Integrated Hydrometallurgical
Jarosite Treatment
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Jarosite Treatment

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To Marieke

To my parents
Contents

Chapter 1
Introduction

1.1 Occurrence, properties and applications of zinc 1
1.2 Primary zinc refining 3
1.3 Hydrometallurgical zinc refining processes
   1.3.1 The goethite process 5
   1.3.2 The paragoethite process 7
   1.3.3 The hematite process 8
   1.3.4 The conventional jarosite process 9
   1.3.5 The low-contaminant jarosite process 10
   1.3.6 The Dor jarosite process 11
   1.3.7 Direct leach processes 11
   1.3.8 New options for hydrometallurgical zinc refining processes 13
1.4 Hydrometallurgical zinc refining residues 15
1.5 Aim and scope of this thesis 18
1.6 References 21

Chapter 2

Acidic dissolution of zinc ferrite

Abstract 25

2.1 Introduction 26
2.2 Experimental 27
2.3 Data analysis 28
2.4 Results
   2.4.1 Characterization of zinc ferrite 28
   2.4.2 Applicability of the shrinking core model 29
   2.4.3 Dependence of the rate constant on the temperature 33
   2.4.4 Dependence of the rate constant on the H⁺ and HSO₄⁻ activity 35
   2.4.5 Dependence of the rate constant on the Fe³⁺ concentration 36
   2.4.6 Dependence of the rate constant on the Fe²⁺ concentration 36
   2.4.7 Dependence of the rate constant on the Zn²⁺ concentration 38
   2.4.8 Differences between synthetic and industrial zinc ferrite 39
Chapter 3

Reductive dissolution of zinc ferrite

Abstract

3.1 Introduction

3.2 Theory

3.3 Experimental

3.4 Data analysis

3.5 Results and discussion

3.5.1 Characterization of zinc ferrite

3.5.2 Applicability of the leaching model and reproducibility of the experiments

3.5.3 Dependency of the dissolution rate in H₂O on the Fe²⁺ concentration

3.5.4 Dependency of the dissolution rate in H₂SO₄ on the solvent

3.5.5 Dependency of the dissolution rate in HClO₄ on the solvent

3.5.6 Dependency of the dissolution rate in HClO₄ in the presence of Fe³⁺ on the solvent

3.6 Conclusions

3.7 References

Chapter 4

Simultaneous dissolution of zinc ferrite and precipitation of ammonium jarosite

Abstract

4.1 Introduction

4.2 Theory
4.2.1 The dissolution rate of zinc ferrite 68  
4.2.2 The precipitation of ammonium jarosite 68  
4.2.3 Simultaneous dissolution of zinc ferrite and precipitation of jarosite 69  
4.3 Experimental  
4.3.1 Synthesis of zinc ferrite and ammonium jarosite 71  
4.3.2 Characterization of zinc ferrite and ammonium jarosite 71  
4.3.3 Determination of the solubility product of ammonium jarosite 72  
4.3.4 Simultaneous dissolution of zinc ferrite and precipitation of ammonium jarosite 72  
4.4 Results and discussion  
4.4.1 Characterization of zinc ferrite and ammonium jarosite 73  
4.4.2 Determination of the solubility product of ammonium jarosite 74  
4.4.3 Simultaneous dissolution of zinc ferrite and precipitation of ammonium jarosite 76  
4.5 Consequences for industrial practice 86  
4.6 Conclusions 86  
4.7 References 87  
Appendices to chapter 4 88  

Chapter 5

Precipitation of jarosite

I. Chemical factors affecting the production rate

Abstract 95  
5.1 Introduction 96  
5.2 Theory 97  
5.3 Experimental 98  
5.4 Results and discussion  
5.4.1 Check on reproducibility and determination of the solubility product 100  
5.4.2 Calculation of the supersaturation 100  
5.4.3 Influence of the synthesis temperature 102  
5.4.4 Influence of the ionic strength 102  
5.4.5 Influence of the NH₄⁺ concentration 103  
5.4.6 Influence of the SO₄²⁻ concentration 104  
5.4.7 Influence of the Zn²⁺ concentration 106  
5.5 Conclusions 107  
5.6 References 108
Chapter 6

Precipitation of jarosite

II. Incorporation of zinc in continuous experiments

Abstract

6.1 Introduction

6.2 Theory

6.3 Experimental

6.3.1 Chemicals

6.3.2 Continuous crystallization equipment

6.3.3 Treatment of samples

6.3.4 Experimental procedure

6.3.5 Experimental conditions

6.4 Results and discussion

6.4.1 Determination of the residence time distribution

6.4.2 The applicability of factorial design analysis

6.4.3 Factors affecting the precipitation

6.4.4 Effect of the pH

6.5 Conclusions

6.6 Optimized conditions for jarosite precipitation

6.7 References

Appendices to chapter 6

111

112

112

115

115

117

118

118

121

121

122

135

136

136

138

138

Chapter 7

Precipitation of jarosite

III. Incorporation of impurities in batch experiments

Abstract

7.1 Introduction

7.2 Theory

7.3 Experimental

7.4 Results and discussion

7.4.1 Composition of the mother liquor

7.4.2 Precipitation of jarosite

7.4.3 Incorporation of impurities

7.5 Conclusions

7.6 References

147

148

149

152

155

155

157

165

165
Chapter 8

Incorporation of zinc in ferrous sulfate monohydrate

Abstract 169
8.1 Introduction 170
8.2 Theory 171
8.3 Experimental 173
8.3.1 Determination of the solubility of FeSO₄·H₂O in aqueous FeSO₄/ZnSO₄-solutions
8.3.2 Continuous crystallization of FeSO₄·H₂O at 140 - 160°C 174
8.4 Results and discussion 180
8.4.1 Solubility of FeSO₄·H₂O in the presence of ZnSO₄
8.4.2 Results of the continuous crystallization of FeSO₄·H₂O 181
8.5 Consequences for operating an integrated hydrometallurgical jarosite treatment process 186
8.6 Conclusions 186
8.7 References 187

Chapter 9

Integrating jarosite residue treatment processing in hydrometallurgical zinc winning - comparison of five potential processes

Abstract 189
9.1 Introduction and aim 190
9.2 Methodology 192
9.3 Raw materials and energy sources 193
9.4 Description of the processes 195
9.4.1 Process option I
9.4.2 Process option II
9.4.3 Process option III
9.4.4 Process option IV
9.4.5 Process option V
9.5 Mass balances; results 204
9.6 Energy balances; results 207
9.7 Conclusions 214
9.8 References 215
Appendices to chapter 9 217
Chapter 10

Emission factors for aqueous industrial cadmium emissions in the Rhine River basin; a historical reconstruction for the period ’70-’88

Abstract 239

10.1 Introduction and aim 240
10.2 Methodology 240
10.3 Monitoring data 243
10.4 Legislation 245
10.5 Industrial overview 246
10.6 Cadmium processing industries 247
    10.6.1 Non-ferrous metal mining 247
    10.6.2 Other in-basin mining activities 249
    10.6.3 Primary zinc refining 250
    10.6.4 Other non-ferrous metal refining industries 252
    10.6.5 Cadmium pigment manufacturing 254
    10.6.6 Cadmium stabilizer manufacturing 256
    10.6.7 Industrial use of cadmium pigments and stabilizers 257
    10.6.8 Cadmium battery manufacturing 259
    10.6.9 Cadmium plating 262
    10.6.10 Wet phosphoric acid manufacturing 264
    10.6.11 Iron and steel industry, including coke production 265
    10.6.12 Summary of aqueous emission factors of cadmium for industrial sources 269

10.7 Results and discussion 270
10.8 Conclusion 271
10.9 References 272

Summary of the thesis 279

Samenvatting van het proefschrift 283

Dankwoord 287
Chapter 1

Introduction

1.1 OCCURRENCE, PROPERTIES AND APPLICATIONS OF ZINC

Zinc in its metallic form was discovered later than less-reactive metals such as copper, gold, silver, iron and lead. The first sign of the use of zinc, however, still dates back to the prehistory. In Transylvania an idol was found which contained 87.5% zinc and 11.4% lead. In the Roman Empire calamine zinc ore was mixed with copper to yield brass with 10 - 27% Zn [1]. The first commercial zinc winning plant in Europe, with a production capacity of 200 ton/year, was built near Bristol (UK) in 1748 [2].

In nature, zinc is not encountered in its metallic form. The most important zinc minerals are sphalerite (ZnS, tetrahedral) which may contain isomorphical FeS and MnS, wurtzite (ZnS, hexagonal), smithsonite (ZnCO$_3$), hydrozincite (Zn$_6$(OH)$_3$(CO$_3$_2)), zincite (ZnO) and willemite (Zn$_2$SiO$_4$) [3]. Currently, sphalerite and wurtzite are the only minerals which are commercially exploited. They typically contain 5 - 10 w% ZnS.

The metal zinc has the atomic number 30, an atomic weight of 65.38 Dalton and is, due to its high density at 25 °C (7133 kg/m$^3$) often referred to as 'heavy' metal. At atmospheric pressure the melting point of zinc is 419.5 °C and its boiling point is 907 °C. Thus, zinc is relatively volatile. The metal exhibits good casting properties [4], which together with the low melting point, explains the applicability of zinc in die-cast products.

The most important property of zinc, from the commercial point of view, is its high reduction potential. Zinc is less noble than iron and displaces iron ions from the solution, thereby preventing the dissolution of iron. This property is combined with a uniform, low corrosion rate. When zinc is exposed to a moist air environment it develops a zinc carbonate/zinc oxide coating which inhibits further degradation [5].
The metal is essential for biological life, since some enzymatic reactions are in need of ionic zinc. The metal has a low toxicity to most species. In the Netherlands, it does not pose a threat to public health, although some aquatic organisms suffer from high aqueous zinc concentrations [6].

The characteristic combination of properties of zinc are utilized in many applications which may be divided in four categories:

i) galvanizing,
ii) die casting,
iii) alloys (e.g. brass) and
iv) chemicals.

Most of the applications are dissipative. This means that the metal is used in such a low concentration in a product or as such small items that recycling is rather difficult or virtually impossible. Examples of dissipative uses of zinc are: the use of zinc as anodic protection of steel on ship bodies and the application of zinc containing agrochemicals. In the first application, zinc is dissolved to protect steel and thus to maintain the integrity of steel constructions over a prolonged period. Zinc itself, however, is lost to the aquatic environment. In the second case the application also inhibits the recycling of zinc.

This, however, does not necessarily mean that these applications should be abandoned. Protecting steel with zinc may, from the point of conservation of natural resources (including energy), be rather attractive, because it inhibits considerable losses of iron and energy by sacrificing relatively small amounts of zinc. What it does mean is that due to limited recycling perspectives and a steadily growing demand for zinc [4,7], zinc winning from natural resources will, for decades to come, remain the dominating production method. Currently, the annual production quantity of primary zinc in the Western World amounts about 6 Mton [7].

This chapter provides an overview of the most important primary zinc refining processes and some of the environmental problems related to these processes. Subsequently, the aim and the scope of this thesis are introduced.
1.2 PRIMARY ZINC REFINING

The previous section indicated the important current and future position of primary zinc refining in the overall zinc supply. This section discusses the process technology of zinc refining in more detail. First, primary and secondary refining are distinguished. Primary zinc refining is the process technology which extracts metallic zinc from mineral ores. Secondary refining uses zinc containing wastes as raw material. Discussion of the latter is beyond the scope of this thesis. A recent overview of the state of the art of secondary zinc refining technology is available [8].

Primary zinc refining is divided in two categories: by pyro- and hydrometallurgical technology. The first category includes the following processes:

i) the horizontal retort or 'Luik' method,
ii) the vertical retort method,
iii) the electrothermic process and
iv) the Imperial Smelting Furnace process.

These processes all use desulfurized and sintered ZnO calcine as feed and obtain gaseous elemental zinc in a hot (1000 - 1200°C) reductive atmosphere. Zinc is subsequently condensed and may have to be distilled, depending on the demanded product specifications. Pyrometallurgical methods have gradually lost their importance. In 1950, these methods together had a market share of 65% [3], which declined to 50% in 1958 [1], 44% in 1969 [4], 20% in 1983 [9] and less than 20% in 1990 [7]. Factors that determined this market loss are:

i) the costly sintering of calcine,
ii) the high labour costs, in particular for the horizontal retort method, which is a batch process,
iii) the difficulties in preventing SO₂ pollution,
iv) the need for an extra distillation to obtain high grade zinc,
v) the relatively low zinc extraction efficiency of the processes,
vi) the environmentally unacceptable residues.
Pyrometallurgical primary refining processes have not been entirely abandoned for two reasons:

i) the Imperial Smelting Furnace enables to treat complex lead-zinc concentrates simultaneously, yielding saleable lead and zinc and

ii) the operating window for processing secondary raw materials, which may have a rather diverse chemical composition, is much larger for pyrometallurgical processes than for hydrometallurgical processes.

Pyrometallurgical zinc refining technology in theory and practice is extensively described in several reviews [1,2,3,5,10].

Hydrometallurgical zinc refining processes have in common that a purified zinc sulfate solution is exposed to a potential of about 3.5 V DC in an electrolysis bath with aluminum cathodes and lead/silver anodes. Because of the importance of hydrometallurgical zinc refining processes for the world zinc production and in order to provide a framework for this thesis, different hydrometallurgical zinc refining processes will be briefly discussed in the following section. A short outline of the chemistry of hydrometallurgical zinc refining is presented here.

Commercial zinc ores contain typically 5 to 10 w% ZnS. In a froth flotation process at the mine, the ore is separated in a hydrophilic fraction containing the worthless gangue and a hydrophobic fraction consisting of zinc concentrate (48 - 60% Zn). The concentrate is then transported to the zinc refineries. Ref. [11] provides an overview of the concentrate composition of 70 mines.

The first step in most refineries is the roasting, at about 910 °C in a fluidized bed, given by:

\[ 2 \text{ZnS} + 3 \text{O}_2 \rightarrow 2 \text{ZnO} + 2 \text{SO}_2 \] (1.1)

Since sphalerite concentrates usually contain 4 - 10% Fe as FeS and FeS\(_2\) the reactions (1.2) and (1.3) occur simultaneously with reaction (1.1).

\[ \text{ZnS} + 2 \text{FeS} + 5 \text{O}_2 \rightarrow \text{ZnO}_x\text{Fe}_y\text{O}_z + 3 \text{SO}_2 \] (1.2)

\[ \text{ZnS} + 2 \text{FeS}_2 + 7 \text{O}_2 \rightarrow \text{ZnO}_x\text{Fe}_y\text{O}_z + 5 \text{SO}_2 \] (1.3)
The zinc oxide formed in reaction (1.1) is easily leached in dilute sulfuric acid at pH 3 to 5 and 70°C (see reaction (1.4)). The zinc ferrite (ZnO. Fe₂O₃) is not soluble in dilute sulfuric acid.

In order not to lose the zinc load incorporated in zinc ferrite with the leach residue, a hot acid leach is used in present day commercial practice. Typical hot acid leach conditions are: pH-values of about 1.0 - 1.5 and a temperature of 95°C (see reaction (1.5)).

\[
\begin{align*}
\text{ZnO} & \quad + \quad 2 \text{ H}^+ \quad \rightarrow \quad \text{Zn}^{2+} \quad + \quad \text{H}_2\text{O} \quad \quad (1.4) \\
\text{ZnO. Fe}_2\text{O}_3 & \quad + \quad 8 \text{ H}^+ \quad \rightarrow \quad \text{Zn}^{2+} \quad + \quad 2 \text{ Fe}^{3+} \quad + \quad 4 \text{ H}_2\text{O} \quad \quad (1.5)
\end{align*}
\]

During reaction (1.5) iron is dissolved as well. Since iron should be bled from the leach circuit, iron is precipitated as either hematite (reaction (1.6)), goethite (reaction (1.7)), or jarosite (reaction (1.8)).

\[
\begin{align*}
2 \text{ Fe}^{3+} & \quad + \quad 3 \text{ H}_2\text{O} \quad \rightarrow \quad \text{Fe}_2\text{O}_3 \quad + \quad 6 \text{ H}^+ \quad \quad (1.6) \\
2 \text{ Fe}^{3+} & \quad + \quad 4 \text{ H}_2\text{O} \quad \rightarrow \quad \text{Fe}_2\text{O}_3\text{H}_2\text{O} \quad + \quad 6 \text{ H}^+ \quad \quad (1.7) \\
3 \text{ Fe}^{3+} & \quad + \quad \text{M}^+ \quad + \quad 2 \text{ SO}_4^{2-} \quad + \quad 6 \text{ H}_2\text{O} \quad \rightarrow \quad \text{MFe}_5(\text{SO}_4)_{2}(\text{OH})_6 \quad + \quad 6 \text{ H}^+ \quad \quad (1.8)
\end{align*}
\]

where \( \text{M}^+ \) represents either \( \text{NH}_4^+ \) or \( \text{Na}^+ \). After further purification a zinc sulfate solution is electrolyzed, as shown in reaction (1.9):

\[
\begin{align*}
2 \text{ Zn}^{2+} & \quad + \quad 2 \text{ H}_2\text{O} \quad \rightarrow \quad 2 \text{ Zn} \quad + \quad \text{O}_2 \quad + \quad 4 \text{ H}^+ \quad \quad (1.9)
\end{align*}
\]

The majority of commercial hydrometallurgical zinc refineries follow this technology.

### 1.3 HYDROMETALLURGICAL ZINC REFINING PROCESSES

The iron removal from zinc refinery process streams is so important that process variations are named after the method of iron removal.

#### 1.3.1 The goethite process

Figure 1.1 shows the leaching and iron precipitation section of a goethite process [12-14]. The dilute acid leach is carried out in two subsequent steps. During the first step air is dispersed in order to oxidize any \( \text{Fe}^{2+} \) to \( \text{Fe}^{3+} \), which then precipitates as ferric hydroxide. This prevents \( \text{Fe}^{2+} \) and \( \text{Fe}^{3+} \) to enter the purification and electrolysis section, where it is unwanted. In the hot acid and
super hot acid leach zinc ferrite is dissolved and a lead/silver-residue remains. The Fe$^{3+}$ in the solution is reduced by adding zinc concentrate, whereafter a sulfur residue is recycled to the roaster. The reduction is carried out in order to avoid the uncontrolled formation of ferric hydroxide. The Fe$^{2+}$ solution is then partly neutralized by adding calcine. After this neutralization step an Fe$^{2+}$ solution and a zinc ferrite and lead/silver residue is obtained. The goethite precipitation finally takes place at 90$^\circ$C after neutralization until the pH = 3, by adding additional calcine and after oxidizing Fe$^{2+}$ to Fe$^{3+}$ by dispersing air. The calcine added in this step preferentially contains no zinc ferrite, since the 'leaching' conditions of the goethite precipitation are such that any zinc ferrite contained in the calcine is lost with the goethite residue. The overall zinc winning efficiency of the goethite process is typically 96 wt%. The composition of the remaining residues is discussed in section 1.4.

![Flowsheet of the goethite process](image)

Figure 1.1 Flowsheet of the goethite process
1.3.2 The paragoethite process

The difference between the goethite and the paragoethite process (see figure 1.2) is the absence of the reduction of Fe\textsuperscript{3+} in the paragoethite process. Any ferric hydroxide formed in the pre-neutralization step is dissolved in the hot acid leach. This eliminates the sulfur slipstream to the roaster as well. The winning efficiency and residue composition of this process are similar to that of the goethite process [15].

Figure 1.2 Flowsheet of the paragoethite process
1.3.3 The hematite process

The hematite process is the most complex hydrometallurgical zinc winning process as will be evident from figure 1.3 [16,17]. In figure 1.3 two separate options are shown in one diagram. The flowsheet shows the lay-out of two commercial hematite processes, one built by Akita in Japan, using calcium carbonate as neutralizing agent, and the other by Ruhrzink in Germany, using calcine as neutralizing agent. The reduction of the ferric/zinc sulfate solution is carried out by adding either concentrate (Ruhrzink) or SO₂ (Akita).

Figure 1.3 Flowsheet of the hematite process
In the case that concentrate is added a sulfur residue is formed which is recycled to the roaster. This is not shown in figure 1.3. The copper precipitation step is specific for the Akita flowsheet; in the Ruhrzink flowsheet this precipitation occurs in the treatment of a bleed stream. If the pre- and post-neutralization are carried out with calcium carbonate ('d' in figure 1.3), the gypsum formed in the pre-neutralization step has commercial applications, whereas the gypsum formed in the post-neutralization step has a too high impurity content and has to be regarded as chemical waste. If calcine ('c' in figure 1.3) is used for neutralization no gypsum is formed.

The hematite precipitation is carried out under 20 bar pressure, in the presence of oxygen, at 180 - 200 °C. The zinc winning efficiency of a hematite process exceeds 98 wt%. Hematite is claimed to find application in the cement industry [16]. More details on the residue composition are given in section 1.4.

1.3.4 The conventional jarosite process

The jarosite process currently applies the most widely used iron precipitation technique in zinc hydrometallurgy, because of its relative ease of operation.

Many different process designs for integrating a jarosite precipitation and zinc ferrite hot acid leach step in an electrolytic zinc plant have been described [18-37]. In this chapter the three most common options are described, which are the conventional process, the low-contaminant process and the Dor process. This section deals with the conventional process. A flowsheet of the leach and the precipitation section of this process is given in figure 1.4. In the conventional process (ammonium or sodium) jarosite residue is obtained separately from a lead/silver residue.
The zinc extraction efficiency in this process is limited by the fact that calcine is used for partial neutralization of the hot acid leach overflow. The calcine used in this step contains zinc ferrite, which, due to the unfavorable dissolution conditions during jarosite precipitation, does not dissolve and is lost with the jarosite residue. The overall zinc winning efficiency is, depending on the iron content of the concentrate, about 95 wt%. The composition of the remaining residues is discussed in section 1.4.

1.3.5 The low-contaminant jarosite process

The low-contaminant jarosite process was developed by Electrolytic Zinc of Australasia [22] and is shown in figure 1.5. Its aim is to reduce the impurity content of jarosite by separating the pre-neutralization step from the jarosite precipitation step and also by lowering the temperature of the pre-neutralization. The latter is done to prevent jarosite formation during the pre-neutralization. After this step the remaining solids are dissolved in the hot acid leach and do not contaminate the jarosite residue. The zinc winning efficiency of this process equals 98.6 wt%. The jarosite residue contains less impurities than the residue formed in the conventional process, as will be shown in section 1.4.

Figure 1.5 Flowsheet of the low-contaminant jarosite process
1.3.6 The Dor jarosite process

The Dor jarosite process is named after C.X. Dor, who developed this option for Budelco B.V. [19]. The process is shown in figure 1.6 and yields a combined lead/silver and jarosite residue. The advantages of this process are the relatively small equipment volume requirements and the high zinc winning efficiency (98.6 wt%). The latter is not limited by the loss of undissolved zinc ferrite from calcine, which has been used for neutralizing purposes, since a pre-neutralization step in this process is not required. The jarosite residue formed in this process is described in section 1.4.

Figure 1.6 Flowsheet of the Dor jarosite process

1.3.7 Direct leach processes

Direct leach processes also utilize sphalerite concentrates but are based on a different process chemistry. The oxidation of sphalerite to zinc oxide and sulfur dioxide is replaced by a sulfuric acid leach of sphalerite in the presence of the redox couple Fe$^{3+}$/Fe$^{2+}$, according to the reactions (1.10) and (1.11) [38]. The iron required for these reactions is supplied by the concentrate.

\[
\text{ZnS} + \text{Fe}_2\text{(SO}_4\text{)}_3 \rightarrow \text{ZnSO}_4 + 2\text{FeSO}_4 + \text{S} \quad (1.10)
\]

\[
2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + 0.5\text{O}_2 \rightarrow \text{Fe}_3\text{(SO}_4\text{)}_3 + \text{H}_2\text{O} \quad (1.11)
\]

Before the concentrate is leached an extra grinding step is used to reduce the size of 80 to 90 wt% of the particles to less than 44 μm.
The commercial processes operate at leach temperatures of about 150°C and under pressures of about 10 bar. Therefore, these processes are usually referred to as direct pressure leaching processes, although it is pressure oxidation. Most of the sulfidic components in the concentrate are leached in reactions similar to reaction (1.10); only about 5% of the non-pyritic sulfur in the concentrate is oxidized to sulfate during the pressure leach. Pyrite, however, will form sulfuric acid under strong oxidation conditions and at elevated temperatures in a sulfate medium:

\[
4 \text{FeS}_2 + 15 \text{O}_2 + 8 \text{H}_2\text{O} \rightarrow 2 \text{Fe}_2\text{O}_3 + 8 \text{H}_2\text{SO}_4 \quad (1.12)
\]

\[
4 \text{FeS}_2 + 15 \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}_3\text{(SO}_4)_3 + 2 \text{H}_2\text{SO}_4 \quad (1.13)
\]

Dissolved ferric sulfate is formed in excess. For its precipitation in practice either jarosite, goethite or hematite are selected.

Figure 1.7 shows a flow-sheet of a two-stage pressure leach process. This process may be used stand-alone, but requires calcine for the pre-neutralisation step, which is not available on site when the sphalerite roasting step is not operated. Although calcine could be obtained from elsewhere, direct pressure leach processes are usually coupled with an already existing roast-leach-electrowin plant. This was first commercially developed by Sherritt-Gordon and installed at the Cominco jarosite process zinc plant in Trail, Canada [39]. Later, Kidd Creek in Timmins
(Canada) has integrated a direct leaching unit with a jarosite process [40]. A similar integration is planned in Belgium, where Vieille Montagne intends to couple a direct leaching unit with a goethite plant [41]. Ruhrzink in Germany has expanded the production capacity of their current hematite process for the period 1989 - 1991 by its coupling with a direct pressure leaching plant [42]. The main reason for substituting the roast step by pressure leaching is the different form in which sulfur is obtained. The market for sulfuric acid is nowadays not as good as for elemental sulfur. Moreover, elemental sulfur is cheaper and easier to store and to transport. In case of the integration of pressure leach operations with existing roast-leach-electrowin plants, the pressure leach also allows production expansion without requiring larger fluidized bed roasters or sulfuric acid plants, which frequently form the bottleneck for production expansion in these plants. In case of Ruhrzink the plant expansion will also lead to an increase of the zinc extraction efficiency to 99%, and a considerable lowering of the impurity content of the hematite product, as will be discussed in section 1.4.

Recently, Electrolytic Zinc of Australasia has presented results of pilot plant experiments with atmospheric direct leaching of zinc concentrate [43]. The NO/NO$_2$-couple was used as oxygen carrier. This process needs further research before it may be regarded as commercially feasible for primary zinc production. The same is true for a direct leaching process based on hydrochloric acid [44], yielding hydrogen sulfide as sulfur product.

1.3.8 New options for hydrometallurgical zinc winning processes
Options for new or modified zinc winning processes frequently occur in literature and aim either at an increase of the zinc winning efficiency, even from complex concentrates, or at the production of environmentally acceptable residues. Two such hydrometallurgical processes are discussed below; one option involves solvent extraction and one applies partial instead of dead roasting of the concentrate.

Figure 1.8 shows a process developed by Thorsen [45] which is based on the selective extraction of zinc and cadmium from leach solutions by using Versatic
acids. The hydrolytic stripping reaction has to be carried out in autoclaves at 180-200°C. Despite the fact that owing to the selectivity of the extractant the hematite will be formed in a readily saleable form, this process appears too costly to become competitive.

Figure 1.8 Flowsheet of the solvent extraction process

Figure 1.9 shows a flowsheet, presented by Spink and Stein [46], for a process with a partial roasting step.

By limiting the residence time of the concentrate in the roaster, a part of the concentrate will remain unoxidized, and iron - due to the reductive gas atmosphere which is caused by the oxygen deficiency in the gas mixture - will not form zinc ferrite but remain divalent as either FeS, or FeO. In the neutral leach, ferrous oxide is dissolved, oxidized by dispersing air and subsequently precipitated as ferric hydroxide, which is reductively dissolved in the hot sulfur

Figure 1.9 Flowsheet of a partial roasting zinc winning process
dioxide leach. This leach is selective for dissolving ferrous bisulfite and does not dissolve unreacted sulfides, originating from the concentrate. Ferrous bisulfite solution is then converted to hematite. This process' advantage is claimed to be the ease of operation, compared to a zinc ferrite/jarosite process, and the quality of the produced hematite. Due to the changes in the roaster operating conditions, the roaster off-gas contains 17 - 20 vol% SO₂. This is about 2.5 times as much as in ordinary roasting off-gases. Moreover, the off-gas is practically oxygen free, so sulfuric acid production from these off-gases is easier.

Integrating pyrometallurgical process steps in zinc hydrometallurgy has also gained renewed interest. Several processes were suggested [8] for treating the neutral leach residue of a hydrometallurgical plant pyrometallurgically. In a reductive gas atmosphere zinc ferrite is then converted into magnetite or hematite and volatilized zinc metal. The zinc metal is then oxidized, condensed and leached yielding a zinc/cadmium sulfate solution and a lead/arsenic residue. The iron either ends up in a slag or gives hematite of poor quality. Chapter 9 of this thesis discusses four hydro/pyro-process designs in detail.

1.4 HYDROMETALLURGICAL ZINC REFINING RESIDUES
Due to increased environmental consciousness many industrial activities have more and more been criticized for their contribution to environmental degradation. As a representative of the lead industry, Zelms concludes that by now, the lead industry depends upon public consent to operate [47].

The same seems to be true for the zinc industry. Jarosite and goethite residues formed during zinc winning are classified as chemical waste because of the content and/or leachability of hazardous elements like Cd, Pb and As. Table 1.1 summarizes the composition of residues formed in different hydrometallurgical plants [13,15,34,42,48,49]. No data on pressure leaching plants were available, apart from data on the Ruhrzink hematite/pressure leach plant.

Since jarosite and goethite residues have not found any application [18,28], their disposal in ponds with impermeable liners requires the acceptance of governments or regulatory bodies.
Table 1.1 Selected element content of hydrometallurgical zinc refining residues (all figures are given in weight percent, based on the dry weight of the residue; n.a. = not available)

<table>
<thead>
<tr>
<th>process</th>
<th>Fe</th>
<th>Zn</th>
<th>Pb</th>
<th>Cu</th>
<th>Cd</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>hematite(^1)</td>
<td>59</td>
<td>1</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>[42]</td>
</tr>
<tr>
<td>gypsum-1-</td>
<td>0.17</td>
<td>0.24</td>
<td>0.01</td>
<td>n.a.</td>
<td>0.01</td>
<td>[48]</td>
</tr>
<tr>
<td>gypsum-2-</td>
<td>9</td>
<td>5</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.01</td>
<td>[48]</td>
</tr>
<tr>
<td>hematite(^2)</td>
<td>65-67</td>
<td>&lt;0.2</td>
<td>&lt;0.01</td>
<td>&lt;0.02</td>
<td>&lt;0.01</td>
<td>[42]</td>
</tr>
<tr>
<td>goethite</td>
<td>40-42</td>
<td>5-9</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>[13]</td>
</tr>
<tr>
<td>Pb/Ag-residue</td>
<td>3-5</td>
<td>1.5-3</td>
<td>25-30</td>
<td>n.a.</td>
<td>n.a.</td>
<td>[13]</td>
</tr>
<tr>
<td>S-residue</td>
<td>7-8</td>
<td>8-15</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>[13]</td>
</tr>
<tr>
<td>paragoethite</td>
<td>40</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>[15]</td>
</tr>
<tr>
<td>conv. jarosite</td>
<td>24-30</td>
<td>2-6</td>
<td>0.2-2</td>
<td>n.a.</td>
<td>.05-.2</td>
<td>[48]</td>
</tr>
<tr>
<td>Pb/Ag-residue</td>
<td>5-30</td>
<td>2-10</td>
<td>2-22</td>
<td>n.a.</td>
<td>.05-.5</td>
<td>[48]</td>
</tr>
<tr>
<td>l.c. jarosite</td>
<td>32.4</td>
<td>0.25</td>
<td>0.05</td>
<td>0.016</td>
<td>0.001</td>
<td>[34]</td>
</tr>
<tr>
<td>Dor jarosite</td>
<td>26</td>
<td>1</td>
<td>4</td>
<td>0.075</td>
<td>0.045</td>
<td>[49]</td>
</tr>
</tbody>
</table>

\(^1\) These data are reported for the Ruhrzink plant before the integration with a direct leaching unit

\(^2\) These data are reported for the Ruhrzink plant after the integration with a direct leaching unit

In the future, the willingness to accept the disposal of large amounts of waste may fade away in many countries, as is already the case in The Netherlands.
The realization that chemical waste ponds will no longer be accepted as a solution for the zinc refiner's residue problem has, particularly during the last decade, stimulated research on producing recyclable residues.

The general classification criteria for residues are composition and/or rate of release of hazardous constituents in natural processes. These criteria have not only become stricter during the past two decades, a tendency that will probably continue, but they have also shown a remarkable variation with geographical location. This can partly be explained by the difference in ecologically acceptable load for some hazardous materials in different areas of the world. Differences in the regulator's opinion on acceptability of risks, however, also create differences in these criteria in different countries and are frequently subject to change.

In several countries, zinc refiners are now already facing a deadline for pond disposal of leach residues. In The Netherlands, such a deadline has been set, demanding the development of a reliable residue treatment process. It is also demanded to treat historically stored residues in the plant to be build according to this process.

In order to produce residues which comply with the environmental rules processes have been suggested, which usually include a calcination step to produce hematite [18,28,50,51,52,53]. These processes, however, do not provide a hematite product which is acceptable to the steel industry and thus solving the residue storage problem.

On behalf of Bodelco B.V. a pyrometallurgical jarosite treatment process has been developed which converts jarosite residues in a fly-ash and in a slag. The flyash contains most of the volatile metals (Zn, Pb, Cd, As) and is suitable for further extraction of zinc, lead and cadmium, yielding an arsenate residue.

The slag reportedly has a low residual content of hazardous metals which are only to a very minor amount released to the environment by leaching [49].
This thesis is focussed on an alternative process for jarosite treatment which is based on hydrometallurgical process operations. The aim is to make a final hematite product which is acceptable to the steel industry, rather than a slag in which iron units are lost for recycling.

1.5 AIM AND SCOPE OF THIS THESIS

This thesis is focussed on the development of a hydrometallurgical zinc refining process wherein hematite is produced which is acceptable as raw material for the steel industry. In short, the iron entering the refining process with the concentrate is precipitated as jarosite residue. This residue is dissolved in a sulfur dioxide leach, yielding a Pb/Ag-residue and a solution containing Zn\(^{2+}\), Fe\(^{2+}\), NH\(_4\)\(^+\) and Cd\(^{2+}\) as sulfates. From this solution ferrous sulfate monohydrate is crystallized at elevated temperatures up to 160°C and pressures up to 8 bar in a so-called fractional crystallization process. By this procedure a relatively pure ferrous sulfate monohydrate can be formed which is calcined into a rather pure hematite. The remaining Zn\(^{2+}\)/Cd\(^{2+}\)/NH\(_4\)\(^+\)-solution is neutralized. Metal hydroxides are then precipitated and recycled to the neutral leach.

In order to evaluate the feasibility of this newly proposed integrated hydrometallurgical jarosite treatment process a research project as described below was carried out. The project was divided in two parts; experimental work and literature based studies. The first part is described in the chapters 2 to 8 and the second part in the chapters 9 and 10. The experimental work covered the following themes:

i)  **Factors affecting the production rate of ammonium jarosite**

In this context the rate of jarosite precipitation as a function of factors such as the temperature and the composition of the mother liquor was studied. The experimental results are discussed in chapter 5.

ii) **The incorporation of zinc in continuous jarosite precipitation experiments**

This study has resulted in a relationship between the supersaturation for the precipitation of jarosite and the incorporation of zinc in the solid
phase. These data are essential for choosing the process conditions in the primary zinc refining plant for which a minimized incorporation is expected. A minimum incorporation of zinc enables an optimized operation of the jarosite treatment unit. This topic is discussed in chapter 6.

iii) *The simultaneous incorporation of different impurities in jarosite*

By dissolving an industrial calcine in $\text{H}_2\text{SO}_4$, a solution was obtained, which was well suited for determining the incorporation of different impurities in jarosite. The obtained results enable the estimation of the concurrent incorporation of impurities in jarosite and are discussed in chapter 7.

iv) *The dissolution of zinc ferrite*

Dissolving zinc ferrite provides the iron that subsequently needs to be precipitated as jarosite; hence the dissolution of zinc ferrite and the precipitation of jarosite are tightly connected. The dissolution rate of zinc ferrite was studied as a function of factors like the acidity of the solution, the temperature, the solvent ($\text{H}_2\text{O}$ or $\text{D}_2\text{O}$), the $\text{Fe}^{3+}$ and the $\text{Fe}^{2+}$ concentration. This has resulted in an improved understanding of the mechanism responsible for the dissolution of zinc ferrite. The results of this study are discussed in chapter 2 and 3.

v) *The simultaneous dissolution of zinc ferrite and precipitation of jarosite*

Combining the information obtained in the steps i, ii, iii en iv has resulted in experiments aimed at the simultaneous dissolution of zinc ferrite and precipitation of jarosite. The reactions proceed as follows: dissolving zinc ferrite yields iron but requires acid, whereas the precipitation of jarosite produces acid but requires iron. In order to transfer iron from zinc ferrite into jarosite a net amount of acid is required. During the experiments this acid demand is fulfilled by operating a pH control at a well chosen pH value. As a consequence, the
incorporation of zinc into jarosite becomes very low. Integrating the dissolution of zinc ferrite and the precipitation of jarosite results in a lower incorporation of zinc in jarosite and in a increase of the winning efficiency of the plant. The experiments carried out to study these simultaneous reactions are described in chapter 5.

vi) **Crystallization of ferrous sulfate modifications at elevated temperatures**
A quantitative estimate of the incorporation of zinc sulfate in ferrous sulfate during high temperature crystallization processes (140 - 180°C) was made by carrying out experiments in a complex, 1.5 litre autoclave, which was operated continuously. The experiments have indicated the potential of this process for separating dissolved Fe²⁺ and Zn²⁺ and have enabled to estimate the number of fractionating steps required in a full scale installation. The experiments and the autoclave itself are described in chapter 8.

Two literature based studies were carried out to supplement the experimental work discussed above.

i) **Environmental and energetic aspects of jarosite treatment processes**
In order to compare the hydrometallurgical jarosite treatment process described above with competing pyrometallurgical jarosite treatment processes, the residue composition and the energy requirements for four pyrometallurgical and the above described hydrometallurgical treatment process were calculated. This study enables comparison of the energy requirements and the expected residue composition for different treatment options. The methodology and the results of this study are provided in chapter 9.

ii) **Defining emission factors for the industrial emission of cadmium in the Rhine River Basin in the period 1970 - 1988.**
This study is not directly linked to the rest of the thesis. It was carried
out under assignment of the International Institute for Applied Systems Analysis in Laxenburg, Austria. Its aim was to investigate the industrial cadmium emissions in the Rhine River Basin in the period 1970 - 1988 per branche and based on this, to define emission factors for aqueous cadmium discharges of these individual branches. The obtained emission factors were calibrated with water quality data available for the Rhine River Basin for this period. The results of this study show the major decrease of the cadmium emissions to the River Rhine as a whole as well as a decrease of the aqueous cadmium emission factors per unit cadmium processed as such. This study is discussed in chapter 10.

1.6 REFERENCES


[38] Collins, M.J., Doyle, B.N., Ozbeek, E. and Masters, I.M., The zinc pressure leaching process. ibid [7], pp. 293 - 311.


[40] Mollison, A.C. and Moore, G.W., Zinc sulfide pressure leaching at Kidd Creek. ibid [7], pp. 277 - 291.


[47] Zelms, J.L., Lead in the 1990's: Continuing growth or beginning of the end?. ibid [7], pp. 5 - 11.


[49] Data provided by Budelco B.V.


Chapter 2

Acidic dissolution of zinc ferrite

ABSTRACT

The dissolution of synthetic and industrial zinc ferrite was studied in HNO₃, HClO₄ and H₂SO₄ solutions, at temperatures ranging from 75 to 95°C and in the presence of an excess of Fe²⁺, Fe³⁺ or Zn²⁺ ions. The rate constant describing this dissolution process was obtained by using a surface reaction controlled shrinking core model, which yielded good results.

The dissolution rate of zinc ferrite depends on the square root of the hydrogen ion activity in H₂SO₄ and HClO₄ solutions. The apparent activation energy for the dissolution equals 74 ±2 kJ/mol in H₂SO₄, 47 ±22 kJ/mol in HClO₄ and 37 ±16 kJ/mol in HNO₃. The order of the rate constant was 0.6 in the Fe²⁺ and -0.5 in the Fe³⁺ concentration. The rate constant for the dissolution of industrial zinc ferrite was 20 to 50 % lower than for synthetic zinc ferrite. The presence of 85 g/L Zn²⁺ in the leach solution retarded the dissolution rate of zinc ferrite by some 50%. A dissolution mechanism is proposed which qualitatively explains the obtained results.

2.1 INTRODUCTION

Hydrometallurgical zinc refining plants frequently use ZnS concentrates which contain up to 10 wt% Fe. During roasting iron combines with zinc to form the spinel ZnO.\textit{Fe}_2\textit{O}_3 (zinc ferrite). In order not to lose zinc incorporated in ZnO.\textit{Fe}_2\textit{O}_3, acidic leaching (pH=1, 90°C) is required to dissolve it. The dissolution yields a Zn/Fe-solution from which iron has to be removed. This is mostly done by operating a jarosite, goethite or hematite process. This paper aims at studying the factors that affect the dissolution rate of ZnO.\textit{Fe}_2\textit{O}_3. Such information is useful for optimizing the current leaching process and is essential for the design of a simultaneous jarosite precipitation/zinc ferrite dissolution process which may have considerable advantages compared to the current subsequent zinc ferrite dissolution - jarosite precipitation process.

In this paper the dependency of the dissolution rate of ZnO.\textit{Fe}_2\textit{O}_3 on the composition of the leach solution is studied, because the solution composition influences the solution potential, which is one of the rate determining factors in the dissolution process. The solution composition is varied by choosing different initial concentrations of Fe\textsuperscript{2+} and Fe\textsuperscript{3+}. Furthermore, the dependency on the hydrogen activity is determined in H\textsubscript{2}SO\textsubscript{4} and HClO\textsubscript{4} leaching and the kinetics are determined by varying the leach temperature between 75 and 95°C in HNO\textsubscript{3}, HClO\textsubscript{4} and H\textsubscript{2}SO\textsubscript{4}. The Zn\textsuperscript{2+} and the HSO\textsubscript{4} concentration are varied independently, in order to study complexation effects in the leach solution which indirectly affect the solution potential. Finally, the dissolution rates of synthetic and industrial ZnO.\textit{Fe}_2\textit{O}_3 are compared.

Although earlier work [1-7] on the dissolution rate of ZnO.\textit{Fe}_2\textit{O}_3 has been published, no systematic study on the relationship between the solution composition and the dissolution rate, as provided in this paper, was available yet.
2.2 EXPERIMENTAL

Synthetic ZnO·Fe$_2$O$_3$ was prepared in amounts of 5 or 10 g by the following procedure. In deionized, distilled water, stoichiometric amounts of ZnSO$_4$·7H$_2$O (72 g/L) and FeSO$_4$·7H$_2$O (139 g/L) were dissolved at 75°C after addition of 1 wt% H$_2$SO$_4$. Upon mixing with a solution containing (NH$_4$)$_2$C$_2$O$_4$ in 10% excess at 90°C ZnFe$_2$(C$_2$O$_4$)$_3$ is formed. The precipitate was filtered, washed and subsequently dried for three hours at 110°C. It was calcined at 700°C for 20 hours to yield ZnO·Fe$_2$O$_3$. A sample of 0.25 g ZnO·Fe$_2$O$_3$ was leached for 2 hours at 25°C in 50 mL of a solution, containing 20 g NH$_4$Cl and 600 ml 25 % NH$_3$ per liter, for determining the residual ZnO-content of the synthetic product [8]. Industrial ZnO·Fe$_2$O$_3$ was isolated from industrial calcine which was formed in a 9.5m diameter fluid bed roaster at 910°C using a ZnS concentrate containing about 52 wt% Zn and 8 wt% Fe. The isolation procedure included the dissolution of ZnO in 0.1M H$_2$SO$_4$ at 20°C until no further increase of the pH was measured. All chemicals used were analytically pure.

The synthetic and the industrial ZnO·Fe$_2$O$_3$ were characterized by scanning electron microscopy (SEM) to establish the crystal size and shape and by X-ray diffraction (XRD) to confirm the crystal structure. Krypton-porosimetry was applied to determine the specific surface area. The particle size distribution was determined using a Coulter Counter Multisizer. A sample of 0.1 g ZnO·Fe$_2$O$_3$ was leached for 15 - 30 minutes in 10 mL 36 % HCl at 25°C. This 'total' leach provided the total amount of zinc and iron in the product.

For determination of the dissolution rate 0.25 or 0.5 g ZnO·Fe$_2$O$_3$ was leached by either HNO$_3$, HClO$_4$ or H$_2$SO$_4$ at temperatures between 75 and 95 °C in a 250-mL round bottom flask, stirred at 610 rpm with a two-blade impeller. Each 3, 5, 10 or 15 minutes a liquid sample was taken and the zinc and iron contents of the solution were determined by AAS and/or ICP. In case Fe$^{2+}$ was added, the flask was operated under a N$_2$-atmosphere. The flask was immersed in a thermostated water bath with a temperature accuracy of ± 0.2°C. The experiments lasted between 20 minutes and 3 hours.

H$_2$SO$_4$ was used because this reflects the industrial practice. HNO$_3$ and HClO$_4$
were used, in order to avoid complexation between the acid anion and \( \text{Zn}^{2+} \) and \( \text{Fe}^{3+} \). \( \text{Fe(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}, \text{ZnSO}_4\cdot7\text{H}_2\text{O}, \text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}, \text{FeCl}_2\cdot4\text{H}_2\text{O} \) and \( \text{FeSO}_4\cdot7\text{H}_2\text{O} \) were used as respective sources for \( \text{Fe}^{3+} \), \( \text{Zn}^{2+} \) and \( \text{Fe}^{2+} \) ions. \( \text{NaHSO}_4\cdot\text{H}_2\text{O} \) was added as a source of excess \( \text{HSO}_4^- \) ions in a \( \text{H}_2\text{SO}_4 \) leach solution.

2.3 DATA ANALYSIS

The conversion data for each experiment were characterized by a rate constant for dissolution obtained from a surface reaction controlled shrinking core model given by:

\[
1 - (1 - x)^{1/3} = \frac{1}{3} k S_o t
\]

(2.1)

Here, \( x \) represents the conversion, \( k \) the rate constant (g/m².min), \( S_o \) the specific surface area of the solids (m²/g) at \( t=0 \) and \( t \) the time (minutes). In deriving equation (2.1) the following assumptions were made: i) the particles dissolve isomorphically, ii) the number of particles remain constant throughout the process and iii) the dissolution rate per unit surface area is constant, thus a constant driving force for the dissolution process is assumed. The conversion \( x \) is defined as the ratio of dissolved iron per gram \( \text{ZnO.Fe}_2\text{O}_3 \) in a sample over dissolved iron per gram \( \text{ZnO.Fe}_2\text{O}_3 \) as obtained during the 'total leach'. The zinc concentration is used for calculating the conversion, in cases where iron ions were added. Appendix 2.1 provides the derivation of the shrinking core model.

2.4 RESULTS

2.4.1 Characterization of zinc ferrite
Synthetic \( \text{ZnO.Fe}_2\text{O}_3 \) was prepared in small charges of 5- or 10-gram product, in order to attain 100 % yield. The free \( \text{ZnO} \) content varied between 2.5 and 5 wt% and the free \( \text{Fe}_2\text{O}_3 \) content between 2 to 7 wt%. Thus, the purity of zinc ferrite samples was about 90 wt%. A typical volume-based particle size distribution of the synthetically obtained product is given in figure 2.1. No
crystalline phases apart from zinc ferrite were detected. The specific surface area of the charges varied between 2 and 7 m²/g (accuracy ± 2%). The figures 2.2a and 2.2b show representative ZnO.Fe₂O₃ particles before and after leaching. In industrial samples, ZnO.Fe₂O₃, Zn₂SiO₄ and PbSO₄ were detected as crystalline phases. Cd and Cu were detected chemically and are assumed to be present as CdO.Fe₂O₃ (0.4 wt%) and CuO.Fe₂O₃ (1.4 wt%). The resulting purity of ZnO.Fe₂O₃ is about 70%. A good particle size analysis could not be obtained, since the industrial samples coagulated during the size analysis. Figure 2.3a, however, gives a representative view of industrial ZnO.Fe₂O₃, which consists of even smaller particles than partly leached synthetic ZnO.Fe₂O₃ (see figure 2.3b).

![Figure 2.1](image)

A representative volume-based particle size distribution of synthetic zinc ferrite

2.4.2 Applicability of the shrinking core model

The shrinking core model adequately describes the dissolution process as long as the conversion increases with time. The model yields a straight line over the whole time range and the slope of this line yields the rate constant k. In figure 2.4a the measured conversion data are properly fitted by a conversion curve
Figure 2.2a  A representative SEM photo of a synthetic zinc ferrite particle before leaching

Figure 2.2b  A representative SEM photo of a synthetic zinc ferrite particle after leaching
Figure 2.3⁴ A representative SEM photo of industrial zinc ferrite before leaching

Figure 2.3⁵ A representative SEM photo of partially leached synthetic zinc ferrite
which is computed with the k-value obtained from the shrinking core model in figure 2.4b.

Figure 2.4 The measured conversion and the conversion predicted by the shrinking core model (a) and the linear dependency of the model value with time (b)

In figure 2.5a the conversion time plot for a typical experiment carried out in the presence of initially added Fe$^{3+}$, Fe$^{2+}$ or Zn$^{2+}$ is given. The shrinking core model no longer yields a straight line when the conversion becomes practically constant (see figure 2.5b) and therefore the drawn straight line was used as the best fit, for the period of progressing conversion.

Table 2.1 provides the results of three experiments, carried out to check the reproducibility (which was ± 2.5 %) using three different charges. The rate constant is calculated assuming the significant internal surface area of ZnO. Fe$_2$O$_3$ to be fully wetted. This assumption was checked by comparing the results obtained with this method, with results obtained by rotating disc experiments with a well-defined exposed surface area [3]. Since the deviation in the rate constant for two experiments performed under similar conditions was within 5%, this assumption is justified.
Figure 2.5  The dissolution grade of zinc ferrite in 2M HClO\textsubscript{4} at 90°C in the presence of 20 g/l Fe\textsuperscript{3+} (a) and the corresponding shrinking core value (b).

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Acid</th>
<th>Acid Strength (mol/L)</th>
<th>added ions</th>
<th>rate constant (g m\textsuperscript{-2} min\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>0.5</td>
<td>-</td>
<td>0.0128</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>0.5</td>
<td>-</td>
<td>0.0133</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>0.5</td>
<td>-</td>
<td>0.0127</td>
</tr>
</tbody>
</table>

2.4.3 Dependency of the rate constant on the temperature

The dependency of the rate constant on the temperature was determined in 0.5M H\textsubscript{2}SO\textsubscript{4}, 1M HNO\textsubscript{3} and 1M HClO\textsubscript{4} from experiments performed at temperatures between 75 and 95°C, which are listed in table 2.2. Plots of ln k versus 1/T are shown in figure 2.6. The apparent activation energies calculated from the slope of the drawn straight line equal 74 ± 2 kJ/mol for H\textsubscript{2}SO\textsubscript{4}, 47 ± 22 kJ/mol for HClO\textsubscript{4} and 37 ± 16 kJ/mol for HNO\textsubscript{3}. 

33
Figure 2.6  The Arrhenius plot for the dissolution of zinc ferrite in 0.5M sulfuric acid, 1M nitric acid and 1M perchloric acid

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Acid</th>
<th>Acid Strength (mol/l)</th>
<th>added ions</th>
<th>rate constant (g m(^{-2}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>H(_2)SO(_4)</td>
<td>0.5</td>
<td>-</td>
<td>0.0043</td>
</tr>
<tr>
<td>80</td>
<td>&quot;</td>
<td>0.5</td>
<td>-</td>
<td>0.0065</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>0.5</td>
<td>-</td>
<td>0.0091</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>0.5</td>
<td>-</td>
<td>0.0133</td>
</tr>
<tr>
<td>95</td>
<td>&quot;</td>
<td>0.5</td>
<td>-</td>
<td>0.0174</td>
</tr>
<tr>
<td>80</td>
<td>HNO(_3)</td>
<td>1.0</td>
<td>-</td>
<td>0.0011</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>1.0</td>
<td>-</td>
<td>0.0013</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>1.0</td>
<td>-</td>
<td>0.0013</td>
</tr>
<tr>
<td>95</td>
<td>&quot;</td>
<td>1.0</td>
<td>-</td>
<td>0.0020</td>
</tr>
<tr>
<td>75</td>
<td>HClO(_4)</td>
<td>1.0</td>
<td>-</td>
<td>0.00040</td>
</tr>
<tr>
<td>80</td>
<td>&quot;</td>
<td>1.0</td>
<td>-</td>
<td>0.00095</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>1.0</td>
<td>-</td>
<td>0.00091</td>
</tr>
<tr>
<td>95</td>
<td>&quot;</td>
<td>1.0</td>
<td>-</td>
<td>0.00123</td>
</tr>
</tbody>
</table>
2.4.4 Dependency of the rate constant on the H⁺ and HSO₄⁻ ion activity

The dependency of the rate constant on the H⁺ activity was determined for dissolution in H₂SO₄ and HClO₄ solutions, from experiments presented in Table 2.3. The H⁺ ion activity was calculated using Pitzer's method [9]. The required data were obtained from ref.[10]. The dissolution of Fe and Zn ions during the experiment was neglected in the calculation of the activity coefficients. Figure 2.7 shows the obtained plots of log k as a function of log [H⁺] ((a) HClO₄, (b) H₂SO₄). For both acids an order in the H⁺ activity of 0.50 was found. The activity calculations showed that the SO₄²⁻ activity was, surprisingly, independent of the H₂SO₄ concentration. Four experiments were carried out where NaHSO₄·H₂O was added, in concentrations ranging from 0.25 to 1.5 M. The addition caused an increase of the rate constant of about 20 %, compared to a similar experiment without HSO₄⁻ addition.

Figure 2.7  The order of the rate constant for zinc ferrite dissolution in the hydrogen activity in HClO₄ at 90°C (a) and in H₂SO₄ at 90°C (b)
TABLE 2.3 Zinc ferrite dissolution experiments III: dependency on H⁺ activity

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Acid</th>
<th>Acid Strength (mol/l)</th>
<th>added ions (g/l)</th>
<th>rate constant (g m⁻² min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>H₂SO₄</td>
<td>0.25</td>
<td>-</td>
<td>0.0078</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>0.5</td>
<td>-</td>
<td>0.0128</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>1.0</td>
<td>-</td>
<td>0.0172</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>2.0</td>
<td>-</td>
<td>0.0249</td>
</tr>
<tr>
<td>90</td>
<td>HClO₄</td>
<td>0.25</td>
<td>-</td>
<td>0.0004</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>0.5</td>
<td>-</td>
<td>0.0006</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>1.0</td>
<td>-</td>
<td>0.0009</td>
</tr>
<tr>
<td>90</td>
<td></td>
<td>2.0</td>
<td>-</td>
<td>0.0015</td>
</tr>
</tbody>
</table>

| 85        | H₂SO₄  | 0.5                   | 24.3             | 0.0116                     |
| 85        |        | 0.5                   | 48.6             | 0.0113                     |
| 85        |        | 0.5                   | 72.9             | 0.0112                     |
| 85        |        | 0.5                   | 145.8            | 0.0109                     |

2.4.5 Dependency of the rate constant on the Fe³⁺ concentration

The dependency of the rate constant on the Fe³⁺ concentration was established for H₂SO₄ and HClO₄ solutions from experiments given in table 2.4. The results of the experiments are shown in figure 2.8 (a), where log k versus the initial Fe³⁺ concentration in log(ppm) is plotted. In 0.5M H₂SO₄ the order in the Fe³⁺ concentration equals -0.5 ± 0.2. In 2M HClO₄ the order is -0.50 ± 0.06. For calculating the order in 2M HClO₄, the results from the experiment with 2 g/l Fe³⁺ were not used.

2.4.6 Dependency of the rate constant on the Fe²⁺ concentration

The dependency of the rate constant on the Fe²⁺ concentration was determined for dissolution in H₂SO₄ and HClO₄ solutions (see table 2.5). Six experiments were carried out with initial Fe²⁺ concentrations between 0 and 800 ppm in a
### TABLE 2.4 Zinc ferrite dissolution experiments IV: dependency on the Fe$^{3+}$ concentration

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Acid</th>
<th>Acid Strength (mol/l)</th>
<th>added ions (g/l)</th>
<th>rate constant (g m$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>H$_2$SO$_4$</td>
<td>0.5</td>
<td>3.8</td>
<td>0.0076</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>0.5</td>
<td>3.9</td>
<td>0.0067</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>0.5</td>
<td>5.5</td>
<td>0.0066</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>0.5</td>
<td>6.4</td>
<td>0.0052</td>
</tr>
<tr>
<td>90</td>
<td>HClO$_4$</td>
<td>2.0</td>
<td>2.0</td>
<td>0.0015</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>2.0</td>
<td>4.5</td>
<td>0.0017</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>2.0</td>
<td>10.0</td>
<td>0.0013</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>2.0</td>
<td>15.0</td>
<td>0.00095</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>2.0</td>
<td>20.0</td>
<td>0.00080</td>
</tr>
</tbody>
</table>

### TABLE 2.5 Zinc ferrite dissolution experiments V: dependency on the Fe$^{2+}$ concentration

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Acid</th>
<th>Acid Strength (mol/l)</th>
<th>added ions (g/l)</th>
<th>rate constant (g m$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>85</td>
<td>H$_2$SO$_4$</td>
<td>0.5</td>
<td>0.073</td>
<td>0.0080</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>0.5</td>
<td>0.164</td>
<td>0.0072</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>0.5</td>
<td>0.240</td>
<td>0.0066</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>0.5</td>
<td>0.421</td>
<td>0.0075</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>0.5</td>
<td>0.806</td>
<td>0.0076</td>
</tr>
<tr>
<td>85</td>
<td>&quot;</td>
<td>0.5</td>
<td>4.0</td>
<td>0.0166</td>
</tr>
<tr>
<td>90</td>
<td>HClO$_4$</td>
<td>2.0</td>
<td>1.8</td>
<td>0.0104</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>2.0</td>
<td>3.9</td>
<td>0.0102</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>2.0</td>
<td>8.9</td>
<td>0.0148</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>2.0</td>
<td>17.6</td>
<td>0.0455</td>
</tr>
</tbody>
</table>
0.5M H$_2$SO$_4$ solution. The rate constants did not differ significantly. The addition of 4 g/l Fe$^{2+}$ as FeSO$_4$.7H$_2$O, however, increased the rate constant by 80%, compared to a similar experiment in the absence of Fe$^{2+}$.

