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

A THESIS PRESENTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

by


School of Mathematical and Physical Sciences
Murdoch University
Perth, Western Australia

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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 (5Fe$_2$O$_3$.9H$_2$O) 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 (Mg$_4$Fe(OH)$_8$Cl.xH$_2$O), 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 (CaSO$_4$) 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 $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$
(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 ferrihydrite.
<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>
<td>0.02</td>
</tr>
<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>
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<tr>
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<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>
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<tr>
<td>7</td>
<td>Fe (II) - Cl - 70°C - NaOH</td>
<td>MAGHEMITE, MAGNETITE</td>
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</tr>
<tr>
<td>8</td>
<td>Fe (II)/Fe(III) - Cl - 20°C - NaOH</td>
<td>FERRIHYDRITE, MAGHEMITE, AKAGANEITE</td>
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<td>10</td>
<td>Fe (III) - Cl - 60°C - CaO</td>
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<td>15</td>
<td>Fe (II)/Fe(III) - Cl - 20°C - CaO</td>
<td>FERRIHYDRITE, AKAGANEITE, CALCITE</td>
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<tr>
<td>16</td>
<td>Fe (III) - Cl - 20°C - MgO</td>
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<td>Fe (III) - Cl - 60°C - MgO</td>
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<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 ferrihydrite. 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 outline 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.
CHAPTER 1
INTRODUCTION

The study of iron chemistry is of traditional importance to the geological and metallurgical industries. Other sciences including fields such as environmental, biological and soil science have become increasingly concerned with iron chemistry, as well as the pigment and magnetic tape industries. Iron is frequently the principal metal contaminant in metallurgical waste streams and acid mine drainage. As a possible pollutant of the environment, iron must be removed prior to the release of such liquors. To achieve this, the method of removal must be both effective and economic. A fundamental understanding of the chemistry of iron is required to address these criteria.

Little research has been conducted on low temperature precipitation of iron oxides and oxyhydroxides, which are notoriously polymeric, gelatinous and unsuitable for settling or dewatering. This work aims to provide a fundamental investigation into how the solution conditions and type of alkali affects the precipitation of iron at ambient temperatures. The study is directed to the application of industrial effluent dewatering processes and is therefore confined to the precipitation of iron (III) oxides and oxyhydroxides from chloride or sulphate media using caustic soda, lime and magnesia as neutralising agents.
The manipulation of solution conditions to induce the precipitation of a product suitable for dewatering has been studied previously; and several different techniques have been reported depending upon prevailing conditions within the initial liquor (Craigen 1975, Dutrizac 1987).

One of the techniques, the "goethite process", precipitates goethite from iron (II) or (III) sulphate solutions and akaganeite from strong chloride solutions. In this process, the concentration of iron (III) must be below 1 g dm$^{-3}$ and the solution temperature above 70°C (Davey and Scott 1976).

The "hematite process" uses a long retention time and a temperature in excess of 90°C. Factors such as complicating anions and cations can dramatically influence the precipitation process (Majima et al. 1985).

The "jarosite process" requires the presence of an alkali cation (such as Na$^+$ or K$^+$) or the ammonium ion and control of parameters such as pH, the ratio of alkali to iron and temperature. Typically much higher concentrations of iron (III) are in solution and jarosite [M$^+$Fe$_3$(OH)$_6$(SO$_4$)$_2$] precipitates at a lower pH (around 1.5) than for the goethite process. However the iron is only partially removed and the solutions are recycled (Dutrizac 1987).
The above processes each have variations suited to particular circumstances, yet they all require high temperatures to produce crystalline precipitates suitable for settling (Dutrizac 1987). Consequently, these processes are costly in industrial practice.

While individual iron oxides and oxyhydroxides produced at high temperatures have been well characterised, fundamental studies of the inter-relationships between these oxides and oxyhydroxides are rare, especially at ambient temperature. In particular, the coupling of these inter-relationships with the intrinsic settling qualities of the iron oxide / oxyhydroxides has not been examined. Figure 1.1 is an attempt to summarise the literature and show the inter-relationships between the various iron oxide / oxyhydroxide minerals. These minerals are briefly described in this section and their XRD data are given later in Figure 4.1.

