_3 + NaOH \longrightarrow NaAl(OH)_4$$

in the form of aquo-complexes. After pressure release, the aluminate liquor is cooled, diluted and freed of red mud by decantation in gravity concentrators. Subsequent fine filtration removes the small residue of insoluble constituents. The clarified liquor, still at ca. 95°C, is an important starting point for aluminum hydroxide manufacture.

Upon cooling, the liquor becomes supersaturated and aluminum hydroxide precipitates out in a reversal of the formation reaction. The solution is seeded with solid aluminum hydroxide to increase the precipitation rate. The hydrargillite formed is filtered off and washed. A large part of it is mashed and returned as seed for the following precipitation and the rest is carefully dried. Coarse particulate aluminum hydroxide is obtained, which can be processed by grinding and sieving to particulate particle size fractions between 10 and 100 µm.

In the "normal" Bayer process coarse particulate aluminum hydroxide is formed, which is processed by grinding and sieving to particle sizes between 10 and 100 µm

Fine particulate aluminum hydroxide is obtained either by introducing special seeding processes into the Bayer process or by precipitation processes: precipitation from cooled and strongly diluted aluminate liquors.

- precipitation by neutralization of aluminate liquor with e.g. CO_2, $NaHCO_3$, H_2SO_4,
- precipitation from aluminum salt solutions with bases such as e.g. NH_3, amines, NaOH,
- precipitation from aluminum salt solutions with sodium aluminate solutions.

Fine particulate aluminum hydroxide (particle size < 1 µm) obtained by:

- modified Bayer processes,
- precipitation processes.

Properties can be influenced during the precipitation processes by:

- temperature,
- pH value,
- rate of precipitation,
- concentration,
- ripening time.

The average particle sizes of commercial products are generally below 1 µm with specific surface areas (BET) generally between 4 and ca. 60 m^2/g. The $Al(OH)_3$-content is > 99.5% by weight. Products posttreated with organic compounds are also available.

5.8.4.3 Carbonates

Calcium carbonate is virtually the only important filler in the processing industry. Barium and magnesium carbonates are only manufactured for special purposes and will thus only be briefly mentioned here.

Synthetic carbonate fillers:

- calcium carbonate,
- (barium carbonate),
- (magnesium carbonate).

Calcium carbonate fillers are synthesized by precipitation processes. This accounts for the usual term "ccp" being an abbreviation of: calcium carbonicum praecipitatum. The following three precipitation processes are used:

Manufacture of calcium carbonate (ccp) by precipitation processes:

(1): neutralization of milk of lime with carbon dioxide

Product properties influenced by:

- temperature,
- concentration,
- pressure.

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \qquad (1)$$

This process is directly coupled to the manufacture of quicklime. Milk of lime is obtained by slaking and then carbon dioxide, produced by the calcining of limestone, is passed into the suspension forming calcium carbonate (see Sections 5.3.2.3 and 5.3.2.4).

(2) and (3): reaction of calcium salts, which are formed as byproducts, with carbonates in aqueous solutions

$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3 + 2\ NaCl \qquad (2)$$

Calcium chloride is formed as a waste product in the manufacture of sodium carbonate by the Solvay process (see Section 3.1.1.3.3).

$$Ca(NO_3)_2 + 2\ NH_3 + CO_2 + H_2O \longrightarrow CaCO_3 + 2\ NH_4NO_3 \qquad (3)$$

Calcium nitrate is produced as a byproduct in the manufacture of fertilizers (see Section 2.1.2.4).

Process (1) supplies purer products and is easier to control than processes (2) and (3).

The calcium carbonate can precipitate either with a calcite or an aragonite structure and can be obtained with a pure white color. The average particle size is in the range 0.01 to 1 µm with specific surface areas (BET) in the range 5 to 100 m^2/g. The surface treatment of calcium carbonate with organic compounds is also becoming increasingly important.

5.8.4.4 Sulfates

Only synthetic sulfate filler:
barium sulfate (blanc fixe)

Blanc fixe *powder*:
by reacting barium sulfide with sodium sulfate in aqueous solution and working up the precipitated product

The only synthetic sulfate manufactured as a filler is barium sulfate and it is known as "blanc fixe". As with calcium carbonate it is produced by precipitation reactions:

$$BaS + Na_2SO_4 \longrightarrow BaSO_4 + Na_2S \qquad (1)$$

The barium sulfide is obtained by reducing heavy spar, with as little silica as possible, with coke. The reaction product is filtered, washed and ground. It is pure white and has particle sizes between ca. 0.3 and 10 µm.

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2\,NaCl \quad (2)$$

Commercially available blanc fixe qualities in the form of ca. 25 to 30% aqueous pastes (blanc fixe paste) are manufactured by reacting barium chloride solution with a solution of Glauber's salts. The barium chloride solution is produced in the manufacture of lithopone or is produced by the reaction of barium sulfide with hydrochloric acid.

Blanc fixe *pastes*:

by reacting barium chloride with sodium sulfate in aqueous solution and working up the suspension

5.8.4.5 Other Synthetic Fillers

For some time titanium oxide and aluminum oxide manufactured by flame hydrolysis (see Section 5.8.4.1.1) have been marketed as fillers.

5.8.5 Properties and Applications

The multitude of described fillers make it impossible to describe the properties of every one. Their application possibilities are not only dependent upon their chemical composition but also to a large extent upon their physical properties and their posttreatment, if any. Purity is an additional criterion, particularly in the case of natural fillers.

A distinction between inactive and active fillers is at present hardly relevant, since the properties of the final product depend more or less strongly upon all the fillers utilized and their use has for a long time not been primarily determined in terms of cost reduction. The efforts of the filler producers in the direction of improved processing methods and dedicated manufacturing processes take this development into account. The surface treatment of natural and synthetic fillers has also acquired great importance. For years there have been products which in the classic sense are not fillers at all, but are in fact active substances (e.g. silica aerosols). Apart from any cost reduction considerations, fillers have essentially the following functions:

- rheological:
  thickening and, if necessary, rendering thixotropic by controlled adjustment of the time dependent structural

Application possibilities of fillers substantially determined by:

- particle size,
- particle shape,
- particle structure,
- specific surface area,
- density,
- color,
- refractive index,
- interaction with the matrix,
- chemical composition,
- type of surface treatment.

Trend:

away from purely cost-reducing fillers to high grade multifunctional fillers viscosity (e.g. talc, wollastonite, kaolin, silica aerosols), in general: change of the flow behavior in lacquers, coatings, printing inks, liquid polymers, sealing compounds;

- optical properties:
  - improvement in whiteness and hiding power as a (partial) replacement for real white pigments e.g. by synthetic silicates, blanc fixe, finest particulate calcium carbonate (homogeneous pigment distribution, supercritical pigmentation) in emulsion paints;
  - as white pigments in paper coating dyes: kaolin, ground natural calcium carbonate;
  - gloss reduction of lacquers and printing inks: wet chemically manufactured silicas, kieselguhrs;
  - opacification of plastics: barium sulfate;
  - as a mineral UV-absorber: mica;
- mechanical properties:
  - reinforcing agent for rubber: e.g. calcium carbonate, synthetic silicas (for the industrial utilization of reinforcing carbon black types see Section 5.7.6.3);
  - improvement of the mechanical properties of plastics: e.g. quartz, novaculite, wollastonite, glass microbeads and flakes ;
- improvement in the resistance of paints and coating to weathering and chemicals (corrosion protection) with e.g. mica, micaceous iron oxide, barium sulfate.

Fillers can influence:

- rheological behavior,
- optical properties,
- resistance to weathering and chemicals.

and in addition can:

- improve in the dispersion behavior of pigments,
- increase fire resistance (aluminum hydroxide),
- improve the surface of paper,
- change the adhesion behavior between foils,
- reduce weight (perlite, hollow glass microbeads).

Other functions of fillers are listed in the marginal notes. The main utilization areas of the above-discussed fillers are summarized in Table 5.8-3.

Table 5.8-3. Main Application Fields for Fillers.

filler	plastics	rubber	lacquers, paints, coatings	printing inks	paper
natural SiO_2:					
quartz	X		X		
tripolite	X				
novaculite	X				
kieselguhr	X	(X)	X		(X)
siliceous earth		X	X		
synthetic SiO_2:					
cristobalite	X		X		
pyrogenic silica	(X)	(X)	X		

filler	plastics	rubber	lacquers, paints, coatings	printing inks	paper
wet chemical silica	X	X	X	X	
natural silicates:					
talc, pyrophyllite	X	X	X		(X)
kaolin	X	X	X		X
mica	X	X	X		
wollastonite	X		X		
perlite	X		(X)		
synthetic silicates:					
wet chemical silcates	(X)	X	X		X
glass (flakes and full and hollow microspheres)	X		X		
micaceous iron oxide:			X		
$CaCO_3$:					
calcite, dolomite	X		X		X
chalk	X	X	X		X
ccp (synthetic carbonate)	X	X	X	X	
aluminum hydroxide	X	(X)	X	(X)	(X)
$BaSO_4$:					
heavy spar	X		X		
blanc fixe	(X)	(X)	X	(X)	(X)
$CaSO_4$:					
light spar		(X)		X	

References for Chapter 5.8: Fillers

Ullmann's Encyclopedia of Industrial Chemistry. 1992. 5. Ed., Vol. A 23, 583 – 660, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1994. 4. Ed., Vol. 10, 745 – 760, John Wiley & Sons, New York.

Katz, H. S., Milewski, J. V. 1987. *Handbook of Fillers and Reinforcements for Plastics*. Van Nostrand Rheinhold Co., New York.

Gaechter, R. and Müller, H. 1990. *Taschenbuch der Kunststoff-Additive*. 3. Ausgabe, Carl Hanser Verlag, München.

Seymour, R. B. Popular Plastics and Rubber **25(4)**, 13 – 19 (1991).

Chem. Week. **149(14)**, 40 (1991).

Kastien, H. Applica **87(11)**, 6 – 12 (1980).

5.9 Inorganic Pigments

5.9.1 General Information and Economic Importance

Pigments: fine paritculate inorganic colorants insoluble in the binder

The DIN definition of the term colorant includes both dyes and pigments. In contrast to dyes, pigments are practically insoluble in the binder. They consist of solid particles generally with a uniform chemical composition and are mainly transition metal oxides, oxide hydrates, sulfides, silicates, sulfates or carbonates (see Table 5.9-1).

Table 5.9-1. Inorganic Pigments: a Survey.

	oxides	sulfides	chromates	various
white	titanium dioxide zinc oxide	zinc sulfide lithopone ($ZnS/BaSO_4$)		white lead (formerly)
red	red iron oxide red lead	cadmium red cadmium orange	molydate red	
yellow	yellow iron oxide nickel titanate yellow chromium titanate yellow	cadmium yellow	chrome yellow zinc chromate	($BiVO_3$) bismuth vanadate
green	chromic oxide green spinel green		chrome green	
blue	cobalt blue	ultramarine		manganese blue prussian blue
brown	brown iron oxide ferrites			iron oxide & pigment blacks
black	black iron oxide spinel black			pigment blacks

Pigment blacks (see Section 5.7-9) and functional pigments for which optical effects are unimportant but whose functions are important (e.g. magnetic pigments) are also included. Table 5.9-2 gives the classification of inorganic pigments according to DIN 55 943, their functions and a few examples.

Table 5.9-2. Classification of Inorganic Pigments.

type		function	examples
natural inorganic pigments			ochre, sienna, graphite, green earth
synthetic inorganic pigments			
1	uncolored pigments		
1.1	white pigments	mainly nonselective light scattering	titanium dioxide, zinc sulfide, lithopone, zinc oxide
1.2	black pigments	mainly nonselective light absorption	pigment blacks, black iron oxide
2	colored pigment	color by selective light absorption mostly with light scattering	iron oxide, cadmium sulfide, ultramarine, chrome yellow, cobalt blue
3	specialty pigments		
3.1	stains and oxides (pigments)	as for colored pigments	cobalt-aluminum-spinel, nickel-chromium spinel, nickel titanate yellow
3.2	corrosion-inhibiting pigments	electrochemical, chemical or physical protection of metallic surfaces	red lead, zinc potassium chromate, zinc phosphate, zinc dust
3.3	magnetic pigments	information storage by magnetization	magnetic iron oxides, chromium dioxide, metallic iron pigments
3.4	luster pigments	luster effect by directed reflection of light from oriented flake-shaped metallic or strongly refracting pigment particles	
3.4.1	metal effect pigments		gold bronze, aluminum bronze, copper bronze
3.4.2	pearlescent pigments	pearlescence is due to multiple reflection on parallelly oriented lamellae.	TiO_2-coated mica, basic lead chromate, mother of pearl pigments
3.4.3	interference pigments	lamellae of a particular thickness exhibit additional iridescent effects by interference	
3.5	luminescent pigments		
3.5.1	fluorescent pigments	selective light absorption and undelayed luminescence excited by high energy radiation (e.g. X-rays, cathode rays, UV and short wavelength visible light)	pigments for cathode ray and X-ray screens, fluorescent lamps, "radioactive" luminous pigments
3.5.2	phosphorescent pigments	selective light absorption and scattering, superimposed on delayed luminescence excited by high energy radiation	zinc and alkaline earth sulfides doped with heavy metal ions (e.g. Cu, Ag, Au, Mn etc.)

Important pigment properties:
- hiding power,
- coloring power (colored pigments),
- color purity,
- lightening power (white pigments).

Important pigment properties are their hiding power, their lightening power in the case of white pigments and their coloring power in the case of colored and black pigments. In pigmented systems the perceived color, as for all nonluminescent body colors, is based on subtractive color mixing. Colored pigments absorb a particular part of the spectrum of the illuminating light, so that the eye only sees the residual spectrum.

White pigments are characterized by their nonselective light scattering and black pigments by their nonselective absorption in the whole of the visible spectrum.

The selective light absorption of colored pigments is due to the interaction of visible light with the valence electrons in the solid. The electronic structure and energy levels of a solid and hence the electronic transitions are determined by the elements present (cations and anions), their oxidation state and their electronic configuration as well as by the lattice geometry. The coloring power of a pigment increases with the number of light absorption-induced electronic transitions. The steeper the absorption edge, the brighter the color will be.

High refractive index and optimum particle size are prerequisites for high light scattering power

The scattering power of pigments, and therefore the hiding power of a pigment coating, mainly depend upon the refractive index of the pigment and its particle size. For high scattering power the refractive index should be as high as possible above that of the binder. For a particular refractive index, there is an optimum particle size to achieve maximum scattering power. This optimum particle size is between 0.1 and 1 μm for white and colored pigments. In large scale manufacture a particle size distribution is required which is as narrow as possible.

The increasingly colored nature of our surroundings has meant increasing use of colorants. Since many colored materials contain at least some inorganic pigment, their demand has steadily increased.

Worldwide production of natural inorganic pigments in 1995:

$120 \cdot 10^3$ t/a

The natural deposits have long not been able to satisfy the demand, partly due to the application-related steady tightening of qualitative specifications. Nevertheless, the production of natural pigments, mainly iron oxides, amounted in 1995 to ca. $0.12 \cdot 10^6$ t/a.

Worldwide production capacity for synthetic inorganic pigments in 1995:
$5 \cdot 10^6$ t/a
- 66% TiO_2
- 15% iron oxides

The worldwide capacity in 1995 for synthetic inorganic pigments and pigment blacks, on the other hand, was $5 \cdot 10^6$ t/a. A survey of the worldwide production capacities for the most important inorganic pigments is given in Table 5.9-3. TiO_2-white pigments and iron oxide-colored pigments together account for more than 80% of the worldwide capacity, the main producers being in the USA and Western Europe with a strong contribution from the Federal Republic of Germany.

Table 5.9-3. Worldwide Production Capacities for Synthetic Inorganic Pigments in 1995 (in 10^3 t/a).

	10^3 t/a	%
titanium dioxide	3170	66
iron oxides	720	15
pigment blacks	530	11
lithopone	190	4
chromate yellow	145	3
cyanide iron blue pigments	<25	<0.5
chromium oxide green	48	1
ultramarine	<25	<0.5
molybdate red/lead chromate	<50	<1
mixed-metal oxide pigments	<25	<0.5
luster pigments	<50	<1
	4800	100.0

Whereas mass-produced pigments such as TiO_2 and iron oxides sell for a few US\$/kg, the prices for individual pigments may be 55 US\$/kg or more. The worldwide turnover in 1995 was > 11 · 10^9 US\$.

Worldwide consumption of inorgnaic pigments in 1995: > 11 · 10^9 US\$

The application fields of the individual pigment groups are very diverse. The main applications in Western Europe are: TiO_2 and mixed phase pigments in the paint and lacquer sector, iron oxide pigments in the construction materials sector. The applications spectrum for inorganic pigments in Western Europe is given in Table 5.9-4.

Application fields for inorganic pigments:

- lacquers and paints,
- construction materials,
- plastics,
- paper,
- enamel and ceramics,
- printing inks,
- various.

Table 5.9-4. Applications Spectrum for Inorganic Pigments in Western Europe in %.

	titanium dioxide	iron oxides	chromium oxide	mixed phase pigments
paints and lacquers	64	29	50	65
construction materials	4	60	25	5
plastics	19	6	10	20
paper	8	2	-	-
enamels and ceramics	4	1	10	10
others	1	2	5	-
	100	100	100	100

5.9.2 White Pigments

5.9.2.1 General Information

The production of white coatings or bulk white solids and the lightening of formulations with colored pigments is currently only possible by pigmentation with white pigments. All white pigments are produced synthetically.

If an average worldwide price of ca. 3.20 DM/kg TiO_2 is assumed, the worldwide turnover is ca. $10.2 \cdot 10^9$ DM.

Largest group of inorganic pigments are the white pigments.

Production in 1995:

$3.42 \cdot 10^6$ t/a

Table 5.9-5. Production in 1995 of the More Important White Pigments Worldwide and in the Federal Republic of Germany (in 10^3 t/a)

	World (10^3 t/a)	FR Germany (10^3 t/a)
titanium dioxide	3200	300
lithopone and zinc sulfide	220	32
zinc oxide white, without lead	n.a.	25
zinc oxide white, with lead	n.a.	18
total	3420	375

TiO_2: white pigment with excellent properties

For achieving maximum hiding power or lightening power, a high refractive index is required and an optimum particle size, upon which it is dependent. Titanium dioxide is more effective in this than any other white pigment (see Table 5.9-6).

Table 5.9-6. Refractive Index and Optimum Particle Sizes of Several White Pigments.

compound	average refractive index, versus vacuum	optimum particle size when using organic binders D_{opt}, in µm	relative scattering power
TiO_2, rutile	2.80	0.19	up to 800
TiO_2, anatase	2.55	0.24	600
ZnS, zinc blende	2.37	0.29	350
ZnO, zinkite	2.01	0.48	100
($BaSO_4$, baryte)*	1.64	1.60	25

* for comparison

5.9.2.2 Titanium Dioxide Pigments

5.9.2.2.1 Economic Importance

Due to its excellent properties (see Table 5.9-6), TiO_2-pigments have a 75% market share of the production of white pigments. White lead, lithopone and zinc white are being increasingly supplanted in the market by TiO_2 (see Table 5.9-5). The worldwide production capacities for TiO_2 have increased in the period 1970 to 1995 from $1.9 \cdot 10^6$ t/a to $3.9 \cdot 10^6$ t/a, the newest plants being chloride process plants (see Table 5.9-7).

TiO_2: by far the most important white pigment

Table 5.9-7. Worldwide Capacities for TiO_2-Manufacture in the Period 1970 to 1995 (in 10^3 t/a).

year	sulfate process	chloride process	total
1970	1499	437	1936
1980	1757	964	2721
1990	1795	1643	3438
1995	1800	2100	3900

5.9.2.2.2 Raw Materials for TiO_2 Pigments

The starting materials for TiO_2 production are ilmenite and titanium slag in the case of the sulfate process (see Section 5.9.2.2.3) and leucoxene, rutile, synthetic rutile, titanium slag and in the future possibly also anatase for the chloride process (see Section 5.9.2.2.3).

Ilmenite $(Fe,Mg,Mn)TiO_3$ occurs naturally in primary and secondary deposits. The TiO_2-content is 43 to 61% and the iron oxide content 34 to 39%. The impurities are mainly Mn, Mg, Al, Si, Cr, V, Nb and Sb. Primary deposits of ilmenite are found in Norway, Russia, Finland, Canada and the USA. However, secondary deposits are more important raw materials due to their easier processing (sands). They are found in South Africa, Australia, India, Brazil, Malaysia and Egypt.

Raw material for TiO_2-pigments

natural:

- ilmenite,
- leucoxene,
- anatase,
- rutile.

synthetic:

- titanium slags,
- synthetic rutile.

Rutile is extracted from river, coastal and dune sands yielding concentrates with 90 to 98% TiO_2, which may be contaminated with Fe, Zr, V, Cr, Al, Si, Mg etc. Australia is the leading producing country supplying $216 \cdot 10^3$ t in 1994.

Anatase deposits with a TiO_2 content of 30 to 40% have been discovered in Brazil. They contain $220 \cdot 10^6$ t TiO_2, being more titanium dioxide than in all the currently known rutile deposits. It can possibly be used as a starting material for $TiCl_4$ in the production of TiO_2 pigments or in the production of metallic titanium.

Production of titanium slags:

by reduction of ilmenite at 1200 to 1600°C and separation of the liquid iron

Titanium slags from ilmenite are important raw materials for the sulfate and chloride processes, due to their high TiO_2-content. The iron contained in ilmenite is largely reduced with carbon to the metal in an arc furnace at 1200 to 1600°C and is separated off. The slags formed have a TiO_2-content of 70 to more than 85%, depending upon the ilmenite used. The main producers are the Quebec Iron and Titanium Corp. (QIT) in Canada and Richards Bay Minerals Ltd. (RBM) in South Africa. The capacity of QIT is $800 \cdot 10^3$ t/a, that of RBM also $800 \cdot 10^3$ t/a.

Production of synthetic rutile from ilmenite:

by removal of iron using various processes while retaining the granular form of the starting material

Synthetic rutile. In recent years the prices for natural rutile have increased due to the increasing scarcity of economically exploitable deposits. Processes for removing iron from ilmenite ore have been developed, to provide a cheap raw material for the chloride process in which the particle form is retained, as this is particularly favorable for fluidized bed chlorination.

Synthetic rutile has a TiO_2-content of 85 to 90%. In all these processes iron is either removed in the form of a salt solution which has to be worked up or as valueless oxide. In the process for the production of titanium slag, on the other hand, metallic iron is obtained, which makes this process more interesting both ecologically and economically. As a result, a large proportion of the synthetic rutile manufacture plants has been closed down.

5.9.2.2.3 Manufacturing Processes for TiO_2 Pigments

Manufacturing processes for TiO_2 pigments:

- sulfate process,
- chloride process.

TiO_2-pigments are either manufactured using the older sulfate process or newer chloride process. The economics of the two processes are very much dependent upon the raw materials available.

Sulfate Process

The sulfate process (see Figure 5.9-1) utilizes ilmenite or titanium slag.

Sulfate process:

- digestion of ilmenite or titanium slag with H_2SO_4,
- reduction of Fe(III) to Fe(II),
- separation of $FeSO_4 \cdot 7H_2O$,
- hydrolysis of $TiOSO_4$,
- washing and "bleaching",
- calcination.

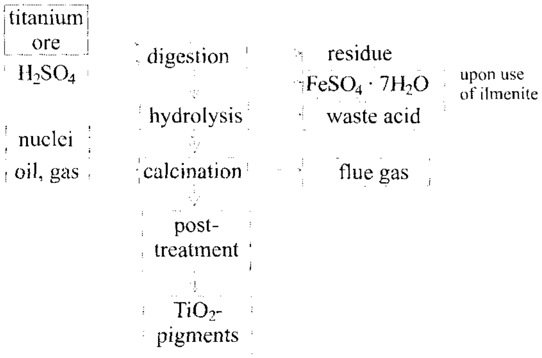


Fig. 5.9-1. TiO_2-pigment manufacture using the sulfate process.

The finely ground raw materials are digested with concentrated sulfuric acid in an exothermic reaction, the digested cake dissolved in cold water and the residue separated off. To prevent coprecipitation of iron(III) ions during the subsequent hydrolysis, they are reduced to iron(II) by adding a Ti(III) solution or scrap iron. Upon evaporating the solution, the large quantities of iron(II) sulfate heptahydrate produced when ilmenite is used, crystallize out. The titanium sulfate is then hydrolyzed by feeding in steam at 95 to 110°C. TiO_2 seed-crystals are added or are formed before hydrolysis to ensure yields of 93 to 96% TiO_2 and to obtain a hydrolysis product which yields the optimum particle size of ca. 0.2 μm upon firing. During hydrolysis sulfuric acid is produced as a dilute aqueous solution, so-called "waste acid".

The hydrolysis product is washed, treated with a Ti(III) solution to remove adsorbed heavy metal ions (Fe, Cr, Mn, V) or bleached with aluminum and acids and calcined at temperatures of ca. 1000°C. With doping or an appropriate choice of additive, latterly rutilization nucleating seeds, before calcination, anatase or rutile pigments can be produced in the calcination process.

Disposal of the waste products from the sulfate process:

- upgrading of waste acid and recycling,
- thermal decomposition of $FeSO_4$ to iron oxide and SO_2 ($\rightarrow H_2SO_4$)

The byproducts produced, dilute sulfuric acid (waste acid) and ferrous sulfate heptahydrate, if ilmenite is used, are to an increasing extent being processed further (see Fig. 5.9-2). In a process operated by Bayer AG since 1958, the waste acid is concentrated to 65% in lined vessels with the aid of a submerged burner. After separation the 65% sulfuric acid can be used as such or is evaporated in a distillation step to 96% sulfuric acid, which can be reused for the digestion of ilmenite or titanium slag.

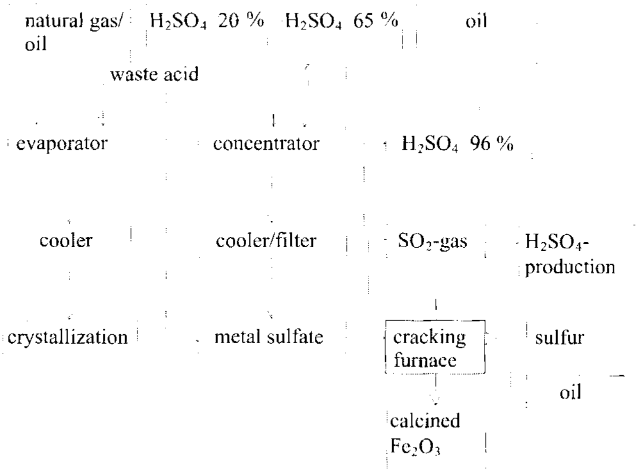


Fig. 5.9-2. Upgrading of waste acid and cracking of metal sulfate.

Iron sulfate is cracked to sulfur dioxide and iron oxide in a fluidized bed reactor at 800 to 1000°C. The energy is provided by the combustion of sulfur or other fuels, the sulfur dioxide formed being, after purification, processed to sulfuric acid. The iron oxide residue can be employed in the cement industry.

An alternative to the concentration of waste acid and reuse thereof, is neutralization of waste acid with calcium carbonate and using the gypsum formed either in the construction industry or for land infill, depending upon purity.

Chloride Process

Chloride process:

- fluidized bed chlorination of rutile ore,
- removal of vanadium,
- $TiCl_4$ distillation,
- $TiCl_4$ combustion to TiO_2 and Cl_2.

In the chloride process natural rutile ore or synthetic rutile with a TiO_2-content of up to 96% is chlorinated in a fluidized bed reactor with oil-coke and chlorine. The raw $TiCl_4$ produced is mixed with reducing agents to convert impurities, such as vanadium oxychloride, to lower valency state vanadium compounds. The titanium tetrachloride formed is then distilled yielding titanium tetrachloride in almost any required purity. Finally it is burnt with pure oxygen to TiO_2 and chlorine, which is reused in the chlorination process (see Fig. 5.9-3).