Four experiments were carried out to determine the influence of the FeCl$_2$.4H$_2$O addition on the rate constant in 2M HClO$_4$. The results are shown in figure 2.8 (b), where log k is plotted versus the initial Fe$^{2+}$ concentration in log (ppm). The order of the rate constant in the Fe$^{2+}$ concentration equals 0.62 ± 0.25, if the results are fitted with a straight line.

### 2.4.7 Dependency of the rate constant on the Zn$^{2+}$ concentration

The rate constant was measured in a 1.8M H$_2$SO$_4$ solution in the presence of 1.3M Zn$^{2+}$ added either as Zn(NO$_3$)$_2$ or as ZnSO$_4$. Table 2.6 shows that in the presence of NO$_3^-$, the addition of 85 g/l Zn$^{2+}$ decreases the rate constant by 55%. In the presence of an equivalent amount of SO$_4^{2-}$ the rate constant reduces by 42%.
TABLE 2.6 Zinc ferrite dissolution experiments VI: dependency on the Zn$^{2+}$ concentration

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Acid</th>
<th>Acid Strength (mol/l)</th>
<th>added ions (g/l)</th>
<th>rate constant (g m$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>H$_2$SO$_4$</td>
<td>1.8</td>
<td>-</td>
<td>0.0243$^a$</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>1.8</td>
<td>85</td>
<td>0.0109$^b$</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>1.8</td>
<td>85</td>
<td>0.0140$^c$</td>
</tr>
</tbody>
</table>

$^a$ estimated value  
$^b$ zinc nitrate was used as zinc source  
$^c$ zinc sulfate was used as zinc source

2.4.8 Differences between synthetic and industrial zinc ferrite

In a 4M HClO$_4$ solution the rate constant of industrial ZnO.Fe$_2$O$_3$ was about 80% of that of synthetic ZnO.Fe$_2$O$_3$, as follows from table 2.7. In a 0.5M H$_2$SO$_4$ solution the ratio of the rate constants was about 0.5. Thus, the rate constant for the dissolution of industrial ZnO.Fe$_2$O$_3$ is lower than for synthetic ZnO.Fe$_2$O$_3$ which is leached under similar conditions. Since the purity of industrial ZnO.Fe$_2$O$_3$ is only about 70%, part of the specific surface should be regarded as 'non-active', which partly explains the difference.

An attempt to measure the dissolution kinetics of synthetic ZnO.Fe$_2$O$_3$ in an industrial hot acid leach solution was not successful because the increase in zinc or in iron concentration, upon leaching, could not be measured against the high background values of the iron (10 g/l) and zinc ( >40 g/l) concentration in the solution.
TABLE 2.7 Zinc ferrite dissolution experiments VII: comparison with industrial zinc ferrite

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Acid</th>
<th>Acid Strength (mol/l)</th>
<th>ferrite type</th>
<th>rate constant (g m⁻² min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>HClO₄</td>
<td>4.0</td>
<td>synthetic</td>
<td>0.0026</td>
</tr>
<tr>
<td>80</td>
<td>&quot;</td>
<td>4.0</td>
<td>industrial</td>
<td>0.0021</td>
</tr>
<tr>
<td>90</td>
<td>H₂SO₄</td>
<td>0.5</td>
<td>synthetic</td>
<td>0.0133</td>
</tr>
<tr>
<td>90</td>
<td>&quot;</td>
<td>0.5</td>
<td>industrial</td>
<td>0.0066</td>
</tr>
</tbody>
</table>

2.5 DISCUSSION AND CONCLUSIONS

It is still unknown whether the dissolution kinetics of ZnO,Fe₂O₃ in acidic media can be fully explained by the dissolution mechanism proposed for hematite by Warren and Devuyst [11], as suggested by Lu and Muir [2]. In this mechanism two options for dissolution are distinguished:

step 1: surface hydroxylation

\[ r_s \text{Fe}^{III}_2\text{O} + \text{H}_2\text{O} \leftrightarrow r_s \text{Fe}^{III}_2(\text{OH})_2 \]  \hspace{1cm} (2.2)

step 2: surface protonation

\[ r_s \text{Fe}^{III}\text{-OH} + \text{H}_3\text{O}^+ \leftrightarrow r_s \text{Fe}^{III}\text{OH}_2^+ + \text{H}_2\text{O} \]  \hspace{1cm} (2.3)

step 3*: direct dissolution

\[ r_s \text{Fe}^{III}\text{OH}_2^+ \rightarrow r_s + \text{Fe}^{III}\text{OH}_2^+ \]  \hspace{1cm} (2.4)

step 3*: anion adsorption and subsequent dissolution

\[ r_s \text{Fe}^{III}\text{OH}_2^+ + X \leftrightarrow r_s \text{Fe}^{III}\text{OH}_2\text{X} \]  \hspace{1cm} (2.5)

\[ r_s \text{Fe}^{III}\text{OH}_2\text{X} \rightarrow r_s + \text{Fe}^{III}\text{OH}_2\text{X} \]  \hspace{1cm} (2.6)
2.5.1 Dependency of the rate constant on the H\(^+\) and HSO\(_4\)\(^-\) activity

The order of the rate constant in the H\(^+\) activity equals 0.50 as well in HClO\(_4\) as in H\(_2\)SO\(_4\) solutions. This is in accordance with a theoretical relationship for the acidic dissolution of a metal hydroxide derived by Vermilyea [12]. This relation may only be applied when H\(^+\) is the only complexing agent on the particle surface. Since metal oxides at pH values below that corresponding to the zero point of charge (ZnO.Fe\(_2\)O\(_3\), pH\(_{zpc}\) = 3.5 [13]) are hydroxylated (step 1 in the model), the same relationship may also be applied for describing the acidic dissolution of metal oxides.

\[ r_r = n_r \frac{k_r^+}{k_r^-} \left( \frac{n_r - k_r^- C}{n_r - k_r^+} \right)^{\alpha_r \frac{z_r}{z_r}} \]

Here C is the H\(^+\) concentration (mol/l), \(\alpha^+\) and \(\alpha^-\) are the electrochemical transfer coefficients which are usually equal to 0.5 [14], \(n_r\) is the number of ions/cm\(^2\), \(z_r\) is the charge number of H\(^+\), \(k_r^+\) and \(k_r^-\) are constants and \(r\) is the dissolution rate (mol l\(^{-1}\) cm\(^{-2}\)). With \(z_r = 1\) for H\(^+\) and \(z_r = -1\) for the transferred electron it becomes clear that the dissolution rate depends upon the square root of the H\(^+\) concentration.

Additions of 0.25 to 1.5 M HSO\(_4\)\(^-\) to 0.5M H\(_2\)SO\(_4\) solutions all increase the rate constant for dissolution similarly by 20%, probably as a consequence of the excess of HSO\(_4\)\(^-\) already present.

3.5.2 The dependency of the rate constant on the redox potential of the solution

The presence of Fe\(^{2+}\) and Fe\(^{3+}\) directly influences the redox potential of the solution and thereby the potential difference between suspended zinc ferrite solids and the solution. This affects the dissolution rate of ZnO.Fe\(_2\)O\(_3\), which is determined by the potential difference between the surface of the particles and the bulk of the solution. The reductive dissolution, here in the presence of Fe\(^{2+}\) in solution, has been described by Lieser [15] for the dissolution of anhydrous Fe\(_2\)(SO\(_4\))\(_3\). The rate determining step was the reduction of a Fe\(^{3+}\) ion in the surface layer by a hydrogen atom which is claimed to be formed in the double layer due to the oxidation of a dissolved Fe\(^{2+}\) ion. If Fe\(^{2+}\) is present in the leach
solution in the absence of other reductants, it becomes the solution potential determining ion. The lower solution potential due to the presence of Fe\textsuperscript{2+} increases the dissolution rate (step 3\textsuperscript{a} in the model), because Fe\textsuperscript{3+} dissolves more easily from the surface layer, after being indirectly reduced by dissolved Fe\textsuperscript{2+}.

Nii and Hisamatsu [7] presented the dependency of the rate constant for ZnO.Fe\textsubscript{2}O\textsubscript{3} dissolution on the addition of 0 - 1 g/l Fe\textsuperscript{2+} as FeSO\textsubscript{4} .7H\textsubscript{2}O to a 9 wt% H\textsubscript{2}SO\textsubscript{4} solution at 50 °C. The order of the rate constant in the Fe\textsuperscript{2+} concentration was 0.5. The results obtained in this study, however, show that at 85°C in a 0.5M H\textsubscript{2}SO\textsubscript{4} solution, the addition of 0 - 1 g/l Fe\textsuperscript{2+} did not change the rate constant as is shown in table 2.5. This is probably due to the fact that at higher temperatures the dissolution proceeds so much faster that a small decrease in redox potential, due to a small Fe\textsuperscript{2+} addition, is no longer significant.

In 2M HClO\textsubscript{4} at 90°C using FeCl\textsubscript{2}.4H\textsubscript{2}O, the order of the dependency on the Fe\textsuperscript{2+} concentration equals 0.62 ±0.25. It is, however, questionable whether a linear fit is applicable. In the presence of Cl\textsuperscript{-} and Fe\textsuperscript{2+} the direct dissolution rate is increased by the presence of Fe\textsuperscript{2+}, but indirect dissolution via Cl\textsuperscript{-} adsorption (step 3\textsuperscript{b} in the model) may also occur. Since FeCl\textsubscript{2}.4H\textsubscript{2}O was used as Fe\textsuperscript{2+} source, both the Cl\textsuperscript{-} concentration and the Fe\textsuperscript{2+} concentration increased. This probably caused the deviation from the straight line. Further research on the separate influence of Fe\textsuperscript{2+} is therefore still to be done.

No experiments have been reported in the literature in which ZnO.Fe\textsubscript{2}O\textsubscript{3} was dissolved in the presence of Fe\textsuperscript{3+}. The above results show that the order of the rate constant in the Fe\textsuperscript{3+} concentration equals -0.5. No activities for the Fe\textsuperscript{2+} or Fe\textsuperscript{3+} addition experiments were calculated, because no appropriate data for Pitzer’s models were available. The authors, using concentrations, are in reasonable agreement with a theoretically derived equation, presented by Gorichev and Kipriyanov [16], for the dependency of the rate constant for the dissolution of magnetite (Fe\textsubscript{3}O\textsubscript{4}) on the Fe\textsuperscript{2+}/Fe\textsuperscript{3+} concentration:
\[ k = k_0 a_{H^+}^{0.5} a_{Fe^{2+}}^{0.5} a_{Fe^{3+}}^{-0.5} \]  \hspace{1cm} (2.8)

The model of Gorichev and Kipriyanov [16] contains the same rate determining step as the model by Lieser [15] and additionally includes the influence of the presence of Fe\(^{3+}\) for determining the redox potential. The redox potential is indirectly influenced by the presence of Zn\(^{2+}\), SO\(_4^{2-}\) or Cl\(^{-}\). Zn\(^{2+}\) ions compete with Fe\(^{3+}\) ions for complex formation with SO\(_4^{2-}\). The decelerating influence of Zn\(^{2+}\) can be understood by assuming that Zn\(^{2+}\) ions form complexes with SO\(_4^{2-}\). As a consequence, the free Fe\(^{3+}\) concentration increases and thereby the redox potential, causing a reduction of the dissolution rate. Moreover, the free SO\(_4^{2-}\) concentration decreases which also decreases the dissolution rate, due to a decrease of the concentration of complexing agents. Both SO\(_4^{2-}\) and Cl\(^{-}\) play a similar role. By complexation of Fe\(^{3+}\) with either Cl\(^{-}\) or SO\(_4^{2-}\), the free Fe\(^{3+}\) concentration decreases which decreases the redox potential. The complexation stimulates dissolution via anion adsorption (step 3b). This explains the considerably lower leaching rate in HNO\(_3\) and HClO\(_4\) solutions, when no complexation is expected, compared to the rate in H\(_2\)SO\(_4\) and HCl solutions. Surprisingly, the apparent activation energies of the dissolution in H\(_2\)SO\(_4\) (74 ±2 kJ/mol) and HCl (83 kJ/mol [4]) are higher than the corresponding values in HNO\(_3\) (37 ±16 kJ/mol) and HClO\(_4\) (47 ±22 kJ/mol), which fact points at a less favorable reaction path. For this apparent discrepancy no explanation is currently available.

The reason for the large degree of uncertainty in the values for the activation energy in HNO\(_3\) and HClO\(_4\) is unknown. Thus, further research is required in order to obtain these data with a higher accuracy. Despite the limited accuracy, the experiments clearly show the significant difference in activation energy for the dissolution of zinc ferrite in H\(_2\)SO\(_4\), compared to the values in HNO\(_3\) and HClO\(_4\).
2.6 CONSEQUENCES FOR INDUSTRIAL PRACTICE

The above results indicate that high Fe$^{3+}$ concentrations decelerate the dissolution of ZnO$\cdot$Fe$_2$O$_3$. By dissolving ZnO$\cdot$Fe$_2$O$_3$, however, Fe$^{3+}$ is released. It is therefore desirable to introduce a sink for Fe$^{3+}$. A suitable sink for Fe$^{3+}$ is jarosite (NH$_4$)$_2$Fe$_3$(SO$_4$)$_2$(OH)$_6$. By simultaneously dissolving ZnO$\cdot$Fe$_2$O$_3$ and precipitating jarosite, the dissolution of zinc ferrite will not be retarded by the presence of Fe$^{3+}$. Meanwhile, the precipitation of jarosite is taking place under controlled conditions, because the supersaturation for the precipitation is determined by the dissolution of Fe$^{3+}$ from ZnO$\cdot$Fe$_2$O$_3$. This is beneficial for the produced crystal size and shape and consequently improves the filterability of the solids. A better filterability reduces the zinc losses in the jarosite residue. Experiments where this simultaneous conversion is studied are reported in chapter four of this thesis.

ACKNOWLEDGEMENT

The Dutch Ministry of Housing, Physical Planning and the Environment is acknowledged for sponsoring this research. F. Kamst and F. van der Ham are acknowledged for their contribution to this study.

2.7 REFERENCES


Appendix 2.1 The shrinking core model

The mass balance over the dissolving solid phase equals:

\[ \rho_s \frac{dV}{dt} = -kA \]  \hspace{1cm} (2.9)

Dividing equation (2.9) by the initial area and the initial volume yields equation (2.10):

\[ \frac{\rho_s}{A_o} \frac{d(V/V_o)}{dt} = - \frac{k}{V_o} \frac{A}{A_o} \]  \hspace{1cm} (2.10)

This equals:
\[
\frac{d(V/V_o)}{dt} = -k \frac{A_o}{V_o \rho_s} \frac{A}{A_o} \tag{2.11}
\]

Equation (2.12) defines \( S_o \) as specific surface area per unit weight:

\[
S_o = \frac{A_o}{V_o \rho_s} \tag{2.12}
\]

The relative volume ( \( V/V_o \) ) as well as the relative area ( \( A/A_o \) ) are described as functions of the relative length ( \( L/L_o \) ) regardless of particle shape:

\[
\frac{A}{A_o} = \left( \frac{L}{L_o} \right)^2 \tag{2.13}
\]

\[
\frac{V}{V_o} = \left( \frac{L}{L_o} \right)^3 \tag{2.14}
\]

This leads to:

\[
\frac{A}{A_o} = \left( \frac{V}{V_o} \right)^{\frac{2}{3}} \tag{2.15}
\]

Substituting equations (2.12) and (2.15) into equation (2.11) yields:

\[
\frac{d(V/V_o)}{dt} = -kS_o \left( \frac{V}{V_o} \right)^{\frac{2}{3}} \tag{2.16}
\]

The dissolved fraction of the solids is given by:

\[
x = 1 - \frac{V}{V_o} \tag{2.17}
\]

This is substituted in equation (2.16):

\[
\frac{dx}{dt} = -kS_o (1 - x)^{\frac{2}{3}} \tag{2.18}
\]

Equation (2.18) is integrated with the boundary condition (\( t=0, x=0 \)):

\[
1 - (1 - x)^{\frac{1}{3}} = \frac{1}{3} k S_o t \tag{2.19}
\]
Chapter 3

Reductive dissolution of zinc ferrite

ABSTRACT

Synthetic zinc ferrite (ZnO.\(\text{Fe}_2\text{O}_3\)) samples were dissolved in 1M HClO\(_4\) solutions with dissolved Fe(ClO\(_4\))\(_2\) at 90°C. The dissolution rate of ZnO.\(\text{Fe}_2\text{O}_3\) depended on the Fe\(^{2+}\)-concentration with an order of 0.43 ± 0.03. It was shown that equivalent leach experiments carried out in D\(_2\)O and H\(_2\)O in the presence of 5 g/L Fe\(^{2+}\) resulted in a dissolution rate which was in H\(_2\)O twice as high as in D\(_2\)O. Three mechanisms are proposed describing the dissolution of ZnO.\(\text{Fe}_2\text{O}_3\) in the presence and in the absence of complexing or reducing agents in H\(_2\)O or D\(_2\)O.

paper by F. Elgersma, G.J. Witkamp and G.M. van Rosmalen, submitted to Hydrometallurgy
3.1 INTRODUCTION

Dissolution of ZnO·Fe₂O₃ is common practice in hydrometallurgical zinc winning plants which use sphalerite concentrates containing over 2 wt% iron. This is a consequence of the fact that the roasting of iron containing sphalerite not only yields ZnO which is easily dissolved in dilute H₂SO₄ (pH = 3 - 5, T = 70°C) but also ZnO·Fe₂O₃ which is much harder to dissolve. Equation (3.1) gives the dissolution reaction of ZnO·Fe₂O₃:

\[ \text{ZnO·Fe}_2\text{O}_3 + 8 \text{H}^+ \rightarrow \text{Zn}^{2+} + 2 \text{Fe}^{3+} + 4 \text{H}_2\text{O} \]  \hspace{1cm} (3.1)

Depending on the iron concentration in the concentrate, ZnO·Fe₂O₃ contains up to 15% of the total amount of zinc in the calcine. Therefore, in order to avoid the loss of the valuable zinc, it has to be dissolved entirely which is usually accomplished by operating a leaching process at pH < 1 and 90 - 95°C.

This paper discusses the acidic dissolution of ZnO·Fe₂O₃ under reductive conditions. It also proposes a mechanism for the acidic dissolution of ZnO·Fe₂O₃ in the absence as well as in the presence of Fe³⁺ complexing or reducing agents.

3.2 THEORY

The dissolution rate of ZnO·Fe₂O₃ is affected by factors such as the temperature, the acidity, the type of acid anion and the presence of ions like Cu⁺, Fe²⁺, Fe³⁺ and Zn²⁺ if added to the leach solution in such an amount that either the redox potential of the solution or the effective concentration of complexing anions is changed.

Recently, Filippou and Demopoulos [1] have presented a review of earlier work on the dissolution of synthetic ZnO·Fe₂O₃ in the absence of redox agents. Additionally, they published results on the dissolution of industrial ZnO·Fe₂O₃.

The reductive dissolution of ZnO·Fe₂O₃ was first studied by Nii and Hisamatsu [2] who showed that at 50°C in 0.9 M H₂SO₄ the dissolution rate was proportional to the square root of the Fe²⁺ concentration at excess Fe²⁺ concentrations up to 1 g/l. Excess here refers to the Fe²⁺ ions added as Fe⁰ salts to the leach solution.
Compared to these amounts the Fe$^{2+}$ concentration originating from the Fe$^{2+}$/Fe$^{3+}$ redox equilibrium of dissolved Fe$^{3+}$ from ZnO.Fe$_2$O$_3$ is negligible.

At 85°C, however, no such a difference between the dissolution rate of ZnO.Fe$_2$O$_3$ in 0.5 M H$_2$SO$_4$ in the presence of 0 or 1 g/l excess Fe$^{2+}$ at 85°C has been found by Elgersma et al.[3]. The difference between the results observed by Nii and by Elgersma must be caused by the difference in temperature for both cases, because the lower H$_2$SO$_4$ concentration in the experiments by Elgersma, compared to the experiments by Nii, would emphasize rather than obscure the effect of Fe$^{2+}$ addition, because SO$_4^{2-}$ ions increase the dissolution rate via Fe$^{III}$ complexation at the ZnO.Fe$_2$O$_3$ surface. The addition of 4 g/l Fe$^{2+}$ (as FeSO$_4$.7H$_2$O) accelerated the dissolution rate in 0.5 M H$_2$SO$_4$ at 85°C with a factor of about two [3]. This shows that higher concentrations of Fe$^{2+}$ accelerate the dissolution at 85°C since the rate increase can not only be explained from the rise of the SO$_4^{2-}$ concentration by some 15 wt%, due to the larger addition of FeSO$_4$.7H$_2$O.

Lu and Muir [4] demonstrated that the dissolution rate of ZnO.Fe$_2$O$_3$ at 25°C in 1 M HCl containing 0.01 M Cu$^+$ was significantly higher than without Cu$^+$. Theoretically, it has been derived that the dissolution rate k of ZnO.Fe$_2$O$_3$ increases with the square root of both the Fe$^{2+}$ and the H$^+$ activities [2,5], as is expressed in equation (3.2).

$$k = k_0 a_{H^+}^{0.5} a_{Fe^{2+}}^{0.5} a_{Fe^{3+}}^{-0.5} \text{ (g m}^{-2} \text{ min}^{-1})$$  \hspace{1cm} (3.2)

Experiments using FeCl$_2$.4H$_2$O as Fe$^{2+}$ source in 2M HClO$_4$ at 90°C were carried out to validate equation (2). It was shown that the dissolution rate increased significantly with the increasing excess Fe$^{2+}$ concentration and the twice as quickly increasing Cl$^-$ concentration [3]. The increase was expressed by an apparent order of the dissolution rate of 0.62 ± 0.25 in the Fe$^{2+}$ concentration. The order in the Fe$^{2+}$ concentration is called apparent because the increasing Cl$^-$ concentration also affects the dissolution rate via Fe$^{III}$ complexation at the ZnO.Fe$_2$O$_3$ surface.

Figure 1A shows the increase of the dissolution rate with the FeCl$_2$ concentration and shows that the observed trend resembles the trend reported by Valverde [6], see Figure 1B, for the dissolution of magnetite (FeO.Fe$_2$O$_3$) in HCl at 50°C. Valverde equally increased the H$^+$ and the Cl$^-$ concentration by adding HCl.
Fig. 1A The increase of the rate constant for ZnO.\text{Fe}_2\text{O}_3 dissolution with the Fe\text{\textsuperscript{2+}} concentration, added as FeCl\text{\textsubscript{2}}

Fig. 1B The increase of the rate constant for Fe\text{\textsubscript{3}}O\text{\textsubscript{4}} dissolution with the HCl concentration in mol/l

Comparison of the results is not unreasonable because the dissolution rates of both Fe\text{\textsubscript{3}}O\text{\textsubscript{4}} and ZnO.\text{Fe}_2\text{O}_3 are determined by the detachment of the Fe\text{\textsuperscript{3+}} ions from the octahedral positions in the spinel [7] and because the influence of an increasing H\textsuperscript{+} concentration on the dissolution rate is approximately equal to the influence of an increase in the Fe\text{\textsuperscript{2+}} concentration, see equation (3.2).

Elgersma [3] proposed to apply a mechanism suggested by Warren and Devuyst [8] for Fe\text{\textsubscript{2}}O\text{\textsubscript{3}} dissolution to the dissolution of ZnO.\text{Fe}_2\text{O}_3, because the detachment of the Fe\text{\textsuperscript{3+}} ions in both cases is rate determining for the dissolution. In the mechanism the following steps are distinguished:

step 1: surface hydroxylation
\[ \text{\textit{\textit{\textit{r}_a Fe}}^{\text{\textsuperscript{3+}}}_2\text{O} + \text{H}_2\text{O} \leftrightarrow \text{\textit{\textit{\textit{r}_a Fe}}^{\text{\textsuperscript{3+}}}_2\text{(OH)}_2} \] (3.3)

step 2: surface protonation
\[ \text{\textit{\textit{\textit{r}_a Fe}}^{\text{\textsuperscript{3+}}}_3\text{OH} + \text{\textit{H}_3\text{O}^+} \leftrightarrow \text{\textit{\textit{\textit{r}_a Fe}}^{\text{\textsuperscript{3+}}}_3\text{OH}_2^+ + \text{H}_2\text{O}} \] (3.4)
step 3a: direct desorption (slow)

\[ r_s \text{Fe}^{III}\text{OH}_2^+ \rightarrow r_s + \text{Fe}^{III}\text{OH}_2^+ \]  (3.5)

step 3b: anion adsorption and subsequent desorption (slow)

\[ r_s \text{Fe}^{III}\text{OH}_2^+ + X^- \leftrightarrow r_s \text{Fe}^{III}\text{OH}_2X \]  (3.6)

\[ r_s \text{Fe}^{III}\text{OH}_2X \rightarrow r_s + \text{Fe}^{III}\text{OH}_2X \]  (3.7)

The rate-determining step in the absence of complexing agents for Fe\(^{3+}\) was supposed to be the direct desorption of a protonated Fe\(^{3+}\)-complex. In the presence of complexing agents, such as SO\(_4^{2-}\) or Cl\(^-\), the desorption of an anion Fe\(^{3+}\)-complex is rate-determining [8]. The latter dissolution process proceeds much faster than direct desorption due to the fact that the ligands bring negative charge into the coordination sphere of a Lewis acid center which polarizes the critical Fe-oxygen lattice bonds and facilitates detachment [9]. In chapter 2 of this thesis it was made plausible that this mechanism correctly describes characteristics of the dissolution of ZnO.\text{Fe}_2\text{O}_3\) such as: i) the dependency of the dissolution rate on the H\(^+\) activity, (Osseo-Asare demonstrated for a generalized case that theoretically the order of 0.5 should be expected [10]) and, ii) the difference between the dissolution rate in HCl and H\(_2\)SO\(_4\) compared to that in HClO\(_4\) and HNO\(_3\) is caused by the lower detachment rate of a protonated Fe\(^{3+}\) complex compared to that of an anion Fe\(^{3+}\)-complex.

The mechanism does not, however, include the influence of redox agents. It therefore needs to be expanded to include the influence of ions such as Fe\(^{2+}\) or Fe\(^{3+}\) on the dissolution rate, if added in such an amount that the redox potential of the solution is affected.

Lieser [11-13] studied the dissolution of Fe\(_2\)(SO\(_4\))\(_3\) in dilute H\(_2\)SO\(_4\) at 20°C in H\(_2\)O and in D\(_2\)O and in the presence of reducing agents like Fe\(^{2+}\), Cu\(^+\), Ti\(^{3+}\), SO\(_2\) and I\(^-\). He suggested a mechanism to explain the accelerating influence of the reducing agents, in particular Fe\(^{2+}\), on the dissolution of Fe\(_2\)(SO\(_4\))\(_3\). The dissolution of ZnO.\text{Fe}_2\text{O}_3 and Fe\(_2\)(SO\(_4\))\(_3\) are likely to have common characteristics, since in both cases the detachment of Fe\(^{3+}\) ions is regarded to be the essential step in the dissolution process. The suggested mechanism consists of the following steps:
Fe^{II}(H_2O)_{6}^{2+}_{(aq)} ↔ Fe^{II}(H_2O)_{6}^{2+}_{(ads)} \quad (3.8)
Fe^{II}(H_2O)_{6}^{2+}_{(ads)} ↔ Fe^{III}OH(H_2O)_{5}^{2+}_{(ads)} + H_{(ads)} \quad (3.9)
Fe^{3+}_{(s)} + H_{(ads)} ↔ Fe^{2+}_{(s)} + H^{+}_{(aq)} \quad (3.10)
Fe^{III}OH(H_2O)_{5}^{2+}_{(ads)} + H^{+}_{(aq)} ↔ Fe^{III}(H_2O)_{6}^{3+}_{(aq)} \quad (3.11)
Fe^{2+}_{(s)} + 6 \ H_2O ↔ Fe^{II}(H_2O)_{6}^{2+}_{(ads)} \quad (3.12)
Fe^{II}(H_2O)_{6}^{2+}_{(ads)} ↔ Fe^{II}(H_2O)_{6}^{2+}_{(aq)} \quad (3.13)

In the presence of excess Fe^{2+} the dissolution rate of Fe_2(SO_4)_3 was found to be two times lower in D_2O than in H_2O [11-13]. This difference was explained from charge transfer from an adsorbed Fe^{2+} ion to an Fe^{3+} ion positioned at the surface (via the reactions (9) and (10)) proceeds via a hydrogen or deuterium atom. This step was supposed to be rate-determining. The difference in dissolution rate in H_2O and D_2O was explained from the difference in mass of H and D.

There is considerable evidence that the detachment of an Fe^{2+} ion proceeds much faster than that of an Fe^{3+} ion, even in the case of FeO_{4} where an Fe^{2+} ion in the crystal surface is claimed to dissolve much slower than an Fe^{2+} which is formed by reducing a structural Fe^{3+} [11,14,15]. The reason why the detachment of Fe^{2+} proceeds faster is that the Madelung energy of the Fe^{II} -oxygen bond in a crystalline lattice is much smaller than that of the Fe^{III} -oxygen bond [9].

This idea is also sustained by the fact that Lieser [11-13] found the dissolution rate of Fe_2(SO_4)_3 in the absence of dissolved Fe^{2+} to be proportional to the Fe^{2+} concentration present in the solid as impurity. Similarly, Nii and Hisamatsu [16] showed that the anion vacancy (i.e. oxygen deficiency) which varied due to differences in the synthesis procedure, determined the dissolution rate of ZnO.Fe_2O_3 in leach solutions without additional redox agents.

It therefore seems likely that the reduction of Fe^{3+} to Fe^{2+} at the surface plays a predominant role in the dissolution mechanism of ZnO.Fe_2O_3, regardless whether such a reduction follows from the presence of reducing agents such as excess Fe^{2+} ions in solution or from e.g. the application of cathodic polarization on the ZnO.Fe_2O_3 crystals which was also shown to enhance the dissolution rate [2].

In order to confirm the applicability of Lieser’s mechanism to the reductive dissolution of ZnO.Fe_2O_3, it had to be verified that i) also in this case the

52
dissolution rate of ZnO·Fe₂O₃ in the presence of excess Fe²⁺ was higher than in H₂O than in D₂O and whether ii) the order of the dependency of the dissolution rate of ZnO·Fe₂O₃ on the Fe²⁺ concentration was 1/2.

3.3 EXPERIMENTAL

Synthetic zinc ferrite was prepared according to a method described in the previous chapter. For determining the free ZnO content of the synthetic product a sample of 0.25 g ZnO·Fe₂O₃ was leached for 2 hours at 25°C in 50 ml of a solution, containing 20 g NH₄Cl and 600 ml 25 wt% NH₃ per liter. A sample of 0.1 g ZnO·Fe₂O₃ was leached for 15 - 30 minutes in 10 ml 36% HCl at 25°C. This 'total' leach provided the total amount of zinc and iron in the product. By assuming all non-ZnO zinc to be ZnO·Fe₂O₃ the quantity of iron contained in ZnO·Fe₂O₃ was determined and thereby the quantity of free Fe₂O₃ was obtained.

The product was further characterized by Scanning Electron Microscopy (SEM) to establish the crystal size and shape and by X-ray Diffraction (XRD) to confirm the crystal structure. A krypton BET-measurement was carried out to determine the specific surface area. The particle size distribution was measured with a Coulter Counter Multisizer.

Samples of 0.25 g from the two different ZnO·Fe₂O₃ charges, synthesized specifically for the reductive dissolution experiments reported here, were leached in 250 ml 0.5M H₂SO₄ solution at 90°C in order to determine the dissolution rate of these charges. The obtained values were compared with the rates obtained in comparable experiments with other charges [3] and indicated whether the synthesized product dissolved at the same rate as the other charges which would allow a comparison of the various experiments, regardless of the charges used.

For the determination of the dissolution rate of ZnO·Fe₂O₃ in the presence of Fe²⁺ it was leached in a 200 ml 1M HClO₄ solution in H₂O or D₂O at 90°C with added excess Fe²⁺. Additionally, ZnO·Fe₂O₃ leach experiments were carried out without excess Fe²⁺ at 90°C in H₂O and D₂O and in 1.0M HClO₄ and 0.5M H₂SO₄ as 'blanks'. All experiments were carried out in a round bottom flask. The solution was stirred at 610 rpm.
It should be noticed that despite the fact that $\text{HClO}_4$ and $\text{H}_2\text{SO}_4$ were used in experiments in $\text{H}_2\text{O}$ as well as in $\text{D}_2\text{O}$, the molar ratio of H/D in $\text{D}_2\text{O}$ experiments was below 0.04. Perchloric acid was used because perchlorate does not form complexes with Fe$^{3+}$ which could obscure the determination of the influence of Fe$^{2+}$ on the dissolution rate. The leach solution contained Fe$^{2+}$ from dissolved Fe($\text{ClO}_4$)$_2$ which was prepared by adding a 5 - 10% molar excess of Ba(OH)$_2$.8H$_2$O to a HClO$_4$ solution of FeSO$_4$.7H$_2$O. The produced BaSO$_4$ was removed by filtration under a N$_2$ blanket to prevent the oxidation of Fe$^{2+}$.

During the experiments the suspension in the flask was kept under a N$_2$ atmosphere. The flask was immersed in a thermostated water bath. The temperature in the flask differed by ±0.2°C. At time intervals of 2.5 or 5 minutes liquid samples were taken. The iron and zinc contents of the solution were determined by Inductively Coupled Plasma atomic emission spectroscopy. The experiments lasted 30 or 60 minutes. All chemicals used were analytical grade. All water used was deionized and distilled in an all pyrex glass apparatus.

3.4 DATA ANALYSIS

The conversion data for each experiment were characterized by a rate constant for dissolution obtained from a surface reaction controlled shrinking core model [2]. The applicability of this model for describing the dissolution process is discussed in the previous chapter.

$$1 - (1 - x)^{1/3} = 1/3 \; k \; S_o \; t$$  \hspace{1cm} (3.14)$$

Here, $x$ represents the conversion, $k$ represents the rate constant ($g/(m^2$.min)), $S_o$ the specific surface area of the solids ($m^2/g$) at $t=0$ and $t$ the elapsed time (minutes). In deriving equation (3.14) the following assumptions were made: i) the particles dissolve isomorphically, ii) the number of particles remains constant throughout the process (this leads to the assumption that all particles were of the same size) and iii) the dissolution rate per unit surface area is constant, thus a
constant driving force for the dissolution process is required. The conversion $x$ is defined as the ratio of dissolved zinc per gram ZnO$\cdot$Fe$_2$O$_3$ in a sample over dissolved zinc per gram ZnO$\cdot$Fe$_3$O$_5$ as obtained during the 'total leach'. A correction was made for the free ZnO content of ZnO$\cdot$Fe$_2$O$_3$.

3.5 RESULTS AND DISCUSSION

3.5.1 Characterization of zinc ferrite

Synthetic ZnO$\cdot$Fe$_2$O$_3$ was prepared in two charges. The free ZnO content was equal to 3.6 and 4.6 wt% respectively. The free Fe$_2$O$_3$ content was below 3 wt%. The median volume particle size of ZnO$\cdot$Fe$_2$O$_3$ was about 11 $\mu$m. The size distribution of the particles was symmetrical and narrow; 16 vol% of the particles was smaller than 7 $\mu$m and 84 vol% was smaller than 14 $\mu$m. No crystalline phases apart from ZnO$\cdot$Fe$_2$O$_3$ were detected by XRD. The specific surface area of the particles was 3.66 m$^2$/g ($\pm$ 2%) for charge I and 2.61 m$^2$/g ($\pm$ 2%) for charge II respectively.

3.5.2 Applicability of the leaching model and reproducibility of the experiments

The experimental results were adequately described by the surface reaction controlled shrinking core model. In most experiments a straight line with a correlation coefficient of above 0.99 was obtained.

The experiments $1^a$ and $1^b$ (see table 3.1) were carried out in the absence of reducing agents to compare the dissolution rate obtained by leaching of the ZnO$\cdot$Fe$_2$O$_3$ charges used for the reductive dissolution experiments, with former results obtained using other charges [3]. In 0.5M H$_2$SO$_4$ at 90°C the resulting dissolution rates obtained in the experiments $1^a$ and $1^b$ were equal to 0.0127 and 0.0122 g m$^{-2}$ min$^{-1}$ respectively. This deviated less than 2 respectively 6% from an average value of 0.0129 g m$^{-2}$ min$^{-1}$ obtained from three other charges [3]. Thus, results obtained in the experiments reported below may be quantitatively compared with results reported in chapter 2 of this thesis.

55
Table 3.1: Zinc ferrite dissolution experiments I: comparability of the leach experiments with experiments carried out with other charges

<table>
<thead>
<tr>
<th>Exp.no.</th>
<th>medium</th>
<th>added acid</th>
<th>temperature</th>
<th>rate constant k</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(mole l(^{-1}))</td>
<td>( °C )</td>
<td>(g m(^{-2}) min(^{-1}))</td>
</tr>
<tr>
<td>1(^A)</td>
<td>H(_2)O</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>90</td>
<td>0.0127</td>
</tr>
<tr>
<td>1(^B)</td>
<td>H(_2)O</td>
<td>0.5 M H(_2)SO(_4)</td>
<td>90</td>
<td>0.0122</td>
</tr>
</tbody>
</table>

3.5.3 Dependency of the dissolution rate in H\(_2\)O on the Fe\(^{2+}\) concentration

Table 3.2 gives the results of the experiments 2 to 6 carried out to determine the dependency of the dissolution rate of ZnO.Fe\(_2\)O\(_3\) on the Fe\(^{2+}\) concentration which due to the dissolution of a comparatively small amount of ZnO.Fe\(_2\)O\(_3\) remained constant throughout the experiment. The Fe\(^{2+}\) concentration was varied between 0 and 14 g l\(^{-1}\). All experiments were carried out in H\(_2\)O containing 1M HClO\(_4\) at 90°C. The dependency of the rate constant on the Fe\(^{2+}\) concentration is of the order of 0.43 ± 0.03. Figure 3.2 shows the corresponding log k/log C\(_{Fe^{2+}}\)-plot. This result sustains the hypothesis of Gorichev and Kipriyanov [5] for the dissolution of Fe\(_3\)O\(_4\) and the experimental results of Nii and Hisamatsu [2]. The reason why the experimentally determined order is slightly below the theoretically expected order of 0.5 is unknown.

3.5.4 Dependency of the dissolution rate in H\(_2\)SO\(_4\) on the solvent

The value of the dissolution rate of ZnO.Fe\(_2\)O\(_3\) in 0.5M H\(_2\)SO\(_4\) in D\(_2\)O without reducing agents at 90°C is 11% lower than the average value obtained from five equivalent experiments carried out with five different charges in H\(_2\)O. The result of this experiment (no. 7) is given in table 3.3. Although the differences between the rates in H\(_2\)O and D\(_2\)O are small, they are regarded significant. An explanation could be the lower dissociation constant of D\(_2\)SO\(_4\) (formed via D from D\(_2\)O exchanging for H\(^+\)) compared to H\(_2\)SO\(_4\) and of D\(_2\)O compared to H\(_2\)O. The lower dissociation constants result in a lower acidity and consequently a lower rate.

56
Figure 3.2 The dependency of the rate constant for ZnO\(\cdot\)Fe\(_2\)O\(_3\) dissolution on the Fe\(^{2+}\) concentration in \(\ln (\text{concentration}/(\text{g l}^{-1}))\).

Table 3.2: Zinc ferrite dissolution experiments II: dependency of the rate constant \(k\) on the Fe\(^{2+}\) concentration in H\(_2\)O containing 1.0 M HClO\(_4\) at 90°C.

<table>
<thead>
<tr>
<th>Exp. no.</th>
<th>Fe(^{2+}) concentration (g l(^{-1}))</th>
<th>rate constant (k) (g m(^{-2}) min(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0</td>
<td>0.00091</td>
</tr>
<tr>
<td>3</td>
<td>1.9</td>
<td>0.00132</td>
</tr>
<tr>
<td>4</td>
<td>3.1</td>
<td>0.00163</td>
</tr>
<tr>
<td>5(^A)</td>
<td>4.6</td>
<td>0.00192</td>
</tr>
<tr>
<td>5(^B)</td>
<td>5.4</td>
<td>0.00193</td>
</tr>
<tr>
<td>5(^C)</td>
<td>5.4</td>
<td>0.00198</td>
</tr>
<tr>
<td>6</td>
<td>14.4</td>
<td>0.00317</td>
</tr>
</tbody>
</table>
Table 3.3: Zinc ferrite dissolution experiments III: dependency of the rate constant k on the solvent

<table>
<thead>
<tr>
<th>exp. no.</th>
<th>medium</th>
<th>added acid</th>
<th>rate constant k (g m⁻² min⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>D₂O</td>
<td>0.5M H₂SO₄</td>
<td>0.0113</td>
</tr>
<tr>
<td>8ᴬ</td>
<td>H₂O</td>
<td>1.0M HClO₄</td>
<td>0.00091</td>
</tr>
<tr>
<td>8ᴮ</td>
<td>D₂O</td>
<td>1.0M HClO₄</td>
<td>0.00113</td>
</tr>
</tbody>
</table>

3.5.5 Dependency of the dissolution rate in HClO₄ on the solvent

Table 3.3 also gives the results from the experiments 8ᴬ and 8ᴮ in which ZnO·Fe₂O₃ was dissolved in 1.0 M HClO₄ at 90°C in H₂O and D₂O respectively. In experiment 8ᴬ a lower rate constant is measured than in experiment 8ᴮ.

Although the dissociation constant of H₂O is higher than that of D₂O, the dissociation constant of DClO₄ and HClO₄ are not expected to be different. The latter is a consequence of the fact that total dissociation occurs with HClO₄ and/or DClO₄ and therefore the free H⁺ or D⁺ concentration is equal for both experiments. For the difference between the results of the experiments 8ᴬ and 8ᴮ currently no explanation is available.

3.5.6 Dependency of the dissolution rate in HClO₄ in the presence of Fe²⁺ on the solvent

Table 3.4 provides the results from the experiments 5ᴬ, 5ᴮ, 5ᶜ and 9ᴬ in which ZnO·Fe₂O₃ was dissolved in 1.0 M HClO₄ at 90°C in H₂O and D₂O respectively. The average rate constant of the experiments 5ᴬ, 5ᴮ, 5ᶜ was twice as high as the average rate constant of the experiments 9ᴬ. It is remarkable that the dissolution of ZnO·Fe₂O₃ in D₂O is not accelerated by the presence of 5 g l⁻¹ Fe²⁺, since the rate constant of e.g. experiment 9ᴮ is practically equal to the value of experiment 8ᴮ. Lieser [11-13] observed that the rate constant for the dissolution of Fe₂(SO₄)₃ at
Table 3.4: Zinc ferrite dissolution experiments IV: dependency of the rate constant $k$ on the solvent in the presence of Fe$^{2+}$

<table>
<thead>
<tr>
<th>exp. no.</th>
<th>Fe$^{2+}$ conc. (g l$^{-1}$)</th>
<th>medium</th>
<th>rate constant $k$ (g m$^{-2}$ min$^{-1}$)</th>
<th>average $k$-value (g m$^{-2}$ min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5$^A$</td>
<td>4.6</td>
<td>H$_2$O</td>
<td>0.00192</td>
<td></td>
</tr>
<tr>
<td>5$^B$</td>
<td>5.4</td>
<td>H$_2$O</td>
<td>0.00193</td>
<td>0.00194</td>
</tr>
<tr>
<td>5$^C$</td>
<td>5.4</td>
<td>H$_2$O</td>
<td>0.00198</td>
<td></td>
</tr>
<tr>
<td>9$^A$</td>
<td>4.3</td>
<td>D$_2$O</td>
<td>0.00080</td>
<td></td>
</tr>
<tr>
<td>9$^B$</td>
<td>4.9</td>
<td>D$_2$O</td>
<td>0.00112</td>
<td>0.00096</td>
</tr>
</tbody>
</table>

20°C in the presence of Fe$^{2+}$ was twice as high in H$_2$O than in D$_2$O in further similar experiments. Thus, the results for ZnO·Fe$_2$O$_3$ and Fe$_2$(SO$_4$)$_3$ are comparable in case Fe$^{2+}$ is added.

In experiments where Lieser added Cu$^{1}$-Cl complexes to the leach solution the rate constant for the dissolution of Fe$_2$(SO$_4$)$_3$ did not depend on the solvent (H$_2$O or D$_2$O), probably because the Cu$^+$ was shielded by Cl$^-$ and did not transfer its charge to the Fe$_2$(SO$_4$)$_3$ via a H or D atom, as suggested for Fe$^{2+}$.

It seems therefore likely that in order to observe differences between the dissolution rate of ZnO·Fe$_2$O$_3$ in the presence of a reducing agent in H$_2$O or D$_2$O no strong complexing agents (like Cl$^-$) may be allowed to interfere. It is supposed that only when a Me$^{n}$-OH or a Me$^{n}$-OD complex is in equilibrium with a Me$^{n+}$-H$_2$O or a Me$^{n+}$-D$_2$O complex (see reaction (9)) a reduction mechanism as proposed by Lieser is correct.

Below, a dissolution mechanism for ZnO·Fe$_2$O$_3$ is suggested which involves steps for three different situations:

I) no complexing agents, no reducing agents

II) complexing agents, no reducing agents

III) no complexing agents, reducing agents
I) In the first case, the mechanism proposed by Warren and Devuyst [8] applies, which is slightly extended here to include the importance of bulk electrons and the relative ease of the detachment of a Fe^{2+} ion:

step 1: surface hydroxylation with H_2O from the solution bulk and protonation
\[ \frac{r_s}{r_s} \text{Fe}^{3+}_2 \text{O} + H_2O \leftrightarrow \frac{r_s}{r_s} \text{Fe}^{3+}_2(\text{OH})_2 \] \[ (3.15) \]
\[ \frac{r_s}{r_s} \text{Fe}^{3+} \text{OH} + H_3O^+ \leftrightarrow \frac{r_s}{r_s} \text{Fe}^{3+} \text{OH}_2^+ + H_2O \] \[ (3.16) \]

step 2: charge transfer from a bulk electron to the surface
\[ \frac{r_s}{r_s} \text{Fe}^{3+} \text{OH}_2^+ + e^- \leftrightarrow \frac{r_s}{r_s} \text{Fe}^{2+} \text{OH}_2 \] \[ (3.17) \]

step 3: release of the Fe^{2+} ion (slow)
\[ \frac{r_s}{r_s} \text{Fe}^{2+} \text{OH}_2 + 5 H_2O \rightarrow \frac{r_s}{r_s} + \text{Fe}^{2+}(H_2O)_6^{2+}\text{(ads.)} \] \[ (3.18) \]

step 4: oxidation of the adsorbed Fe^{2+} and desorption
\[ \text{Fe}^{2+}(H_2O)_6^{2+}\text{(ads.)} \rightarrow e^- + \text{Fe}^{3+}(H_2O)_6^{3+}\text{(aq)} \] \[ (3.19) \]

II) In the second case the influence of complexing agents is included. This yields:

step 1: surface hydroxylation with H_2O from the bulk and protonation
\[ \frac{r_s}{r_s} \text{Fe}^{3+}_2 \text{O} + H_2O \leftrightarrow \frac{r_s}{r_s} \text{Fe}^{3+}_2(\text{OH})_2 \] \[ (3.20) \]
\[ \frac{r_s}{r_s} \text{Fe}^{3+} \text{OH} + H_3O^+ \leftrightarrow \frac{r_s}{r_s} \text{Fe}^{3+} \text{OH}_2^+ + H_2O \] \[ (3.21) \]

step 2: complexation and charge transfer from the anion to the surface Fe^{3+} complex
\[ \frac{r_s}{r_s} \text{Fe}^{3+} \text{OH}_2^+ + X^- \leftrightarrow \frac{r_s}{r_s} \text{Fe}^{3+} \text{OH}_2X^{(n-1)-} \] \[ (3.22) \]
\[ \frac{r_s}{r_s} \text{Fe}^{3+} \text{OH}_2X^{(n-1)-} \leftrightarrow \frac{r_s}{r_s} \text{Fe}^{2+} \text{OH}_2X^{(n-2)-} \] \[ (3.23) \]

step 3: detachment of the complex (slow) and charge transfer from Fe to X
\[ \frac{r_s}{r_s} \text{Fe}^{2+} \text{OH}_2X^{(n-2)-} + 5 H_2O \rightarrow \frac{r_s}{r_s} + \text{Fe}^{3+}(H_2O)_6X^{(3-n)+}\text{(ads.)} \] \[ (3.24) \]
step 4: desorption of the adsorbed Fe$^{3+}$ - complex

\[
\text{Fe}^{III}(\text{H}_2\text{O})_6\text{X}^{(3-n)^+}_{(\text{ads})} \rightarrow \text{Fe}^{III}(\text{H}_2\text{O})_6\text{X}^{(3-n)^+}_{(\text{aq})}
\]  (3.25)

III) The dissolution process in the presence of reducing agents is given by the following steps:

step 1: surface hydroxylation with a H$_2$O ligand attached to a Fe$^{2+}$ ion

\[
\begin{align*}
&\quad \quad \quad \quad r_s \ \text{Fe}^{III}_a \text{O} + \text{H}_2\text{O} - \text{Fe}^{II}_b(\text{H}_2\text{O})_5^{2+} \leftrightarrow \quad \quad \quad r_s \ \text{Fe}^{III}_a(\text{OH})_2 - \text{Fe}^{II}_b(\text{H}_2\text{O})_5^{2+} (3.26) \\
&\text{step 2: charge transfer via hydrogen transfer to an adjacent Fe}^{III} \text{ on the surface (slow)}
\end{align*}
\]

\[
\begin{align*}
&\quad \quad \quad \quad r_s \ \text{Fe}^{III}_a(\text{OH})_2 - \text{Fe}^{II}_b(\text{H}_2\text{O})_5^{2+} \leftrightarrow \quad \quad \quad r_s \ \text{Fe}^{III}_a(\text{OH})_2 - \text{Fe}^{III}_b(\text{H}_2\text{O})_4^{2+} + \quad r_s \ \text{H} (3.27) \\
&\quad \quad \quad \quad r_s \ \text{Fe}^{III}_a \text{Kink} + \quad r_s \ \text{H} \leftrightarrow \quad r_s \ \text{Fe}^{III}_a \text{Kink} + \text{H}^{(\text{aq})} (3.28)
\end{align*}
\]

step 3: desorption of the reaction products

\[
\begin{align*}
&\quad \quad \quad \quad r_s \ \text{Fe}^{III}_a \text{Kink} + \quad 6 \ \text{H}_2\text{O} \rightarrow \quad \quad \quad \text{Fe}^{II}_c(\text{H}_2\text{O})_6^{2+} (3.29) \\
&\quad \quad \quad \quad r_s \ \text{Fe}^{III}_a(\text{OH})_2 - \text{Fe}^{III}_b(\text{H}_2\text{O})_4^{2+} + \text{H}^+ \rightarrow \quad \quad \quad r_s \ \text{Fe}^{III}_a \text{O} + \quad \text{Fe}^{III}_b(\text{H}_2\text{O})_6^{3+} (3.30)
\end{align*}
\]

In principle, the mechanisms I, II and III may occur simultaneously and are therefore in competition. In most cases, however, it is assumed that only one mechanism is prevailing for the dissolution process at a given situation.

In case I where no complexing agents are assumed to be present, the dissolution rate of ZnO.Fe$_2$O$_3$ is determined by the release of the Fe$^{2+}$ complex which is formed by reaction (3.17). The dissolution rate of ZnO.Fe$_2$O$_3$ via mechanism I may be enhanced by three factors:

i) by lowering the redox potential by addition of a reducing species which does not operate via mechanism III, like a Cu$^\text{II}$Cl-complex,

ii) by cathodic polarization of the solids and

iii) by changing the synthesis conditions for ZnO.Fe$_2$O$_3$ in such a way that a higher vacancy concentration is realized.

Factor i) affects the dissolution rate by lowering the redox potential of the solution and thereby increasing the potential difference between the positively charged
hydroxylated surface of the solid and the solution. This increases the driving force for dissolution and consequently facilitates the detachment of Fe$^{2+}$-OH complexes. Oxidizing species which increase the solution potential are known to decelerate the dissolution as was shown in the previous chapter for the dissolution of ZnO$\cdot$Fe$_2$O$_3$ in the presence of increasing amounts of Fe$^{3+}$.

Factor ii) increases the potential difference between the solution and the solids by artificially increasing the potential of the latter and thus increasing the dissolution rate.

Factor iii) increases the number of potentially active sites per unit surface, which also increases the dissolution rate.

Mechanism II where complexing agents are present in the absence of reducing agents is similar to mechanism I but includes the complexation of a surface Fe$^{3+}$ ion with a complexing agent. The rate determining step in this mechanism is also the detachment of a Fe$^{2+}$-complex (reaction 3.24) but much higher dissolution rates are observed compared to the rates observed for mechanism I. In particular SO$_4^{2-}$ and Cl$^-$ are very effective in enhancing the dissolution rate of ZnO$\cdot$Fe$_2$O$_3$ via complexation.

In mechanism III the rate determining step is the reduction of a surface Fe$^{3+}$ to Fe$^{2+}$ (reaction 3.28). Lieser [11-13] explains the difference of a factor two in the dissolution rate measured in H$_2$O and D$_2$O, which is unique for this mechanism, by assuming that elementary H or D is involved in one of the steps of the mechanism.

The reason why the dissolution rate of ZnO$\cdot$Fe$_2$O$_3$ in the presence of excess Fe$^{2+}$ in H$_2$O is two times higher than in D$_2$O is not fully understood. The temperature does not seem to affect this phenomenon because the experiments carried out by Lieser [11-13] were performed at 20$^\circ$C and the experiments in this study at 90$^\circ$C, but the same factor two was observed. It seems no coincidence that the ratio of the dissolution rates corresponds to the ratio of the mass of H and D, but no mechanistic explanation is available which relates the rate of charge transfer from an adsorbed Fe$^{2+}$ to a surface Fe$^{3+}$ via H or D to the reciprocal value of their mass.
3.6 CONCLUSIONS

The dependency of the dissolution rate of ZnO.\(\text{Fe}_2\text{O}_3\) upon the Fe\(^{2+}\) concentration is of the order 0.43 ± 0.03 in 1 M HClO\(_4\) solutions at 90°C.

Three different dissolution mechanisms for ZnO.\(\text{Fe}_2\text{O}_3\) were suggested. The various dissolution mechanisms may compete under particular conditions, but usually one mechanism determines the dissolution rate.

A difference of a factor of two of the rate constant for the dissolution of ZnO.\(\text{Fe}_2\text{O}_3\) is observed in 1 M HClO\(_4\) at 90°C in the presence of 5 g/L Fe\(^{2+}\) in H\(_2\)O compared to D\(_2\)O. This difference is caused by the reductive dissolution mechanism for ZnO.\(\text{Fe}_2\text{O}_3\) but not yet fully understood. In the absence of Fe\(^{2+}\) no significant difference in the dissolution rate of zinc ferrite in 1M HClO\(_4\) at 90°C in H\(_2\)O or D\(_2\)O was measured. This indicates that for reductive dissolution a step involving proton transfer is rate determining.

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3.7 REFERENCES


Simultaneous dissolution of zinc ferrite and precipitation of ammonium jarosite

ABSTRACT
Zinc ferrite (ZnO$_2$Fe$_3$O$_4$) was converted in a single-step seeded batch process into ammonium jarosite (NH$_4$Fe$_6$(SO$_4$)$_2$(OH)$_6$) at 95°C and at pH values, which were kept constant at either 1.7 or 1.95. The conversion consists of the dissolution of zinc ferrite, which could be described by a surface reaction controlled shrinking core model, and the simultaneous precipitation of ammonium jarosite which is also a surface reaction controlled process. The supersaturation during conversion for the precipitation of jarosite was calculated from the solution composition.

At pH = 1.7 virtually 100% conversion of zinc ferrite is achieved. This leads to a residual zinc content of the produced solids below 0.1 wt%. XRD-analyses of the product showed correspondingly small amounts of zinc ferrite. This indicates that the zinc incorporation in the jarosite lattice is practically negligible. The advantages of such a controlled conversion process for industrial practice are discussed.

paper by F. Elgersma, G.J. Witkamp and G.M. van Rosmalen, submitted to Hydrometallurgy
4.1 INTRODUCTION

In the Western World over 80% of the primary production of zinc originates from electrolytic zinc refining plants [1]. Despite the increasing popularity of direct (pressure) leaching technology, most of the plants are still operating a roast-leach-electrowinning process.

During the roasting process of zinc blende, zinc oxide and sulfur dioxide are produced, as well as zinc ferrite in case iron is present in the concentrate. Rodier [2] has published a list of zinc mine concentrate contents which shows that only 9 out of 74 concentrates contain less than 2 wt% iron and that the average iron content of the concentrates is 6.6 wt%. Since usually VM-Lurgi fluidized bed roasting technology is applied, the formation of zinc ferrite is unavoidable.