Starting with the hexahydro coordinated iron (III) monomer, partial hydrolysis produces an iron (III) dimer (Johnston and Lewis 1986). This dimer is the precursor to the other iron (III) oxides and oxyhydroxides. While many consider ferrihydrite to be the growth precursor (Pollard et al. 1992), in fact it must dissolve to reform the dimer prior to the precipitation of goethite, or undergo dehydration and internal rearrangement to form hematite (Cornell et al. 1989).
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. Ferrihydrite \( 5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O} \)
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) \( \delta\text{-FeOOH} \)
Of all the iron oxides and oxyhydroxides, the formation of ferrihydrite is kinetically favoured at ambient temperature. Rapid elevation in pH of the iron (III) dimer will produce poorly ordered ferrihydrite (1). The crystallinity of the ferrihydrite depends upon the rate and temperature of the hydrolysis reaction. Well ordered ferrihydrite can have 4 - 6 weak X-ray diffraction lines, while poorly ordered ferrihydrite has two very broad lines and sometimes none at all. There is debate whether the supposed zero line ferrihydrite is merely amorphous iron (III) oxide hydroxide or a proto-ferrihydrite type material (see Section 3.1). With time and elevated temperatures, the poorly ordered ferrihydrite will recrystallise forming the more ordered 6-XRD line ferrihydrite. This material will transform into hematite with further elevation of temperature. At ambient temperature over an extended period of time, the poorly ordered ferrihydrite will redissolve back to the dimer and the thermodynamically favoured goethite will be precipitated (2).

The polymerisation of dimer at ambient temperature to give goethite, is extremely slow in the presence of chloride or nitrate and can take years to produce an ordered crystalline material (Flynn 1984).
The iron (III) dimer can also lead to the precipitation of a mixture of goethite and hematite (3) when hydrolysed relatively slowly at solution temperatures in excess of 60°C. The minerals are well ordered and highly crystalline. However, rapid hydrolysis produces poorly crystalline goethite and hematite as well as ferrihydrite.

Slow elevation of the pH at ambient temperatures in a highly concentrated chloride solution (>3 mol dm⁻³) will produce poorly crystalline akaganeite (4). The high concentration of chloride appears to block the formation of goethite while promoting the formation of akaganeite. At elevated temperature (70°C) and in the absence of chloride ions, akaganeite can transform to goethite and hematite via a dissolution and reprecipitation process (Cornell and Giovanoli 1990).

The presence of iron (II) ions complicates the precipitation process. When iron (II) is oxidised in air at pH 7 to 8, green complexes (5) form as intermediates. With an elevated pH of 9 to 10, aerial oxidation produces green rusts (6).

Green rusts (6) will transform into magnetite (7) by slow aerial oxidation, or by violent oxidation into the zeta iron oxyhydroxide (10) or synthetic feroxyhite.
Maghemite (8) is formed through the slow controlled oxidation of iron (II) solutions at ambient temperatures via the green rust intermediates (6). Maghemite can also be produced by oxidation of finely divided magnetite (7).

The green complexes (5) will also directly transform into magnetite (7) by the use of high pH and slow aerial oxidation.

Rapid aerial oxidation of the green complexes will produce lepidocrocite (9). In the presence of more iron (II), lepidocrocite will be converted to magnetite. Lepidocrocite can transform into other iron oxides and oxyhydroxides depending on pH, Eh, iron (II), and temperature (Ward 1989). Oosterhout (1967) described such transformations as via competitive mechanisms of dissolution / precipitation and solid state internal rearrangement.

With such a multitude of iron oxides and oxyhydroxides that can form both directly and via transformations, it is not surprising that complicated mixtures often result which are difficult to characterise.
CHAPTER 2
THE STRUCTURE OF IRON OXIDES AND OXYHYDROXIDES

Iron oxides and oxyhydroxides are the hydrolysis products of iron (III) and iron (II) solutions. At ambient temperature the products are usually X-ray amorphous polymeric materials containing short chain cationic species. With time and appropriate solution conditions, these polymeric species can convert to a crystalline precipitate. The formation of a variety of oxides and oxyhydroxides are possible and often a mixture is produced as a result of two or more competing mechanisms.

To understand the overall chemistry of the reactions involved in the precipitation and inter-conversion of the various iron oxides / oxyhydroxides, it is first necessary to understand their structure and formation. Each of the known iron oxides and oxyhydroxides are briefly discussed below.