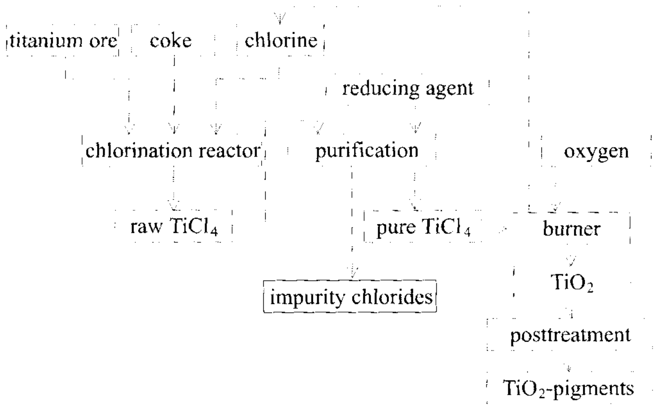


Fig. 5.9-3. TiO_2-manufacture by the chloride process.

The formation of impurity metal chlorides is dependent upon the raw material. If there were sufficient rutile available, this process would be particularly ecologically favorable. However, in view of its scarcity and hence its high price, raw materials with low titanium contents, such as 85% RBM slag (see Section 5.9.2.2.2), are currently being used in the chloride process. Allowance has then to be made for the resulting increased formation of impurity metal chlorides. TiO_2-pigment manufacture without byproducts is not possible. These byproducts are disposed of by the "deep well process" (USA), dumped or, after processing, used for water processing.

Posttreatment of TiO_2

Most TiO_2 pigments undergo an inorganic and organic posttreatment to increase their weathering resistance and to improve their dispersibility in paints and plastics.

Untreated anatase pigments, in particular, exhibit poor weathering resistance due to absorption of near UV-light not only by TiO_2, but also by paint binders and plastics. This leads to UV-induced degradation of the organic materials and to the formation of OH- and HO_2-radicals on the surface of the TiO_2-pigments. These accelerate the photochemical degradation of the binder resulting in the

Posttreatment of TiO_2 pigments to:

- improve their dispersibility,
- increase their weathering resistance.

exposure of pigment particles, which are washed out (chalking).

These effects can be suppressed or even reversed by using the more stable rutile pigments, by doping the hydrolysis product with Zn^{2+}, Al^{3+}, Zr^{4+} or Si^{4+} prior to calcination and by precipitation of poorly soluble colorless inorganic compounds such as hydrated SiO_2, $Al(OH)_3$, hydrated ZrO_2, water-containing aluminum silicates, aluminum phosphates etc. onto the TiO_2-surface. The so-treated stabilized rutile pigment still absorbs UV-light, but without secondary photochemical reactions and hence protects the organic binder by screening it from UV-light.

5.9.2.2.4 Applications for TiO_2 Pigments

Application fields for TiO_2 pigments:

- paints and coating materials,
- plastics,
- printing inks,
- fibers,
- papers,
- laminates,
- construction materials,
- enamel and ceramics,
- cosmetics.

The high covering and lightening powers of TiO_2-pigments, their chemical stability, nontoxicity and favorable price/effect ratio has gained them entry into many application fields, thereby supplanting the other white pigments. TiO_2-pigments are thus used in the manufacture of paints and coating materials, plastics, printing inks, fibers (delustering), papers, laminate papers (laminates based on melamine or urea-formaldehyde resins), construction materials, enamels and ceramics, powders, ointments, toothpaste and even cigar wrappers. There is hardly a white-colored or tinted object in our environment, which does not contain TiO_2-pigments.

Table 5.9-8. Applications Spectrum for TiO_2-pigments in the World, the USA and Western Europe.

	World (%)	Western Europe (%)	USA (%)
paints & lacquers	57	57	51
plastics	18	22	21
paper	12	11	20
others	13	10	8

TiO_2 slurries:

highly concentrated, flowing, pumpable and volumetrically dosable TiO_2-suspensions

Recently the use of TiO_2-pigments as highly concentrated, easy flowing, pumpable and volumetrically dosable suspensions (so-called slurries) has increased. These slurries with up to 75% by weight of TiO_2 are rheologically designed so that no sediment is formed even after long storage times. Such TiO_2-pigments are dust-free.

5.9.2.3 Lithopone and Zinc Sulfide Pigments

Lithopones: mixtures of ZnS and $BaSO_4$

The lithopones comprise a group of white pigments obtained by the calcination of coprecipitated zinc sulfide and barium sulfate. The zinc sulfide content of the types of lithopone, which determines the quality of the pigment, varies between 29 and 60%. Special pigments may consist of pure zinc sulfide. ZnS-containing white pigments are used for special paints, printing inks for wallpaper and in the plastics and rubber industries. Their use has declined steadily in recent decades and is currently with $215 \cdot 10^3$ t/a less than 10% of the TiO_2 production (see Table 5.9-5).

Manufacture of lithopones:
- precipitation: $ZnSO_4 + BaS \rightarrow ZnS + BaSO_4$
- firing of the mixture.

The lithopones are manufactured by mixing zinc sulfate and barium sulfide solutions:

$$ZnSO_4 + BaS \longrightarrow ZnS + BaSO_4$$

Purification of the $ZnSO_4/ZnCl_2$ solution by removal of foreign metals:
- oxidation with chlorine,
- precipitation of nobler metals with zinc dust.

The zinc salt solutions, which currently mainly come from zinc and copper smelters, contain impurities which have to be completely removed prior to use, because all heavy metals form colored sulfides. For the purification step the solution is oxidized with chlorine (pH 4), which precipitates most of the iron and manganese as the oxide-hydrate and part of the cobalt, nickel and cadmium present as their hydroxides. In the second step, the elements nobler than zinc (Ni, Co, Cd, In, Tl, Pb, Cu, Ag) are precipitated as their metals by adding zinc dust and the metals returned to the copper smelters for noble metal extraction. After purification the solutions are adjusted to a particular zinc content. Mixtures of zinc sulfate and zinc chloride solutions are used for manufacturing lithopone types with more than 30% ZnS.

Preparation of the BaS solution: $BaSO_4 + 2C \rightarrow BaS + 2CO_2$

Barium sulfide solutions are obtained by reduction of low silica natural heavy spar with coke or coal in rotary kilns at ca. 1250°C and leaching with water. Since all the heavy metal sulfides remain in the residue, the filtered solution can be directly used for the precipitation of the zinc salt.

Light stability of lithopones increased by doping with 0.02 to 0.5% Co

The precipitated raw pigment does not exhibit pigment properties due to its too small particle size and has to be subsequently calcined at a particular firing temperature (dependent upon the residual salt content) to yield the optimum particle size of ca. 0.35 μm. Lithopones with satisfactory light stability are obtained by incorporating 0.02 to 0.5% of cobalt. Chemical or mechanical posttreatment (e.g. steam-jet grinding with organic grinding and dispersion aids, if required) yields optimum lithopone types for particular application fields.

5.9.2.4 Zinc Oxide White Pigments

5.9.2.4.1 Manufacture

Zinc oxide white pigments are known as "zinc white" or zinc oxide depending upon the manufacturing process.

"Zinc White" (ZnO) by the French Process

Manufacture of zinc white (ZnO) by the "French" process:

- melting of metallic Zn,
- evaporation of the Zn,
- vapor phase oxidation with air to ZnO.

In the manufacture of zinc white by the "French" process, metallic zinc is melted, evaporated and oxidized in the vapor state to zinc oxide with air. If the starting material is insufficiently pure, the zinc has to be purified by evaporation and condensation prior to the oxidation step. The size and shape of the zinc oxide crystals can be controlled by the oxidation conditions. After combustion the ZnO is precipitated from the ZnO/air mixture in settling chambers, in which classification of the zinc oxide particles takes place according to their size.

Zinc Oxide by the American Process

Manufacture of zinc oxide by the "American" process:

- reduction of oxidic zinc compounds,
- subsequent direct oxidation to ZnO.

The raw materials for the manufacture of zinc oxide by the "American" process are roasted ores, concentrates of zinc ores or more recently zinc hydroxide or zinc carbonate from the processing of scrap. These are reduced with coal and directly reoxidized to ZnO in the same reaction chamber. The purity of the zinc oxide is normally somewhat inferior to that from the "French" process. Grades of various purities can be produced by fractionation.

Zinc Oxide by the Wet-Chemical Process

Manufacture of zinc oxide wet-chemically:

- precipitation of zinc hydroxide or carbonate,
- calcination.

Zinc is precipitated from purified zinc salt solutions as the hydroxide, basic carbonate or carbonate, which is washed, filtered and dried. The pigment is obtained by subsequent calcination. Pigments suitable for particular applications can be obtained by varying the precipitation and calcination conditions. At low calcination temperatures particularly fine particles are produced, so-called transparent zinc oxide, which is actually the basic carbonate. Wet-chemically produced zinc oxides are particularly pure, since very pure zinc salt solutions can be produced (see Section 5.9.2.3).

5.9.2.4.2 Applications

Zinc oxides is mainly used in the rubber industry in which it serves as an activator in the vulcanization process. Its low hardness and high compatibility with polymers are important for its utilization in chemical materials. In its utilization in paints, its tendency to form zinc soaps, which hinder the attack of coatings by fungus and improve the aging resistance (UV-absorption), is important. Further application fields for zinc oxide are in copier paper, glues, pharmaceutical products, cosmetic products and dental cements.

Applications for ZnO:

- rubber industry,
- coloration of plastics,
- paints,
- photocopier paper,
- pharmaceutical and cosmetic products.

5.9.3 Colored Pigments

5.9.3.1 Iron Oxide Pigments

With a worldwide production in 1995 of ca. $600 \cdot 10^3$ t/a of synthetic pigments and ca. 110 to $120 \cdot 10^3$ t/a of natural pigments, iron oxide pigments represent by far the most important group of colored pigments (see Section 5.9.1). This group consists of chemically very different coloring substances e.g. α-FeOOH (yellow), γ-FeOOH (yellow-orange), Fe_3O_4 (black), γ-Fe_2O_3 (brown) and α-Fe_2O_3 (red), from which a wide range of brown hues can be produced by blending. The production of mixed oxides and the control of hue by adjustment of particle size are also important. Iron oxide pigments are the cheapest inorganic pigments and therefore have found widespread use, particularly in products for the construction industry and in coating materials.

Iron oxide pigments:

group of colored pigments with largest consumption quantitywise

Worldwide production in 1995:

ca. $0.72 \cdot 10^6$ t/a

5.9.3.1.1 Natural Iron Oxide Pigments

The naturally occurring mineral pigments owe their color to iron compounds and contain impurities which are a function of where they are found. Their poor tinting strength and less saturated color purity, compared with synthetic pigments, are due to their low purity and broader particle size distributions. Natural iron pigments are therefore, with a few exceptions, only used for less demanding applications. Their fastness, which they have in common with synthetic products, is the reason for our still being able to admire the colored cave paintings from 15 000 BC.

Natural iron oxides:

- natural reds such as Spanish red or Persian red,
- ochre,
- sienna,
- umber,
- micaceous iron oxide.

Natural reds such as persian red (found at Hormuz in the Persian Gulf), spanish red and burnt sienna contain ca. 50% iron oxide and represent the most important group of natural mineral pigments. Their tinting strength increases with increasing α-Fe_2O_3 content, which can amount to 95% in the purest sorts. Their utilization is mostly limited to primers, cheap ships' paints and house paints (USA, Scandinavia).

Ochre, whose color is almost exclusively due to limonite, (α-FeOOH), is still mined in nominal quantities in South Africa and France. It is being increasingly supplanted by synthetic pigments, because of its low α-FeOOH content (20% Fe_2O_3 in French ochre, up to 55% in South African ochre and ca. 87% Fe_2O_3 in synthetic α-FeOOH) and the poorer consistency of its coloristic properties.

Sienna, consisting mainly of a mixture of finely crystalline goethite and colloidal silica (Fe_2O_3 content ca. 50%), has translucent (semi-transparent) properties and as a result is particularly important in artists' paints and other special fields. Raw sienna has a brown-yellow hue due its manganese oxide content (up to 1%), which changes to bright red-brown upon burning.

Umber (Fe_2O_3 content between 45 and 70%, MnO_2 content between 5 and 20%), whose largest deposits are on Cyprus, is mainly exported from there in a calcined form.

Micaceous iron oxide, a flake-shaped α-Fe_2O_3 with a metallic gray color, is mainly mined in Carinthia (Austria). It is used in the top coat of corrosion protection coatings. Application fields are steel superstructures (stations, Eifel tower), petrochemical plants and ship building. The annual capacity worldwide is $10 \cdot 10^3$ t/a.

Table 5.9-9. Natural and Synthetic Iron Oxide Pigments.

	natural	synthetic	hue shift with increasing particle size
yellow	limonite yellow ochre	goethite, α-FeOOH	green-yellow → brown-yellow
	sienna (bog ore)	lepidokrokite, γ-FeOOH	yellow → orange
red	hematite persian red, spanish red, red ochre, siderite (burnt), sienna (burnt)	hematite, α-Fe_2O_3	yellow-red → red-violet
brown	umber (untreated and burnt)	maghemite, γ-Fe_2O_3	bright brown → dark brown
	siderite (burnt)	mixtures of hematite, goethite and magnetite	
	sienna (burnt)		
black	magnetite	magnetite (Fe_3O_4)	green-brown → blue-tinged black

5.9.3.1.2 Synthetic Iron Oxide Pigments

General Information

The high demands of the paint and construction materials industries, can virtually only be satisfied by synthetic iron oxide pigments. They possess the required chemical purity and can be produced in different particle sizes, which enables variation in both hiding power and hue to be achieved. Iron oxide pigments attain their maximum scattering power at a particle size of ca. 0.2 μm, the hiding power being lower for both larger and smaller particles. Particles smaller than ca. 0.01 μm lose their scattering power completely and are used for transparent colorants.

Hue adjustment with synthetic iron oxide pigments:

- chemically through choice of materials:
  - α-FeOOH yellow,
  - α-Fe_2O_3 red,
  - Fe_3O_4 black,
- physically through particle size variation:
  - ca. 0.2 μm for optimum hiding power,
  - < 0.01 μm for transparent iron oxide pigments.

The production sites for synthetic iron oxide pigments are mainly in the Federal Republic of Germany, the USA, Japan and China. The largest manufacturer is Bayer AG (FRG). The different production processes can, in principle, all be used to manufacture differently mixed iron oxides and thus all the different colors. The economics of the processes is the deciding factor.

The purity of raw materials, such as ferrous sulfate and ferrous chloride from steel industry pickling plants and scrap iron from the metal-working industries, determines their suitability for pigment manufacture.

Table 5.9-10. Particle Size, Hue and Hiding power of Iron Oxide Pigments.

	particle diameter (μm)		
	0.001 → 0.01	0.1 → 1.0	10.0 → 100.0
pigment type:	transparent iron oxides	hiding iron oxides	micaceous iron oxide
hue:			gray-brown (metallic effect)
red iron oxide (α-Fe_2O_3)	yellow-red	yellow-red to violet	-
yellow iron oxide (α-FeOOH)	lemon yellow	green-yellow to orange-yellow	-
black iron oxide (Fe_3O_4)	-	brown-black to blue-black	-
hiding power:	low	optimum	low

Manufacture

Thermal Decomposition of Iron Compounds

Manufacture of synthetic iron oxide pigments:

- thermal decomposition of iron compounds,
- oxidative processes in aqueous media.

Thermal decomposition of iron compounds to α-Fe_2O_3:

- roasting of $FeSO_4$,
- calcination of α-FeOOH,
- oxidative calcination of Fe_3O_4,
- oxidative high temperature decomposition of $FeCl_2$.

Red iron oxide pigments are mainly obtained by roasting and calcining processes. α-Fe_2O_3 is obtained by oxidative calcination of all decomposable iron compounds. Decomposition of iron sulfate and α-FeOOH and the oxidation of Fe_3O_4 are industrially important.

After prior dehydration to the monohydrate, ferrous sulfate heptahydrate is oxidatively roasted at temperatures above 650°C, producing clear red-colored α-Fe_2O_3 pigments (copperas reds):

$$6\,FeSO_4 \cdot H_2O + 3/2\,O_2 \longrightarrow Fe_2O_3 + 2\,Fe_2(SO_4)_3 + 6\,H_2O$$
$$2\,Fe_2(SO_4)_3 \longrightarrow 2\,Fe_2O_3 + 6\,SO_3$$

The sulfur dioxide formed can be processed to sulfuric acid. A disadvantage of this process is the contamination of the effluent with the soluble unroasted sulfate when the roasted charge is washed, due to the incomplete roasting of the sulfate.

Ferrous chloride, the salt available in the largest quantities from pickling plants, can also be thermohydrolytically decomposed. The iron oxide formed does not, however, possess the usual pigment qualities and is normally pelletized and reused in steel manufacture. $FeCl_2$ solutions from the Ruthner process are an exception. These are utilized in the hard- and soft-ferrite industries.

In principle, all the α-FeOOH or Fe_3O_4 pigments produced by the precipitation process, the Penniman-Zoph process and the Laux process can be calcined to red α-Fe_2O_3 pigments. The oxidative calcination of Fe_3O_4 from the Laux process is the most important process. A complete range of red tones can be obtained by rotary kiln calcination, by varying the particle size through the choice of material and temperature conditions. Working up only requires a grinding step, a washing step being unnecessary due to the purity of the starting materials. The calcination of yellow pigments also leads to needle-shaped red pigments. Transparent α-Fe_2O_3 pigments result from the calcination of very fine α-FeOOH particles. These can also be obtained by oxidative thermal decomposition of $Fe(CO)_5$.

Oxidative processes used for the manufacture of:

- yellow α-FeOOH pigments,
- black Fe_3O_4 pigments,
- red α-Fe_2O_3 pigments.

Oxidation Processes in Aqueous Media

FeOOH-yellow, Fe_3O_4-black and Fe_2O_3-red pigments are obtainable by an air oxidation process from iron(II) sulfate solutions with appropriate choice of reaction conditions and the use of certain nucleating seeds. The manufacture of α-FeOOH-yellow pigments is very important. The first reaction step is the production of the nucleating seeds, so important to the properties of the final pigment, by adding sodium hydroxide to a $FeSO_4$ solution and converting the resulting basic ferrous sulfate precipitate into a suspension of α-FeOOH-nuclei by air oxidation:

Oxidation processes in aqueous media take place in two steps:

- nucleating seeds formation,
- pigment particle growth.

$$2\,FeSO_4 + 4\,NaOH + \tfrac{1}{2}\,O_2 \longrightarrow 2\,FeOOH + 2\,Na_2SO_4 + H_2O$$

The crystalline α-FeOOH-nuclei are very small and can be used as transparent pigments. Pigments with covering properties are obtained by crystal growth on the α-FeOOH nuclei, by adding iron sulfate solution, sodium hydroxide and air, to obtain the particle size corresponding to the hue required (precipitation process).

Particles can also be grown by adding scrap iron and oxidizing it with air without the consumption of any other chemicals (Penniman-Zoph process).

Pigment particle growth:

- by the precipitation process through the addition of $FeSO_4$,
- by the Penniman-Zoph process through the dissolution of scrap iron.

$$\begin{aligned} 2FeSO_4 + 3H_2O + 1/2O_2 &\longrightarrow 2FeOOH + 2H_2SO_4 \\ Fe + H_2SO_4 &\longrightarrow FeSO_4 + H_2 \end{aligned}$$

The effluent from this process does not contain any additional salt, because the sulfuric acid formed reacts with the scrap to $FeSO_4$. The reaction is accelerated by maintaining the temperature at 70 to 90°C with steam.

In the manufacture of black pigments by the precipitation process, iron(II) salt solutions are neutralized and oxidized with air at 90 to 100°C to a Fe(II)/Fe(III) ratio of 0.5 (Fe_3O_4). Using a similar process and appropriate nuclei formation conditions, small α-Fe_2O_3 nuclei are formed upon complete oxidation, which after growth yield easily dispersible red α-Fe_2O_3 pigments with high tinting strength (direct red process).

Aniline process:

- reduction of nitrobenzene with scrap iron to α-FeOOH or Fe_3O_4 pigments and aniline,
- distillative separation of aniline.

The long known reaction of nitrobenzene with metallic iron, previously used exclusively for the manufacture of aniline, has been so adapted by Laux (Bayer AG) that high tinting strength Fe_3O_4 pigment is formed instead of the previously unstable iron oxide-containing residue. This pigment can either be used directly or calcined to strongly tinted red α-Fe_2O_3 pigments. The addition of aluminum chloride to the reaction mixture yields yellow α-FeOOH pigments.

The raw materials for this "Laux process" are ground and sieved largely degreased cast iron or wrought iron chips. Particle size, metallurgical state and addition rate determine the quality of the resulting pigments. The reaction is started by feeding in steam and is exothermic:

$$C_6H_5NO_2 + 2\,Fe + 2\,H_2O \xrightarrow{AlCl_3} C_6N_5NH_2 + 2\,FeOOH$$

or

$$4\,C_6H_5NO_2 + 9\,Fe + 4\,H_2O \xrightarrow{FeCl_3} 4\,C_6N_5NH_2 + 3\,Fe_3O_4$$

Pigment is formed in the absence of bases and nitrobenzene is used as an oxidation agent. At the end of the reaction most of the aniline is separated off, the residue being distilled off by steam distillation. The pigment suspension is freed from excess iron chips by sieving and is then washed free of salt in a series of sludge thickeners and vacuum rotary filters. The pigment paste is dried in belt driers, drum driers, spray driers or fluidized bed driers and is then ground or micronized (pulverized in a jet mill).

Applications for Iron Oxide Pigments

There are considerable regional differences in the applications of iron oxide pigments. In Western Europe the construction materials sector is dominant, whereas in the USA it is the paint and coatings sector.

Applications for iron oxide pigments:

- construction material colorant,
- paints and lacquers,
- coloring of plastics,
- as a raw material for hard and soft ferrites.

Table 5.9-11. Applications Spectra for Iron Oxide Pigments in Western Europe and the USA (%).

	Western Europe (%)	USA (%)
construction material colorants	64	23
paints and lacquers	30	47
coloring of plastics	4	12
others	2	18

In the construction materials colorant sector, the chemical stability, light fastness and weathering stability of synthetic iron oxide pigments are important. Concrete bricks, paving stones, roofing tiles, asbestos cement, mortar, bitumen and facade plaster are all currently colored with iron oxide pigments.

Natural and synthetic iron oxides not possessing pigment properties are used as raw materials in the production of hard and soft ferrites (see Section 5.5.5.2, Electro- and Magneto-Ceramics) for radio, television and telephone technology, for adhesive magnets, for rotors in dynamos, for low-loss magnetic layers, for DC-motors, for transformer cores, for electronic calculators and high frequency furnaces. This amounts to an annual worldwide production of more than $300 \cdot 10^3$ t/a.

α-FeOOH or α-Fe_2O_3 pigments with particle sizes less than 0.01 μm (transparent pigments) are mainly used in metallic paints and in transparent wood-protection lacquers (UV protection). The annual worldwide production of transparent iron oxide pigments is of minor importance compared with that of covering iron oxide pigments.

5.9.3.2 Chromium(III) Oxide Pigments

5.9.3.2.1 Manufacture

All the industrially important production processes for chromium(III) oxide pigments start from chromates or dichromates, which are obtained by alkaline oxidative digestion of chrome ores.

Manufacturing Processes in Aqueous Media

Chromium hydroxide or chromium oxide hydrate are formed when chromates are used as oxidizing agents in organic chemistry. These can be calcined to α-Cr_2O_3 or directly used as a pigment. Such processes have declined in importance, due to the increasing use of catalytic oxidation in organic chemistry.

Manufacture of Cr_2O_3 pigments:

- in aqueous media:
  reduction of chromate or dichromate solutions with organic waste products or polysulfides and subsequent calcination to α-Cr_2O_3

Organic waste products such as molasses or sawdust and sulfur are particularly cheap reducing agents for chromates or dichromates. Polysulfide-containing sulfur suspensions are the most widely used reducing agents producing chromium hydroxide which is difficult to filter together with sodium thiosulfate, which can be used for reducing further chromate. This is achieved by mixing the thiosulfate-containing suspension with additional sodium dichromate in a kneader. The resulting granulate is then calcined to α-chromium(III) oxide at 900 to 1100°C.

Manufacturing Processes in the Solid State

- in the solid state or melt:
  reduction of dichromate with sulfur or ammonium salts

Sodium dichromate is reduced with sulfur by intensively mixing the components and then calcining in rotary kilns or rotary-plate furnaces at 800 to 1000°C.

$$Na_2Cr_2O_7 + S \longrightarrow Cr_2O_3 + Na_2SO_4$$

The calcination product, which contains sodium sulfate in addition to chromium oxide and also possibly unreacted chromate, is purified by mashing with water, filtering and washing.

The presence of fluxes such as NaCl or Na_2SO_4 during the decomposition of ammonium dichromate ensures that Cr_2O_3-pigments are formed in addition to nitrogen and water, instead of extremely fine powders. The isolation of ammonium dichromate can therefore be dispensed with by calcining mixtures of sodium dichromate and ammonium chloride or ammonium sulfate at 800 to 1000°C.

$$Na_2Cr_2O_7 + 2\,NH_4Cl \longrightarrow Cr_2O_3 + 2\,NaCl + N_2 + 4\,H_2O$$

$$Na_2Cr_2O_7 + (NH_4)SO_4 \longrightarrow Cr_2O_3 + Na_2SO_4 + N_2 + 4\,H_2O$$

To ensure a good yield and high quality pigments, it is important that the intermediate formation of ammonium dichromate be as complete as possible.

The use of stoichiometric quantities of ammonium chloride or slightly under stoichiometric quantities of ammonium sulfate in the reaction mixture yields low sulfur chromium(III) oxide for the manufacture of chromium metal.

The Cr_2O_3-pigments produced by the different processes are further processed by washing, filtering, drying and grinding.

5.9.3.2.2 Properties and Applications of Chromium(III) Oxide

Cr_2O_3 was already in use in 1802 as a green stain (colorant) in the manufacture of Sèvres porcelain, due to its extreme thermal and chemical stability. Some hue variation is possible by changing the pigment particle size (0.3 to 0.5 µm). As the particles become coarser the color changes from green to green-blue and the hiding power decreases. A yellow-green hue can be obtained by precipitating aluminum and titanium hydroxide onto the pigment particles and then calcining at 1200°C.

A permanent green coloring in cement or lime-bonded construction materials can only be achieved using Cr_2O_3. Particularly high purity chromium oxide is used in the aluminothermic manufacture of metallic chromium.

Applications for Cr_2O_3:

- as a pigment for paints, plastic, construction materials, enamels,
- for the aluminothermic manufacture of metallic chromium,
- in refractory ceramics.

The importance of green chromium oxide hydrate pigments (CrOOH, Guignet's green) has decreased considerably with the introduction of phthalocyanine pigments.

The worldwide production capacity for Cr_2O_3 is ca. $48 \cdot 10^3$ t/a. In Western Europe ca. 50% is used in paints and coatings, 25% in construction materials, 10% in enamels and ceramics and 5% for other applications such as in refractory ceramics.

5.9.3.3 Chromate and Molybdate Pigments

Chromate and molybdate pigments:

- chrome yellow,
- chrome orange,
- chrome red,
- molybdate orange,
- molybdate red.

Most important properties:

- brilliant hue,
- high tinting strength,
- high hiding power.

Chromate and molybdate pigments include chrome yellow, molybdate orange, molybdate red, chrome orange and chrome red. This pigment group is characterized by its brilliant hues, high hiding power, high tinting strength, light fastness and stability to solvents, migration and weathering.

By far the most important products are chrome yellow and molybdate red. The chrome yellow pigments are $Pb(Cr,S)O_4$ mixed phases or pure $PbCrO_4$ and are produced by precipitation from the aqueous phase. The different hues from green-tinged yellow to bright and mid-yellow to golden yellow can be controlled by the crystal modification (orthorhombic or monoclinic) or by varying the lead sulfate content.

Table 5.9-12. Properties of Chromate and Molybdate Pigments.

pigment type	formula	color	particle size in µm
chrome yellow			
orthorhombic	$Pb(Cr, S)O_4$	green-tinged yellow	0.2 to 0.6
monoclinic (needle-shaped)	$Pb(Cr, S)O_4$ $PbCrO_4$	bright to mid-yellow golden yellow	0.1 to 0.8 long, length to width 3 to 1
molybdate orange: (tetragonal)	$Pb(Cr, Mo, S)O_4$	orange to red	0.15 to 0.25
molybdate red: (tetragonal)			0.5 to 0.75
chrome orange (minoclinic)	$PbCrO_4 \cdot PbO$	orange to red	0.1 to 1.0
chrome red			1 to 12

Most important pigments:

- chrome yellow: $Pb(Cr,S)O_4$-mixed phases, or $PbCrO_4$,
- molybdate orange or red: $Pb(Cr,Mo,S)O_4$-mixed phases.