Zinc oxide which is quickly dissolved in dilute sulfuric acid (pH = 3 - 5, T = 70 °C) and zinc ferrite which only dissolves under more severe conditions (pH = 1, T = 95°C) are leached in subsequent steps. The dissolution of zinc ferrite is required to avoid the loss of its zinc content. It, however, also introduces iron in the leaching circuits, which has to be withdrawn because iron is a harmful impurity in the electrowinning process. It interferes with the electrolyte purification of dissolved Cu²⁺, Cd²⁺ and Co²⁺ with zinc dust and promotes anode corrosion and uptake of lead and iron in cathodic zinc [3].

For the removal of iron from zinc leaching circuits three commercial processes are available. These processes are usually named after the minerals which precipitate, namely hematite (Fe₂O₃), goethite (FeOOH) or jarosite (MFe₃(SO₄)₂(OH)₆ with M = Na⁺ or NH₄⁺). The jarosite and goethite processes are more easy to operate than the hematite process and therefore these processes are most commonly installed. Although iron precipitation processes are mature technology by now, improvements have become essential because the impure goethite and jarosite have never found any application and require disposal. Their impurity not only results from the uptake of elements like Cd, Pb and As which are present as trace metals in the ore, but also from zinc ions which incorporate in and adhere to the lattice.

Residue disposal is now heavily criticized in several countries. In The Netherlands, disposal not only has to be stopped in the near future, even historically disposed
jarosite residues have to be converted into environmentally acceptable products. This calls for jarosite or goethite residue treatment processes which are currently developed [4]. In these processes a low initial zinc content of the residue is beneficial, not only because of the higher refining efficiency of the valuable metals but also because it lowers the energy requirements during further treatment [4]. This study describes a potential improvement of the current hydrometallurgical zinc refining process. This improvement is realized by a careful control of the conversion of zinc ferrite into ammonium jarosite. The supersaturation with respect to jarosite is kept low by imposing a slow release of iron from the simultaneously dissolving zinc ferrite. This can be achieved by control of the pH of the solution. The advantage of having a lower supersaturation during the precipitation is that this usually leads to a reduced uptake of most impurities in the crystalline phase.

A controlled conversion of zinc ferrite into ammonium jarosite has not received much attention in literature yet. Huggare et al.[5] have indicated that the direct conversion route was feasible, but did not provide details about reaction kinetics or supersaturation levels. In this paper the simultaneous dissolution of zinc ferrite and precipitation of ammonium jarosite and the determination of the rate-determining step of this process are described, as well as the residual uptake of zinc in jarosite.

4.2 THEORY

The conversion of zinc ferrite into ammonium jarosite is a two-step solvent-mediated process, which is summarized by the following two reaction equations:

\[
\text{ZnO}_{.4} \text{Fe}_{.6} \text{O}_3 + 8 \text{H}^+ \rightarrow \text{Zn}^{2+} + 2 \text{Fe}^{3+} + 4 \text{H}_2\text{O} \quad (4.1)
\]

\[
\text{NH}_4^+ + 3 \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 6 \text{H}_2\text{O} \rightarrow \text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 6 \text{H}^+ \quad (4.2)
\]

First, the two processes are discussed separately and thereafter it will be explained why the simultaneous dissolution of zinc ferrite and precipitation of jarosite offers opportunities for obtaining a higher jarosite purity by controlling the process pH. The progress of the two processes is quantified by conversions, one based on the fraction of dissolved zinc ferrite and the other on the ratio of iron.
precipitated as jarosite over iron dissolved from zinc ferrite. Equations (4.1) and (4.2) may be added to yield:

\[ 3 \text{ZnO}\cdot\text{Fe}_2\text{O}_3 + 2 \text{NH}_4^+ + 4 \text{SO}_4^{2-} + 12 \text{H}^+ \rightarrow 3 \text{Zn}^{2+} + 2 \text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 \]  

(4.3)

### 4.2.1 The dissolution rate of zinc ferrite

The dissolution process of zinc ferrite in mineral acids has been the subject of several investigations. Recently, it was concluded [6] that the dissolution rate \( k \) (g min\(^{-1}\).m\(^{-2}\)) of zinc ferrite depends on the Fe\(^{3+}\) concentration and the hydrogen activity:

\[ k = k_0 \sqrt[3]{\frac{a_{H^+}}{a_{Fe^{3+}}}} \]  

(4.4)

Here \( k_0 \) represents a constant (g m\(^{-2}\) min\(^{-1}\)). In order to determine this dissolution rate, a surface reaction controlled shrinking core model was used which was shown to fit the experimental data in chapter two of this thesis adequately. This model is given by the equations (4.5) and (4.6):

\[ 1 - (1 - x)^{1/3} = K t \]  

(4.5)

with:

\[ K = \frac{1}{3} k S_0 \]  

(4.6)

Here, \( K \) is the proportionality constant (min\(^{-1}\)), \( x \) is the fraction dissolved zinc ferrite (which is defined in equation (7)) and \( S_0 \) is the initial specific surface area (m\(^2\).g\(^{-1}\)) of zinc ferrite, determined by krypton BET-measurement. It was shown that the dispersed porous zinc ferrite particles are 100% wetted and therefore the use of the entire specific surface area is justified [6]. The conversion is defined below:

\[ x = \frac{[\text{Zn}]}{[\text{Zn}]}_{t=t} / \frac{[\text{Zn}]}{[\text{Zn}]}_{t=\infty} \]  

(4.7)

### 4.2.2 The precipitation of ammonium jarosite

This process step is described by equation (4.2). The conversion into jarosite is defined by the ratio of iron precipitated as jarosite over iron dissolved from zinc ferrite. This ratio was corrected for the initial concentration of Fe\(^{3+}\) (see equation 4.10). The corresponding production rate is given by the time derivative of the
production of jarosite, calculated from the iron balance. It can also be defined as:

$$r_p = \rho_c G A$$  \hspace{1cm} (4.8)

Here, $r_p$ is the production rate (kg s$^{-1}$), $\rho_c$ is the jarosite density (2960 kg m$^{-3}$), $G$ is the linear crystal growth rate (m s$^{-1}$) and $A$ is the surface area of the crystals (m$^2$).

The linear growth rate depends on the driving force for crystallization and is thus directly related to the relative supersaturation, given by equation (4.9). The derivation of equation (4.9) is given in appendix 4.1.

$$\sigma = \left( \frac{[Fe^{3+}]^3 [NH_4^+] [SO_4^{2-}]^2 [OH^-]^6}{([Fe^{3+}]^3 [NH_4^+] [SO_4^{2-}]^2 [OH^-]^6)_{eq}} \right)^{1/12} - 1$$  \hspace{1cm} (4.9)

For calculating the free concentrations of Fe$^{3+}$, SO$_4^{2-}$, NH$_4^+$ and OH$^-$ in these mixed ferric and ammonium sulfate solutions, complex constants have to be known. The appendices 4.2 to 4.4 provide the complexation reactions and the method which is used to determine the concentrations of the different species.

4.2.3 Simultaneous dissolution of zinc ferrite and precipitation of jarosite

In a process where one phase dissolves and thereby provides the source material for another phase that precipitates, usually either the dissolution or the precipitation step is rate-determining. In case the dissolution process is rate-determining the concentration of the common constituents of the dissolving and the precipitating phase remain comparatively low. Its concentration approaches the value dictated by the equilibrium concentration of the precipitating phase. Inversely, when the precipitation process is rate-determining the concentration of the constituent ions is comparatively high and approaches the equilibrium concentration of the dissolving phase. Figure 4.1 provides a schematic diagram for a batch experiment which shows the concentration of the constituent that is transferred from the one phase to the other, as a function of time for the two extremes.

In case of the dissolution of zinc ferrite and the precipitation of jarosite this common constituent is iron. The dissolution rate of zinc ferrite and the precipitation rate of jarosite are both affected by the acidity of the solution and by
the Fe$^{3+}$ concentration. As shown in equation (4.4) the dissolution rate of zinc ferrite increases with an increasing H$^+$ activity and with a decreasing Fe$^{3+}$ concentration. Equation (4.9) shows that, via the supersaturation, the precipitation rate of jarosite increases with an increasing Fe$^{3+}$ concentration. The Fe$^{3+}$ equilibrium concentration decreases by increasing the pH. For a given Fe$^{3+}$ concentration, this results in a supersaturation which increases with an increasing pH. Therefore, the pH is the parameter which allows simultaneous control over the supersaturation and the dissolution rate.

Figure 4.1: A schematic diagram for a simultaneous dissolution and precipitation reaction. The concentration of the constituent ion, in this case Fe$^{3+}$, will follow the trend shown by line I if the precipitation is rate limiting and will follow line II if the dissolution is rate limiting. The dashed line shows the solubility of the precipitating phase.

At too high values of the pH, the supersaturation becomes too high, due to the dependency of the Fe$^{3+}$ equilibrium concentration on the pH. At too low values of the pH the dissolution of zinc ferrite is no longer rate determining and the Fe$^{3+}$ concentration either leads to a too high supersaturation, or the conversion into jarosite remains low owing to the fact that the equilibrium solubility of Fe$^{3+}$ has increased considerably.
A pH optimization pursues operating conditions, where the process is dominated by a slow dissolution of zinc ferrite, while the supersaturation in the solution reaches a (sufficiently) low value. It is demonstrated in ref. [7] that in continuous crystallization experiments the incorporation of impurities increased with increasing supersaturation. Therefore, by keeping the solution at this pH value the incorporation of impurities also remains low.

4.3 EXPERIMENTAL

4.3.1 Synthesis of zinc ferrite and ammonium jarosite
Synthetic zinc ferrite was prepared in a batch charge of 50 g, following the procedure described in chapter two of this thesis. For determining the residual ZnO-content of the synthetic product, a sample of 0.25 g ZnO.\textsubscript{Fe}\textsubscript{2}O\textsubscript{4} was leached for two hours at 25°C in 50 ml of a solution, containing 20 g NH\textsubscript{4}Cl and 600 ml 25% NH\textsubscript{3} per liter. A sample of 0.1 g ZnO.\textsubscript{Fe}\textsubscript{2}O\textsubscript{4} was leached for 30 minutes in 10 ml 36% HCl at 25°C. This 'total' leach provided the total amount of zinc and iron in the product. The \textsubscript{Fe}\textsubscript{2}O\textsubscript{3} content of the sample was determined via the material balance.

Jarosite seed crystals were prepared in a continuous crystallization process at 95°C using the equipment and procedure described in [8]. The residence time of the continuous experiment was on the average 1.25 hour. The feed concentration of the iron(III) sulfate solution was 0.92 mole l\textsuperscript{-1} Fe\textsuperscript{3+} and the feed ammonium sulfate solution contained 0.88 mole l\textsuperscript{-1} NH\textsubscript{4}\textsuperscript{+}. The solutions were added in a stoichiometric ratio. During the experiments a pH of 1.5, when measured at 25°C, was maintained by adding lithium hydroxide. The resulting crystal slurry was filtered and dried. Due to the presence of Li\textsubscript{2}SO\textsubscript{4}.H\textsubscript{2}O which was formed with the seeds due to insufficient washing some large seeds clusters (size: 1 to 20 mm) were formed, which were separated before using the solids as seeds.

4.3.2 Characterization of zinc ferrite and ammonium jarosite
Ammonium jarosite and zinc ferrite were characterized by scanning electron microscopy (SEM) to establish their crystal size and shape and by x-ray diffraction
(XRD) to confirm their crystal structure. Krypton-BET measurements were used to determine the specific surface area of zinc ferrite. The particle size distributions were determined using a Coulter Counter Multisizer.

4.3.3 Determination of the solubility product of ammonium jarosite
To measure the solubility product, defined as the equilibrium ionic concentration product, 8.00 g ammonium jarosite was dissolved in 200.0 g deionized and distilled water, kept at 95 ± 0.2 °C, in a 250 ml round bottom flask, which was brought at a pH value of 1.7 or 1.95 at 95°C, by adding H₂SO₄. The flask was immersed in a thermostated water bath. The solution was stirred at 610 rpm with a two-bladed stirrer.

A change of pH due to dissolution of jarosite was avoided by adding accurately known acid quantities of a mixture of H₂SO₄ and HClO₄. Liquid samples were taken at regular time intervals. The iron content of the solution was determined by Inductively Coupled Plasma-atomic emission spectroscopy (ICP).

4.3.4 Simultaneous dissolution of zinc ferrite and precipitation of jarosite
All chemicals used were analytically pure. Deionized and distilled water was used. In order to decrease the pH of a solution of 5.50 g (NH₄)₂SO₄ in 200.0 g water to a value of either 1.70 or 1.95 at 25°C sulfuric acid (96 - 98 wt%) was added. The solution was heated in a 250 ml round bottom flask which was immersed in a thermostated water bath. The solution was kept at 95 ± 0.2°C and stirred at 610 rpm. At 95°C, either 8 or 16 g NH₄Fe₃(SO₄)₂(OH)₆ seeds were added. In order to compensate for the acid consumption due to the slight dissolution of the seeds, so-called 'control acid' was dosed. Control acid contained 34.55 ml HClO₄ (70-72 wt%) and 9.7 ml H₂SO₄ (96-98 wt%) supplemented to an aqueous solution up to a total volume of 100 ml. If the dissociation of H₂SO₄ is assumed to deliver one H⁺ per H₂SO₄, control acid yields about six H⁺ over every two SO₄²⁻ (present as HSO₄⁻). This ratio corresponds to that directed by equation (4.3) for the conversion of zinc ferrite into jarosite and was chosen in order to keep an approximately constant SO₄²⁻ concentration, regardless of the amount of acid required to maintain a constant pH. A constant SO₄²⁻ concentration throughout the experiment is needed.
to keep the driving force for the dissolution of zinc ferrite constant, since this parameter is known to be very sensitive to the $\text{SO}_4^{2-}$ concentration [6].

At an arbitrarily chosen moment, denoted by $t=0$, 6.00 g ZnO.\(\text{Fe}_2\text{O}_3\) was added. Liquid samples were taken at regular time intervals and the zinc and iron contents of the solution were determined by ICP. During the experiments the pH was measured by shortly immersing a pH-electrode in the solution. The pH was kept at a constant value of 1.70 or 1.95 (at 95°C) by adding control acid in accurately known quantities.

Six experiments were carried out in which the dissolution of zinc ferrite and the precipitation of jarosite proceeded simultaneously. Table 4.1 provides the experimental details and also shows that in one experiment no pH control was used. That experiment started with an initial acidity which was sufficiently high to dissolve all zinc ferrite present.

4.4 RESULTS AND DISCUSSION

4.4.1 Characterization of zinc ferrite and ammonium jarosite seeds

The free ZnO content of ZnO.\(\text{Fe}_2\text{O}_3\) was equal to 3.6 wt\%. Based on the results of the total leach (Zn: 29.15 wt\% and Fe: 43.68 wt\%) it was concluded that 2.93 wt\% Zn in ZnO.\(\text{Fe}_2\text{O}_3\) was present in the form of free ZnO. Using a material balance an iron deficiency of 1.1 wt\% was calculated when assuming all non ZnO-zinc to be ZnO.\(\text{Fe}_2\text{O}_3\). This result gives the impression that no free \(\text{Fe}_2\text{O}_3\) is present in this charge. This result is not confirmed by the XRD analysis of the final jarosite product formed in experiment 2, which revealed that an \(\text{Fe}_2\text{O}_3\) content of 3 wt\% was originally present in ZnO.\(\text{Fe}_2\text{O}_3\).

The reason why \(\text{Fe}_2\text{O}_3\) was not observed by XRD in the pure ZnO.\(\text{Fe}_2\text{O}_3\) charge, is that using the XRD method, small quantities of \(\text{Fe}_2\text{O}_3\) are hard to detect in the presence of excess ZnO.\(\text{Fe}_2\text{O}_3\). In the final jarosite product, however, zinc ferrite was almost absent, but apparently, \(\text{Fe}_2\text{O}_3\) was not dissolved during the experiment, which allowed its identification. This also justifies the use of the Fe$^{3+}$ concentration in the solution as originating only from the dissolution of ZnO.\(\text{Fe}_2\text{O}_3\) and not from the dissolution of \(\text{Fe}_2\text{O}_3\). The small uncertainty in the Fe$^{3+}$ source
concentration does not affect the calculation of the degree of dissolution of zinc ferrite either, because for that purpose the overall Zn content of the ZnO Fe₂O₃ charge minus the amount of Zn in ZnO was used. The dissolution rate in 0.5M H₂SO₄ at 90°C of 0.25 g ZnO Fe₂O₃ of this charge deviated less than 2% from the results for three ZnO Fe₂O₃ charges, prepared in different synthesis experiments, reported in [6]. This indicates that a comparison between the results here and in ref.[6] is allowed.

The median volume based particle diameter of the ZnO Fe₂O₃ charge equals 10.7 μm, with 16 wt% of the particles smaller than 7.4 μm and 16 wt% larger than 14.4 μm. This indicates a small, symmetric particle size distribution. The specific surface area of the charge was equal to 3.66 m²/g (±2%). Figure 4.2 shows representative, porous ZnO Fe₂O₃ particles.

Figure 4.3 shows SEM views of the jarosite seed crystals, which were in the size range up to about 20 μm. The particle size measuring instrument only allows measurement of particles with a diameter larger than 1.4 μm. Ignoring the particles below this size, the median volume based diameter of the jarosite seed crystals was 5.0 μm. XRD confirmed the jarosite structure of the seeds, but also indicated that they were contaminated with Li₂SO₄·H₂O and traces of NH₄Fe(SO₄)₂. This was confirmed by chemical analysis. The impurities originated from insufficient washing of the seeds directly after their precipitation. The presence of these impurities did not affect the process because both substances instantaneously dissolved in the hot acidic solution. Lithium does not influence the precipitation of jarosite [19]. In the calculation of the initial total sulfate concentration which is required for the calculation of the supersaturation, the sulfate contribution of Li₂SO₄·H₂O and NH₄Fe(SO₄)₂ was taken into account.

4.4.2 Determination of the solubility product of ammonium jarosite
Two experiments were carried out to determine the solubility product of ammonium jarosite in an aqueous solution at 95°C and at a pH of 1.7 or 1.95. Figure 4.4 shows the measured iron concentration for both experiments in time. The decreasing iron concentration in time is explained by the fact that
Figure 4.2: SEM-view of a representative zinc ferrite particle

Figure 4.3: SEM-view of representative jarosite seeds
NH₄Fe(SO₄)₂ was present in the seeds which dissolved instantaneously. This resulted in a high initial Fe³⁺ concentration which later decreased due to jarosite precipitation.

![Graph](image)

**Figure 4.4:** The Fe³⁺ concentration measured in jarosite solubility experiments operated at a constant pH; line A refers to pH = 1.7, B to pH = 1.95

The extrapolated value after 10 hours was used for determination of the solubility product which was about equal to 10⁻⁹¹ (mole l⁻¹)¹² for both experiments at pH = 1.7 and pH = 1.95. This value was obtained after carrying out a species calculation such as described in the appendices 4.2 to 4.4, in which the free concentrations of Fe³⁺, SO₄²⁻, OH⁻ (via H⁺) and NH₄⁺ were calculated.

4.4.3 Simultaneous dissolution of zinc ferrite and precipitation of jarosite

In these experiments the dissolution of zinc ferrite and the precipitation of jarosite occur simultaneously. Since the incorporation of zinc during the precipitation of jarosite is negligible, as will be shown below, the increasing Zn²⁺ concentration in time could be used for calculating the conversion of ZnO·Fe₂O₃.

The Fe³⁺ concentration in the solution at t=0 was a result of the dissolution of NH₄Fe(SO₄)₂ which was inadvertently present in the seeds. After t=0 the dissolution of ZnO·Fe₂O₃ enhanced the Fe³⁺ concentration but due to the growth of jarosite the Fe³⁺ concentration does not increase stoichiometrically with the zinc
concentration but less or can even decrease. As an example figure 4.5 shows the concentration-time plot for Fe$^{3+}$ and Zn$^{2+}$ related to experiment 1. The Zn$^{2+}$ concentration in figure 4.5 is corrected for the instantaneous dissolution of zinc oxide present in the ZnO. Fe$_2$O$_3$ sample. From the combined Zn(t) and Fe(t) curves the jarosite conversion can be derived. In the following the simultaneous dissolution of ZnO. Fe$_2$O$_3$ and the precipitation of jarosite are discussed separately, although they occurred simultaneously in the experiments.

![Graph showing concentration of Zn and Fe over time](image)

Figure 4.5: The Zn$^{2+}$ and Fe$^{3+}$ concentration during the conversion in experiment 1. The Zn$^{2+}$ concentration is directly proportional to the amount of dissolved zinc ferrite, while the Fe$^{3+}$ concentration is determined by both the dissolved zinc ferrite and the precipitated jarosite.

**The dissolution of zinc ferrite**

The observed Zn$^{2+}$ concentration as a function of time can be described with a surface reaction controlled shrinking core model. Figure 4.6 shows the shrinking core fit for the dissolution rate of ZnO. Fe$_2$O$_3$ in the experiments 4 and 6 (see table 4.1). In experiment 4, where the pH was kept constant at 1.95 throughout the experiment, the shrinking core model describes the dissolution process accurately, which points at a constant driving force for dissolution. In experiment 6, which
Figure 4.6: The shrinking core fit (scm = shrinking core model value; \((1-(1-x)^{1/3})\) with \(x = \) conversion) for Zn\(^{2+}\) for the experiments 6 (line A) and 4 (B)

Table 4.1  Process conditions and results related to the dissolution of zinc ferrite in the direct conversion experiments of zinc ferrite into jarosite

<table>
<thead>
<tr>
<th>#</th>
<th>pH</th>
<th>jarosite seeds (g)(^1)</th>
<th>duration (hr)</th>
<th>dissolution of zinc ferrite t = 2 hr (%)</th>
<th>t = 4 hr (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.7</td>
<td>8</td>
<td>5.1</td>
<td>29</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>1.7</td>
<td>8</td>
<td>28.2</td>
<td>37</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>1.7</td>
<td>16</td>
<td>4.5</td>
<td>33</td>
<td>51</td>
</tr>
<tr>
<td>4</td>
<td>1.95</td>
<td>8</td>
<td>4.4</td>
<td>14</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td>1.95</td>
<td>16</td>
<td>4.6</td>
<td>19</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>var.</td>
<td>8</td>
<td>5.7</td>
<td>67</td>
<td>77</td>
</tr>
</tbody>
</table>

\(^1\) The quantities of the seeds include the impurities Li\(_2\)SO\(_4\)\(\cdot\)H\(_2\)O and NH\(_4\)Fe(SO\(_4\))\(_2\)
was designed to start with a high initial acidity and in which the pH increased during the experiment, the driving force is decreasing with time. This is reflected by the change in slope of the Zn versus time curve of this experiment, given in Figure 4.6.

The change of the dissolution rate of ZnO\textsubscript{2}Fe\textsubscript{3}O\textsubscript{8} with time was also calculated. Figure 4.7 shows the obtained results for the experiments 2, 4 and 6.

![Graph showing dissolution rate as a function of time](image)

**Figure 4.7:** The rate constant for the dissolution of zinc ferrite as a function of time for the experiments 2, 4 and 6. The pH values of the experiments are: #4 (pH = 1.95), #2 (pH = 1.7) and #6 (pH = variable).

Experiment 6 starts with a high initial dissolution rate which decreases due to increasing Fe\textsuperscript{3+} and decreasing H\textsuperscript{+} concentrations, whereas the dissolution rates for the experiments 2 and 4 are initially lower, but remain more or less constant. The higher rate in experiment 2 compared to 4 can be explained from the higher H\textsuperscript{+} and SO\textsubscript{4}\textsuperscript{2-} concentrations in experiment 2. The SO\textsubscript{4}\textsuperscript{2-} concentration strongly affects the dissolution rate of ZnO\textsubscript{2}Fe\textsubscript{3}O\textsubscript{8} [6] and is higher in experiment 2 because a larger amount of acid was required to reach the constant pH level of 1.7, compared to the pH of 1.95 in experiment 4.

Table 4.1 gives the conversion of ZnO\textsubscript{2}Fe\textsubscript{3}O\textsubscript{8} in all experiments, as defined in equation (4.7), after two and four hours. The conversion rather than the dissolution rate is presented, because the dissolution rate was not a constant for
most experiments. The conversion is clearly depending on the acidity. A higher conversion is observed for those experiments which start with a higher H\(^+\) and a coupled higher SO\(_4\)^{2-} concentration.

*The production rate of ammonium jarosite*

The precipitation of ammonium jarosite starts directly after the suspension was heated to 95°C, because due to the instantaneous dissolution of NH\(_4\)Fe(SO\(_4\))\(_2\) originating from the seeds, the solution becomes supersaturated with regard to jarosite precipitation.

As soon as ZnO.Fe\(_2\)O\(_3\) is added at t=0, ZnO.Fe\(_2\)O\(_3\) starts to dissolve and provides additional Fe\(^{3+}\) for jarosite growth. Table 4.2 gives the Fe\(^{3+}\) concentration at t=0 and at t= 4h for the various experiments. The conversion of iron at t=t which originated from ZnO.Fe\(_2\)O\(_3\) and yielded jarosite is defined by equation (4.10):

\[
\xi = 1 - \frac{[\text{Fe}^{3+}]_{t=t} - [\text{Fe}^{3+}]_{t=0}}{[\text{Fe}^{3+}]_{ZF} - [\text{Fe}^{3+}]_{t=0}}
\]  

(4.10)

Here, \(\xi\) is the dimensionless conversion, [Fe\(^{3+}\)]\(_{t=t}\) is the Fe\(^{3+}\) concentration at t=t (ppm) and [Fe\(^{3+}\)]\(_{ZF}\) is the quantity of Fe\(^{3+}\) released by dissolved ZnO.Fe\(_2\)O\(_3\) (ppm). The latter quantity is calculated by multiplying the measured Zn\(^{2+}\) concentration which is corrected for the initial ZnO dissolution, by a factor of two. The concentration at t=0 of about 0.7 g/kg Fe\(^{3+}\) is due to the dissolution of NH\(_4\)Fe(SO\(_4\))\(_2\).

If higher concentrations are observed, these can only be assigned to the dissolution of jarosite from the seeds due to the low pH (e.g. in experiment 6). In case of experiment 3 a conversion of more than one was calculated, caused by the fact that not only all Fe\(^{3+}\) ions originating from ZnO.Fe\(_2\)O\(_3\) were precipitated, but also part of the Fe\(^{3+}\) which originated from dissolved seeds. In case of experiment 6 the negative conversion shows that no nett growth of jarosite had taken place, because at t=0 more Fe\(^{3+}\) from seeds was dissolved than was reprecipitated at t=4h.

It is clear from table 4.2 that the Fe\(^{3+}\) concentration in solution effectively remains low, when the pH is kept constant at values of 1.7 or 1.95 during the experiments, compared to the Fe\(^{3+}\) concentration observed in experiment 6 for an initially lower pH. In the experiments in which the pH was controlled a high conversion of Fe\(^{3+}\)
from ZnO Fe₂O₃ to jarosite was achieved. The high conversion in the case of the experiments 1 to 5 and the low conversion in the case of experiment 6 show that in the experiments 1 to 5 the dissolution of ZnO Fe₂O₃ was rate-determining for the entire process, whereas in experiment 6 the precipitation of jarosite was rate-determining (see figure 4.1).

| Table 4.2 Jarosite precipitation from simultaneously dissolving zinc ferrite |
|---|---|---|
| # | Fe³⁺ conc. (g/kg) | ξ, t = 4 hr. |
|   | t = 0 | t = 4 hr | ( - ) |
| 1  | 0.7  | 1.7  | 0.80  |
| 2  | 1.6  | 4.0  | 0.63  |
| 3  | 3.0  | 2.1  | 1.21  |
| 4  | 0.7  | 1.0  | 0.90  |
| 5  | 0.7  | 0.8  | 0.97  |
| 6  | 4.4  | 9.7  | -0.03 |

The different results in conversion for various experiments in which 8 or 16 g seeds were added (e.g. exp. #4 and #5), are at first sight not expected for a dissolution controlled conversion process, but follow from a higher initial SO₄²⁻ concentrations with a higher seeds quantity. The higher SO₄²⁻ concentration originates from the impurities in the seeds and increases the dissolution rate of zinc ferrite as well as the supersaturation with regard to jarosite.

Figure 4.8 presents the production rate as a function of time for all experiments. In the experiments 2, 3 and 6 higher initial production rates as well as higher initial Fe³⁺ concentrations are observed than in the experiments 1, 4 and 5. The reason why the initial production rate in experiment 6 is lower than expected on the basis of its high initial Fe³⁺ concentration is that the jarosite seeds partly dissolved due to the low pH at t=0. The solubility of jarosite, as shown in figure
4.4, increases with a decreasing pH and therefore the driving force for precipitation is lower.

The fact that a higher jarosite production rate is observed with a higher Fe$^{3+}$ concentration in the solution sustains the reasoning that the jarosite precipitation step in this process in the experiments 1 to 5 is not rate-determining.

![Production rate vs time graph](image)

**Figure 4.8:** The jarosite production rate as a function of time for all experiments

*Calculation of the supersaturation*

Calculation of the supersaturation was carried out using the method described in the appendices 4.2 to 4.4. Plots of the supersaturation versus time, as obtained for the experiments 1, 5 and 6 are presented in figure 4.9. The results of the calculations for the experiments 2, 3 and 4 were comparable to the findings of the experiments 1, 5 and 6. The 'dip' observed in the supersaturation level of experiment 5 was caused by a too long time interval between two pH-measurements and, as a result, the pH-value increased which affected the supersaturation. The supersaturation in the experiments 1 and 6 reached a maximum, which was reached earlier in experiment 1. The supersaturation of experiment 6 started below zero because the initial acidity of the solution (pH < 0.7 at 95°C) made the solution undersaturated with respect to jarosite.
Figure 4.9: The supersaturation with regard to jarosite as a function of time for the experiments 1 (pH = 1.7), 5 (pH = 1.95) and 6 (pH = variable).

The calculated supersaturation value slightly suffered from inaccuracy for various reasons. The complex constants for one of the iron and one of the zinc species were only estimated (see appendices 4.2 and 4.3). In order to investigate the influence of changes in the values of these complex constant estimates on the final value of the supersaturation, the estimates were varied by multiplying them with a factor of 0.4 or 2.5 respectively. The corresponding supersaturation changed less than 0.1% in case of changing the iron complex constant and less than 5% in case of changing the zinc complex constant. This showed that the calculated supersaturation was not very sensitive to the value of these complex constants. Moreover, changing these estimates did not affect the trends in supersaturation. A more serious problem was that the species calculation method did not always correctly predict the H⁺ concentration which was checked by measurement of the pH-value for the experiments assuming an activity coefficient of 0.7 for H⁺. The calculated pH values appeared to be higher than the observed ones. Consequently, the supersaturation levels were also higher than predicted. It was found that deviation of the results depended on the molar ratio of (the total H⁺ concentration) over (the total SO₄²⁻ concentration), regardless the species in which H⁺ or SO₄²⁻ were present. If the ratio was below 0.8, the calculated pH was more than 10%
higher than the observed pH. It has not become clear what caused this deviation. The problem is demonstrated in figure 4.9 where the supersaturation calculated for experiment 5 (with \( [H^+]/[SO_4^{2-}] < 0.8 \)) is too high compared with the values shown for the other experiments (with \( [H^+]/[SO_4^{2-}] > 0.8 \)). Additional proof for the assumption that the supersaturation was too high was obtained by comparing the jarosite production rates for the experiments 1 and 6 with the rate for experiment 5. Despite the higher supersaturation predicted for experiment 5, a lower production rate was observed, which justifies the statement that the calculated value of the supersaturation level for experiment 5 is too high.

Due to this problem, the calculated supersaturation level could unfortunately not be used to demonstrate that a lower supersaturation for the precipitation of jarosite prevails at process conditions where the dissolution rate of zinc ferrite becomes rate-determining for the conversion process.

**Analysis of the ammonium jarosite product**

The composition of the final product obtained at the end of experiment 2 was analyzed chemically for its element concentrations, by X-ray diffraction and by scanning electron microscopy. The particle size distribution was obtained via measurement with a Coulter Counter Multisizer.

The size distribution of the jarosite seeds and of the product, obtained in experiment 2 did not significantly differ.

The iron content of the solids was equal to 33.2 wt\% (theoretically 34.9 wt\%) and the sulfate content was equal to 39.8 wt\% (theoretically 40.1 wt\%). The fact that the iron content of the jarosite product is below the theoretically expected value has been observed by Dutrizac as well, who found 30.92 wt\% iron in synthetic ammonium jarosite [9]. The reason for the higher value observed in this study comes from residual hematite and undissolved zinc ferrite as detected by XRD.

The combined hematite and zinc ferrite quantity was estimated to be less than 2 wt\%. Since the X-ray diffraction patterns of hematite and zinc ferrite are difficult to distinguish, this technique does not allow estimation of the residual zinc ferrite content.
Chemical analysis showed that the residual zinc content was 0.094 wt% after washing of the crystals with water and with 2% H₂SO₄. This corresponds with 0.35 wt% ZnO·Fe₂O₃ if the incorporation of zinc in jarosite is assumed to be negligible and yields a 1:4 ratio of zinc ferrite to hematite. The XRD Guinier de Wolff photograph showed lines representative for zinc ferrite, but based on their weak intensity it is not possible to determine whether e.g. 0.25 or 0.35 wt% ZnO·Fe₂O₃ was present in the jarosite product. The results, however, proof that only a very small quantity of Zn²⁺ is incorporated in the jarosite lattice, since the zinc still present with the jarosite originates from undissolved zinc ferrite.

Figure 4.10 shows a SEM photograph of jarosite solids produced in experiment 2. The separate crystals have clearly developed faces, in contrast to the more agglomerated seeds.

Figure 4.10: SEM-view of a single jarosite crystal formed during the simultaneous dissolution of zinc ferrite and precipitation of jarosite in an experiment with a controlled pH
4.5 CONSEQUENCES FOR INDUSTRIAL PRACTICE

The simultaneous dissolution of zinc ferrite and precipitation of jarosite which was discussed on the basis of bench scale experiments requires further study in continuous processes but provides interesting opportunities for hydrometallurgical zinc refining plants in which the impurity uptake of valuable metals in jarosite should be reduced. The results presented in this paper show that the impurity uptake in jarosite can be reduced by controlling the rate of the conversion process via the pH of the solution. The pH should be kept at a level where the process is dominated by the dissolution of zinc ferrite and where the supersaturation for the precipitation of jarosite remains low.

4.6 CONCLUSIONS

- The equilibrium ionic concentration product for the dissolution of ammonium jarosite at 95°C is $10^{-91} \text{ (mole l}^{-1}\text{)}^{12}$.

- In simultaneous conversion experiments the nett conversion of iron out of ZnO. Fe$_2$O$_3$ into jarosite was about 60 - 100% after four hours in the experiments with a controlled pH, whereas in comparable experiments with an uncontrolled pH the nett conversion was still below zero, due to partial dissolution of the seeds.

- The dissolution rate of zinc ferrite determines the rate of the conversion process, if it is operated at a controlled pH of 1.7 or 1.95.

- The calculation of the supersaturation could not be used for comparing the different experiments, because for those experiments where the total H / total SO$_4$ - concentration was below 0.8 the method did not yield reliable results of the H$^+$ concentration.
The incorporation of zinc in jarosite formed at a constant pH value of 1.7 amounted 0.094 wt%, after washing the solids with water and 2 wt% H₂SO₄. A major part of the zinc content was present as undissolved zinc ferrite, which proves that the Zn²⁺ incorporation can be controlled by pH control.

SEM-photos reveal that the crystals produced during the conversion from zinc ferrite into ammonium jarosite have a large size, compared to jarosite crystals grown in unseeded batch experiments, and are not agglomerated.

ACKNOWLEDGEMENT
The authors want to acknowledge the Dutch Ministry of Housing, Physical Planning and the Environment for funding this research study. F. van den Ham, M. Koppelaar - van der Aa, J.F. van Lent, N.M. van der Pers and H.L. Jansma are gratefully acknowledged for their contributions to this work.

4.7 REFERENCES


Appendix 4.1  The definition of the supersaturation and its application to jarosite precipitation

The driving force for crystallization $\Delta \mu$ (J mole$^{-1}$) is related to the activity of ions in the mother liquor by:

$$\frac{\Delta \mu}{R T} = \ln \frac{\prod a_i^{y_i}}{(\prod a_i^{y_i})_{eq}}$$  \hspace{1cm} (4.11)

Here, $R$ is the universal gas constant ($8.314$ J mole$^{-1}$K$^{-1}$), $T$ is the temperature in K, $a_i$ represents the activity of the ion (mole l$^{-1}$) and $v$ its valency. The subscript $eq$ refers to the equilibrium state, i.e. the activity product which corresponds to the solubility product of the salt at that temperature. The relative supersaturation is then defined as:

$$\sigma = \left(\frac{\prod a_i^{y_i}}{(\prod a_i^{y_i})_{eq}}\right)^{\frac{1}{v}} - 1$$  \hspace{1cm} (4.12)

with:
\[ v = \sum v_i \]  

(4.13)

In case of ammonium jarosite equation (4.12) becomes:

\[ \sigma = \left( \frac{(a_{F_{\text{eq}}})^3 (a_{NH_4}) (a_{SO_4^2})^2 (a_{OH})^6}{(a_{F_{\text{eq}}})^3 (a_{NH_4}) (a_{SO_4^2})^2 (a_{OH})^6 \text{eq}} \right)^{1/12} - 1 \]  

(4.14)

Since \( a_i = \gamma_i C_i \), equation (4.14) is useful for calculating the supersaturation if the activity coefficient \( \gamma_i \) and all concentrations \( C_i \) are known for the supersaturated and the saturated solution at a particular temperature. Despite the progress in the description of the thermodynamics of complex and concentrated aqueous solutions, it still remains difficult to obtain accurate values for the activity coefficients in this solution. If, however, that the supersaturation is not excessively high, e.g. smaller than 2, the assumption that the activity coefficient for a given ion in the saturated solution is approximately equal to that in the supersaturated solution seems acceptable. Thus, \( \gamma_{Fe(3+)} = \gamma_{Fe(3+)} \text{eq} = \gamma_{Fe(3+)} \text{eq} \text{etc.} \)

In order to calculate the supersaturation the concentration of hydroxide is also required. This concentration is obtained via the dissociation equilibrium of water. The equilibrium constant at 95°C equals \( 3.98 \times 10^{13} \). Equation (4.9) in the theory section is obtained by replacing the activities in equation (4.14) by concentrations.

Appendix 4.2  The calculation of the complex constants in the acid - ferric sulfate - water system at 95°C

The solution which is used as medium for the conversion process consists of a mixture of dissolved sulfuric acid, perchloric acid and ammonium sulfate. The reason for the simultaneous use of sulfuric acid and perchloric acid is given in the section 'experimental'. In this mixture the following reactions are expected:

\[
\begin{align*}
\text{H}_2\text{SO}_4 & \rightarrow \text{H}^+ + \text{HSO}_4^- \quad (4.15) \\
\text{HSO}_4^- & \leftrightarrow \text{H}^+ + \text{SO}_4^{2-} \quad (4.16) \\
\text{HClO}_4 & \rightarrow \text{H}^+ + \text{ClO}_4^- \quad (4.17) \\
\text{(NH}_4\text{)}_2\text{SO}_4 & \rightarrow 2 \text{NH}_4^+ + \text{SO}_4^{2-} \quad (4.18)
\end{align*}
\]
It is assumed that the reactions (4.15), (4.17) and (4.18) have a conversion of 100%. Thus, the following species are present: $H^+$, $NH_4^+$, $HSO_4^-$, $SO_4^{2-}$ and $ClO_4^-$. The equilibrium constant $K_s$ equals 0.00173 at 95°C [10].

\[
K_s = \frac{a_{SO_4^{2-}}}{a_{HSO_4^{-}}}
\]  

(4.19)

The complexation of iron(III) in a sulfate containing aqueous solution includes basically eight equilibrium reactions [11,12], which are given below.

\[
\begin{align*}
Fe^{3+} + OH^- & \leftrightarrow FeOH^{2+} \quad (4.20) \\
Fe^{3+} + 2 OH^- & \leftrightarrow Fe(OH)_2^+ \quad (4.21) \\
2 Fe^{3+} + 2 OH^- & \leftrightarrow Fe_2(OH)_4^{4+} \quad (4.22) \\
Fe^{3+} + HSO_4^- & \leftrightarrow FeHSO_4^{2+} \quad (4.23) \\
Fe^{3+} + HSO_4^- + SO_4^{2-} & \leftrightarrow FeHSO_4SO_4 \quad (4.24) \\
Fe^{3+} + SO_4^{2-} & \leftrightarrow FeSO_4^+ \quad (4.25) \\
Fe^{3+} + 2 SO_4^{2-} & \leftrightarrow Fe(SO_4)_2^{2-} \quad (4.26) \\
Fe^{3+} + 2 HSO_4^- & \leftrightarrow Fe(HSO_4)_2^+ \quad (4.27)
\end{align*}
\]

The complex constants for these reactions are usually measured at 25°C [12-14] and are given in table 4.2.1 together with the calculated complex constants at other temperatures.

In order to obtain the complex constants at 140°C, McAndrew et al.[11] used a method which is based on the fact that the complex constant for a given reaction may be calculated at any temperature using equation (4.28):

\[
\Delta G_T = RT \ln K_T
\]  

(4.28)

Here, $\Delta G$ represents the free energy (J mole$^{-1}$). Thus, at 25°C and standard conditions the measured complex constant for a given reaction provides the value of $\Delta G_{298}$. If $\Delta G$ for this system is calculated at any other temperature, the corresponding value of the complex constant is obtained. In order to calculate $\Delta G$ at other temperatures, the equations (4.29) to (4.33) are used.

\[
\Delta G_T = \Delta H_T - T \Delta S_T
\]  

(4.29)

\[
\Delta H_T = \Delta H_{298} + \int_{298}^{T} C_p \, dT
\]  

(4.30)
Table 4.2.1 The complex constants in the ferric sulfate - water system at different temperatures, given an ionic strength of 3M NaClO₄ unless otherwise specified [12-14]

<table>
<thead>
<tr>
<th>reaction</th>
<th>complex constants at different temperatures</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>$^{10}\log K_{298}$</td>
</tr>
<tr>
<td>4.20</td>
<td>11.21</td>
</tr>
<tr>
<td>4.21</td>
<td>22.0</td>
</tr>
<tr>
<td>4.22</td>
<td>25.4</td>
</tr>
<tr>
<td>4.23</td>
<td>0.78</td>
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<tr>
<td>4.24</td>
<td>2.58</td>
</tr>
<tr>
<td>4.25</td>
<td>2.03</td>
</tr>
<tr>
<td>4.26</td>
<td>3.00</td>
</tr>
<tr>
<td>4.27</td>
<td>2.11</td>
</tr>
</tbody>
</table>

1 measured in 1.2 M NaClO₄
2 measured in 1.0 M NaClO₄
3 estimated value

\[ \Delta S_T = \Delta S_{298} + \int_{298}^{T} \frac{C_P}{T} \, dT \]  \hfill (4.31)

\[ \Delta S_{298} = \sum \, n_i \, S_{298,i} - \sum \, n_j \, S_{298,j} \]  \hfill (4.32)

\[ C_{p,av} = a_T + \beta_T \, S_{298,obs} \]  \hfill (4.33)

In these equations $\Delta H$ represents the enthalpy (J mole⁻¹), $\Delta S$ the entropy (J mole⁻¹ K⁻¹), $C_p$ the specific heat (J mole⁻¹ K⁻¹) at temperature $T$ and $C_{p,av}$ the average specific heat of the substance in the temperature range (298 $\rightarrow$ T) in (J mole⁻¹ K⁻¹). Equation (4.32) shows that the standard entropy change for a reaction equals the sum of the standard entropies of the products minus the sum of the standard entropies of the reactants.
entropies of the reactants $j$. The stoichiometric coefficients are represented by $n$.
Equation (4.33) was derived empirically by Criss and Cobble [15], who also provided the proportionality constants $\alpha_T$ (J mole$^{-1}$ K$^{-1}$) and $\beta_T$ ($) at different temperatures.

Table 4.2.2 Proportionality constants for calculating the average specific heat of ionic compounds over temperature ranges between 0 and 200°C

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Cations$^1$</th>
<th>Anions$^2$</th>
<th>Anions$^4$</th>
<th>Oxy Anions$^3$</th>
<th>Acid Oxy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\alpha^5$</td>
<td>$\beta^6$</td>
<td>$\alpha$</td>
<td>$\beta$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>60</td>
<td>146</td>
<td>-0.41</td>
<td>-192</td>
<td>-0.28</td>
<td>-531</td>
</tr>
<tr>
<td>95$^7$</td>
<td>185</td>
<td>-0.53</td>
<td>-236</td>
<td>-0.04</td>
<td>-572</td>
</tr>
<tr>
<td>100</td>
<td>192</td>
<td>-0.55</td>
<td>-243</td>
<td>0</td>
<td>-577</td>
</tr>
<tr>
<td>150</td>
<td>192</td>
<td>-0.59</td>
<td>-255</td>
<td>-0.03</td>
<td>-556</td>
</tr>
<tr>
<td>200</td>
<td>(209)$^8$</td>
<td>(-0.63)</td>
<td>(-272)</td>
<td>(-0.04)</td>
<td>(-607)</td>
</tr>
</tbody>
</table>

1 This category includes simple cations, but does not contain H$^+$
2 This category includes the halides and OH$^-$
3 This category includes e.g. HSO$_4^-$, HPO$_4^{2-}$ and H$_2$PO$_4^-$
4 This category includes e.g. SO$_4^{2-}$, NO$_3^-$ and ClO$_3^-$
5 The unit of the constant $\alpha$ is J mole$^{-1}$ K$^{-1}$
6 The constant $\beta$ is dimensionless
7 These values are intrapolated for this study
8 Parenthetical values are derived from extrapolated values of the corresponding entropy terms from lower temperatures and are thus subject to greater error [15].

Table 4.2.2 provides the original constants and shows the interpolated values at 95°C. $S_{298,abs.}$ represents the partial molal entropy at 298 K, taking the value for
\[ S_{298,\text{abs.}} = S_{298} - 20.9 \ z \]  

(4.34)

in which \( z \) represents the charge of the ion. Additional data were obtained from [16-18]. Finally, the value of \( \Delta G_T \) is given by equation (4.35):

\[ \Delta G_T = \Delta G_{298} - \Delta S_{298} (T - 298) + C_{p,\text{avg.}} (T - 298) - T C_{p,\text{avg.}} \ln \left( \frac{T}{298} \right) \]  

(4.35)

The resulting complex constants at 95°C are given in table 4.2.1. The value for the complex constant from reaction (4.24) at 95°C could not be obtained from tabulated thermodynamic data (\( \Delta H, \Delta S \) etc.) and was interpolated from data provided by McAndrew et.al. The value for the constant in reaction (4.27) was estimated, based on similar trends for the other equilibria. Due to the inaccuracy in these complex constant estimates, the resulting concentrations of the species may also be inaccurate. In calculating the supersaturation, however, the ratio of the concentrations of Fe\(^{3+}\), NH\(_4^+\), SO\(_4^{2-}\) and OH\(^-\) under supersaturated and saturated conditions is used. Thus, the resulting inaccuracy in the calculated supersaturation may remain limited.

**Appendix 4.3  The calculation of complex constants in the zinc sulfate - water system**

A sulfuric acid solution in which zinc ferrite dissolves will contain Zn\(^{2+}\) and complexes of Zn\(^{2+}\) with other dissolved species. The following reactions are expected:

\[ \text{Zn}^{2+} + \text{OH}^- \leftrightarrow \text{ZnOH}^+ \]  

(4.36)

\[ \text{Zn}^{2+} + \text{HSO}_4^- \leftrightarrow \text{ZnHSO}_4^+ \]  

(4.37)

\[ \text{Zn}^{2+} + \text{SO}_4^{2-} \leftrightarrow \text{ZnSO}_4 \]  

(4.38)

The reactions (4.36) and (4.37) have complex constants measured at 25°C in 3.0M NaClO\(_4\) of 4.74 and 0.70 \( (^{10}\log K \text{- values}) \) respectively. Using the method described
in the previous appendix, the complex constants at 95°C were calculated as 4.47 and 0.56 (\(10\log K\) - values) respectively.

The complex constant for reaction (4.38) is given as 1.71 (\(10\log K\) - value) at 25°C in a saturated \(\text{KClO}_3\)-solution, extrapolated to zero ionic strength [13]. This figure is in reasonable agreement with data given by Pitzer [10]. Insufficient data were available for using the method given in the previous appendices. Thus an educated guess was made and \(10\log K\), corresponding to reaction (4.38), was estimated at 2.18.

Appendix 4.4 The calculation of the species present in an acidic solution of ferric, zinc and ammonium sulfate at 95°C

The solution which is used as medium for the conversion process is described in appendix 4.2. The reactions (4.15) to (4.18) are thus to be expected. In addition, the dissolution of zinc ferrite will initiate the reactions (4.20) to (4.27) and (4.36) to (4.38), described in the previous appendices.

Thus, 13 equilibrium reactions ((4.16), (4.20 to 4.27), (4.36 to 4.38) and the water equilibrium) remain, in which 17 different species occur. Four more equations are thus required for calculating the quantities of the individual species. These equations are the mass balances for Fe, S, Zn and H. The total amount of dissolved iron and zinc as a function of time is known for each sample. This enables, together with knowledge of the added quantity of control acid in time and the reaction stoichiometry, to calculate the progress of the dissolution of zinc ferrite, the quantity of newly-formed jarosite and the total amount of sulfate, ammonium and hydrogen (as \(H^+\), \(\text{HSO}_4^-\) or \(\text{HSO}_4^-\)-complexes) in the solution. These total amounts provide the missing link in calculating the free concentrations of the individual species for each sample, which are used for calculating the supersaturation.
Chapter 5

Precipitation of jarosite
I. Chemical factors affecting the production rate

ABSTRACT
Batch experiments at 95°C were carried out to determine the dependency of the production rate of ammonium jarosite (NH₄Fe₃(SO₄)₂(OH)₆) in a supersaturated (Fe³⁺/NH₄⁺/SO₄²⁻) solution on factors such as temperature, ionic strength and the NH₄⁺ concentration, the SO₄²⁻ concentration and the Zn²⁺ concentration. The solubility product for jarosite was also determined.
For a jarosite conversion above 10% in six hours, a temperature above 75°C is needed, while an optimal conversion occurs at a temperature of about 95°C since this temperature does not yet require pressurized operation and already provides a satisfactory production rate. The solubility product of ammonium jarosite at 95°C equals 10⁻⁹¹.
An increasing Zn²⁺ concentration in a mother liquor containing a rather small excess of SO₄²⁻ (e.g. 150%) slightly reduces the free SO₄²⁻ concentration and thereby the production rate of jarosite.

5.1 INTRODUCTION

The precipitation of alkali jarosite (XFe$_3$(SO$_4$)$_2$(OH)$_6$ with usually X = Na$^+$, K$^+$, Ag$^+$, NH$_4^+$ or Pb$_{0.5}^+$) has been the subject of numerous papers which were mostly related to zinc hydrometallurgy [1-12]. The relationship between the precipitation of this basic ferric sulfate and zinc hydrometallurgy is a consequence of the fact that jarosite has found large application as an outlet for iron and arsenic in zinc winning processes. The corresponding jarosite process has now been applied for about 25 years and is worldwide operated in zinc plants with a total production capacity of about two million ton slab zinc per year, which is about a third of the annual worldwide primary zinc production [13,14]. Other mineral industries also apply the jarosite process in some form to remove iron from leach solutions, but the application in the zinc winning industry is quantitatively the most important [15].

Due to the close relationship between the zinc industry and jarosite precipitation, most of the previously published papers have approached the jarosite precipitation process as part of a method aimed at iron removal and not as a precipitation reaction as such. Thus, a large number of data on jarosite product composition and yield are available as a function of precipitation conditions such as temperature, stirrer speed and an overall solution composition. Relatively little attention, however, has been paid to jarosite from the viewpoint of 'precipitation' rather than of 'iron removal'. The work carried out by Zerella and Headington forms an exception in this context [16-18]. Their studies, however, are not of direct interest for application in the usual roast-leach-electrowin zinc hydrometallurgy because they discuss pressurized operations which are rather expensive.

This paper aims to describe the chemistry of jarosite precipitation in relation to the zinc industry. The precipitation is studied as a function of the individual concentrations of the NH$_4^+$ and SO$_4^{2-}$ ions, the ionic strength and the Zn$^{2+}$ concentration in the solution at a preselected temperature. The influence of these parameters is e.g. quantified by their impact on the production rate. The ionic strength of the solution was adjusted by the addition of LiNO$_3$, which ions were formerly proven to have no effect on the precipitation of jarosite.
5.2 THEORY

Jarosite is formed in solutions of ferric and alkali sulfate at low pH-values (1 - 2). In order to obtain a reasonable reaction rate (more than 10% conversion within 24 hours) temperatures above 75°C are required. In this study alkali sulfate is limited to ammonium sulfate, which was used in the experiments. The precipitation reaction is given by equation (5.1):

\[ \text{NH}_4^+ + 3 \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 6 \text{H}_2\text{O} \rightarrow \text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 6 \text{H}^+ \]  

(5.1)

The driving force for the precipitation is quantified by the supersaturation which is given by equation (5.2):

\[ \beta = \ln \left( \frac{(a_{\text{Fe}^{3+}})^3 a_{\text{NH}_4^+} (a_{\text{SO}_4^{2-}})^2 (a_{\text{OH}^-})^6}{(a_{\text{Fe}^{3+}})^3 a_{\text{NH}_4^+} (a_{\text{SO}_4^{2-}})^2 (a_{\text{OH}^-})^6}_{\text{eq}} \right) \]  

(5.2)

This may be simplified by substituting the activity \( a_i \) by the concentration \( C_i \) (mole m\(^{-3}\)), thereby neglecting the influence of the activity coefficients:

\[ \beta = \ln \left( \frac{[\text{Fe}^{3+}]^3 [\text{NH}_4^+] [\text{SO}_4^{2-}]^2 [\text{OH}^-]^6}{([\text{Fe}^{3+}]^3 [\text{NH}_4^+] [\text{SO}_4^{2-}]^2 [\text{OH}^-]^6)_{\text{eq}}} \right) \]  

(5.3)

Here \( \beta \) represents the supersaturation. Calculation of the supersaturation requires the knowledge of the concentration of the free species in the solution and of the equilibrium concentration of the free species in solution. A method for determining the concentration of the species in the solution as a function of the overall concentration of Fe, S, N and H and of the temperature is presented in ref. [19]. It is shown in ref. [19] that the method does not lead to satisfactory results if the molar ratio of the overall concentrations of H\(^+\) and SO\(_4^{2-}\) is too small, i.e. if \([\text{H}^+] / [\text{SO}_4^{2-}] < 0.8\), which is mostly the case during batch jarosite precipitation experiments. Too low free H\(^+\) concentrations are then calculated, compared to the measured pH values (assuming an activity coefficient of 0.7 for H\(^+\)). The free H\(^+\) (via the OH\(^-\)) concentration has a strong effect on the supersaturation. The restricted applicability of this method, which is only due to numerical problems, forms a serious drawback.

97
An alternative would be to measure the pH during a batch experiment and then use the obtained $a_{H^+}$ to estimate $c_{H^+}$ by making an educated guess for the activity coefficient of $H^+$. The estimated $c_{H^+}$ may then be introduced as a parameter with a known value rather than as a variable in the species calculation. This method is applied below, but only for one experiment.

The production rate of jarosite is calculated using the mass balance. The production rate $r_p$ is related to the growth rate and thereby indirectly to the relative supersaturation, since it is also defined as:

$$ r_p = GA \rho_c $$  \hspace{1cm} (5.4)

Here $r_p$ is the production rate (kg s$^{-1}$), $G$ is the crystal growth rate (m s$^{-1}$), $A$ is the crystal surface area (m$^2$) and $\rho_c$ represents the crystal density (kg m$^{-3}$). The crystal growth rate $G$ is related to the relative supersaturation $\beta$:

$$ G = k \beta^n $$  \hspace{1cm} (5.5)

Here, $k$ and $n$ are constants depending on process parameters such as the ionic strength. The ionic strength of the solution was quantified by using equation (5.6) in which $c_i$ equals the concentration of an ion $i$ in mole l$^{-1}$ and $z_i$ is the charge of the ion $i$.

$$ I = 1/2 \Sigma c_i z_i^2 $$  \hspace{1cm} (5.6)

The conversion of Fe$^{3+}$ into ammonium jarosite is defined by equation (5.7):

$$ \xi = \left( C_{Fe^{3+}}(t=0) - C_{Fe^{3+}}(t=t) \right) / C_{Fe^{3+}}(t=0) $$  \hspace{1cm} (5.7)

### 5.3 EXPERIMENTAL

The batch crystallization experiments were carried out in a round bottom hard glass vessel of 500 ml immersed in an oil bath. The temperature could be controlled within 0.5°C accuracy. Before the solutions of NH$_4^+$ and Fe$^{3+}$ (which also contained Zn$^{2+}$ or Li$^+$ ions if these were added) and SO$_4^{2-}$ and NO$_3^-$, were fed into the heated vessel, both streams were heated separately up to the reaction temperature. The experiments were not seeded. The reaction mixture was stirred vigorously at 800 - 1000 rpm to prevent or at least minimize scale formation on the vessel walls. The experimental conditions are summarized in table 5.1.
<table>
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<th>code</th>
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<th>NO$_3^-$</th>
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<td>-</td>
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<td>-</td>
<td>0.47</td>
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<td>2.3</td>
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<tr>
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<td>0.10</td>
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<td>-</td>
<td>0.45</td>
<td>1.25</td>
<td>4.1</td>
<td>95</td>
</tr>
</tbody>
</table>

During the experiments 3 ml samples were taken at regular time intervals from which, after filtration over a 0.45 μm filter, the Fe$^{3+}$ concentration was measured by automatic titration with EDTA. The concentration of Zn$^{2+}$ was measured by Atomic Absorption Spectroscopy (AAS). All water used has been deionized and subsequently distilled in an all pyrex glass water distillation apparatus.
5.4 RESULTS AND DISCUSSION

5.4.1 Check on reproducibility and determination of the solubility product
Two similar experiments (#1 and #2) were carried out to check the reproducibility of these unseeded precipitation reactions. Figure 5.1 shows the measured Fe$^{3+}$ concentration as a function of the reaction time for experiment 1. The data obtained in experiment 2 resembled the data for experiment 1, but showed a somewhat lower conversion over the time range (0 - 50 hours), despite the slightly higher initial NH$_4^+$ concentration. Table 5.2 provides conversion data of Fe$^{3+}$ into ammonium jarosite for the two experiments. It shows that the reproducibility is sufficient to justify comparisons of results for experiments with reasonably large differences in the initial NH$_4^+$, Zn$^{2+}$ or SO$_4^{2-}$ concentrations.

