PRECIPITATION AND CHARACTERISATION OF IRON (III) OXYHYDROXIDES FROM ACID LIQUORS.

A THESIS PRESENTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

by


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I declare that this thesis is my own account of my research and contains work which has not previously been submitted for a degree at any University.

Evan John Jamieson
January, 1995
INDUSTRIAL EXECUTIVE SUMMARY

A detailed literature review on the nature and characteristics of iron oxides & oxyhydroxides has been compiled from the fields of soil science, environmental science, hydrometallurgy, mineral processing, mineralogy and spectroscopy. However, very little has been published discerning the factors controlling precipitation of these iron oxides and oxyhydroxides, particularly at ambient temperature. This thesis aims at providing such information as a set of fundamental guidelines for industry to be able to neutralise and precipitate iron from solution at ambient temperature.

- The structure of ten iron oxides and oxyhydroxides have been reviewed along with associated formation mechanisms. This review was used to compile Figure 1.1 (p4) on the inter-relationship of formation mechanisms.

- A variety of instrumental techniques were reviewed to understand the best methods for identification and characterisation of precipitates. These techniques include XRD (p49), Mössbauer spectroscopy (p54), chemical dissolution (p77), surface area (p84), transmission electron microscopy (p87), thermal gravimetry (p89) and settling ability (p99). The background theory behind each technique is briefly described along with reported data on iron oxides and oxyhydroxides.

- A critical evaluation of these instrumental techniques was conducted (Chapter 6) using a set of samples covering the amorphous to highly crystalline range of iron oxides and oxyhydroxides. Mössbauer spectroscopy used in conjunction with high resolution XRD was found to be the superior technique. However, time and cost constraints related to Mössbauer spectroscopy would prevent its widespread industrial use. A discussion regarding the reliability of other individual techniques concluded that each one taken alone can be very misleading. It is recommended that at least two separate techniques be used to identify and characterise iron oxide and oxyhydroxide precipitates.
The superiority of the Mössbauer technique is best demonstrated in Section 7.3.3 (p173), where the technique was used to investigate charged short chain polymeric species formed at low pH. These results were used to compose Figure 7.11 (p180), which is a new model for the formation of ferrihydrite from polymeric iron oxyhydroxide.

The Mössbauer technique was also paramount to the interpretation of molecular growth and polymer formation during ageing (Section 7.3, p160-186). It was proposed that as caustic is added to an iron (III) chloride solution, localised pH gradients arise. Since the point of zero charge for most iron oxides and oxyhydroxides is between pH 6.6 and 8.2, the possibility exists for both positive (from bulk solution) and negative (from point of caustic addition) charged iron polymers to coexist for a short period of time. Charge balance results in pseudo-chemical agglomeration resulting in larger particles. This theory explained the importance of intermediate polymer ageing, rate of alkali addition etc, and became important for interpreting data from the sulphate, lime and magnesia systems.

For the caustic - iron (III) sulphate system, evidence was presented that the adsorption of FeSO\(_4^+\) complex during precipitation followed by sulphate expulsion, assisted the goethite crystallisation process (Section 7.4.2, p190). It was also proposed that the sulphate ions adsorbed onto the red polymeric iron colloid, lowering surface charge and enhancing agglomeration and crystallisation.

The use of lime or magnesia combined with the sulphate system precipitated a highly crystalline form of ferrihydrite (DABFS, p214, p226), however the lime system co-precipitated gypsum. It appears that the diffusion layer surrounding the dissolving alkali (lime or magnesia) particle has a high localised pH. Ferrihydrite precipitated in this region would have a negative surface charge and would attract positive surface charged colloid from solution (low bulk solution pH) enhancing agglomeration. The formation of this surface layer would slow the release of hydroxide into bulk solution resulting in less polymer being formed. The action of iron sulphate complex within this localised high pH agglomerated layer, assisted formation of dense ferrihydrite by physically orientating incoming iron species giving ordered precipitation.
Factors effecting the formation of precipitates suitable for settling were vigorously pursued for the industrial reader. Many useful observations were discovered during the course of this investigation using pure synthetic liquors.