The orthorhombic modification can be stabilized by mixed crystal formation with lead sulfate ($PbSO_4$ content ca. 35 ± 15%), appropriate precipitation conditions and precipitation of protective colloids on it e.g. aluminum hydroxide. The stable monoclinic modification of the golden yellow $PbCrO_4$ is formed at precipitation temperatures above 50°C. Monoclinic lead chromate pigments with bright to mid-yellow hues can be produced by mixed-metal oxide formation with lead sulfate ($PbCr_xS_{1-x}O_4$ with up to 50% $PbSO_4$). The tetragonal $Pb(Cr,Mo,S)O_4$ pigments can be produced by incorporating white tetragonal $PbMoO_4$ resulting in the composition: 75 to 80% $PbCrO_4$, 10 to 15% $PbMoO_4$ and 3 to 10% $PbSO_4$ (molybdate orange or molybdate red pigments).

The chrome orange and red pigments are manufactured by precipitating the starting materials in the presence of alkali and then boiling. Starting materials for the precipitation reactions are sodium dichromate, sodium sulfate or sulfuric acid, lead salts such as lead nitrate, PbO suspensions and litharge. The latter is converted into lead salt solutions by dissolution in nitric or acetic acid. Their application-related properties are improved by posttreatment with phosphates, colorless oxides and hydroxides and amorphous SiO_2. This considerably improves their light fastness, temperature stability and chemical inertness.

The high tinting strength, light fastness, hiding power, brilliant hue and good price/performance ratio of these pigments has led to their widespread application in paints, printing inks and plastics. Chrome green or fast chrome green is formed by mixing chrome yellow with iron blue or phthalocyanine blue. Since the mixing ratio of the two components can be varied within a wide range, a wide range of green hues can be obtained.

Applications in:
- paints,
- printing inks,
- plastics.

Despite the adoption of appropriate safety measures during manufacture, such as closed units and dust removal plants, ensuring emission values for chromate and lead below their respective MAK values (0.1 mg/m^3 as CrO_3 and 0.1 mg/m^3 as Pb), chromate pigments are being increasingly substituted by other pigments.

5.9.3.4 Mixed-Metal Oxide Pigments and Ceramic Colorants

Colored mixed-metal oxide pigments result from the incorporation of color-giving transition metal ions into an oxide host-lattice (see Table 5.9-13). Depending upon the particle size and properties of the chosen host, pigments (0.2 to 2 µm) or ceramic colorants (stains) (up to ca. 10 µm) result, which in many cases are characterized by high thermal and chemical stability and thus are suitable for the coloring of enamels and ceramics.

Mixed-metal oxide pigments and ceramic colorants (stains):

obtained by the incorporation of color-giving transition metal ions into an oxide host-lattice

Particle size:

• pigments:	0.2 to 2 µm
• stains and oxides:	average size up to 10 µm

Table 5.9-13. Mixed-metal oxide Pigments.

pigment group	chemical composition	crystal structure	color
cobalt aluminate blue	$CoAl_2O_4$ $Co(Al, Cr)_2O_4$	spinel	red-tinged blue to green-tinged blue
spinel green	$(Co, Ni, Zn)_2TiO_4$	spinel	green
zinc iron brown	$ZnFe_2O_4$	spinel	bright to mid-brown
Fe-Cr-Mn brown	$Zn(Cr, Fe)_2O_4$	spinel	red-brown
spinel black	$Cu(Fe, Cr)_2O_4$	spinel	black
Ti-Sb-Cr buff	$(Ti, Cr, Sb)O_2$	rutile	orange-yellow
Ti-Sb-Ni yellow	$(Ti, Ni, Sb)O_2$	rutile	lemon-yellow
Ti-Sb-Mn brown	$(Ti, Mn, Sb)O_2$	rutile	bright to dark brown
pseudobrookite yellow	$Fe_2TiO_5 \cdot xTiO_2$	pseudobrookite	yellow-brown
iron manganese black	$(Fe, Mn)_2O_3$	bixbyite	black
iron manganese brown	$(Fe, Mn)_2O_3$	hematite	bright to red-brown
iron chrome brown	$(Fe, Cr)_2O_3$	corundum	red-brown to black-brown
manganese blue	$BaSO_4 \cdot Ba_3(MnO_4)_2$	barite	green-tinged blue

Manufacture by solid state reactions at 1000 to 1400°C

The starting materials in the manufacture of mixed-metal oxide pigments (as a rule carbonates, hydroxides, oxides and oxide-hydrates) are intimately mixed and heated, if necessary with added flux, at temperatures of 1000 to 1300°C. The particle size can be controlled, and thus the coloristic properties influenced, by varying the calcination temperature and the added flux. The 0.2 to 2 μm particles required for the pigment sector are obtained by intensive grinding of the calcined clinker in ball or sand mills.

Applications in the pigmentation:

- paints,
- plastics,
- enamels and ceramics.

Stains and oxides (ceramic colorants) with an average particle size up to ca. 10 μm and a broad particle size distribution, are in some cases manufactured at still higher temperature, up to 1400°C. The higher primary particle sizes are necessary because a more or less strong solubilization of the particles takes place during the firing of the enamel or ceramic frits. The component to be enameled or glazed is coated with a mixture of intensively mixed frits and colorants then fired at temperatures between 500 and 1200°C.

The thermal stability of stains and oxides is particularly important in view of the high processing temperatures and therefore oxide host-lattices with spinel-, corundum-, rutile- and silicate-phases are favored as well as zircon, phenacite, garnet and sphene structures.

The color range can be considerably widened by incorporating several color-giving or lattice-modifying ions (Table 5.9-14). The pure red-tinged blue pigment cobalt aluminum spinel can thus be changed into a green-tinged blue pigment by the additional incorporation of chromium. The further incorporation of nickel and titanium leads to an inverse titanium spinel with a brilliant green color. Brown iron-chromium-zink spinel is converted into a black pigment (spinel black) by replacing the zinc copper.

The rutile lattice is particularly suitable for incorporating color-giving ions. Almost all of the transition ions can be accommodated in the rutile lattice. The most important rutile mixed-metal oxide pigments contain nickel and chromium (lemon yellow and ochre colors respectively). By incorporating manganese a brown pigment is obtained. Niobium or antimony is incorporated to compensate for charges lower than 4+. This incorporation principle is used to a considerable extent in stains and oxides for enamels and ceramics. In this case, the number of possible element combinations is further expanded, since host-lattices such as zircon, phenacite and sphene, which have lower refractive indices and hence are less interesting as pigments but have a very high thermal stability, can be used. Ca. $10 \cdot 10^3$ t of ceramic colorants (oxides and stains) are currently produced annually in the USA and Europe.

5.9.3.5 Cadmium Pigments

Cadmium pigments based on yellow CdS or its mixed phases are among the most brilliant inorganic colored pigments. As a result of their high thermal stability and their not bleeding in plastics, they are mainly incorporated into plastics with high processing temperatures such as styrene-polymers, poly(ethene), poly(propene) and poly(carbonate), in which organic pigments with comparable brilliance suffer from thermal degradation. They are also used in especially brilliant paints. Their UV absorption protects the organic matrix (the binder) from UV degradation.

Most important properties of cadmium pigments:

- high tinting strength,
- high brightness,
- thermal stability during the pigmentation of plastics.

Table 5.9-14. Colorants for Enamels and Ceramics (Stains and Oxides) (Selection).

colorant	chemical composition	crystal structure	temperature up to which colorant is stable, °C
blues:			
cobalt blue	$CoAl_2O_4$	spinel	1450
(Co, Cr)-blue	$(Co, Ni, Zn)_2, (Cr, Al)_2O_4$	spinel	1450
zircon blue	$(Zr, V)SiO_4$	zircon	1350
greens:			
cobalt titanate	$(Co,Ni,Zn)_2TiO_4$	spinel	1350
cobalt chromite	$Co(Cr, Al)_2O_4$	spinel	1400
yellows:			
zircon yellow	$(Zr, Pr)SiO_4$	zircon	1200 to 1300
zirconium vanadium yellow	$(Zr, V)O_2$	baddeleyite	1400
tin vanadium yellow	$(Sn, V)O_2$	rutile	1350
cadmium yellow	$(Cd, Zn)S$ coated with $ZrSiO_4$	wurtzite	1250
oranges and reds:			
pink red	$Ca(Sn, Cr)SiO_5$	sphene	1250
zircon iron pink	$(Zr, Fe)SiO_4$	zircon	1250
manganese pink	$(Al, Mn)_2O_3$	corundum	
cadmium red	$Cd(S, Se)$ coated with $ZrSiO_4$	wurtzite	1250
violets:			
cobalt olivine	Co_2SiO_4	olivine	1250
pink violet	$(Sn, Cr)O_2$	rutile	1250
browns:			
mixed-metal oxides	$Zn(Cr, Fe, Ni) (Cr, Fe, Mn)_2O_4$	spinel	1300
	$Fe(Fe, Cr)_2O_4$	spinel	1300
	$(Fe, Co) (Fe, Cr)_2O_4$	spinel	1300
	$(Ti, V, Sb)O_2$	corundum	
blacks:			
mixed-metal oxides	$(Cu, Co, Ni) (Cr, Fe, Mn)_2O_4$	spinel	1300
	$CuCr_2O_4$	spinel	1300
	$(Fe, Co) (Fe, Cr)_2O_4$	spinel	1300
	$(Ti, V, Sb)O_2$	rutile	1000
grays:			
tin antimony gray	$(Sn, Sb)O_2$	rutile	1250
zircon gray	$(Zr, Co, Ni)SiO_4$	zircon	1250

Variation of the hue of yellow cadmium sulfide pigments by mixed-crystal formation:

- with ZnS, greenish yellow,
- with HgS or CdSe, orange to bordeaux red

In yellow CdS, which is the basis of the cadmium pigments, both the cadmium and the anion can, within certain limits, be replaced by ions with similar radii. The incorporation of zinc is industrially important in the manufacture of greenish yellow pigments, (Cd,Zn)S, as is that of mercury in (Hg,Cd)S and selenium in Cd(S,Se) for the production of a color range from orange to red to bordeaux red.

Manufacture of cadmium pigments by:

- precipitation with $Na_2S(Se)$ and calcination,
- calcination of $CdCO_3$, a zinc salt and S (yellow pigment) or calcination of $CdCO_3$, S and Se (red pigments).

Cadmium yellow pigments (CdS) are manufactured by adding sodium sulfide to dissolved metallic cadmium or a cadmium salt solution to precipitate the fine particle raw colorant, which does not yet have pigment properties. Calcination at temperatures between 600 and 700°C induces particle growth to ca. 0.2 μm at which optimum tinting strength and hiding power are attained.

An alternative frequently used process is the calcination of a mixture of $CdCO_3$ (from metallic cadmium), zinc salt and sulfur (for the manufacture of yellow pigments), or with selenium in the place of zinc salt in the case of red pigments.

Optimum particle size:

0.2 to 0.4 μm

In the manufacture of orange to deep red cadmium sulfoselenides using the precipitation process, selenium is dissolved in the sodium sulfide solution in an amount consistent with the color required. Particularly brilliant hues are obtained, if the precipitated raw colorant undergoes brief heat treatment in molten salt at ca. 800°C whereby an optimum particle size of ca. 0.2 to 0.4 μm can be obtained.

LD_{50} of cadmium pigments:

> 10 g/kg rat

Cadmium sulfide pigments belong to the least soluble cadmium compounds and therefore their toxicity cannot be compared with that of soluble cadmium compounds. The LD_{50}-values are greater than 10 g/kg rat oral. The cadmium solubility of commercial pigments in stimulated stomach acid (0.1% hydrochloric acid) is less than 0.1% and that of cadmium pigments incorporated in paints and plastics orders of magnitude lower, so that cadmium pigment-colored plastics can be used in the manufacture of household apparatus and packaging materials without reservation. However, their worldwide use has declined between 1980 and 1995.

5.9.3.6 Cyanide Iron Blue Pigments

Cyanide iron blue pigments (formerly known as prussian blue, milori blue or turnbull's blue) have the composition:

$$Me^+[Fe^{2+}Fe^{3+}(CN)_6] \cdot xH_2O \text{ with } Me(Na^+, K^+, NH_4^+)$$

Manufacture of cyanide iron blue pigments $Me^+[Fe^{2+}Fe^{3+}(CN)_6]$:

- precipitation with Fe(II)-salts with hexacyanoferrate(II),
- oxidation with chlorates or dichromates.

They are precipitated as a white dough when ferrous salts react with complex iron(II)-cyanides. This is then converted to cyanide iron blue by oxidation with chlorates or dichromates.

$$Fe^{2+} + Me_4^+[Fe^{2+}(CN)_6] \cdot (x + y)H_2O \longrightarrow$$
$$Me_2^+[Fe^{2+}Fe^{2+}(CN)_6] \cdot xH_2O + 2Me^2 + yH_2O$$
$$Me_2^+[Fe^{2+}Fe^{2+}(CN)_6] \cdot xH_2O \xrightarrow{\text{oxidation}}$$
$$Me+[Fe^{2+}Fe^{3+}(CN)_6] \cdot xH_2O + Me^+$$

The white dough is either precipitated by adding the hexacyanoferrate(II) solution to the iron(II)-solution or the simultaneous addition of the dissolved components to an agitator vessel at pH values between 2 and 6. The particle size can be influenced by the choice of temperature (20 to 60°C) and the concentrations of the initial solutions. The white dough is aged by boiling and then oxidized to the cyanide iron blue pigment which is filtered off, gently dried and ground.

Applications for cyanide iron blue pigments:

- car paint,
- printing ink,
- colored paper.

Dark cyanide iron blue types have particle sizes from 0.01 to 0.05 µm and almost black pure tones, whereas the bright-blue types have particle sizes between 0.05 and 0.2 µm. Cyanide iron blue pigments have extremely high tinting strengths, but are difficult to disperse, due to their tendency to agglomerate. They are stable over short periods at temperatures up to 180°C and hence are usable in stoving enamels. They are mainly used in printing inks (particularly gravure), in the coloring of fungicides (cyanide iron blue is used e.g. in vineyards as a leaf fertilizer), in paints (car paints) and in the manufacture of colored paper.

Mixtures of cyanide iron blue pigments with chrome yellow and zinc yellow are known as chrome green and zinc green respectively and are used in paints and printing inks.

LD_{50} of cyanide iron blue pigments:
8 to 10 g/kg rat

The DL_{50} of cyanide iron blue pigments is 8 to 10 g/kg rat.

5.9.3.7 Ultramarine Pigments

Ultramarine pigments are sodium aluminum silicates with the composition $Na_8[Al_6Si_6O_{24}] \cdot S_x$ (Na-rich) or $Na_{8-y}[Al_{6-y}Si_{6+y}O_{24}] \cdot S_x$ (Si-rich), which can have a blue, green, red or violet tone, depending upon the composition of the chromogenic S_x-group.

Ultramarine pigments:
blue, green, red, violet tones

The multistage manufacture of ultramarine pigments begins with careful partial calcination of the mineral kaolinite (china clay) to metakaolinite:

$$\underset{\text{(kaolinite)}}{Al_4(OH)_8Si_4O_{10}} \xrightarrow[-xH_2O]{500\text{ bis }600\,^\circ C} \underset{\text{(metakaolinite)}}{Al_4(OH)_{8-2x}O_xSi_4O_{10}}$$

A wide mesh three-dimensional zeolite structure is built up out of metakaolinite and the other raw materials (Na_2SO_3, S, reducing agent) in a very complex firing process in a reducing atmosphere (SO_2):

$$1.5Al_4(OH)_{8-2x}O_xSi_4O_{10} + 3Na_2CO_3 \xrightarrow[48\text{ bis }80\text{ h}]{750\text{ bis }800\,^\circ C}$$
$$Na_6[Al_6Si_6O_{24}] + 3CO_2 + (6 - 1.5x)H_2O \text{ (silica poor)}$$

Manufacture of ultramarine pigments:

- partial calcination of kaolinite to metakaolinite,
- formation of a zeolite structure by calcination with Na_2CO_3 in a SO_2 atmosphere,
- reaction with Na_2S_x to white prae-ultramarine,
- slow oxidation to ultramarine.

The reaction with the intermediately formed Na_2S_x yields white prae-ultramarine:

$$Na_6[Al_6Si_6O_{24}] + Na_2S_x \longrightarrow \underset{\text{(pre-ultramarine)}}{Na_6[Al_6Si_6O_{24}] \cdot Na_2S_x}$$

Blue ultramarine (with the chromogenic group S_3^-, herein generally represented as S_x) is formed by slow (up to 20 days!) oxidation of the sulfur in the cavities and channels in the zeolite cage:

$$2Na_6[Al_6Si_6O_{24}] \cdot Na_2S_x + \xrightarrow[-SO_4^{2-}]{O_2,\,SO_2} \underset{\text{(Na-rich)}}{2Na_8[Al_6Si_6O_{24}] \cdot S_x}$$

Recently new continuous processes have been introduced, which have reduced the manufacturing time to several hours and has clear ecological advantages.

Silica-rich ultramarine blue pigments are obtained with the same reaction sequence. Green ultramarine requires 1/7 to 1/8 of the sulfur required for the blue pigment, but 2.5 times the amount of reducing agent. The firing process occurs at temperatures between 900 and 1000°C in a

Variation in manufacturing conditions produces:

- blue ultramarine,
- green ultramarine,
- violet ultramarine,
- red ultramarine.

reducing atmosphere and the reaction and cooling times (20 to 25 h) are much shorter than for ultramarine blue rich in sodium. The color-giving species are S_2^- and S_3^- in cavities in the cage-structure. Oxidation of ultramarine blue or green with air at 130 to 280°C in the presence of ammonium chloride results in ultramarine violet with the chromophore S_4^-. Ultramarine red is obtained from ultramarine blue or green by air oxidation at 100 to 150°C in the presence of HCl and Cl_2.

5.9.4 Corrosion Protection Pigments

Modes of operation of active corrosion inhibiting pigments:

Paints pigmented with active corrosion inhibiting pigments are applied as corrosion-protecting coatings or primers to metallic surfaces. Active corrosion protection pigments should inhibit the corrosion processes. These can occur by a multiplicity of corrosion processes, which explains the wide range of corrosion protection pigments (Table 5.9-15 and Table 5.9-16).

Inhibition of corrosion processes by
- passivation,
- cathodic protection,
- formation of protective layers,
- formation of metal soaps,
- pH change,
- neutralization of corrosion promoters.

As a rule, corrosion protection pigments possess several of the cited inhibition properties, so that corrosion protection with a particular pigment is by a combination of different mechanisms. Optimum efficiency requires combination with a suitable binder. For example the utilization of a corrosion protection pigment which forms metal soaps only makes sense, if the binder is able to form soaps.

The use of the optimum pigment concentration, which can vary consideration, is equally important. Thus zinc salts of nitro-isophthalic acid are used at a concentration of ca. 0.5% by weight in paints, whereas ca. 90% is necessary in the case of zinc-dust pigments, to guarantee the zinc-iron contact necessary for cathodic protection.

Corrosion protection coatings also contain inactive corrosion protection pigments as additives (TiO_2, Fe_2O_3, fillers, $CaCO_3$ etc.), which support the operation of the active pigments.

Toxicological reservations in connection with several corrosion protection pigments has led to the increased use of nontoxic pigments and to new developments such as Sicorin® or the calcium or zinc ferrite pigments (see Table 5.9-15).

Table 5.9-15. Active Corrosion Protection Pigments.

classification	materials	formula	manufacture	world production quantities (t/a)
lead-containing	red lead	Pb_3O_4	oxidation of PbO	50 000
	lead cyanamide/lead phosphate/lead phosphite	$Pb(CN)_2/Pb_3(PO_4)_2 \cdot 3H_2O$ $2PbO \cdot PbHPO_3 \cdot 0.5H_2O$	precipitation	3 000
	basic lead silicochromate	$PbSiO_3 \cdot 3PbO/SiO_2$ $PbCrO_4 \cdot PbO/SiO_2$	precipitation on SiO_2	6 000
	calcium plumbate	Ca_2PbO_4	PbO + CaO	3 000
chromate-containing	zinc yellow	$3ZnCrO_4 \cdot K_2CrO_4 \cdot Zn(OH)_2 \cdot 2H_2O$	precipitation with ZnO	20 000
	basic zinc chromate	$ZnCrO_4 \cdot 4Zn(OH)_2$	ZnO + CrO_3	2 000
	strontium chromate	$SrCrO_4$	precipitation	3 000
phosphate-containing	zinc phosphate	$Zn_3(PO_4)_2 \cdot$ 2 to 4 H_2O	precipitation	5 000
	chromium phosphate	$CrPO_4 \cdot 3H_2O$	precipitation	< 1 000
borate-containing	barium borate	$BaO \cdot B_2O_3 \cdot H_2O$	precipitation	2 000
metallic	zinc dust	Zn	sublimation	70 000
	lead powder	Pb	melt spraying	1 000
oxide	zinc oxide	ZnO	oxidation of Zn	7 000
mixed oxide	calcium ferrite/zinc ferrite	$CaO \cdot xFe_2O_3/ ZnO \cdot xFe_2O_3$	calcination	n.a.
inhibitor-containing	Sicorin®	Zn-salts of nitro-isophthalic acid	precipitation	n.a.

Table 5.9-16. Corrosion Protection Processes with Different Pigment Types.

type of process	mode of protection	typical examples
electrochemical	passivation by development of an appropriate potential	chromates, Pb_3O_4
	cathodic protection	zinc dust
chemical	formation of protective layers on metal surfaces	chromates, phosphates
	formation of metal soaps with fatty acids of binder	ZnO, Pb_3O_4
	pH shift of metal soaps with fatty acids of binder (no Fe-corrosion at pH 11 to 12)	Ca_2PbO_4, ferrites such as $CaO{\cdot}xFe_2O_3$, $ZnO{\cdot}xFe_2O_3$
	neutralization of corrosion promoters (Cl^-, SO_4^{2-})	Pb_3O_4, alkali reacting corrosion protection pigments
physical	coverage of undercoat	micaceous iron oxide
	improvement in physical properties of the coating layer (improved flexibility and adhesion, reduced water permeability)	Pb_3O_4, $Pb(CN)_2$, ferrites: $CaO{\cdot}xFe_2O_3$, $ZnO{\cdot}xFe_2O_3$

5.9.5 Luster Pigments

The term luster pigments includes:

- metal effect pigments,
- nacreous pigments,
- interference pigments.

The term luster pigments includes metallic, nacreous and interference pigments. The luster effect is due to directed reflection on planar-shaped and ordered pigment particles.

5.9.5.1 Metal Effect Pigments

Metal effect pigments:

flakes or lamella-shaped metal particles of

- aluminum,
- copper,
- gold bronze.

Metal effect pigments consist of high luster flakes or lamella-shaped particles of soft ductile metals such as aluminum, copper and gold bronze. They are produced by cold forming of granules or pieces of sheet, foil or wire in specially constructed ball mills. Cold welding is hindered by the addition of fatty acids or alkylamines as lubricants, which coat the freshly formed surfaces. Particles from a few mm to µm's in diameter with aspect (thickness to diameter) ratios of 1 : 50 to 1 : 250 can be produced, depending upon the grinding technique and grinding time. The metal effect pigments are used in paints, printing inks and plastics, either alone (mass tone) or colored with transparent colorants.

5.9.5.2 Nacreous Pigments

Manufacture of synthetic nacreous luster pigments by precipitating TiO_2 on mica platelets

Pearlescence comes about by multiple partial reflection of every incident ray of light on several platelet-shaped particles at different depths in the coating.

The naturally occurring nacreous pigment fish-scales (guanine) is no longer available in sufficient quantities. Basic lead carbonate serves as a synthetic substitute, but is suspect on toxicological grounds. Bismuth oxychloride nacreous pigments are expensive and are being supplanted by cheaper products. Synthetic titanium dioxide nacreous pigments, produced by the precipitation of hydrous titanium dioxide onto colorless mica fractions of uniform platelet size and subsequent calcination, are very important. The uncoated mica platelets should be at most 200 to 500 μm thick and the double-sided titanium dioxide coating is ca. 50 μm thick. Normally the particle diameter is 10 to 30 μm.

5.9.5.3 Interference Pigments

Interference pigments are nacreous pigments, which fulfill the interference criteria and hence exhibit color effects

If the interference condition is fulfilled by the nacreous pigments produced by the precipitation process i.e. the product of oxide coating thickness and refractive index lies in the 200 to 500 nm range, interference colors are observed. Precise maintenance of coating thickness is important for a uniform color effect. The color effects possible with interference pigments (complementary colors in transmission and reflection) are utilized in the manufacture of cosmetics, artificial mother of pearl and costume jewelry. Ca. 35% of car paintings are carried out with interference pigments. An example of an industrial application is the manufacture of infra-red reflecting light-cupolas from acrylic glass. The color range can be strongly extended with colorants (Fe_2O_3, C_2O_3). The worldwide consumption of nacreous and interference pigments in 1995 was ca. $12 \cdot 10^3$ t.

5.9.6 Luminescent Pigments

Luminescent pigments:

fine particulate activated and sensitized solids, producing luminescence upon excitation

Luminescent pigments are solid fine particulate (1 to 5 μm) luminescent materials, which reemit absorbed energy as light at lower energy than the energy absorbed (mainly in the visible spectral region) either almost simultaneously with (fluorescence), or subsequent to (phosphorescence) excitation. Depending upon the structure and composition of the luminescent material, the stored energy can be reemitted within fractions of a second or up to several hours after excitation.

Activators (e.g. transition metal and rare earth ions) which act as luminescent centers optionally with sensitizers (e.g. Sb^{3+}, Pb^{2+}, Ce^{3+}, Eu^{3+}, Tb^{3+}) are incorporated in concentrations of 10^{-2} to 10^{-4} g/mol into a crystal lattice generally consisting of colorless oxides, oxysulfides, sulfides, silicates, phosphates, borates or halides of zinc, alkaline earth or rare earth metals. The impurity level must be well below the activator concentration, since impurities act as quenching centers and considerably reduce the emission yield. Emission decay time and color are mainly dependent upon the choice of activators and the crystal field influences of the matrix.

Applications in:

- cathode ray tubes,
- fluorescent lights,
- television screens,
- radar screens,
- flying spot scanners,
- image intensifiers,
- X-ray screens,
- safety marketing.

Luminescent pigments are manufactured by the repeated calcination/sintering of homogeneously mixed raw material at 1000 to 1400°C under reducing conditions, depending upon the activator(s) and the crystal lattice, interspersed with gentle grinding. They are coated in thin layers from suspensions which contain an adhesive e.g. by precipitation. Table 5.9-17 gives several selected examples.

5.9.7 Magnetic Pigments

5.9.7.1 General Information and Properties

Important properties of magnetic pigments:

- ferri- or ferromagnetic,
- needle-shaped,
- aspect ratios of 5 : 1 to 10 : 1,
- coercive forces between 300 and 1500 Oe,
- tape remanences between 1200 and 3200 Gauß.

Magnetic information storage on tapes, drums and rigid and floppy discs is based on the magnetization of miniscule solids, the so-called magnetic solids, dispersed in organic binders. These are needle-shaped particles 0.03 to 0.1 µm in diameter with aspect (length/width) ratios of 5 : 1 to 10 : 1. The products used are based on the ferrimagnetic compounds γ-Fe_2O_3 and Fe_3O_4 or ferromagnetic substances such as CrO_2 and metallic iron. The composition, shape and size of the needles are crucial for obtaining the desired magnetic properties in the tape (see Table 5.9-18).

The coercive force I_{HC} and remanence I_R achievable in the storage medium are important properties*).

The coercive force I_{HC} represents the resistance of the tape to re- and demagnetization. An oppositely directed field strength of the size of I_{HC} is necessary to demagnetize an already magnetized object.