The results obtained in the experiments 1 and 2 were also used to estimate a maximally attainable conversion after infinite residence time by extrapolation of the Fe$^{3+}$/time curves. Experiment 2 was operated for over ten days to enable estimation of this maximum conversion. Table 5.2 includes these results. Based on the 'infinite' conversion a solubility product was calculated, using the species method given in ref.[19], since the ratio of total H$^+$ concentration over total SO$_4^{2-}$ concentration exceeded 0.8 at the end of these experiments. For experiment 1 the equilibrium ionic concentration product K$_s$ equals 4 *10$^{-91}$; for experiment 2 K$_s$ equals 2*10$^{-91}$. The obtained results are thus of the same order of magnitude. Moreover, they resemble the solubility product (K$_s$ = 10$^{-91}$) based on the dissolution of jarosite at 95°C, reported in ref. [19]. It should be noted that the impact of the differences solubility products by a factor of 4 on a calculated supersaturation is minor, due to the logarithmic term in equation (5.3).

5.4.2 Calculation of the supersaturation
For experiment 1 the supersaturation β was calculated as a function of time by substituting the free H$^+$ concentrations estimated from the measured pH values in the equations applied in ref.[19] for the calculation of the concentrations of the various ionic species. This yielded the results shown in figure 5.2 for exp. #1.
Figure 5.1: The Fe$^{3+}$ concentration as a function of time for exp. #1. The dashed line shows the extrapolated Fe$^{3+}$ concentration at infinite residence time

The method used for calculating the supersaturation for experiment #1 could not be applied to all other experiments, because in some cases, where comparatively low initial SO$_4^{2-}$ concentrations were present (e.g. exp. # 14 to 17 and 8 and 9) the mathematical routine which was used to determine the species distribution did not converge. Since the method described in ref. [19] could only be applied in the final stage of most of the experiments, where the ratio of total H$^+$/total SO$_4^{2-}$ is above 0.8, which is not the most interesting part of the conversion, no supersaturation estimates were made for the other experiments.

The production rate for jarosite is proportional to the supersaturation in experiment #1. Thus, the growth rate in equation (5.5) is proportional to the supersaturation, which is not really surprising given the extremely high initial supersaturation. Additionally, the total surface area must remain constant, probably owing to agglomeration of the individual crystals.
5.4.3 Influence of the synthesis temperature

Three experiments (#3, 4 and 5) were performed at 75°C, 85°C and 95°C at further similar operating conditions. Plots of the Fe³⁺ concentration versus time are given in figure 5.4. The yield as well as the rate of conversion are strongly dependent on temperature. At 75°C hardly any precipitation occurs, while at 85°C an induction time of 1.5 hours seems to precede the actual conversion. At 95°C an acceptable conversion rate is obtained and therefore this temperature was selected for all other experiments. In zinc winning practice the precipitation is also carried out at 95°C.

5.4.4 Influence of the ionic strength

Variations in composition of the crystallizing solutions unavoidably induce differences in the prevailing ionic strengths. The influence of a substantial variation in ionic strength upon the conversion process was therefore first investigated by comparing the results of experiment #6 with a similar experiment #7 where 1.2 mole l¹ LiNO₃ was added to the solution. From the Fe³⁺ concentration
versus time plots given in Figure 5.5, it follows that both curves almost coincide. This similarity in Fe\(^{3+}\) consumption during precipitation can only occur if the driving force for crystallization is the same in both cases. This implies that the ionic strength of the saturated solution is apparently so high, that further changes in ionic strength do not affect the activity coefficients of the ions. It also shows that nitrate ions do not lower the driving force for conversion e.g. by complex formation.

5.4.5 Influence of the NH\(_4\)\(^+\) concentration
Two experiments were performed, one with a stoichiometric amount of NH\(_4\)\(^+\) ions (exp. #8), the other with a three times higher amount of NH\(_4\)\(^+\) ions (exp. #9) at further similar conditions. The difference in ionic strength in both experiments has already been shown to be of no influence upon the conversion process. A higher NH\(_4\)\(^+\) concentration not only affects the stoichiometry but also yields an increase in pH. A higher NH\(_4\)\(^+\) concentration as well as a higher pH-value both
raise the supersaturation. As a result the initial conversion of Fe$^{3+}$ into jarosite proceeds faster in the presence of more NH$_4^+$, as is shown in figure 5.6. Based on the Fe$^{3+}$ conversion data, the jarosite production rate (in kg m$^{-3}$ hr$^{-1}$) was calculated. The resulting plot is shown in figure 5.7.

It was not possible to distinguish the separate influence of the increase in the NH$_4^+$ concentration and of the increase in pH, caused by the increase in the NH$_4^+$ concentration, on the differences in the initial production rates of both experiments. It seems, however, likely that the difference in the initial production rates for these experiments is mainly caused by the increase of the pH, because changes in the OH$^-$ concentration affect the supersaturation much more than changes in the NH$_4^+$ concentration.

![Graph](image)

Figure 5.6: The influence of the NH$_4^+$ concentration on the Fe$^{3+}$ concentration in time; (A) = exp. 8, (B) = exp. 9.

![Graph](image)

Figure 5.7: The production rate of jarosite; line (A) relates to exp. 9, line (B) relates to exp. 8.

5.4.6 *Influence of the SO$_4^{2-}$ concentration*

Four experiments (#10 to # 13) were carried out with initial SO$_4^{2-}$ concentrations ranging from 0.45 to 0.8 mole l$^{-1}$ at further similar conditions. All experiments initially also contained 0.3 M Zn$^{2+}$.
The plots for the Fe$^{3+}$ concentration as a function of time for these experiments are given in figure 5.8. From figure 5.8 it can be concluded that the difference in the conversion-time functions for the experiments #10 and #11 is small. The observed differences might even be within the spread of the data which would be expected if two similar experiments are carried out. About the same counts for the experiments #12 and #13, albeit that experiment #13, showing an induction period of about 1 hour, finally reaches a somewhat higher conversion.

In order to compare the influence of the increase of the SO$_4^{2-}$ concentration on the production rate the experiments #11 and #12 are compared as representative examples.

Figure 5.9 shows the difference in the production rate for the experiments #11 and #12. The figure was obtained by plotting the smoothed time derivative of the calculated jarosite production as a function of time. The plot shows that the initial production rate in experiment #12 is 2.4 times larger than the value for exp. #11.

![Figure 5.8: The influence of the SO$_4^{2-}$ concentration on the Fe$^{3+}$ concentration in time.](image1)

![Figure 5.9: The production rate of jarosite; line (A) relates to exp. 12, line (B) relates to exp. 11.](image2)

It may therefore qualitatively be concluded that an increasing concentration of SO$_4^{2-}$ in the concentration range studied, increases the production rate considerably as a result of the higher supersaturation.
5.4.7 Influence of the Zn\(^{2+}\) concentration

Three experiments (#15 to #17) were performed with increasing Zn\(^{2+}\) concentrations up to 0.6 mole l\(^{-1}\) for comparison with the blank (#14). The resulting Fe\(^{3+}\) concentrations as a function of time are given in figure 5.10. Based on figure 5.11, which shows, as an example, the plot of the jarosite production rate as a function of time for the experiments # 14 and # 17, it can be concluded that Zn\(^{2+}\) ions retard the precipitation of jarosite. The retardation is a consequence of the fact that Zn\(^{2+}\) forms complexes with SO\(_4^{2-}\) and thereby limits the free SO\(_4^{2-}\) concentration for precipitating with Fe\(^{3+}\) ions.

These results are not at odds with results presented in the next chapter of this thesis for continuous jarosite precipitation experiments. In the continuous experiments a higher total Zn\(^{2+}\) concentration enhanced the conversion of Fe\(^{3+}\) into jarosite. The difference, however, is that in the continuous experiments SO\(_4^{2-}\) was present in such a large excess that this limited the free Fe\(^{3+}\) concentration. Addition of Zn\(^{2+}\) reduced the complexation of Fe\(^{3+}\) and as a consequence the relevant ionic product (Fe\(^{3+}\))^3(SO\(_4^{2-}\))^2 increased more due to the increasing free Fe\(^{3+}\) concentration than it decreased due to the smaller free SO\(_4^{2-}\) concentration, with as a result a higher conversion.

Figure 5.10: The influence of the Zn\(^{2+}\) concentration on the Fe\(^{3+}\) concentration in time.

Figure 5.11: The production rate of jarosite; line (A) relates to exp. 14 line (B) relates to exp. 17
In the batch experiments in this study the free $\text{SO}_4^{2-}$ concentration decreases more strongly than the free $\text{Fe}^{3+}$ concentration rises, because in these experiments the $\text{SO}_4^{2-}$ excess is not so high. Due to problems with the species calculation, this reasoning can unfortunately not be sustained by quantitative data.

A lower production rate is observed with a higher total $\text{Zn}^{2+}$ concentration, which was expected, given the relation between the $\text{Fe}^{3+}$ concentration and time for these experiments.

5.5 CONCLUSIONS

The batch experiments on jarosite synthesis from a mixture of ammonium and ferric sulfate proved to be reasonably well reproducible. The solubility product given by the equilibrium ionic concentration product for jarosite was measured by operating a batch synthesis experiment for 245 hours and 71 hours at 95°C and was equal to $10^{a1}$; this value was also obtained by similar measurements after dissolving jarosite in a neutral solution at 95°C.

Increases in temperature, $\text{SO}_4^{2-}$ concentration or $\text{NH}_4^+$ concentration enhance the jarosite production rate. The production rate at temperatures up to 75°C is approximately zero. At 95°C the conversion of $\text{Fe}^{3+}$ into jarosite equals more than 50% within 24 hours for most of the experiments. Additions of $\text{LiNO}_3$ to vary the ionic strength in the range from 2 to 4 mole $\text{l}^1$ did not significantly affect the production rate.

Increasing the concentration of $\text{Zn}^{2+}$ ions in a solution with a relatively small excess of $\text{SO}_4^{2-}$ ions (i.e. 150 %) retards the precipitation rate, due to complexation of $\text{Zn}^{2+}$ with $\text{SO}_4^{2-}$ which decreases the free $\text{SO}_4^{2-}$ concentration and thereby the driving force for jarosite precipitation.

ACKNOWLEDGEMENT

The financial support of the Dutch Ministry of Housing, Physical Planning and the Environment is gratefully acknowledged. M. Koppelaar - van der Aa, N. den Breejen and H. Verver are acknowledged for their contribution to this study.
5.6 REFERENCES


19. Chapter 4, this thesis.
Chapter 6

Precipitation of jarosite

II. Incorporation of zinc in continuous experiments

ABSTRACT

Ammonium jarosite was precipitated in a 1.5 l continuous Mixed Suspension Mixed Product Removal-crystallizer in the presence of varying feed Zn$^{2+}$, Mg$^{2+}$, Li$^+$ and NH$_4^+$ concentrations. The feed Fe$^{3+}$ concentration and SO$_4^{2-}$ concentration were chosen at the constant level of 0.25 mole l$^{-1}$ and 1.6 mole l$^{-1}$ respectively. The experiments were carried out at 95°C, pH 1.5 and using residence times varying between 0.8 and 2.0 hours. The following parameters were determined: steady state conversion, the jarosite crystal growth rate, the nucleation rate, the specific surface area, the solids density in the suspension, the production rate, the supersaturation and the incorporation of zinc respectively magnesium in the jarosite lattice. The residence time distribution of the system was determined by adding alunite as tracer. Additional experiments were carried out at a pH of 1.2 and 1.8 respectively, in order to determine the influence of the pH on the precipitation.

Based on the obtained results the incorporation of zinc in jarosite or the jarosite production rate may be predicted for a wide range of process conditions. The incorporation of zinc in ammonium jarosite, probably via isomorphous substitution, equals about 2 - 10 g/kg depending on the process conditions. This implies that in industrial practice the loss of zinc due to the removal of iron as jarosite ranges between 0.12 and 0.6 wt%, for a zinc concentrate containing 52 wt% zinc and 8 wt% iron.

6.1 INTRODUCTION

The precipitation of ammonium jarosite (NH₄Fe₃(SO₄)₂(OH)₆) is mostly applied in hydrometallurgical zinc refining to remove iron as a solid substance from acidic zinc leach solutions. Jarosite is suitable for this purpose, since the incorporation of zinc in jarosite is relatively low compared with the zinc loss in untreated neutral leach residue. Jarosite is also used as an outlet for impurities which would otherwise accumulate in the leaching circuits and which originate from the zinc ore. Examples of these are arsenic, gallium, indium and other trace elements.

Dissolving zinc ferrite and subsequently precipitating jarosite enables to recover most of the zinc contained in zinc ferrite, but in the industrial process the solid phase inevitably gets contaminated with lead, silver, cadmium, zinc, copper, cobalt and other metals and with arsenic and antimony. This contamination has hampered all potential applications of this residue and therefore many zinc refining plants have built large storage ponds for jarosite. This practice has now become subject of criticism for environmental reasons. In the Netherlands the storage of jarosite will in the near future become prohibited and even historically disposed stock will have to be treated in order to produce an environmentally acceptable residue. Recently, an overview is given on integrated jarosite treatment processes [1].

These treatment processes consume large amounts of energy. The energy requirements partly depend on the zinc content of the residue. The aim of this study is to investigate to what extent the zinc incorporation in jarosite can be reduced by changing the precipitation conditions. For this purpose continuous jarosite precipitation experiments were carried out. Despite the fact that jarosite synthesis has been the subject of many investigations [2-12], surprisingly little attention has been paid to continuous syntheses, such as reported here.

6.2 THEORY

The precipitation of jarosite is given by the following reaction:

\[
\text{NH}_4^+ + 3 \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 6 \text{H}_2\text{O} \rightarrow \text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 6 \text{H}^+ \tag{6.1}
\]
Continuous crystallization experiments allow to determine the crystal growth rate, the nucleation rate and the specific surface area of the growing crystals as a function of the specific operating conditions. Randolph and Larson [13] have shown that for a so-called Continuous Mixed Suspension Mixed Product Removal (CMSMPR) crystallization system the relations (6.2) to (6.4) can be derived. Equation (6.2) gives the number distribution of the crystal size in a CMSMPR system and enables to calculate the linear crystal growth rate $G$ (m s$^{-1}$) from experimentally determined Crystal Size Distribution (CSD)-data. Despite the fact that, as will be shown later, the particles formed in precipitating jarosite are no single crystals but agglomerates, the theory developed for evaluating single crystal precipitation processes will be used. Consequently, 'crystal' growth rates, nucleation rates and 'crystal' size distributions are related to the agglomerates rather than to the individual crystallites and are to be interpreted with great care.

$$n = n_0 \exp \left( -\frac{L}{G \tau} \right)$$

(6.2)

Here $n$ represents the population density of crystals of length $L$ (in m), $n_0$ is the population density of nuclei extrapolated to zero size, and $\tau$ represents the residence time of the suspension in the crystallizer (in s). The nucleation rate $B^o$ (# m$^{-3}$ s$^{-1}$) is given by:

$$B^o = n_0 G$$

(6.3)

Appendix 6.1 shows the method which was used to calculate the crystal growth rate and the nucleation rate from the obtained experimental data.

The solids concentration in the suspension $M_i$ (kg m$^{-3}$) is obtained from the iron and the mass balance (see appendix 6.2).

The specific surface area $A_i$ (m$^2$ kg$^{-1}$) of the crystals equals:

$$A_i = \frac{k_a}{3 k_r \rho_c G \tau}$$

(6.4)

In equation (6.4) $k_r$ is a shape factor which equals $\pi/6$ for spherical particles, $\rho_c$ represents the crystal density (kg m$^{-3}$) and $k_a$ is a shape factor which equals $\pi$ for spherical particles.
In order to check the applicability of the CMSMPR concept for the jarosite precipitation experiments carried out in this study the residence time distribution for the crystalline phase was experimentally determined and compared with the residence time distribution which could theoretically be calculated for an ideal CMSMPR system. Appendix 6.3 provides the theoretical background of the calculation method used for this purpose.

The partition coefficient for the incorporation of impurities in the jarosite lattice quantifies the selectivity of the process under different conditions. It is defined as:

\[ D = \frac{\left( \frac{[Zn^{2+}]}{[Fe^{3+}]} \right)_j}{\left( \frac{[Zn^{2+}]}{[Fe^{3+}]} \right)_i} \]  

(6.5)

In equation (6.5) \([Zn^{2+}]_t\) and \([Fe^{3+}]_t\) represent the overall concentrations of Zn\(^{2+}\) and Fe\(^{3+}\) in the solution, regardless of the species. Dutrizac [15] has demonstrated that the degree of incorporation of foreign ions in the jarosite lattice increases with an increasing first hydrolysis constant \(K\), which is given by:

\[ K = \frac{[MOH^{n-1}]}{[M^{n+}] [OH^-]} \]  

(6.6)

It is thus assumed that the ions are incorporated in their hydrolyzed form. In this study, the partition coefficient is therefore also calculated using the concentrations of ZnOH\(^{+}\) and Fe(OH)\(^{2+}\) instead of the total concentrations of Fe\(^{3+}\) and Zn\(^{2+}\) in the liquid phase:

\[ D = \frac{\left( \frac{[ZnOH^{+}]}{[FeOH^{2+}]} \right)_j}{\left( \frac{[ZnOH^{+}]}{[FeOH^{2+}]} \right)_i} \]  

(6.7)

The calculation of the concentrations of the species was carried out using a method described in ref.[16].

The driving force for the precipitation of jarosite is given by:

\[ \beta = \ln \left( \frac{[NH_4^+] [Fe^{3+}]^3 [SO_4^{2-}]^2 [OH^-]^6}{([NH_4^+] [Fe^{3+}]^3 [SO_4^{2-}]^2 [OH^-]^6)_{eq}} \right) \]  

(6.8)

In equation (6.8) \(\beta\) represents the growth affinity, here referred to as dimensionless supersaturation, the numerator represents the concentrations of the
constituent free ions in the mother liquor, whereas the denominator represents the free concentrations of these ions in a saturated solution. The value of the supersaturation is obtained with a method described in chapter four of this thesis. The ionic product given in the denominator is obtained by carrying out a dissolution experiment at a constant pH of 1.5. The ionic product in a saturated solution equals $10^{01}$ (mole l$^{-1}$)$^{12}$. In order to estimate the supersaturation for experiments carried out at constant pH equation (6.9) was used. Appendix 6.4 shows the assumptions made in deriving equation (6.9).

$$\beta = \ln \left( \frac{[NH_{4}^{+}] [Fe^{3+}]^3 [SO_{4}^{2-}]^2}{([NH_{4}^{+}] [Fe^{3+}]^3 [SO_{4}^{2-}]^2)_{eq}} \right)$$ \hspace{1cm} (6.9)

The degree of removal of iron is quantified as the conversion, which is defined as follows:

$$\xi = \frac{\varphi_{Fe,feed} - \varphi_{Fe,aq}}{\varphi_{Fe,feed}}$$ \hspace{1cm} (6.10)

Here, $\varphi_{Fe,feed}$ represents the molar feed flux of dissolved $Fe^{3+}$ and $\varphi_{Fe,aq}$ is the molar flux of dissolved $Fe^{3+}$ leaving the continuous crystallizer.

The rate of production is expressed as the jarosite mass production per unit volume and per unit time.

6.3 EXPERIMENTAL

6.3.1 Chemicals

All chemicals used were analytical grade. All water used has been deionized and subsequently distilled in an all pyrex glass water distillation apparatus.

6.3.2 Continuous crystallization equipment

A schematic drawing of the equipment used for the continuous syntheses is presented in figure 6.1. The glass storage vessels (1) and (2) contained a ferric and an ammonium sulfate solution. In case zinc or lithium sulfate were dosed, these salts were added to the iron sulfate solution. The precipitation vessel (3) was a thermostated double-wall borosilicate glass reactor with an effective volume of 1.5 l. The feed rates of the two components to the crystallizer were controlled by a
computer. The dosages, fed by means of the peristaltic pumps (4) and (5), were based upon the signals of the two electronic balances (10) and (11). Since the feed quantities were very small, dosage control based on weight differences was more accurate than based on flow rates. The reaction mixture was stirred vigorously at 800 - 1000 rpm with a three-bladed teflon stirrer. The solution in the crystallizer was kept at a constant level by using two level electrodes attached to a peristaltic pump. The temperature in the crystallizer was measured by a Pt 100 electrode and kept at \(95 \pm 0.2^\circ C\). The feed streams were heated to \(95^\circ C\) in two parallel glass heat exchangers (12) and (13).

![Figure 6.1: The continuous jarosite precipitation equipment](image)

The pH-level was measured continuously and was kept constant within 0.15 pH units for some experiments and after implementing a better pH control procedure.
within 0.03 pH units for the other experiments. The pH was corrected during the process by addition of a 8 wt% LiOH-solution from a storage vessel (16), which is in contrast to experiments carried out by Dutrizac [2] who used Li₂CO₃ for this purpose.

In most experiments the pH was 1.5. The pH-electrode was operated at 25°C by measuring the solution after withdrawal by the peristaltic pump (6) and cooling down to 25°C. This set-up was chosen in order to increase electrode life-time and to avoid scaling at the electrode surface.

6.3.3 Treatment of samples

Samples of the solid and the liquid phase were taken after the level control pump (6). Liquid samples were also taken directly from the crystallizer in order to check whether the two sampling procedures yielded the same results. Directly after a liquid sample was taken, it was filtered on a 20 mm diameter Büchner funnel equipped with 0.45 μm filter paper. The Fe³⁺ concentration of the liquid samples was determined by automatic titration with EDTA. In order to check the accuracy of this method the Fe³⁺ concentration of some samples was also determined by Induced Coupled Plasma (ICP) atomic emission spectroscopy.

Samples of the solid phases were taken as follows. During a period of about 1/25 of the expected residence time the peristaltic pump 6 was electrically disconnected. During this period the level in the crystallizer increased with about 60 ml. Pump 6 was then switched on and was manually controlled to flush about 120 ml suspension at once. This suspension quantity contained about 0.5 to 3 gram jarosite which was required for the different crystal phase analyses. The described procedure minimizes the disturbance of the crystallization conditions. In order to be sure that the suspension sample was taken from the inside of the reactor and not from the intermediate piping, the first 20 ml of the sample were discarded. The suspension sample of 100 ml was put in a 100 ml glass flask and was immediately cooled down to 25°C by immersing the flask in cold water. This procedure prevented the outgrowth of jarosite after sampling, because the crystal growth rate at 25°C is negligible. Moreover, the solubility of jarosite increases at pH 1.5 with decreasing temperature [17], so in these samples the actual
supersaturation would also be reduced. Even if an undersaturated solution would result from this procedure it still seems unlikely to assume that jarosite would dissolve to any significant extent, because jarosite dissolution at 25°C is also very slow.

After the mixture was cooled down, it was filtered on a Büchner funnel, thoroughly washed several times with water and diluted (5 wt%) H₂SO₄ and dried at 100°C. The obtained solids were analyzed by x-ray diffraction to confirm the jarosite crystal structure and were observed by scanning electron microscopy. A Coulter Counter Multisizer was used to determine the particle size distribution after dispersing the particles in a saturated NaCl-solution at 25°C. The instrument was equipped with a tube which enabled to measure particle sizes between 1.4 and 66 µm. The zinc concentration in the solids was determined by dissolving the crystals in (2 wt%) HCl and by subsequently measuring the Zn²⁺ concentration in the solution by Atomic Absorption Spectroscopy (AAS). The Fe- and S-concentrations of solid samples were determined by ICP analysis.

6.3.4 Experimental procedure

The experiments started with 25 g dry seeds, obtained from a previous continuous experiment, which were dispersed in a fresh mixture of dissolved ferric and ammonium sulfate, which were pumped from the storage vessels in a well defined ratio, controlled by the process computer. After the level in the crystallizer had reached 1.5 liter the process was left for typically one hour in order to start the precipitation of jarosite on the still limited surface of the seeds. After this batch period the continuous crystallization process was started. Each experiment lasted for nine or more residence times. Liquid samples were taken at least once per residence time. After the sixth residence time four or five solid samples were taken at regular time intervals.

6.3.5 Experimental conditions

In order to relate the incorporation of zinc to the composition of the mother liquor a two-level factorial design set-up was used for the selection of the experimental conditions of experiments in which the NH₄⁺ and Zn²⁺ concentration as well as the
residence time were varied. Varying three factors on two levels implies that at least $2^3$ or 8 experiments are required [18]. In this case the set-up included 15 experiments. All experiments with their corresponding feed concentrations are given in table 6.1. In table 6.1 the added quantity of Li$_2$SO$_4\cdot$H$_2$O is included as well. This addition was required in order to maintain a constant background concentration of total SO$_4^{2-}$ throughout the experiments.

The experiments c1 to c10 represent an extended $2^2$ factorial design [18]. The values for the Fe$^{3+}$ and Zn$^{2+}$ concentrations (0.25 mole l$^{-1}$ and 1.0 mole l$^{-1}$ respectively) are constant and are the same order of magnitude as in industrial practice. The NH$_4^+$ concentration and the residence time were varied. The experiments c11 to c15 complete the set-up for a $2^3$ factorial design.

Additionally, six experiments were carried out for other purposes. Two experiments were used to study the influence of the pH, and constant pH values of either 1.2 or 1.8 were chosen respectively, which were different from the pH 1.5 level in the other experiments.

Two other experiments were carried out where Zn$^{2+}$ was substituted by Mg$^{2+}$ in order to compare the influence of Zn$^{2+}$ and Mg$^{2+}$ on the precipitation. Magnesium is known hardly to incorporate in the jarosite lattice [15,19]. Magnesium concentrations in the solid and the liquid samples were measured by AAS.

Finally, two experiments were carried out to determine the residence time distribution to verify whether the use of the CMSMPR concept for this crystallization system is allowed. In these experiments alunite (KAl$_3$(SO$_4$)$_2$(OH)$_6$) was used as a tracer. The tracer was added after five residence times to a continuous jarosite precipitation experiment. Alunite is isostructural with jarosite and forms solid solutions [20]. It is therefore assumed that the very fine alunite particles are incorporated in the jarosite agglomerates and that the alunite residence time distribution is representative for that of jarosite. The tracer (0.4 g) could, despite its small quantity, be detected well because the aluminum concentration in a solid sample could be measured easily with AAS. The alunite sample was produced in a 250 ml batch crystallization experiment, using an 0.3M Al$_2$(SO$_4$)$_3\cdot$0.1 M K$_2$SO$_4$ solution at 95°C. The tracer experiments were carried out with a high Fe$^{3+}$ and SO$_4^{2-}$ feed concentration compared to the other experiments.
Table 6.1  The average residence time and the composition of the mixed feed stream for continuous jarosite precipitation experiments

<table>
<thead>
<tr>
<th>code</th>
<th>residence time</th>
<th>Fe$^{3+}$</th>
<th>NH$_4^+$</th>
<th>Zn$^{2+}$</th>
<th>SO$_4^{2-}$</th>
<th>Li$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hour</td>
<td>mol/l</td>
<td>mol/l</td>
<td>mol/l</td>
<td>mol/l</td>
<td>mol/l</td>
</tr>
<tr>
<td>c1</td>
<td>0.94</td>
<td>0.267</td>
<td>0.079</td>
<td>1.066</td>
<td>1.661</td>
<td>0.309</td>
</tr>
<tr>
<td>c2</td>
<td>1.84</td>
<td>0.261</td>
<td>0.078</td>
<td>1.043</td>
<td>1.624</td>
<td>0.303</td>
</tr>
<tr>
<td>c3</td>
<td>0.92</td>
<td>0.261</td>
<td>0.364</td>
<td>1.040</td>
<td>1.665</td>
<td>0.104</td>
</tr>
<tr>
<td>c4</td>
<td>1.72</td>
<td>0.253</td>
<td>0.354</td>
<td>1.007</td>
<td>1.614</td>
<td>0.100</td>
</tr>
<tr>
<td>c5</td>
<td>1.35</td>
<td>0.264</td>
<td>0.226</td>
<td>1.054</td>
<td>1.686</td>
<td>0.247</td>
</tr>
<tr>
<td>c6</td>
<td>1.36</td>
<td>0.267</td>
<td>0.223</td>
<td>1.071</td>
<td>1.711</td>
<td>0.254</td>
</tr>
<tr>
<td>c7</td>
<td>1.50</td>
<td>0.251</td>
<td>0.024</td>
<td>1.003</td>
<td>1.605</td>
<td>0.427</td>
</tr>
<tr>
<td>c8</td>
<td>0.76</td>
<td>0.253</td>
<td>0.217</td>
<td>1.011</td>
<td>1.619</td>
<td>0.240</td>
</tr>
<tr>
<td>c9</td>
<td>1.37</td>
<td>0.251</td>
<td>0.407</td>
<td>1.003</td>
<td>1.604</td>
<td>0.044</td>
</tr>
<tr>
<td>c10</td>
<td>2.02</td>
<td>0.260</td>
<td>0.227</td>
<td>1.028</td>
<td>1.649</td>
<td>0.234</td>
</tr>
<tr>
<td>c11</td>
<td>0.99</td>
<td>0.250</td>
<td>0.080</td>
<td>0.400</td>
<td>1.562</td>
<td>1.493</td>
</tr>
<tr>
<td>c12</td>
<td>1.91</td>
<td>0.251</td>
<td>0.080</td>
<td>0.401</td>
<td>1.565</td>
<td>1.495</td>
</tr>
<tr>
<td>c13</td>
<td>1.01</td>
<td>0.256</td>
<td>0.358</td>
<td>0.409</td>
<td>1.634</td>
<td>1.327</td>
</tr>
<tr>
<td>c14</td>
<td>1.84</td>
<td>0.255</td>
<td>0.358</td>
<td>0.409</td>
<td>1.634</td>
<td>1.327</td>
</tr>
<tr>
<td>c15</td>
<td>1.39</td>
<td>0.255</td>
<td>0.219</td>
<td>0.711</td>
<td>1.632</td>
<td>0.860</td>
</tr>
<tr>
<td>c15 pH1.2</td>
<td></td>
<td>0.255</td>
<td>0.219</td>
<td>0.711</td>
<td>1.632</td>
<td>0.860</td>
</tr>
<tr>
<td>c15 pH1.8</td>
<td></td>
<td>0.254</td>
<td>0.221</td>
<td>0.709</td>
<td>1.628</td>
<td>0.857</td>
</tr>
<tr>
<td>c13 Mg</td>
<td>0.97</td>
<td>0.246</td>
<td>0.345</td>
<td>1.04$^1$</td>
<td>1.575</td>
<td>0.096</td>
</tr>
<tr>
<td>s16 Al</td>
<td>0.86</td>
<td>0.978</td>
<td>0.082</td>
<td>1.133</td>
<td>2.747</td>
<td>0</td>
</tr>
<tr>
<td>s18 Al</td>
<td>0.79</td>
<td>0.978</td>
<td>0.360</td>
<td>1.133</td>
<td>2.765</td>
<td>0</td>
</tr>
</tbody>
</table>

$^1$ The figure represents the Mg$^{2+}$ concentration in mol/l
6.4 RESULTS AND DISCUSSION

6.4.1 Determination of the residence time distribution

The residence time distribution was determined in experiment s16 Al and s18 Al. Table 6.1 shows the experimental conditions in all experiments. Using the method described in appendix 6.3 the results given in table 6.2 are obtained.

Table 6.2 The residence time estimates obtained using the method of the mass balance and using the residence time distribution experiments

<table>
<thead>
<tr>
<th>code</th>
<th>$\tau_{\text{mass bal.}}$ (hr)</th>
<th>$\tau_{\text{exp.}}^1$ (hr)</th>
<th>$\tau_{\text{MSMPR}}^2$ (hr)</th>
<th>$\sigma_{\text{exp.}}$</th>
<th>$\sigma_{\text{MSMPR}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>s16 Al</td>
<td>0.86</td>
<td>0.78</td>
<td>0.87</td>
<td>0.72</td>
<td>0.76</td>
</tr>
<tr>
<td>s18 Al</td>
<td>0.79</td>
<td>0.73</td>
<td>0.82</td>
<td>0.76</td>
<td>0.67</td>
</tr>
</tbody>
</table>

1 The subscript exp. refers to the evaluation of the experimental data with the general method

2 The subscript MSMPR refers to the evaluation of the experimental data with the MSMPR method

The different approaches for calculating the residence time yield results which do not deviate largely. This is sustained by the results shown in figure 6.2 in which the measured E(t)-curve is compared with the E(t)-curve which corresponds to an MSMPR-crystallizer. Despite the fact that some differences between the MSMPR and the general approach are observed, there is sufficient proof that the reactor operated as an MSMPR-crystallizer.

6.4.2 The applicability of factorial design analysis

The initial feed concentrations (which represent the values after mixing of the Fe$^{3+}$ and the NH$_4^+$ feed streams) were chosen according to factorial design rules. The evaluation of the obtained experimental responses with a factorial design approach
Figure 6.2: Comparison of the residence time distribution expected for an ideal MSMPR crystallizer with the experimentally measured residence time distribution.

is, however, not allowed because one of the five factors, namely the residence time, is depending upon the conversion (via the hydroxide addition) which on its turn is dependent upon the feed streams. Independency of the factors is an essential constraint when applying factorial design tools. Therefore the evaluation of the results proceeded without factorial design analysis.

6.4.3 Factors affecting the precipitation
Table 6.3 provides the calculated results for all experiments: the conversion $\xi$, the growth rate $G$, the nucleation rate $B^o$, the specific surface $A_o$, the solids density in the suspension $M_o$, the production rate $r_p$, the supersaturation $\sigma$ and the partition coefficient $D$.

Using a factorial design approach facilitates an evaluation of the impact of a change in process conditions. This $2^3$ factorial design is represented by a cube.
<table>
<thead>
<tr>
<th>code</th>
<th>$\xi$</th>
<th>G</th>
<th>B$^2$</th>
<th>$A_i$</th>
<th>$M_i$</th>
<th>$r_p$</th>
<th>$\beta$</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(-)</td>
<td>nm/s</td>
<td>#/(m$^3$/s)</td>
<td>m$^2$/kg</td>
<td>* 10$^{-9}$</td>
<td>m$^2$/kg</td>
<td>* 10$^{-2}$</td>
<td>kg/(m$^3$.hr)</td>
</tr>
<tr>
<td>c 1</td>
<td>0.36</td>
<td>1.2</td>
<td>4</td>
<td>2</td>
<td>14</td>
<td>15</td>
<td>9.8</td>
<td>1.2</td>
</tr>
<tr>
<td>c 2</td>
<td>0.54</td>
<td>0.5</td>
<td>10</td>
<td>2</td>
<td>20</td>
<td>11</td>
<td>7.9</td>
<td>1.1</td>
</tr>
<tr>
<td>c 3</td>
<td>0.57</td>
<td>1.5</td>
<td>5</td>
<td>1</td>
<td>22</td>
<td>24</td>
<td>9.7</td>
<td>2.7</td>
</tr>
<tr>
<td>c 4</td>
<td>0.82</td>
<td>1.0</td>
<td>2</td>
<td>1</td>
<td>28</td>
<td>17</td>
<td>6.3</td>
<td>1.2</td>
</tr>
<tr>
<td>c 5</td>
<td>0.77</td>
<td>1.0</td>
<td>5</td>
<td>1</td>
<td>29</td>
<td>22</td>
<td>6.6</td>
<td>1.4</td>
</tr>
<tr>
<td>c 6</td>
<td>0.73</td>
<td>0.7</td>
<td>17</td>
<td>2</td>
<td>28</td>
<td>21</td>
<td>7.2</td>
<td>1.5</td>
</tr>
<tr>
<td>c 7</td>
<td>0.23</td>
<td>0.6</td>
<td>6</td>
<td>2</td>
<td>9</td>
<td>6</td>
<td>8.2</td>
<td>1.4</td>
</tr>
<tr>
<td>c 8</td>
<td>0.35</td>
<td>1.4</td>
<td>9</td>
<td>2</td>
<td>13</td>
<td>18</td>
<td>10.8</td>
<td>2.5</td>
</tr>
<tr>
<td>c 9</td>
<td>0.75</td>
<td>1.0</td>
<td>4</td>
<td>1</td>
<td>27</td>
<td>20</td>
<td>7.8</td>
<td>2.0</td>
</tr>
<tr>
<td>c10</td>
<td>0.77</td>
<td>0.5</td>
<td>9</td>
<td>2</td>
<td>29</td>
<td>14</td>
<td>6.8</td>
<td>1.5</td>
</tr>
<tr>
<td>c11</td>
<td>0.12</td>
<td>0.8</td>
<td>5</td>
<td>2</td>
<td>5</td>
<td>5</td>
<td>8.6</td>
<td>6.5</td>
</tr>
<tr>
<td>c12</td>
<td>0.46</td>
<td>0.4</td>
<td>8</td>
<td>2</td>
<td>17</td>
<td>9</td>
<td>6.0</td>
<td>3.7</td>
</tr>
<tr>
<td>c13</td>
<td>0.21</td>
<td>1.0</td>
<td>5</td>
<td>2</td>
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<td>c14</td>
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<td>2</td>
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<td>13</td>
<td>6.3</td>
<td>5.8</td>
</tr>
<tr>
<td>c15</td>
<td>0.58</td>
<td>0.6</td>
<td>14</td>
<td>2</td>
<td>22</td>
<td>16</td>
<td>7.4</td>
<td>3.2</td>
</tr>
<tr>
<td>c 3 Mg</td>
<td>0.30</td>
<td>0.7</td>
<td>14</td>
<td>2</td>
<td>11</td>
<td>12</td>
<td>13.3</td>
<td>0.2</td>
</tr>
<tr>
<td>c13 Mg</td>
<td>0.25</td>
<td>1.0</td>
<td>7</td>
<td>2</td>
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<td>9.3</td>
<td>0.6</td>
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<tr>
<td>c15 pH 1.2</td>
<td>0.32</td>
<td>0.7</td>
<td>5</td>
<td>2</td>
<td>13</td>
<td>9</td>
<td>10.0$^{12}$</td>
<td>3.2</td>
</tr>
<tr>
<td>c15 pH 1.8</td>
<td>0.92$^3$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1. Assuming the equilibrium ionic product $[\text{NH}_4^+][\text{Fe}^{3+}]$.$\text{SO}_4^{2-}$.$\text{OH}^-$ to be equal to $10^{-90}$ (mole L$^{-1})^{12}$ and $[\text{OH}^-] = 10^{-12.4} \cdot 1.2 = 6.3 \cdot 10^{-12}$ mole L$^{-1}$; consequently: $[\text{NH}_4^+][\text{Fe}^{3+}]$.$\text{SO}_4^{2-}$.$\text{OH}^-$ = $1.6 \cdot 10^{-24}$ (mole L$^{-1})^{8}$.

2. An appropriate value for $[\text{OH}^-]$ and a corresponding value for $[\text{H}^+]$ were also used in calculating the species.

3. In experiment c 15 pH 1.8 two separate solid phases were formed, which inhibited the calculation of the crystallization parameters like the growth and nucleation rate etc.
For the bottom plane of the cube \([Zn^{2+}] = 0.4 \text{ mole l}^{-1}\) and for the top plane \([Zn^{2+}] = 1.0 \text{ mole l}^{-1}\). For the left side plane of the cube \([NH_4^+] = 0.08 \text{ mole l}^{-1}\) and for the right side \([NH_4^+] = 0.35 \text{ mole l}^{-1}\). For the front plane the residence time is about 1 hour, for the back plane it is 1.8 hours. In the following the conversion, the production rate, the supersaturation, the growth rate and the zinc incorporation are individually discussed as a function of the feed composition and the residence time and the results are, among others, presented by using this cube.

**conversion**

The conversion increases with an increasing residence time, an increasing feed \(NH_4^+\) concentration and an increasing feed \(Zn^{2+}\) concentration, as is shown in figure 6.3. For the upper plane of the cube the observed results were used to predict iso-conversion lines. This was only justified for the upper plane because these ten measurements, with the duplicate experiment in the centre, provided enough data to estimate the contour lines with a sufficient accuracy.

![Figure 6.3: The conversion of the precipitation reaction as a function of the feed concentrations and the residence time](image-url)
Figure 6.4 presents the iso-conversion lines. A feed NH$_4^+$ concentration of 0.16M (twice the stoichiometric value) is required for achieving a conversion above 70%. Feed NH$_4^+$ concentrations above 0.2M, however, no longer cause a significant increase in conversion. Similarly, the residence time must exceed 4500 s to reach a conversion of 70% but higher residence times no longer increase the conversion noticeably. The response of the conversion to the feed NH$_4^+$ concentration and to the residence time is explained by the increasing supersaturation corresponding to an increasing NH$_4^+$ concentration and by the increasing reaction time available for growth and thus conversion, respectively.

![Residence Time vs Feed NH$_4^+$ Concentration](image)

Figure 6.4: The conversion plotted with iso-conversion lines as a function of the feed NH$_4^+$ concentration and the residence time

The influence of the feed Zn$^{2+}$ concentration on the conversion is exerted via the Zn$^{2+}$ - SO$_4^{2-}$ complexation which affects the free Fe$^{3+}$ concentration. Table 6.4 provides the total and the calculated free Fe$^{3+}$ and SO$_4^{2-}$ concentrations for the experiments c1 to c4 and c11 to c14 which form the angular points of the cube. Jarosite precipitation requires three Fe$^{3+}$ and two SO$_4^{2-}$ ions per molecule. Thus, the relevant ionic product is (Fe$^{3+}$)$^3$(SO$_4^{2-}$)$^2$. For the experiments listed in table 6.4
the ratio of the free ion over the total ion concentrations of both Fe\(^{3+}\) and SO\(_4^{2-}\) were calculated and used in calculating the above mentioned ionic product. The reason why the ratio's and not the absolute values were used, is that the figures require normalization to correct for the difference in conversion in the various experiments.

Table 6.4  The total and the free [Fe\(^{3+}\)] and [SO\(_4^{2-}\)] and the ratio of respective free concentrations for comparable experiments with [Zn\(^{2+}\)] = 0.4M (c11 to c14) respectively 1.0M (c1 to c4) and [Mg\(^{2+}\)] =0.4M and 1.0M.

<table>
<thead>
<tr>
<th>code</th>
<th>Fe(^{3+}),tot. (mole l(^{-1}))</th>
<th>Fe(^{3+}),free (mole l(^{-1})) (*10^7)</th>
<th>SO(_4^{2-}),tot. (mole l(^{-1}))</th>
<th>SO(_4^{2-}),free (mole l(^{-1})) (*10^2)</th>
<th>free/total (*10^6)</th>
<th>(R_{Fe^{3+}}) (*10^2)</th>
<th>(R_{SO_4^{2-}}) (*10^{20})</th>
</tr>
</thead>
<tbody>
<tr>
<td>c1</td>
<td>0.162</td>
<td>26.4</td>
<td>1.59</td>
<td>2.14</td>
<td>16.2</td>
<td>1.34</td>
<td>77</td>
</tr>
<tr>
<td>c11</td>
<td>0.220</td>
<td>10.0</td>
<td>1.54</td>
<td>4.05</td>
<td>4.5</td>
<td>2.63</td>
<td>6</td>
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<td>c2</td>
<td>0.113</td>
<td>15.2</td>
<td>1.53</td>
<td>2.35</td>
<td>13.5</td>
<td>1.54</td>
<td>58</td>
</tr>
<tr>
<td>c12</td>
<td>0.132</td>
<td>4.5</td>
<td>1.49</td>
<td>4.67</td>
<td>3.4</td>
<td>3.14</td>
<td>4</td>
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<tr>
<td>c3</td>
<td>0.104</td>
<td>11.7</td>
<td>1.56</td>
<td>2.58</td>
<td>11.2</td>
<td>1.65</td>
<td>38</td>
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<tr>
<td>c3 Mg</td>
<td>0.167</td>
<td>57.3</td>
<td>1.52</td>
<td>1.47</td>
<td>34.3</td>
<td>0.97</td>
<td>376</td>
</tr>
<tr>
<td>c13</td>
<td>0.204</td>
<td>7.6</td>
<td>1.60</td>
<td>4.47</td>
<td>3.7</td>
<td>2.79</td>
<td>4</td>
</tr>
<tr>
<td>c13 Mg</td>
<td>0.180</td>
<td>7.2</td>
<td>1.54</td>
<td>4.32</td>
<td>4.0</td>
<td>2.80</td>
<td>5</td>
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<tr>
<td>c4</td>
<td>0.040</td>
<td>3.7</td>
<td>1.47</td>
<td>2.87</td>
<td>9.1</td>
<td>1.95</td>
<td>29</td>
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<tr>
<td>c14</td>
<td>0.090</td>
<td>2.4</td>
<td>1.52</td>
<td>5.28</td>
<td>2.7</td>
<td>3.46</td>
<td>2</td>
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A higher Zn\(^{2+}\) concentration 'consumes' a larger part of the total SO\(_4^{2-}\) concentration. Although this reduces the remaining SO\(_4^{2-}\) concentration available for jarosite precipitation, it also reduces the quantity of SO\(_4^{2-}\) available for Fe\(^{3+}\) complexation, which leads to a higher free Fe\(^{3+}\) concentration. The latter relatively outweighs the influence of the decreasing SO\(_4^{2-}\) concentration (see table 6.4) and explains why increasing the Zn\(^{2+}\) concentration increases the conversion.

126
This reasoning is sustained by comparing the influence of \( \text{Zn}^{2+} \) ions with \( \text{Mg}^{2+} \) ions on jarosite precipitation (see table 6.1). The experiments c 3 Mg and c13 Mg are equivalent to the experiments c 3 Zn and c13 Zn but with \( \text{Mg}^{2+} \) substituted for \( \text{Zn}^{2+} \).

The experiments c13 Zn and c13 Mg yield practically the same results for the conversion, the crystal growth rate, the nucleation rate, the solids density in the suspension, the production rate and the supersaturation (see table 6.3). The calculation of the species, using the method described in ref.[16] and using data for the complexation of \( \text{Mg}^{2+} \) with respectively \( \text{OH}^- \), \( \text{SO}_4^{2-} \) and \( \text{HSO}_4^- \) [21-23], yielded results which did not significantly deviate between the experiments c13 Zn and c13 Mg, as becomes clear from table 6.4. The partition coefficient for the incorporation of impurities is, however, considerably lower for \( \text{Mg}^{2+} \), as expected, given the relationship between the partition coefficient and the comparatively low value of the first hydrolysis constant of \( \text{Mg}^{2+} \).

The experiments c 3 and c 3 Mg yield, despite their equal reaction conditions, considerably different results for the species and thus for the conversion, the production rate, the crystal growth rate and the supersaturation. Despite the considerable increase of the relevant ionic product for experiment c 3 Mg, compared to experiment c 13 Mg (see table 6.4), only a small increase of the conversion was observed. The supersaturation in experiment c 3 Mg, however, has doubled, compared to the experiments c 13 Mg and c 3. The reason why the addition of a large excess of \( \text{Mg}^{2+} \) ions did not further increase the conversion of \( \text{Fe}^{3+} \) to jarosite, despite of its nett positive effect on the free \( \text{Fe}^{3+} \) and \( \text{SO}_4^{2-} \) concentration, might be growth limitation of the individual crystallites which form jarosite aggregates due to growth retardation in case of \( \text{Mg}^{2+} \). This explains the low conversion, the comparatively high supersaturation and the low crystal growth rate observed in experiment c 3 Mg. Large amounts of \( \text{Mg}^{2+} \) ions (e.g. 1.0M) are also known to retard the growth of other mineral salts [25,26].

The reason why these effects were only observed for a feed \( \text{Mg}^{2+} \) concentration of 1.0M and not for 0.4M was also provided by the species calculation. For a feed \( \text{Mg}^{2+} \) concentration of 0.4M the free \( \text{Mg}^{2+} \) concentration was 0.018M, but for a feed concentration of 1.0M the free \( \text{Mg}^{2+} \) concentration was 0.12 M. It is assumed that
this large increase in free Mg$^{2+}$ concentration determines the fact that the retarding influence of Mg$^{2+}$ on the growth of jarosite was only observed in experiment c 3 Mg.

**Production rate**
The production rate per unit volume increases with an increasing feed NH$_4^+$ concentration as is shown in figure 6.5, except in the case of the duplicate experiment c 5/c 6 versus experiment c 9 where an increase in the feed NH$_4^+$ concentration leads to about the same production rate.

The production rate also increases with an increasing feed Zn$^{2+}$ concentration and this is a consequence of the increasing conversion as discussed in the previous section. The highest production rate of 24 kg m$^{-3}$ hr$^{-1}$ is observed for experiment c 3 but for the duplicate experiments c 5/c 6 it is only slightly lower. The production rate is linearly proportional to the solids density in the suspension and therefore the solids density in the suspension shows the same trend as the production rate. The solids density itself ranges from 0.5 to 2.9 wt%.

![Figure 6.5: The jarosite production rate as a function of the feed concentrations and the residence time](image-url)
**supersaturation**

Figure 6.6 shows the calculated supersaturation for the different experiments. The supersaturation increases with a decreasing residence time but did not show a clear dependency on the feed Zn\(^{2+}\) or the feed NH\(_4^+\) concentration. Figure 6.7 shows the relationship between the supersaturation and the residence time. For a feed Zn\(^{2+}\) concentration of 1.0M the supersaturation is relatively low in the experiments c4, c 5/c 6 and c10. In these experiments a high feed NH\(_4^+\) concentration and a high residence time were chosen. The feed Zn\(^{2+}\) concentration itself did apparently not directly influence the supersaturation.

![Graph showing supersaturation as a function of feed concentrations and residence time.](image1)

**Figure 6.6: The supersaturation β as a function of the feed concentrations and the residence time**

![Graph showing supersaturation as a function of residence time.](image2)

**Figure 6.7: The supersaturation β as a function of the residence time**

**crystal growth rate**

Appendix 6.1 describes the method used to determine the crystal growth rate. Since in each experiment agglomeration occurs, the crystal growth rate itself cannot be determined by this method. Instead the obtained 'growth rate' is a function of both the real crystal growth and the agglomeration rate. This becomes clear when observing figure 6.8, which shows four representative SEM photographs from jarosite crystals precipitated at different levels of supersaturation.
Figure 6.8a: A representative jarosite agglomerate formed in a continuous experiment at supersaturation $\beta = 6.0$

Figure 6.8b: A representative jarosite agglomerate formed in a continuous experiment at supersaturation $\beta = 7.8$
Figure 6.8c: A representative jarosite agglomerate formed in a continuous experiment at supersaturation $\beta = 9.6$

Figure 6.8d: A representative jarosite agglomerate formed in a continuous experiment at supersaturation $\beta = 10.8$
The obtained results for the growth rate, given in figure 6.9, lead to the conclusion that the growth rate increases with either a decreasing residence time, an increasing feed Zn$^{2+}$ concentration or an increasing feed NH$_4^+$ concentration. The accuracy of the results, however, is limited, as is shown in the duplicate experiments c5/c6 where a considerable difference in growth rate for the two experiments is observed.

![Figure 6.9: The growth rate as a function of the feed concentrations and the residence time](image)

Figure 6.9 shows the relationship between the growth rate and the supersaturation for the experiments c1 to c15. Owing to the inaccuracy, the growth rate figures do not allow to determine the dependency of the growth rate on the supersaturation. Since, however, both growth and agglomeration rates are expected to increase with the supersaturation, the tendency seems reasonable. A typical number-based crystal size distribution, as measured with the Coulter Counter Multisizer, is given in appendix 6.1. Given the shape of the particles observed in figure 6.8, the assumption that the agglomerates are spherical seems justified.
Based on the growth rate, estimates of the nucleation rate and the specific surface area of the crystals were obtained. Due to the inaccuracy in the growth rate, inaccurate results for the nucleation rate and the specific surface area were inevitable. Thus, regardless of the process conditions within the studied range, the nucleation rate is equal to \((8 \pm 4) \times 10^9 \text{ m}^3\text{s}^{-1}\). This nucleation rate has the usual order of magnitude for precipitation systems. The specific surface area equals 1.7 \(\pm 0.5 \text{ m}^2 \text{ kg}^{-1}\).

**incorporation of zinc**

The incorporation of zinc was quantified by the partition coefficient \(D\) as calculated from equation (6.5) using the total \(\text{Fe}^{3+}\) and \(\text{Zn}^{2+}\) concentrations in the solution. This approach enables to directly estimate the incorporation of \(\text{Zn}^{2+}\) in jarosite from a solution containing \(\text{Fe}^{3+}\) and \(\text{Zn}^{2+}\). The partition coefficient for the conditions studied in this paper is typically 0.002. It decreases with an increasing feed \(\text{Zn}^{2+}\) concentration, an increasing feed \(\text{NH}_4^+\) concentration and with an increasing residence time. Zinc is assumed to substitute the lattice \(\text{Fe}^{3+}\) ions in jarosite isomorphously.
Figure 6.11A shows the relationship between the partition coefficient, based on the total Fe\(^{3+}\) and the total Zn\(^{2+}\) concentration, and the supersaturation. Despite the considerable spread in the results, an increase of the partition coefficient with the supersaturation is observed. Figure 6.11B shows the relationship between the partition coefficient, based on the FeOH\(^{2+}\) concentration and the ZnOH\(^+\) concentration (see equation 6.7), and the supersaturation. The results show that the partition coefficient increases with an increase in the supersaturation. The value of the partition coefficient calculated from equation (6.7) is much higher than the value calculated from equation (6.5). This higher value indicates that the tendency of the jarosite lattice to incorporate a hydrolyzed Zn\(^{2+}\) ion is high, compared to the apparent tendency calculated on basis of the total Zn\(^{2+}\) concentration. The comparatively low incorporation of Zn\(^{2+}\) in jarosite is therefore not believed to be caused by the high selectivity of the jarosite lattice but rather by the lower first hydrolysis constant of Zn\(^{2+}\) compared to the one of Fe\(^{3+}\), which reduces the ratio of ZnOH\(^+\) over Zn\(^{2+}\) in the solution.

![Graph A: Partition coefficient vs. Supersaturation](image1)

**Fig. 6.11A:** The partition coefficient, D, calculated from the total Zn\(^{2+}\) and Fe\(^{3+}\) concentrations, as a function of the supersaturation

![Graph B: Partition coefficient vs. Supersaturation](image2)

**Figure 6.11B:** The partition coefficient D, calculated from the ZnOH\(^+\) and the Fe(OH)\(_2^+\) concentrations, as a function of the supersaturation

The zinc loss in jarosite was also quantified using the zinc concentration in the jarosite agglomerates as a measure. This yields the results presented in figure
6.12. The loss of zinc in jarosite remains below 1 wt% and decreases with a decreasing feed NH$_4^+$ concentration. The reason why the loss of zinc seems to be related to the feed NH$_4^+$ is not fully clear.

Figure 6.12: The incorporation of zinc in jarosite in g kg$^{-1}$ solids as a function of the feed concentrations and the residence time

6.4.4 Effect of the pH
Two experiments were carried out at pH-levels different from 1.5 which was used in the other experiments. Apart from the changed pH, the experiments c15 pH 1.2 and c15 pH 1.8 were equal to experiment c15. The results of the experiments are given in table 6.3.

The results of the experiment at pH 1.2 were similar to the results for the experiment at pH 1.5, except for the supersaturation and the conversion which both decreased. Experimental results provided by Zyuzikov [26] showed that jarosite has an increasing solubility with an increasing H$^+$ concentration. Therefore, using the same feed Fe$^{3+}$ concentration yields at lower pH a lower supersaturation and consequently a lower conversion.
The experiment at pH 1.8 yielded a mixed solid precipitate and reached a very high conversion of 92%. Using XRD-Guinier de Wolff diffractograms ammonium jarosite and traces of goethite were identified. Based on the blackening of the photo it was concluded that amorphous substances were also present. The precipitate had turned brown, in contrast to yellowish-brown which is the typical color of ammonium jarosite. Chemical analysis showed that the precipitate contained 57.6 wt% Fe, only 10.7 wt% SO₄ and 1.1 wt% Zn. Calculating a mass balance over the solid phase confirmed that goethite was formed simultaneously with jarosite. The observation of the simultaneous co-formation of goethite and jarosite in the presence of high Zn²⁺ concentrations was also reported by Dutrizac [15].

6.5 CONCLUSIONS

The precipitation of jarosite from aqueous solutions of Fe³⁺ and SO₄²⁻ at 95°C in continuous experiments yielded conversions of dissolved Fe³⁺ into jarosite varying between 12 and 82 %, dependent on the process conditions and the residence time. The corresponding production rate for jarosite varied between 5 and 24 kg jarosite m³ reactor hr⁻¹. A higher production rate was obtained at high feed NH₄⁺ concentrations and at low residence times.

The incorporation of zinc was quantified with a partition coefficient based on the total Zn²⁺ and the total Fe³⁺ concentration. It resulted in a value of about 0.001 - 0.003. This corresponds with a zinc load of 2.5 to 11 g/kg in jarosite. The incorporation of Zn²⁺ in the jarosite lattice increased with an increase in the supersaturation for the precipitation. A lower zinc uptake was obtained at low NH₄⁺ concentrations.