2.1 FERRIHYDRITE

It is generally accepted that well ordered (i.e. 4-6 XRD line) ferrihydrite has a defective hematite structure (Figure 2.1) with hexagonally close packed layers of O, OH, or H$_2$O, forming octahedral sites containing the iron (III) ions (Johnston and Lewis 1986, Murad and Johnston 1987, Cornell et al. 1989).
2.2 GOETHITE

Goethite (α-FeOOH) was one of the first iron oxyhydroxides to be assigned a formal structure. The structure is given below in Figure 2.2, with the iron atoms at the centre of the octahedra.

Misawa et al. (1974) reported the structure of goethite as orthorhombic (based on the hexagonal close packed framework of oxygen), citing X-ray and neutron diffraction data. Russell et al. (1974) state that the goethite structure is built from twin condensed strips of FeOOH octahedra, having shared O$^2-$ ions along the edges. Flynn (1984) also reports that the goethite structure is based upon double chains of edge shared Fe(O$_2$OH)$_6$ octahedra. Russell et al. (1974) state that bridging occurs with hydrogen bonding. This is in agreement with structures proposed by Kauffman and Hazel (1975), Ishikawa et al. (1986, 1988) and Hiemstra et al. (1989).
Figure 2.1. The structure of hematite. (A) View is down the hexagonal $c$ axis showing the arrangements of octahedra and central $Fe^{3+}$ ions. Oxygen triplets are shown for two of the octahedra. (B) View is down the $a$ axis showing the close packed array of oxygen and the arrangements of $Fe^{3+}$ in alternate pairs. From Murad and Johnston (1987).

Figure 2.2. The structure of goethite. (A) Showing the way in which the double chains of octahedra are linked to neighbouring double chains by sharing octahedral apices along the $c$ axis. Hydrogen bonding is shown as double lines across the tunnel cavities. (B) The double chain unit of $Fe(O,OH)_6$ octahedra. From Murad and Johnston (1987).
2.3 HEMATITE

Hematite ($\alpha$-Fe$_2$O$_3$) consists of planes of hexagonally close packed oxygen atoms, with iron only filling two thirds of the octahedral sites (Murad and Johnston 1987). Due to the partial filling of the sites, the octahedra are substantially distorted, with the iron atom resting closer to the unshared face than to the shared face.

Figure 2.1 shows the close packing of the oxygen and the partial filling of the octahedral sites with iron. The view is down the a axis.

2.4 AKAGANEITE

Akaganeite (ß-FeOOH) is the iron (III) oxyhydroxide formed from hydrolysis in a chloride medium. Its structure, similar to that of goethite, consists of twinned chains of Fe(O,OH)$_6$ octahedra having shared corners (Flynn 1984, Cornell and Giovanoli 1988a). The structure is based upon the body centred cubic packing of oxygen. It is generally accepted that the structure of akaganeite is the same as hollandite (Ishikawa et al. 1986, 1988), as shown in Figure 2.3.
In early literature, there was some debate whether the structure contained larger pores. The hollandite structure contains pores of 0.5 nm, however pores within the akaganeite structure of up to 3.0 nm diameter have been proposed (Watson et al. 1962, Gallagher 1970, Braun and Gallagher 1972). Based on surface area (BET) data and electron micrographs from Gallagher (1970), Howe and Gallagher (1975) proposed a "supercell" structure incorporating the large pores, having a formula of Fe_{128}O_{116}(OH)_{152}.

More recently, Galbraith et al. (1979) used high resolution electron microscopy to dispute the supercell claim. They have shown akaganeite to be crystallographically homogeneous and hence the "supercell" could not exist. They also demonstrated that the evidence presented by Gallagher (1970) was radiation damage from the microscope. This presumably is also the explanation for the hollow tubes observed by Watson et al. (1962).

2.5 GREEN COMPLEXES

The exact composition of green complex I and green complex II is still unclear. The complexes can be distinguished by the ratio of iron (II) to iron (III). Green complex I has a ratio of 2:1, while green complex II has a ratio of 1:1 (Misawa et al. 1974).
2.6 GREEN RUSTS

Both green rust I (formed in a chloride solution) and green rust II (formed in a sulphate solution) are dark green precipitates having a hexagonal crystal system. Their crystal dimensions vary, depending upon the anion present (Misawa et al. 1974).