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*) the internationally used units Oersted, Gauß and emu/g (electromagnetic units) are converted to SI-units as follows:

1 Oe = $10^3/4\pi$ [Am^{-1}]; 1 Gauß = 10^{-4} T (Tesla); 1 emu/g = $12.56 \cdot 10^4$ [Tcm^3g^{-1}]

Table 5.9-17. Selected Examples of Luminescent Pigments and their Fields of Application

activator	phosphor composition		main emission maxima (nm)	color	fields of application
Mn^{2+}	zinc orthosilicate	Zn_2SiO_4	525	green	oscilloscopes
Mn^{2+}/Sb^{3+}	calcium halogen phosphates	$Ca_5(PO_4)_3(Cl,F)$	480 580	blue yellow-orange	fluorescent lights
Mn^{4+}	magnesium fluorogermanate	$Mg_2GeO_4 \cdot 1.5MgO \cdot 0.5MgF_2$	710	red	high pressure mercury lamps
Sn^{2+}	(Sr,Mg)-orthophosphate	$(Sr,Mg)_3(PO_4)_2$	630	rose-red	fluorescent lights & high pressure mercury lamps
Ce^{3+}	yttrium aluminum garnet	$Y_3Al_5O_{12}$	550	yellow	flying spot scanners
Eu^{2+}	barium fluorobromochloride	BaF(Br,Cl)	440	blue	X-ray screens
Eu^{3+}	yttrium oxide	Y_2O_3	625	red	fluorescent lights and television tubes
Tb^{3+}	yttrium oxysulfide	Y_2O_2S	540 440	green blue	television tubes television tubes, radar tubes & X-ray screens
Tb^{3+}	gadolinium oxysulfide	Gd_2O_2S	540	green	X-ray screens
Ag$^+$/Cl$^-$ Cu$^+$/Cl$^-$	zinc sulfide	ZnS	525	green	radar tubes
Zn^{2+}	zinc oxide	ZnO	505	green	flying spot scanners
none	calcium wolframate	$CaWO_4$	415	blue-violet	fluorescent lights & X-ray screens

The higher the residual magnetization (I_R, remanence) in the tape after switching off the magnetizing field, the higher will be the intensity of the signal reproduced. The remanence of a tape depends upon the degree of filling as well as the choice of pigment. Depending on the tape quality, remanences of 1200 to 1700 Gauß are attained with oxidic magnetic materials and 2600 to 3200 Gauß with metallic iron pigments.

Operating points for tape recorders are set on the basis of the coercivity of the tapes:

I. normal (γ-Fe_2O_3),
II. CrO_2,
III. double-layer tapes CrO_2/γ-Fe_2O_3,
IV. metal.

To obtain optimum reproduction, the apparatus has to be adapted to the different coercive forces of these materials. This is accomplished by setting operating points (OP):

OP I: normal (γ-Fe_2O_3);
OP II: chromium oxide (and higher coercivity iron oxides);
OP III: ferrochrome (doubly coated tapes with CrO_2/iron oxide; largely historical);
OP IV: metal (iron or alloys).

5.9.7.2 Manufacture of Magnetic Pigments

Manufacture of CrO_2:

1. $CrO_3 \xrightarrow[200 \text{ to } 300 \text{ bar}]{250\ ^\circ\mathrm{C}} CrO_2 + \frac{1}{2}O_2$

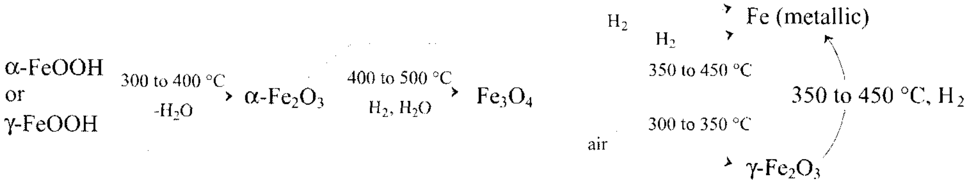
2. $2CrOOH + CrO_3 \xrightarrow[50 \text{ to } 800 \text{ bar}]{300 \text{ to } 450\ ^\circ\mathrm{C}} 3CrO_2 + H_2O$

Very complicated processes are currently necessary for the production of needle-shaped magnetic pigment particles. As regards needle-shaped pigments, chromium dioxide with a rutile structure is favored. It tends to crystallize as needles under hydrothermal production conditions (decomposition of CrO_3 in an oxygen atmosphere or reaction of CrOOH with CrO_3).

Manufacture of the iron-based magnetite pigments γ-Fe_2O_3, Fe_3O_4 and Fe from needle-shaped α-FeOOH or γ-FeOOH

The manufacture of iron oxide-based needle-shaped magnetic pigments is much more complicated as γ-Fe_2O_3, Fe_3O_4 and metallic iron (all cubic) do not crystallize in a needle-shape. It is therefore necessary to start from needle-shaped precursors. Nonmagnetic α-FeOOH (goethite) or γ-FeOOH (lepidokrokite) produced by precipitation and oxidation from Fe(II)-salt solutions are suitable precursors which can be converted into ferrimagnetic magnetite by dehydration and reduction and into ferromagnetic metallic iron by complete reduction.

In the synthesis of γ-Fe_2O_3, careful oxidation of magnetite in a spinel lattice to a superstructure of crystallizing ferrimagnetic γ-Fe_2O_3 (maghemite) under well-defined conditions is necessary:



Since the starting material is chemically and structurally changed several times, it is important that the initial needle shape be retained as completely as possible during the synthesis by, for example, using protective layers.

Coercivity increase for iron oxide magnetic pigments by Co-doping or Co-ferrite coating

Recently ever more use has been made of the coercivity-increasing effect of cobalt in the magnetic iron oxides. The cobalt is either incorporated homogeneously into the iron oxide lattice (bulk doping) or the needles of the finished γ-Fe_2O_3 or Fe_3O_4 magnetic pigment are epitaxially coated with a layer of cobalt ferrite. Coercive forces of 380 to 750 Oe require ca. 1 to 4% Co. Such products have comparable properties to CrO_2-pigments (see Table 5.9-18).

The world production capacity for magnetic pigments in 1991 was ca. $40 \cdot 10^3$ t, magnetic iron oxide pigments accounting for over 90% of this. Metallic iron pigments are preferred for 8 mm camcorders tapes.

It is mainly utilized in the manufacture of video tapes (VHS) Metal pigments are increasingly being used in 8 mm video formats and R-DAT.

The importance of audio cassettes has waned, since the introduction of the compact disc.

Table 5.9-18. Properties of Magnetic Pigments.

magnetic pigment	coercivity I_{HC}	saturation magnetization, σ_s in emu/g		typical application fields
	in Oe	theoretical	practical	OP I to OP IV (Operating Points)
γ-Fe_2O_3	330 to 370	74	70 to 73	audio cassettes OP I, amateur & professional tape recorders, computer tapes, floppy discs
γ-Fe_2O_3-pigments	370 to 450			audio cassettes, OP I
Co-modified	550 to 650		84	audio cassettes, OP II
	650 to 750			video tapes (e.g. VHS)
Fe_3O_4		84		
F_3O_4/γ-Fe_2O_3	400 to 440		80	audio cassettes, OP !
berthollide Fe_3O_4/γ-Fe_2O_3	550 to 650		84	audio cassettes, OP II
Co-modified Fe_3O_4/γ-Fe_2O_3	650 to 750			video tapes (home video recorder)
CrO_2	450 to 650		75	audio cassette, OP II
	600 to 700			video tapes (home video recorder)
Fe (metal)	1100 to 1200	150	120 to 140	audio cassettes, OP IV
	1400 to 1500			video tapes, e.g. 8 mm

References for Chapter 5.9: Inorganic Pigments

Pigments in general and colored pigments:

Winnacker-Küchler: Chemische Technologie, 4. Aufl., 1983. Bd. 3, 349.

Ullmann's Encyclopedia of Industrial Chemistry. 1992. 5. Ed., Vol. A 20, 243 – 369, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1996. 4. Ed., Vol. 19, 1 – 40, John Wiley & Sons, New York.

Winter, G., Fortschr. Miner. **57.2**, 172 – 202 (1979).

Kittel, H., Lehrbuch der Lacke und Beschichtigung, Vol. I - VII, Verlag W. A. Colomb, Berlin (1974).

Bittler, K. and Ostertag, W., Angew. Chem. **92**, 18 – 194 (1980).

Hund, F., Angew. Chem. **93**, 763 – 771 (1981).

Buxbaum, G., Ed., Inorganic Industrial Pigments, VCH, 2nd. Ed., 1998.

White pigments:

Barksdale, J., Titanium, 2nd Ed., New York, Ronald Press Comp., 1966.

The Economics of Titanium, 2nd Ed., Roskill information Services Ltd., 1976.

Wooditsch, P., defazet **33(6/7)**, 191 – 194 (1979).

Fischer, J., Industrial Minerals, August 1996, 47 – 55.

Skillen, A., Industrial Minerals, July 1996, 25 – 35.

Special pigments:

Wienand, H., and Ostertag, W., Farbe und Lack **88(3)**, 183 – 188 (1982).

Broll, A., Breyer, H. H. and Kleinschmitt, P., Chem-Z. **101(7/8)**, 319 – 323 (1977).

Industrial inorganic Chemistry
Karl Heinz Büchel, Hans-Heinrich Moretto & Peter Woditsch

6 Nuclear Fuel Cycle

6.1 Economic Importance of Nuclear Energy

Nuclear energy is today a developed and established technology in the energy market. Its contribution to the worldwide provision of energy is currently similar to that from water power at about a sixth of the worldwide production of electricity. The share of electricity production from nuclear power technology in France and Lithuania is over 70% and in four other countries it accounts for about half of the electricity production. In the Federal Republic of Germany and a number of other countries it accounts for about a third of the electricity production (FRG in 1994: 34% of public electricity provision). At the beginning of 1996 there were 428 nuclear power station complexes in operation in 34 countries with a capacity of 363 GWe, with 62 complexes then under construction (see Table 6.1-1). Nuclear energy is currently almost exclusively employed for electricity production.

The prognosis for the future development of nuclear energy involves a number of uncertainties. In some Western industrialized countries more or less large parts of the population have decided to dispense with nuclear energy, in other countries, e.g. France, these groups have little support. The example of Sweden shows that these preferences can also change, when difficulties emerge regarding concrete steps in the direction of exiting from nuclear energy. A number of Asian countries and several former communist countries in Eastern and Central Europe plan further expansion in nuclear energy.

Public electricity provision from power stations in 1994 in the FRG, net (in TWh):

coal	108.1
lignite	123.7
oil	4.3
natural gas	19.5
nuclear energy	141.8
water power	16.2
other	3.6
	417.5

Table 6.1-1. Nuclear Power Station Complexes in the World according to Country (as of 01.02.1996).

	on stream		under construction		total	
country	number	brutto capacity 10^3 MWe	number	brutto capacity 10^3 MWe	number	brutto capacity 10^3 MWe
Argentina	2	1	1	1	3	2
Armenia	-	-	2	1	2	1
Belgium	7	6	-	-	7	6
Brazil	1	1	2	2	3	3
Bulgaria	6	4	2	2	8	6
China	3	2	4	3	5	5
FR Germany	20	23	-	-	20	23
Finland	4	2	-	-	4	2
France	56	61	4	6	60	67
Great Britain	29	15	-	-	29	15
India	10	2	4	1	14	3
Iran	-	-	2	3	2	3
Japan	50	41	5	5	55	46
Canada	21	16	-	-	21	16
Kasakhstan	1	0.2	-	-	1	0.2
Korea (South)	10	9	10	9	20	18
Cuba	-	-	2	1	2	1
Lithuania	2	3	-	-	2	3
Mexico	2	1	-	-	2	1
Netherlands	2	1	-	-	2	1
Pakistan	1	0.1	1	0.3	2	0.4
Romania	-	-	2	2	2	2
Russia	29	21	6	6	35	27
Sweden	12	10	-	-	12	10
Switzerland	5	3	-	-	5	3
Slovak Republic	4	2	4	2	8	4
Slovenia	1	1	-	-	1	1
Spain	9	7	-	-	9	7
South Africa	2	2	-	-	2	2
Taiwan	6	5	-	-	6	5
Czech Republic	4	2	2	2	6	4
Ukraine	16	15	5	5	21	20
Hungary	4	2	-	-	4	2
USA	109	105	4	5	113	110
World	428	363.3	62	56.3	490	419.6

Overall it is unlikely that the share of nuclear energy in global energy provision will change in the medium term i.e. that nuclear power station capacity will increase (according to WEC/IIASA, depending upon the assumptions made, by 20 to 100% by 2020). In the Federal Republic of Germany nuclear power station capacity will probably be maintained at least at the present level in the medium term. The long term perspectives are difficult to gauge, they depend particularly upon what stringent climate protection measures become necessary are and their being internationally carried out, and to what extent renewable energies win acceptance in the market, this being decisive in determining the future not yet predictable cost reductions in solar technology. A significantly higher share of nuclear energy in the energy provision is technically and economically feasible, it potentially also providing part of the heat requirements in addition to electricity.

Primary energy consumption:

- worldwide in 1993 in 10^9 t SKE, according to energy source*):

oil	4.460
gas	2.550
coal	3.060
nuclear energy	0.800
water power	0.850
public provision	11.720
biomass etc.	1.500
renewable (wind, solar, geothermal)	0.031
total	13.251

*) calculated according to substitution methods

Worldwide energy consumption has risen in the last 40 years by a factor of four. The global energy demand will continue to increase in the future. This is partly due to the necessity of raising the standard of living of the poorer regions of the World and partly due to the continuing growth in the World population from the present $5.5 \cdot 10^9$ to ca. $10 \cdot 10^9$ by the middle of the twenty-first century. Maintenance of recent growth rates in energy provision will experience increasing problems as regards the provision of raw materials. Therefore current predictions are that the energy intensity of the Gross National Product will be reduced more in the future than in the past by the application of improved technology for the conversion and utilization of energy and that the proportion of fossil energy sources will decline strongly in the long term. Despite such energy saving efforts, worldwide energy consumption will double by the middle of the twenty-first century (band width of the WEC/IIASA study 1995: increase of a factor of 1.6 to 2.7 by 2050).

- distribution according to world regions of publicly provided energy:

North America	28.3%
Asia/Australia	24.7%
Western Europe (OECD)	18.1%
Rest of Europe	17.8%
Latin America	5.0%
Middle East	3.3%
Africa	2.8%

An important precondition for future energy provision is climate protection. Since the beginning of industrialization the CO_2-concentration in the Earth's atmosphere has increased from 283 ppm to 354 ppm. This is predominantly due to increasing combustion of coal, oil and natural gas. It has been scientifically proved that the increase in so-called greenhouse gases in the air, brings about a climatically relevant heat contribution in the Earth's atmosphere in the radiation equilibrium between solar radiation and re-radiation from the Earth. Complicated secondary effects can both ameliorate and exacerbate this.

Consumption per person (t SKE/a):

North America	10.8
Europe (OECD) and others	4.8
Rest of world	0.9
World average	2.0

Probable climate change due to ever increasing consumption of fossil fuels worldwide and consequent increase in CO_2-emission

Reduction in CO_2-emission only possible by immediate reduction in fossil fuel energy consumption

Despite remaining uncertainties in the climate models and global warming prognoses, it is currently regarded as probable that the average temperature of the atmospheric layer close to the Earth's surface will increase by several degrees Kelvin, if the emission of greenhouse gases, particularly CO_2, increases as in the past. If grave harm to humanity is to be avoided with any certainty, carbon dioxide emission has to be strongly reduced in the future, which is generally held to require an immediate reduction in fossil fuel consumption. The quantitative prerequisites therefor are currently being discussed internationally. The gap between increasing worldwide demand on the one hand and the required reduction in fossil fuel utilization on the other can not only be covered by renewable energy and energy saving measures but also a large proportion will probably have to be covered by nuclear energy. In the long term this can mean a tenfold increase in worldwide nuclear capacity.

There are a wide range of measures for reducing CO_2-emissions, which either are aimed at energy saving or at a shift to low emission or emission-free energy sources. Most of them are associated with additional costs. Typical avoidance costs are between 100 DM per ton of avoided CO_2-emission to more than 2000 DM for utilization of solar cells. Nuclear energy on the other hand can reduce the emission of CO_2 without additional costs or, e.g. by utilization for average load electricity or industrial process heat, with costs, which are at least well below the above-mentioned amounts.

Fuel cycle costs in nuclear power stations (January 1995, Pf/kWh):

natural uranium and conversion	0.19
uranium enrichment	0.26
fuel element production	0.52
reprocessing and storage of waste	1.39
total	2.36
for future EPR* (higher burn-up, direct storage)	1.60

* jointly developed European pressurized water reactor

At the current low world market prices for fossil fuels there is no clear cost advantage of nuclear energy over favorably sited power stations fired with imported coal and modern combined gas and steam power stations. More accurate comparisons depend upon the assumed interest on capital, the actual fuel prices and local conditions. Furthermore, there is no construction experience with the new generation of nuclear reactors. Despite this and independent of the above-mentioned cost advantages for climate protection, the constructioned of new nuclear reactors is economically justified. The nuclear share in energy provision of a country is at a fixed price and is reliable. This is due to the high fixed costs. Nuclear fuel uranium currently only accounts for 2% of electricity production costs. Due to its low price and extremely high energy density, national demand for uranium can, without doubt, be covered for many years.

6.2 General Information about the Nuclear Fuel Cycle

In nuclear power stations electrical current is produced from nuclear energy. Efficient operation requires provision of the nuclear power station with fuel elements and the disposal of spent materials. These operations are brought together in the nuclear fuel cycle, which embraces on the provision side the extraction and dressing of uranium ores to uranium concentrates, their conversion to uranium(VI) fluoride, enrichment of the uranium isotope U^{235} from 0.7% in natural uranium to ca. 3%, the conversion of uranium(VI) fluoride into nuclear fuel and the production of fuel elements.

Disposal comprises the reprocessing of spent fuel elements i.e. the separation and recycling of unused uranium and of the plutonium produced in the reactor and the treatment and secure permanent storage of the radioactive fission products.

Since 1994 it has been legally permissible in the Federal Republic of Germany to store the fuel elements directly.

It has not yet been decided in the Federal Republic of Germany which option is to be preferred long term.

Nuclear fuel cycle:

1. Provision of the nuclear power station with fuel elements:

- extraction and dressing of uranium ores,
- production of UF_6,
- enrichment of the U^{235} isotope,
- production of nuclear fuel from UF_6,
- manufacture of fuel elements.

2. Nuclear power station waste disposal by:

- reprocessing of spent elements i.e. separation of U and Pu from one another and from the other radioactive fission products,
- recycling of the fissile materials in the fuel element production and
- treatment and permanent storage of radioactive waste.

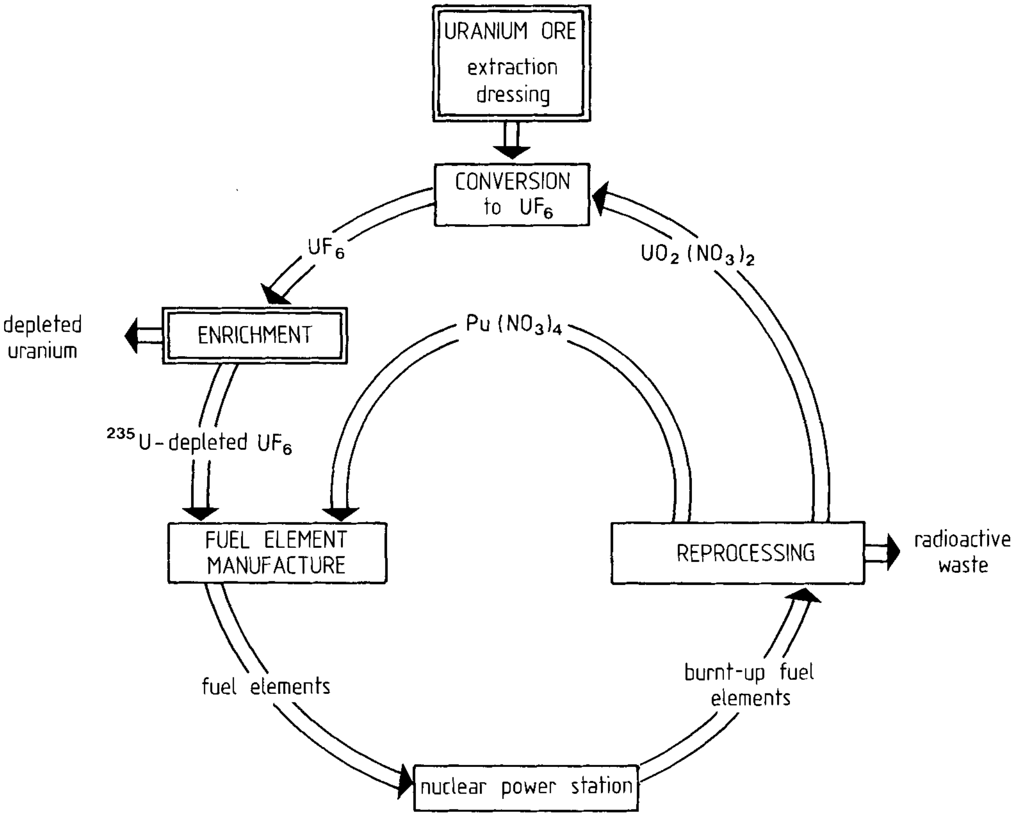


Fig. 6.2-1. Fuel Cycle for Light-water Reactors.

6.3 Availability of Uranium

The annual demand for uranium is currently just over $60 \cdot 10^3$ t (1994: $62 \cdot 10^3$ t/a). Assuming a doubling of the demand in 30 years, the cumulative requirement of natural uranium from 1996 to 2020 will be $2 \cdot 10^6$ t and $5 \cdot 10^6$ t to 2040. These prognoses can be compared with the natural reserves in Table 6.3-1.

Uranium is widely distributed in nature. The Earth's crust contains ca. 4 ppm uranium and seawater 3 ppb uranium. The total inventory in the upper Earth's crust is in the billions of tons, in the oceans $4 \cdot 10^9$ t. However, only a small part of this is sufficiently highly concentrated to make extraction worthwhile. Table 6.3-1 gives a summary of the resource situation.

The known and probable deposits (< 130$/kg) are sufficient for over 250 years

The deposits with over 130$/kg uranium have up to now, as a result of lack of economic interest, hardly been prospected for. The figures given in Table 6.3-1 have been estimated on the basis of general dependencies between concentration and the size of the deposit.

A comparison of possible demand and reserves shows that the currently known reserves will be consumed in the first half of the twenty-first century However, the probable additional reserves are, assuming increasing demand and depending upon the final level, sufficient for several hundred years. An increase in the price of uranium only has a marginal impact on electricity production costs, see Section 6.1.

Table 6.3-1. Uranium Resources. (from "Energy for Tomorrow's World", WEC 1993)

cost class	known reserves (in 10^6t)	probable reserves (in 10^6t)
up to 80$/kg U (current price 25 to 50$/kg U depending on contractual arrangements)	2.4	
up to 130$/kg U	3.7	13
up to 260$/kg U		50 – 100 (based on geological analogies)

The natural uranium requirements of a reactor can be influenced by technical measures. Thus increasing the degree of burn up from 40 to 50 MWd/kg reduces the required quantity by 5% and the recycling of plutonium from reprocessed fuel elements reduces the requirement by about 30% compared with direct permanent storage. A prolonging of the loading cycle, on the other hand, increases the uranium requirement.

Recycling of plutonium from processing reduces uranium consumption by 30%

With fast breeder reactors the known uranium reserves would last for many hundreds of years

Should the probable reserves not be confirmed or be unusable for other reasons, a technology is available which solves the resource problem anyway, the fast breeder reactor. In fast breeder reactors the known uranium reserves would last for many hundreds of years, even in the event of a vast expansion in nuclear energy provision.

The thorium bred from Uranium-233 has lost its importance as a nuclear fuel, because the minor advantages of the reactor type do not outweigh the disadvantages of a second nuclear fuel cycle. Thorium-fed reactors will, in all probability, not play a role in the energy market.

6.4 Nuclear Reactor Types

6.4.1 General Information

Nuclear power stations, worldwide, according to reactor type (situation at beginning of 1996):

	on stream	under construction
• light-water reactor		
boiling water	93	4
pressurized water	249	44
• graphite		
AGR, GGR	30	1
HTR	-	2
H_2O-graphite	20	1
• heavy water, Candu	32	9
• fast breeder	4	3
	428	64

There are a number of different nuclear reactor types. The most widely used is the light-water reactor, but graphite-moderated types, which are cooled with light-water or gas, are in operation, also heavy-water reactors. The graphite-moderated high temperature reactor is in a state of halted development, as are gas-cooled reactors and fast breeder reactors.

6.4.2 Light-water Reactors

Two types of light-water reactors:

- boiling water reactors,
- pressurized water reactors.

H_2O used as a neutron moderator and coolant.

Light-water reactors are the most important nuclear reactors

There are two types of light-water reactor: boiling water and pressurized water reactors. Both reactor types use water both as a coolant and as a moderator for slowing down the fast neutrons (2 MeV) produced during nuclear fission to the thermal energies (ca. 0.025 eV) required for the fission of further ^{235}U-nuclei. The economic importance of light-water reactors is shown by the fact that of the 490 nuclear reactors operating or under construction in 1996, 390 were light-water reactors. Of the nuclear reactors operating in the Federal Republic of Germany in 1996, 7 were boiling water reactors and 18 were pressurized water reactors.

6.4.2.1 Boiling Water Reactors

Boiling water reactors:

- H_2O coolant is evaporated at ca. 70 bar in the reactor core,
- steam fed directly into turbines.

- fuel:
  ^{235}U-enriched UO_2.

In this reactor type water is brought to its boiling point in the reactor core at a pressure of 70 bar. The resulting steam is directly fed from the pressurized reactor vessel to turbines. Fuel element bundles, each consisting of fuel rods in a lattice-like (6 x 6 to 8 x 7) array are to be found in the reactor core. The core fuel consists of ^{235}U-enriched uranium(IV) oxide. The reactors are controlled and closed down by cross-shaped control rod assemblies, which consist of steel tubes containing neutron-absorbing boron carbide.

6.4.2.2 Pressurized Water Reactors

In pressurized water reactors the heat produced in the reactor core is transferred by a closed primary loop at 155 bar and ca. 320°C without steam formation to a nonradioactive secondary loop in which steam is produced. The water of the primary loop flows through the reactor core and the closely packed square bundles of fuel rods about 3 to 5 m long and 10mm in diameter. A typical fuel element consists of 236 fuel rods and 20 control rods in a 16 x 16 array. 193 such fuel rods totaling 117 t of ^{235}U-enriched uranium(IV) oxide nuclear fuel make up the heat producing core of a 1300 MW nuclear reactor. The control rod tubes contain neutron-absorbing elements, such as boron, with which the chain reaction is regulated (moderated). The components of the primary loop are enclosed in a hermetically sealed cylindrical or spherical pressure containment vessel which is designed to withstand the pressure build-up in the event of damage and to protect the environment from the release of any of the radioactive materials formed inside.

Pressurized water reactors:

- heat produced in the reactor core is absorbed by a primary coolant loop at 155 bar and ca. 320°C in which no steam is produced and is transferred to a nonradioactive secondary loop
- Fuel:
  ^{235}U-enriched UO_2, fuel complement for a 1300 MW nuclear power station: 117 t UO_2,
- Primary coolant loop enclosed in a hermetically sealed safety containment vessel

6.4.3 Graphite-Moderated Reactors

6.4.3.1 Gas-Cooled

The first self-sustaining nuclear reactor built by Fermi in Chicago, which came on stream in 1942, was a gas-cooled graphite-moderated reactor.

The Magnox reactors, developed in Great Britain and France in the 1950's and still operating there, operate with CO_2 as coolant. The gas temperatures attain a maximum of 420°C and the fuel is natural uranium in metal or oxide form.

The *advanced gas-cooled reactors* (AGR) are a further development of the Magnox-reactors. They were only built in Great Britain. They utilize lightly-enriched uranium in oxide form. The gas exit temperatures are significantly

Graphite-moderated reactors:

- cooling agent: CO_2,
- moderator: graphite,
- fuel: originally natural uranium (Magnox-reactor), as metal or UO_2, later ^{235}U-enriched UO_2 (AGR)

higher at 690°C than with the Magnox-reactors, which is advantageous in steam production.

In contrast with AGR-reactors, the *high temperature reactors* (HTR) currently in development, which are also gas-cooled graphite-moderated reactors, helium is the cooling gas, thereby avoiding the troublesome corrosion of graphite by carbon dioxide, according to the equation:

$$C + CO_2 \rightleftharpoons 2\,CO$$

High temperature reactors:

- coolant: helium,
- operates up to 950°C,
- fuel: highly enriched U/Th-mixed oxides or weakly enriched UO_2 embedded in so-called coated particles with SiC and graphite,
- fuel elements: balls or hexaganol blocks.