6.6 OPTIMIZED CONDITIONS FOR JAROSITE PRECIPITATION

The process conditions for jarosite precipitation must be optimized to achieve a high conversion leading to an output Fe³⁺ concentration below e.g. 2 g/l, a low alkali consumption, a sufficiently high production rate and a limited incorporation
of Zn\(^{2+}\) in the jarosite residue. On an industrial scale the optimized conditions for jarosite precipitation depend on factors such as the available reactor capacity, the costs of alkali, the energy costs and the costs due to the loss of zinc with jarosite. In the following, two cases are discussed as examples of how to use the data presented in the foregoing study for optimization of an industrial jarosite precipitation process.

-i- In the first case it is assumed the loss of zinc determines the process conditions' choice, e.g. as a consequence of the required subsequent treatment process. Conditions with a low feed alkali concentration (< 0.1M) and a residence time of one hour seem preferable. This choice necessitates a large reactor capacity.

-ii- In the second case when a comparatively small reactor capacity is assumed to be available, a feed NH\(_4^+\) concentration of 0.2M and a residence time of 1.5 hours are required for obtaining the production rate needed to cope with the reactor capacity. This, however, inevitably increases the loss of Zn\(^{2+}\) to the jarosite residue.

For a commercial hydrometallurgical zinc refining plant which uses 400,000 ton/a zinc concentrate containing 52 wt% zinc and 8 wt% iron a jarosite production of 103,000 ton/a is expected (assuming jarosite to contain 31 wt% iron). For a jarosite precipitation process with a feed containing 0.25M Fe\(^{3+}\), 1.0M Zn\(^{2+}\), 0.08M NH\(_4^+\) and 1.6M SO\(_4^{2-}\) and a residence time of 1 hour (case -i-) a production rate of 15 kg jarosite m\(^{-3}\) hr\(^{-1}\) was measured with a corresponding incorporation of 2.6 g zinc per kg jarosite. If the plant operates for 7000 hours/a (± 80% availability), a reactor volume of about 1000 m\(^3\) is required. The annual loss of zinc due to incorporation in jarosite then equals about 270 tons, which is 0.13 wt% of the zinc quantity in the concentrate.

For a feed containing 0.17M NH\(_4^+\) instead of 0.08M NH\(_4^+\), all other concentrations remaining equal, and a residence time of 1.4 hours (case -ii-), a production rate of 21 kg m\(^{-3}\) hr\(^{-1}\) was measured with a corresponding incorporation of about 9 g zinc per kg jarosite. For an operation of 7000 hours/a a reactor volume of 700 m\(^3\) is required. The annual loss of zinc due to the incorporation in jarosite is then
equal to about 930 tons which is 0.45 wt% of the zinc quantity in the concentrate. The figures presented above are calculated for a single continuous stirred tank reactor. In industrial practice jarosite precipitation will always be carried out in a cascade of reactors which will enhance the conversion per unit volume for the same process conditions. The above given examples illustrate the potential use of this study's results for designing or optimizing jarosite precipitation processes given different constraints.

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6.7 REFERENCES

[1] Chapter 9, this thesis.


[16] Chapter 4, this thesis.


[22] ibid. [21], Special publication no. 25 (1971).


Appendix 6.1  Calculation of the crystal growth rate and the nucleation rate from experimental data

A Coulter Counter Multisizer measures a volume-based agglomerate/crystal size. This is converted into a volume-based size distribution or a number-based size distribution. The latter is required for calculating the growth rate and is obtained by assuming that all crystals are spheres which is a crude simplification. A relationship between the length (diameter) of the crystal and the number of crystals with that particular length is given in equation (6.11):

\[
\ln n = - \frac{1}{G \tau} L + \ln n_0
\]  

(6.11)

Figure 6.13 shows the experimentally obtained crystal size distribution and the calculated straight line fit. The fit does not adequately describe the part of the results at the higher crystal size range, due to the fact that the number of crystals is too small in that range.

Figure 6.13: The relationship between the log number size distribution and the length of the crystals. The dashed line represents the straight line which was used in calculating the growth rate.

140
Using equation (6.11), the nucleation rate $B^o$ may also be calculated after taking into account the dilution of the sample. For this purpose a normalization factor $N$ is defined:

$$N = \frac{k_v \rho_f \int_{e}^{\infty} n L^3 dL}{M_i}$$  \hspace{1cm} (6.12)

This equation can be solved since the coordinates $(L, n)$ were obtained from the Coulter Counter analysis and $M_i$ (the solids density in the suspension) was available from the iron and the mass balance. A normalized distribution is obtained by dividing $n(L)$ through $N$. The intercept (limit value at $L \rightarrow 0$) of the straight line of $\ln (n(L)/N)$ against $L$ yields the value for $n_v$, the population density of crystals at zero size, which is used for calculating the nucleation rate $B^o$ via equation (6.3).

**Appendix 6.2 Calculation of the residence time and the slurry density**

The suspension residence time $\tau$ (s) and the slurry density $M_s$ (kg m$^{-3}$) can not be measured accurately and were therefore calculated from the input parameters and the Fe$^{3+}$ concentration in the effluent. The suspension residence time $\tau$ follows from:

$$\tau = \frac{V}{\Phi_{out}}$$  \hspace{1cm} (6.13)

In equation (6.13) $V$ represents the volume of the reactor (m$^3$) and $\Phi_{out}$ is the outflux (m$^3$ s$^{-1}$). An overall mass balance for the system is given by equation (6.14):

$$\Phi_{out} \rho_{out} = \Phi_1 \rho_1 + \Phi_2 \rho_2 + \Phi_3 \rho_3$$  \hspace{1cm} (6.14)

Here, $\Phi$'s represent fluxes (m$^2$ s$^{-1}$) and $\rho$'s represent solution densities (kg m$^{-3}$); the subscripts 1, 2 and 3 refer to the NH$_4^+$, Fe$^{3+}$ and OH$^-$ feed streams respectively. In Figure 6.14 a scheme of the equipment is given. The figure also shows the symbols used. The iron balance is given by equation (6.15):

$$\frac{3M_i}{M_w} \Phi_{out} + \left(1 - \frac{M_i}{\rho_{jar}}\right) \Phi_{out} C_{Fe, out} = \Phi_2 C_{Fe, 2}$$  \hspace{1cm} (6.15)
Here $M_w$ is the molecular weight of ammonium jarosite which is $479.6 \text{ g mole}^{-1}$ and $\rho_{jar}$ is the crystal density of ammonium jarosite ($2960 \text{ kg m}^{-3}$).

In order to calculate the $\text{OH}^-$ consumption it is assumed that the average pH of the $\text{NH}_4^+$ and $\text{Fe}^{3+}$ feed streams equals 1.5. This is a somewhat rough assumption, because the pH value of the added mixture depends on the feed composition which was varied for the various experiments, but since the $\text{OH}^-$ feed stream was small compared to the $\text{NH}_4^+$ and $\text{Fe}^{3+}$ feed streams, the resulting inaccuracy was irrelevant.

The $\text{OH}^-$ flow needed for acid neutralization due to jarosite precipitation was calculated from:

$$\phi_3 \, c_{\text{OH}^-,3} = \frac{6 \, \phi_{\text{out}} \, M_t}{M_w}$$

(6.16)

The density of the suspension leaving the crystallizer is given by equation (6.17):

$$\rho_{\text{out}} = M_t + (1 - \frac{M_t}{\rho_{jar}}) \, \rho_{l,\text{out}}$$

(6.17)

The equations (6.13) to (6.17) contain 17 variables. The crystallizer volume $V$ is determined by the experimental equipment. The molecular weight and the crystal density of jarosite are known from literature.

From the remaining 14 variables nine are measured to solve the equations. These are: the fluxes $\phi_1$ and $\phi_2$ and their corresponding densities $\rho_1$ and $\rho_2$, the influx
concentrations $C_{\text{Fe},2}$ and $C_{\text{OH},3}$, the solution densities of the OH$^-$ stream, $\rho_3$, and the liquid outflux $\rho_{\text{liq},\text{out}}$ (after filtration) as well as the Fe$^{3+}$ concentration $C_{\text{Fe},\text{out}}$. Algebraic manipulation leads to explicit expressions for $\phi_{\text{out}}$, $\rho_{\text{out}}$, $\phi_3$, $\tau$ and $M_t$.

Appendix 6.3    Determination of the residence time distribution

Levenspiel [14] described a tracer method which is applicable to determine the residence time distribution of a solid phase in a chemical reactor. The general result, which yields an average residence time and the spread of the residence time distribution, is compared with the result obtained by assuming the crystallizer to operate as an ideal stirred tank reactor, which in crystallization literature is equivalent to an CMSMPR reactor. In order to be allowed to use the MSMPR equations derived for the crystal size distribution and thus for the crystal growth rate, the nucleation rate and the specific crystal surface area it is essential to know whether the results obtained by the tracer method satisfy the MSMPR concept. Moreover, the calculated residence times found by these two methods should not deviate from the value obtained from the iron and the mass balance (see appendix 6.2).

In the tracer method a normalized concentration function $E(t)$ is defined:

$$E(t) = \frac{\phi_v C_m(t)}{m} \quad (6.18)$$

Here, $m$ is the quantity of the tracer (g) at $t=0$, $\phi_v$ is the flow rate of the solution (l h$^{-1}$) and $C_m(t)$ is the concentration of the tracer (g l$^{-1}$) at $t=t$ in the outlet stream. Based on the measurement of $C_m(t)$ and $\phi_v$, $E(t)$ may be obtained. According to Levenspiel the average residence time can be found by solving the definite integral:

$$\tau_{av} = \int_0^\infty t E(t) \, dt \quad (6.19)$$

The spread of the residence time distribution, $\sigma^2$, is given by equation (6.20):

143
\[ \sigma^2 = \int_0^\infty t^2 \ E(t) \ dt - \tau^2 \] (6.20)

The value of the average residence time and the corresponding spread is found by integration using experimental data. The results from the tracer approach are now compared with the results obtained by assuming MSMPR behavior. In that case, a relationship between \( C_m(t) \) and \( t \) may be derived theoretically and yields:

\[ C_m(t) = C_{m,0} \exp \left( -t / \tau \right) \] (6.21)

This approach directly yields an average residence time from the slope of a plot of \( \ln C_m \) against time. The value of the spread of the residence time distribution is, in the MSMPR case, obtained by substituting the equations (6.18) and (6.21) into equation (6.20). This yields:

\[ \sigma^2_{\text{MSMPR}} = \frac{\Phi_v C_{m,0}}{m} \int_0^\infty t^2 \exp \left( -t \right) \ dt - \tau^2 \] (6.22)

with:

\[ \frac{\Phi_v C_{m,0}}{m} = \frac{1}{\tau} \] (6.23)

The definite integral is of the form

\[ \int_0^\infty x^n \exp \left( -ax \right) \ dx \] (6.24)

For \( n \) is a positive integer and for \( a > 0 \) (in this case \( a = 1/\tau \)) this integral equals: \( n! / a^{n+1} \) or, in this case, \( 2 \tau^3 \). Consequently, \( \sigma^2_{\text{MSMPR}} = \tau^2 \) in the MSMPR case.

**Appendix 6.4 The calculation of the supersaturation**

The supersaturation, as given in equation (6.8), is calculated by determining the free concentrations of \( \text{NH}_4^+, \text{Fe}^{3+}, \text{SO}_4^{2-} \) and \( \text{OH}^- \) from the total concentrations of \( \text{Fe}^{3+}, \text{SO}_4^{2-}, \text{NH}_4^+ \) and \( \text{H}^+ \). This is realized by defining the complexation equilibria,
by estimating the complex constants at 95°C and by solving a set of 17 equations with 17 variables [16]. It was shown [16], however, that this set-up did not yield correct values of the H⁺ activity, when the molar ratio of (total H⁺/total SO₄²⁻) was below 0.8. Because for all experiments carried out here this ratio is below 0.8, the method is unapplicable.

A significant difference between the batch experiments for which the method was developed and the continuously operated experiments in this study is that here the pH-level is kept constant. Thus, since the OH⁻ concentration is constant, it does not need to be included in the calculation routine.

A reasonable estimate for the supersaturation during these continuous experiments can thus be obtained from equation (6.9).

The OH⁻ concentration at pH = 1.5 equals $10^{(12.4+1.6)} = 1.3 \times 10^{-11}$ mole l⁻¹, since at 95°C, $k_w = 10^{-12.4}$. An equilibrium free ionic product which equals $2.1 \times 10^{-26}$ (mole l⁻¹)⁶ is obtained when substituting $1.3 \times 10^{-11}$ mole l⁻¹ for the OH⁻ concentration in the equilibrium free ionic product $\text{NH}_4^+ \times (\text{Fe}^{3+})^3 \times (\text{SO}_4^{2-})^2 \times (\text{OH}^-)^6 = 10^{-91}$ (mole l⁻¹)¹², determined by jarosite dissolution experiments. The free concentrations of Fe³⁺, SO₄²⁻ and NH₄⁺ are calculated using the method given in ref.[16].
Chapter 7

Precipitation of jarosite

III. Incorporation of impurities in batch experiments

ABSTRACT

The incorporation of Zn$^{2+}$, Cu$^{2+}$, Cd$^{2+}$, Co$^{2+}$, SbO$\_3^-$ and AsO$_4^{3-}$ in jarosite $(\text{NH}_4)_w(\text{H}_2\text{O})_x\text{Na}_y\text{K}_z\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ with $w + x + y + z = 1$ was studied from seeded batch experiments at $95^\circ$C. A mother liquor prepared by dissolving industrially calcined zinc concentrate in concentrated H$_2$SO$_4$, was neutralized with LiOH to a pH of 1.5 prior to the addition of the seeds as an ammonium containing suspension.

The incorporation of the divalent metals Zn, Cd, Co and Cu was quantified by a partition coefficient. The incorporation mechanism for these metals was isomorphous substitution of Fe$^{3+}$.

The AsO$_4^{3-}$ ions formed a separate phase, which included most of the SbO$_3^-$ ions although some SbO$_3^-$ and AsO$_4^{3-}$ ions may also be incorporated in the jarosite lattice. Factors affecting the incorporation behavior of impurities in jarosite are discussed.
7.1 INTRODUCTION

An iron precipitation process is essential in most hydrometallurgical zinc refining plants because zinc concentrate (50 - 60 wt% Zn) may contain up to 12 wt% iron, which combines during the roasting process with zinc to zinc ferrite. Zinc ferrite has to be dissolved in order to avoid the loss of zinc, but thereby yields dissolved iron. Iron must be removed, because it interferes with the zinc electrolysis process. Moreover, by precipitating an iron compound under the right conditions, other undesirable impurities contained in the concentrate, like arsenic, are effectively removed as well.

The negative aspect of precipitating iron, however, is the inadvertent loss of metals which have a sales value for a zinc plant, such as zinc, cadmium and copper. Defining the process' optimum from that point of view, processes are favored where iron, arsenic and some other impurities are effectively removed and zinc, cadmium and copper are not.

For the past 25 years the removal of iron from many hydrometallurgical zinc refining circuits was mostly carried out by operating the jarosite process, because this process fulfills the described demands at reasonable costs [1]. The jarosite precipitation reaction is given by equation (7.1):

\[ \text{X}^{+} + 3 \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 6 \text{H}_2\text{O} \rightarrow \text{XFe}_6(\text{SO}_4)_3(\text{OH})_6 + 6 \text{H}^+ \]  

(7.1)

where X = Na\(^+\), K\(^+\), NH\(_4\)\(^+\) or H\(_3\)O\(^+\). These four cations can easily substitute each other in the jarosite lattice.

In many industrial plants ammonia is added to generate the supersaturation required for jarosite precipitation. In that case the major part of the cations in the lattice will become NH\(_4\)\(^+\) ions. Since, however, the concentrate always contains Na\(^+\) and K\(^+\) and because H\(_3\)O\(^+\) is present since the precipitation occurs from a strongly acidic solution, a solid solution of H\(_3\)O\(^+\), Na\(^-\), K\(^-\) and NH\(_4\)-jarosite is unavoidable. Despite the fact that the name jarosite refers to the potassium containing mineral, it will here be adopted for the solid solutions.

Although jarosite precipitation for iron removal is mainly applied to zinc refining, it has also found application in manganese and copper processing [2,3].
A serious drawback is the fact that the produced jarosite residue has not found any application and is nowadays often stored in HDPE-lined ponds close to the zinc refineries, with precautions to prevent leakage of contaminated percolation water to groundwater resources. In some countries this solution is no longer regarded as acceptable and in the Netherlands, for instance, regulatory measures are in place which in the future will demand zinc refineries not only to produce an environmentally more acceptable residue, but also to treat historically disposed residues.

This calls for research focussed on the development of jarosite residue treatment processes [4], but also for a better understanding of the jarosite precipitation itself, in particular with respect to its tendency to incorporate impurities. The impurities are now not only important because of the loss of economic benefits, but also because of their influence on residue treatment costs.

This paper quantifies the incorporation of Co²⁺, SbO⁵⁺, Cd²⁺, AsO₄³⁻, Cu²⁺ and Zn²⁺ ions during a batchwise seeded jarosite precipitation from a dissolved industrial calcine sample. Attempts will also be made to explain their mode of uptake in the jarosite crystals.

7.2 THEORY

For the incorporation of foreign ions in crystal lattices three different modes are distinguished [5], viz. interstitial incorporation, coprecipitation and isomorphous substitution.

In case of *interstitial incorporation* the foreign ions are accomodated at interstitial lattice positions between the host lattice ions. Interstitial uptake is strongly dominated by the available interionic and interatomic space in the crystal lattice and its occurrence is rather hard to identify.

*Coprecipitation* is defined as the simultaneous precipitation of separate crystalline phases one being of the host crystals and the other consisting of a salt, which is usually less soluble than the host crystals. Usually, the crystals or conglomerates formed by the foreign phase have a smaller size than the host crystals and are attached to the host crystal surfaces or are even intergrown with these. In the
latter case this incorporation mode is hard to distinguish from the other uptake modes.

*Isomorphous substitution* is taking place when a foreign ion replaces a host lattice ion. In this case, the host ion and the impurity ion compete for the same lattice position. In order to quantify to what extent the impurity becomes distributed between the solid phase and the solution, a partition coefficient \( D \) is given by [5]:

\[
D = \frac{[M]_s / [H]_s}{[M]_l / [H]_l}
\]  
(7.2)

Here, \([M]\) represents the concentration of the foreign ions in the crystalline or solid phase and \([H]\) gives the concentration of the host ions for which the foreign ions can substitute. The subscripts \( s \) and \( l \) refer to the solid and the liquid phase respectively. The value of \( D \) is not only determined by thermodynamic, but also by kinetic factors.

The thermodynamic value of \( D \) for a given combination of host lattice and foreign ions can in principle be predicted theoretically, but this requires the knowledge about parameters such as:

i) the activity coefficients of the host ion and the foreign ion in the solution and the solid phase,

ii) the free energy required for transforming the MX lattice into a lattice, isomorphous with the HX lattice,

iii) the elastic deformation energy required for stretching the host lattice if the impurity ion is smaller or larger than the substituted ion and

iv) the thermodynamic solubility product of the MX and the HX solid phases.

Mostly, the required parameters are not known with a sufficient accuracy. Consequently, experimental data are often indispensable in determining the thermodynamically expected degree of incorporation of different impurities in a given host lattice.

In the above discussion, merely thermodynamical parameters were emphasized which are related to equilibrium conditions. Crystal growth and thereby impurity
uptake, however, requires a supersaturated solution which is characterized by a driving force towards equilibrium. Obviously, the value of the driving force, in other words, the kinetics of growth, also affect the degree of incorporation. The partition coefficient may either rise or fall with an increasing supersaturation but approaches an asymptotic value of one at very high crystal growth rates regardless of its thermodynamic equilibrium value. When the foreign ions have a strong attraction to the crystal surface, their concentration at the surface increases when more time is available for surface adsorption before the next growth layer is formed. This is the case at lower growth rates, which explains why D decreases from a thermodynamic value higher than one, to lower values at increasing supersaturation.

When, however, the foreign ions have a small affinity towards the crystal surface the thermodynamic D-value is smaller than one, and rises with an increasing growth rate, due to an enhanced chance to become entrapped by the faster propagating subsequent growth layers.

Despite the fact that a quantitative prediction of the partition coefficient is not feasible yet, some physical/chemical properties of the foreign ions in combination with the mother liquor seem to determine their degree of incorporation in the host lattice. These properties are:

i) the ionic radius; the closer the ionic radius of the impurity resembles the ionic radius of the host ion, the larger the uptake, owing to a minor increase in lattice strain caused by its uptake.

ii) the coordination number; if the coordination number of a foreign ion in its comparable salt is equal to that of the host ion the incorporation of the foreign ion is strongly favored.

iii) the valency; if the valency of a foreign is higher or lower than the valency of the the host ion, the degree of incorporation is expected. In practice, however, this rule is seldom obeyed, because other factors overrule the influence of the valency.
iv) the chemical nature; the mutual attractiveness of ions is influenced by the polarizability of their bonding orbitals. This is expressed as 'hardness' or 'softness'. 'Hard' cations preferably combine with 'hard' anions, so incorporation is favored by a comparable 'hardness' of host and impurity ions.

v) the dehydration free energy; a lower value of this parameter for the foreign ion compared to the host ion stimulates the incorporation, because in that case the foreign ion exchanges its hydration shell comparatively easily, which facilitates incorporation in the host crystal lattice.

vi) the dehydration frequency; the value of this parameter only influences the dependency of the incorporation on the growth rate. A host ion with a lower dehydration frequency than the foreign ion will give rise to an increasing incorporation with a higher growth rate, because the impurity becomes rather easily entrapped due to the relative ease by which it attains and loses its coordinating ligands.

vii) the activity coefficients of the host and the foreign ion; these represent the escaping tendency of a particular ion in a solution and are influenced by the mutual interaction of dissolved ions. Consequently, the activity coefficient itself is a response rather than a factor.

Since a number of the above mentioned properties are closely interrelated, observed relations between a change in properties of various impurities and a corresponding change in their incorporation are not necessarily causal.

For a number of impurities, which incorporation in jarosite will be determined below, the available data on their properties relevant for their incorporation, are listed in table 7.1.

7.3 EXPERIMENTAL

Two, in principle duplicate, batch precipitation experiments were carried out. The mother liquor for the experiments was prepared by mixing two solutions; a suspension which contained jarosite seeds and NH$_4^+$ ions and a clear liquid which contained dissolved industrial calcine.
<table>
<thead>
<tr>
<th>Property</th>
<th>Cd$^{2+}$</th>
<th>Cu$^{2+}$</th>
<th>Zn$^{2+}$</th>
<th>Co$^{2+}$</th>
<th>AsO$_4^{3-}$</th>
<th>SbO$_3^{-}$</th>
<th>SO$_4^{2-}$</th>
<th>Fe$^{3+}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic radius (pm)</td>
<td>109</td>
<td>87</td>
<td>88</td>
<td>72$^2$</td>
<td>246$^3$</td>
<td>168$^3$</td>
<td>244</td>
<td>69$^4$</td>
<td>[14-17]</td>
</tr>
<tr>
<td>Coordination no.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(with OH$^-$)</td>
<td>6</td>
<td>6</td>
<td>6</td>
<td>4</td>
<td>6-18$^6$</td>
<td>-</td>
<td>8$^6$</td>
<td>6$^7$</td>
<td>[16-19]</td>
</tr>
<tr>
<td>Hardness$^8$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( - )</td>
<td>soft</td>
<td>mod.</td>
<td>mod.</td>
<td>mod.</td>
<td>-</td>
<td>-</td>
<td>hard</td>
<td></td>
<td>[15]</td>
</tr>
<tr>
<td>$\Delta$H$_{\text{dehyd.}}$$^9$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(MJ mole$^{-1}$)</td>
<td>-1.69</td>
<td>-1.97</td>
<td>-1.92</td>
<td>-1.92</td>
<td>-</td>
<td>-</td>
<td>-4.2</td>
<td></td>
<td>[20]</td>
</tr>
<tr>
<td>$\nu$$_{\text{dehyd.}}$$^9$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Hz)</td>
<td>4*10$^8$</td>
<td>10$^9$</td>
<td>3*10$^7$</td>
<td>2*10$^5$</td>
<td>-</td>
<td>-</td>
<td>3*10$^2$</td>
<td></td>
<td>[21,22]</td>
</tr>
<tr>
<td>$K_{eq.}$ (95°C)$^{10}$</td>
<td>3.8</td>
<td>5.67</td>
<td>4.47</td>
<td>3.44</td>
<td>-</td>
<td>-</td>
<td>11.04</td>
<td></td>
<td>[23-27]</td>
</tr>
</tbody>
</table>

1. The As$^{5+}$ ion and Sb$^{5+}$ ion do not exist under the given conditions. Based on predominance diagrams AsO$_4^{3-}$ is the most abundant species containing As$^{5+}$ [10-12] and SbO$_3^{-}$ is the most abundant species containing Sb$^{5+}$ [13].
2. The radius corresponds to the high spin configuration in tetraedric Co$^{3+}$ complexes.
3. No ionic radius for AsO$_4^{3-}$ and SbO$_3^{-}$ was reported [15,17]. The estimate for AsO$_4^{3-}$ is the value of V$_{O_4}^{5-}$. This value is used because As$^{5+}$ and V$^{5+}$ have ionic radii in a 4-coordination of 47.5 and 49.5 pm respectively. The ionic radius of SbO$_3^{-}$ is estimated by using the value of V$_{O_4}^{5-}$. Both Sb and V have a 6-coordination in this configuration [16]. Since the ionic radii of V$^{5+}$ and Sb$^{5+}$ differ slightly for this coordination (68 and 74 pm resp.) the radius of SbO$_3^{-}$ is probably a few pm larger.
4. This ionic radius corresponds to a low spin electron configuration.
5. This figure is estimated by using PO$_4^{3-}$ data.
6. A coordination number of 8 is reported in H$_2$SO$_4$; in di- and trivalent metal solutions of SO$_4^{2-}$ coordination numbers between 6.4 and 9.6 are reported [17].
7. The coordination number of Fe$^{3+}$ in jarosite is 6 [19].
8. The 'hardness' of ions was not quantified, because the rule of the thumb that the hardness may be estimated by dividing the ionic radius of an ion (in pm) by its charge, does not reveal all characteristics of the hardness which may affect the incorporation of a foreign ion in a host lattice.
9. These data are related to 25°C.
10. This is the first hydrolysis constant, calculated at 95°C, for the reaction:

\[
M^{n+} + \text{OH}^- \rightarrow M\text{OH}^{(n+)}^-
\]

with:

\[
K = \frac{[M\text{OH}^{(n+)}^-]}{([M^{n+}] \cdot [\text{OH}^-])}
\]
preparation of the dissolved industrial calcine solution

Industrially produced calcine was used as a component for the mother liquor, since it not only consisted of ZnO and ZnO. Fe₂O₃, but also contained alkali ions and a mixture of all the relevant impurities. The calcine was obtained from a zinc refinery, operating a 9.5 m diameter fluid bed roaster at 910°C.

In total 150 g calcine was dissolved in a solution containing 375 ml H₂SO₄ (96 wt%) and 575 ml H₂O at 100°C. This solution was diluted, filtered and then partly neutralized with LiOH until the pH of the solution was 1.5 at 95°C. Lithium hydroxide was used for that purpose because lithium was proven not to affect the precipitation of jarosite [6]. The obtained solution is further called 'leach acid'.

preparation of the seeds

The jarosite seeds were prepared in a continuous process at 95°C at an average residence time of 1.25 hour. The feed Fe³⁺ concentration was 0.92 mole l⁻¹ and the feed NH₄⁺ concentration was 0.88 mole l⁻¹. The solutions were added in a stoichiometric ratio for jarosite formation. During the synthesis the pH was kept constant at 1.5 by adding LiOH. Details on the equipment are given in chapter five of this thesis [7].

preparation of the seeds solution and the mother liquor

For each experiment 17 g dry jarosite seeds were suspended in 200 ml of a dilute (NH₄)₂SO₄ solution and aged at 95°C for 115 hours for experiment 1 and 18 hours for experiment 2. The composition of the 'leach acid' and the solution of the seeds suspension was determined prior to their mixing. The 'leach acid' and the seeds suspension were separately heated to 95°C. After mixing, the slurry density of the obtained mother liquor was about 40 kg m⁻³ jarosite, which equals the slurry density used in the industrial jarosite precipitation process.

equipment, sampling and analytical procedures

The precipitation took place in a 500 ml round-bottom glass container which was immersed in an oil bath, kept at a temperature of 95°C and stirred vigorously at 800 rpm to avoid scaling.
During an experiment 18 solution samples were taken at regular time intervals over a period of 6.5 hours and immediately filtered. Solid samples were taken after about three hours and at the end of the experiment, by removing 25 ml solution. The solids were filtered, washed with diluted (5 wt%) \( \text{H}_2\text{SO}_4 \) to remove adhered and adsorbed impurities and subsequently dried at 35°C for two weeks. The elements Co, Zn, Fe, Cd, Cu, As and S in all solution samples were analyzed by Inductively Coupled Plasma atomic emission spectroscopy (ICP). Part of the solid samples were dissolved in 2 wt% HCl solution and analyzed in another way. The elements Cd, Cu, Zn, Fe, S and As were analyzed by ICP. The elements Cd, Zn and As in these samples were additionally analyzed by Atomic Absorption Spectroscopy (AAS, flame) and the elements Cd in the solid phase and Sb in the liquid phase were also determined with the AAS (furnace) technique. The elements Zn, Cd, Cu, Fe, As, Co, Sb, Na and K were analyzed in the solid phase by Inductive Neutron Activation Analysis (INAA). The reason why different analytical methods were required for determining the composition of the samples, is the difficulty in obtaining accurate results for elements like Co, Cu and Cd which are present in concentrations of typically 0.1-10 ppm in a solid phase which contains about 31 wt% Fe.

7.4 RESULTS AND DISCUSSION

7.4.1 Composition of the mother liquor

The composition of the 'leach acid' and of the solution filtered from the seeds suspension is given in table 7.2 with, for some elements, their standard deviations calculated on basis of six samples. Table 7.2 also gives the composition of the solution which is obtained by mixing the seeds suspension with the 'leach acid'.

7.4.2 Precipitation of jarosite

The precipitation of jarosite was followed by determining the \( \text{Fe}^{3+} \) concentration in the mother liquor in time. Figure 7.1 shows the decrease of the \( \text{Fe}^{3+} \) concentration for both experiments. Despite the fact that both experiments were duplicates, the final \( \text{Fe}^{8+} \) concentrations were different for both experiments.
Table 7.2  The composition of the 'leach acid', the seeds solution and the mother liquor for both experiments in ppm

<table>
<thead>
<tr>
<th>element</th>
<th>'leach acid'</th>
<th>'seeds' solution</th>
<th>mother liquor at t = 0 exp. #1</th>
<th>exp. #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>(3.10 ± 0.02) * 10³</td>
<td>89</td>
<td>1.70 * 10³</td>
<td>1.70 * 10³</td>
</tr>
<tr>
<td>Zn</td>
<td>(12.8 ± 0.2) * 10³</td>
<td>0</td>
<td>7.64 * 10³</td>
<td>7.6 * 10³</td>
</tr>
<tr>
<td>Cu</td>
<td>80.3 ± 0.7</td>
<td>0</td>
<td>44.0</td>
<td>44.0</td>
</tr>
<tr>
<td>Cd</td>
<td>62.4 ± 0.9</td>
<td>0</td>
<td>34.4</td>
<td>34.4</td>
</tr>
<tr>
<td>As</td>
<td>59.5 ± 2.1</td>
<td>0</td>
<td>32.0</td>
<td>32.0</td>
</tr>
<tr>
<td>S</td>
<td>(69.5 ± 0.6) * 10³</td>
<td>10.9 * 10³</td>
<td>41.9 * 10³</td>
<td>42.0 * 10³</td>
</tr>
<tr>
<td>K</td>
<td>45</td>
<td>3</td>
<td>26.4¹</td>
<td>26.4¹</td>
</tr>
<tr>
<td>Na</td>
<td>15</td>
<td>9</td>
<td>11.5¹</td>
<td>11.5¹</td>
</tr>
<tr>
<td>Co</td>
<td>2.35</td>
<td>0</td>
<td>1.3¹</td>
<td>1.3¹</td>
</tr>
<tr>
<td>Sb</td>
<td>6.9</td>
<td>0</td>
<td>3.9</td>
<td>3.7</td>
</tr>
</tbody>
</table>

¹ Calculated on basis of the concentration in the 'leach acid' and in the solution which contained the seeds.

Figure 7.1: The Fe³⁺ concentration in solution as a function of time for the experiments #1 (line (A)) and #2 (line (B))
The longer aging period of the seeds in experiment 2 can only explain a difference in their total surface area and thus in their conversion rate, but not in their ultimate conversion. Apparently the difference indicates the reproducibility of the experiments.

Figure 7.2 shows the production rate of jarosite (in mg min⁻¹) as a function of the conversion time. The production rate at t = 0 starts at 50 respectively 75 mg min⁻¹ for experiment 1 and 2, which corresponds to 7 respectively 10 kg m⁻³ hr⁻¹.

![Figure 7.2: The jarosite production rate for the experiments #1 (line (B)) and #2 (line (A))](image)

In table 7.3 the Na⁺, K⁺ and Fe³⁺ concentrations in the newly formed phase are given. The observed Fe³⁺ deficiency (theoretical value: 34.9 wt% Fe in e.g. NH₄Fe₃(SO₄)₂(OH)₇) seems characteristic for jarosite and was also reported by Dutrizac [9]. The alkali concentration in the jarosite phase is below stoichiometrical (theoretical: 7.8 wt% K in KFe₃(SO₄)₂(OH)₇ or 4.8 wt% Na in NaFe₃(SO₄)₂(OH)₇). The remainder (about 75 %) of the monovalent positions in the jarosite lattice is therefore supposed to be occupied with NH₄⁺ or H₂O⁺ ions.

### 7.4.2 Incorporation of impurities

In the following the incorporation of the divalent metals zinc, cadmium, copper and cobalt will be discussed first, followed by a separate discussion of arsenic and antimony, which appeared to behave in a different way.
Table 7.3 The concentration Na⁺, K⁺ and Fe³⁺ in the solid samples

<table>
<thead>
<tr>
<th>code</th>
<th>Fe³⁺ wt%</th>
<th>Na⁺ wt%</th>
<th>K⁺ wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3¹</td>
<td>31.3 ± 0.6</td>
<td>0.44</td>
<td>1.19</td>
</tr>
<tr>
<td>1.6</td>
<td>30.7 ± 0.4</td>
<td>0.44</td>
<td>1.19</td>
</tr>
<tr>
<td>2.3</td>
<td>30.2 ± 0.4</td>
<td>0.37</td>
<td>0.98</td>
</tr>
<tr>
<td>2.6</td>
<td>31.8 ± 0.4</td>
<td>0.37</td>
<td>0.98</td>
</tr>
</tbody>
</table>

¹ The code is: number of experiment, reaction time when sampling (hours)

**incorporation of Zn²⁺, Cu²⁺, Cd²⁺ and Co²⁺**

The incorporation is quantified by the partition coefficient D defined in equation (7.2) which is only relevant in case of isomorphous substitution of Fe³⁺. This assumption seems reasonable given the results of Dutrizac [28] who shows that an increasing incorporation of the metal ions Co²⁺, Cu²⁺ and Zn²⁺ in jarosite proceeds parallel with a decreasing Fe³⁺ concentration in the solid phase without the formation of a non-jarosite phase and without a decrease of the alkali concentration in the jarosite phase.

For a comparison of the incorporation behavior of the various ions, their partition coefficient is needed, since at least its thermodynamic value should be independent of the operating conditions like the value of the impurity concentration in the solution.

It is, however, also interesting to know the mass percentage of the impurity MPI in the solid phase since this ratio is a direct measure of the absolute amount of impurities taken up by the solids under the given conditions. Both the D-values and the mass percentage impurity MPI in jarosite are given in table 7.4 for all four cationic impurities.

For Zn²⁺ the D value as well as the total uptake of jarosite are about the same as those reported in chapter six of this thesis for the continuous precipitation of ammonium jarosite from chemically pure starting materials. The results obtained
for Co$^{3+}$, Cd$^{2+}$ and Cu$^{2+}$ are therefore also considered to be reliable estimates for their values in continuous jarosite processing.

These results can also be compared with those obtained by Yaroslavtsev [29], who quantified the uptake of 16 elements in potassium jarosite at 90°C by K values.

$$K = \frac{\text{mass percentage impurity of jarosite}}{\text{dissolved concentration of the impurity} \ (g/100cc)}$$ (7.3)

For much higher Zn$^{2+}$ concentrations in the solution ranging from 3.2 - 16.3 g/100 cc, he reported K values of 0.20 - 0.08, while in this study with a Zn$^{2+}$ solution concentration of 0.76 g/100 cc and a mass Zn$^{2+}$ percentage in jarosite of 0.38, a K value of 0.38 was found. This higher K value for a jarosite consisting mainly of ammonium jarosite is unexpected, since Dutrizac [28] reported earlier that more Zn$^{2+}$ was incorporated in potassium than in ammonium jarosite under the same synthesis conditions. If the partition coefficients for Zn$^{2+}$ are calculated from Dutrizac's experimental data [28], D values are found between 0.001 and 0.0025, which match very well with the D value of 0.0019 obtained here.

Table 7.4  The incorporation of Zn$^{2+}$, Cd$^{2+}$, Cu$^{2+}$ and Co$^{2+}$ in jarosite

<table>
<thead>
<tr>
<th></th>
<th>D, exp.1</th>
<th>MPI,exp.1</th>
<th>D, exp.2</th>
<th>MPI,exp.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(-)</td>
<td>(g/kg)</td>
<td>(-)</td>
<td>(g/kg)</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>1.9 * 10$^{-3}$</td>
<td>3.8</td>
<td>1.9 * 10$^{-3}$</td>
<td>3.8</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>2 - 6 *10$^{-4}$</td>
<td>0.004$^2$</td>
<td>2 - 6 *10$^{-4}$</td>
<td>0.004</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>1.5 * 10$^{-2}$</td>
<td>0.18</td>
<td>1.6 * 10$^{-2}$</td>
<td>0.18</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>9.5 * 10$^{-3}$</td>
<td>0.0038</td>
<td>1.2 * 10$^{-2}$</td>
<td>0.0045</td>
</tr>
</tbody>
</table>

In calculating the partition coefficient for these ions the average Fe$^{3+}$ concentration in solution (1200 ppm) was used. It is shown that the incorporation of Zn$^{2+}$ is related to the supersaturation [8] and thereby to the growth rate. In this study, as a first estimate, the average partition coefficient is used.

2 The analysis of Cd in the solid phase yielded a considerable spread in the results which is also reported in the D-value. The concentration value in g/kg is averaged.
For the incorporation of Cu\(^{2+}\) in jarosite, Yaroslavtsev [29] reported a K-value of 1.0 - 0.56 for solutions containing 0.32 - 1.60 (g/100 cc). In this study (Cu\(^{2+}\) = 4.4 \times 10^{-3} \text{ g/100 cc}, \text{ mass percentage Cu}\(^{2+}\) in jarosite: 0.018) a K value of 4.1 was calculated. Dutrizac [28] reported results, which, if quantified by the partition coefficient D, range between 0.004 and 0.01, whereas in this study D = 0.016 was found. Differences in K or D of about one order of magnitude can easily be explained from kinetic effects such as differences in the production rates, which have not been taken into account here.

For Cd\(^{2+}\) incorporation Yaroslavtsev [29] reported a K-value of 0.02 for solution concentrations of 0.056 - 1.12 (g/100 cc). In this study (Cd\(^{2+}\) = 3.4 \times 10^{-3} \text{ g/100 cc}, \text{ mass percentage Cd}\(^{2+}\) in jarosite: 4 \times 10^{-4}) a higher K value of 0.12 was calculated. The partition coefficient D, based upon the results reported by Dutrizac [28] ranges between 10^{-4} and 10^{-3} for Cd\(^{2+}\). In this study D = 2 - 6 \times 10^{-4} was found which is in good accordance with the results of Dutrizac.

For the incorporation of Co\(^{2+}\) Yaroslavtsev [29] reported a K-value of 0.5 - 1.2 for a solution concentration range of 0.008 - 0.02 (g/100 cc). In this study (Co\(^{2+}\) = 1.3 \times 10^{-4} \text{ g/100 cc}, \text{ mass percentage Co}\(^{2+}\) in jarosite: 3.6 - 4.5 \times 10^{-4}) a slightly higher K value of 2.8 - 3.5 was calculated. The partition coefficient D, based upon the results reported by Dutrizac [28] ranges between 1.4 - 2.6 \times 10^{-3} while in this study a significantly higher D = 1.0 - 1.2 \times 10^{-2} was found. It is not clear what has caused the differences between the results of Dutrizac and of this study.

In summary the partition coefficient for the incorporation of the divalent metals decreases in the sequence: Cu > Co > Zn > Cd. Apart from the Co\(^{2+}\) incorporation, this sequence resembles the one reported by Dutrizac [28], which was equal to the sequence of the first hydrolysis constant of the respective divalent metal ions, Cu > Zn > Cd > Co as given in table 7.1. The difficulty in determining the low Co concentration in jarosite in these experiments may have caused an error in the D value for Co.
The formula of jarosite may be written as $X(\text{Fe(OH})_2)_2(\text{SO}_4)_2$. In this structure $\text{Fe(OH})_2^+$ is probably substituted by a monovalent foreign cation which is likely to be $\text{M(OH})^+.\text{H}_2\text{O}$ where $\text{M}$ is $\text{Zn}^{2+}$, $\text{Co}^{2+}$, $\text{Cu}^{2+}$ or $\text{Cd}^{2+}$.

The ionic radius is usually the most important parameter determining the incorporation of a foreign ion in a crystal lattice. In this case, where the incorporating cation still has two ligands, the radius of the substituting complex cations is not known, but due to the presence of the two ligands might be less critical. Another factor related to metal-ligand complexation is the coordination number of the metal. For $\text{Co}^{2+}$ a coordination number of four is reported for the tetraedric hydroxide complex [16], which is different from the usual coordination number of six observed for the other metals discussed in this study. This is also a factor that determines the comparatively low incorporation of $\text{Co}^{2+}$ as observed by Dutrizac [28].

The 'hardness' of the ions $\text{Zn}^{2+}$, $\text{Co}^{2+}$ and $\text{Cu}^{2+}$ is classified as moderate, $\text{Fe}^{3+}$ is classified as hard and $\text{Cd}^{2+}$ is classified as soft. This additionally explains why the incorporation of $\text{Cd}^{2+}$ is comparatively low.

Although $\text{Fe(OH})_2^+$ and $\text{M(OH})^+.\text{H}_2\text{O}$ are made up of metal ions with a different valency, there are sufficient possibilities for the lattice to remain neutral. In this case the co-incorporation of $\text{H}_2\text{O}$ simultaneously leads to a charge-neutral and probably an isostructural substitution. Therefore, the charge of an incorporating foreign ion often does not allow to predict the degree of incorporation of that ion. The dehydration energy of the divalent metal ions $\text{Cd}^{2+}$, $\text{Cu}^{2+}$, $\text{Co}^{2+}$ and $\text{Zn}^{2+}$ is considerably lower than the value for $\text{Fe}^{3+}$. This, however, does not simply justify to assume that their mutual difference is not important. In case of the impurity incorporation in jarosite this factor is, however, probably not of importance, since e.g. $\text{Cd}^{2+}$, having the lowest dehydration energy which would facilitate incorporation, shows a comparatively small incorporation.

The dehydration frequency of the four divalent metal ions is considerably higher than the value of $\text{Fe}^{3+}$. This means that a higher ligand exchange rate exists for these metals compared to $\text{Fe}^{3+}$, but no direct relationship between this exchange rate and the incorporation of $\text{M(OH}}^+.\text{H}_2\text{O}$ complexes in the jarosite lattice is observed.
The behavior of $\text{AsO}_4^{3-}$ and $\text{SbO}_3$

In contrast to the concentration of the divalent ions in the liquid phase which remained about constant throughout the experiments 1 and 2, the concentration of dissolved $\text{AsO}_4^{3-}$ and $\text{SbO}_3^-$ decreased with time. This points at a significant uptake of both species either by incorporation in the jarosite lattice or by coprecipitation. Figure 7.3 shows the arsenic concentration in the solution for the experiments 1 and 2 as a function of time.

![Graph showing arsenic concentration over time](image)

Figure 7.3: The arsenic concentration in the solution as a function of time for the exp. #1 (line (B)) and #2 (line (A)). For experiment #1 a steady decrease of the concentration was measured, whereas for experiment #2 a more or less constant arsenic concentration was measured.

The antimony concentration in the solution shows a similar pattern for both experiments. The antimony concentration starts at about 3.8 ppm for both experiments and decreased in six hours to 1.9 ppm in experiment 1 and to 3.5 ppm in experiment 2. Despite the fact that experiment 1 and 2 were meant to be duplicates, a difference in the behavior of arsenic and antimony was observed in the two experiments. In experiment 2 the arsenic concentration only decreases as long as the $\text{Fe}^{3+}$ concentration decreases. After the precipitation of jarosite had virtually stopped the concentration of arsenic (and antimony) remained constant. The arsenic concentration of the newly formed solid phase (corrected for the presence of seeds) was $3.4 \times 10^3$ ppm.
In experiment 1 the arsenic concentration in solution decreased proportionally with the Fe$^{3+}$ concentration during the first 30 minutes of the experiment. After the jarosite precipitation rate had become negligible, the decrease of the arsenic (and antimony) concentration, however, continued with time. At the end of experiment 1 the newly formed solids contained $5.9 \times 10^3$ ppm As.

A material balance comparing the initially dissolved arsenic and antimony quantities with the observed liquid and solid contents of arsenic and antimony after six hours, showed that about 50 wt% of both arsenic and antimony have been taken up by the solid phase. The explanation for the observed behavior of antimony and arsenic could be as follows. In experiment 2 the decrease of the arsenic concentration as a function of time resembles the decrease of the Fe$^{3+}$ concentration which points at a direct relationship between jarosite growth and the decrease of the arsenic concentration. Due to the low AsO$_4$$^{3-}$ concentration (<1000 ppm) in the solid phase (including the seeds) no XRD-identification of a crystalline arsenate form is feasible, even if all arsenate were coprecipitated as a separate phase.

Robins and co-workers claim that a basic ferric arsenate, in this case a jarosite phase in which sulfate is substituted by arsenate, is non existent [10,21,30]. Even the existence of the mineral beudantite (PbFe$_3$SO$_4$AsO$_4$(OH)$_6$) is questioned. The results obtained in experiment 2, should according to Khoe [31], be interpreted as interstitial incorporation rather than as isomorphous substitution. The reason why interstitial incorporation may occur is that jarosite characteristically grows with lattice defects. In the jarosite formula MFe$_x$(SO$_4$)$_y$(OH)$_6$ the value of $x$ is usually lower than three. These lattice defects provide the space for interstitial incorporation of impurities. Dutrizac and Jambor [32], however, suggest that up to 2% of the sulfate in jarosite may be substituted isomorphously by the incorporation of AsO$_4$$^{3-}$, although Dutrizac points out that the size of AsO$_4$$^{3-}$ is somewhat larger than that of SO$_4$$^{2-}$ (see table 7.1). This, in comparing beudantite and lead jarosite lattices, does not significantly affect the unit cell parameters, which for beudantite (a = 7.32 Å; c = 17.02 Å) are almost similar to those for lead jarosite (a = 7.32 Å; c = 16.90 Å). The results obtained in experiment 2 do not enable to determine the incorporation mechanism for this system.
In experiment 1 initially the decrease of the arsenic concentration is also related to the growth of jarosite but after the jarosite precipitation has stopped the arsenic and antimony concentration remain decreasing linearly with time. This shows that at this later stage the precipitation of arsenic and antimony is independent from the precipitation of jarosite. This was shown earlier by Karoleva and co-workers [33], Dutrizac [32] and Robins [10]. The arsenate may then precipitate as scorodite (FeAsO$_4$.2H$_2$O) in either a crystalline or an amorphous form. Apparently the solution prepared for the precipitation of jarosite is also supersaturated for the coprecipitation of scorodite. The fact that in experiment 1 the coprecipitation of scorodite does occur and in experiment 2 apparently not or not to the same extent, shows that this scorodite precipitation is badly reproducible. This lack of reproducibility could follow from the induction time for this precipitation process which may vary in different experiments, although the process conditions are equal.

The behavior of antimony is similar to that of arsenic. Antimony, in experiment 2, incorporates in some form in the jarosite structure, probably via interstitial incorporation. The newly produced jarosite in experiment 2 contained $1.0 \times 10^2$ ppm Sb. In experiment 1, however, antimony is contained in the solid phase to a much higher extent since at the end of the experiment the newly formed solids contained $7.0 \times 10^2$ ppm Sb. This indicates that Sb coprecipitates with or incorporates into the scorodite phase more easily than it coprecipitates into the jarosite phase.

Because of the observed behavior of AsO$_4^{3-}$ and SbO$_3^-$ it does not make sense to define a partition coefficient for these elements based on isomorphous substitution as incorporation mechanism. Therefore a quantitative comparison of the results obtained in this study with the results obtained by Yaroslavtsev [29] does not make sense.

The knowledge that in precipitating jarosite, arsenic and in particular antimony may to a large extent be present as a crystalline/amorphous solid product which is coprecipitated as a separate phase from jarosite may be useful in designing jarosite treatment processes in which arsenic and antimony need to be separated from most of the iron precipitate.
7.5 CONCLUSIONS

The degree of incorporation of divalent metals in ammonium jarosite is primarily related to the first hydrolysis constant of these metals although, probably due to an experimental inaccuracy, this was not sustained by the obtained data for the incorporation of Co$^{2+}$ in jarosite. The higher the hydrolysis constant, the larger the incorporation of these metals in the jarosite lattice. The mechanism of the incorporation of divalent metals in the jarosite lattice is probably isomorphous substitution of M(OH)$^\cdot$H$_2$O for Fe(OH)$_2^+$ ions. The incorporation of arsenic and antimony in the jarosite lattice is limited. Controversy exists in literature whether the arsenate ion can substitute for a sulfate ion or not. The results obtained in this study show that there is a relationship between the production rate of jarosite and the rate of incorporation of arsenic. The removal of arsenic from a solution can also proceed via coprecipitation of a iron arsenate phase, which may be scorodite. The uptake of antimony either in or coprecipitated with the scorodite phase is much higher than its incorporation in the jarosite phase.

ACKNOWLEDGEMENT

The Dutch Ministry of Housing, Physical Planning and the Environment is gratefully acknowledged for the financial support for this study. M. Koppelaar-van der Aa is acknowledged for her contribution to this study.

7.6 REFERENCES


[8] Chapter 6, this thesis.


[25] Chapter 4, this thesis.

166
Chapter 8

Incorporation of zinc in ferrous sulfate monohydrate

ABSTRACT

Continuous crystallization experiments of FeSO$_4$.H$_2$O in aqueous solutions containing Zn$^{2+}$ were carried out at temperatures of 140 - 165°C in a stainless steel/glass 1.1 liter autoclave. The experiments were aimed at determining the incorporation of Zn$^{2+}$ in FeSO$_4$.H$_2$O as a function of process parameters such as the temperature and the residence time. Additionally the solubility of FeSO$_4$.H$_2$O in this temperature region in the presence of ZnSO$_4$ was determined.

The crystallization of FeSO$_4$.H$_2$O yielded a product which contained between 2 and 3 wt% Zn$^{2+}$, depending on the process conditions. The incorporation of Zn$^{2+}$ was also quantified using a partition coefficient which, together with the calculated results for the supersaturation in the various experiments, revealed that the incorporation of Zn$^{2+}$ in FeSO$_4$.H$_2$O increased with the supersaturation, but mainly by the thermodynamic value of the partition coefficient, i.e. a supersaturation value of zero equal to 0.3.

The separation of Fe$^{2+}$ and Zn$^{2+}$ from aqueous solutions by crystallization of FeSO$_4$.H$_2$O has a too low selectivity to justify its use in an integrated hydrometallurgical jarosite treatment process.
8.1 INTRODUCTION

In hydrometallurgical zinc winning processes large quantities of iron containing residues are formed because 2 - 12 wt% iron is inadvertently present in zinc concentrate. The iron residues jarosite (NH₄Fe₃(SO₄)₂(OH)₆) and goethite (FeOOH) have not found any applications because of their contamination with heavy metals such as lead, zinc and cadmium and with arsenic. Therefore, they have to be disposed in HDPE-lined ponds which have been built in the neighborhood of zinc winning companies. Despite the fact that protective measures are taken to prevent leakage of contaminated water from the disposal ponds to the soil, more and more pressure is nowadays exerted on zinc winning companies to search for processes which yield environmentally more acceptable residues. In The Netherlands even the historically disposed jarosite residue will have to be reprocessed in the near future.

This calls for residue treatment processes aimed at converting iron residues formed in hydrometallurgical zinc winning to products which may find application in civil engineering or in (non ferrous) metal industries. Recently, five residue treatment processes aimed at processing a jarosite residue [1] were described in literature. One of these processes, the integrated hydrometallurgical jarosite treatment process, includes a process-step in which a ferrous and zinc sulfate solution is crystallized in a cascade of autoclaves at a temperature of about 160°C. Under these conditions ferrous sulfate monohydrate (FeSO₄.H₂O) is formed which contains a small amount of zinc, which means that the remaining mother liquor has become enriched in zinc compared to the feed. The process is based on the considerably lower solubility of pure FeSO₄.H₂O compared with pure ZnSO₄.H₂O at 160°C, which should lead to a comparatively high selectivity for the crystallization of FeSO₄.H₂O. Figure 9.1 shows the solubility of pure FeSO₄.H₂O and pure ZnSO₄.H₂O as a function of temperature.

This paper discusses the equipment required to perform the crystallization experiments and provides the obtained results.
Figure 8.1: The solubility of pure FeSO₄·H₂O and pure ZnSO₄·H₂O as a function of temperature [2]

8.2 THEORY

The driving force for the crystallization of FeSO₄·H₂O is quantified in equation (8.1) by defining a dimensionless supersaturation $\beta$:

$$\frac{\Delta \mu}{RT} = \beta = \ln \left( \frac{a_{Fe^{2+}} a_{SO_{4}^{2-}} a_{H_{2}O}}{(a_{Fe^{2+}} a_{SO_{4}^{2-}} a_{H_{2}O})_{eq}} \right)$$ (8.1)

In equation (8.1) $a_i$ represents the activity of species $i$ in the solution, $\Delta \mu$ is the driving force for the phase transition (J mole⁻¹), $R$ represents the gas constant 8.314 J mole⁻¹ K⁻¹ and $T$ is the absolute temperature in K. The subscript eq in the nominator indicates the equilibrium situation which is strongly depending on temperature. The activity of a species $i$ is given by equation (8.2):

$$a_i = \gamma_i C_i$$ (8.2)

where $\gamma_i$ is the dimensionless activity coefficient and $C_i$ is the concentration expressed in mole l⁻¹. Calculation of the activity coefficients for FeSO₄·H₂O at
elevated temperatures, using Pitzer's equations [3,4], requires knowledge of the constants in these equations for FeSO₄ and ZnSO₄. The constants for FeSO₄ are not known at temperatures beyond 70°C and extrapolating these temperature-dependent constants to 140 - 165°C seemed unacceptable. Consequently, it was not possible to calculate the activity coefficients for this FeSO₄/ZnSO₄ mixture at temperatures of 140 - 165°C. For this reason, and because the water activity of the supersaturated solution is not expected to be much different from that of the saturated solution, equation (8.1) was simplified to equation (8.3):

\[
\beta = \ln \left( \frac{c_{Fe^{2+}} \cdot c_{SO_4^{2-}}}{(c_{Fe^{2+}} \cdot c_{SO_4^{2-}})_{eq}} \right)
\]

(8.3)

Here the ionic product at equilibrium no longer equals the thermodynamic solubility product. In order to calculate \( \beta \) it is essential to know the ionic product of FeSO₄·H₂O in the FeSO₄/ZnSO₄ solutions used in the experiments at temperatures from 140 to 165°C. The solubility of FeSO₄·H₂O is, however, affected by the presence of zinc sulfate in the solution, owing to the presence of the additional sulfate ions, and may therefore not be calculated from solubility data obtained for pure ferrous sulfate solutions. For this reason the solubility data were obtained from a solution with a Zn²⁺/Fe²⁺ molar ratio of 0.1 which was the same as the solution fed into the continuous crystallization experiments.

The incorporation of zinc in FeSO₄·H₂O was quantified by a partition coefficient \( D \) as:

\[
D = \frac{[Zn]_s / [Fe]_s}{[Zn]_l / [Fe]_l}
\]

(8.4)

These \( D \) values were determined from continuous crystallization experiments. Factors affecting the partition coefficient for a particular system of a host crystal and an impurity were already discussed in the previous chapter of this thesis.
8.3 EXPERIMENTAL

8.3.1 Determination of the solubility of FeSO$_4$.H$_2$O in aqueous FeSO$_4$/ZnSO$_4$-solutions

The solubility of FeSO$_4$.H$_2$O in the presence of Zn$^{2+}$ was determined from two batch experiments. In these experiments an aqueous solution was used which contained 1.62 mole l$^{-1}$ Fe$^{2+}$, 0.162 mole l$^{-1}$ Zn$^{2+}$ and 1.809 mole l$^{-1}$ SO$_4^{2-}$. In order to prevent oxidation of Fe$^{2+}$ during the preparation of the solution, the solution was acidified by adding H$_2$SO$_4$ which caused the SO$_4^{2-}$ concentration to be slightly higher than the sum of the Fe$^{2+}$ and the Zn$^{2+}$ concentrations. For the same purpose, in preparing the solution, as well as during the experiments itself, an N$_2$ blanket was applied. The N$_2$ gas contained less than 3 ppm O$_2$.

The solution was heated in a 1.5 liter autoclave with a heating jacket filled with oil. This enabled control of the temperature in the autoclave within ± 0.3 °C. In order to prevent boiling phenomena, the reactor pressure was kept at least 1 bar above the boiling pressure of H$_2$O at that temperature by using N$_2$ gas. Changes in pressure of this order of magnitude had no effect on the solubility data through their influence on the water activity.