Murad and Johnston (1987) describe the green rusts as cations octahedrally packed with oxygen, which are separated by layers of water and anions. Cuttler et al. (1990) used Mössbauer spectroscopy to characterise the presence of iron (II) in green rust II. They estimated the iron (II) to iron (III) ratio to be between 2 and 2.5.

2.7 MAGNETITE

Magnetite (Fe₃O₄), considered to be a spinel Fe³⁺(Fe²⁺Fe³⁺)O₄ (Murad and Johnston 1987), is cubic in structure and ranges in colour from black to red black. Misawa et al. (1974) report that magnetite has in fact an inverse spinel structure, while Kunda and Hitesman (1977) claim that it is a composite of iron (II) and iron (III) oxides (FeO.Fe₂O₃). Figure 2.4, is a representation of the spinel group.
Figure 2.3. The structure of akaganeite showing the linking of the double chains of octahedra to form tunnels with an approximately square shaped cross section. (A) The individual atoms and (B) the overall structure. From Murad and Johnston (1987).

Figure 2.4. The spinel structure of magnetite with the position of ions shown in only two sets of octahedra for clarity. The perspective is indicated by the bolder lined circles being those closer to the viewer. From Murad and Johnston (1987).
2.8 MAGHEMITE

Maghemite (γ-Fe$_2$O$_3$) has been reported to possess a cubic lattice structure and is the magnetic form of hematite, though it is thermodynamically less stable (Swaddle and Oltmann 1980). Murad and Johnston (1987) report that maghemite is a non-stoichiometric spinel (see Figure 2.4).

Kassim et al. (1981) claim that results from high resolution electron microscopy have shown maghemite to have a tetragonal structure. Johnson and Merrill (1972) claim maghemite contains bound water, essential to its structural formation.

2.9 LEPIDOCROCITE

The structure of lepidocrocite (γ-FeOOH) (Figure 2.5) has been shown to be similar to the twin octahedral chains of Fe(O,OH)$_6$ (Ishikawa et al. 1988). These twin chains form into sheets of edge sharing octahedra, with each sheet being bound to the other via hydrogen bonding (Kauffman and Hazel 1975, Flynn 1984, Cornell and Giovanoli 1988a). Lepidocrocite is orthorhombic, but the structure is based upon a face centred cubic framework of oxygen (Misawa et al. 1974), elsewhere described as cubic close packed (Kauffman and Hazel 1975).
Figure 2.5. The structure of lepidocrocite showing the linking of double chains by edge sharing of the octahedra to form sheets, which are hydrogen bonded together as indicated by the double lines. From Murad and Johnston (1987).
2.10 FEROXYHITE

Misawa et al. (1974) report feroxyhite (ascribed $\delta'$-FeOOH) as having a hexagonal based crystal system similar to a disordered CdI$_2$ structure. Patrat et al. (1983) used powder X-ray diffuse scattering data to suggest the structure was made of similar and dissimilar paired chains.

Murad and Johnston (1987) describe the mineral feroxyhite as the disordered modification of the synthetic form, preferring to distinguish between the two forms for Mossbauer studies, as have Pollard et al. (1992). Both ascribe feroxyhite as $\delta'$-FeOOH, with $\delta$-FeOOH being the synthetically derived species. Newman (1987) stated that feroxyhite was poorly crystalline and resembled ferrihydrite in being composed of poorly ordered 4Fe(O,H) octahedral units. He suggested that feroxyhite was probably more crystalline than ferrihydrite as it had sharper XRD peaks and was less soluble in acid ammonium oxalate.

2.11 SUMMARY

The structural representation of each of the iron oxides and oxyhydroxides depicts how each form consists of octahedrally coordinated iron. Chapter 3 will illustrate how twin strips of iron octahedra condense into the structural formations observed.
CHAPTER 3
FORMATION OF IRON OXIDES AND OXYHYDROXIDES

The formation of the various oxides and oxyhydroxides follow different reaction paths. Some of these paths are competitive, while others are effectively blocked by the formation solution conditions and other ionic species present.

When a base is added to an acid solution of iron (III) ions, polymerisation begins to take place. Initially the process forms an iron dimer which nucleates a red colloidal polycationic material (Flynn 1984) which settles slowly and is difficult to filter. It appears that although the short chain polymeric material is unstable, it can take years to transform at neutral to acidic pH (Flynn 1984). The degree of subsequent polymerisation depends on the hydroxide to iron ratio and other solution factors such as temperature and anions present (Flynn 1984).