The fuel in the high temperature reactors consists either of highly enriched uranium together with thorium oxide or weakly enriched uranium(IV) oxide (ca. 10% enrichment). A characteristic of HTR-reactors is the configuration of the fuel. Small fuel particles are utilized 500 μm in diameter and with a uranium(IV) oxide core. These are coated with three thin layers (pyrolytic graphite/silicon carbide/pyro lytic graphite) forming so-called coated particles. These coated fuel particles permit very high fuel burn-up (100,000 MWd/t) and exhibit exceptional properties regarding the release of radioactive fission products. Thus in normal operation only about 10^{-6} of the fission products is released i.e. only every millionth coated particle releases fission products and even in the event of breakdown these particles can be thermally stressed for several hundred hours at temperatures up to 1600°C, without release of more than 10^{-5} of the fission products contained.

These particles are embedded in a graphite matrix, the fuel elements either being manufactured as balls (6 cm in the diameter) or hexagonal blocks (key width 360 mm).

High temperature rectors were very successful in Germany as pebble bed reactors (PBR's) with the AVR-reactor in Jülich over 20 years, 50 MW t/h, and with the THTR 300 in Hamm-Ueontrop with 300 MW, which was tested electrically for 3 years.

- high potential for nuclear process heat and power-heat-coupling due to inherent physical law safety properties

The systematic utilization of the physical law-determined safety properties of high temperature reactors was the basis for the development of the HTR-reactor for power-heat-coupling and nuclear process heat up to 950°C in reactor sizes of 200 MWth. This reactor type was approved for industrial and public use in the Federal Republic of Germany by a nuclear-independent commission due to its inherent safety properties.

The Chernobyl catastrophe and the resulting pressure of public opinion prevented the further development of this interesting reactor line in the Federal Republic of Germany.

High temperature reactor technology is currently being developed further, particularly in Japan and China. In Japan a 30 MWth-HTR prototype unit is being commissioned and was scheduled to achieve its first criticality in 1997. In China a 10 MWth-HTR is being built, completion being scheduled for 1999. For these countries the aspects of a very high degree of inherent safety, good utilization of fissile material, flexible utilization in the energy economy, good storage behavior of spent fuel, completely ceramic fuel elements and a simple operating principle are important.

6.4.3.2 Light-Water Cooled

RBMK-type reactors were developed in the former USSR and have acquired infamy since the reactor catastrophe at Chernobyl. Currently in the former States of the USSR and Lithuania, 15 reactors of this type are still in operation and a further 5 reactors of its predecessor the GLWR-type. The worst shortcomings of this reactor type, which at the time decisively contributed to the triggering of the catastrophe: the design of the shutting down rods and the void coefficient of reactivity, have in the meantime been modified in all the RBMK-reactors still operating. In these reactors parallel pressure tubes, which form the reactor core and are filled with slightly enriched uranium fuel, are arranged in a cylinder of graphite blocks. Water is used as the coolant. The pressure tubes are designed for 100 to 150 bar. Steam at 500 to 520°C is produced in the reactor.

H_2O-cooled graphite-moderated reactors:

- fuel: slightly enriched Uranium compounds,
- coolant: H_2O, under high pressure: steam at >500°C,
- moderator: graphite.

6.4.4 Heavy-Water Reactors

Heavy-water reactors utilize heavy water (D_2O) as a moderator. They can be operated with natural uranium, since the capture cross-section for the thermal neutrons, necessary for controlling nuclear chain reactions, is very low for D_2O compared with H_2O. Enrichment of ^{235}U is therefore not necessary. The high price of heavy water (only present as 0.015% in natural water) is, however, a disadvantage. The resulting higher investment costs

Heavy water reactors:

- fuel: natural uranium or enriched uranium,
- moderator: D_2O
  production very costly, hence reactor type not widely used.

compared with light-water reactors and the lower power density have hindered a wider use of this reactor type (Candu). Only in Canada and India has this reactor type been installed in large numbers.

6.4.5 Fast Breeder Reactors

Fast breeder reactors:

- operated with "fast" neutrons,
- breeding reaction in a blanket of ^{238}U or ^{232}Th; core consists of suppliers of fast neutrons (^{239}Pu, ^{233}U or ^{235}U). Fuel is highly enriched UO_2 or PuO_2,
- more fissile material can be bred than is consumed,
- new fissile material is bred (^{239}Pu, ^{233}U) with unmoderated neutrons.

Fast breeder reactors are not operated, as e.g. light-water reactors, with slow neutrons, but with unmoderated "fast" neutrons as they occur immediately upon nuclear fission. These fast neutrons are necessary to sustain the chain reaction. The neutron yield per fission is here larger, since more neutrons are left over for the breeding process, once the neutrons lost by absorption and leakage have been subtracted. They are absorbed by ^{238}U or ^{232}Th, which are converted into fissile ^{239}Pu and ^{233}U respectively. A new fissile material is therefore bred from the non-fissile ^{238}U and ^{232}Th. A breeder reactor consists, therefore, in principle of a fissile material-rich core of ^{239}Pu and ^{233}U or ^{235}U, surrounded by a blanket of ^{238}U or ^{232}Th, from which more fissile material can be bred as it is consumed. Experimentally breeding rates of 1.1 have been attained in breeder reactors. Fast breeder reactors do not contain a moderator.

- fast breeder reactors do not need moderators.

Uranium (ca. 20% ^{235}U) is used as the fuel, but mainly with ^{239}Pu in the form of a UO_2/PuO_2 mixture. The breeding blanket consists of depleted uranium from isotope separation plants or from reprocessing plants for spent nuclear fuels. Axially movable boron carbide absorbers are distributed in the fuel zone for shutting down purposes. The uranium utilized can be ca. 100 times better utilized than e.g. in light-water reactors.

- uranium is almost 100 times better utilized than e.g. in light-water reactors.

Since with this high uranium utilization less rich uranium deposits (down to the uranium concentration in seawater) also become economically viable, nuclear energy from breeder reactors is a practically inexhaustible energy source.

Light-water cannot be used as a heat transporting agent, since the fast neutrons may not be slowed down. The preferred heat transferring medium is liquid sodium.

- liquid sodium is used for heat transfer in both the primary and secondary loops

Sodium-cooled fast breeder reactors, in which the heat is transferred via liquid sodium from the primary radioactive loop to an inactive secondary loop onto a conventional water/steam loop, are technically realizable. This is shown by the experience built up with experimental and prototype plants in the USA (since 1951), the former States of the USSR (since 1958), Great Britain (since 1974), France (since 1967), the Federal Republic of Germany (1977 - 1991, Karlsruhe) and Japan (since 1977) in reactors producing up to 1200 MW of electricity. The sodium technology is demanding, but is manageable. Russia, France and Japan have the most advanced development programs in the world for fast breeder reactors. In these countries demonstration breeders operate with 600 and 1200 MW electrical outputs (Super-Phenix in France, with 1200 MW). In the Federal Republic of Germany (at Kalkar) a sodium-cooled fast breeder reactor was under construction with a capacity of 327MW, but construction was stopped for political and financial reasons shortly before commissioning. Japan has built and is presently commissioning an analogous plant (280MW).

Sodium-cooled fast breeder reactors are technically realizable.

Russia, France and Japan operate fast breeder reactors.

6.5 Nuclear Fuel Production

The most important fuel for currently operated nuclear power stations (mainly light-water reactors) is ^{235}U-enriched uranium(IV) oxide. Also of importance are metallic uranium for the Magnox reactors and a few research reactors and uranium-plutonium mixed oxides for light-water reactors. Fuel production comprises: extraction and dressing of uranium ores to uranium concentrates, conversion into UF_6, the uranium compound used for enrichment of the ^{235}U-isotope, enrichment of ^{235}U and production of fuel from enriched UF_6 (reconversion).

The starting materials for uranium nuclear fuels are uranium compounds from natural uranium deposits and fissile material separated by reprocessing from spent uranium fuel rods.

Provision of nuclear power stations with fuel (^{235}U-enriched UO_2 or U-metal):

- conversion of uranium concentrate to UF_6,
- enrichment of ^{235}U-isotope,
- reconversion of UF_6 to UO_2 or U-metal.

Nuclear fuels from:

- natural uranium,
- spent uranium fuel rods.

6.5.1 Production of Uranium Concentrates ("Yellow Cake")

Uranium deposits:

- vulcanites,
- pegmatites,
- discordance, gangue, conglomerate and sandstone deposits,
- phosphates, coal, bituminous shale,
- uranium is then worked, if U_3O_8-content > 0.5% (for conventional deposits).

Uranium occurs naturally in discordance-pegmatite, vulcanite gangue, conglomerate and sandstone deposits In addition it occurs as phosphates, in coal, bituminous shale and seawater. For extraction with convention mining techniques (underground and overcast mining) contents of at least 0.5% U_3O_8 are necessary. In addition to conventional mining techniques in-situ leaching (ISL-process) is used. The ISL-technique is suitable for extracting uranium from sandstone deposits, for which particular mineralogical and geological conditions have to be fulfilled.

Worldwide production of uranium (1997): 32,188 t

The most important uranium producing countries in 1997 were: Canada (30%), Niger (9.2%), Russia (9.2%), Kazakhstan (7%), Australia (6.8%), Uzbekistan (6.3%), Namibia (5.9%), South Africa (5.2%), USA (4.3%), France (3.2%). The worldwide production of uranium in 1997 was 32,188 t.

6.5.1.1 Uranium from Uranium Ores

Uranium-containing ores are crushed, ground, leached, enriched and precipitated

The ore extracted by open cast or underground mines is coarsely ground in crushers and then finely ground, the thereby released radon being sucked off as a radiation prevention measure. The uranium content is extracted with the help of hydrometallurgical processes, in which the enrichment of uranium via ion exchange or extraction processes and a precipitation process follow the leaching step.

6.5.1.1.1 Leaching Processes

Leaching of uranium ores can proceed with acid or alkali.

For tetravalent uranium leaching has to be carried out oxidatively

The leaching of uranium ores proceeds with acid or alkali, depending upon the composition of the ore. Ores with alkaline gangue are preferably leached with alkali. If uranium(IV) compounds are present, the leaching is carried out under oxidative conditions. Uranium is leached from low grade uranium ores by trickling the leaching medium through heaps of roughly crushed ore or into the seam itself (in situ leaching). Heap leaching is currently only used sporadically. In-situ leaching is industrially important particularly in Kazakhstan, Uzbekistan and the USA.

In-situ leaching in the seams themselves proceeds with sulfuric acid or carbonate solutions. The leaching agent is fed in via injection tubes into the rock seam and brought to the surface via a central tube. In situ uranium leaching efficiency is 60 to 85%. Currently ca. 5000 t of uranium are extracted in this way.

In situ leaching in seams proceeds with alkali or acid.

Uranium leaching efficiency 60 to 85%, important growing.

Leaching with Acid

Dilute sulfuric acid is generally used as the acidic leaching agent. This digests the uranium(VI) oxide, which mainly occurs in secondary deposits, to uranyl sulfate:

$$UO_3 + H_2SO_4 \longrightarrow UO_2SO_4 + H_2O$$

The uranium in primary pitch blend is mainly present as uranium(IV) oxide and must first be oxidized to hexavalent uranium. This is most easily achieved with the Fe^{3+} ions, which come from the ore itself:

$$UO_2 + 2\,Fe^{3+} \longrightarrow UO_2^{2+} + 2\,Fe^{2+}$$

If insufficient trivalent iron is present, it is produced from divalent iron by blowing in air or oxygen or by adding chlorate solution continuously to the leaching sludge.

Acid leaching:

- preferred leaching agent: dilute sulfuric acid
- UO_3 from secondary deposits is digested to uranyl sulfate
- UO_2 in primary pitch blend must be initially oxidized with trivalent iron

Between 20 and 1100 kg of sulfuric acid is used per t ore. Acid leaching generally proceeds at atmospheric pressure.

Sulfuric acid consumption:

20 to 1100 kg/t ore

Bacterial leaching with thiobacillus thiooxidans is also an acid leaching process. Sulfidic sulfur, e.g. in pyrites, is oxidized to sulfate and iron(II) is oxidized to iron(III), which itself oxidizes uranium(IV) to uranium(VI). This process has not yet been operated industrially.

Acid leaching is also possible bacteriologically

Leaching with Alkali

Alkaline leaching with:

- Na_2CO_3,
- $NaHCO_3$,
- $(NH_4)_2CO_3$.

Uranium(VI) is converted into uranyl tricarbonato-complexes

Leaching with alkali always takes place at high temperatures, either under pressure (5 to 6 bar, 95 to 120°C) or at atmospheric pressure (75 to 80°C). The leaching agent used is sodium carbonate, sodium hydrogen carbonate or ammonium carbonate. Uranium(VI) oxide is converted in this process into uranyl tricarbonato-complexes:

$$UO_3 + Na_2CO_3 + 2\ NaHCO_3 \longrightarrow Na_4[UO_2(CO_3)_3] + H_2O$$

U(IV) is oxidized in alkali media with oxygen to U(VI)

The uranium(IV) is first oxidized in the alkaline medium by ambient oxygen to uranium(VI). Leaching with alkali under pressure has been carried out for a long time.

6.5.1.1.2 Separation of Uranium from the Leaching Solutions

Separation of uranium from the leaching solutions by:

- ion exchange,
- extraction.

Combinations of ion exchange and ion extraction are also used.

Ion exchange and extraction with organic solvents have proved effective in separating uranium from the leaching solutions. Combinations of the ion exchange process with solvent extraction are also known. This is normally preceded by separation of the leaching solution from solids by multistage filtration or countercurrent decantation followed by clarification e.g. over a bed of sand.

Uranium separation by ion exchange:

strongly or weakly basic ion exchange resins are used. Elution with nitrate or chloride solutions

Separation by ion exchange: Strongly basic or weakly basic ion exchange resins are used to separate selectively the uranium from the weakly acidic or alkaline solutions from the leaching step. The uranium is eluted from the ion exchange resins with nitrate or chloride solutions as anionic (carbonato- or sulfato-) complexes.

Ion exchange by three processes:

- in fixed beds,
- in suspension,
- continuous.

The ion exchange is carried out according to different processes. Separation from solid-free solutions can, in addition to conventional fixed bed processes, be carried out continuously with cylindrical columns' mounted in series. Ion exchange can also be carried out on unclarified turbid leaching solutions, if baskets with ion exchange resin are moved in the turbid leaching solution or by continuous ion exchange. The advantage of the ion exchange process is that uranium can be extracted from very dilute solutions as well as from turbid unclarified solutions.

Separation by solvent extraction: Uranium can be extracted from aqueous solutions using extraction agents into the solvent phase, from which it can be stripped. The extraction agents used are phosphorus compounds such as di-(2-ethylhexyl)-phosphate, tri-n-butyl-phosphate and tri-n-octylphosphine oxide as well as primary, secondary and tertiary amines in salt form or as quaternary ammonium salts. The extraction agents are diluted with inert hydrocarbons, preferably kerosene, to concentrations of 4 to 10% by volume. The solubility of the amine salts, particularly the hydrogen sulfates, chlorides and nitrates is increased by adding long chain alcohols (e.g. isodecanol).

Uranium separation by extraction:

extraction agents:

- phosphorus compounds,
- amines.

Following processes are utilized:

- AMEX: amine extraction,
- PURLEX: amine extraction,
- DAPEX: dialkylphosphate extraction,
- ELUEX: combination of ion exchange with extraction,
- BUFLEX: combination of ion exchange with extraction.

The extraction processes, which are mainly carried out in mixer-settler plants, are preferably carried out with acidic leaching solutions. For the different processes see the marginal notes.

Stripping of the uranium compounds from the organic phase with aqueous salt solutions

Stripping of the uranium compounds proceeds by mixing the separated uranium-containing organic phase with an aqueous solution of sodium chloride, sodium carbonate or ammonium sulfate at a slightly acid or alkaline pH. The uranium present in the organic phase, e.g. as $(R_3NH)_4[UO_2(SO_4)_3]$, goes into the aqueous phase, e.g. in the form of a carbonato-complex:

$$\begin{aligned}&(R_3NH)_4\,[UO_2(SO_4)_3]\ (\text{org.}) + 5\ Na_2CO_3\ (\text{aq.})\\ &\rightleftharpoons\ 4\ R_3N + Na_4\,[UO_2(CO_3)_3]\ (\text{aq.}) + 2\ H_2O + 2\ CO_2\\ &\qquad + 3\ Na_2SO_4\end{aligned}$$

6.5.1.1.3 Manufacture of Marketable Uranium Compounds (“Yellow Cake”)

High quality requirements particularly as regards uranium concentration and the maximum quantities of undesirable ions such as Mo, V and P are stipulated by the processors for the end product, so-called “yellow cake” produced by the uranium ore mines. Uranium is generally precipitated as diuranates from the aqueous solutions produced by the ion exchange and solvent extraction processes under precise conditions.

Uranium concentrate, “yellow cake”, must be very pure.

The diuranate can be precipitated from alkaline solutions by two processes:

1. with sodium hydroxide at pH > 12 and 80°C:

Precipitation of uranium from alkaline solution as diuranate with:

- NaOH,
- NH_3 or MgO after prior acidification of the solution.

$$2\,Na_4\,[UO_2(CO_3)_3] + 6\,NaOH \longrightarrow Na_2U_2O_7 + 6\,Na_2CO_3 + 3\,H_2O$$

2. with ammonia or magnesium oxide after prior acidification of the solutions.

In the first process vanadium is coprecipitated and the sodium diuranate contains a nominal stoichiometric excess of sodium. The vanadium can be removed by roasting the "yellow cake" in the presence of sodium carbonate at 850°C followed by washing. The sodium carbonate solution from the washing is converted into sodium hydrogen carbonate and the sodium hydroxide solution into sodium carbonate by passing hot carbon dioxide into the solutions, which are returned to the leaching process. The consumption of solid sodium hydroxide is 10 to 20 kg/t ore.

In the second process the alkaline solution is mixed with acid and the carbon dioxide liberated driven of by boiling. The resulting acidic solution is then neutralized with ammonia or magnesium oxide, whereupon uranium precipitates together with molybdenum and vanadium. The process is therefore only used if uranium ores have low concentrations of molybdenum and vanadium.

Uranium can de separated from alkaline solutions as UO_2 by reduction of carbonato-complexes with H_2, instead of as diuranates

Uranium can also be obtained as uranium(IV) oxide from the alkaline solutions by reduction with hydrogen at 140 to 150°C under pressures of 6 to 10 bar in the presence of a nickel catalyst:

$$Na_4\,[UO_2(CO_3)_3] + H_2 \longrightarrow UO_2 + Na_2CO_3 + 2\,NaHCO_3$$

This very expensive process is no longer carried out industrially.

Uranium precipitated from acid solutions as diuranates:

- NH_3 at pH 5,
- $Mg(OH)_2$, $Ca(OH)_2$.

In the case of acidic solutions, uranium is generally precipitated with ammonia at pH 5 as ammonium diuranate, but magnesium and calcium hydroxides are also used as the precipitating agent:

$$2\,UO_2SO_4 + 6\,NH_3 + 3\,H_2O \longrightarrow (NH_4)_7U_2O_7 + 2\,(NH_4)_2SO_4$$

Before diuranate precipitation the excess sulfate and iron have to be removed.

Should it be necessary, excess sulfate and iron can be removed by preliminary precipitation with milk of lime or magnesium oxide to gypsum and iron hydroxide. If the phosphate concentration is too high, it can be precipitated as iron phosphate by adding iron ions. A better crystalline ammonium diuranate is obtained by simultaneously blowing in air or steam during the precipitation. In the case of salt-rich acidic uranium solutions, precipitation can be carried out with hydrogen peroxide, this type of precipitation being very selective.

$$UO_2SO_4 + H_2O_2 \longrightarrow UO_4 + H_2SO_4$$

The thereby formed sulfuric acid is neutralized by adding magnesium hydroxide. Independently of the production method, the precipitated uranium concentrate is washed to remove adhering salt solution and then dried. The precipitates produced with ammonia are subsequently calcined in a multiple hearth kiln at 750°C, ammonia, sulfite and chloride being driven off and U_3O_8 being formed:

Diuranate precipitates are washed and dried:

- ammonium diuranate at ca. 750°C; converted into U_3O_8,
- sodium diuranate and uranoxy-hydrate at 120 to 175°C.

$$9\ (NH_4)_2U_2O_7 \longrightarrow 6\ U_3O_8 + 14\ NH_3 + 15\ H_2O + 2\ N_2$$

With sodium diuranate or uranoxy-hydrate a drying temperature of 120 to 175°C is sufficient.

Independently of their color (calcined uranium oxide is dark-green to black), the resulting uranium concentrate is known as "yellow cake". The name refers to the yellow color of the uranium precipitate.

6.5.1.2 Uranium from Phosphate Ores and Wet Phosphoric Acid

Ionic radius of U^{4+} comparable with Ca^{2+}; hence U^{4+} in apatites.

Wet process phosphoric acid from apatites contains 50 to 200 ppm U_3O_8

Separation of U_3O_8 from raw wet process phosphoric acid:

1. by extraction with
   - mixture of trioctylphosphine oxide and di-(2-ethylhexyl)-phosphate,
   - mixture of mono- and dioctylphenylesters of phosphoric acid.

Uranium is present in apatites, because the ionic radius of uranium(IV) is comparable to that of the calcium ion. In the wet process the apatite is digested with dilute sulfuric acid producing wet process phosphoric acid. Raw phosphoric acid produced by the wet process contains, depending upon the ore used, between 50 and 200 ppm U_3O_8. The uranium can be recovered from wet process acid by extraction. The extraction agents used are preferably a mixture of trioctylphosphine oxide (TOPO) and di-(2-ethylhexyl)-phosphate (DEHPA) in kerosene (process developed by the Oak Ridge National Laboratory) or a mixture of mono- and dioctylphenylesters of phosphoric acid. Further developments of the Oak Ridge National Laboratory process are the reduction stripping and oxidation stripping processes.

2. by the reduction stripping process:

- oxidation of U^{4+} to U^{6+},
- extraction of U^{6+} with trioctylphosphine oxide/di-(2-ethylhexyl)phosphate in kerosene,
- reduction stripping of the organic phase with Fe^{2+} in water,
- reoxidation of U^{4+} to U^{6+},
- renewed extraction of U^{6+},
- stripping of the organic phase with aqueous $(NH_4)_2CO_3$; $(NH_4)_4[UO_2(CO_3)_3]$ precipitates out.

In the reduction stripping process uranium(IV) in the raw wet process acid is oxidized to uranium(VI) by treatment with sodium chlorate, hydrogen peroxide or air at 60 to 70°C, the uranium(VI) formed being extracted with trioctylphosphine oxide/di-(2-ethylhexyl)phosphate in kerosene and the resulting solution finally reductively stripped repeatedly with aqueous iron(II) solutions. This results in an enrichment by a factor of 40. After oxidation of the stripped solution with sodium chlorate or ambient oxygen and renewed extraction of the uranium(VI) formed with trioctylphosphine oxide/di-(2-ethylhexyl)phosphate, the phosphoric acid is removed from the organic phase by washing. The uranium(VI) is then stripped with ammonium carbonate and precipitated as the ammonium diuranyl-tricarbonato-complex. This is filtered off, washed and calcined.

3. by the oxidation stripping process:

- with mono/dioctyphenyl phosphoric acid ester mixture,
- oxidation of U^{4+} to U^{6+} in aqueous phosphoric acid,
- extraction with trioctylphosphine oxide/di-(2-ethylhexyl)phosphate.

In the oxidation stripping process the uranium(VI) in the raw wet process acid is initially reduced to uranium(IV), which is extracted with a mixture of mono and dioctylphenyl esters of phosphoric acid in kerosene. Oxidation with sodium chlorate in phosphoric acid transfers the uranium to the aqueous phase and it is then extracted with trioctylphosphine oxide/di-(2-ethylhexyl)-phosphate, as in the reduction stripping process.

6.5.1.3 Uranium from Seawater

Uranium content in seawater very low compared with other deposits:

seawater	0.003 ppm
phosphates	100 – 200 ppm
conventional uranium ores	350 – 5000 ppm

The average uranium-content in seawater is at 0.003 ppm significantly lower than in conventional uranium ores (350 to 5000 ppm) or in phosphates (100 to 200 ppm). About 27 $\cdot 10^3$ t of uranium is fed annually into the sea via rivers.

Uranium is present in seawater as uranyl carbonate or carbonato-complexes.

The uranium in seawater is present, depending upon the pH and carbon dioxide concentration, as UO_2CO_3, $[UO_2(CO_3)_2H_2O]^{2-}$ or $[UO_2(CO_3)_3]^{4-}$.

It is technically feasible to extract uranium from seawater. There are, however, sufficient quantities of terrestrial uranium deposits, with extraction costs well below the extraction costs of uranium from seawater.

6.5.2 Conversion of Uranium Concentrates to Uranium Hexafluoride

6.5.2.1 General Information

The main task in the conversion of uranium concentrate ("yellow cake") to UF_6 is the purification of the concentrate and its conversion into a chemically suitable form for further processing or enrichment of the ^{235}U-isotope for the different reactor types. Isotope enrichment proceeds in the gas phase via uranium(VI) fluoride, the only uranium compound which boils at low temperatures and is stable in the vapor phase. It is advantageous that fluorine only occurs naturally in a single isotope.

Conversion of uranium concentrates into UF_6, which is used for:

- uranium purification,
- ^{235}U-isotope enrichment.

Two processes are employed for the production of uranium(VI) fluoride, namely the wet and dry processes. In both processes uranium(IV) oxide and uranium(IV) fluoride are formed as intermediates. In the wet process the uranium(IV) oxide is produced from the uranium concentrate by way of uranyl nitrate, whereas in the dry process the uranium concentrate is directly reduced to uranium(IV) oxide. The methods of purification used are also different: in the wet process the purification proceeds at the uranyl nitrate stage, by solvent extraction, whereas in the dry process the end product uranium hexafluoride is itself distillatively purified.

Conversion to UF_6 by two processes:

- wet process:
  uranium concentrate $\rightarrow UO_2(NO_3)_2$ (purification) $\rightarrow UO_2 \rightarrow UF_4 \rightarrow UF_6$
- dry process:
  uranium concentrate $\rightarrow UO_2 \rightarrow UF_4 \rightarrow$ UF_6 (purification)

6.5.2.2 Wet Process for Uranium(VI) Fluoride Manufacture

In the production of uranium(IV) oxide in the wet process, the uranium concentrate is first converted into a uranyl nitrate solution with nitric acid. After the purification of the uranyl nitrate by solvent extraction, it can be converted into uranium(IV) oxide by two different routes: either by thermal denitration to uranium(VI) oxide which is then reduced to uranium(IV) oxide or by conversion of uranyl nitrate into ammonium diuranate which is reduced to uranium(IV) oxide. Purification proceeds by extraction of the uranyl nitrate hydrate from the acidic solution with tri-n-butylphosphate in kerosene and stripping this organic phase with water, whereupon uranium goes into the aqueous phase.

Wet process:
two routes of $UO_2(NO_3)_2$ to UO_2

1st route:

$UO_2(NO_3)_2 \cdot 6H_2O$
$\downarrow$
UO_3
$\downarrow$
UO_2

2nd route (Comurhex process):

$UO_2(NO_3)_2 \cdot 6H_2O$
$\downarrow$
$(NH_4)_2U_2O_7$
$\downarrow$
UO_2

This diluted aqueous uranyl nitrate solution is evaporated to uranyl nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$, which is then calcined to uranium(VI) oxide in a fluidized bed furnace:

$$UO_2(NO_3)_2 \cdot 6\,H_2O \longrightarrow UO_3 + NO + NO_2 + 6\,H_2O + O_2$$

The temperature must not exceed 400°C, to prevent the formation of U_3O_8. The nitrous gases produced are processed to nitric acid, which is recycled. The subsequent reduction of uranium(VI) oxide to uranium(IV) oxide with hydrogen at 500°C also proceeds in the fluidized bed furnace.

The second route to uranium(IV) oxide consists of precipitation of ammonium diuranate from the solvent extraction-purified aqueous uranyl nitrate solution by adding ammonia and then reducing it with hydrogen to uranium(IV) oxide (Comurhex process developed in France).