1: PRECIPITATION FROM IRON (III) CHLORIDE SOLUTIONS.

- Caustic (NaOH) strength, rate and mixing efficiency had little impact upon the precipitate. Neither chloride concentration nor ageing of the intermediates had significant effect (Chapter 7, p146). In all cases, amorphous or poorly crystalline ferrihydrite (5Fe₂O₃.9H₂O) was produced.

- Slaked or dry lime (CaO) and magnesia (MgO) showed little benefit relative to caustic in the settling of precipitates. However their cost saving over the use of caustic will ensure their industrial use (Sections 8.1, p209; 9.1, p223). Magnesia was found to assist with the precipitation of small quantities of iowaite (Mg₆Fe(OH)₈ClₓxH₂O), but the predominant product was ferrihydrite.

- Crystalline precipitates suitable for settling were only achieved using elevated temperatures (>60°C) in line with current industrial processes (Section 7.2, p156).

2: PRECIPITATION FROM IRON (III) SULPHATE SOLUTIONS.

- Caustic was found to precipitate fine crystalline goethite (α-FeOOH) rather than ferrihydrite, however settling was still quite slow (Sections 7.4.2, p190).

- Lime was found to precipitate a highly crystalline ferrihydrite that had exceptional settling ability. However, the co-precipitation of gypsum (CaSO₄) hindered the settling rate (Sections 8.3.1 & 8.3.2, p214).

- Precipitation using magnesia produced a highly crystalline ferrihydrite that was able to settle rapidly in the absence of co-precipitated gypsum (Sections 9.2.1 & 9.2.2, p226).
3: PRECIPITATION FROM IRON (II) CHLORIDE SOLUTIONS

- **Caustic** precipitated highly crystalline maghemite ($\gamma$-Fe$_2$O$_3$) at ambient temperature, that settled very rapidly (Section 10.1, p240). This result was heavily influenced by the rate of caustic addition due to air oxidation of iron (II) to iron (III). Precipitation at elevated temperature assisted the formation of magnetite, however this also increased the formation of slow settling ferrihydrite; the end result being a slower settling precipitate than that formed at ambient temperature.

- **Lime and magnesia** gave poorly crystalline maghemite and slow settling ferrihydrite due to air oxidation of iron (II) to iron (III) being catalysed by adsorption at the solid particle surfaces.

COMPARISON OF NEUTRALISATION MEDIA FOR CHLORIDE AND SULPHATE SOLUTIONS.

A comparison of settling rates achieved for the various systems is given in Figure 11.1 (p267), and tabulated in Tables 11.1 - 11.3 (p265). It is recommended that further work be conducted by industry on mixes of iron (II), iron (III), chloride and sulphate, which may be unique to their process. In particular...

- An investigation into a wider range of iron and counter anion concentrations.

- The use of pulp recycle technology for the precipitation of solids from iron (III) chloride solutions at ambient temperature should be investigated further (Section 11.6, p270).

- The dramatic influence of lime and particularly magnesia upon precipitates from iron (III) sulphate solutions at ambient temperature requires more extensive investigation for possible industrial application, especially when combined with pulp recycle technology.
Figure 1.1. The interrelationship in formation conditions between various iron oxides and oxyhydroxides. The chemical formulae for these iron compounds are given below.