During the experiments the solution was stirred at 400 rpm with a two-blade impeller.

In experiment 1 the solution was heated to 140°C with a temperature increase rate of 1 K min$^{-1}$ and then kept at 140°C for three hours. The time interval of three hours included a safety margin, because equilibrium was reported to be obtained already after two hours in comparable experiments [5]. After 2, 2.5 and 3 hours liquid samples were taken, using a procedure which will be described in a subsequent section. The concentrations of Fe$^{2+}$ and Zn$^{2+}$ in the solution samples were determined by Atomic Absorption Spectroscopy (AAS). After three hours at 140°C the solution was heated to 150°C and the sampling procedure was repeated. The same procedure was also carried out after heating to 160°C and 170°C respectively.

In experiment 2 the solution was directly heated to 165°C (dT/dt = 1 K min$^{-1}$) and kept at 165°C for three hours while liquid samples were taken after 1, 2, 2.5 and
3 hours. The sampling procedure was then repeated with a time interval of an hour for four hours after the solution was cooled down to 155°C and thereafter to 145°C respectively.

8.3.2 Continuous crystallization of FeSO₄·H₂O at 140-160°C

preparation of the solution

The solution which was fed into the continuous crystallizer was prepared by dissolving 0.582 kg FeSO₄·7H₂O and 0.0602 kg ZnSO₄·7H₂O per kg demineralized water. Before and during the preparation as well as during the experiments N₂ gas was bubbled through the solution to remove dissolved O₂ and to provide an N₂ blanket over the solution which was kept in a closed vessel. Additionally, 1 ml of 96 wt% H₂SO₄ was added to further prevent the oxidation of Fe²⁺. The solution was stored during the experiments in a 25 l steel double wall cylindrical vessel, which was heated with water via a heating jacket to 40°C. The heating was required to dissolve all the solids because below 80°C the solubility of both FeSO₄ and ZnSO₄ still increases with increasing temperature (see figure 8.1). During the preparation the solution was stirred with a teflon-coated two-blade stirrer at 200-300 rpm.

installed equipment

A schematic of the installed equipment is given in figure 8.2. Here some pieces of the equipment will be described. The procedures which were used for carrying out the experiments and taking the samples will be discussed in following sections. Unit A in figure 8.2 represents a 50 liter, 200 bar N₂ cylinder which is used for the supply of N₂ gas in storage vessel C and for maintaining the desired pressure in reactor G and product vessel K. The supply of N₂ gas to storage vessel C is controlled by operating a flow-adjusting valve V6 and a rotameter to measure the flow. The N₂ gas is bubbled through a perforated plate which is located at the bottom of vessel C, just below the stirrer. The liquid level in vessel C was observed by using a float. Additionally, thermostat bath B and vessel C were both put on a 150 kg range balance with an accuracy of ± 0.5 gram to register the (nett)
weight of the solution. The balance was connected to a personal computer which registered the weight and calculated the flow rate during the continuous experiments. The balance and the PC are not included in figure 8.2.

![Figure 8.2: A schematic of the installed equipment](image)

The feed solution was pumped from vessel C to reactor G via membrane pump F. Membrane pump F could yield a flow rate which corresponded with suspension residence times varying between 0.5 and 2.0 hours. The inaccuracy of the flow was below 1 wt%.

The connecting pipe between vessel C and reactor G was heated with a heating tape. This enabled heating of the feed to temperatures of 105°C. Preheating of the feed was essential to reach the desired steady state temperature in reactor G. Reactor G was a 1.5 liter cylindrical (L:D = 2:1) double-wall autoclave with a jacket filled with heating oil. The cylinder was made from glass because this allowed observation of the liquid level, which was essential for manual control of
the liquid level during the continuous process. The level control procedure will be discussed in a subsequent section.

The bottom and the topside of reactor G as well as all piping and valves and the storage and the product vessel (C and K) were made of AISI 316 L - stainless steel. The effective volume of reactor G was 1.1 liter, because space was required for internals (stirrer, sampling pipe, thermo-element tube etc.) and because in the continuous experiments the reactor was not entirely filled.

The heating oil was thermostated in a 4 kW heating unit H. The temperature in reactor G was automatically controlled by adjusting the oil flow from the heating unit H. The resulting inaccuracy in the suspension temperature was below ±0.3°C. The temperature in reactor G was measured with a Pt-100 element immersed in a tube filled with heating oil. Temperatures were recorded of the feed in vessel C, of the feed in the heated piping to the reactor, of the suspension in reactor G and of the heating oil. The temperature difference between the heating oil and the suspension in the reactor was not allowed to exceed 50°C for safety reasons. This constraint and the fact that for safety reasons the temperature of the heating oil had to be kept below 210°C determined the maximum temperature of the suspension. As a result this maximum suspension temperature in the reactor was limited to 150°C for a suspension residence time of 0.5 hours, to 155°C for 1 hour, to 160°C for 1.5 hours and to 165°C for 2 hours.

The suspension in the reactor was stirred at 400 rpm with a two-blade impeller. The pressures in reactor G and product vessel K were measured independently. In order to prevent boiling phenomena, the reactor pressure was kept at least 1 bar above the boiling pressure of H₂O at that temperature by using N₂ gas. A safety valve V18 was installed in direct connection with reactor G and was adjusted to open at pressures in excess of 13 bars, since the glass cylinder was guaranteed to withstand pressures of 13 bars at 200°C.

Product vessel K had a volume of 4 liter and in an experiment at steady state was operated under the same pressure as reactor G. This separate vessel was essential for the level control in reactor G and was operated as a sluice for removing the product, formed in reactor G at elevated temperature and pressure, from the installation.
level control procedure

The aim is to operate reactor G as a Continuous Mixed Solid Mixed Suspension Removal (CMSMPR) crystallizer [6]. This requires a (semi-) continuous withdrawal of a representative mixed suspension from reactor G. In order to be sure that no crystal settling occurs in the piping during the suspension withdrawal, which takes place via an outlet through the topside of reactor G, a high removal velocity of the suspension is required. Just to open and close a valve in the removal tube will not suit this purpose, because the suspension contains crystalline material which would damage the valve and/or the packing material if the pressure before the valve is e.g. 7 bar higher than the ambient pressure after the valve. Opening and closing such a valve for only a few times would, due to wear, lead to unacceptable leakage.

To achieve leakage-free suspension withdrawal, product vessel K was installed. When suspension has to be withdrawn from reactor G two valves (V15 and V16) in a pipe on top of vessel K are opened which reduce the pressure in vessel K and allow \( \text{N}_2 \) gas to escape. The reason why \( \text{N}_2 \) gas escapes instead of suspension is that vessel K is never entirely filled with suspension. Since vessel K and reactor G are in direct connection (valve V13 is only closed if vessel K has to be emptied during the experiments), the lower pressure in vessel K causes a rapid flow (velocities up to 2 m/s in the pipe) of suspension from reactor G to vessel K via V13. As the desired level of the suspension is reached in reactor G the \( \text{N}_2 \) escape valve V15 on top of vessel K is closed.

In order to prevent blockage of the connecting pipe between reactor G and vessel K the pressure in vessel K is first adjusted to the pressure in reactor G via valve V10. Subsequently valve V14 is very shortly opened to reduce the pressure in reactor G compared to vessel K. Thereby the connecting pipe is emptied by \( \text{N}_2 \) gas flowing from vessel K to reactor G.

Per level control step 10 wt% of the reactor volume is withdrawn, which does not disturb the MSMPR crystallization process. The above described level control device using \( \text{N}_2 \) gas as auxiliary phase proved to be very useful.
**experimental set-up**

The feedstock for a continuous experiment was prepared one day ahead of the experiment in order to allow the salts to dissolve. The experiments were started by quickly filling the reactor with feedstock and then heating the first batch of reactor contents to the desired temperature at which the continuous process would be operated. As soon as this batch reached the desired process temperature the experiment was started. All experiments lasted nine residence times or even longer. Liquid samples were taken at least every residence time and solid samples were taken from the fifth residence time onwards once per residence time.

**sampling procedure and analytical methods**

Liquid samples (usually 15 ml) could be taken directly from the reactor because a 25 μm filter was positioned in front of valve V19. By opening the valves V19, V22 and by slightly opening throttle valve V23 a practically crystal-free liquid entered heat exchanger E at the reactor pressure. When heat exchanger E was entirely filled with liquid, which was the case when liquid started coming out of throttle valve V23, V23 was closed again. The pressure of the liquid in heat exchanger E was maintained by closing valve V22 before cleaning the rest of the liquid sampling device with N₂ gas. Heat exchanger E was a double-wall tube with a jacket filled with flowing cold water. This cooled the liquid sample to ambient temperature and thereby reduced the pressure of the sample without flashing, which, due to water evaporation, would have changed the solution composition.

After the sample was cooled, it was removed from the heat exchanger which was subsequently cleaned and dried with N₂ gas. The liquid sample was directly filtered on a 0.45 μm filter and subsequently diluted in a 2 wt% HCl solution. The Fe²⁺ and Zn²⁺ concentrations in the sample were determined by AAS.

Solid samples were taken using sluice L. The first step in the procedure was opening valve V27, through which sluice L was filled, whereafter valve V27 was closed again. By opening valve V28 the hot and still pressurized suspension flashed into a beaker, from which it was immediately removed by filtering the obtained suspension over a Büchner funnel connected to an oil vacuum pump. Owing to the cooling caused by this flashing some dissolution of the crystal can

178
occur. The crystals were immediately washed with acetone to displace residual mother liquor. Due to this method the packing material of valve V28 only lasted about five samples.

The washed crystals were dried. Subsequently the solids were analyzed with x-ray diffraction (XRD) to confirm the crystal structure and with scanning electron microscopy (SEM) to observe the size and the shape of the crystals. The chemical composition of the crystals was determined by dissolving them in a 2 wt% HCl solution and by subsequent analysis of the Fe$^{2+}$ and Zn$^{2+}$ concentrations of the solution with AAS.

**Experimental conditions of the continuous experiments**

Nine experiments were carried out in which from a ferrous and zinc sulfate solution initially containing 1.62 mole l$^{-1}$ Fe$^{2+}$ and 0.162 mole l$^{-1}$ Zn$^{2+}$ was crystallized under different conditions given in table 8.1. The molar ratio and concentration of Fe$^{2+}$ and Zn$^{2+}$ were chosen such that the solution would resemble a solution leaving a reductive leach autoclave in a hydrometallurgical jarosite treatment process [1].

**Table 8.1** Experimental conditions for continuous crystallization of FeSO$_4$.H$_2$O; the figures in the table represent the codes of the experiments

<table>
<thead>
<tr>
<th>temperature (°C)</th>
<th>residence time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.5</td>
</tr>
<tr>
<td>140</td>
<td>c1</td>
</tr>
<tr>
<td>145</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>c5</td>
</tr>
<tr>
<td>155</td>
<td></td>
</tr>
<tr>
<td>160</td>
<td></td>
</tr>
<tr>
<td>165</td>
<td></td>
</tr>
</tbody>
</table>

179
8.4 RESULTS AND DISCUSSION

8.4.1 Solubility of FeSO₄·H₂O in the presence of ZnSO₄

Two experiments were carried out to determine the solubility of FeSO₄·H₂O in the presence of Zn²⁺ in aqueous solutions at temperatures ranging between 140 and 170°C.

Figure 8.3 shows the results obtained for these experiments as far as the Fe²⁺ concentration is concerned. The results obtained in experiment 1 where the solubility was measured at a rising temperature program of 140 - 150 - 160 - 170°C and those obtained in experiment 2 at a decreasing temperature program of 165 - 155 - 145°C lead to identical solubility curves. Figure 8.4 shows the results obtained in both experiments for the Zn²⁺ concentration. The results in experiment 1 show a higher Zn²⁺ concentration than those obtained in experiment 2. The dashed line shows the 'average' value used in the calculations of the supersaturation, where the Zn²⁺ concentration is used as a measure for its contribution to the overall SO₄²⁻ concentration.

![Figure 8.3: The saturation Fe²⁺ concentration as a function of temperature](image1)

![Figure 8.4: The Zn²⁺ concentration as a function of temperature. The dashed line gives an estimated, average curve.](image2)
The difference in the results of experiment 1 and 2 is explained by the fact that in experiment 1 the experimental procedure included the fast rise of the suspension temperature to 140°C, whereas in experiment 2 the suspension temperature fastly went up to 165°C. In the latter experiment the major part of the crystals was formed at temperatures between 140 and 165°C, because in that temperature range the conversion increased from 25 to 75%. The rapid increase of the temperature from 140 - 165°C has resulted in a high supersaturation value which caused a higher uptake of zinc in FeSO₄·H₂O. Consequently, the crystals grown in experiment 2 contained more zinc than those grown in experiment 1 with a slow increase of temperature in the range 140 - 165°C and therefore a lower supersaturation.

In subsequently decreasing the temperature via 155°C to 145°C in experiment 2 the Fe²⁺ concentration has reached a new, higher level of solubility with a correspondingly higher Fe²⁺ concentration. The solid phase, however, still has its 'fast growth history' and therefore the Zn²⁺ concentration observed in experiment 2, although increasing, remains lower than in experiment 1.

Since the substitution of Fe²⁺ by Zn²⁺ ions in the FeSO₄·H₂O lattice gives no change in the SO₄²⁻ concentration in the solution, no influence of the growth history on the FeSO₄·H₂O solubility was observed.

8.4.2 Results of the continuous crystallization of FeSO₄·H₂O

The results obtained in the experiments c1 to c9 are summarized in table 8.2.

characterization of the product

Figure 8.5 is a representative SEM-micrograph of a single FeSO₄·H₂O crystal. The rounding of the crystal edges reveals that during the sampling some dissolution has occurred. In figure 8.6 more crystals can be seen. Using a Büchner funnel it was qualitatively shown that the filtration behavior of the solids was excellent. Some dissolution of fines, could, however, have happened during sampling. XRD-Guinier de Wolff diffractograms indicate the presence of FeSO₄·H₂O as the only crystalline phase in the obtained crystalline material.
Figure 8.5: A SEM-view showing a few representative FeSO$_4$.H$_2$O crystals. The rough surfaces indicate that during sampling some dissolution has taken place.

Figure 8.6: A SEM-view showing the particle size distribution of the FeSO$_4$.H$_2$O crystals
conversion values

The conversion of Fe$^{2+}$ to FeSO$_4$.H$_2$O is higher at higher temperatures (compare e.g. exp. c1 with c5) or longer residence times (compare e.g. exp. c1 with c2). The reproducibility of the achieved conversion is, as is obvious from the experiments c4 and c6, about 10%.

Table 8.2 Results of continuous crystallization experiments of FeSO$_4$.H$_2$O in the presence of ZnSO$_4$ at 140 - 160°C

<table>
<thead>
<tr>
<th>#</th>
<th>temperature</th>
<th>residence time</th>
<th>conversion$^1$</th>
<th>supersaturation</th>
<th>Zn-load</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>hours</td>
<td>%</td>
<td>(-)</td>
<td>g/kg solids</td>
<td>(-)</td>
</tr>
<tr>
<td>c1</td>
<td>140</td>
<td>0.5</td>
<td>24</td>
<td>1.80</td>
<td>19</td>
<td>0.41</td>
</tr>
<tr>
<td>c2</td>
<td>140</td>
<td>1.5</td>
<td>60</td>
<td>0.74</td>
<td>23</td>
<td>0.35</td>
</tr>
<tr>
<td>c3</td>
<td>150</td>
<td>1.5</td>
<td>83</td>
<td>2</td>
<td>28</td>
<td>0.31</td>
</tr>
<tr>
<td>c4</td>
<td>145</td>
<td>1.0</td>
<td>67</td>
<td>0.76</td>
<td>25</td>
<td>0.36</td>
</tr>
<tr>
<td>c5</td>
<td>150</td>
<td>0.5</td>
<td>65</td>
<td>1.22</td>
<td>25</td>
<td>0.34</td>
</tr>
<tr>
<td>c6</td>
<td>145</td>
<td>1.0</td>
<td>58</td>
<td>1.12</td>
<td>25</td>
<td>0.35</td>
</tr>
<tr>
<td>c7</td>
<td>155</td>
<td>1.0</td>
<td>81</td>
<td>0.22</td>
<td>28</td>
<td>0.30</td>
</tr>
<tr>
<td>c8</td>
<td>160</td>
<td>1.5</td>
<td>85</td>
<td>0.014</td>
<td>30</td>
<td>0.31</td>
</tr>
<tr>
<td>c9</td>
<td>165</td>
<td>2.0</td>
<td>89</td>
<td>0.002</td>
<td>30</td>
<td>0.31</td>
</tr>
</tbody>
</table>

$^1$ The conversion is defined as (C$_{Fe}$ feed - C$_{Fe}$) / C$_{Fe}$ feed

$^2$ For unknown reasons a negative supersaturation was calculated for this experiment

High conversions of over 80% are obtained only in experiments at temperatures of 150°C or above. No explanation is available for the unexpectedly high conversion observed in experiment c3, which also resulted in the calculation of a negative supersaturation for that experiment following from a too low Fe$^{2+}$ concentration in the solution.
supersaturation values

The supersaturation values were calculated from the determined Fe$^{2+}$ concentration in the solution using equation (8.3). It was assumed that the SO$_4^{2-}$ concentration was the sum of the Fe$^{2+}$ and Zn$^{2+}$ concentrations plus the contribution of the H$_2$SO$_4$ addition. High $\beta$ values were obtained for experiments with a low conversion and low values for experiments with a high conversion.

incorporation of Zn$^{2+}$ in FeSO$_4$.H$_2$O

The incorporation of Zn$^{2+}$ in FeSO$_4$.H$_2$O is expressed by two parameters; by the absolute quantity of zinc in FeSO$_4$.H$_2$O in g/kg solids as well as by the partition coefficient D which is a more proper measure for the selectivity of the process. The reproducibility of the data on the incorporation, expressed in the partition coefficient D, is ± 0.01, which is sufficiently high to distinguish between the various experiments.

Experiment c1 shows a comparatively high D-value, which is related to a comparatively high value of the supersaturation of 0.90. The experiments c2, c4, c5 and c6 together form a group of experiments with D-values ranging between 0.34 and 0.36 and corresponding supersaturation values ranging between 0.74 and 1.22. Finally, the experiments c3, c7, c8 and c9 form a group with D-values of 0.30 and 0.31 and low supersaturation levels of 0.22 or less. Figure 8.7 shows the relation between D and $\sigma$ for these experiments, assuming a $\beta$-value of 0.2 for experiment c3.

Figure 8.7 obscures the effect of the temperature on the D-value, because the D-values depend on both the temperature and the supersaturation. It is not possible to distinguish between the influence of the temperature and the supersaturation. Comparing, however, the D-values measured in the experiments c1 and c2 or c5 and c3 it becomes clear that these couples of isothermal experiments show considerable differences in D-value which may only be related to the different supersaturation levels in the various experiments. This provides evidence that the supersaturation probably has a larger influence on the D-value than the temperature. This is disappointing, because upon increasing the temperature a significantly lower D-value was also expected due to the lower ratio of the
solubilities of pure FeSO$_4$.H$_2$O and pure ZnSO$_4$.H$_2$O (see figure 8.1). A relationship between D and the ratio of the solubilities of salts was given by Balarew [7] and Witkamp [8].

![Partition coefficient D vs. Supersaturation β](image)

Figure 8.7: The partition coefficient D as a function of the supersaturation

The zinc load in FeSO$_4$.H$_2$O ranges between about 2 and 3 wt% and reaches the highest values for experiments with a high conversion. Despite the fact that the partition coefficient D decreases with increasing conversion the zinc load in FeSO$_4$.H$_2$O increases. This rather unexpected result is caused by the fact that the zinc load in the solid phase is a product of two terms, as shown in equation (8.5).

$$\frac{[Zn^{2+}]_s}{[Fe^{2+}]_s} = D \frac{[Zn^{2+}]_l}{[Fe^{2+}]_l} \quad (8.5)$$

An increasing conversion is accompanied by a low equilibrium concentration which yields a lower value of the partition coefficient D. Simultaneously, however, an increasing conversion also leads to a large decrease of the Fe$^{2+}$ concentration in the solution, which compared to a smaller decrease of the Zn$^{2+}$ concentration, increases the ratio of the Zn$^{2+}$ over the Fe$^{2+}$ concentration in the solution. The resulting zinc concentration in the solid phase is higher because the decrease of the partition
coefficient with a decreasing supersaturation is smaller than the increase of the Zn\(^{2+}\)/Fe\(^{2+}\) -ratio in the solution for high conversion experiments. The main conclusion which can be drawn from these experiments is that, despite the considerable differences in the solubilities of the pure salts FeSO\(_4\).H\(_2\)O and ZnSO\(_4\).H\(_2\)O, the selectivity for the crystallization of FeSO\(_4\).H\(_2\)O in the presence of Zn\(^{2+}\) is poor. Although the incorporation of Zn\(^{2+}\) is to some extent determined by the supersaturation, because an increasing supersaturation induces an increasing zinc incorporation, the relatively large value of the partition coefficient is mainly due to the high thermodynamic equilibrium concentration of Zn\(^{2+}\) in FeSO\(_4\).H\(_2\)O.

8.5 CONSEQUENCES FOR OPERATING AN INTEGRATED HYDROMETALLURGICAL JAROSITE TREATMENT PROCESS

For successful operation, the integrated hydrometallurgical jarosite treatment process as described in [1], heavily depended on the selectivity of the separation of Fe\(^{2+}\) and Zn\(^{2+}\) by crystallization of FeSO\(_4\).H\(_2\)O at temperatures between 140 and 165°C.

A single-step crystallization process itself yields FeSO\(_4\).H\(_2\)O crystals which are well-filterable at conversions of over 85%, but with a residual zinc content of 2 - 3 wt%. The residual zinc content is to a large extent determined by the D-value at zero supersaturation, which means that changing the supersaturation does not significantly affect the selectivity of the process.

As follows from the material and energy balances calculated in [1], for D = 0.3 the selectivity of this separation process is too poor to justify its application as a key-step in an integrated hydrometallurgical jarosite treatment process.

8.6 CONCLUSIONS

The crystallization of FeSO\(_4\).H\(_2\)O from an aqueous solution containing Zn\(^{2+}\) in a continuously operated 1.1 liter autoclave at 140 - 165°C yielded a well-filterable, crystalline product, of which the filtration properties might have been obscured somewhat by the dissolution of fines.
The incorporation of Zn$^{2+}$ in FeSO$_4$.H$_2$O ranged between 2 and 3 wt% and depended slightly on the process conditions, such as the temperature and the residence time.

The partition coefficient D for the incorporation of Zn$^{2+}$ in FeSO$_4$.H$_2$O varied between 0.30 and 0.41 and was shown to increase with increasing supersaturation. The partition coefficient was mainly determined by the D-value at zero supersaturation and not so strongly by its kinetics.

The separation of Fe$^{2+}$ and Zn$^{2+}$ from aqueous solutions by crystallization of FeSO$_4$.H$_2$O has a too low selectivity to justify its use in an integrated hydrometallurgical jarosite treatment process.

ACKNOWLEDGEMENTS

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8.7 REFERENCES

Chapter 9

Integrating jarosite residue processing in hydrometallurgical zinc refining - comparison of five potential processes

ABSTRACT

Hydrometallurgical zinc refining processes are frequently based on iron containing concentrates which yield a goethite, jarosite or hematite residue. Jarosite and goethite are usually stored in lined ponds, which in some countries is no longer regarded acceptable for environmental reasons. Thus, treatment processes for jarosite-like residues are required.

This paper provides the comparison of five different process designs for integrated jarosite treatment in a hydrometallurgical zinc refining plant leading to environmentally acceptable residues. The processes are designed for producing 200 ktons/yr zinc and for treating 80 ktons/yr historical jarosite. Mass and energy balances are used to determine parameters such as:

- the energy use per ton waste treated and
- the amount and composition of final residues.

The conclusion of the work is that pyrometallurgical jarosite treatment integrated in hydrometallurgical zinc refining is preferable to hydrometallurgical jarosite treatment. Integrated pyrometallurgical processes lead to a smaller quantity of remaining hazardous residues and require less energy.

9.1 INTRODUCTION AND AIM

The refining of primary non-ferrous metals from concentrates inevitably leads to the formation of residue materials, since naturally occurring undesirable impurities and valuable metals are part of the same concentrate. Since metal users impose strict specifications on their raw material, the primary metal industry has to separate the desired metal from the impurities. The metal is sold, but impurities frequently remain close to the metal refining plant in a storage facility. Fortunately many 'impurities' are no longer regarded as such, since process technology has become available to win more and more metals economically as by-product. In particular iron and arsenic, however, which are found in many concentrates, are still ending up in residues [1,2].

This paper limits its scope to hydrometallurgical zinc refining. Worldwide, an annual production of about 6 Mton of zinc is realized. About 80 % of this quantity is produced in hydrometallurgical zinc refining plants which consist of a roasting, leaching and electrowinning step. The problem of the dissolution of iron in the leach circuit is solved by precipitating either jarosite, goethite or hematite from the leach solution. Precipitating these iron containing residues also prevents the built-up of some of the other impurities (e.g. Ge, As) which accompany zinc in the concentrate, in the electrolyte. Most hydrometallurgical zinc refining plants separately produce a lead-silver residue which may be commercially used for lead and/or silver winning and a gypsum residue which is formed after bleeding spent acid in order to prevent the accumulation of a.o. magnesium and manganese.

The quantity of iron residue formed during zinc refining depends on the iron content of the concentrate and on the particular iron residue that is precipitated. For a given iron content the overall mass of jarosite residue exceeds the mass of goethite and of hematite. Operating a jarosite precipitation step in a plant, however, is relatively easy and gives the highest zinc recovery, which has led to the current situation in which jarosite forming plants dominate the zinc refining industry. For this reason this paper only deals with
jarosite. The jarosite residue formed during historical and current zinc refining finds no application and is therefore either disposed off in storage ponds, discharged in sea or stored in artificial caves in granite rock. The situation with respect to goethite is similar. Hematite is claimed to find application in cement industries [3].

In the Netherlands storage ponds containing jarosite are lined with HDPE-foils. Percolating water is withdrawn from the deposit and decontaminated before discharge. Despite such measures, more and more pressure is exerted on zinc companies to treat their (historical) residues and to produce environmentally acceptable residues. The criterion which determines this acceptability is the potentiality of leaching out hazardous elements by natural processes. Since current jarosite does not fulfill this criterion, it is regarded as hazardous chemical waste [4]. Society's criticism on (further) storage of hazardous chemical waste has increased, since it is conflicting with the aim to develop a sustainable world economy [5].

In the Netherlands three geographical factors add to the concern on hazardous waste. The first factor is the high population density (± 450 inhabitants/km²) which means that space for whatever purpose is limited. The second factor is that almost 15 million people are depending on drinking water which to a large extent is extracted from ground water resources. The third factor is the groundwater table (freatic surface), which is very near the surface. Some aqueous pollutants (e.g. nitrate) have already been shown to percolate to these resources as a consequence of human (agricultural) activities. In order to prevent the storage of jarosite residues in the Netherlands from remaining a potential hazard to drinking water resources and, of course, to the soil itself, it has been decided that further storage of jarosite will be prohibited in the near future. Moreover, current storage facilities are to be emptied. The jarosite residue will have to be converted into an iron product which does no longer possess unacceptable leaching properties. This conversion process is preferentially combined with the primary zinc refining plant.
The aim of this paper is to compare five hydrometallurgical zinc refining processes for integrated residue treatment on residue quantity and composition as well as on energy requirements. The choice for the individual options has been made as follows. Option I considers a treatment unit which is almost entirely complementary to a conventional primary zinc refining plant. A single recycle stream returns the zinc recovered from the jarosite residue to the primary plant. The second option interferes with the primary plant, since two characteristic unit operations in the primary plant are abandoned. The third and fourth option introduce further changes in the primary plant. The fifth option, however, utilizes the same primary plant as the first option, but introduces a principally different treatment method. The five options together cover only a small range of possible flow sheets for primary zinc refining plants with integrated residue treatment, but include basically new developments which are worthwhile to be discussed in more detail. Due to the fact that the technology presented in this study has never been built on an industrial scale, it is not possible to include a section on capital costs with any significant accuracy.

This paper might also be useful for zinc refining companies in other countries which face a comparable residue problem, but have to cope with other constraints (e.g. geographical factors, energy prices, residue specifications etc.).

9.2 METHODOLOGY

In the subsequent sections the five processes are discussed as a combination of (unit) operations for which mass and energy balances are calculated. Mass balances are based on chemical reaction equations (see appendix 9.1) which are supposed to have a conversion of 100% (apart from one well defined exception). This assumption is justified by the fact that recycling flows which are required to cope with conversions below 100%, do not influence the overall mass balance of the process. Solid/gas phase separation devices are assumed to be ideal, i.e. solids are completely separated from the gases. In order to calculate the required energy for drying residues, a residual moisture content
after liquid filtration of 40 wt% is assumed, which is a conservative estimate, based on data from industrial practice [6]. In the hydrometallurgical treatment process all filter and washing devices are assumed to yield a filter cake with a 40 wt% moisture content. For the hydrometallurgical treatment plant the fluxes of the recycle flows were calculated because they partly determined the required amounts of sulfuric acid, sodium hydroxide and energy. For calculating energy balances some of the pyrometallurgical equipment was sized, because furnace sizes, operation temperatures and residence times are major parameters determining the overall process energy requirements. All processes are designed to produce 200 ktons/yr zinc and simultaneously treat the residue due to this production as well as 80 ktons/yr historical jarosite residue. In order to facilitate the calculations a constant concentrate and residue composition is assumed.

9.3 RAW MATERIALS AND ENERGY SOURCES

Hydrometallurgical zinc refining processes use sphalerite concentrates which contain a number of impurities. The assumed composition of the concentrate is given in table 9.1. The presence of impurity elements such as e.g. germanium, cobalt, nickel, aluminum and indium is neglected. This is justified because these elements are not of major importance for calculating the overall mass and energy balances. The elements lead, zinc, copper, cadmium and iron are assumed to be present as sulfides. The other elements are assumed to be present as oxides. The composition of historical jarosite residues is determined by the composition of the concentrate but also by the process lay-out of the zinc refining plant. Differences between jarosite residues obtained from different zinc refining plants are caused by the fact that the lead/silver residue is not always separated from the jarosite residue. This paper uses a worst case scenario in which the lead/silver residue is part of the jarosite residue. The composition of the historical jarosite residue is also given in table 9.1.
<table>
<thead>
<tr>
<th>element</th>
<th>wt% in Zn conc.</th>
<th>mass/year (ton)</th>
<th>wt% in hist. jarosite</th>
<th>mass/year (ton)</th>
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<tr>
<td>Zn</td>
<td>54</td>
<td>205200</td>
<td>1</td>
<td>800</td>
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<td>Pb</td>
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<td>2</td>
<td>1600</td>
</tr>
<tr>
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<td>2280</td>
<td>1.5</td>
<td>1200</td>
</tr>
<tr>
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<td>628</td>
<td>0.2</td>
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<td>122</td>
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<tr>
<td>Mn</td>
<td>0.025</td>
<td>95</td>
<td>0.08</td>
<td>64</td>
</tr>
<tr>
<td>H</td>
<td>--</td>
<td>--</td>
<td>1.91</td>
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<td>--</td>
<td>1.74</td>
<td>1392</td>
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<td>33</td>
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<td>12.97</td>
<td>10384</td>
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<td><strong>380001</strong></td>
<td><strong>100</strong></td>
<td><strong>80075</strong></td>
</tr>
</tbody>
</table>

In historical jarosite 80 wt% of the iron is present as ammonium and 20 wt% as hydronium jarosite. Other metals are assumed to be present as (hydrated) sulfates. Arsenic is assumed to be present as arsenic(V)oxide and 25 wt% of the zinc load as (unreacted) sphalerite.

Additional essential raw materials are zinc dust, ammonia, lime, oxygen, sand, sulfuric acid, ferric sulfate and sodium hydroxide. All these raw materials are assumed to be 100% pure except oxygen. Sand, required for slag formation, is assumed to consist of 100% silicium dioxyde. Oxygen is assumed to be technically pure (95 %), the remainder being nitrogen. The overall energy requirements for the integrated zinc refining and residue treatment operations
are split up in electricity requirements and natural gas consumption. The electricity is generated in a natural gas fired power station. Natural gas is only assumed to be the energy source because this reflects the Dutch situation best. Natural gas and electricity are compared by using the following conversion factor which includes energy losses in power generation and power transport: 3.0 kWh/Nm³ gas or 10.8 MJₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑₑᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉᵉ(115,185),(884,893)
further refining and the remaining acidic zinc solution is returned to the leach circuit. Spent acid from the electrolysis is recycled to the neutral leach, the acid leach and to the fly-ash leaching process in the treatment unit. The sulfuric acid production during electrolysis can not fulfill the demand in the leaching processes. Therefore fresh sulfuric acid is added to the acid leach. This results in excess water in the leach-electrowin circuit which necessitates a bleed stream. The bleed stream consists of spent acid, which has a low zinc concentration. This minimizes zinc losses and simultaneously prevents the accumulation of manganese and magnesium in the circuit. Lime is added to the bleed in order to precipitate metal hydroxides. This operation yields a contaminated gypsum residue and a purified neutral aqueous solution which, after passing further waste water treatment units, is discharged without environmental risks.

The gypsum residue, together with the solid residue that remains after the acid leach (jarosite and lead/silver residue) and the historical jarosite residue are dried and subsequently fed into a flash furnace. The purpose of this first treatment operation is to produce an iron-silicate slag with a low heavy metal content and a negligible leachability of those heavy metals that remain in the slag. Sand and natural gas are essential for obtaining the optimum slag formation conditions (± 1300°C). In order to cope with the demands of environmental legislation, secondly a batch slag fuming is operated at ± 1300°C, during which coal is used as reductant and lances are inserted in the slag bath for enhancing the mass transfer between the liquid slag and the gas phase. In this step the slag is fumed to further decrease the volatile heavy metal content. The two operations together yield an iron-silica slag which also contains calcium, barium, magnesium and manganese and fly-ashes which contain lead, cadmium, arsenic, copper and zinc.

The fly-ashes are leached in a complicated set of unit operations which prevent the accumulation of arsenic, yield a saleable lead sulfate residue and enable the recovery of cadmium, copper and zinc. A more detailed discussion of this leach unit is beyond the scope of this paper. Finally, a ferric arsenate residue is precipitated simultaneously with gypsum in the leach unit. This residue does
not have any application and has to be stored in a suitable hazardous chemical waste pond. The volume of hazardous chemical waste that has to be stored is, however, reduced to 5% of the original jarosite waste, since the slags produced in this process are suitable for civil engineering purposes.

Figure 9.1 Simplified flow-sheet showing the option I integrated jarosite treatment process

9.4.2 Process option II
Figure 9.2 presents a simplified flow-sheet of an alternative process for integrated zinc refining and residue treatment. This option only differs from option I in that no jarosite precipitation and no acid leach plant are incorporated. The elimination of these steps is justified by the fact that the zinc content of the neutral leach residue will, after passing the residue treatment
process, finally end up in the neutral leach in a dissolved form. Thereby equipment and maintenance costs are reduced and the energy requirements in the primary plant are decreased.

Figure 9.2 Simplified flow-sheet showing process option II

9.4.3 Process option III

Figure 9.3 represents a second alternative process. This process resembles process option II, but is more complicated. In order to avoid the major increase of the initial zinc load to the flash furnace this process operates a reductive roasting step. This step reduces the zinc ferrite content of calcine by exposing the calcine to \( \pm 850^\circ C \) in a reductive gas atmosphere. Zinc ferrite is then converted to zinc oxide which is easily soluble in the neutral leach and to magnetite which is very slightly soluble [9,10]. Simultaneously, a fly ash is formed, which is leached in the fly-ash leach in the treatment unit. The advantage of reducing the zinc ferrite content in calcine is gained by introducing an extra process step which increases the energy requirements.
Another difference between the options II and III regards the gypsum bleed. In this option the neutral leach solution which contains a lot of zinc at a low acidity is partly bled off. Lime is added to the bleed in order to precipitate waste gypsum which contains the metals as hydroxides. All zinc contained in the gypsum residue is recovered in the flash furnace and the slag fumer. Compared to option II, savings are made on fresh sulfuric acid inputs, because the amount of acid neutralized by lime has decreased.

Figure 9.3 Simplified flow-sheet showing process option III

9.4.4 Process option IV

Figure 9.4 shows the simplified flow sheet for the fourth option. This option closely resembles option III. The only difference is that in option III historical jarosite residue is fed into the flash furnace, whereas in option IV this residue
is fed into the oxidative roaster. Neglecting the technical difficulties which may
arise from feeding a very fine ($d_{50,\text{vol.}} < 20 \mu m$) pulverized material into a
fluidized bed roaster, it is easily demonstrated that the energy required for
decomposing 80 ktons/yr historical jarosite residue is much smaller than the
energy obtained by roasting 380 ktons/yr of sphalerite concentrate. By feeding
the jarosite residue to the oxidative roaster the combustion energy of the
concentrate is utilized efficiently because the heat transfer in fluidized beds is
excellent. Combining the jarosite residue and the concentrate does decrease the
steam production in the waste heat boiler following the oxidative roaster, but
the main application of this steam, heating the acid leach and jarosite
precipitation vessels, has also vanished.

Figure 9.4 Simplified flow-sheet showing process option IV
By adding historical jarosite residue to the concentrate it is essentially enriched in iron, leading to a considerable increase in zinc ferrite production. However, the oxidative roasting step is followed by a reductive roasting step which eliminates the major part of the zinc ferrite. The flash furnace is thus fed with a smaller quantity of residue.

9.4.5 Process option V

Option V is schematically presented in figure 9.5. This option includes a hydrometallurgical treatment unit. The primary refining unit resembles the unit described for option I and leads a.o. to a combined jarosite and lead/silver residue as well as to a bleed gypsum residue. The fresh jarosite residue combined with historical jarosite is leached under reductive conditions by adding sulfur dioxyde [11]. This yields a solid residue containing lead, barium, calcium, arsenic and silica. The obtained solution contains zinc, copper, cadmium, ammonium, magnesium, manganese and, most of all, iron(II). Ferrous sulfate is then crystallized as smozolkonite (monohydrate) in a fractional crystallization unit. The unit as such is described in appendix 9.3. It is operated at 160 °C in order to improve crystal purity, since the relative solubility of ferrous sulfate monohydrate, compared to zinc sulfate monohydrate is small at elevated temperatures (140-160°C). The partition coefficient for the incorporation of zinc in ferrous sulfate is defined as follows:

\[
D= \frac{[Zn]_g/ [Fe]_g}{[Zn]_l/ [Fe]_l}
\]  

(9.1)

in which l represents the liquid phase and s the solid phase.

In this study this coefficient is assumed to be constant. Its value is assumed to be equal to 0.2. This is still far beyond the thermodynamically feasible value at 160°C which, based on the ratio of the solubility products, equals about 0.05.

The value of 0.2 was based on extrapolating preliminary results for the D-value obtained in early experiments. The assumed D-value, compared to the later obtained experimental results, reported in the previous chapter, was too low. This means that the calculated results for the energy and raw material
requirements will in practice be higher than reported here. Zinc is chosen as the impurity which determines the effectiveness of this operation for three reasons:

i) The site is a zinc winning plant which benefits from selling zinc instead of losing it in residues.

ii) The potential application of hematite in the primary iron and steel industry sets very strict specifications.

iii) Zinc is the most abundant 'impurity' while producing clean iron residues.

Figure 9.5 Simplified flow-sheet showing process option V
The fractional crystallization unit yields a relatively pure ferrous sulfate which is roasted at 600 - 800°C to yield hematite and sulfur dioxyde. The so-produced hematite has to meet the standards for use as a raw material in the steel industry. The remaining liquid phase contains, after oxidation, iron(III), zinc, cadmium, copper, manganese, ammonium and magnesium. The metals are precipitated by adding caustic soda, which removes ammonium as ammonia. The precipitate is returned to the neutral leach in the primary plant, since zinc, cadmium and copper are valuable. Magnesium and manganese are finally removed with the bleed gypsum. The sodium sulfate solution remaining after the hydroxide precipitation is recycled for its heat content. However, a bleed is required to limit the accumulation of sodium and sulfate ions. This bleed may be treated with lime to yield a relatively pure gypsum which will find application in the building industry and a diluted caustic soda solution which may be utilized in waste water neutralization.

This option does not include processes which are operated at very high temperatures. Therefore, it is interesting to calculate whether the energy consumption per unit waste will be lower.

The remaining residues, however, are assumed to have quite different properties from those that have experienced a pyrometallurgical treatment. The impurity content of hematite is determined by the final composition of ferrous sulfate monohydrate. This composition is determined by the partition coefficient as given in equation (9.1). Since the partition coefficient and the aqueous ferrous concentration are constant for a given temperature, the uptake of zinc in the crystals is influenced by the slurry density, which is defined as the quantity of ferrous sulfate monohydrate crystals per 1000 kg of water. In this study three different values are chosen for the slurry density i.e. 50, 100 and 200 kg/1000 kg water. Since the output of produced ferrous sulfate monohydrate is constant, regardless of the slurry density, the differences in slurry density are realized by changing the quantity of water, i.e. by varying the dilution of the pregnant solution.
9.5 MASS BALANCES; RESULTS

Appendix 9.1 provides all reaction equations which were used to calculate the mass balances for the different processes. The overall results for the pyrometallurgical treatment process are given in Table 9.2 and for the hydrometallurgical treatment process in Table 9.3. Since the raw materials are the same for all processes, the options I to IV yield about the same amount of products. Minor differences occur in lime and sulfuric acid use and sulfur dioxide and slag production. Major differences, however, occur between the options I to IV and option V in residue composition and amount. Obviously, the hydrometallurgical option produces a larger quantity of residues. The Pb/As/Ba-residue contains about 20 wt% lead. Although this lead content is in itself probably sufficient for economic lead recovery [12], the presence of silver which was not considered in this study may further add to the saleability of this stream [13,14].

Table 9.3 shows that with a decrease of the slurry density the amount of chemicals required for operating this process increases drastically. The chemical use at low slurry densities clearly reaches unacceptably high levels. The aqueous bleed containing sodium sulfate rises as a consequence of this. The reason for the increased chemical use is lying in the fact that with a lower slurry density the fraction dissolved iron over crystallized iron is enhanced and therefore the recycling of ferric ions increases. Each recycled ferric ion is precipitated as ferric hydroxide, consuming caustic soda, and redissolved with sulfuric acid. Redissolved ferric hydroxide is then precipitated as jarosite, consuming extra ammonia. These mass balances also confirm the decreasing zinc content in the hematite product with decreasing slurry density. However, even at a slurry density of 50 kg/1000 kg H₂O the hematite product still contains 229 ppm of zinc, which exceeds the steel industry's limit of 120 ppm Zn in pig iron [15], which corresponds to 81 ppm in hematite, assuming pig iron to contain 4% carbon. In case a lower value of the partition coefficient D is practically feasible, the corresponding final contamination of hematite also decreases and enables the utilization of hematite in the steel industry.
Table 9.2: Results obtained from mass balance calculations for four pyrometallurgical jarosite treatment options (all figures in kton/yr)

<table>
<thead>
<tr>
<th></th>
<th>option I</th>
<th>option II</th>
<th>option III</th>
<th>option IV</th>
</tr>
</thead>
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<tr>
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<td>380.0</td>
<td>380.0</td>
<td>380.0</td>
</tr>
<tr>
<td>zinc dust</td>
<td>2.7</td>
<td>2.7</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>hist. jarosite</td>
<td>80.1</td>
<td>80.1</td>
<td>80.1</td>
<td>80.1</td>
</tr>
<tr>
<td>ammonia</td>
<td>2.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lime</td>
<td>3.8</td>
<td>3.8</td>
<td>6.2</td>
<td>6.5</td>
</tr>
<tr>
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<td>2.0</td>
<td>2.1</td>
<td>2.1</td>
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<tr>
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<td>13.0</td>
<td>13.0</td>
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<tr>
<td>slag</td>
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<td>111.4</td>
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<td>sulfur dioxide</td>
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<td>283.2</td>
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<td>arsenate/gypsum</td>
<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
</tr>
</tbody>
</table>

The residues obtained with the hydrometallurgical process consist next to the Pb/As/Ba-residue of waste gypsum which has to be stored because its heavy metal content inhibits applications.
Table 9.3: Results obtained from mass balance calculations for the hydro-metallurgical treatment process for three different values of the slurry density in the fractional crystallizers (all figures in kton/yr)

<table>
<thead>
<tr>
<th></th>
<th>( M_0 = 50 \text{kg/ton} )</th>
<th>( M_1 = 100 \text{kg/ton} )</th>
<th>( M_2 = 200 \text{kg/ton} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw materials</td>
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<td></td>
</tr>
<tr>
<td>concentrate</td>
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<td>380.0</td>
<td>380.0</td>
</tr>
<tr>
<td>zinc dust</td>
<td>2.7</td>
<td>2.7</td>
<td>2.7</td>
</tr>
<tr>
<td>hist. jarosite</td>
<td>80.1</td>
<td>80.1</td>
<td>80.1</td>
</tr>
<tr>
<td>ammonia</td>
<td>12.8</td>
<td>5.7</td>
<td>3.7</td>
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<tr>
<td>lime</td>
<td>2.3</td>
<td>3.2</td>
<td>3.4</td>
</tr>
<tr>
<td>sulfuric acid</td>
<td>206.4</td>
<td>99.7</td>
<td>70.3</td>
</tr>
<tr>
<td>caustic soda</td>
<td>326.8</td>
<td>111.5</td>
<td>51.5</td>
</tr>
<tr>
<td>Products</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>zinc</td>
<td>208.1</td>
<td>207.8</td>
<td>207.2</td>
</tr>
<tr>
<td>cadmium</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>copper</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>hematite</td>
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<td>73.2</td>
<td>73.2</td>
</tr>
<tr>
<td>zinc in hematite</td>
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</tr>
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<td>sulfur dioxyde</td>
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<td>257.0</td>
<td>271.0</td>
</tr>
<tr>
<td>Residues</td>
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<td></td>
</tr>
<tr>
<td>Pb/As/Ba-residue</td>
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<td>44.2</td>
<td>44.2</td>
</tr>
<tr>
<td>waste gypsum</td>
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<td>11.3</td>
<td>11.9</td>
</tr>
<tr>
<td>zinc in gypsum</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
</tr>
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<td>aqueous bleed</td>
<td>4,186.9</td>
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<td>499.5</td>
</tr>
<tr>
<td>dissolved ( \text{Na}_2\text{SO}_4 )</td>
<td>579.8</td>
<td>197.9</td>
<td>91.4</td>
</tr>
</tbody>
</table>
9.6 ENERGY BALANCES; RESULTS

Estimates were made of the energy requirements of all five options described in section 9.4. Table 9.4 provides the obtained results for the options I to IV. The energy requirements of the primary winning plant are based on literature [16]. The relations used for estimating the energy use of 'classical' unit operations in zinc hydrometallurgy are given in appendix 9.4. Appendix 9.5 discusses the estimates of the energy use of the reductive roasting step. Appendix 9.6 provides the calculations of the energy requirements for the residue dryers. The design aspects and energy requirements of the flash furnaces are discussed in appendix 9.7. The batch slag fumers are discussed briefly in appendix 9.8.

In options I to IV the flash furnace and the batch slag fumer yield large quantities of hot combustion gases, which are suitable for power generation. In the options III and IV the hot gases leaving the reductive roaster and in the options II to IV part of the hot gases obtained during oxidative roasting are also used for this purpose. The gases are utilized to produce saturated steam at 100 bar (312 °C). This steam is subsequently superheated in a separate unit which utilizes natural gas as fuel. The energy requirements of the superheater and the resulting power production are described in appendix 9.9. Appendix 9.10 discusses the energy requirements of the fly-ash leaching in the options I to IV.

Table 9.4 indicates the importance of on-site power generation. The main differences in the power consumption are related to the flash furnace. This is explained by the fact that the flash furnace requires technical oxygen, for which a power consumption of 400 kWh/ton technical oxygen is assumed. The flash furnace in option I has the largest oxygen demand and consequently the largest power consumption.
Table 9.4A  The electrical energy requirements for the options I to IV (in kWh/ton SHG zinc, negative signs indicate energy releases)

<table>
<thead>
<tr>
<th>step</th>
<th>option I</th>
<th>option II</th>
<th>option III</th>
<th>option IV</th>
</tr>
</thead>
<tbody>
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<td>roasting</td>
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<td>110</td>
<td>110</td>
<td>183</td>
</tr>
<tr>
<td>sulfuric acid production</td>
<td>300</td>
<td>278</td>
<td>281</td>
<td>285</td>
</tr>
<tr>
<td>reductive roasting</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>leaching</td>
<td>179</td>
<td>72</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>electrolysis</td>
<td>3,373</td>
<td>3,373</td>
<td>3,373</td>
<td>3,373</td>
</tr>
<tr>
<td>melting and casting</td>
<td>127</td>
<td>127</td>
<td>127</td>
<td>127</td>
</tr>
<tr>
<td>others</td>
<td>71</td>
<td>71</td>
<td>71</td>
<td>71</td>
</tr>
<tr>
<td>residue drying</td>
<td>36</td>
<td>32</td>
<td>32</td>
<td>14 + 26</td>
</tr>
<tr>
<td>flash furnace</td>
<td>140</td>
<td>86</td>
<td>99</td>
<td>59</td>
</tr>
<tr>
<td>electrostatic precipitator</td>
<td>0.7</td>
<td>0.5</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>slag fumer</td>
<td>132</td>
<td>132</td>
<td>137</td>
<td>137</td>
</tr>
<tr>
<td>flyash leach &amp;miscellaneous</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>on-site power generation</td>
<td>-1,477</td>
<td>-1,366</td>
<td>-1,503</td>
<td>-1,161</td>
</tr>
<tr>
<td>net use</td>
<td>3,092</td>
<td>3,016</td>
<td>3,000</td>
<td>3,386</td>
</tr>
</tbody>
</table>

Table 9.4B shows that option I has a small low pressure steam deficiency. This steam deficiency is converted into Nm³ natural gas equivalents by assuming an energetical efficiency of 85 % during steam production and additionally 10 % heat losses to the environment during the utilization of the steam. Thus, 1 ton of steam (130 °C, H=2.72 MJ/kg) is produced by burning 111 Nm³ of natural gas (heat of combustion 32 MJ/kg). The options II to IV generate just as much low pressure steam during the oxidative roasting as is required for the leaching processes. The remaining energy is used to generate high pressure steam which is utilized, after superheating, for power generation.

The natural gas consumption, which is given in table 4C, increases significantly due to the on-site power generation.
Table 9.4A  The (saturated) steam balance for the options I to IV (in ton steam/ton SHG zinc, negative signs indicate steam releases).

<table>
<thead>
<tr>
<th>step</th>
<th>option I</th>
<th>option II</th>
<th>option III</th>
<th>option IV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>low pressure ($T = 130 , ^\circ C$)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oxidative roasting</td>
<td>-1.92</td>
<td>-0.25</td>
<td>-0.25</td>
<td>-0.14</td>
</tr>
<tr>
<td>leaching</td>
<td>2.23</td>
<td>0.45</td>
<td>0.45</td>
<td>0.45</td>
</tr>
<tr>
<td>residue drying</td>
<td>-0.44</td>
<td>-0.40</td>
<td>-0.40</td>
<td>-0.51</td>
</tr>
<tr>
<td>fly-ash leaching</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>deficiency</td>
<td>0.07</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>high pressure ($T = 312 , ^\circ C$)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oxidative roasting</td>
<td>-</td>
<td>-1.28</td>
<td>-1.28</td>
<td>-1.22</td>
</tr>
<tr>
<td>reductive roasting</td>
<td>-</td>
<td>-</td>
<td>-0.24</td>
<td>-0.24</td>
</tr>
<tr>
<td>flash furnace</td>
<td>-3.72</td>
<td>-2.06</td>
<td>-2.22</td>
<td>-1.16</td>
</tr>
<tr>
<td>fumer</td>
<td>-1.13</td>
<td>-1.13</td>
<td>-1.18</td>
<td>-1.18</td>
</tr>
<tr>
<td>superheater</td>
<td>4.85</td>
<td>4.47</td>
<td>4.92</td>
<td>3.80</td>
</tr>
</tbody>
</table>

Table 9.4C  The natural gas requirements for the options I to IV (in Nm$^3$/ton SHG zinc)

<table>
<thead>
<tr>
<th>step</th>
<th>option I</th>
<th>option II</th>
<th>option III</th>
<th>option IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>reductive roasting</td>
<td>-</td>
<td>-</td>
<td>31</td>
<td>33</td>
</tr>
<tr>
<td>residue drying</td>
<td>90</td>
<td>81</td>
<td>81</td>
<td>36 + 65</td>
</tr>
<tr>
<td>flash furnace</td>
<td>226</td>
<td>142</td>
<td>154</td>
<td>99</td>
</tr>
<tr>
<td>slag fumer</td>
<td>125</td>
<td>125</td>
<td>130</td>
<td>131</td>
</tr>
<tr>
<td>superheater</td>
<td>94</td>
<td>87</td>
<td>95</td>
<td>74</td>
</tr>
<tr>
<td>net use</td>
<td>535</td>
<td>435</td>
<td>491</td>
<td>438</td>
</tr>
</tbody>
</table>
In order to compare the overall energy requirements for the options I to IV, the Nm³ natural gas equivalent is defined. The equivalent of 1 MJ electric energy is 2.963 MJ heat obtained by combustion of natural gas. This relates to an energetic efficiency of 30.7 % during power generation. Table 9.4\textsuperscript{D} provides the overall results of the energy requirements.

Table 9.4\textsuperscript{D} The overall energy requirements for the options I to IV (in Nm³ natural gas equivalents/ton SHG zinc)

<table>
<thead>
<tr>
<th>energy carrier</th>
<th>option I</th>
<th>option II</th>
<th>option III</th>
<th>option IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas</td>
<td>535</td>
<td>435</td>
<td>491</td>
<td>438</td>
</tr>
<tr>
<td>electricity</td>
<td>1,031</td>
<td>1,005</td>
<td>1,000</td>
<td>1,129</td>
</tr>
<tr>
<td>steam</td>
<td>8</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>overall use</td>
<td>1,574</td>
<td>1,440</td>
<td>1,491</td>
<td>1,567</td>
</tr>
</tbody>
</table>

Table 9.4\textsuperscript{D} shows the minor differences in energy consumption between the four options. Option I is consuming more energy than option II, because option I maintains jarosite precipitation and hot acid leach steps in the primary plant, whereas these two steps are abandoned in option II. Introducing a reductive roaster in option II, which yields option III, increases the energy consumption and makes the plant somewhat more complex. Option IV, which is equivalent to option III in all respects but the location of the historical jarosite feed, shows that this alternative even further increases the energy consumption.

Before conclusions are drawn it is essential to emphasize that the differences in energy consumption are relatively small. It is even doubtful whether based on the accuracy of the estimates which were used, it is justified to conclude that the differences reported on the bottom line of table 9.4\textsuperscript{D} are significant. It is, however, evident that the energy consumption of the options I to IV equals in average $1.5 \times 10^3$ Nm³/ton SHG zinc.

The energy calculations for option V are given in the tables 9.5\textsuperscript{A,B,C,D}. The rotary furnace which is utilized for roasting ferrous sulfate is described in appendix 9.11. Three different types of steam are used in the treatment plant. The
medium pressure steam (180 °C or 200 °C) is used for heating the (feed) streams to the fractional crystallizer. The low pressure steam is used for the leaching steps in the primary winning units, as well as for heating the reductive leach. The off-gases of the residue dryer and the rotary furnace are used for generating medium and low pressure steam. Steam is generated by combustion of natural gas with an assumed energetical efficiency of 85%. The heat losses to the environment while using steam are assumed to be 10%. As far as reasonably possible, waste heat is used for heating purposes and water is recycled. The steam circuits are closed loops between the crystallizers and the boilers, thus utilizing the heat content of the condensate as efficient as possible. The heat content of the waste water stream which leaves the hydroxide precipitation is not lost since this stream is partly recycled as feed wash stream to the fractional crystallization unit and the reductive leach.

Table 9.5\textsuperscript{A} Power requirements for option V for different values of the slurry density $M_i$ (in kg FeSO$_4\cdot$H$_2$O/1000 kg H$_2$O) (in kWh/ton SHG zinc)

<table>
<thead>
<tr>
<th>step</th>
<th>$M_i = 50$ kg/ton</th>
<th>$M_i = 100$ kg/ton</th>
<th>$M_i = 200$ kg/ton</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxidative roasting</td>
<td>110</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>acid production</td>
<td>213</td>
<td>255</td>
<td>269</td>
</tr>
<tr>
<td>leaching</td>
<td>751</td>
<td>365</td>
<td>247</td>
</tr>
<tr>
<td>electrolysis</td>
<td>3,373</td>
<td>3,373</td>
<td>3,373</td>
</tr>
<tr>
<td>melting and casting</td>
<td>127</td>
<td>127</td>
<td>127</td>
</tr>
<tr>
<td>others</td>
<td>71</td>
<td>71</td>
<td>71</td>
</tr>
<tr>
<td>residue dryer</td>
<td>29</td>
<td>29</td>
<td>29</td>
</tr>
<tr>
<td>rotary furnace</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>fractional crystallizer and reductive leach</td>
<td>77</td>
<td>77</td>
<td>77</td>
</tr>
<tr>
<td>sum</td>
<td>4,755</td>
<td>4,411</td>
<td>4,307</td>
</tr>
</tbody>
</table>

Table 9.5\textsuperscript{A} shows the power requirements for the options V. Comparing table 9.5\textsuperscript{A} with table 9.4\textsuperscript{A} it becomes evident that the fact that no power is generated
by using waste heat, increases the net power consumption for the options V considerably. Table 9.5 gives the steam consumption for the hydro-metallurgical option.

Table 9.5 Steam requirements in option V for different values of the slurry density \( M_t \) (in kg \( \text{FeSO}_4\cdot\text{H}_2\text{O}/1000 \text{ kg H}_2\text{O} \)) and the redissolution percentage \( RD \) (all figures in ton steam/ton SHG zinc, negative signs indicate steam releases).