Conversion of UO_2 to UF_4 proceeds with anhydrous hydrogen fluoride (dry process) in fluidized bed, screw-reactor or moving bed reactor

Moving bed reactors possess above one another:

- a reduction zone for reduction of UO_3 with hydrogen and
- a hydrofluorination zone for UF_4 production.

Uranium(IV) oxide is the starting material for uranium(IV) fluoride production in which uranium(IV) oxide is generally reacted with anhydrous hydrogen fluoride. This difficult to carry out exothermic reaction proceeds either in a fluidized bed, in moving bed reactors, or in screw-reactors. To achieve as complete as possible reaction in fluidized bed reactors, two fluidized bed reactors are connected in series. Screw-reactors are also preferably connected in series. In moving bed reactors the reduction zone and the hydrofluorination are arranged above one another in a plant. The uranium(IV) oxide produced by the reduction of uranium(VI) oxide with hydrogen is very reactive and is completely reacted with HF at temperatures between 500 and 650°C to uranium(IV) fluoride.

Wet process for UF_4-manufacture (EXCER-process):

purification of uranium(VI) in solution
↓
reduction to uranium(IV)
↓
precipitation of $UF_4 \cdot 0.75H_2O$
↓
dehydration to UF_4

A wet process is also utilized for the production of uranium(IV) fluoride, namely the EXCER process (Ion **Ex**change **C**onversion **E**lectrolytic **R**eduction). In this process the ion exchange- or extraction-purified uranium(VI) solution is either electrolytically or chemically reduced to uranium(IV), which is precipitated with hydrofluoric acid as uranium(IV) fluoride hydrate ($UF_4 \cdot 0.75H_2O$). This is subsequently dehydrated at 400 to 450°C.

Manufacture of UF_6 from $UF_4 + F_2$ in flame-reactors or fluidized bed reactors

The conversion of uranium(IV) fluoride to uranium(VI) fluoride proceeds exclusively with elemental fluorine, either in flame-reactors or in fluidized bed reactors. The uranium(VI) fluoride formed is recovered from the reaction gases by freezing it out.

The wet process for uranium(VI) fluoride manufacture is utilized in the Kerr-McGee process, in which the reduction proceeds with a H_2/N_2-mixture from ammonia cracking and hydrofluorination is carried out in a two stage fluidized bed. British Nuclear Fuel Ltd and Eldorado Nuclear Ltd/Canada also use wet processes.

Wet processes:

- Kerr-McGee process,
- British Nuclear Fuel process,
- Eldorado Nuclear process.

6.5.2.3 Dry Process for Uranium(VI) Fluoride Manufacture

In the dry process, introduced by Allied Chemical Corp., the uranium concentrate is pelletized and directly reduced with hydrogen to uranium(IV) oxide at temperatures between 540 and 650°C in a fluidized bed reactor. Hydrofluorination to uranium(IV) fluoride proceeds in two fluidized bed reactors connected in series. After fluorinating the uranium(IV) fluoride formed in a production unit consisting of a flame-reactor and a fluidized bed reactor, the uranium(VI) fluoride produced is purified in a two stage pressure distillation process. This distillative purification process is necessary, because, in contrast with the wet process, no purification is carried out in earlier stages.

Dry process for production of UF_6 from Allied Chemical Corp.:

uranium concentrate
↓
reduction to UO_2
↓
hydrofluorination to UF_4
↓
fluorination to UF_6
↓
UF_6 purification by fractional distillation

The uranium conversion capacity in Western industrialized countries in 1995 was nominally $385 \cdot 10^3$ t/a UF_6, of which about 73% is accounted for by wet processes. The capacity in the former States of the USSR is estimated to be ca. $14 \cdot 10^3$ t/a UF_6. In 1995 the total conversion was $51.3 \cdot 10^3$ t UF_6.

Uranium conversion capacities in 1995 (in 10^3 t/a):

USA	11.5
Canada	9.5
Great Britain	5.5
France	12.0
Western industrialized countries:	38.5
former States of USSR:	14.0
other countries	1.5

6.5.3 ^{235}U-Enrichment

Enrichment of the ^{235}U-isotope from the 0.711% in natural uranium to ca. 4% can proceed by gas diffusion, with a gas centrifuge and with separation nozzles. The separation nozzle process is no longer important. Pure uranium(VI) fluoride is utilized.

Enrichment of ^{235}U-isotopes from 0.711% in natural uranium to ca. 4% proceeds via:

In the *gas diffusion process* uranium(VI) fluoride is forced through a cascade of fine pore membranes connected directly in series. This process exploits the

- gas diffusion process,

different diffusion rates of isotopes with different masses. To achieve an ^{235}U-enrichment of 3 to 5%, this process has to be repeated 1000 to 1500 times and is very energy intensive.

- gas centrifuge process,

The *gas centrifuge process* uses long multipy overcritically rotating cylinders, in which the heavy uranium isotope ^{238}U is enriched at the cylinder wall and the lighter isotope ^{235}U is enriched at the center of the centrifuge. Enrichment to 3 to 5% ^{235}U is achieved in less than ten stages connected in series. The energy consumption is ca. 50 kWh/kg SWU (SWU = separation work units).

- nozzle separation process.

The *nozzle separation process* utilizes the centrifugal forces which occur upon diversion of a gas stream. A gas stream of uranium(VI) fluoride, helium and hydrogen is directed along a curved wall and then split by a peeling off plate into two gas streams with enrichment of the heavier and lighter isotopes respectively.

Laser separation of isotopes is in development.

Laser separation of isotopes for enrichment of ^{235}U is in development and is not yet ripe for industrial exploitation

Uranium enrichment capacities in 1995 (10^3 t SWU/a):

• USA	19.2
• France	10.8
• FRG/Great Britain/Netherlands (Urenco):	3.5
• Russia:	14.0
• Japan:	0.6

In 1995 the worldwide enrichment capacity was ca. 48.1 · 10^3 t SWU/a. The annual requirement of a 1300 MW reactor is ca. 120 t SWU. The separation work is dependent upon the degree of depletion.

6.5.4 Reconversion of Uranium(VI) Fluoride into Nuclear Fuel

6.5.4.1 Into Uranium(IV) Oxide

6.5.4.1.1 General Information

Conversion of UF_6 into UO_2 by:

- two wet processes,
- a dry process.

There are three processes which are industrially convert enriched uranium(VI) fluoride into sinterable uranium(IV) oxide: two wet processes and one dry process.

In the manufacture of enriched UO_2 avoidance of critical mass has to be taken into account.

In all processes criticality avoidance safety features have to be incorporated, as in general when enriched uranium is being processed, i.e. there must be measures for hindering an uncontrolled chain reaction, which occurs upon attaining the critical mass. This is dependent upon the degree of ^{235}U-enrichment, the chemical form of the uranium, the degree of moderation and geometric dimensions. Thus by increasing the surface area of a vessel, the loss of neutrons to the surroundings is increased with the result that the neutron population necessary for achieving a critical condition is not attained. The diameter of apparatuses or the height of the filtration layer is thus limited and additional heterogeneous neutron poisons are incorporated into the vessel e.g. boron carbide or cadmium.

6.5.4.1.2 Uranium(IV) Oxide by Wet Processes

In the wet processes poorly soluble uranium compounds are precipitated, whereby the fluoride left in the filtrate is reacted with lime to fluorspar or processed to other inorganic fluorine compounds by fluorine processing companies.

Wet processes for the production of UO_2:

precipitation of poorly soluble uranium compounds from the hydrolysis of UF_6:

- ADU process,
- AUC process.

Ammonium diuranate (ADU) process: This process was developed in the USA in the 1950's and is currently still the most important process. However, the raw uranium(IV) oxide produced with this process contains up to 2% by weight of fluoride and hence requires aftertreatment before it is suitable for pressing into fuel pellets. This disadvantage is not shared by the other two processes. New reconversion plants do not, therefore, in the main, utilize the ADU-process.

ADU-process supplies fluoride-containing UO_2; its importance is hence on the wane

In the ADU process the uranium(VI) fluoride from the enrichment plant is first evaporated and hydrolyzed with water:

$$UF_6 + 2\,H_2O \longrightarrow UO_2F_2 + 4\,HF$$

The UO_2F_2 solution is treated with ammonia, whereupon ammonium diuranate precipitates out, although not in a strictly stoichiometric composition:

$$2\,UO_2F_2 + 8\,HF + 14\,NH_3 + 3\,H_2O \longrightarrow (NH_4)_2\,U_2O_7 + 12\,NH_4F$$

ADU process:

hydrolysis of UF_6 to UO_2F_2
↓
conversion with NH_3 to "$(NH_4)_2U_2O_7$"
↓
filtration, extraction, recrystallization to reduce the fluoride content
↓
drying
↓
reductive decomposition with H_2/H_2O to U_3O_8
↓
reduction to UO_2
↓
weak reoxidation

The precipitate is largely freed of fluoride ions after filtration by extraction or recrystallization. After drying at 200°C, the ammonium diuranate is reductively decomposed by a H_2/H_2O mixture at ca 500°C to U_3O_8, which is then reduced with hydrogen at 500 to 800°C to uranium(IV) oxide. The reductive decomposition to U_3O_8 and its reduction can be carried out in a single step e.g. in a rotary kiln. Since the uranium(IV) oxide formed can be pyrophoric, it is weakly reoxidized.

AUC process supplies low fluoride UO_2:
UF_6 reacted with CO_2, NH_3, H_2O to $(NH_4)_4[UO_2(CO_3)_3]$
↓
filtration, washing
↓
decomposition in H_2/H_2O to UO_2
↓
weak reoxidation

Ammonium uranyl carbonate (AUC) process: This process was developed in the 1960's in the Federal Republic of Germany. It comprises the simultaneous feeding of uranium(VI) fluoride, carbon dioxide and ammonia into an aqueous ammonium carbonate solution at 70°C, whereupon tetra-ammonium tricarbonato-dioxo-uranate (ammonium uranyl carbonate) precipitates out:

$$UF_6 + 5\ H_2O + 3\ CO_2 + 10\ NH_3 \longrightarrow (NH_4)_4[UO_2(CO_3)_3] + 6\ NH_4F$$

The properties of the product are significantly influenced by the precipitation conditions, which therefore have to be carefully controlled. The filtered and with a ammonium carbonate solution-washed product contains less than 0.5% by weight of fluoride.

The ammonium uranyl carbonate is reductively converted to uranium(IV) oxide via uranium(VI) oxide in a fluidized bed kiln at 500 to 700°C by feeding in water as the fluidizing medium and using hydrogen or a H_2/N_2-mixture, from the cracking of ammonia, as the reducing agent. At this high temperature the fluoride content is further reduced to 100 ppm by the action of the water vapor. The resulting fine particulate uranium(IV) oxide can be pyrophoric and therefore on cooling is weakly reoxidized at temperatures below 100°C.

6.5.4.1.3 Uranium(IV) Oxide by the Dry (IDR) Process

IDR process:
reaction of UF_6 gas with superheated steam to solid UO_2F_2. Reduction to UO_2.

The IDR (**I**ntegrated **D**ry **R**oute) process consists of reacting gaseous uranium(VI) fluoride with superheated steam, whereupon solid UO_2F_2 is formed, which is reduced with hydrogen to uranium(IV) oxide. This reaction can be carried out in both a fluidized bed reactor and in a rotary kiln, whereby the latter appears more suitable.

6.5.4.1.4 Manufacture of Uranium(IV) Oxide Pellets

UO_2-sintered pellets are produced by pressing and sintering in the presence of H_2 at ca. 1700°C

The uranium(IV) oxide produced by the above-described processes is used for the manufacture of uranium(IV) oxide sintered pellets. The uranium(IV) oxide is ground, pressed in e.g. hydraulic presses, then sintered at ca. 1700°C in the presence of hydrogen and thereby shrink to the desired density. The pellets (diameter 10 mm, tolerance ± 10 to ± 25 μm) are ground with a cylindrical grinder, then washed and dried.

6.5.4.2 Other Uranium Nuclear Fuels

Uranium metal: Metallic uranium as a nuclear fuel is unimportant compared with uranium(IV) oxide. It is manufactured by reducing uranium(IV) fluoride with metallic magnesium or calcium, whereby the mixture as a result of the temperature increase (Mg), or with the help of ignition pellets, burns up producing liquid uranium metal:

Uranium metal unimportant as a fuel compared with uranium(IV) oxide.

Manufactured by reduction of uranium(IV) fluoride with Mg or Ca.

$$UF_4 + 2\,Mg \longrightarrow U + 2\,MgF_2$$

The starting material for the manufacture of ^{235}U-enriched uranium metal, uranium(IV) fluoride, is produced by reducing enriched uranium(VI) fluoride with hydrogen or chlorohydrocarbons.

Uranium-plutonium mixed oxides: Uranium-plutonium mixed oxides (MOX) are becoming increasingly important, since plutonium is produced during the reprocessing of spent fuel elements. In these mixed oxide fuel elements a mixture of uranium(IV) and plutonium(IV) oxides with a plutonium content of 3 to 4% is utilized instead of ca. 4% ^{235}U-enriched uranium(IV) oxide. Such fuel elements have similar nuclear physical properties to the standard elements with ^{235}U and can therefore be used in their place.

U-Pu mixed oxides utilize Pu isolated during the reprocessing of spent fuel elements.

In their manufacture uranium(IV) oxide is mixed with the appropriate quantity of plutonium(IV) oxide, the mixture pressed into pellets and then sintered (termed coprocessing in the USA). Uranium(IV) oxide is produced by one of the above-described processes and plutonium(IV) oxide from the aqueous nitrate solution produced during reprocessing by precipitating it as plutonium oxalate and calcining the oxalate.

Manufacture of U-Pu mixed oxides:

1. By mixing UO_2 and PuO_2

These mixed oxides can also be manufactured by mixing the uranium and nitrate solutions produced during the reprocessing of spent nuclear fuels and converting these metal nitrate mixtures into a mixed oxide (coprecipitation). In this process the plutonium is first reoxidized, then gaseous ammonia and carbon dioxide are introduced into the aqueous nitrate mixture, whereupon ammonium uranyl-plutonyl carbonate is precipitated. This can be calcined to

2. by mixing the nitrate solutions of U and Pu

↓

precipitation of ammonium uranyl-plutonyl carbonate with NH_3 and CO_2

↓

calcined to U-Pu mixed oxide

uranium(IV)-plutonium(IV) mixed oxides at temperatures above 500°C.

6.5.5 Fuel Element Manufacture

Fuel elements consist of nuclear fuel in cladding tubes

The nuclear fuel pellets are generally filled in thin-walled cladding tubes to hinder leaching by coolant in the reactor core and to prevent release of fission products into the coolant circuit. In light-water reactors, for example, zirconium alloy (zirkaloy) cladding is used.

The fuel rods for boiling and pressurized water reactors are constructed similarly. They are filled with helium to improve the heat transfer from the pellets to the cladding tube and to withstand better the pressure in the reactor and contain no fuel at the top end of the fuel rods to improve fission gas retention. The latter can be ensured by holding the fuel in place with the aid of a spiral spring. Both ends of the cladding tube are welded gas tight. The fuel rods for pressurized water reactors are manufactured with a helium pressure of ca. 23 bar and ca. 5 bar for fuel rods for boiling water reactors.

Fuel elements consist of a bundle of fuel rods

The actual fuel elements in pressurized water reactors consist of individual fuel rods and control rod tubes mounted in a self-supporting construction of spacers fitted with a top and feet. Fuel elements for boiling water reactors, by comparison, have no control rod tubes, the fuel element zirkaloy claddings being used to guide the control rods and the coolant.

6.6 Disposal of Waste from Nuclear Power Stations

6.6.1 General Information

The spent fuel elements contain in addition to radioactive fission products considerable quantities of fissile uranium and plutonium, which are produced in the nuclear reactor. For a burn up, which gives the ratio of the energy produced with the nuclear fuel to the mass of heavy metals in the nuclear fuel, of e.g. 33,000 MWd per t uranium, a spent fuel, originally consisting of 3.2% ^{235}U and 96.8% ^{238}U, still contains 0.76% uranium, 0.9% plutonium (70% fissile) and about 3.5% of fission products. To recycle the not yet utilized ^{235}U and the bred plutonium, they have to be separated from each other and from the fission products.

Transmutation of nuclear fuel in a reactor:

original fuel	after burn up (33 000 MWd/t U)
3.2% ^{235}U	→ 0.76% ^{235}U
	→ 0.44% ^{236}U
	→ 2.0% fission products
96.8% ^{238}U	→ 1.5% fission products
	→ 94.3% ^{238}U
	→ 0.9% Pu
	→ 0.1% Np, Am, Cm

The legal basis for waste disposal from nuclear power stations in the Federal Republic of Germany is laid down in the Atom law, the waste concept of the Government of the Federal Republic of Germany, which establishes the legal basis for the disposal for nuclear power station waste. The disposal of waste in the conventional sense (from a 1000 MW reactor, for example, fuel elements with in total ca. 30 t of spent fuel and 12.5 t of cladding materials have to be taken away and replaced) consists of interim storage of the spent fuel elements, the reprocessing of nuclear fuel with recycling of the separated fissile products in the fuel element production, or the permanent storage of spent fuel elements and the handling and permanent storage of radioactive waste.

Disposal of nuclear power station waste in conventional sense consists of:

- interim storage of spent fuel elements,
- reprocessing the spent nuclear fuel,
- recycling of spent fissile material in the production of fuel elements,
- direct permanent storage of spent fuel elements,
- handling and end storage of radioactive waste.

The German electricity industry in 1989 gave up its original plans for building its own reprocessing plant in favor of a European solution and transferred the reprocessing to plants in France and Great Britain. The contracts cover all reprocessing quantities up to and including the year 2005. In addition there are options for extending these reprocessing arrangements for a further ten years.

The precedence of reprocessing spent fuel elements to dispose of the radioactive waste was abandoned in the middle of 1994. Since then direct permanent storage has been awarded equal legal precedence to a waste disposal option on the basis of reprocessing. It is expected that the electricity industry will make increasing use of this

Since 1994 direct permanent storage on an equal footing in the Federal Republic of Germany possibility. In the context of research and development work regarding component development, the feasibility of permanent storage has been demonstrated.

The conventional waste disposal in energy and economically more advantageous:

- considerable saving in
  - natural uranium;
  - separation energy for ^{235}U-enrichment,
- utilization of fast breeder reactors possible and thereby 60 times increase in uranium-utilization.

The nuclear power station operators in the Federal Republic of Germany an required to provide proof of their arrangements for the disposal of spent fuel elements for the coming 6 years on a rolling basis. This is a legally binding prerequisite for the operation of nuclear power stations. The disposal evidence is currently provided almost exclusively via contracts with the reprocessing plants in France and Great Britain.

Direct permanent storage is currently less expensive than further processing

Cost comparison studies have shown that direct permanent storage offers significant cost advantages over reprocessing. The current low uranium price due to overproduction also favors direct permanent storage. A shortage of uranium, on the other hand, would favor the recycling of reprocessed nuclear fuel. In addition to the cost considerations, other criteria have to be weighed up. It would be favorable to the energy industry and the economy to reprocess the spent fuel elements and thereby reuse the recovered energy raw materials. This recycling of uranium and plutonium represents a considerable saving in natural uranium: ca. 17% upon recycling uranium and ca. 34% upon recycling uranium and plutonium.

The aim of fuel use is as high as possible utilization of the fuel. Technical development is not yet at an end. Average burn ups of 50,000MWd/t uranium appear thoroughly realistic. The economic and ecological usefulness of reprocessing highly spent fuel elements can only be evaluated, when this has been achieved. The then pertaining circumstances have also to be taken into account in the decision regarding waste disposal options together with the physically less favorable composition of the plutonium isotope in the case of higher burn-up.

- plutonium misuse is avoided

It is, however, also important that through the return of plutonium in the fuel elements to light-water reactors, the possible misuse of plutonium is avoided in the future.

6.6.2 Stages in Nuclear Waste Disposal

6.6.2.1 Interim Storage of Spent Fuel Elements

Interim storage of spent fuel elements is initially carried out in pools of water at nuclear power stations

The spent fuel elements have to be temporarily stored during the decay of short-lived, very energetic radioactivity and associated afterheating for several years in the case of reprocessing and for several decades in the case of direct permanent storage. The interim storage generally takes place initially under water in so-called decay pools at nuclear power stations. There are decades of experience with wet storage. No weakening of the cladding tubes or structural components of a fuel element has been observed.

Compact storage sites have been built at nuclear power stations to increase the storage capacity

To increase the interim storage capacity at nuclear power stations compact storage frames have been incorporated into the decay pools.

Further storage capacity has been provided by the construction of external interim storage sites at Ahaus and Gorleben each for 1000 t of heavy metals. An expansion of the storage capacity by changing the storage concepts is in motion. Interim storage will then take place in specially developed large containers (e.g. CASTOR) for transport and long term-storage. They are so designed to safely encapsulate the radioactive materials even in the event of a very serious accident, to dissipate the afterheat from the heating elements and to keep the external radiation to a legally permissible level. Loaded containers of this type weigh up to 120 t.

6.6.2.2 Reprocessing of Spent Fuel Elements

Purex process utilized for reprocessing

The essential functions of the reprocessing of spent fuel elements is to separate uranium and plutonium from one another and both of them from the radioactive fission products. For this purpose, the PUREX process (**P**lutonium and **U**ranium **R**ecovery by **Ex**traction), based on extractive separation, has become accepted worldwide. It is currently used in all modern reprocessing plants.

Decades of experience operating the Purex process

The Purex process was developed between 1945 and 1949 in the USA for military purposes and since 1954 has been operated industrially in more than 10 countries in reprocessing plants of various sizes. Decades of experience with this process exist in the USA, Great Britain and France. In the Federal Republic of Germany operational experience has been acquired over 20 years with the reprocessing plant at Karlsruhe. The Purex process is also used in Japan and Russia.

Reprocessing capacity in t/a:

France:	1600
Great Britain	700

Sufficient for the next 30 to 40 years.

At the end of the 1970's the civil reprocessing plant in the USA was closed down for political reasons. The spent fuel elements have been stored since then at interim storage sites. The only reprocessing plants operated in Western Europe, those in France and Great Britain, have successively expanded their capacities and have currently a joint capacity of 2300 t heavy metal per year.

With the plants UP 2-800 and UP 3 (each with a capacity of 800 t/a) in France and Thorp (with 700 t/a) in Great Britain, there is sufficient capacity in Europe to reprocess the waste of 100 nuclear power stations and thereby to cover the total demand for the next 30 to 40 years. Japan disposes over an operating pilot plant and an industrial plant has been in the planning phase for a number of years.

The Purex process is in principle also suitable for the reprocessing of fuel from fast breeder reactors, as shown by the results from development work in France, Great Britain and the Federal Republic of Germany. The important differences compared with the reprocessing of light-water reactor fuel elements are a ca. ten-fold greater plutonium content and much shorter spent fuel element cooling times before reprocessing (these should only be ca. 6 months to 1 year).

Purex process consists of the steps:

- cutting up of the fuel elements with
  - rod shears,
  - bundle shears,
- dissolution of fuel in boiling nitric acid,

Purex process: The actual reprocessing process begins with the cutting up of the fuel elements taken from entry basins. This can be carried out in two process variants: cutting up in ca. 5 cm long pieces with rod shears, whereby initially the head pieces are separated off and the individual fuel rods withdrawn from the rod bundle, or direct cutting with hydraulic bundle shears.

In the second step the nuclear fuel is selectively dissolved in hot nitric acid in an apparatus with criticality avoidance features, the zirkaloy cladding tubing not being dissolved. The dissolution process itself can also be carried out in two process variants: cutting of the fuel elements in a given quantity of acid in the dissolver or cutting and then adding acid. The second process variant has the advantage that the gases liberated during the dissolution (nitrogen(II) oxide, ^{85}Krypton, ^{131}Xenon, tritium, ^{129}Iodine) are continuously liberated. The cladding is left behind in the dissolution process in so-called dissolver baskets. All of the process steps proceed by remote control in bunker-type rooms with meter-thick concrete walls (hot cells) to prevent exposure to the intensively radioactive radiation.

The nitric acid solution from the dissolution of the fuel rod contents is filtered [poly(propene) fleece] or centrifuged, to remove suspended solids (zirconium- or molydenum- compounds and ruthenium and palladium alloys). The thus obtained fuel solution contains uranium, plutonium and the radioactive fission products. It is, after its composition is adjusted to the extraction conditions (3 molar in nitric acid and 240 to 300 g/L uranium) subjected to multi-cyclic extraction with tributylphosphate (dissolved in dodecane). Uranium and plutonium pass into the organic phase and are thereby separated from the fission products, which remain in the aqueous phase.

- removal of solids from the fuel solution,
- 1st extraction cycle:
  separation of U and Pu from fission products by extraction with tributylphosphate in dodecane,

In the case of large throughputs, pulse-type sieve plate columns or mixer-settlers are used as extraction apparatuses both for this process step and for the later extraction steps.

In the next step uranium and plutonium are separated from one another by adding hydrazine, whereupon the uranium present as a uranium(IV) salt forms a complex with hydrazine which remains in the organic phase, but the plutonium present in the organic phase as a plutonium(IV) salt is reduced to plutonium(III), which is insoluble in the organic phase and therefore goes into the aqueous phase. A separation of the uranium from the plutonium is thereby achievable. Recent development work has shown that the plutonium(IV) can be electrolytically reduced to plutonium(III) in situ, which results in more efficient separation.

- separation of U from Pu by:
  - reduction of Pu(IV) to Pu(III) by U(IV)
    or electrolytically,
  - extraction of Pu(III) in aqueous phase

In the next process step the uranium is stripped with 0.01M nitric acid into the aqueous phase.

- stripping of U with dilute HNO_3 into the aqueous phase

Separation of the fuel solution into three aqueous solutions containing uranium, plutonium and the fission products respectively has thereby been achieved in the first extraction cycle.

In two further extractive uranium purification cycles, each consisting of extraction and stripping, the uranium solution is further purified to remove residual plutonium, neptunium and technetium.

- 2nd & 3rd *uranium purification cycles* (extraction/stripping): for removal of residual quantities of Pu, Np, Tc in uranium. Permitted Pu-content: 10 ppb.

In two extractive plutonium purification cycles plutonium is separated from small quantities of co-extracted fission products. The plutonium(III) is oxidized with nitrogen(IV) oxide to plutonium(IV), which is extracted with tributylphosphate. This oxidation can also take place anodically.

- 2nd & 3rd *plutonium purification cycles*: for removal of co-extracted fission products. Pu(III) is oxidized with NO_2 or electrolytically to Pu(IV).

Contamination of U and Pu with fission products: 0.1 to 1 ppm

U and Pu recovery efficiency: 98 to 99%

With the help of this multicyclic extraction the contamination of uranium and plutonium with fission products is reduced to 0.1 to 1 ppm. The residual concentration of plutonium in uranium may not exceed 10 ppb, since the uranium must be able to be processed without protective measures. The recovery efficiency for uranium and plutonium is 98 to 99%.

Uranyl nitrate and plutonyl nitrate solutions concentrated

After the purification cycles, the dilute plutonium nitrate solution is concentrated to ca. 250 g/L and the uranium nitrate solution to ca. 450 g/L.

Tributylphosphate reused after removal of interfering impurities

Tributylphosphate is recycled, it being scrubbed, e.g. with sodium carbonate, to remove associated interfering impurities such as dibutylphosphate produced by radiation, before being reused.

The Purex process is carried out at temperatures up to 130°C, at, or slightly below, atmospheric pressure and uses aqueous dissolution and extraction processes, which are tried and tested in the chemical industry. In addition, it has proved possible to limit the places in the plant with high radiation activity to a few areas.

6.6.2.3 Further Processing of Uranium and Plutonium Solutions

Further processing of uranium directed to further uranium enrichment:

- for low ^{235}U-contents: conversion to UO_3,
- for sufficient ^{235}U-content: conversion to UF_4 or UF_6.

The further processing of the uranyl nitrate solution, which in some plants is postpurified with silica gel, is directed towards further enrichment of the uranium. If this is not worthwhile due to a too low ^{235}U-content, the product is converted into uranium(VI) oxide, a storable compound. This can serve as a starting material for possible later utilization in fast breeder reactors. The uranium(VI) oxide is either produced indirectly by way of ammonium diuranate or by direct calcination. If further enrichment is foreseen, uranium(VI) fluoride or uranium(IV) fluoride is produced, the latter being fluorinated in the enrichment plant to uranium(VI) fluoride.