(1) Ferrhydrite  \(5\text{Fe}_2\text{O}_3.9\text{H}_2\text{O}\)
(2) Goethite  \(\alpha\text{-FeOOH}\)
(3) Hematite \(\alpha\text{-Fe}_2\text{O}_3\)
(4) Akaganeite \(\beta\text{-FeOOH}\)
(5) Green complex  
(6) Green rust  
(7) Magnetite  \(\text{Fe}_3\text{O}_4\)
(8) Maghemite  \(\gamma\text{-Fe}_2\text{O}_3\)
(9) Lepidocrocite  \(\gamma\text{-FeOOH}\)
(10) Zeta FeOOH (Feroxyhite)  \(\delta\text{-FeOOH}\)
Figure 7.11. Model for the growth and formation of polymeric material into ferricydrite.
<table>
<thead>
<tr>
<th>KEY</th>
<th>THE SYSTEM</th>
<th>MAJOR PRECIPITATES</th>
<th>SETTLING RATE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe (III) - Cl - 20°C - NaOH</td>
<td>FERRIHYDRITE</td>
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<tr>
<td>2</td>
<td>Fe (III) - Cl - 40°C - NaOH</td>
<td>FERRIHYDRITE, GOETHITE</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>Fe (III) - Cl - 60°C - NaOH</td>
<td>FERRIHYDRITE, GOETHITE, HEMATITE</td>
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</tr>
<tr>
<td>4</td>
<td>Fe (III) - SO4 - 20°C - NaOH</td>
<td>GOETHITE</td>
<td>0.04</td>
</tr>
<tr>
<td>5</td>
<td>Fe (III) - SO4 /Cl - 20°C - NaOH</td>
<td>FERRIHYDRITE</td>
<td>0.01</td>
</tr>
<tr>
<td>6</td>
<td>Fe (II) - Cl - 20°C - NaOH</td>
<td>MAGHEMITE</td>
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<tr>
<td>7</td>
<td>Fe (II) - Cl - 70°C - NaOH</td>
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</tr>
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<td>8</td>
<td>Fe (II)/Fe(III) - Cl - 20°C - NaOH</td>
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<tr>
<td>10</td>
<td>Fe (III) - Cl - 60°C - CaO</td>
<td>FERRIHYDRITE, CALCITE</td>
<td>0.02</td>
</tr>
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<td>Fe (III) - SO4 - 20°C - CaO</td>
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<td>12</td>
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<td>15</td>
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<td>FERRIHYDRITE, AKAGANEITE, CALCITE</td>
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<td>16</td>
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<tr>
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</tr>
<tr>
<td>21</td>
<td>Fe (II)/Fe(III) - Cl - 20°C - MgO</td>
<td>FERRIHYDRITE, IOWAITE</td>
<td>0.05</td>
</tr>
</tbody>
</table>

Figure 11.1. A comparison of settling rates between systems.

NOTE: Systems 1, 2 & 3 show the effect of temperature with pure iron (III) chloride using NaOH.

Systems 4 & 5, 11 & 12 and 18 & 19 show the influence of sulphate.

Systems 6, 7 & 8, 13, 14 & 15 and 20 & 21 show the influence of iron (II).
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1 Peter 4:11.
"If anyone ministers, let him do it as with the ability that God supplies, that in all things God may be glorified through Jesus Christ, to whom belong the glory and the dominion forever and ever." NKJV
ABSTRACT

An important problem in the mineral processing industry is the removal of iron (III) from process and waste streams by precipitation as the metal hydroxide by elevation of pH. Caustic (NaOH), lime (CaO) and slaked lime (Ca(OH)$_2$), are cheap and effective reagents for this purpose, however iron (III) oxyhydroxides often form polymeric chains when precipitated at ambient temperature. This gelatinous material is slow to settle and difficult to filter, unlike the crystalline solids obtained at higher temperature.

A systematic fundamental study was undertaken to assess the suitability of various characterisation techniques to the iron oxide and oxyhydroxide group of minerals. Techniques such as chemical dissolution methods, surface area, TEM and thermal gravimetry were found to be very useful for comparative purposes, but were not recommended as primary characterisation techniques. Mössbauer spectroscopy proved to be the most reliable method for determination of phase composition especially when used in conjunction with XRD. However cost and time for analysis prevent this technique being used extensively. It was found that XRD, settling rate and settled sediment volume were broadly applicable and able to identify variation between samples cheaply and efficiently.

This study also methodically compared the settling rates, sediment volumes and iron oxide phases associated with using caustic solution, dry & slaked lime and dry & slaked magnesia.