<table>
<thead>
<tr>
<th>( M_t )</th>
<th>50</th>
<th>50</th>
<th>100</th>
<th>100</th>
<th>200</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>( RD = 0 )</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>

| low pressure \( (T = 130^\circ C) \) |
| oxi. roaster | -1.92 | -1.92 | -1.92 | -1.92 | -1.92 | -1.92 |
| leaching | 9.31 | 9.31 | 4.42 | 4.42 | 3.07 | 3.07 |
| reduct. leach | - | - | 0.10 | - | 0.07 | - |
| residue dryer | - | - | - | - | -0.07 | - |
| rotary furnace | - | - | - | - | -0.08 | - |
| deficiency | 7.39 | 7.39 | 2.60 | 2.50 | 1.07 | 1.15 |

| med. pressure \( (T = 180^\circ C) \) |
| fractional |
| crystallizer | 3.40 | 3.42 | 0.70 | 1.10 | 0.09 | 0.58 |
| residue dryer | -0.59 | -0.59 | -0.59 | -0.59 | -0.09 | -0.58 |
| rotary furnace | -0.08 | -0.08 | -0.08 | -0.08 | - | - |
| deficiency | 2.73 | 2.75 | 0.03 | 0.43 | 0 | 0 |

| med. pressure \( (T = 200^\circ C) \) |
| fractional |
| crystallizer | 1.41 | 1.41 | 0.60 | 0.60 | 0.37 | 0.37 |
| residue dryer | - | - | - | - | -0.37 | - |
| rotary furnace | - | - | - | - | -0.06 | - |
| deficiency | 1.41 | 1.41 | 0.60 | 0.60 | 0 | 0.31 |

212
For all values of the slurry density there is a steam deficiency. However, in particular for lower values of the slurry density, this steam deficiency becomes very large. This has an important effect on the natural gas requirements which are given in table 9.5\textsuperscript{c}. It is also obvious that the influence of whether or not dissolution is required in the fractional crystallizer is not of influence on the energy requirements for low values of the slurry density.

Table 9.5\textsuperscript{c}  The natural gas consumption for option V for different values of the slurry density $M_i$ (in kg FeSO$_4$.H$_2$O/1000 kg H$_2$O) and the redissolution percentage RD (in Nm$^3$ natural gas/ton SHG zinc).

<table>
<thead>
<tr>
<th>RD</th>
<th>$M_i = 50$</th>
<th>$M_i = 50$</th>
<th>$M_i = 100$</th>
<th>$M_i = 100$</th>
<th>$M_i = 200$</th>
<th>$M_i = 200$</th>
</tr>
</thead>
<tbody>
<tr>
<td>residue dryer</td>
<td>72.1</td>
<td>72.1</td>
<td>72.1</td>
<td>72.1</td>
<td>72.1</td>
<td>72.1</td>
</tr>
<tr>
<td>rotary furnace</td>
<td>38.3</td>
<td>38.3</td>
<td>38.3</td>
<td>38.3</td>
<td>38.3</td>
<td>38.3</td>
</tr>
<tr>
<td>steam production</td>
<td>1,179.2</td>
<td>1,180.9</td>
<td>342.3</td>
<td>366.1</td>
<td>119.0</td>
<td>154.0</td>
</tr>
<tr>
<td>sum</td>
<td>1,289.6</td>
<td>1,291.3</td>
<td>452.7</td>
<td>476.5</td>
<td>229.4</td>
<td>264.4</td>
</tr>
</tbody>
</table>

The results in table 9.5\textsuperscript{c} are added to the results in table 9.5\textsuperscript{a} by using the same conversion factor as used for the options I to IV.

Table 9.5\textsuperscript{d}  The overall energy requirements for the option V (in Nm$^3$ natural gas equivalents/ton SHG zinc)

<table>
<thead>
<tr>
<th>energy carrier</th>
<th>$M_i = 50$</th>
<th>$M_i = 50$</th>
<th>$M_i = 100$</th>
<th>$M_i = 100$</th>
<th>$M_i = 200$</th>
<th>$M_i = 200$</th>
</tr>
</thead>
<tbody>
<tr>
<td>RD = 0</td>
<td>1,289.6</td>
<td>1,291.3</td>
<td>452.7</td>
<td>476.5</td>
<td>229.4</td>
<td>264.4</td>
</tr>
<tr>
<td>gas</td>
<td>1,585.0</td>
<td>1,585.0</td>
<td>1,470.3</td>
<td>1,470.3</td>
<td>1,435.7</td>
<td>1,435.7</td>
</tr>
<tr>
<td>power</td>
<td>2,874.6</td>
<td>2,876.3</td>
<td>1,923.0</td>
<td>1,946.8</td>
<td>1,665.1</td>
<td>1,700.1</td>
</tr>
<tr>
<td>overall use</td>
<td>2,874.6</td>
<td>2,876.3</td>
<td>1,923.0</td>
<td>1,946.8</td>
<td>1,665.1</td>
<td>1,700.1</td>
</tr>
</tbody>
</table>

Table 9.5\textsuperscript{d} clearly shows the steep rise of the natural gas requirements of this option with decreasing slurry density. Comparing the results presented in table
9.4 and table 9.5 it is evident that option V requires more energy than the options I to IV despite the fact that the process temperatures in option V are much lower.

This demonstrates the advantage of high temperature processes; waste heat may be used as a source of energy with a high intrinsic value, which in this case is used for power generation. The hydrometallurgical process uses energy of a lower quality since the applied temperatures are much lower, but because of that, its waste heat can not be used for power generation.

9.7 CONCLUSIONS

The following conclusions are drawn:

-i- The hydrometallurgical zinc refining processes with integrated pyrometallurgical jarosite treatment processes as discussed in this paper (options I to IV) reduce the quantity of residue to be stored to less than 5 wt% of the original amount of jarosite residue.

-ii- The options I to IV show relatively small differences in energy requirement per unit zinc produced. The most energy-efficient process appears to be option II. Its energy consumption is below 1500 Nm³ natural gas equivalents/ton SHG zinc.

-iii- The hydrometallurgical zinc refining process with integrated jarosite treatment process as discussed in this paper as option V produces two residue streams which have no application: waste gypsum and Pb/Ba/As-residue. The two streams combined amount about 25 - 30 % by weight of the original amount of jarosite residue. In order to apply the produced hematite in the steel industry the zinc content should be very low, which complicates the process and requires large amounts of chemicals and energy. The process parameter which determines the incorporation of zinc in ferrous sulfate monohydrate is the partition coefficient D. The relatively high value of this partition coefficient inhibits the practical application of an integrated hydrometallurgical treatment process.
Hydrometallurgical integrated jarosite treatment with fractional crystallization of ferrous sulfate monohydrate is an interesting technique, but given the final residue quantity and the high energy requirements it is not competitive with a pyrometallurgical treatment process, which offers better opportunities for waste-heat use and yields a smaller amount of unapplicable residue.

ACKNOWLEDGEMENTS

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9.8 REFERENCES


215


Appendix 9.1 Chemical reaction equations used for calculating the mass and energy balances

1. **Oxidative roasting (all options)**

   *concentrate*

   \[
   \begin{align*}
   2 \text{ZnS} + 3 \text{O}_2 & \rightarrow 2 \text{ZnO} + 2 \text{SO}_2 \quad \text{(ditto for Pb and Cd)} \\
   4 \text{CuS} + 5 \text{O}_2 & \rightarrow 2 \text{Cu}_2\text{O} + 4 \text{SO}_2 \\
   \text{ZnS} + 2 \text{FeS} + 5 \text{O}_2 & \rightarrow \text{ZnO} . \text{Fe}_2\text{O}_3 + 3 \text{SO}_2 \\
   \text{ZnS} + 2 \text{FeS}_2 + 7 \text{O}_2 & \rightarrow \text{ZnO} . \text{Fe}_2\text{O}_3 + 5 \text{SO}_2
   \end{align*}
   \]

   *historical jarosite (option IV)*

   \[
   \begin{align*}
   4 \text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 & \rightarrow 6 \text{Fe}_2\text{O}_3 + 8 \text{SO}_2 + \text{O}_2 + 2 \text{N}_2 + 20 \text{H}_2\text{O} \\
   2 \text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6 & \rightarrow 3 \text{Fe}_2\text{O}_3 + 4 \text{SO}_2 + 2 \text{O}_2 + 9 \text{H}_2\text{O} \\
   2 \text{PbSO}_4 & \rightarrow 2 \text{PbO} + 2 \text{SO}_2 + \text{O}_2 \\
   2 \text{ZnSO}_4 . 7\text{H}_2\text{O} & \rightarrow 2 \text{ZnO} + 2 \text{SO}_2 + \text{O}_2 + 14 \text{H}_2\text{O} \quad \text{(ditto for Mg)} \\
   2 \text{3(CdSO}_4)_2 . 8\text{H}_2\text{O} & \rightarrow 6 \text{CdO} + 6 \text{SO}_2 + 3 \text{O}_2 + 16 \text{H}_2\text{O} \\
   4 \text{CuSO}_4 . 5\text{H}_2\text{O} & \rightarrow 2 \text{Cu}_2\text{O} + 4 \text{SO}_2 + 20 \text{H}_2\text{O} + 3 \text{O}_2 \\
   2 \text{MnSO}_4 . \text{H}_2\text{O} & \rightarrow 2 \text{MnO} + 2 \text{SO}_2 + \text{O}_2 + 2 \text{H}_2\text{O} \\
   2 \text{CaSO}_4 . 2\text{H}_2\text{O} & \rightarrow 2 \text{CaO} + 2 \text{SO}_2 + \text{O}_2 + 4 \text{H}_2\text{O} \\
   \text{ZnO} + \text{Fe}_2\text{O}_3 & \rightarrow \text{ZnO} . \text{Fe}_2\text{O}_3
   \end{align*}
   \]

2. **Reductive roasting (options III and IV)**

   \[
   \begin{align*}
   12 \text{ZnO} . \text{Fe}_2\text{O}_3 + \text{CH}_4 & \rightarrow 12 \text{ZnO} + 8 \text{Fe}_3\text{O}_4 + \text{CO}_2 + 2 \text{H}_2\text{O} \\
   \text{CH}_4 + \text{CO}_2 & \rightarrow 2 \text{CO} + 2 \text{H}_2
   \end{align*}
   \]

After the reductive roasting step, regardless of the zinc ferrite content of the calcine, 96 wt% of the zinc metal is assumed to be zinc oxide and 4 wt% has remained zinc ferrite. Additionally 0.5-1.0 wt% of the concentrate ends up in a fly-ash. The fly-ash is reported to contain: Pb 52%, Cd 8.1% and Zn 5.5%. These elements are assumed to be present as oxides, which makes them contribute
72.1 wt% to the fly-ash weight. The remainder is assumed to be all of the arsenic(III) oxide present in the calcine. The total amount of fly-ash then equals 3729 ton/a which indeed lies in the range of 0.5-1.0 wt% of the concentrate mass. The figures are based on results reported by Püllenberg [9].

3. Neutral leach (all options)

calcine

ZnO + 2 H⁺ → Zn²⁺ + H₂O (ditto for Cd, Pb, Mg, Ba, Ca and Mn⁺)

Manganese is supposed to be present as MnO; Mn₃O₄ or Mn₂O₃ may also occur, but are neglected

Cu₂O + 2 H⁺ → 2 Cu⁺ + H₂O
4 Cu⁺ + O₂ + 4 H⁺ → 4 Cu²⁺ + 2 H₂O
Pb²⁺ + SO₄²⁻ → PbSO₄(s) (ditto for Ba)
Ca²⁺ + SO₄²⁻ + 2 H₂O → CaSO₄.2H₂Oₙ

magnetite (options III and IV)

Despite the fact that magnetite is slightly soluble in the neutral leach solution, its solubility is neglected. Any dissolved Fe²⁺ will be oxidized to Fe³⁺ and then precipitate as ferric hydroxide by aerating the neutral leach solution.

hydroxide precipitate (option V)

Zn(OH)₂ + 2 H⁺ → Zn²⁺ + 2 H₂O (ditto for Cd, Cu, Mn and Mg)
Fe(OH)₃ + 3 H⁺ → Fe³⁺ + 3 H₂O

4. Jarosite precipitation (options I and V)

NH₄⁺ + 3 Fe³⁺ + 2 SO₄²⁻ + 6 H₂O → NH₄Fe₃(SO₄)₂(OH)₆·₉H₂O + 6 H⁺
3 Fe³⁺ + 2 SO₄²⁻ + 7 H₂O → H₃[Fe₃(SO₄)₂(OH)₆·₉H₂O] + 5 H⁺
NH₃ + H⁺ → NH₄⁺
5. Acid Leach (options I and V)

\[ \text{ZnO} \cdot \text{Fe}_2\text{O}_3 + 8 \text{H}^+ \rightarrow \text{Zn}^{2+} + 2 \text{Fe}^{3+} + 4 \text{H}_2\text{O} \]
\[ \text{H}_2\text{SO}_4 \rightarrow 2 \text{H}^+ + \text{SO}_4^{2-} \]

6. Purification (all options)

\[ \text{Cu}^{2+} + \text{Zn} \rightarrow \text{Cu} + \text{Zn}^{2+} \] (ditto for Cd)

In order to get an effective cementation process a 50% molar excess of zinc dust is added to the first step. After separating the Cd-Cu-Zn-cement from the solution, cadmium is selectively redissolved. Subsequently, cadmium is once more cemented with 50% molar excess zinc dust. The zinc dust used in the cementation process is recycled to either the neutral leach or the jarosite precipitation as an acidic zinc solution.

7. Electrolysis (all options)

\[ \text{Zn}^{2+} + 2 \text{H}_2\text{O} \rightarrow 2 \text{Zn} + 4 \text{H}^+ + \text{O}_{2(g)} \]

In the options I, II and V the bleed to remove excess water and to prevent the accumulation of magnesium and manganese consists of spent acid, which is formed during the electrolysis process. Therefore, the reactions used to describe the gypsum precipitation in the bleed stream are discussed in this section.

\[ \text{Zn}^{2+} + 2 \text{OH}^- \rightarrow \text{Zn(OH)}_{2(s)} \] (ditto for Mg\(^{2+}\) and Mn\(^{2+}\) (all options) and Cd\(^{2+}\) and Cu\(^{2+}\) (options III and IV))

\[ \text{CaO} + 2 \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{O} \]
\[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2 \text{OH}^- \]
\[ \text{Ca}^{2+} + \text{SO}_4^{2-} + 2 \text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O}_{(s)} \]
8. Flash Furnace and Slag Fuming (options I to IV)

\[ \text{waste gypsum} \]
\[ 2 \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow 2 \text{CaO} + 2 \text{SO}_2 + 4 \text{H}_2\text{O} + \text{O}_2 \]
\[ \text{Mg(OH)}_2 \rightarrow \text{MgO} + \text{H}_2\text{O} \]
(ditto for Zn and Mn and Cd and Cu (option II and III))

\[ \text{historical jarosite (options I, II and III)} \]
\[ \text{fresh jarosite (option I)} \]
\[ 4 \text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 \rightarrow 6 \text{Fe}_2\text{O}_3 + 8 \text{SO}_2 + \text{O}_2 + 2 \text{N}_2 + 20 \text{H}_2\text{O} \]
\[ 2 \text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6 \rightarrow 3 \text{Fe}_2\text{O}_3 + 4 \text{SO}_2 + 2 \text{O}_2 + 9 \text{H}_2\text{O} \]
\[ 2 \text{PbSO}_4 \rightarrow 2 \text{PbO} + 2 \text{SO}_2 + \text{O}_2 \]
\[ 2 \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} \rightarrow 2 \text{ZnO} + 2 \text{SO}_2 + 14 \text{H}_2\text{O} + \text{O}_2 \]
(ditto for Mg)
\[ 2 \text{3(CdSO}_4)_8\text{H}_2\text{O} \rightarrow 6 \text{CdO} + 6 \text{SO}_2 + 16 \text{H}_2\text{O} + 3 \text{O}_2 \]
\[ 4 \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow 2 \text{Cu}_2\text{O} + 4 \text{SO}_2 + 20 \text{H}_2\text{O} + 3 \text{O}_2 \]
\[ 2 \text{MnSO}_4 \cdot \text{H}_2\text{O} \rightarrow 2 \text{MnO} + 2 \text{SO}_2 + 2 \text{H}_2\text{O} + \text{O}_2 \]
\[ 2 \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow 2 \text{CaO} + 2 \text{SO}_2 + 4 \text{H}_2\text{O} + \text{O}_2 \]
\[ 2 \text{ZnS} + 3 \text{O}_2 \rightarrow 2 \text{ZnO} + 2 \text{SO}_2 \]
\[ \text{As}_2\text{O}_5 \rightarrow \text{As}_2\text{O}_3 + \text{O}_2 \]
\[ 4 \text{Cu}_2\text{O} + \text{CH}_4 \rightarrow 8 \text{Cu} + \text{CO}_2 + 2 \text{H}_2\text{O} \]
\[ 4 \text{ZnO} + \text{CH}_4 \rightarrow 4 \text{Zn} + \text{CO}_2 + 2 \text{H}_2\text{O} \]
(ditto for Pb and Cd)
\[ 2 \text{MgO} + \text{SiO}_2 \rightarrow \text{Mg}_2\text{SiO}_4 \]
(ditto for Ca)
\[ \text{MnO} + \text{SiO}_2 \rightarrow \text{MnSiO}_3 \]
(ditto for Ba)
\[ 2 \text{Fe}_2\text{O}_3 + 2 \text{SiO}_2 \rightarrow 2 \text{Fe}_2\text{SiO}_4 + \text{O}_2 \]

specific for options II, III and IV:
\[ 2 \text{ZnO} \cdot \text{Fe}_2\text{O}_3 + 2 \text{SiO}_2 \rightarrow 2 \text{ZnO} + 2 \text{Fe}_2\text{SiO}_4 + \text{O}_2 \]

specific for options III and IV:
\[ 2 \text{Fe}_3\text{O}_4 + 3 \text{SiO}_2 \rightarrow 3 \text{Fe}_2\text{SiO}_4 + \text{O}_2 \]

220
The so-obtained Cu,Cd,Zn,Pb,As - fly-ash reoxidizes during cooling:

\[ 2 \text{Zn} + \text{O}_2 \quad \rightarrow \quad 2 \text{ZnO} \quad (\text{ditto for Pb and Cd}) \]

\[ 4 \text{Cu} + \text{O}_2 \quad \rightarrow \quad 2 \text{Cu}_2\text{O} \]

9. Fly-Ash leaching unit  \text{(options I to IV)}

\[ \text{ZnO} + 2 \text{H}^+ \quad \rightarrow \quad \text{Zn}^{2+} + \text{H}_2\text{O} \quad (\text{ditto for Cd, Pb and Ca}) \]

\[ \text{Pb}^{2+} + \text{SO}_4^{2-} \quad \rightarrow \quad \text{PbSO}_{4(s)} \]

\[ \text{Ca}^{2+} + \text{SO}_4^{2-} + 2 \text{H}_2\text{O} \quad \rightarrow \quad \text{CaSO}_4.2\text{H}_2\text{O}_{(s)} \]

\[ \text{Cu}_2\text{O} + 2 \text{H}^+ \quad \rightarrow \quad 2 \text{Cu}^+ + \text{H}_2\text{O} \]

\[ 4 \text{Cu}^+ + \text{O}_2 + 4 \text{H}^+ \quad \rightarrow \quad 4 \text{Cu}^{2+} + 2 \text{H}_2\text{O} \]

\[ \text{Fe}_2(\text{SO}_4)_{3}6\text{H}_2\text{O} \quad \rightarrow \quad 2 \text{Fe}^{3+} + 3 \text{SO}_4^{2-} + 6 \text{H}_2\text{O} \]

\[ 2 \text{As}_2\text{O}_3 + 2 \text{O}_2 + 4 \text{Fe}^{3+} + 6 \text{H}_2\text{O} \quad \rightarrow \quad 4 \text{FeAsO}_4 + 12 \text{H}^+ \]

10. Reductive leaching \text{(option V)}

\[ \text{NH}_4\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 6 \text{H}^+ \quad \rightarrow \quad \text{NH}_4^+ + 3 \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 6 \text{H}_2\text{O} \]

\[ \text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_9 + 5 \text{H}^+ \quad \rightarrow \quad 3 \text{Fe}^{3+} + 2 \text{SO}_4^{2-} + 7 \text{H}_2\text{O} \]

\[ 2 \text{Fe}^{3+} + \text{SO}_2 + 2 \text{H}_2\text{O} \quad \rightarrow \quad 2 \text{Fe}^{2+} + 4 \text{H}^+ + \text{SO}_4^{2-} \]

\[ \text{ZnSO}_4.7\text{H}_2\text{O} \quad \rightarrow \quad \text{Zn}^{2+} + \text{SO}_4^{2-} + 7 \text{H}_2\text{O} \quad (\text{ditto for Mg}) \]

\[ 3(\text{CdSO}_4)\text{.8H}_2\text{O} \quad \rightarrow \quad 3 \text{Cd}^{2+} + 3 \text{SO}_4^{2-} + 8 \text{H}_2\text{O} \]

\[ \text{CuSO}_4.5\text{H}_2\text{O} \quad \rightarrow \quad \text{Cu}^{2+} + \text{SO}_4^{2-} + 5 \text{H}_2\text{O} \]

\[ \text{MnSO}_4.\text{H}_2\text{O} \quad \rightarrow \quad \text{Mn}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O} \]

11. Fractional ferrous sulfate crystallization \text{(option V)}

\[ \text{Fe}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O} \quad \rightarrow \quad \text{FeSO}_4.\text{H}_2\text{O} \]

12. Ferrous sulfate roasting \text{(option V)}

\[ 4 \text{FeSO}_4.\text{H}_2\text{O} \quad \rightarrow \quad 2 \text{Fe}_2\text{O}_3 + 4 \text{SO}_2 + \text{O}_2 + 4 \text{H}_2\text{O} \]

221
13. Hydroxide precipitation (option V)

\[
\begin{align*}
\text{Zn}^{2+} + 2 \text{OH}^- & \rightarrow \text{Zn(OH)}_2 \quad \text{(ditto for Cd, Cu, Mg and Mn)} \\
\text{NH}_4^+ + \text{OH}^- & \rightarrow \text{NH}_3 + \text{H}_2\text{O} \\
\text{H}^+ + \text{OH}^- & \rightarrow \text{H}_2\text{O} \\
\text{Fe}^{3+} + \text{OH}^- & \rightarrow \text{Fe(OH)}_3
\end{align*}
\]

Appendix 9.2 The composition of Groningen natural gas in vol. %

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vol. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_4)</td>
<td>81.29</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>2.87</td>
</tr>
<tr>
<td>C(_3)H(_8)</td>
<td>0.38</td>
</tr>
<tr>
<td>C(_4)H(_10)</td>
<td>0.15</td>
</tr>
<tr>
<td>C(_5)H(_12)</td>
<td>0.04</td>
</tr>
<tr>
<td>C(_6)H(_14)</td>
<td>0.05</td>
</tr>
<tr>
<td>N(_2)</td>
<td>14.32</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.01</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Appendix 9.3 Details on the hydrometallurgical treatment process

In order to obtain the (model) results presented in table 9.3 the following design assumptions have been made.

1. Zinc content of process jarosite

Process jarosite consists of ammonium and hydronium jarosite and of an insoluble residue which consists of lead sulfate, barium sulfate, arsenic(III)oxide, gypsum and silicium dioxyde. The jarosite residue still contains water in which zinc sulfate remains dissolved. It is assumed that in
spite of the washing procedure operated in the primary refining plant 3 % of the dry weight of jarosite residue consists of (soluble) zinc sulfate (which equals 1.21 wt% zinc). This is a conservative estimate because newly developed belt filter washing techniques are claimed to yield lower levels of soluble zinc in jarosite residue [17]. This estimate leads to an increasing zinc load to the reductive jarosite leach with increasing jarosite production. Given the same concentrate intake, an increasing jarosite production is the consequence of a larger recycle from the treatment unit.

2. Zinc content of historical jarosite

Historical jarosite has a lower zinc content (1 wt%), since due to water percolation through the ponds, part of the zinc content has been 'washed' out and been recovered by the drainage system.

3. Reductive leach

The reductive leach is operated at 100 °C. Sulfur dioxide is first dissolved in water (200 kg/m³) at 15 °C. The slurry density of the feed to the reductive leach equals 300 g/kg H₂O. After the reductive leach the remaining solids are filtered and subsequently washed with recycled hot sodium sulfate solution. The wash-solution is added to the ferrous sulfate solution produced in the reductive leach and fed into the first crystallizer of the fractional crystallization unit.

4. Description of the fractional crystallization unit

Crystallization processes are used because of their potentiality of producing high purity solids with only limited energy requirements. In the case of zinc and ferrous sulfate the selectivity for producing relatively pure ferrous sulfate crystals is determined by the ratio of the solubility of zinc sulfate over ferrous sulfate. The higher this ratio, the higher the selectivity. The solubility
diagrams of ferrous and zinc sulfate are given in figure 9.6 [18]. The solubility of zinc sulfate is still substantial above 140 °C, whereas the solubility of ferrous sulfate is low in that temperature range. For this reason the unit which is aimed at crystallizing 'clean' ferrous sulfate is designed to operate at 160 °C.

![Solubility diagram](image)

**Figure 9.6** The solubility diagram of zinc and ferrous sulfate as a function of temperature (in g anhydrous salt/kg H₂O)

The proportionality constant between the composition of the liquid phase and the resulting composition of the crystalline phase is called the partition coefficient and is defined in section 9.4.5. Lowering the ratio of zinc over iron in the liquid phase obviously decreases the zinc content of the obtained crystals. Thus, a unit operation is designed in which the ratio of zinc over iron in the liquid phase gradually decreases towards the point where the crystals leave the unit. This technique is called 'fractional crystallization'. The fractional crystallization concept is frequently used in organic crystallization. The operation principle is as follows. The pregnant solution enters the first of a group of five subsequent crystallizers and yields relatively contaminated crystals, which were grown at a high supersaturation. The latter factor
stimulates the formation of highly agglomerated crystals with inclusions of contaminated liquid. These crystals are filtered. Subsequently, they are washed with the filtrate originating from the second crystallizer. The filtrate and the wash liquid leave the unit and are used to preheat the feed streams before they enter the hydroxide precipitation step. After the crystals from the first step are washed they enter the second step. Two extremes should now be distinguished. The first extreme is that no cooling is required in order to obtain a crystalline phase in equilibrium with its surrounding solution, which has a lower zinc over iron ratio. The driving force for this process is the discrepancy between the feed crystal composition and the crystal composition in equilibrium with the solution present in the second crystallizer. The process described above may thermodynamically be feasible, but still be unpractical for kinetical reasons. In that case, the kinetics of the process may be speeded up by redissolving the crystalline phase at a lower temperature. One unit of a fractional crystallizer with complete redissolution is shown in figure 9.7 and forms the second extreme.

![Diagram](image)

**Figure 9.7** One crystallizer in a fractional crystallization unit, in this case with complete dissolution
In figure 9.7 a redissolution step at 120 °C is used. This temperature is applicable for slurry densities up to 100 kg FeSO\textsubscript{4}.H\textsubscript{2}O/1000 kg H\textsubscript{2}O. For a slurry density of 200 kg FeSO\textsubscript{4}.H\textsubscript{2}O/1000 kg H\textsubscript{2}O a redissolution temperature of 100 °C is required.

For this particular application no research results are available which enable to predict the extent to which redissolution is required in a practical process. For this reason the energy consumption of the designed unit is presented as a range. The lower value is valid when redissolution is not required, the higher value includes 100 % redissolution.

The second step in the crystallization unit is equivalent to the third and fourth step. The fifth step utilizes water (instead of filtrate) to wash the crystals. In order to prevent redissolution during washing, the wash water temperature is designed to be higher than 175°C. The justification for choosing five crystallizers is given in figure 9.8, which shows the residual zinc content of ferrous sulfate monohydrate for different numbers of crystallizers and different values of the slurry density. Obviously, the slow increase in crystal purity with an increasing number of crystallizers limits its number at about five.

![Graph showing the zinc content in FeSO\textsubscript{4}.H\textsubscript{2}O](image)

Figure 9.8 The zinc load in FeSO\textsubscript{4}.H\textsubscript{2}O after a different number of crystallizers for T = 160°C and D = 0.2. M\textsubscript{t} is given in (kg crystal/1000 kg H\textsubscript{2}O) which is about equal to kg/m\textsuperscript{3} H\textsubscript{2}O.
Figure 9.8 is valid for any redissolution percentage between zero and 100, because for every step it is assumed that equilibrium between the solid and the liquid phase is reached. Additional water is added in step 2, 3 and 4 in order to limit the slurry density to the desired value, i.e. 50, 100 or 200 kg FeSO₄·H₂O/1000 kg H₂O. Figure 9.8 reveals the importance of this slurry density for obtaining FeSO₄·H₂O of sufficient purity. Despite the fact that a slurry density of 50 kg FeSO₄·H₂O/1000 kg H₂O yields a low residual zinc content, it is obvious from table 9.3 in section 9.5 that the chemicals demands for this low value of the slurry density rise to an unacceptable high level. This is due to the high recycle rate which is required for obtaining high purity crystals.

Figure 9.9 shows the importance of the partition coefficient for the feasibility of this process. The lower the value of the partition coefficient, the more promising this process is likely to be. For this particular application the hydrometallurgical option can not reasonably reach the desired purity of FeSO₄·H₂O, because the value of the partition coefficient is too high.

Figure 9.9  The resulting zinc load in FeSO₄·H₂O using five crystallizers operated at T = 160°C for different values of the slurry density Mₘ (kg crystal/1000 kg H₂O) and the partition coefficient D.
5. Drying and roasting

The resulting ferrous sulfate monohydrate crystals are obtained as a 60 wt% slurry, which is dried in a pneumatic dryer. This yields a dried crystalline product and a hot off-gas which contains over 50% (mole) of water vapour. The off-gas is used to produce steam (180°C, 10 bar) and is subsequently partly condensed in a heat exchanger, heating the feed to the reductive leach. The solids are fed to a rotary furnace which converts ferrous sulfate to hematite and sulfur dioxide. The solids heat recovery in this step is limited to heating of the incoming combustion air. The hot gas which is rich in sulfur dioxide, is used to produce steam (180°C, 10 bar) and is subsequently fed to a sulfuric acid plant.

Appendix 9.4 The energy use in primary electrolytic zinc winning operations

In order to estimate the energy use in the 'classical' electrolytic zinc winning operations the results of a survey published by Kellogg [16] were used. The concentrate used in Kellogg's calculations resembles the concentrate assumed in this paper. This justifies the use of his figures and assumptions. This study uses the following energy use relations (per unit operation).

1. Roasting

Roasting is an exothermic process, which yields 1.05 ton steam/ton concentrate in option I and V. The obtained steam has an energy content of 2.72 MJ/kg at a temperature of 130°C. The options II, III and IV produce steam which is used for heating (130°C) and steam which, after being superheated, is used for power generation. The balance between the two products is determined by the demand for 'heating steam' in the different options. The surplus of energy is used for power generation, as is shown in table 9.4°C.

The roasting process includes the electrostatic precipitators, filters, fluid bed
blowers etc. The power requirements of the roasting process are estimated at 60 kWh/ton concentrate. In option IV historical jarosite is fed into the roaster, which reduces the steam production, due to its endothermic decomposition. The power requirements for option IV are estimated at 100 kWh/ton concentrate.

2. Sulfuric acid production

For the production of sulfuric acid a double contact process is assumed. The electrical power requirements for this process are given as 135 kWh/ton acid (100 %). The sulfur dioxide formed during the concentrate roasting as well as during the thermal jarosite or ferrous sulfate treatment is assumed to be fed into the sulfuric acid plant.

3. Leaching, precipitation and purification

Included in the operations leaching, precipitation and purification are the pumps, filters, stirring devices etc. The electrical power requirements are given as 177 kWh/ton zinc. However, in this 'ton zinc', drosses and zinc dust required in the purification are included. For each ton of Special High Grade (or SHG, 99.995 %) zinc which may be sold, R tons of zinc are required, in which R represents the ratio of (SHG zinc + dross + zinc powder) over SHG zinc. In this study the value of R is chosen as 1.0129, which is slightly lower than the value reported by Kellogg. Thus, a slight increase of the energy efficiency since the publication of Kellogg's survey (1980) is taken into account. For the leaching, precipitation and purification section in option I the value of 177 kWh/ton zinc is multiplied by R to yield 179.3 kWh/ton SHG zinc.

In the options II, III and IV however, no jarosite precipitation and hot acid leach are operated. Arbitrarily it is assumed that the electrical energy requirements for the neutral leach and purification section amount 40 % or 71.7 kWh/ton SHG zinc.

Option V does operate a jarosite precipitation and hot acid leach step, but in option V, due to the large recycle of iron, the relationship between a ton SHG
zinc and the precipitation and hot acid leaching of iron is no longer valid. In
order to compensate for the increased electrical energy requirements the
literature value of (177*R) kWh/ton SHG zinc is multiplied by the ratio P which
equals (ton jarosite residue formed) over (ton jarosite residue formed in option
I). This ratio probably overestimates the increase in the leach-precipitate
section, because the neutral leach and purification flows are not significantly
higher. In order to compensate for the overestimated value here, no correction
for the magnitude of the recycle is made in the hydrometallurgical treatment
plant's electrical energy requirements.

The steam requirements reported in literature vary considerably. This study
uses the value of (2.2*R) ton steam/ton SHG zinc, which equals 2.23 ton
steam/ton SHG zinc. This value is multiplied by 0.2 for the options II, III and
IV which yields 0.45 ton steam/ton SHG zinc. This correction is made because
these options do not include hot acid leach and jarosite precipitation which are
the major steam consuming steps in this section. For option V the value of the
steam requirement equals (2.2*R*P) ton steam/ton SHG zinc.

4. Electrolysis

Included in the electrical energy requirements for the electrolysis are a.o.
pumps. The stripping of the cathodes is also included. It is reported that the
overall requirement equals 3330 kWh/ton zinc or (3330*R=) 3373 kWh/ton SHG
zinc.

5. Melting and casting

This procedure requires 125 kWh/ton zinc or (125*R=) 128.6 kWh/ton SHG zinc.

6. Others

The 'others' include laboratory facilities, offices, heating etc. They require 70
kWh/ton zinc or (70*R=) 70.9 kWh/ton SHG zinc.
Appendix 9.5 Energy requirements for reductive roasting

The reductive roaster is operated to convert the calcine which is obtained in the oxidative roaster into a calcine low in zinc ferrite. The net reaction equation for this process is given in appendix 9.1, section 2. For calculating the thermal and electrical energy requirements for this step more detailed assumptions were required.

In order to obtain a gas atmosphere with sufficient reductive potential a CO₂/CO-ratio of 1.5 is taken, based on [9] and references therein. This ratio is almost comparable to the one used in the nickel industry for reduction of nickeliferrous iron oxide to magnetite and Ni/Fe-metal [19].

The roaster is operated at 800 °C. At that temperature and for a CO₂/CO-ratio of 1.5 the heat of combustion of Groningen natural gas (see appendix 9.2) equals 433 kJ/mole. Heat is required for:

i) the decomposition of zinc ferrite into zinc oxide and hematite,
ii) the conversion of hematite into magnetite,
iii) the reduction of arsenic(V)oxide to arsenic(III)oxide,
iv) the heat of vaporization of lead oxide, arsenic(III)oxide, cadmium and zinc and
v) the heat losses due to radiation and convection.

The conversion of cadmium and zinc to its metallic form is not included, since these metals volatilize and re-oxidize inside the roaster which consumes no nett energy for the respective chemical reactions.

The process is assumed to be carried out in a rotary kiln. The heat transfer from the gas to the solids is assumed to take place in the first 33 % of the length of the kiln. The solids which originate from the oxidative roaster were assumed to have a temperature of 600 °C at the entrance and have to be heated up to 800 °C by a gas which reaches a final temperature of 850 °C. The heat losses are estimated at 3 kW/m². The heat transfer coefficient is estimated at 50 W m⁻² K⁻¹ and the logarithmic mean temperature equals 440 K, given a
combustion temperature of natural gas of 1800 °C for this CO₂/CO-ratio. Assuming the thermal isolation to have a thickness of 0.20 m and the kiln to have a length/diameter-ratio of 20, the following data are obtained:

Option III: natural gas consumption 31.2 Nm³ gas/ton SHG zinc
kiln length 47 m
kiln diameter 2.33 m

Option IV: natural gas consumption 32.7 Nm³ gas/ton SHG zinc
kiln length 50 m
kiln diameter 2.46 m

Electrical energy requirements are assumed to be equal for the kilns, and are estimated to be 100 kWh/ton SHG zinc.

The heat content of the off-gases is used to generate steam (312 °C, 100 bar). This steam is superheated in a separate heater and used for power generation.

Appendix 9.6 Energy requirements for residue drying

Wet solids are dried before they are fed into pyrometallurgical processes like roasting or slag production. This is especially important in the latter case, because the gas volume produced, determines the equipment size.

In this paper pneumatic dryers were selected as equipment. For pneumatic dryers the following electrical and thermal energy requirement estimates are available in literature [20]:

i) electrical energy requirement 0.2 MJ/kg vaporized water

ii) thermal energy requirement 4.5 MJ/kg vaporized water

Thus, the thermal energy efficiency is equal to about 50 %, since the heat of vaporization of water equals 2.26 MJ/kg at 100 °C. The dryer off-gases are used to generate saturated steam (130 °C) in the options I to IV and 180°C in option
V. They are also used in option V for preheating the feed to the reductive leach. The residual moisture content in the solids is 1 wt% for all dryers except the one in option V. In option V a negligible water content of the solids is essential in order to avoid the formation of FeSO₄·OH during the roasting of ferrous sulfate. FeSO₄·OH is a relatively stable intermediate which is formed in the presence of water. The formation of FeSO₄·OH increases the sulfur content of hematite which is undesirable.

In option IV two pneumatic dryers are applied. The first dryer is used to evaporate water from historical jarosite residue which is fed into the oxidative roaster. The second dryer is required to dry the feed of the flash furnace.

Appendix 9.7 The flash furnace: design aspects and energy requirements

The flash furnace is chosen as a first process step towards reducing the content of cadmium, zinc, lead, arsenic and to some extent copper in the final slag residue. The technology of flash furnaces in itself is not new, but they have not found application in low-grade residue treatment.

In a flash furnace a liquid slag bath is obtained at temperatures ranging from 1200 - 1400 °C, depending on the melting point of the slag. During its continuous operation the relatively volatile heavy metals evaporate during suspension smelting and are collected as their oxides or sulfates in the fly-ash.

1. The specific gas flow

Flash furnaces are commonly used for smelting copper and copper/nickel sulfide concentrates. Their capacities are reported on the basis of tons of solid feed treated per unit bath area or per unit furnace volume per day [21,22]. This is not a solid design basis because the corresponding gas flow varies considerably with the degree of oxygen enrichment of the combustion air.

Commercial furnaces vary in gas flow from less than 500 m³/m² bath.hour
INCO, Copper Cliff) to more than 2200 m³/m² bath.hour for Outokumpu-type furnaces using pre-heated air only for combustion of fuel. This leads to corresponding variations in dust carry-over. Traditional reverberating furnaces have gasflows close to 1000 m³/m² bath.hour, with a dust load of about 1 % of the charge. Since this is about intermediate for the range calculated for flash furnaces a gas flow of 1000 m³/m² bath.hour was chosen as basis for our design. The gases originate from the combustion of natural gas and from the partial decomposition of the residue during the process. It is economical to limit the required gas flow to a minimum, since the bath size is linearly proportional to it and so are the equipment costs and the energy losses. This aim is achieved by using oxygen-enriched air. Using technically pure oxygen as a fuel, however, is expensive, so an optimum should be chosen. In this study, without further optimization, it is assumed that 67 % of the oxygen demand which is not fulfilled by the oxygen liberated by the decomposition of the residue, is supplied as technically pure oxygen (95 % O₂, 5% N₂), the remaining 33 % originating from air.

2. Energy supply and demand

Groningen natural gas (see appendix 9.2) is used as fuel. Its heat of combustion is estimated at 700 kJ/mole gas. The combustion energy is used for:

i) endothermic decomposition reactions;

ii) heating the resulting gases, slag and fly-ash;

iii) coping with the heat losses to the environment.

Based on the composition of the slag which for all pyrometallurgical options predominantly consists of a mixture of FeO, SiO₂ and CaO, melting points of the slags were obtained by using ternary phase diagrams. For each option the operation temperature of the flash furnace was chosen 100 °C above the so-determined slag melting point. In order to ensure good heat transfer, the gas was assumed to have a temperature of 200 °C above the slag melting point. The
heat content of the slag at 1200 °C was estimated at 1600 kJ/kg, for 1300 °C it was 1700 kJ/kg and for 1400 °C it was 1800 kJ/kg. The specific heat content of the fly-ash was assumed to be equal to the specific heat content of the slag.

The energy required for decomposition reactions is obtained by calculating the heat effect of the chemical reactions, mentioned in appendix 9.1 for the options I to IV. This also yields the heat content of the product gases. The differences in the zinc feed content in different options have no influence on the composition of the slag leaving the flash furnace, since the reduction potential of the gas atmosphere is for each option adjusted to the feed zinc load of the furnace.

The energy lost to the environment is obtained assuming the following:

i) the thickness of the isolation of the furnace is 0.30 m;
ii) the thermal conductivity of the isolation is 2 W/m.K;
iii) the outer temperature of the furnace is 125 °C;
iv) the outer surface area of the apparatus equals five times the slag bath surface area;
v) water cooling is applied in order to prevent hot-spots.

The energy losses to the environment constitute between 10 and 16 % of the overall energy inputs for the different options.

Having determined the entire energy requirement, the overall gas flow, the natural gas consumption and the slag bath size are calculated. Table 9.6 summarizes the results for the options I to IV.

After the flash furnace the hot gases are used to produce steam (312 °C, 100 bar) which, after additional heating, is used for power generation. After the waste heat boiler, the fly-ashes are collected in electrostatic precipitators. The energy requirements of electrostatic precipitators are described in literature [23]. For this application a specific energy consumption of 0.85 kW/m³.s is assumed, given a gas temperature of 312 °C.
The technically pure oxygen is produced in a cryogenic turn-key air separation unit, which will not be discussed here. The energy requirement for obtaining technically pure oxygen is estimated at 400 kWh/ton O₂ (technically pure).

Table 9.6 Calculation results for the flash furnace application as low-grade residue convertor

<table>
<thead>
<tr>
<th>option #</th>
<th>feed ton/hour¹</th>
<th>bath temp °C</th>
<th>techn. O₂ Nm³/hour</th>
<th>air Nm³/hour</th>
<th>nat. gas Nm³/hour</th>
<th>bath area m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>32.57</td>
<td>1,400</td>
<td>7,436</td>
<td>16,801</td>
<td>6,721</td>
<td>277</td>
</tr>
<tr>
<td>II</td>
<td>29.50</td>
<td>1,300</td>
<td>4,566</td>
<td>10,317</td>
<td>4,205</td>
<td>162</td>
</tr>
<tr>
<td>III</td>
<td>29.78</td>
<td>1,300</td>
<td>5,239</td>
<td>11,834</td>
<td>4,579</td>
<td>178</td>
</tr>
<tr>
<td>IV</td>
<td>25.29</td>
<td>1,200</td>
<td>3,146</td>
<td>7,110</td>
<td>2,924</td>
<td>97.5</td>
</tr>
</tbody>
</table>

¹ A year is assumed to include 7008 productive hours; thus an availability of 80% is assumed

Appendix 9.8 Calculation of the energy requirement of the batch slag fumer

The batch slag fumer is applied to produce a slag which meets the environmental standards with respect to the leaching of hazardous metals by natural processes and with respect to the composition.

Pilot plant experiments, carried out the Pasminco Research Centre under assignment of Budelco B.V. have confirmed that the composition and the leaching properties of slags produced from jarosite residue fulfil the requirements of the Dutch Government for use in building materials. The contents and background of the Dutch 'building materials directive' are beyond the scope of this paper [4]. It should be noted that this directive demands a residual antimony concentration below 100 ppm, before a material is accepted for use as natural gravel substitute in concrete. Achieving this limit results in a zinc concentration below 1000 ppm.
In order to reach these very low residual zinc concentrations in the slag, a high CO/CO$_2$-ratio is required. This is obtained by using natural gas as fuel and coal as reductant. The carbon requirements are about 800 kg/ton zinc which is to be removed [24]. The zinc load to the slag fumer equals about 1.25 % of the quantity of slag. The slag leaving the fumer contains about 0.1 % of zinc. This means that the net zinc removal equals about 1300 tons/year. This requires about 2000 tons of coal/year, assuming the carbon content of coal to be 50 %, which is reasonable for a coal containing a medium amount of volatiles.

For this paper the quintessence of the pilot plant tests is the quantity of energy required for slag fuming. This equals 233 Nm$^3$ natural gas/ton slag [25]. The data given in the tables in section 9.6 are obtained by relating the zinc and the slag production.

The electrical energy is required for producing technical oxygen (95 % O$_2$, 5 % N$_2$) which is needed for obtaining a bath temperature of 1300 °C at that particular CO/CO$_2$-ratio.

**Appendix 9.9 The superheater and the on-site power station**

In the options I to IV the hot combustion gases resulting from the flash furnace and the batch slag fumer are suitable for use in power generation. In the options III and IV the off-gases of the reductive roaster are also used. After these high temperature steps waste heat boilers are used to produce saturated steam at 312 °C (100 bar). Steam, which is useful for power generation has to be superheated in order to prevent condensation on turbine blades. The final temperature of superheated steam prepared for power generation is typically 560 °C. In order to heat steam from 312 °C to 560 °C, 0.528 MJ/kg is required. This energy is obtained by burning natural gas, with a supposed energetic efficiency of 85 %. Since for the options I to IV the amount of 100 bar steam is known, the natural gas consumption is easily calculated.

The superheater produces steam which is used for generating power with an efficiency of 30.7 %. Thus, the power production equals 1.10 MJ$_{\text{elec.}}$/kg steam (100 bar, 560 °C).
Appendix 9.10 Fly-ash leaching unit and miscellaneous

The fly-ash leaching unit uses energy for redissolving the fly-ash and for selectively precipitating ferric arsenate. The overall energy requirements for the fly-ash leaching unit are assumed to be:

i) 0.2 ton steam (low pressure, 130 °C)/ton SHG zinc
ii) 50 kWh/ton SHG zinc

The options I to IV have similar fly-ash leaching units, so for all options the same estimates are used. For the options I to IV a power consumption of 50 kWh/ton SHG zinc is assumed for miscellaneous purposes.

Appendix 9.11 The rotary furnace for ferrous sulfate roasting

The feed of this furnace is assumed to consist of anhydrous ferrous sulfate which decomposes to hematite and sulfur dioxyde. The heat effect of this reaction is 195 kJ/mol FeSO$_4$ at 670°C [26]. This temperature is chosen because the higher the temperature, the faster the reaction proceeds. However, above 670 °C a phase transition of hematite occurs which increases the required heating energy, without increasing the reaction speed [27].

The rotary furnace is operated countercurrently. Its calculated length equals 60 m. The internal diameter equals 2.6 m and the wall thickness is assumed to be 0.2 m. Given a heat transfer coefficient of 50 W/m$^2$.K, the overall heat losses to the environment are calculated at 6 %. The energy required for operating the furnace in option V equals 38.3 Nm$^3$ natural gas/ton SHG zinc. The hot gases leaving this unit are used for generating medium pressure steam.
Chapter 10

Emissions factors for aqueous industrial cadmium emissions in the Rhine River basin; a historical reconstruction for the period 1970 - 1988

ABSTRACT

Aqueous emission factors are obtained for industrial cadmium discharges to the Rhine River basin in the period 1970 - 1988. The emission factors are calibrated by comparing the predicted cadmium emissions with monitoring data. The agreement between the predicted and the monitored emissions justifies the use of these emission factors in time as parameters showing the environmental burden of (industrial) activities independent of production quantities.

The emission factors for most of the cadmium processing industries have decreased between 80 and 98 % in the period 1970 - 1988. The overall industrial cadmium discharges to the Rhine River basin have decreased by 90 % from about 140 ton/year in the period 1970 - 1972 to about 13.5 ton in 1988.

published by F. Elgersma, S. Anderberg* and W.M. Stigliani* (*affiliated with the International Institute for Applied Systems Analysis, schloßplatz 1, 2361 Laxenburg, Austria) in: Proc. 7th International Cadmium Conference, New Orleans (1992). This paper is a summary of the IIASA working paper 91/5 by the same authors.
10.1 INTRODUCTION AND AIM

An emission factor is defined here as the emission of a particular pollutant (in this case: cadmium) to the environment per unit of production of a given product. The product can either be one in which the pollutant is deliberately embodied (e.g. Cd in nickel-cadmium batteries), or one in which the pollutant is an unwanted waste material released during production (e.g. Cd in steel production).

Emission factors are useful in quantifying the environmental burden of (industrial) activities. The factors are not constant over time, due to ever improving process technologies which reduce hazardous emissions to the environment. Despite that, little attention has been paid in literature to the historical change of emission factors.

This study analyses such changes for the aqueous industrial cadmium discharges to the Rhine River basin (see figure 10.1) in the period 1970 - 1988. This study is part of a wider investigation of chemical pollution in the Rhine basin currently being undertaken at the International Institute for Applied Systems Analysis, IIASA. Cadmium is a priority substance in environmental policy, because the metal and its compounds are toxic to humans and many other species. The period 1970 - 1988 is of particular interest because during this time the industrial aqueous cadmium emissions to the Rhine have decreased by over 90%. The emission factors obtained in this study may well be applicable for studying historical aqueous emissions in other industrialized river basins.

10.2 METHODOLOGY

Table 10.1 provides an overview of those cadmium processing industries that are relevant to this study. It also indicates in which part of the basin the branches are mainly represented.
Figure 10.1 The geography of the Rhine River and its main tributaries
Table 10.1 Relevant cadmium processing industries and their locations

<table>
<thead>
<tr>
<th>Intentional Use of cadmium</th>
<th>main representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc and lead mining industry</td>
<td>FRG(^1), Ruhr area</td>
</tr>
<tr>
<td>Zinc and lead winning industry</td>
<td>FRG, Duisburg</td>
</tr>
<tr>
<td>Battery manufacture</td>
<td>FRG, Ruhr area</td>
</tr>
<tr>
<td>Pigment manufacture</td>
<td>FRG, Nordrhine Westfalia and Stuttgart</td>
</tr>
<tr>
<td>Stabilizer manufacture</td>
<td>FRG, Stuttgart</td>
</tr>
<tr>
<td>Stabilizer application (PVC) industry</td>
<td>FRG, Nordrhine Westfalia</td>
</tr>
<tr>
<td>Cadmium plating</td>
<td>FRG, Ruhr area</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Inadvertent Use of Cadmium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet phosphoric acid manufacture</td>
</tr>
<tr>
<td>Iron and steel industry</td>
</tr>
<tr>
<td>Other non-ferrous metal industry</td>
</tr>
<tr>
<td>Other mining activities</td>
</tr>
</tbody>
</table>

\(^1\) FRG stands for the former Federal Republic of Germany


Aqueous emission factors for cadmium are reported in literature. As will be shown the reported factors from different literature sources may differ more than one order of magnitude discussing the same industrial activity. However,
a rather uniform change for the different branches in the period 1970 - 1988 is expected for two reasons.

- **i-** Increasing regulatory pressure was exerted on cadmium emitting industries (see section 10.4 of this chapter).

- **ii-** The use of industrial waste water treatment plants started in the 1970's and was greatly expanded in the 1980's. Thus, technology was available and was applied for improving the water quality in the Rhine basin.

Emission factor estimates are based on data obtained by literature search, taking into account the two reasons for a rather uniform change of the factors in time, regardless of the branches.

### 10.3 MONITORING DATA

The Rhine River basin supplies drinking water for parts of the FRG and The Netherlands and therefore the water quality is monitored extensively on different locations. For cadmium, monitoring data are collected since 1973. The locations Village-Neuf, Seltz, Koblenz and Lobith are indicated in figure 10.1. The monitoring data present the overall aqueous pollutant load, regardless of the phase in which cadmium is present. This overall load is the sum of all pollutant inputs into the river, regardless of their origin. Two categories are distinguished:

- **i-** point sources (including both industrial and non-industrial point sources like sewage treatment plants treating municipal waste water) and

- **ii-** non-point sources (run-off, natural origin, air pollution etc.)

A statistical method for analysis of monitoring data has been developed by Behrendt and Böhme [1]. Their method distinguishes the fraction of the two pollutant source categories for a given overall pollutant input into a river. Discussing this method is beyond the scope of this paper. Figure 10.2, which
shows time trends in emission of cadmium, is based on monitoring data. One may observe a strong decrease of the cadmium concentrations in the Rhine over the period 1973 - 1987. It also indicates that this decline is mainly due to decreasing point source emissions. Table 10.2 contains the point source emissions, calculated according to this method, showing the importance of the Rhine sector between Koblenz and Lobith.

Figure 10.2 Analysis of point and nonpoint loads of cadmium to the Rhine River in the period 1973 - 1987, based on water quality monitoring data (source: [1])

Monitoring data obtained in The Netherlands, downstream of Lobith, have not been used because extensive sedimentation and resuspension of cadmium is known to occur in this part of the river. Thus, measurement of cadmium concentrations of the river water is no longer directly correlated with aqueous emissions from point sources. In contrast, very little accumulation of cadmium occurs in the Rhine between Village-Neuf and Lobith [2].
Table 10.2  Cadmium point source discharges to the Rhine in the period 1973 - 1987 in ton/year. Source: [1]

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Village-Neuf</td>
<td>---</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Seltz</td>
<td>---</td>
<td>23 - 28&lt;sup&gt;1&lt;/sup&gt;</td>
<td>1 - 2</td>
</tr>
<tr>
<td>Koblenz</td>
<td>2 - 7</td>
<td>6 - 9</td>
<td>---</td>
</tr>
<tr>
<td>Lobith</td>
<td>109 - 123</td>
<td>72 - 77</td>
<td>6 - 9</td>
</tr>
</tbody>
</table>

<sup>1</sup> The fact that the cadmium load decreased between Seltz and Koblenz in the period 1978 - 1982 is in disagreement with the assumption that no net accumulation occurs in this part of the river.

This is not true for the main tributaries to the Rhine, in which net sedimentation of cadmium does occur because of slower-flowing water with regulated flow [2,3]. Hydrological studies are in preparation to take into account this sedimentation problem [4].

**10.4 LEGISLATION**

In 1976 the Council of the European Communities published Directive 76/464/EEC on the prevention of water pollution, which contained list 1 (often referred to as the 'black list') and list 2 (the 'grey list') [5]. These lists were also accepted in the international negotiations on the prevention of the pollution of the River Rhine [6]. Cadmium and its compounds were among the first chemicals listed on the 'black list'. This list obliged EC-member states to prevent pollution with 'black list' chemicals with the best technical means. In 1983 the Council of the European Community published a revision of Directive 76/464/EEC. The 1983 Directive (83/513/EEC) contained specific limit values according to the type of industry concerned and quality objectives for the aquatic environment into which cadmium is discharged by such industries [7]. The limit values had to be met by January 1<sup>st</sup> of 1986 and replaced earlier limit...
values [8]. The branche related limit values are given in the emission factor review. In addition the FRG government increased the fee for the residual discharge of cadmium considerably in the period 1982 - 1986 [9]. The discharge of 1 kg Cd/year had a fee of DM 180.-- in 1982 and a fee of DM 400.-- in 1986. The first ten kg Cd discharge per year remained free of charge. In The Netherlands for aqueous heavy metal discharges no fees had to be paid in the period 1970 - 1988. In 1989 the Dutch Parliament accepted a proposal for introducing fees in the Dutch law for prevention of surface water pollution (Wet Verontreiniging Oppervlaktewater). The introduction of fees is planned for January 1st of 1992. The discharge of 1 kg Cd/year will be feed with Hfl 420.-- (≈ DM 375,--) [10].

It is obvious that the discussion of emission factors for aqueous heavy metal discharges would be much easier if the authorities (had) published the fees which were received from emitting industries. If, in addition, the legal discharge permission per company would also be available, a much more accurate and detailed analysis of aqueous heavy metal discharges could be made. The fees and the discharge permissions, however, are confidential and therefore unavailable for use in this paper.

10.5 INDUSTRIAL OVERVIEW

All branches of the cadmium processing industry given in table 1 are represented in the Rhine River basin. The non-ferrous metal industry includes zinc and lead mining, winning and recycling. The iron and steel industry and the wet phosphoric acid industry are relevant because of the cadmium impurities in their raw materials. The cadmium product manufacturers and industrial users in the basin are divided over six categories:

-i- cadmium pigment manufacturing,
-ii- cadmium stabilizer manufacturing,
-iii- PVC manufacturing,
-iv- cadmium plating,
-v- alloy manufacturing and processing and
-vi- nickel-cadmium battery manufacturing.
The pigment, stabilizer, PVC and battery branches are all represented by a few large companies. The plating industry, however, is divided over a large number of generally small companies, most of which are concentrated in the Ruhr area. The alloy manufacturing and processing industry is not important as source of aqueous cadmium emissions, and is not further considered here.

Figure 10.3 shows the quantities of the major cadmium products (in ton cadmium/year) produced in the entire FRG for the period 1970 - 1988. Figure 10.4 shows the relative importance of each product in percentages. The figures 10.3 and 10.4 indicate the decrease of cadmium plating in time and the increase of battery manufacturing. The overall use of cadmium decreased 47% in the period 1975 - 1988.

The following section contains a branch-wise description of the different in-basin cadmium processing industries, their locations, the obtained production data, the estimated aqueous emission factors and the calculated emissions.