Further processing of plutonium:

- production of plutonium(IV) oxide via plutonium oxalate,
- conversion into U-Pu-mixed oxide fuel.

Years of experience in the manufacture of mixed oxide fuel

Plutonium is usually precipitated in reprocessing plants as its oxalate, which is converted into plutonium(IV) oxide from which mixed oxide fuel elements for light-water reactors or fast breeder reactors can be manufactured. Considerable knowledge over the manufacture of mixed oxide fuel elements has been built up over the years in the USA, France, Great Britain, Japan, Belgium and the Federal Republic of Germany. Thus up to the end of 1993, just in the Federal Republic of Germany, 4.5t of fissile plutonium had been incorporated into more than 100,000 fuel rods, mainly for utilization in light-water reactors. The 26,000 fuel rods destined for use in the fast breeder reactor at Kalkar, have not been able to be used.

6.6.2.4 Treatment of Radioactive Waste

The solid, liquid and gaseous radioactive waste (see marginal notes) produced during the reprocessing of spent fuel elements has to be safely stored, to prevent entry into the biosphere.

The waste includes the high activity aqueous refined product (HAW) from the first extraction cycle, the medium activity (MAW) and low activity (LAW) liquid salt-containing waste, which mainly arises from scrubbing the extraction agent with sodium carbonate, and the active cladding and structural components of the fuel elements in which small quantities (ca. 0.1%) of fuel and tritium are present. In addition there is solid waste of all types, such as paper, plastic and glass, solvent residues, gaseous waste and tritium-containing effluent.

Typical quantities of waste per t of irradiated uranium fuels with a burn up of 30 000 MWd/t U:

HAW	7 m^3
MAW	8 m^3
LAW	3 m^3
- with T-content	0.7 m^3
cladding	0.45 m^3
solid waste	3 m^3
gases	0.2 Nm^3

The process for treatment of liquid radioactive waste is directed to concentrating the activity into the smallest possible volume. The high activity fission product solutions are thus concentrated to ca. 1/10 of their initial volume by distilling off the nitric acid. The resulting waste is a self-heating liquid, which can be stored in cooled stainless steel containers. For long term storage, this highly activity waste must be converted into a solid and leach-resistant form. Vitrification, i.e. embedding the radioactive fission products in a glass matrix, has proved to be particularly useful in this regard, particularly using borosilicate glass. Such glasses can embed up to 20 to 30% of their own weight of fission product oxides.

Treatment of high activity solutions (HAW):

- concentration to ca. 1/10 of the initial volume by distilling off the nitric acid
- vitrification by embedding in a glass matrix

These glasses are stable to irradiation and are only very slightly leached by water or aqueous salt solutions, which is important in the envisaged permanent storage of the radioactive fission products, and dissipates the decay-heat efficiently to the environment. The vitrification of highly active waste also enables above ground long term interim storage e.g. in air-cooled dry stores.

Glasses are stable to irradiation, resistant to leaching and dissipate the decay-heat efficiently to the environment.

Vitrification processes consist of:

- concentration,
- drying,
- calcination,
- production of the glass smelt,
- solidification of the glass.

A number of processes have been developed for the vitrification of high activity waste. These consist of concentrating the waste solutions, optional denitration, drying, calcination, smelting of the glass and solidification of the glass. In the so-called Pamela vitrification plant set up by a German company in Mol in Belgium, ground glass frit is added to the fission product concentrate and the mixture fed into a glass furnace. There calcination and thermal denitration take place and at ca. 1200°C a borosilicate smelt is produced. This can either be dropped onto a slowly rotating steel disc, whereupon glass beads are formed, with which steel cylinders are filled and whereover molten lead is poured, or be discharged through a valve in the bottom into an ingot mold, where glass blocks are formed.

Treatment of low activity water (LAW):

- distillative concentration,
- solidification of the radioactive concentrate.

The low activity waste water is generally processed by distillation, whereupon a decontaminated distillate is obtained, which can be fed back into the process or discharged from the plant, and a residue in which radioactive nuclides are present in concentrated form. This residue can be bituminized or encased in concrete.

Ca. 60 L glass produced per t spent fuel (30 000MWd/t U).

The annual yield in vitrified high activity waste from the spent fuel elements of a 1000 MW nuclear power only amounts to 3 m^3.

Treatment of medium activity waste (MAW):

- concentration of 8 m^3 to 0.8 m^3 per t spent fuel (30 000 MWd/t U),
- solidification by stirring into bitumen (gives 1.6 m^3 per t fuel) or in concrete

Medium activity waste, from extraction agent scrubbing and the decontamination operations particularly important in connection with repairs and maintenance work, is first treated by evaporation to ca. 1/10 of its initial volume. The concentrate obtained can then be solidified by stirring into hot bitumen or embedded in concrete resulting in ca. 1.6 m^3 bituminized mass/t fuel. A new development can avoid the production of contaminated salt in the scrubbing of the extraction agent, enabling the scrubbing solutions to be very highly concentrated. In this new process hydrazine carbonate is utilized as the scrubbing agent (instead of sodium carbonate) and the hydrazine is electrolytically oxidized to gaseous products. This strongly reduces the quantity of MAW.

A new scrubbing process for the extraction agent makes it possible to reduce strongly the quantity of MAW

Treatment of medium activity solid waste (cladding, structural component):

- embedding in cement barrels: 1 t spent fuel (30 000 MWd/t U) produces ca. 1 m^3 of concrete.

The medium activity residue from the dissolution of the nuclear fuel, consisting of cladding and structural components, is encased in concrete barrels.

Treatment of miscellaneous solid waste (low activity):

- volume reduction by burning, then embedded in cement: 1 t spent fuel (30 000 MWd/t U) produces ca. 0.65 m^3 of concrete

The waste from contaminated, no longer usable, process materials has a low activity. It is burnt to reduce its volume then encased in concrete barrels.

Dissolver sludge from fuels from light-water reactors can, due to its high ruthenium content, only be embedded in concrete after long cooling times. A technical solution requiring shorter cooling times is being investigated.

The gaseous radioactive products released by dissolution of nuclear fuel: ^{129}Iodine, radioactive aerosols, ^{85}Krypton, $^{14}CO_2$, Tritium; are handled in different ways. Radioactive aerosols are removed by scrubbing and with electrostatic and air filters. ^{129}Iodine was absorbed on silver nitrate-impregnated silica-based solid bed filters in the closed German reprocessing plant at Karlsruhe. The decontamination factors achievable in this process being very high ($> 10^3$). ^{85}Krypton is currently vented into the atmosphere from all reprocessing plants. In the Federal Republic of Germany, the possibility of isolating ^{85}Krypton in cold test plants by low temperature rectification was evaluated. ^{85}Krypton would be stored in gas cylinders after separation. The irreversible fixing of krypton in special zeolites and the implanting of krypton in metals could replace cylinder storage.

Treatment of gaseous radioactive products:

- Aerosols:
  removed by scrubbers and filters,
- ^{129}Iodine:
  in the FRG absorption on $AgNO_3$ - impregnated silica,
- ^{85}Krypton:
  is currently vented in the atmosphere. Retention by low temperature rectification in development,

60% of the tritium formed in the nuclear reactor is bound by the zirconium of the cladding material and is disposed of with the cladding as medium activity waste. Of the remaining tritium very little is to be found in the dissolver gasand its radiological environmental impact is negligibly small. The rest of the tritium is present in tritium-containing water in the distillate. It can be pressed into deep geological formations or enriched by isotope exchange.

- Tritium:
  60% bound by zirconium, is disposed of with solid waste. Gaseous tritium vented.

6.6.2.5 Permanent Storage of Radioactive Waste

The last stage in the disposal of nuclear power station waste is long-term secure permanent storage of the solidified high, medium and low activity waste. Annually 5000 m^3 of radioactive waste is produced in the Federal Republic of Germany, of which only half comes from nuclear power stations.

Permanent storage sites for radioactive waste must be stable over geological periods. Under discussion in the FRG are:

- rock salt formations deep underground,
- granite,
- clay,
- anhydrite.

In the Federal Republic of Germany permanent storage of all types of radioactive waste in deep geological formations is striven for. The exclusion of radioactive waste from the biosphere is guaranteed by a system of natural and technical barriers and therewith impermissible environmental pollution is also excluded in the long term.

Since reunification the Federal Republic of Germany has at its disposal the permanent storage site for weakly radioactive at Morsleben, an existing permanent storage site in salt-rock, whose permit expires on 30.06.2000, under the terms of the reunification treaty. Worldwide only Sweden practises underground permanent storage for medium and low activity waste.

In the Federal Republic of Germany two further permanents storage sites have been at the planning stage for years. The furthest advanced in the planning process is the Konrad pit in Salzgitter, a former iron ore mine. This permanent storage site is foreseen for the reception of radioactive waste with negligible heat-output. A large proportion, quantitywise, of all radioactive waste from nuclear power station operations, from medicine, research and from industry falls into this category. The permanent storage site disposes over a permanent storage capacity of 650 000 m^3.

Since 1979, the suitability of a second project concerning the salt dome at Gorleben in the Lower Saxony administrative area Lüchow-Dannenberg is being investigated as a permanent storage site for all types of solid and solidified radioactive waste and also for the reception of glass ingots with high activity waste from the reprocessing of spent fuel elements for their direct permanent storage. The results to date of above-ground and underground investigations have confirmed the hoped for suitability of this salt dome. The underground mining phase of the investigation of the salt dome is currently being carried out. Two borings have been sunk to ca. 840 m. Since 1996 the mine chambers necessary for the investigation have been completed. Due to the, for thermal reasons, necessary interim storage for several decades of the glass ingots and spent fuel elements, the electricity industry has taken the view that this permanent storage site would first be used after 2020.

References for Chapter 6: Nuclear Fuel Cycle

General Information:

Ullmann's Encyclopedia of Industrial Chemistry. 1996. 5. Ed., Vol. A 17, 589 – 789, VCH Verlagsgesellschaft, Weinheim.

Gärtner, E., *Uran, Produktion und Gewinnung, Brennstoffkreislauf und möglicher Beitrag zur Energieversorgung*, Jahrbuch für Bergbau, Energie, Mineralöl und Chemie, 1977/78.

Jahrbuch der Atomwirtschaft 1996, Handelsblatt GmbH, Düsseldorf.

Specific Information:

Economic Importance of Nuclear Energy:

Leuschner, H. J., *Kohle und Kernenergie - Basis einer sicheren Energieversorgung*, Braunkohle 306 – 308 (1980).

Fossile Energieträger und Kernenergie, Berichtsband der Fachtagung des Deutschen Atomformums e.V.; Okt. 1981, Bonn, Deutscher Atomform e.V., Bonn.

Energie-Perspektiven 1950 – 1980 – 2000. Studie der Deutschen BP Akteingesellschaft (1981).

International Nuclear Fuel Cycle Evaluation (INFCE) International Energy Agency, IAEA, Vol. 1 to 9, Vienna (1980).

Taurit, R. and Wagner, M. *Künftige Entwicklung von Stromgestehungspreisen,* Brennst. - Wärme - Kraft **32**, 554 – 556 (1980).

Schmitt, D. and Junk, H. *Kostenvergleich der Stromerzeugung auf der Basis von Kernenergie und Steinkohle,* Zeitschr. Für Energiewirtschaft, 77 – 86 (1981).

Harding, C. G. F. *The Future of Nuclear Energy in Western Industrialized Nations*, ATW Atomwirtschaft Atomtech. **33**, 543 – 546 (1988).

Spalthoff, F. J. *Zur Rolle der Kernenergie für die Energieversorgung der Bundesrepublik,* Atomwirtschaft **26**, 140 – 143 (1981).

Kohlmaier, G. H. *Energiestrategien und CO_2-Risiko,* Umschau Wiss. Tech. **81**, 648 – 651 (1981).

Gerstler, R., Kaiser, H. and Wagner, H.-F. *Bedarf an Kernbrennstoffen und Brennstoffkreislaufdiensten* (Erhebungen und Befunde der International Nuclear Fuel Evaluation), Atomwirtschaft **25**, 269 – 272 (1980).

Schlüter, A. *Kernfusion und das Energieproblem,* Naturwissenschaften **69**, 226 – 235 (1982).

Kernreaktoren:

Ullmann's Encyclopedia of Industrial Chemistry. 1991. 5. Ed., Vol. A 17, 617 – 714, VCH Verlagsgesellschaft, Weinheim.

Eckey, H., Emmert, K. G. and Kilian, P. *Kernphysikalische Schwerpunkte der Reaktortechnik,* Physik in unserer Zeit **11**, 18 – 21, 47 – 59 (1980).

Status of Advanced Technology and Design for Water Cooled Reactors: LWR, IAEA TECDOC-479.

Status of Advanced Technology and Design for Water Cooled Reactors: Heavy Water Reactors, IAEA TECDOC-510 (1989).

Status of Metal Cooled Fast Breeder Reactors, IAEA (Ed.), Tech. Pep. Ser. IAEA No. 246 (1985).

Kugeler, K., Schulten, R. *Hochtemperaturreaktotechnik,* Springer-Verlag, Berlin (1989).

Reutler, H. and Lohnert, G. H. *Advantages of Going Modular in HTR's,* Nucl. Eng. Des **78**, 129 (1984).

Michaelis, H. and Mayer, H. *Schnelle Brutreaktoren,* Handbuch der Kernenergie, 105 – 117, Econ-Verlag, Düsseldorf (1986).

Supply:

Ullmann's Encyclopedia of Industrial Chemistry. 1991. 5. Ed., Vol. A 17, 732 – 749, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1996. 4. Ed., Vol. 17, 376 – 391, John Wiley & Sons, New York.

Atomwirtschaft, Atomtechnik **2(2)**, 79 – 97 (1996).

Gmelin, Handbuch der anorg. Chemie. 1979. 8. Aufl. *Uran*, Ergänzungsband A 1, *Uranlagerstätten,* Springer-Verlag, Berlin.

Gmelin, Handbuch der anorg. Chemie. 1981. 8. Aufl. *Uran*, Ergänzungsband A 3, *Technologie, Verwendung,* Springer-Verlag, Berlin.

Braatz, U. and Dibbert, H. J. *Kernbrennstoffversorgung: Gerüstet für mehr Kernenergie.* Jahrbuch der Atomwirtschaft **13**, A 45 – A 58 (1982).

Uranium resources,Production and Demand. OECD/IAEA, Paris (1988).

Mehner, A. W. et al. *Spherical Fuel Elements for Advanced HTR Manufacture and Qualification by Irradiation Testing,* J. Nucl. Mater. **171**, 9 – 18 (1990).

Die Uranversorgung der Welt. Atomwirtschaft **25**, 583 – 585 (1980).

Bacher, W. and Jacob, E. *Uranhexafluorid – Chemie und Technologie eines Grundstoffs des nuklearen Brennstpff-Kreislaufs,* Chem. Z. **106**, 117 – 136 (1982).

Mohrhauer, H., Krey, M. and Severin, D. *Urananreicherung mit Zentrifugen,* Atomwirtschaft **26**, 186 – 191 (1981).

Ehrfeld, W. and Ehrfeld, U. *Uranisotopentrennung,* Chem. Z. **101**, 53 – 63 (1977).

Nuclear Waste Disposal:

Ullmann's Encyclopedia of Industrial Chemistry. 1991. 5. Ed., Vol. A 17, 749 – 790, VCH Verlagsgesellschaft, Weinheim.

Kirk-Othmer, Encyclopedia of Chemical Technology. 1996. 4. Ed., Vol. 17, 409 – 428, John Wiley & Sons, New York.

Baumgartner, F. *Chemie der nuklearen Entsorgung,* Verlag K. Theimig, München (1978).

Schüller, W. *Entsorgung der Kernkraftwerke - eine ökologische Notwendigkeit,* Umschau **77**, 41 – 49 (1977).

Koch, G. *Wiederaufarbeitung von Kernbrennstoffen,* Kerntechnik **20**, 363 – 369 (1978).

Levi, H. W. *Die Entsorgung von Kernkraftwerken,* Phys. Bl. **36**, 299 – 303 (1980).

Kroebel, R. *Die Entsorgung von Kernkraftwerken,* Nachr. Chem. Tech. Lab. **30**, 372 – 377 (1982).

Entsorgung von Kernkraftwerken. Tagungsbericht vom November 1980, Essen, Verlag TÜV Rheinland GmbH, Köln (1981).

Closs, K. D. *Direkte Endlagerung oder Wiederaufarbeitung?,* Umschau Wiss. Tech. **81**, 290 – 296 (1981).

Benedict, M., Pigford, T., Levi, H. *Fuel Cycles for Nuclear Reactors,* in: Nuclear Chemical Engineering, Chap. 3, 91 pp., McGraw Hill, New York (1981).

Kleykamp, H. *Der chemische Zustand von AUPuC- und OKOM-Mischoxid in verschiedenen Stadien der Brennstoffkreislaufs,* Kernfirschungszentrum, Karlsruhe Ber. KfK-4430 (1988).

Delange, M. *LWR Spent Fuel Reprocessing at La Hagie: Ten Years On,* Proc. Int. Conf. Nucl. Fuel Reprocess.

Waste Management, Vol. 1, 228, Soc. Française Nucléaire, Paris (1987).

Mandel, H. *Die energiepolitische Bedeutung der Entsorgung*, At. U. Strom. **23**, 7 – 10 (1977).

Schmidt-Küster, W.-J. *Das Entsorgungskonzept der Bundesregierung*, Atomwirtschaft **25**, 294 – 299 (1980).

Diefenbacher, W. and Jocher, W. G. *Wiederaufarbeitung und thermische Rückführung*, Atomwirtschaft **25**, 371 – 375 (1980).

Müller-Christiansen, K. and Willessen, M. *Plutonium*. Gesellschaft für Reaktorsicherheit mbH, Reihe Stellungnahmen zu Kernenergiefragen (GRS-S-27), Köln (1979).

Kroebel, R. and Krause, H. *Endlagerung von radioaktiven Abfällen*, Kerntechnik **20**, 371 – 377 (1978).

Koelzer, W. *Auswirkungen radioaktiverEmissionen von Kernkraftwerken und Wiederaufarbeitungsanlagen auf die Umgebung*, Reihe "Kernthemen", Deutsches Atomform e.V., Bonn (1979).

Industrial inorganic Chemistry
Karl Heinz Büchel, Hans-Heinrich Moretto & Peter Woditsch

Company Abbreviations Index

Abbreviation	Official Name and Headquarters
Air Industries	Air Industries, Allentown, USA.
American Chrome	American Chrome & Chemicals Inc., Corpus Christi, USA; Daughter of Harrisons & Crossfield PLC, London, UK.
Asahi Chemical	Asahi Chemical Industry Co. Ltd., Tokio, Japan.
Asahi Glass	Asahi Glass Co. Ltd., Tokio, Japan.
BASF	BASF AG, Ludwigshafen, Federal Republic of Germany.
Bayer	Bayer AG, Leverkusen, Federal Republic of Germany.
Bayer Corp.	Bayer Corp., Pittsburgh, USA; Daughter of Bayer AG, Leverkusen, Federal Republic of Germany
Breyer Heurty	Heurty SA, Paris, France.
British Chrome & Chemicals	British Chrome & Chemicals, Eagles Cliff, UK.
Business Communications Co.	Business Communications Co., Stamford, USA
Buss	Buss Ltd., Pratteln, Switzerland.
CdF-Chimie	Charbonnage de France, Paris, France.
Central Prayon	Central Prayon
CERPHOS	CERPHOS
Chemetals	Chemetals Inc., Baltimore, USA.
CIBA-Geigy	CIBA-Geigy AG, Basel, Switzerland.
Davy McKee	Davy McKee AG, Frankfurt/M., Federal Republic of Germany.
Dead Sea Bromine	Dead Sea Bromine, Israel.
Dorr	Dorr Co. Inc., Stamford, USA.
Dorr-Olivier	Dorr-Olivier Inc., Milford, USA.
Dow Chemical	Dow Chemical Corp., Midland, USA.
DSM	NV DSM, Nederlands Staatsmijnen, Heerlen, The Netherlands.
DuPont	E. I. Dupont de Nemours and Comp. Inc., Wilmington, USA.
Elf-Atochem	Elf-Atochem, Paris, France.
Erco	Erco Industries Ltd., Islington, Canada.

Company Abbreviations Index (cont.)

Abbreviation	Official Name and Headquarters
Ethyl Corp.	Ethyl Corp., Richmond, USA.
Fisons	Fisons Ltd., Felixstowe, UK.
Gesellschaft f. Elektrometallurgie	GfE, Gesellschaft für Elektrometallurgie mbH, Düsseldorf, Federal Republic of Germany; Daughter of Metturg Inc., New York, USA.
Great Lake Chemicals	Great Lake Chemicals, West Lafayette, USA.
Hoechst	Hoechst AG, Frankfurt/M., Federal Republic of Germany.
Hooker	Hooker Electrochemical Co., New York, USA.
ICI	Imperial Chemical Industries Ltd., London, UK.
Inventa	Inventa AG für Forschung und Patentverwertung, Zürich, Switzerland.,
Kellog-Lopker	Kellog-Lopker Int. Corp., Houston, USA; Daughter of Pullmann Inc., Chicago, USA.
Knauf	Gebr. Knauf, Westdeutsche Gipswerke Iphoven, Federal Republic of Germany.
Lurgi	Lurgi Gesellschaften, Frankfurt, Federal Republic of Germany; Daughter of Metallgeschallschaft AG, Frankfurt/M., Federal Republic of Germany.
3M Corp.	Minnesota Mining and Manufacturing Comp., St. Paul, USA.
Merck	Merck AG, Darmstadt, Federal Republic of Germany.
Mitsubishi	Mitsubishi Gas Chem. Ltd., Tokio, Japan.
Mitsui Mining	Mitsui Mining, Tokio, Japan.
Mitsui-Toatsu	Mitsui Toatsu Chemicals Inc., Yokohama, Japan.
Monsanto	Monsanto Corp., St. Louis, USA.
Montedison	Montedison SpA, Milan, Italy.
Nippon Carbon	Nippon Carbon Co. Ltd., Tokio, Japan.
Nippon Chemical	Nippon Chemical Ind., Tokio, Japan.
Nippon Denko	Nippon Denko K. K., Tokio, Japan.
Nissan	Nissan Chemical Ind. Ltd., Tokio, Japan.
Occidental Chemicals	Occidental Chemicals, Dallas, USA.
Olin	Olin-Mathieson Chem. Corp., New York, USA.
Otsuka	Otsuka Kagaku Yakuhin K.K., Osaka, Japan.
Oxychem	Oxychem, Dallas, USA.
PCUK	Produits Chimiques, Ugine Kuhlmann, Paris, France; Daughter of Pechiney Ugine Kuhlmann (up to 1982).
Pennwalt	Pennwalt Corp., Buffalo, USA.
Pilkington	Pilkington Brothers, St. Helens, UK.

Company Abbreviations Index (cont.)

Abbreviation	Official Name and Headquarters
PPG	Pittsburgh Plate Glass, Pittsburgh, USA.
Prayon	Société de Prayon SA, Forêt-Trooz, Belgium.
Rhône-Poulenc	Société des Usines Chimiques Rhône-Poulenc, Paris, France.
Saphikon	Saphikon Inc., Hampshire, USA.
Sedema	Sedema, Daughter of Dadachem SA, Tertre, Belgium.
Shieldalloy	Shieldalloy Corp., Newfield, USA.
Shell	Royal Dutch Shell Group, The Hague, The Netherlands.
Siemens	Siemens AG, Berlin-München, Federal Republic of Germany.
Solvay	Solvay & Cie, Brussels, Belgium.
Stamicarbon	Stamicarbon BV, Daughter of Nederlandse Staatsmijnen, Heerlen, The Netherlands.
St. Gobain	Compagnie des Saint Gobain SA, Paris, France.
Stoppani	Stoppani, Milan, Italy.
Texaco	Texaco Inc., New York, USA.
Textron Inc.	Textron Inc., Providence, USA.
Thann	Fabriques der Produits Chimiques de Thann et de Mulhouse, Thann, France.
Tokai Carbon	Tokai Carbon, Tokio, Japan.
UBE Industries	UBE Industries
UCC	Union Carbide Corp., New York, USA.
Uhde	Krupp Uhde GmbH, Dortmund, Federal Republic of Germany.
UKF	Unie van Kunstmestfabrieken BV, Utrecht, The Netherlands.
VAW	Vereinigte Aluminiumwerke, Berlin-Bonn, Federal Republic of Germany.

Industrial inorganic Chemistry
Karl Heinz Büchel, Hans-Heinrich Moretto & Peter Woditsch

Subject Index

activated carbon 527 ff
activated carbon manufacture 528 ff
active aluminas 252
active carbon black 517 ff
ADU process 611 ff.
alkali bromates 179 ff.
– applications 181
alkali bromides 178 ff.
alkali chromates
– manufacture 258 ff.
alkali compounds
– general information 213
alkali metals
– general information 213
alkaline earth compounds
– general information 230 ff.
alkaline earth metals
– general information 230 ff.
alkali silicates 338 ff.
– applications 340
– economic importance 338
– manufacture 338
alkali peroxodisulfates
– applications 28
– economic importance 21
– production 26
alumina cement 411
aluminum 246 ff.
– applications 249 ff., 517
– economic importance 248
– general information 246
– manufacture 298 ff.
– occurrence 247 ff.
aluminum chloride 253 ff.
– applications 254
– economic importance 253
– manufacture 253
aluminum fluoride 138 ff.
– manufacture
- - Chemie Linz process 139
- - from hexafluorosilic acid 139 ff.
- - from hydrogen fluoride 138
- - Lurgi process 138
- - UKF process 139 ff.
aluminum hydroxide
– applications 251 ff., 514
– economic importance 250
– manufacture 250 ff.
- - Bayer process 250 ff.
aluminum hydroxide fillers 542 ff.
aluminum nitride products 482
aluminum oxide 250 ff.
– applications 251 ff., 470
aluminum oxide ceramics 460
aluminum oxide fibers 389 ff.
aluminum silicates 327 ff.
aluminum sulfate 4, 252 ff.
ammonia 29 ff.
– applications 43 ff.
– economic importance 29
ammonia manufacture 29 ff.
– ammonia separation 41
– process steps 30
– single train plants 41
– synthesis gas conversion 29 ff., 39 ff.
- - catalysts 30 ff.
- - compression 38
- - reactor types 39 ff.
– synthesis gas production 32 ff.
- - coal gasification 35
- - conversion of carbonmonoxide 36
- - partial oxidation of heavy fuel oil 34
- - raw materials 32
- - steam reforming of naphta 33
– synthesis gas purification 36 ff.
ammonium bromide 179
ammonium carbonate 602
ammonium dichromate
– applications 266
– manufacture 262
ammonium diuranate 604, 611
ammonium fluoride 611
ammonium hydrogen carbonate 51
ammonium hydrogen fluoride 141

ammonium nitrate 52, 197 ff.
- economic importance 197 ff.
- manufacture 200 ff.

ammonium perchlorate
- applications 174
- economic importance 166 ff.
- manufacture 172

ammonium peroxodisulfate
- applications 28
- economic importance 21
- production 26

ammonium phosphate
- economic importance 79 ff.

ammonium phosphates 76, 79, 192 ff.
- applications 80 ff.
- economic importance 189
- liquid fertilizer manufacture 193 ff.
- manufacture 79, 192 ff.
- solid fertilizer manufacture 192 ff.

ammonium sulfate
- economic importance 197
- manufacture 199 ff.

ammonium thiosulfate 121 ff.
- applications 122
- manufacture 122

ammonium uranyl(VI) carbonate 612
anhydrite, natural 415 ff.
anhydrite, synthetic 135, 415 ff.
Anhydrite I, II, III 417 ff.
apatite 65 ff., 190 ff.
asbestos cement 411
asbestos fibers 356 ff.
- applications 361 ff.
- deposits 333
- economic importance 356 ff.
- extraction 359 ff.
- general information 361
- in asbestos textiles and filter materials 364
- in composite materials 362 ff.
- properties and structure 357 ff.
- toxic properties 354 ff.
- types and compositions 357 ff.