Pure sodium hydroxide and iron (III) chloride solutions were used to represent the simplest system. Factors such as temperature, mixing, neutralisation rate, heterogeneous precipitation, sulphate addition, the presence of divalent cations (Mg$^{2+}$) and strong iron (III) ligands (e.g. citrate, oxalate) were investigated with this system. Generally the predominant iron phase precipitated was the poor order 0 or 2 XRD line ferricydrite. The temperature during precipitation was found to be the only critical parameter in changing product crystallinity and morphology. However, some other factors were able to produce small changes in agglomeration and settling rates, suggesting processes such as pulp recycle may prove beneficial. The iron (III) sulphate system induced a change in precipitates producing microcrystalline goethite, although settling rates were not improved.
The use of slowly dissolving lime in the iron (III) chloride system was unable to improve precipitate crystallinity or settling rate, however results suggest that lime and caustic can be used interchangeably. The lime / iron (III) sulphate system produced a co-precipitate of ferrihydrite and gypsum of enhanced settling ability relative to the caustic system.

The use of sparingly soluble magnesia failed to improve the precipitate of the iron (III) chloride system, however substantial improvement was found in the crystallinity and settling rate when using the iron (III) sulphate and mixed chloride / sulphate system, provided a range of conditions were met. This product resembled "dense amorphous basic ferric sulphate" (DABFS) and was identified as a highly ordered form of ferrihydrite by Mössbauer studies. It is suggested that this precipitate may form the basis for a new low temperature industrial precipitation process.

To further investigate the iron precipitation process, iron (II) and mixed iron (II)/(III) chloride solutions were hydrolysed with the addition of sodium hydroxide, calcium oxide and magnesium oxide under well aerated conditions. Dense maghemite was produced with the caustic system at ambient temperature which settled faster than magnetite precipitated at 70°C. The divalent cations Ca²⁺ and Mg²⁺ appear to hinder precipitation of crystalline maghemite at ambient temperature, forming the gelatinous poorly ordered ferrihydrite.

This fundamental and systematic study of the precipitation process of iron oxides and oxyhydroxides has led to an improvement in the integral understanding of iron (III) hydrolysis. The investigation of characterisation techniques has also led to an enhanced knowledge of their interaction with these precipitates and hence their strengths and weaknesses.
STRUCTURE OF THE THESIS

An introduction to the problem facing industry regarding the treatment of iron burdened effluent and subsequent precipitate removal is presented in Chapter 1. It includes a summary of what is known about the iron precipitation process and current industrial procedures.

Chapter 2, reviews the structure of each of the various iron oxides and oxyhydroxides. This gives a basis for understanding the formation process of these structures which is reviewed in Chapter 3.

Chapter 4 discusses the standard characterisation techniques frequently performed upon these iron minerals. These techniques are both physical and chemical in orientation. This chapter seeks to out line the relative strengths of each technique as well as giving an insight into how each technique operates.

Chapter 5 outlines the experimental procedures used, along with descriptions of how some of the procedures and techniques were conceived. Particular attention was paid to the reactor design.

Chapter 6 looks at a series of experimentally prepared samples which cover a range of the iron oxides and oxyhydroxides. These samples were used to evaluate the various chemical and physical characterisation techniques and relate these findings to those observed by others. The evaluation of results was used to reflect upon the reliability and practicality of each of the techniques involved.
Chapters 7, 8 and 9 report the various factors which influence iron (III) precipitation using sodium hydroxide, calcium oxide and magnesium oxide, respectively.

Chapter 10 looks at the related precipitation process for iron (II) solutions, including the use of sodium hydroxide, calcium oxide and magnesium oxide as the source of alkali. Other factors such as temperature and oxidation rate of iron (II) are also investigated.

Chapter 11 summarises the basic findings of this report and describes its limitations. The application of the knowledge gained by this thesis to industrial operations and areas that require further investigation are also discussed.

Chapter 12 contains a list of relevant references used throughout the text.