10.6 CADMIUM PROCESSING INDUSTRIES

10.6.1 Non-ferrous metal mining

During the period 1970 - 1987 three non-ferrous metal mines were operational in the basin. Despite the rather fragmentary data, estimates of the in-basin zinc and zinc/lead concentrate production data were obtained [18-28]. Waterborne dispersal is claimed to be the major route of cadmium loss from non-ferrous metal mines [29]. For the mid 1970's an overall aqueous cadmium emission of 60 - 150 ton/year in the EC is estimated [29]. Calculating the emission factor for Western Germany with 29.4% of the EC mining capacity yields an emission factor of 74 - 176 g Cd/ton Zn concentrate produced [19].

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Figure 10.3 The production of cadmium products in the FRG for 1970 - 1988

Figure 10.4 The relative percentages of cadmium products manufactured in the FRG for 1970 - 1988

These numbers correspond to an accompanying zinc loss of 2.5 - 5.9 % of the total concentrate production, which clearly is far too high. For a mine producing 120,000 tons of concentrate, an overall cadmium emission of 0.29 ton
is estimated [30]. This yields an emission factor of 2.4 g Cd/ton Zn concentrate
produced. This emission factor is used for the period 1970 - 1977. For the
period 1978 - 1987 an emission factor of 1 g Cd/ton Zn concentrate is used. The
dercrease is justified by taking into account stricter environmental legislation
and consequently improved on-site housekeeping. Due to lack of data no
estimate for 1988 is available. Table 10.3 summarizes the in-basin production,
emission factors and emissions due to non-ferrous metal mining.

Table 10.3  Zn concentrate production, Cd emission factor and emissions from
non-ferrous mining in the Rhine basin in the period 1970 - 1987

<table>
<thead>
<tr>
<th>period</th>
<th>production Zn concentrate ton / year</th>
<th>emission factor g Cd / (ton Zn concentrate)</th>
<th>emission (ton Cd/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 - 1972</td>
<td>146,000</td>
<td>2.4</td>
<td>0.4</td>
</tr>
<tr>
<td>1973 - 1977</td>
<td>148,000</td>
<td>2.4</td>
<td>0.4</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>135,000</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>100,000</td>
<td>1.0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 10.3 indicates that non-ferrous metal mining does not cause major
cadmium emissions.

10.6.2 Other in-basin mining activities

Some coal and salt mines are also located in the basin area. An overall
cadmium emission to the Rhine from coal mining has been estimated to be 30
kg/year in 1989 [31]. This emission level suggests that coal mining is not a
significant source of cadmium in the basin.

For salt mining an aqueous emission of 520 kg/year is given for 1989 [31]. The
source of emission is located in the French part of the basin. In order to
backcast these emissions to the 1970's a linkage between the point source
chloride discharge to the Rhine and the cadmium emissions due to salt mining
is made. This is justified by the fact that the salt discharges are related to
natural salt resources with an assumed constant composition. Using point source Cl⁻ discharge data, the results presented in table 10.4 are obtained [1].

Table 10.4 Aqueous cadmium emissions due to salt mining in the period 1973 - 1988. Source: [1].

<table>
<thead>
<tr>
<th>period</th>
<th>chloride discharges (kg/s)</th>
<th>Cd emission (ton Cd/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1973 - 1977</td>
<td>114</td>
<td>0.46</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>133</td>
<td>0.53</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>130</td>
<td>0.52</td>
</tr>
<tr>
<td>1988</td>
<td>-</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Table 10.4 is calculated using the proportionality constant of 0.13 g Cd/ton Cl⁻. Assuming the discharged salt to be sodium chloride this constant equals 0.08 g Cd/ton salt. The average cadmium concentration in the earth's crust equals (0.1-0.5 g Cd/ton) [32] which has the expected same order of magnitude. The relative contribution of cadmium emissions due to salt mining was negligible in the 1970's but because of the large reduction in cadmium emissions overall becomes significant by the end of the 1980's.

10.6.3 Primary zinc refining

Aqueous cadmium emissions from the primary zinc industry depends on the applied refining process. Two primary zinc refining plants operate in the basin; one Imperial Smelting Furnace-smelter in Duisburg and one electrolytic plant in Datteln. The production statistics for these plants are based on incomplete literature data and estimates [25-28,33]. The company operating the ISF-smelter claims for 1979 to cause an emission of 1 ton [29]. An ISF-smelter simultaneously produces lead and zinc. Therefore the emission factor is linked to the joint production of lead and zinc, which equalled 95,400 ton in 1979. This yields an emission factor of 10 g Cd/ton (Zn+Pb). For the period 1970 - 1977 the emission factor is assumed to be higher. No literature sources directly justify
this statement, but monitoring data indicate a significant decline of point source emissions in the period 1975 - 1980 (see table 10.2). Between Koblenz and Lobith over 110 tons of cadmium were emitted by point sources in the period 1973 - 1977, whereas 67 tons were emitted in the period 1978 - 1982. The emission factor for 1975 is calculated by multiplying the emission factor for 1978 - 1982 (10 g Cd/ton (Zn+Pb)) by (110/67). This yields an emission factor for 1970 - 1977 of 16 g Cd/ton (Zn+Pb).

According to The Deutsche Kommission zur Reinhaltung des Rheins this particular plant emitted 480 kg cadmium in 1985 [34]. Given the production of 100,500 ton (Zn+Pb) the emission factor equals 5 g Cd/ton (Zn+Pb). The International Centre for Water Studies (ICWS) independently measured and added up all cadmium point source discharges to the River Rhine by the non-ferrous metal industry in 1989. Their result is an emission of 90 kg Cd/year [31]. Even if this primary zinc refining plant is the major emitter, the emission factor remains limited to about 0.5 g Cd/ton (Zn+Pb) for this last period.

For the electrolytic plant with a zinc production capacity of 105,000 tons, the aqueous cadmium emission equaled 10 kg Cd/year in 1977 [30]. This yields an emission factor of 0.1 g Cd/ton Zn. An emission factor of 0.02 g Cd/ton Zn for a comparable 150,000 ton Zn plant in 1982 is also reported [35]. Therefore the emission of the in-basin electrolytic primary zinc refining plant is assumed to be negligible small. Table 10.5 summarizes the in-basin primary lead and zinc production, the corresponding emission factors and the resulting emissions for the period 1970 - 1988.

Primary zinc and lead refining in the Rhine basin in the period 1970 - 1988 has remained approximately constant, but obviously the aqueous emissions of cadmium have decreased significantly, which is reflected by the change of emission factors in time.
Table 10.5  The production of lead and zinc, the cadmium emission factors and the cadmium emissions for primary lead/zinc refining in an ISF-smelter in the Rhine River basin in the period 1970 - 1988

<table>
<thead>
<tr>
<th>period</th>
<th>production lead (ton)</th>
<th>production zinc (ton)</th>
<th>emission factor g Cd/ton(Zn+Pb)</th>
<th>emission (ton Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 - 1972</td>
<td>38,000</td>
<td>84,000</td>
<td>16</td>
<td>2.0</td>
</tr>
<tr>
<td>1973 - 1977</td>
<td>30,300</td>
<td>67,000</td>
<td>16</td>
<td>1.6</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>29,600</td>
<td>65,500</td>
<td>10</td>
<td>1.0</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>31,300</td>
<td>69,200</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>1988</td>
<td>30,000</td>
<td>70,000</td>
<td>0.5</td>
<td>0.05</td>
</tr>
</tbody>
</table>

10.6.4  Other non-ferrous metal refining industries

This category includes secondary zinc refining, secondary cadmium refining and secondary lead refining.

Secondary zinc refining was operational in a large metal recycling plant in Duisburg until 1984. No statistics on production and raw material use are available. This plant however, is assumed to have been the major in-basin cadmium discharger until the beginning of the 1980's [11,36-38]. Two quotes illustrate this: "by the end of the 1970's one non-ferrous metal company emitted 35 to 45 tons cadmium annually, given a total emission of 68 tons due to non-ferrous metallurgy" [37]. The "(...) aqueous cadmium emissions have declined considerably in recent years mainly due to the closure of one plant which had been responsible for about 90 % of the aqueous emissions"[38].

An emission factor for this plant is not defined, because the raw material spectrum is too variable to justify a generalized factor. Aqueous cadmium emissions were assumed to be 50 tons/year for the period 1970 - 1982 and 25 tons/year in 1983 and 1984. No emissions are attributable to this source after its closure in 1984.
Secondary cadmium refining was carried out during the period 1970 - 1979 by one company located in Bonn. The cadmium production capacity of the plant was 300 tons [19]. No data are available with respect to emissions or emission factors. As a worst case scenario an emission factor of 10 kg Cd/ton Cd processed is used. This yields an emission of 3 tons/year in the 1970's.

Secondary lead refining is carried out in five different plants. Two plants are located in Duisburg and one each in Rommerskirchen, Braubach and Nürnberg [33]. No actual secondary lead production data are available. If all companies operate on average at 90 % of their production capacities, the annual production equals about 100,000 tons. An emission factor of 6.2 g Cd/ton Pb is provided [39]. Using this factor yields an emission of 0.6 ton Cd/year for this branch. This figure indicates that in comparison to secondary zinc and cadmium refining, these sources are negligible. Table 10.6 summarizes the presented data.

Table 10.6 Aqueous cadmium emissions due to selected non-ferrous metal industries in the Rhine River basin in the period 1970 - 1988

<table>
<thead>
<tr>
<th>period</th>
<th>secondary zinc refining (ton Cd/year)</th>
<th>secondary cadmium refining (ton Cd/year)</th>
<th>secondary lead refining (ton Cd/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 - 1972</td>
<td>50</td>
<td>3.0</td>
<td>0.6</td>
</tr>
<tr>
<td>1973 - 1977</td>
<td>50</td>
<td>3.0</td>
<td>0.6</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>50</td>
<td>3.0²</td>
<td>0.6</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>25¹</td>
<td>0</td>
<td>0.6</td>
</tr>
<tr>
<td>1988</td>
<td>0</td>
<td>0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

¹ after 1984, this source equals zero
² after 1979, this source equals zero
Table 10.6 indicates that the secondary zinc refining plant has been a dominant aqueous emitter of cadmium in the basin until the mid 1980's. Due to lack of more precise data, however, the emissions quoted here have a large inherent uncertainty, that limits the accuracy with which other estimated emission factors can be calibrated from river monitoring data.

10.6.5 Cadmium pigment manufacturing

The production process for cadmium pigments includes unit operations such as filtration and precipitation [40]. These steps give rise to aqueous pollution which is caused by residual dissolved cadmium or very finely dispersed cadmium sulfide particles. Despite rapid improvements in waste water treatment technology, the entire elimination of cadmium emissions to surface waters is not yet attainable.

Five chemical producers were manufacturing cadmium pigments in the basin [41]. In consulting the pigment industry it was pointed out that during the period 1970 - 1988 three plants, located in Besigheim, Bonn and Leverkusen, dominated the market [42]. The accuracy of data on cadmium use in pigment production was confirmed by industry sources, and cadmium use per plant was obtained by dividing pigment production among the three plants [11-17]. A review of published emission factors is shown in table 10.7. All sources refer to the Rhine basin except ref. [43] which pertains to the USA.

Waste water treatment units which efficiently capture low concentrations of heavy metals were not available in the early 1970's. Therefore the emission factor for cadmium pigment manufacturing is expected to be high in the beginning of the 1970's. It decreases significantly during the 1970's. This is in accordance with the trend observed in analyzing the literature.

Table 10.8 provides the estimated cadmium pigment manufacturing data for the three relevant plants, the estimated emission factors and the resulting in-basin emissions for the period 1970 - 1988.
Table 10.7 Published emission factors for cadmium pigment manufacturing

<table>
<thead>
<tr>
<th>date ref.</th>
<th>emission factor (g Cd/kg Cd)</th>
<th>source</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1973</td>
<td>1.0</td>
<td>[11]</td>
<td></td>
</tr>
<tr>
<td>1978</td>
<td>20</td>
<td>[29]</td>
<td>without waste water treatment</td>
</tr>
<tr>
<td>1978</td>
<td>10</td>
<td>[3,29,44]</td>
<td>waste water treatment, eff. 50 %</td>
</tr>
<tr>
<td>1979</td>
<td>1.46</td>
<td>[36]</td>
<td>calculated: emission/production</td>
</tr>
<tr>
<td>1982</td>
<td>1.0</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>1984</td>
<td>8.2</td>
<td>[3,43,44]</td>
<td>waste water treatment, eff. 50 %</td>
</tr>
<tr>
<td>1984</td>
<td>2.6</td>
<td>[48]</td>
<td>waste water treatment, eff. 90 %</td>
</tr>
<tr>
<td>1983-1985</td>
<td>0.7</td>
<td>[8]</td>
<td>legal emission limit</td>
</tr>
<tr>
<td>1985</td>
<td>0.5</td>
<td>[34]</td>
<td>calculated: emission/production</td>
</tr>
<tr>
<td>since 1986</td>
<td>0.3</td>
<td>[7]</td>
<td>legal emission limit</td>
</tr>
</tbody>
</table>

Table 10.8 The relevant in-basin cadmium pigment manufacturing plants, their production, the estimated emission factors and the related in-basin cadmium emissions for the period 1970 - 1988

<table>
<thead>
<tr>
<th>period</th>
<th>B’heim ton Cd/yr</th>
<th>Leverkusen ton Cd/yr</th>
<th>Bonn ton Cd/yr</th>
<th>sum ton Cd/yr</th>
<th>emission factor g Cd/kg Cd</th>
<th>emission ton Cd/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970-1972</td>
<td>276</td>
<td>339</td>
<td>276</td>
<td>891</td>
<td>10 - 20</td>
<td>9 - 18</td>
</tr>
<tr>
<td>1973-1977</td>
<td>309</td>
<td>378</td>
<td>309</td>
<td>996</td>
<td>4 - 10</td>
<td>4 - 10</td>
</tr>
<tr>
<td>1978-1982</td>
<td>266</td>
<td>326</td>
<td>266</td>
<td>859</td>
<td>1.5</td>
<td>1.3</td>
</tr>
<tr>
<td>1983-1987</td>
<td>175</td>
<td>215</td>
<td>175</td>
<td>565</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>1988</td>
<td>178</td>
<td>0</td>
<td>201</td>
<td>379</td>
<td>0.3</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 10.8 highlights the importance of the decreasing emission factor in time. In the period 1971 - 1988 it decreased by a factor of about 50, while the
decreased by a factor of about 2. Thus, the overall reduction of aqueous emissions of cadmium was about two orders of magnitude.

10.6.6 Cadmium stabilizer manufacturing

Cadmium stabilizer manufacturing involves a wet chemical process for which aqueous cadmium emissions are inherent [45]. The stabilizer industry has been represented in the basin by one company, located in Besigheim in the 1970’s [46]. No data on the production of this plant or the year of termination of stabilizer production are available. It is assumed that this company, being one of four manufacturers of cadmium stabilizers in the FRG, had produced 25 % of the total stabilizer production during the period 1970 - 1977. The cadmium use in the FRG stabilizer industry is available [11-17]. Emission factors are reviewed in table 10.9. All sources refer to the Rhine basin except ref. [43] which refers to the USA.

<table>
<thead>
<tr>
<th>date ref.</th>
<th>emission factor g Cd/kg Cd proc.</th>
<th>source</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1973</td>
<td>1 - 1.5</td>
<td>[11]</td>
<td></td>
</tr>
<tr>
<td>1978</td>
<td>20</td>
<td>[29]</td>
<td>without waste water treatment</td>
</tr>
<tr>
<td>1978</td>
<td>10</td>
<td>[3,29,44]</td>
<td>waste water treatment, eff. 50%</td>
</tr>
<tr>
<td>1979</td>
<td>0.3</td>
<td>[36]</td>
<td>calculated: emission/production</td>
</tr>
<tr>
<td>1982</td>
<td>1.5</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>1982</td>
<td>2.3</td>
<td>[14]</td>
<td>calculated: emission/production</td>
</tr>
<tr>
<td>1984</td>
<td>1.0</td>
<td>[3,43,44]</td>
<td>waste water treatment, eff. 50%</td>
</tr>
<tr>
<td>1984</td>
<td>0.2</td>
<td>[43]</td>
<td>waste water treatment, eff. 90%</td>
</tr>
<tr>
<td>1983-1985</td>
<td>0.8</td>
<td>[8]</td>
<td>legal emission limit</td>
</tr>
<tr>
<td>since 1986</td>
<td>0.5</td>
<td>[7]</td>
<td>legal emission limit</td>
</tr>
</tbody>
</table>
As with cadmium pigment manufacturing the emission factor for the beginning of the 1970's is expected to be high due to lack of the availability of adequate waste water treatment technology. During the 1970's the factor is assumed to decrease significantly. The development of the emission factor is obtained by comparing the different literature sources. Table 10.10 provides the estimated in-basin cadmium stabilizer manufacturing data, the estimated emission factors and the resulting in-basin emissions for 1970 - 1988.

Table 10.10 The estimated in-basin cadmium stabilizer production, the emission factor estimates and the related aqueous emission in the period 1970 - 1988

<table>
<thead>
<tr>
<th>period</th>
<th>production</th>
<th>emission factor</th>
<th>emission</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ton Cd/year</td>
<td>g Cd/kg Cd proc.</td>
<td>ton Cd/year</td>
</tr>
<tr>
<td>1970 - 1972</td>
<td>89</td>
<td>10 - 20</td>
<td>0.9 - 1.8</td>
</tr>
<tr>
<td>1973 - 1977</td>
<td>91</td>
<td>4 - 10</td>
<td>0.4 - 0.9</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>0</td>
<td>2.0</td>
<td>0</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>0</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>1988</td>
<td>0</td>
<td>0.4</td>
<td>0</td>
</tr>
</tbody>
</table>

The emissions calculated for this branch indicate that it has not contributed significantly to the aqueous cadmium pollution of the Rhine. The development of the emission factor resembles the trend for cadmium pigment manufacturing.

10.6.7 The industrial use of cadmium pigments and stabilizers

Cadmium pigments are used in industry for coloring polymers and ceramics. Formerly, they were used in lacquer manufacturing [18,47,48]. Although other published cadmium emission inventories do not mention these uses [29,39,49], the question arises as to whether these industrial applications might be significant sources of aqueous cadmium pollution. The major industrial use of cadmium pigments, ranging from 75 % in the early 1970's to 90 % in the late
1980's is polymer coloring [18,47,48]. This industrial branch is not expected to cause aqueous cadmium emissions, due to the fact that polymer manufacturers send a so-called master batch to the pigment manufacturing company. There it is heavily colored on site and returned to the polymer processing plant, where it is used as a color additive to uncolored polymer. This procedure concentrates cadmium handling and processing on the site of the pigment manufacturer. Consequently, emissions in polymer processing plants are expected to be negligible.

The industrial use of (automobile) lacquer containing cadmium pigments as well as the use of cadmium pigments in coloring ceramics are not expected to cause significant aqueous emissions of cadmium either. Automobile lacquer is dissolved in organic solvents, so no water is involved in the processing. Ceramic processes require high temperatures which may cause atmospheric but not aqueous emissions.

Cadmium stabilizers are only used in PVC-processing. In the beginning of the 1970's many different PVC-products were stabilized by cadmium containing additives. Increased environmental concern has limited the number of PVC-applications in which cadmium stabilizers are still utilized. The market is now dominated by use in PVC outdoor window profiles, which in 1989 had a market share of 75 % [48]. Only recently have PVC-stabilizers been used in master batches [50]. During PVC-processing aqueous emissions of cadmium may occur from processes such as the wet stripping of dust-laden ventilation air.

In the basin area eight companies are involved in PVC-processing. One plant is located in Switzerland (Sins), six plants are located in the FRG (Frankfurt/M., Köln, Ludwigshafen, Marl, Rheinberg and Waldshut) and one plant is located in the Netherlands (Rotterdam). The Swiss plant has a PVC processing capacity of 30 kttons which is too small to justify further analysis. The FRG production capacity of PVC equals 1445 kttons in 1983, of which 69 % is located in the basin [51]. The plant in Rotterdam has a production capacity of approximately 200 kttons PVC. According to the Deutsche Kommission zur Reinhaltung des Rheins the PVC-processing plants in Ludwigshafen, Marl and Rheinberg discharged cadmium in 1985 [34].
Two approaches are used to estimate an aqueous cadmium emission factor for PVC-processing. The first approach assumes the FRG cadmium stabilizer use to be proportional to the PVC-processing capacity and distributed over the three in-basin plants which are mentioned as dischargers [34].

The second approach assumes all in-basin FRG plants to use cadmium stabilizers, proportional to their PVC production capacity. The data for the PVC-processing plant in Marl are used to calculate the emission factor, assuming that the PVC processing is the only cadmium related activity on the site.

The resulting emission factor, using approach 1, equals 1.4 kg Cd/ton Cd processed. Approach 2 yields an emission factor of 1.9 kg Cd/ton Cd processed for the 1980's. For 1990 the company claimed to discharge 60 kg cadmium [52]. The emission factor for 1988 and for 1990 are assumed to be equal: 0.5 g Cd/kg Cd processed. The emission factor is backcasted for the 1970's based on water treatment technology data, supplied by the company in Marl. It is claimed that in the period 1975 - 1990, the organic water pollution was reduced by 90 % [53]. A linear proportionality between organic pollutant reduction and cadmium removal is assumed. This leads to an estimated emission of 600 kg cadmium in the 1970's. This figure is related to the estamited cadmium stabilizer use in the 1970's and yields an emission factor estimate of 4.2 - 5.8 g Cd/kg Cd processed.

Table 10.11 presents the cadmium stabilizer use in the FRG part of the basin, the estimated emission factor and the in-basin emission in the FRG. The emission in The Netherlands is assumed to be negligible, compared to two adjacent wet phosphoric acid production plants in Rotterdam. Table 10.11 indicates the minor importance of this branch as an emitter to the Rhine basin.

10.6.8 Cadmium battery manufacturing

Nickel-cadmium battery manufacturing is a process which includes steps that might cause aqueous cadmium pollution [54]. The only in-basin Ni-Cd battery manufacturer is located in the Ruhr basin. Battery manufacturing data for the period 1970-1988 were estimated and shown in the figures 10.3 and 10.4.
Table 10.11 The estimated in-basin cadmium stabilizer use, the emission factor estimates and the related emissions in the period 1970 - 1988

<table>
<thead>
<tr>
<th>period</th>
<th>stabilizer use ton Cd/year</th>
<th>emission factor g Cd/kg Cd proc.</th>
<th>emission ton Cd/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 - 1972</td>
<td>245</td>
<td>5 - 7</td>
<td>1.2 - 1.7</td>
</tr>
<tr>
<td>1973 - 1977</td>
<td>251</td>
<td>4.2 - 5.8</td>
<td>1.1 - 1.5</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>366</td>
<td>2 - 3</td>
<td>0.7 - 1.1</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>292</td>
<td>1.4 - 1.9</td>
<td>0.4 - 0.6</td>
</tr>
<tr>
<td>1988</td>
<td>233</td>
<td>0.5</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Two types of batteries exist: vented or pocket-plate cells and sealed or sintered-plate cells. The manufacturing processes for these types differ, and so do the aqueous emission factors. The following production ratio is used [11-17]:

<table>
<thead>
<tr>
<th>sealed</th>
<th>vented</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 - 1975</td>
<td>10 %</td>
</tr>
<tr>
<td>1976 - 1985</td>
<td>30 %</td>
</tr>
<tr>
<td>1986 - 1988</td>
<td>60 %</td>
</tr>
</tbody>
</table>

Table 10.12 summarizes the emission factor estimates which are available in literature.

All figures presented in table 10.12 apply to the Rhine basin, except the figures presented in ref. [43] which are based on data collected in the USA. The figures presented in table 10.12 do not offer a consistent view, and therefore the estimated emission factors have a limited accuracy. It was assumed that the emission factors for battery manufacturing have decreased by about a factor 10 in the period 1970 - 1988.
Table 10.12 Published aqueous emission factors for cadmium discharges due to Ni-Cd battery manufacturing in the Rhine basin in the period 1970 - 1988

<table>
<thead>
<tr>
<th>date</th>
<th>emission factor</th>
<th>source</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1975</td>
<td>2.0</td>
<td>[55]</td>
<td></td>
</tr>
<tr>
<td>1975</td>
<td>3.1</td>
<td>[56]</td>
<td></td>
</tr>
<tr>
<td>1979</td>
<td>3.6</td>
<td>[36]</td>
<td>calculated as emission/production</td>
</tr>
<tr>
<td>1982</td>
<td>4.0</td>
<td>[14]</td>
<td></td>
</tr>
<tr>
<td>1982</td>
<td>6.5</td>
<td>[14]</td>
<td>calculated as emission/production</td>
</tr>
<tr>
<td>1982</td>
<td>2.9</td>
<td>[57]</td>
<td>calculated as emission/production</td>
</tr>
<tr>
<td>1982</td>
<td>3.0</td>
<td>[29]</td>
<td>pocket plate cell manufacturing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>no waste water treatment</td>
</tr>
<tr>
<td>1982</td>
<td>1.5</td>
<td>[29,44]</td>
<td>pocket plate cell manufacturing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>waste water treatment efficiency 50%</td>
</tr>
<tr>
<td>1982</td>
<td>13.8</td>
<td>[29]</td>
<td>sintered plate manufacturing</td>
</tr>
<tr>
<td>1984</td>
<td>3.0</td>
<td>[43]</td>
<td>pocket plate cell manufacturing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>no waste water treatment</td>
</tr>
<tr>
<td>1984</td>
<td>0.5</td>
<td>[43]</td>
<td>sintered plate cell manufacturing</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>waste water treatment efficiency 50%</td>
</tr>
<tr>
<td>1986</td>
<td>1.5</td>
<td>[7]</td>
<td>legal emission limit</td>
</tr>
</tbody>
</table>

Table 10.13 contains the calculated Ni-Cd sealed and vented battery production in the basin, the emission factor estimates and the resulting aqueous cadmium emissions due to Ni-Cd battery production. The emission factors were estimated based on the collected data presented in table 10.12.
Table 10.13 Production of sealed and vented cells, emission factor estimates, and the aqueous cadmium emissions in the period 1970 - 1988

<table>
<thead>
<tr>
<th>period</th>
<th>production vented cells ton Cd/year</th>
<th>production sealed cells ton Cd/year</th>
<th>emission factor vented cells g Cd/kg Cd</th>
<th>emission factor sealed cells g Cd/kg Cd</th>
<th>emission ton Cd/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970-1972</td>
<td>243</td>
<td>27</td>
<td>8</td>
<td>15</td>
<td>2.3</td>
</tr>
<tr>
<td>1973-1977</td>
<td>211</td>
<td>52</td>
<td>4</td>
<td>10 - 15</td>
<td>1.3 - 1.6</td>
</tr>
<tr>
<td>1978-1982</td>
<td>177</td>
<td>76</td>
<td>3</td>
<td>5 - 10</td>
<td>0.9 - 1.3</td>
</tr>
<tr>
<td>1983-1987</td>
<td>178</td>
<td>145</td>
<td>1.5</td>
<td>2 - 3</td>
<td>0.6 - 0.7</td>
</tr>
<tr>
<td>1988</td>
<td>136</td>
<td>205</td>
<td>1.0</td>
<td>1.0</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Although battery manufacturing has become the major cadmium application (see figure 10.4), the aqueous cadmium emissions remain limited.

10.6.9 Cadmium plating

In the beginning of the 1970's cadmium plating was the most important cadmium use. Plating is performed by a large number of small companies located in all in-basin countries. The production data for the FRG [11-17], for France and for The Netherlands [35,58,59] are given in table 10.14.

Table 10.14 The production of cadmium in plating in the period 1970 - 1988 in The Netherlands, the FRG and France

<table>
<thead>
<tr>
<th>period</th>
<th>use (Netherlands) (ton Cd/year)</th>
<th>use FRG (ton Cd/year)</th>
<th>use (France) (ton Cd/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 - 1972</td>
<td>50</td>
<td>508</td>
<td>324</td>
</tr>
<tr>
<td>1973 - 1977</td>
<td>50</td>
<td>355</td>
<td>322</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>5</td>
<td>261</td>
<td>271</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>1 - 3</td>
<td>140</td>
<td>242</td>
</tr>
<tr>
<td>1988</td>
<td>0</td>
<td>68</td>
<td>204</td>
</tr>
</tbody>
</table>

262
Table 10.14 shows the strong decline of the cadmium use in plating. No data are available for Switzerland and Luxemburg. These countries are not expected, however, to be major cadmium plate producers (probably less than 10% of the total in-basin production). In-basin emissions due to plating in France can be estimated based on the percentage of population and industrial activities occurring in the part of France located in the basin. This is of the order of 5 - 10% of total French population and industrial activity.

For the Netherlands it is assumed that 50% of all cadmium plating companies are located in the Rhine basin, which is a worst-case scenario. The FRG has a large concentration of plating companies in the Ruhr area [3]. Seventy-five percent of all cadmium plating companies in the FRG is assumed to be located there. Table 10.15 gives an overview of emission factor estimates for the plating industry.

Table 10.15 Published emission factors for the aqueous cadmium emission due to cadmium plating in the period 1970 - 1988 in the Rhine basin

<table>
<thead>
<tr>
<th>date ref.</th>
<th>emission factor</th>
<th>source</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1975</td>
<td>12.6</td>
<td>[55]</td>
<td></td>
</tr>
<tr>
<td>1979</td>
<td>4.7</td>
<td>[36]</td>
<td>calculated: emission/production</td>
</tr>
<tr>
<td>1979</td>
<td>8 - 10</td>
<td>[3]</td>
<td></td>
</tr>
<tr>
<td>1981</td>
<td>1.5 - 1.8</td>
<td>[60]</td>
<td>waste water treatment eff. 50%</td>
</tr>
<tr>
<td>1981</td>
<td>0.5 - 1.0</td>
<td>[60]</td>
<td>best available technology by 1981</td>
</tr>
<tr>
<td>1982</td>
<td>25</td>
<td>[29]</td>
<td></td>
</tr>
<tr>
<td>1983</td>
<td>20</td>
<td>[3,44,61]</td>
<td>waste water treatment eff. 50%</td>
</tr>
<tr>
<td>1984</td>
<td>11.5</td>
<td>[3,43]</td>
<td>waste water treatment eff. 50%</td>
</tr>
<tr>
<td>1986</td>
<td>0.3</td>
<td>[7]</td>
<td>legal emission limit</td>
</tr>
</tbody>
</table>

Table 10.15 shows a range of emission factors that differ by two orders of magnitude. Much of this discrepancy can be explained by different levels of
applied emission control technologies in the cited studies. Since the plating industry is known to have been a major source of aqueous cadmium emissions in the 1970's [3], and since it is known from monitoring data that emissions from point sources have decreased by more than 90 % over the last two decades, it is reasonable to assume that there has been a large and rapid decrease in the emission factor over the period under consideration. It is estimated here that it was reduced by 50 - 100 fold over the period 1970 - 1988. Table 10.16 provides an overview, consistent with the monitoring data, of how these emission factor and cadmium emissions may have changed during the 1970's and 1980's.

Table 10.16 The production of cadmium plate, estimated emission factors and the resulting emissions for 1970 - 1988 in the Rhine basin

<table>
<thead>
<tr>
<th>period</th>
<th>Use NL basin</th>
<th>Use FRG-basin</th>
<th>emission factor g Cd / kg Cd</th>
<th>emission NL ton Cd</th>
<th>emission FRG ton Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970-1972</td>
<td>25</td>
<td>384</td>
<td>20 - 30</td>
<td>0.5 - 0.8</td>
<td>7.7 - 10.6</td>
</tr>
<tr>
<td>1973-1977</td>
<td>25</td>
<td>266</td>
<td>15 - 25</td>
<td>0.4 - 0.6</td>
<td>4.0 - 6.7</td>
</tr>
<tr>
<td>1978-1982</td>
<td>2.5</td>
<td>196</td>
<td>10 - 20</td>
<td>0 - 0.1</td>
<td>2.0 - 3.9</td>
</tr>
<tr>
<td>1983-1987</td>
<td>1</td>
<td>105</td>
<td>1 - 6</td>
<td>0</td>
<td>0.1 - 0.6</td>
</tr>
<tr>
<td>1988</td>
<td>0</td>
<td>54</td>
<td>0.3</td>
<td>0</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

1 The table does not include France, Luxemburg and Switzerland which probably comprise less than 20 % of the in-basin plate production

10.6.10 Wet phosphoric acid manufacturing

Wet phosphoric acid manufacturing is one of the major cadmium discharging processes in the basin. Cadmium is a natural constituent of apatite ore, which is used as raw material to produce phosphoric acid. The cadmium content of the ore ranges from 0.1 to 90 ppm depending on its origin [62]. A fraction (typically 20 - 50 %) of the cadmium contained in the ore ends up in a gypsum
waste product which is formed during the wet phosphoric acid manufacturing process. In the basin two plants are located in Rotterdam and one plant is located in Ottmarsheim (France), each of which discharges gypsum to the Rhine. Since the cadmium discharges depend entirely on the composition of the ore, estimation of emission factors is not a feasible approach. The quantity of cadmium emitted by the two Dutch plants is presented in table 10.17 [59,63-67]. For the period 1970-1973 import/export statistics were used to estimate the Dutch emissions [68]. The emission estimates for the French plant are based on data available for the Dutch plants and on ore import data [39].

Table 10.17 The aqueous in-basin cadmium emissions due to wet phosphoric acid manufacturing in the period 1970 - 1988

<table>
<thead>
<tr>
<th>period</th>
<th>emission Netherlands (ton Cd)</th>
<th>emission France (ton Cd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 - 1972</td>
<td>22.7</td>
<td>3.2</td>
</tr>
<tr>
<td>1973 - 1977</td>
<td>21.8</td>
<td>3.0</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>13.7</td>
<td>1.9</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>13.7</td>
<td>&lt; 1.9</td>
</tr>
<tr>
<td>1988</td>
<td>9.0</td>
<td>&lt; 1.3</td>
</tr>
</tbody>
</table>

Table 10.17 shows a relatively minor decrease in cadmium emissions in this branch during the period 1970 - 1988. By 1988 phosphoric acid manufacturing causes more aqueous cadmium emissions than all other industrial activities combined. It is the aim of the companies in question, however, to limit their combined emissions to less than one ton by 1992.

10.6.11 Iron and steel industry, including coke production
Iron and steel production utilizes different raw materials in which minor amounts of cadmium are contained. The iron and steel industry generally includes coke production, sinter production, crude iron production and, finally, steel production. The two relevant steps with regard to aqueous cadmium
emissions are coke and steel production, each of which are discussed in this section.

**Coke production**

In order to manufacture steel it is essential to reduce oxidic iron ores, for which carbon is used in the form of coke. Coke is obtained by processing coal, which contains cadmium as an impurity in concentrations ranging from 0.22 - 1 ppm [39,69]. Part of the cadmium content is converted into flyash which is captured by wet scrubber devices, causing aqueous emissions. The emissions due to coke production are calculated for the 1970's by using an emission factor which equals \((0.281 \times C)\) g Cd/ton coke produced. Here, \(C\) represents the cadmium content of the coal in ppm. It is assumed that this emission factor correctly describes the emissions in the period 1970 - 1979, assuming \(C\) to be 1 ppm. For the period 1980 - 1988 the emission factor is divided by a factor of 10, to take into account improved process technology.

In the Rhine basin in this period seven coke plants were operating in France and 23 plants in the FRG. Twenty-seven plants are located in tributaries reaching the Rhine between Koblenz and Kobith, whereas three plants are located directly adjacent to the Rhine between Koblenz and Kobith. Table 10.18 presents the overall coke production [70-77] and the resulting emissions.

**Table 10.18 The in-basin coke production and the resulting aqueous cadmium emissions in the period 1970 - 1988**

<table>
<thead>
<tr>
<th>period</th>
<th>coke production (kton/year)</th>
<th>emission factor g Cd/t coke</th>
<th>emission ton Cd/yr</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>France</td>
<td>FRG</td>
<td></td>
</tr>
<tr>
<td>1970 - 1972</td>
<td>3,922</td>
<td>32,227</td>
<td>0.281</td>
</tr>
<tr>
<td>1973 - 1977</td>
<td>3,554</td>
<td>28,198</td>
<td>0.281</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>3,268</td>
<td>23,471</td>
<td>0.129</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>2,261</td>
<td>18,626</td>
<td>0.028</td>
</tr>
<tr>
<td>1988</td>
<td>2,414</td>
<td>15,587</td>
<td>0.028</td>
</tr>
</tbody>
</table>
Table 10.18 shows that coke production has decreased by 50% in the basin in the period 1970 - 1988, but that the major reason for lower emissions has been the rapid decrease in the emission factor. The emission estimates show the importance of aqueous cadmium emissions due to coke production in the 1970's.

**Steel production**

Three different processes exist for steel production; open hearth furnace (OHF), basic oxygen (BO) and electric arc (EA) steelmaking. The OHF-steelmaking method is not applied in the basin and therefore it is not analyzed in this study. In EA-steelmaking, steel scrap provides a large proportion of the input material. The scrap has a relatively high cadmium content (up to 6 ppm) [29] due to the application of cadmium as a surface protection layer on steel. In the basin 22 plants in the FRG and 6 plants in France produced steel in the period 1970 - 1988. One plant, located in Kehl (FRG), is upstream of Koblenz. Seven plants are located directly adjacent to the Rhine. All others are located on tributaries reaching the Rhine between Koblenz and Lobith. Table 10.19 provides the statistics for BO- and EA-steel production in France and the FRG [70-77].

Table 10.19 The in-basin steel production for France and the FRG in the period 1970 - 1988

<table>
<thead>
<tr>
<th>period</th>
<th>BO-steel</th>
<th>EA-steel</th>
<th>EA-steel</th>
<th>BO-steel</th>
<th>EA-steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>FRG</td>
<td>24,466</td>
<td>688</td>
<td>3,217</td>
<td>14,594</td>
<td>1,469</td>
</tr>
<tr>
<td>(kton/yr)</td>
<td></td>
<td>(kton/yr)</td>
<td>(kton/yr)</td>
<td>(kton/yr)</td>
<td>(kton/yr)</td>
</tr>
<tr>
<td>1970-1972</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1973-1977</td>
<td>25,541</td>
<td>718</td>
<td>3,355</td>
<td>15,270</td>
<td>1,536</td>
</tr>
<tr>
<td>1978-1982</td>
<td>23,729</td>
<td>667</td>
<td>3,119</td>
<td>14,159</td>
<td>1,425</td>
</tr>
<tr>
<td>1983-1987</td>
<td>21,061</td>
<td>592</td>
<td>2,768</td>
<td>12,569</td>
<td>1,265</td>
</tr>
<tr>
<td>1988</td>
<td>20,194</td>
<td>568</td>
<td>2,655</td>
<td>12,042</td>
<td>1,212</td>
</tr>
</tbody>
</table>

-1- EA-steel produced in a plant located at the Rhine, upstream of Koblenz
-2- EA-steel produced in plants 'located' between Koblenz and Lobith

267
Table 10.19 shows that in-basin steel production has decreased by about 20\% in the period 1970 - 1988. Nevertheless the overall in-basin production of steel in 1988 still amounted to over 36.6 Mton. Table 10.20 summarizes the estimated aqueous emission factors for steel production.

**Table 10.20** Published aqueous cadmium emission factors for EA- and BO-steel manufacturing in the basin in the period 1970 - 1988

<table>
<thead>
<tr>
<th>date ref.</th>
<th>emission factor (g Cd/ton steel)</th>
<th>source</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1982</td>
<td>not possible</td>
<td>[29]</td>
<td></td>
</tr>
<tr>
<td>1983</td>
<td>0.09 - 0.45</td>
<td>[78]</td>
<td>emission/ton crude iron for entire plant</td>
</tr>
<tr>
<td>1983</td>
<td>0 - 0.28</td>
<td>[29,78]</td>
<td>emission/ton crude iron, excl.coke prdn.</td>
</tr>
<tr>
<td>1983</td>
<td>0 - 0.23</td>
<td>[29,78]</td>
<td>emission per ton BO-steel</td>
</tr>
<tr>
<td>1985</td>
<td>0.007 - 0.01</td>
<td>[59]</td>
<td></td>
</tr>
<tr>
<td>1989</td>
<td>0.18</td>
<td>[39]</td>
<td>emission per ton BO-steel</td>
</tr>
<tr>
<td>1989</td>
<td>0.11</td>
<td>[39]</td>
<td>emission per ton EA-steel</td>
</tr>
</tbody>
</table>

Based on these scattered data the emission factor estimates are made, the results of which are given in table 10.21. Table 10.21 also contains the resulting emissions to the Rhine upstream of Koblenz (Rhine -1-) and between Koblenz and Lobith (Rhine -2-).

The emission factor for steel production is assumed not to change in the period 1970 -1982. During this period environmental measures in the iron and steel industry were focussed mainly on air pollution control. The, by then, recognized aqueous pollution problems in the steel industry originated from the etching of steel in hydrochloric or sulfuric acid. During the 1980's the reduction of aqueous pollution got priority (a.o. due to the stricter environmental legislation) and therefore the estimated emission factors were assumed to decrease. The emission factors for EA- and BO-steel are assumed to be equal, due to lack of data justifying a more detailed approach.
Table 10.21 Emission factor estimates and emissions for steel production in the basin in the period 1970 - 1988

<table>
<thead>
<tr>
<th>period</th>
<th>emission factor (g Cd/ton steel)</th>
<th>emissions Rhine -1- (ton Cd/year)</th>
<th>emissions Rhine -2- (ton Cd/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1970 - 1972</td>
<td>0.4</td>
<td>0.3</td>
<td>17.5</td>
</tr>
<tr>
<td>1973 - 1977</td>
<td>0.4</td>
<td>0.3</td>
<td>18.3</td>
</tr>
<tr>
<td>1978 - 1982</td>
<td>0.4</td>
<td>0.3</td>
<td>17.0</td>
</tr>
<tr>
<td>1983 - 1987</td>
<td>0.2</td>
<td>0.1</td>
<td>7.5</td>
</tr>
<tr>
<td>1988</td>
<td>0.05</td>
<td>0</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 10.21 shows that the iron and steel industry has been a major source of aqueous cadmium emissions to the Rhine basin.

10.6.12 Summary of aqueous emission factors of cadmium for industrial sources
The data-base presented in the sections 10.6.1 to 10.6.11 is summarized in this section. Figure 10.5 provides an overview of the changes in aqueous cadmium emission factors for some of the selected industrial branches. The figure shows that the factors have decreased for all cadmium processing branches, in most cases by 90% or more.

![Diagram](image)

Figure 10.5 The decrease of the emission factors for aqueous industrial cadmium emissions in the Rhine River basin

269
10.7 RESULTS AND DISCUSSION

In the previous sections, the trends in aqueous cadmium emission factors for the most relevant industrial branches were estimated. Based on these estimates an emission profile for the River Rhine as a function of time and location is obtained. In figure 10.6 this emission profile is compared with the estimates from analysis of water quality monitoring data [1]. It should be noted that this comparison is subject to the following uncertainties:

-i- the emissions from a single secondary zinc winning plant during the period from 1970 - 1984 accounted for a significant fraction (on the order of 45 - 70 %) of total emissions. Available information about this source, however, is limited.

-ii- the assumption is made that 100 % of the emissions to tributaries to the Rhine reach the main stream. This is probably a crude simplification.

-iii- the point source discharges to the Rhine as determined by the monitoring data method include e.g. household discharges via large sewage treatment plants. These discharges are not accounted for in the present analysis.

.iv- emission factors in the literature show a wide variation of values for some branches. These discrepancies introduce more uncertainty in the estimated values.

-v- in order to obtain emissions per industrial branch, estimated emission factors were multiplied by production quantities. In some cases production statistics were incomplete or unavailable, subjecting the emission estimates to further uncertainties.

270
Despite these sources of uncertainty, figure 10.6 clearly shows that the results based on the emission factors are consistent with the trends based on the monitoring data.

![Graph showing cadmium emissions from point sources in the Rhine basin from 1973 to 1987.](image)

**Figure 10.6** Aqueous emissions of cadmium from point sources in the Rhine basin (1973 - 1987). Estimates based on historical trends in emission factors (this work) are compared with estimates obtained from river monitoring data (source: [1]).

### 10.8 CONCLUSION

Aqueous emission factors are obtained for industrial cadmium discharges to the Rhine River basin in the period 1970 - 1988. The emission factors are calibrated by comparing the predicted cadmium emissions with monitoring data. The analysis suggests that a large reduction in aqueous emissions of...
cadmium has occurred over this 18 year period. Although part of this reduction is the result of decreased production, much of it is due to increased application of water cleaning technologies, as reflected by large decreases in emission factors for the water-polluting branches.

ACKNOWLEDGEMENTS

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274


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SUMMARY

In the document 'prevention and recycling of waste materials' (1986) issued by the Dutch Ministry of the Environment the development of a treatment process for contaminated jarosite (NH$_4$Fe$_3$(SO$_4$)$_2$(OH)$_6$ with Pb, Cd, As, Zn etc.) was considered to be essential in order to solve the residue problems of the Dutch hydrometallurgical zinc refining industry.

This Ph.D. thesis describes bench scale experiments designed to determine the feasibility of a hydrometallurgical jarosite treatment process. The proposed treatment process consists of three steps. Jarosite is reductively leached with SO$_2$, which yields a (Fe$^{2+}$/Zn$^{2+}$/SO$_4^{2-}$)-solution and a Pb/Ag/As-product. From the Fe$^{2+}$ containing solution FeSO$_4$.H$_2$O is crystallized at 160°C. FeSO$_4$.H$_2$O, which should contain a minimum quantity of Zn$^{2+}$, is subsequently roasted into Fe$_2$O$_3$ which is applicable as a raw material for the steel industry and into SO$_2$ which is used for H$_2$SO$_4$ production.

Chapter one introduces the current methods for hydrometallurgical refining of zinc metal from sulfidic zinc concentrates and the related solid waste problems. A hydrometallurgical zinc refining process usually consists of a roast step in which the sulfidic concentrate (ZnS and FeS$_2$) is roasted to ZnO, ZnO.Fe$_2$O$_3$ and SO$_2$, from which H$_2$SO$_4$ is produced. In two subsequent leach steps ZnO and ZnO.Fe$_2$O$_3$ are dissolved. The iron from ZnO.Fe$_2$O$_3$ and a number of impurities from the concentrate are usually precipitated as jarosite. Some by-products, like Cd and Cu, are separated during purification of the electrolyte. From the clean electrolyte zinc metal is subsequently deposited on cathodes. Jarosite is mostly stored as waste in ponds on the refinery site.

Chapter two discusses factors affecting the dissolution of zinc ferrite. The specific dissolution rate of zinc ferrite increases with increasing acidity, increasing Fe$^{2+}$ concentration in the leach solution and with increasing temperature. An increasing concentration of Fe$^{3+}$ in the leach solution reduces the specific dissolution rate. The rate is also dependent upon the type of acid; in diluted H$_2$SO$_4$ or HCl a larger
dissolution rate for zinc ferrite was measured than in diluted HNO$_3$ or HClO$_4$. In chapter three the dissolution of zinc ferrite in acidic solutions in the presence of Fe$^{2+}$, i.e. under reductive conditions, is discussed. Experiments in which zinc ferrite was dissolved in diluted HClO$_4$ in D$_2$O in the presence of Fe$^{2+}$, have contributed to the proposal for a general dissolution mechanism for ZnO·Fe$_2$O$_3$.

In chapter four the leaching of ZnO·Fe$_2$O$_3$ is carried out simultaneously with the precipitation of jarosite, at a constant pH which was chosen at such a value that the dissolution of zinc ferrite is rate determining for the overall process. In doing so, jarosite is precipitated at a low supersaturation and a lower incorporation of zinc in jarosite (<0.1 wt%) is measured compared to jarosite precipitation under normal conditions. Combining the leaching of ZnO·Fe$_2$O$_3$ and the precipitation of jarosite in a single step at a constant pH thus optimizes the zinc refining process.

The synthesis of jarosite from (Fe$^{3+}$ / NH$_4^+$ /SO$_4^{2-}$)-solutions is studied in the chapters five to seven. In chapter five, batch experiments are used to study the influence of the NH$_4^+$, SO$_4^{2-}$ and Zn$^{2+}$ feed concentrations, the temperature and the ionic strength on the precipitation rate of jarosite. The precipitation rate increases with an increasing NH$_4^+$ and SO$_4^{2-}$ concentration and at increasing temperature. The rate, however, decreases with an increasing Zn$^{2+}$ concentration.

In chapter six continuous jarosite precipitation experiments are described which were carried out at a constant pH using different feed concentrations of NH$_4^+$ and SO$_4^{2-}$ and different residence times. The results show that the conversion of dissolved Fe$^{3+}$ to jarosite increases with increasing NH$_4^+$ and SO$_4^{2-}$ feed concentrations until a maximum level is reached. The same relation is true for the conversion and the residence time. The incorporation of zinc in jarosite is proportional to the supersaturation during precipitation. At a constant pH the supersaturation is mainly determined by the Fe$^{3+}$ concentration in the solution.

In chapter seven the incorporation of Zn$^{2+}$, Cd$^{2+}$, Cu$^{2+}$, Co$^{2+}$, AsO$_4^{3-}$ and SbO$_3^-$ in jarosite is determined. The divalent metals are incorporated in hydrolyzed form

280
in the sequence Cu > Co > Zn > Cd. Arsenate and antimonate appear to coprecipitate in a separate phase.

In chapter eight the crystallization of FeSO$_4$.H$_2$O in an autoclave at 140 - 170°C is described. The partition coefficient of Zn$^{2+}$ in FeSO$_4$.H$_2$O has been determined. The effective separation of Fe$^{2+}$ and Zn$^{2+}$ is essential in the proposed hydrometallurgical jarosite treatment process. The partition coefficient for the incorporation of zinc in FeSO$_4$.H$_2$O was found to be too high to achieve a good separation of Fe$^{2+}$ and Zn$^{2+}$.

Chapter nine presents a comparison of five different jarosite treatment processes. Four of these processes include pyrometallurgical operations and one is the hydrometallurgical process. The energy requirements per ton zinc produced are calculated for a primary zinc refinery coupled with a waste treatment process, where additionally 'historical' waste material is treated. The quantity and the composition of the required raw materials, as well as of the expected waste streams are calculated.

This comparison shows that the hydrometallurgical jarosite treatment process requires more energy and yields a less-acceptable residue, compared to the pyrometallurgical processes which do not differ considerably.

Chapter ten summarizes the results of a study carried out under assignment of the International Institute for Applied Systems Analysis in Laxenburg, Austria. This study was aimed at determining the industrial cadmium emission to the Rhine River basin in the period 1970 - 1988.

The emissions are quantified in ton of Cd/year and via emission factors, in g Cd/kg Cd processed. The emissions as well as the emission factors decline strongly in the period 1970 - 1988. After multiplying cadmium processing data per branche with related emission factors as a function of time an emission profile was obtained. This profile was compared with Rhine water quality data. The results showed that the emission factor approach correctly describes the decrease of the cadmium load in the Rhine as a function of time.
SAMENVATTING

In de notitie *preventie en hergebruik van afvalstoffen* (nov. 1986) van het ministerie van VROM werd het ontwikkelen van een verwerkingsproces voor verontreinigd jarosiet (NH₄Fe₃(SO₄)₂(OH)₆ met daarin Pb, Cd, As, Zn etc.) gezien als een vereiste om de deponie-problematiek van de hydrometallurgische zinkwinning in Nederland op te lossen.

Dit proefschrift beschrijft laboratorium-onderzoek dat dient ter beoordeling van de haalbaarheid van een *hydrometallurgisch* verwerkingsproces voor jarosiet-afval. Het voorgestelde verwerkingsproces bestaat uit drie processtappen. Het jarosiet wordt reductief opgelost m.b.v. SO₂, waarna een (Fe²⁺/Zn²⁺/SO₄²⁻)-oplossing ontstaat en een Pb/Ag/As-reststof achterblijft. Uit de Fe²⁺ houdende oplossing wordt bij 160°C FeSO₄·H₂O gekristalliseerd dat zo min mogelijk Zn²⁺ mag bevatten. Het FeSO₄·H₂O wordt geroost tot Fe₂O₃ dat als grondstof dient voor de staalindustrie en tot SO₂ dat gebruikt wordt voor de H₂SO₄-produktie.

Hoofdstuk één geeft als inleiding een overzicht van de bestaande methoden voor het hydrometallurgisch winnen van zinkmetaal uit sulfidische zinkconcentraten en de ermee verbonden residu-problematiek.

Een hydrometallurgisch zinkwinningsproces bestaat gewoonlijk uit een rooststap waarin het sulfidisch erts (vnl. ZnS en FeS₂) wordt verbrand tot ZnO, ZnO·Fe₂O₃ en SO₂ waarvan H₂SO₄ wordt gemaakt. ZnO en ZnO·Fe₂O₃ worden vervolgens in een zwavelzure oplossing gegooid. Het ijzer uit het ZnO·Fe₂O₃ en een aantal verontreinigingen uit het erts worden meestal geprecipiteerd als jarosiet. Enkele bijproducten, waaronder Cd en Cu, worden apart afgescheiden in de elektrolytzuivering, waarna Zn via elektrolyse kan worden gewonnen. Het jarosiet wordt meestal in bekkens op bedrijfsterreinen opgeslagen als afvalstof.

Hoofdstuk twee beschrijft de factoren die het oplosgedrag van ZnO·Fe₂O₃ bepalen. De specifieke oplossnelheid van ZnO·Fe₂O₃ stijgt met toenemende zuurgraad, toenemende Fe²⁺-concentratie in de logingsoplossing en met toenemende temperatuur. Bij een stijgende concentratie Fe⁵⁺ in de logingsoplossing daalt de specifieke
oplossnelheid. De oplossnelheid is afhankelijk van het zuur; in verdun H₂SO₄ of HCl wordt een hogere oplossnelheid gemeten dan in verdun HNO₃ of HClO₄.

In hoofdstuk drie wordt het oplossen van ZnO. Fe₂O₃ in aanwezigheid van Fe²⁺ in de oplossing, d.w.z. onder reductieve condities, besproken. Experimenten waarin ZnO. Fe₂O₃ in verdun HClO₄ in D₂O in aanwezigheid van Fe²⁺ werd opgelost, leidden tot de formulerings van een algemeen oplosmechanisme voor ZnO. Fe₂O₃.

In hoofdstuk vier wordt de loging van ZnO. Fe₂O₃ gelijktijdig uitgevoerd met de precipitatie van jarosiet, bij een constante pH die zo wordt gekozen dat het oplossen van ZnO. Fe₂O₃ snelheidsbepalend is. Hierdoor wordt jarosiet gevormd bij een lage oververzadiging en wordt een verlaagde inbouw van zink in jarosiet (<0.1 wt%) gemeten ten opzichte van jarosiet precipitatie experimenten onder gangbare condities. Het combineren van de loging van ZnO. Fe₂O₃ en de precipitatie van jarosiet in één processtap bij een constante pH optimaliseert dus het zinkwinningsproces.

De synthese van jarosiet uit (Fe³⁺ / NH₄⁺ / SO₄²⁻)-oplossingen wordt bestudeerd in de hoofdstukken vijf t/m zeven. In hoofdstuk vijf wordt met batch-experimenten de invloed van de NH₄⁺-, SO₄²⁻ en Zn²⁺-voedingsconcentraties, de temperatuur en de ionsterkte op de precipitatie-snelheid van jarosiet bestudeerd. Hieruit blijkt een versnellende invloed van een stijgende NH₄⁺- en SO₄²⁻ concentratie en van een stijgende temperatuur op de precipitatie en een vertragende invloed van een stijgende Zn²⁺ concentratie.

In hoofdstuk zes worden continue jarosiet precipitatie experimenten beschreven bij constante pH en bij verschillende voedingsconcentraties van NH₄⁺ en SO₄²⁻ en verschillende verblijftijden. De resultaten hiervan tonen onder andere aan dat de conversie van opgelost Fe³⁺ naar jarosiet stijgt met stijgende NH₄⁺- en SO₄²⁻-voedingsconcentraties tot een maximum wordt bereikt. Eenzelfde relatie geldt voor de conversie en de verblijftijd. De inbouw van zink in jarosiet is evenredig met de oververzadiging voor de precipitatie. Bij een constante pH wordt de oververzadiging vooral bepaald door de Fe³⁺-concentratie in de oplossing.

In hoofdstuk zeven wordt de inbouw van Zn²⁺, Cd²⁺, Cu²⁺, Co²⁺, AsO₄³⁻ en SbO₃⁻ in
jarosiet bepaald. De divalente metalen worden opgenomen in een gehydrolyseerde vorm in de volgorde Cu > Co > Zn > Cd. Arseen en antimoen lijken soms preferentieel in een separate fase te coprecipiteren.

In hoofdstuk acht wordt de vorming van FeSO₄.H₂O uit een (Fe²⁺ / Zn²⁺ / SO₄²⁻)-oplossing in een autoclaaf bij 140-170°C beschreven. Hiermee is de verdelingscoëfficiënt van Zn²⁺ tijdens continue kristallisatie van FeSO₄.H₂O bepaald. De scheiding van Fe²⁺ en Zn²⁺ middels deze stap is essentieel in het voorgestelde jarosietverwerkingsproces. De verdelingscoëfficiënt voor de inbouw van Zn²⁺ in FeSO₄.H₂O is te hoog om een goede scheiding van Fe²⁺ en Zn²⁺ te waarborgen.

Hoofdstuk negen vergelijkt vijf verschillende jarosietverwerkingsprocessen. Vier ervan zijn pyrometallurgische routes en één ervan is het hydrometallurgisch proces. Van deze processen is nagegaan hoeveel energie per ton zink nodig is in een geïntegreerde primaire zinkwinningsfabriek waaraan het afvalverwerkingsproces is gekoppeld en waar in het afvalproces bovendien historisch afval wordt verwerkt. Tevens is de grootte en de samenstelling van de benodigde grondstoffstromen en van de te verwachten afvalstromen berekend. Deze vergelijking toont aan dat de hydrometallurgische verwerkingsroute meer energie vergt en tot een minder aanvaardbaar produkt leidt dan de pyrometallurgische processen, die onderling betrekkelijk weinig verschillen.

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