AUC process 612

barium
- economic importance 242 ff.
- natural deposits 242

barium carbonate 243 ff., 513
- applications 244 ff.
- economic importance 243
- manufacture 243 ff.

barium sulfate 245, 544
barium sulfate filler 544 ff.
barium sulfide 245
barium titanate 464 f
basic chromium sulfates 265 ff.
beryllium
- applications 231
- economic importance 231
- manufacture 231
- oxide 231, 445, 462)

bismuth oxychloride 581
bleaching powder 168
bonding agents 396
bone china 457
boron carbide products 480
boron fibers 386 ff.
- applications 387 ff.
- manufacture 387
- properties 386

boron nitride products 481
boron trifluoride 142 ff.
brackish water 10
bromates, alkali 179 ff.
bromides 178 ff.
bromine 175 ff.
- applications 179 ff.
- economic importance 175 ff.
- natural deposits 175

bromine manufacture 176 ff.
- from bromide-enriched starting materials 177
- from seawater 177 ff.

cadmium pigments 573 f
cadmium yellow pigments 574
caesium 213
calcium 237 ff.
- manufacture 238
- natural deposits 237

calcium carbide 240 ff.
- applications 241
- economic importance 240
- manufacture 241

calcium carbonate 238 ff.
- applications 238 ff.
- economic importance 238
- mining and manufacture 238

calcium carbonate filler 538
calcium chloride 240
- applications 240

- economic importance 240
- manufacture 240

calcium cyanamide 241
calcium fluoride 127 ff.
calcium hydrogen sulfite 121
calcium hydroxide 239
- applications 6, 239
- economic importance 239
- manufacture 239

calcium hypochlorite
- applications 174
- economic importance 166
- manufacture 167

calcium oxide 239, 398 ff.
- applications 239, 402 ff.
- economic importance 239
- manufacture 239, 398 ff.

calcium phosphates
- applications 77
- economic importance 77
- manufacture 80

calcium sulfate 415 ff.
- economic importance 415 ff.
- manufacture 68 ff., 135, 418 ff.
- modifications 416 ff.
- formation 417 ff.
- properties 417

carbon, synthetic 505 ff
carbon black 517 f
carbon black manufacture 518 f
carbon disulfide 126
carbon felt 381
carbon fibers 377 ff.
- applications 380 ff.
- economic importance 377 ff.
- manufacture 380 ff.
- properties 378 ff.

carbon manufacture 528 f
carbon wool 381
cement
- compositions 404
- economic importance 403 ff.

ceramic fibers 388 ff.
- non oxide fibers 391 ff.
- oxide fibers 389 ff.
- whiskers 394 ff.

ceramics 443 ff
ceramic stains 551, 574
CERPHOS process 423
chloralkali electrolysis 147 ff.
- economic importance 146 ff.
- diaphragm process 154 ff.
- evaluation of the processes 158 ff.
- membrane process 157 ff.
- mercury process 152 ff.
- starting materials 148 ff.

chlorinated trisodium phosphate 169
chlorine 149 ff.
- applications 3 ff., 8, 159 ff., 285
- economic importance 146 ff.
- manufacture 151 ff., 164 ff.

chlorine dioxide
- applications 174
- economic importance 166
- manufacture 173 ff.

(chloro)methylphenysilanes 297 ff.
(chloro)methylsilanes 296 ff.
(chloro)phenylsilanes 297 ff.
chlorosulfonic acid 120
chromate pigments 543 ff.
chrome-tanning agents 265 ff.
chromic acid *see chromium (VI) oxide*
chromite 257 ff.
chromium 266 ff.
- economic importance 266
- manufacture
  - - chemical reduction 267
  - - electrochemical reduction 267 ff.

chromium boride 493 f
chromium carbide 489
chromium compounds 255 ff.
- economic importance 255 ff.
- manufacture 258 ff.
- raw material 257 ff.

chromium manufacture 266
chromium (III) oxide 264 ff.
- applications 266 ff.

chromium(III) oxide pigments 567
chromium(VI) oxide 262 ff.
- applications 266
- manufacture 262 ff.
  - - by electrolysis 263 ff.
  - - with sulfuric acid 262 ff.

clay ceramics *see silicate ceramics*
coarse ceramic products 424 ff.
- expanded products 425 ff.

coloring carbon blacks 517
COMURHEX process 607
concrete 397
- construction materials 396 ff.

– cement 403 ff.
– ceramic products 424 ff.
– lime 397 ff.
– gypsum 415 ff.
corrosion protection pigments 578
cristobalite 509, 514
cryolite *see sodium aluminum hexafluoride* 140 ff.

dental ceramics 457
dialkyl phosphites 98
diamond 496 ff
(dichloro)dimethylsilane 298 ff.
– hydrolysis 309 ff.
– methanolysis 311 ff.
disulfur dichloride 118
dolomite bricks 472 f

electro-ceramics 464
electrochemical fluorination of organic compounds 144 ff.
enamel 432 ff.
– applications 440
– application on sheet steel 436, 439 ff.
- - dry processes 440 ff.
- - wet processes 439 ff.
– classification 433
- - coloring and opacifying systems 435 ff.
- - layer arrangement 433 ff.
- - manufacture 437 ff.
– enameling procedure 436
– firing 441
– general information 432
EXER process 608
expandable clays 403
expanded products 425 ff.
expanded products (foam glass)
– from glasses 430
expanded products from clays and shales 425 ff.
– gas-forming reaction 428
– manufacture 429 ff.

feldspar 445
ferrites 465
ferrochrome 267
ferrocyanate pigments 575 f.
ferrophosphorus 84
fibers, inorganic 351 ff.
fillers 535 ff.
– applications 545 ff.
– economic importance 536
– general information 535 ff.
– properties 545 ff.
fillers, natural 536 ff.
– beneficiation 537 ff.
– silicas and silicon dioxide 536 ff.
– silicates 536 ff.
fillers, synthetic 439
– pyrogenic silicas 539
– wet processes 540 ff.
– posttreatment 541
fine earthenware 455 f
fluorapatite 130
fluorination, electrochemical 144 ff.
fluorine 130 ff.
– applications 132
– economic importance 132
fluorine manufacture 130 ff.
fluorosulfonic acid 120
fluorspar 127 ff.
– applications 129
– extraction 128
foamed carbon 515
forsterite bricks 472
frit manufacture 437 ff.
furnace acid 74 ff.

glass 327 ff.
– applications 338 ff., 542
– compositions 326 ff.
– economic importance 325
– manufacture 329 ff.
- - chemical decoloration 330 ff.
- - container glass 335 ff.
- - flat glass 335
- - float glass 335
- - melting furnaces 332 ff.
- - melting process 331 ff.
- - molding 334 ff.
- - raw materials 329 ff.
- - tank furnaces 313 ff.
– properties 336 ff.
– structure 325 ff.
glass-ceramics 328 ff.
glass fiber *see textile glass fibers*
glass fillers 542
glass wool 372 ff.
glassy carbon 515
graphite 500 ff

graphite, natural 500
graphite, synthetic 505
graphite foils and membranes 516
graphite manufacture 506 ff
graphitization of synthetic carbon 509
Guillini process 423
gypsum 415 ff.
– economic importance 415 ff.
– byproduct 420 ff.
– natural 418 ff.
- - from flue gas desulfurization 421
- - from organic acid manufacture 420
- - from phosphoric acid production 421 ff.

hafnium carbide 488
hafnium nitride 492
heavy water 597 ff.
heraklith 412
hexafluorosilicates 142 ff.
hexafluorosilicic acid 134 ff., 142
HM carbon fibers
– applications 378 ff.
– general information 375 ff.
– manufacture 378 ff.
HT carbon fibers
– applications 378 ff.
– general information 375 ff.
– manufacture 378 ff.
hydrazine 43 ff.
– applications 48 ff.
– economic importance 43
hydrazine manufacture 44 ff.
– Bayer process 46 ff.
– H_2O_2 process 47 ff.
– Raschig process 44 ff.
– urea process ·45
hydrochloric acid 162 ff.
– economic importance 163
– electrolysis 163 ff.
hydrogen 14 ff.
– applications 18 ff.
– as by product 18 ff.
- - by chloralkali electrolysis 152 ff.
– economic importance 14 ff.
– manufacture 15 ff.
- - catalytic decomposition of ammonia 18 ff.
- - coal gasification 16 ff.
- - electrolysis of water 16 ff.
- - petrochemical processes 15 ff.
- - thermal decomposition of water 17 ff.
– storage as hydrides 19 ff.
– transport 19 ff.
hydrogen bromide 178 ff.
– applications 180
hydrogen chloride 162 ff.
– applications 120, 163 ff., 285
– economic importance 163
– manufacture 162
hydrogen fluoride 132 ff.
– applications 136 ff.
– economic importance 132, 137
hydrogen fluoride manufacture 132 ff.
– Bayer process 134 ff.
– Buss process 135
– Du Pont process 135
hydrogen iodide 183
hydrogen peroxide 20 ff., 50
– applications 27
– economic importance 20
– production 21 ff.
- - anthraquinone process 23 ff.
- - electrochemical process 22 ff.
- - isopropanol oxidation process 22
hydrogen sulfide 129
hydroxylamine 50 ff.
– applications 50
– economic importance 50
hydroxylamine manufacture 50 ff.
– nitrate reduction process 52 ff.
– nitric oxide reduction process 51 ff.
– Raschig process 51
hypophosphites 89

IDR process 612
inorganic fibers 351 ff.
– economic importance 352
– general information 351
– insulation materials 372 ff.
– properties 352 ff.
– physiological aspects 354 ff.
– reinforcement sector 369 ff.
inorganic peroxo compounds 20 ff.
interference pigments 581
iodates, alkali 184
iodides
– applications 184 ff.
iodine
– applications 184 ff.
– economic importance 181
– natural deposits 181 ff.

iodine manufacture
- from brines 182
- from niter residual solutions 183

iron(II)sulfate 4
iron oxide pigments 561
iron oxide pigments, synthetic 563

kaolin 445 f.
Knauf process 422

lead glass 328
LECA process 425
light bricks 424
lime 397 ff.
- applications 402 ff.
- economic importance 397 ff.
- raw materials 398 ff.

lime hydrate *see calcium hydroxide*
lithium 213 ff.
- applications 214
- economic importance 214
- occurrence 213

lithium bromide 180
lithium carbonate 214 ff.
lithium chloride 215 ff
lithium hydride 215
lithium hydroxide 215
lithium hypochlorite 169
lithopone pigments 559
luminescent pigments 581
lustrous pigments 580

magnesia bricks 469
magnesia cement 412
magnesium
- applications 233
- economic importance 232
- manufacture 232 ff.
- natural deposits 231

magnesium carbonate 234 ff., 543
- applications 234, 538
- economic importance 234
- manufacture 234
- natural deposits 234

magnesium chloride 236
- applications 236
- economic importance 236
- manufacture 236

magnesium nitrate 62
magnesium oxide 235, 463
- applications 235
- economic importance 235
- manufacture 235

magnesium sulfate 237
- applications 237
- economic importance 237
- manufacture 237

magnetic pigments 582 ff
magneto-ceramics 464
manganese
- electrochemical manufacture 292 ff.
- importance and applications 292 ff.

manganese compounds
- economic importance 282 ff.
- manufacture 284 ff.
- raw materials 283 ff.

manganese(II) carbonate
- applications 292
- manufacture 286

manganese chloride 285
manganese nitrate 288
manganese(II) oxide
- applications 292
- manufacture 284

manganese(II) sulfate
- applications 292
- economic importance 282
- manufacture 285

managanese(II,III) oxide
- applications 292
- manufacture 286

manganese(III) oxide
- applications 292
- manufacture 286

manganese(IV) oxide
- applications 292
- economic importance 282
- manufacture 286 ff.
  - - activation of manganese(IV) oxide minerals 287 ff.
  - - electrolytic manganese(IV) oxide (EMD) 289
  - - oxidation of manganese(II) carbonate 288 ff.
  - - thermal decomposition of manganese nitrate 288

melt phosphates 190
Merck process 172
metal borides 493
metal fibers 384 ff.
- boron fibers 386 ff.
- steel fibers 384 ff.

– tungsten fibers 382 ff.
metallic hard materials 484 ff
metallic pigments 580
metal nitrides 492 f
metal silicides 494
mineral fibers 351 ff.
mineral fiber insulating materials 372 ff.
– applications 377
– economic importance 372 ff.
– fiber manufacture 373
– general information 372 ff.
– manufacture 373 ff.
- - blowing process 374
- - centrifugal process 375 ff.
- - melt manufacture 375
- - processing of fibers into insulating materials 376
- - raw matrials 374
- - two-step centrifugal jet process 376
mixed metal oxide pigments 571 f
molybdate pigments 570 f
molybdenum disilicide 494

nacreous pigments 581
niobium carbide 488
niobium nitride 492
nitric acid, highly concentrated 59 ff.
– direct processes 60 ff.
– indirect extractive distillation processes 62 ff.
nitric acid 53 ff.
– applications 64 ff., 200 ff.
– economic importance 53
nitric acid manufacture 53 ff.
– catalysts 55, 57
– highly concentrated nitric acid 59 ff.
- - Conia-process 61
- - direct process 60 ff.
- - magnesium nitrate process 62
- - Sabar process 61
- - sulfuric acid process 62
- - oxidation of ammonia 54 ff.
- - oxidation of nitric oxide 55 ff.
– nitric oxides, conversion to nitric acid 56
– plant types 57 ff.
– tail gases 62
nitric oxide 55 ff.
nitrogen-containing fertilizers 196 ff.
– economic importance 196 ff.
nitrophosphates
– economic importance 189
nitrophosphates manufacture 195 ff.
– carbonitric process 195
– sulfonitric process 195 ff.
nonoxide ceramics 479 ff
nuclear energy
– economic importance 587 ff.
nuclear fuel
– manufacture 599 ff.
- - fuel elements 614 ff.
- - uranium metal 613
- - uranium-plutonium mixed oxides 613 ff.
– manufacture from uranium ore concentrates 600 ff.
nuclear fuel cycle 587 ff.
– general information 591 ff.
nuclear fuel reprocessing 617 ff.
– PUREX process 618
– separation of uranium and plutonium 619
– working up of uranium and plutonium 620 ff.
nuclear reactor types 594 ff.
– Candu 594
– fast breeder reactors 598 ff.
– general information 594
– graphite-moderated reactors 595 ff.
- - advanced gas-cooled reactors (AGR) 595 ff.
- - gas-cooled reactors 5953 ff.
- - high temperature reactor (HTR) 596
- - light water-cooled reactors 597
– heavy water reactors 597 ff.
– light water reactors 594 ff.
- - boiling water reactors 594 ff.
- - pressurized water reactors 595
– Magnox 595 ff.
nuclear waste disposal 615 ff.
– concrete encasement 622 ff.
– conditioning of radioactive waste 621
– direct permanent storage of irradiated fuel elements 624
– gaseous radioactive products 623
– general information 615 ff.
– interim storage of irradiated fuel elements 617
– liquid radioactive waste treatment 621 ff.
– permanent storage 623 ff.
– reprocessing of spent fuel elements 617 ff.
– vitrification 621 ff.

optical glass 328, 337
oxide ceramics 458
oxide pigments 548

pentasodium triphosphate 75
perchloric acid
– economic importance 166
– from Merck process 172 ff.
perlite 510
phosphates (non fertilizers)
– ammonium phosphates 79 ff.
– calcium phosphates 80
– sodium phosphates 75 ff.
– tetrapotassium diphosphate 80
phosphinic acid 89
phosphonic acids 99 ff.
– applications 100 ff.
phosphoric acid 67 ff.
– applications 67 ff.
– economic importance 67 ff.
– from white phosphorus 74 ff.
phosphoric acid manufacture 68 ff.
– hemihydrate processes 69, 72
– impurity removal 73 ff.
– wet-process acid by dihydrate process 69 ff.
phosphoric acid triesters
– applications 93 ff.
– economic importance 93 ff.
– manufacture 91 ff.
phosphorous acid 89
phosphorous acid esters
– applications 98 ff.
– dialkylphosphites 98
– trialkylphosphites 97
– triarylphosphites 97
phosphoric acid esters 91 ff.
– diarylalkylphosphates 91 ff.
– dithiophosphoric ester acids 94 ff.
- - applications 95
- - economic importance 95
– dithiophosphoric acid diesters 95 ff.
– phosphoric ester acids 94
- - applications 94
- - economic importance 94
- - manufacture 94
– thiophosphoric acid triesters 96
- - applications 96 ff.
– trialkylphosphates 92
- - applications 93 ff.
- - economic importance 93 ff.
- - manufacture 92
– triarylphosphates 91 ff.
- - applications 93 ff.
- - economic importance 93 ff.
- - manufacture 91
– tris(chloroalkyl)phosphate 92 ff.
- - applications 93
- - economic importance 93
- - manufacture 92 ff.
phosphorus 80 ff.
– applications 81
– economic importance 80 ff.
– manufacture 82 ff.
– phosphorus manufacture
- - red phosphorus 84
- - white phosphorus 82 ff.
– raw materials 65 ff.
phosphorus compounds 65 ff.
– inorganic 65 ff.
– organic 91 ff.
– raw materials 65 ff.
phosphorus-containing fertilizers 187 ff.
– economic importance 187 ff.
– manufacture 190 ff.
phosphorus oxychloride 87
phosphorus pentachloride 87 ff.
phosphorus pentasulfide 86
phosphorus pentoxide 85
phosphorus raw materials manufacture 65 ff.
phosphorus sulfochloride 88
phosphorus trichloride 86 ff.
plasters 417 ff.
plaster setting processes 423 ff.
plutonium 598, 615
plutonium(IV) oxide 613, 619
poly(organosiloxanes), branched 314 ff.
poly(organosiloxanes), linear 307 ff.
polyphosphates 11, 78
porcelain 456 f
Portland cement 405 ff.
– applications 409
– clinker compositions 405
– manufacture 405 ff.
- - dry processes 407 ff.
- - half-dry process 407 ff.
- - half-wet process 407 ff.
- - wet process 407 ff.
– raw materials 405
Portland cement solidification processes 412 ff.
posttreatment of silicas 513
potassium 227 ff.
– general information 227
potassium bromide 180

potassium carbonate
- applications 229 ff.
- manufacture 228 ff.
potassium chlorate
- applications 174
- economic importance 166
- manufacture 170
potassium chloride 208 ff.
- extraction 210 ff.
potassium-containing fertilizers 205 ff.
- economic importance 206 ff.
- manufacture 208 ff.
- raw materials 205 ff.
potassium dichromate
- applications 266
- manufacture 262
potassium hydrogen fluoride 141
potassium hydroxide 230
- applications 228
- economic importance 230
- manufacture 228
potassium nitrate 210 ff.
potassium perchlorate
- manufacture 172
potassium permanganate
- applications 292
- economic importance 285
potassium peroxodisulfate
- applications 28
- economic importance 21
- production 26
potassium permanganate manufacture 289 ff.
- single-step liquid phase process 291
- two-step roasting processes 290
potassium salts
- extraction 210 ff.
- occurrence 205 ff.
potassium silicates
- applications 340
- economic importance 338
- general information 338
- manufacture 337
potassium sulfate 210
pozzolan cements 410
PUREX process 617 ff.
pyrogenic silicas 539 ff.
pyrolytic carbon 513
pyrolytic graphite 513

quartz 445
quartz glass 327
quicklime *see calcium oxide*

rapidly fired porcelain 457
red phosphorus 80 ff., 85
refractory ceramics 469
reinforcing carbon fibers *see HT and HM carbon fibers*
reverse osmosis *see water desalination*
rock wool 372 ff.
roofing materials 397, 424 ff.
rubidium 213

Saffil fiber 390
sand-line bricks 402
seawater 10
silanes
- manufacture 296 ff.
silicon carbide 475 ff
silicon carbide fibers 388 ff.
- general information 388 ff.
- manufacture 391 ff.
silicon carbide products 477
silicone products, industrial
- silicone copolymers 323 ff.
- silicone greases 317
- silicone rubbers 317 ff.
  - hot vulcanizing 320 ff.
  - properties 322
  - room temperature vulcanizing 317 ff.
- silicone oils 307 ff.
- silicone oil emulsions 316 ff.
silicon compounds, organic 295 ff.
- acyloxysilanes 300
- aminosilanes 298
- aminoxysilanes 300 ff.
- nomenclature 295
- organoalkoxysilanes 299
- organofunctional silanes 302 ff.
  - alkenylsilanes 302 ff.
  - halo-organosilanes 303
  - organoaminosilanes 303 ff.
  - organomercaptosilanes 304
- organohalosilanes 296 ff.
- organohydrogensilanes 301 ff.
- oximosilanes 300
- silazames 301
- siliconfunctional organosilanes 298 ff.
silicones 305 ff.
- economic importance 306 ff.

– manufacture 307 ff.
- - cyclization 310
- - hydrolysis 307 ff.
- - methanolysis 309 ff.
- - polycondensation 312 ff.
- - polymerization 310 ff.
- - polysiloxanes, branched 314 ff.
- - polysiloxanes, linear 307 ff.
- - starting materials (silanes) 307
– nomenclature 305 ff.
– properties 305 ff.
– structure 305 ff.
silicon nitride products 478 ff
sinter phosphates 189
slag cement 409 ff.
slag fibers 372 ff.
slaked lime *see calcium hydroxide*
sodium 217 ff.
– applications 217 ff., 598
– economic importance 217
– general information 216 ff.
– manufacture 217
sodium aluminate 254 ff.
sodium aluminum hexafluoride 136, 140 ff.
sodium borates 225 ff.
– applications 226 ff.
– extraction 226
– natural deposits and economic importance 225 ff.
sodium bromate 179 ff.
sodium bromide 178 ff.
sodium carbonate 218 ff.
– applications 221 ff.
– economic importance 219
– general information 218
– manufacture of synthetic 220 ff.
– production from natural deposits 219 ff.
sodium carbonate perhydrate
– applications 27 ff.
– economic importance 20
– production 25 ff.
sodium chlorate 170
– applications 174
– economic importance 166
– manufacture 170 ff.
sodium chloride 150 ff., 224 ff.
– applications 173 ff.
– economic importance 148 ff
sodium chlorite 166, 170
sodium dichromate
– applications 266
– manufacture 258 ff.
sodium dichromate dihydrate manufacture
– carbon dioxide process 261
– sulfuric acid process 260 ff.
sodium disulfite 121
sodium dithionite 122 ff.
– applications 123
– production 122 ff.
sodium fluoride 141
sodium hydrogen carbonate 222 ff.
– applications 222 ff.
– economic importance 222
– manufacture 222
– natural deposits 222
sodium hydrogen sulfate 225
sodium hydrogen sulfide 125
sodium hydrogen sulfite 121
sodium hydroxide 45, 146 ff., 213
– applications 121,160 ff., 250, 254
– economic importance 146 ff.
– manufacture 151 ff.
sodium hydroxymethanesulfinate 122 ff.
– applications 124
– manufacture 123 ff.
sodium hypochlorite 166 ff.
– applications 174
– economic importance 166
– manufacture 167 ff.
sodium hypophosphite 89 ff.
sodium metasilicate 339
sodium perborate
– applications 27 ff.
– economic importance 20
– production 24 ff.
sodium percarbonate *see sodium carbonate perhydrate*
sodium perchlorate
– manufacture 172
sodium peroxide
– applications 28
– economic importance 21
– production 26 ff.
sodium peroxodisulfate
– applications 28
– economic importance 21
– production 26 ff.
sodium phosphates 75 ff.
– applications 75 ff.
– economic importance 75 ff.

– manufacture 77
sodium silicates
– applications 340
– economic importance 338
– general information 338
– manufacture 337
sodium sulfate 223 ff.
– applications 224
– economic importance 223
– from natural deposits 223 ff.
– general information 223
– manufacture 223 ff.
sodium sulfide 124 ff.
sodium sulfite 121
sodium tetrahydroborate 128
sodium thiosulfate 121 ff.
– applications 122
– manufacture 122
sol-gel process 390
sorel cement 412
stoneware 456
strontium 242
– applications 242
– natural deposits 242
strontium carbonate 242
sulfur 101 ff.
– applications 104
– economic importance 104
– manufacture 102 ff.
- - Claus process 102 ff.
- - Outukumpu process 103
– occurrence 101 ff.
sulfur dichloride 118
sulfur dioxide 106 ff., 116 ff.
– applications 117
– from flue gas desulfurization 116
– manufacture 106 ff., 116 ff.
sulfur hexafluoride 143 ff.
sulfuric acid 104 ff.
– applications 115
– economic importance 104
– from sulfur dioxide 105 ff.
- - contact process 110 ff.
- - double absorption process 111 ff.
- - fluidized bed process 112
- - moist gas catalysis process 112 ff.
- - nitrous process 113
- - sulfur trioxide absorption 111
- - tailgas treatment 112
– from waste sulfuric acid 113 ff.
- - Bayer Bertrams process 115
- - Plinke process 115
sulfur trioxide 117 ff.
– applications 117
– manufacture 110 ff., 117
sulfuryl chloride 119 ff.
superphosphate
– economic importance 188
– manufacture 190 ff.

talc 537 ff.
tantalum carbide 488
tantalum nitride 492
tetrafluoroboric acid 142 ff.
tetrapotassium diphosphate 77 ff.
– manufacture 80
textile glass fibers
– applications 369 ff.
– classification 365
– economic importance 364 ff.
– general information 364 ff.
– manufacture 366 ff.
- - direct melt process 367
- - marble melt process 367
- - rod drawing process 367
– raw materials 366
textile glass mats 368 ff.
thermal and basic slag phosphates
– economic importance and manufacture 189 ff.
thionyl chloride 123
– applications 123
– manufacture 123
thiophosphoric acid derivatives 94 ff.
Thomas phosphates 190 ff.
thorium carbide 491
thorium(IV) oxide 462
titanates 464
titanium carbide 487
titanium diboride 493
titanium dioxide 553 ff
titanium dioxide pigments 553 ff **titanium nitride** 492 f.
trialkyl phospites 97
triaryl phosphites 97
triple superphosphate
– economic importance 188
– manufacture 191 ff.
tungsten carbide 489 f

ultramarine pigments 577

uranium
- economic importance 592 ff.
- occurrence 592 ff., 600 ff.

uranium 235 enrichment 609 ff.
- gas centrifuge process 610
- gas diffusion process 609 ff.
- laser isotope separation 610
- nozzle separation process 610

uranium carbide 491

uranium hexafluoride 142, 607 ff.
- conversion into nuclear fuel 610 ff.

uranium hexafluoride from uranium concentrates 607 ff.
- dry process 609
- general information 607
- wet process 607 ff.

uranium(IV) oxide 594 ff., 599, 610 ff., 462
- pellet manufacture 612 ff.

uranium(IV) oxide from uranium hexafluoride 610 ff.
- dry process 612
- general information 610 ff.
- wet processes 611 ff.

uranium production
- from phosphates 605 ff.
- from seawater 606 ff.

uranium production from ores 600 ff.
- leaching processes 600 ff.
- separation from leaching solutions 602 ff.

urea 45
- economic importance 198 ff.

urea manufacture 201 ff.
- solution recycling process 202 ff.
- stripping process 204 ff.

vanadium carbide 487

vanadium(V) oxide 84, 110

water 1 ff.
- chlorination 3 ff., 8
- deionized 8
- desalination 2, 8, 10 ff.
- economic importance 1 ff.
- nitrate removal 6
- ozonization 3 ff.
- potable water 2
- production 10 ff.
  - - from sea and brackish water 10 ff.
  - - by destillation 10 ff.
  - - by reverse osmosis 11 ff.
- purification 2 ff.
- removal of inorganic impurities 5 ff.
- removal of organic impurities 8 ff.
- usage 1

water glass 338

wet chemically manufactured silicas 540 ff.

wet chemically manufactured silicates 540 ff.

wet process acid 68 ff.

whiskers 394 ff.

white cement 411

white phosphorus
- manufacture 82 ff.

white pigments 552 ff

woodstone 412

woven carbon 381

yellow cake 600, 603 ff.

yttrium oxide 462

zeolites 340 ff.
- applications 347 ff.
  - - ion exchangers 347
  - - adsorption agents 347 ff.
  - - separation processes 348 ff.
  - - catalysts 349
- characteristics 343
- dehydration 347
- economic importance 340 ff.
- manufacture 344 ff.
  - - by cation exchange 346
  - - from natural raw materials 344
  - - from synthetic raw materials 344 ff.
- natural types 344
- pelletization 346 ff.
- structure 341 ff.
- types 341

zinc bromide 180

zinc oxide white pigments 560 f

zinc sulfide pigments 559 f

zirconium carbide 488

zirconium nitride 492

zirconium(IV) oxide 461

zirkaloy 614