Spiro et al. (1966) suggest that the hydrolysis product from iron (III) nitrate incorporates anions into the polycation structure postulating the formula \([\text{Fe(OH)}_{x}(\text{NO}_3)_{3-x}]_n\). However, it is now generally accepted that the nitrate anions only form part of an extended electrical double layer (Johnston and Lewis 1986).
3.1 FORMATION OF POLYCATIONS

It is believed that prior to oxide and oxyhydroxide formation, iron (III) monomers begin to form dimers and chains of polymeric material (Murad and Johnston 1987). It has been suggested that the polymeric material is an intermediate upon which the known crystalline oxyhydroxides nucleate (Dousma and De Bruyn 1979).

The mechanism for formation of polycations is given below in Figure 3.1, which is a composite of those proposed by Misawa et al. (1974), Dousma and De Bruyn (1976, 1978), Music et al. (1982) and Dutrizac (1987).

The monomer exists as an octahedral complex \([\text{Fe(OH}_2]_6\)\] with the deprotonated species having the formula \([\text{Fe(OH}_2]_5(\text{OH})\]²⁺ and \(\text{cis} - \text{trans} [\text{Fe(OH}_2]_4(\text{OH})_2\] (Flynn 1984). The first step in polycation formation involves the development of a dimer bound by double -OH or ol-bonds (olation).

Misawa et al. (1974) suggested that the ol-bonds would be difficult to form due to electrostatic repulsion between hydroxyl groups. However, other workers have all proposed that the double ol-bond bridges the iron dimer (Dousma and De Bruyn 1976, Music et al. 1982, Dutrizac 1987).
Figure 3.1. Possible mechanism for the formation of polymers by the linking of dimers into double chains of $\text{Fe(O,OH)}_6$ octahedra.
Dousma and De Bruyn (1976) used optical density experiments to argue that oxolation (the process of replacing OH bridges with O bridges, Figure 3.1) of the dimer is unlikely. They found a difference in the kinetic behaviour between the small polymeric material and the long chain polymers. They postulated that the slower reaction rate of the long chain polymers is due to the oxolation of the bridging oxygen. Hence as the small chain polymeric species are reactive, they do not contain oxo-bridging.

Growth of polycations was thought to occur by the addition of monomers to the chain.

$$\text{Fe}_2(\text{OH})_2^{4+} + \text{FeOH}^{2+} + \text{H}_2\text{O} \rightarrow \text{Fe}_3(\text{OH})_4^{3+} + \text{H}^+$$

It was understood that the orientation in which the polymer grows can influence the nature of the ultimate iron oxyhydroxide (Cornell et al. 1989). For example, a simple trimer has five possible orientations (see Figure 3.2), yet the mechanism for building goethite follows only one of these structures. The orientation that the polymer follows depends upon solution conditions, and anions present (Cornell et al. 1989).
Figure 3.2. The structure of a variety of trinuclear iron (III) hydroxo complexes that could form at low pH. From Cornell et al. (1986).
The existence of trimeric species has been questioned following Mössbauer spectroscopic investigations (Johnston and Lewis 1986). It is now generally accepted that polymerisation involves the linking of dimers to form double chains. The orientation in which the double chains link determines the final structure of the iron oxyhydroxide. It can be argued that all of the iron (III) oxyhydroxides and some of the oxides are formed by the linkage of the double chains under specified conditions (see Figure 3.3). The polycations would presumably be twin strips of iron octahedra that have not condensed into crystalline form.

Many scientists believe they have isolated the intermediate polycation material as small spheres of 1.5 - 5 nm diameter. Dousma and De Bruyn (1979) suggest that the spheres do not grow any larger because they have formed a thermodynamically stable sol, which has resulted in a lowering of the interfacial tension by ionic absorption in the electrical double layer.

Murphy et al. (1976a, 1976b, 1976c) found spheres of polycations ranging in size from 1.5 to 3 nm diameter, prior to the formation of known iron oxyhydroxides. It was reported that these species varied from a few linked monomers to an unspecified number of polymer units. The upper limit was not specified. Spiro et al. (1966) isolated polymer spheres of 7 nm diameter, and determined that approximately 900 iron atoms were present in each sphere.
Figure 3.3. Diagrammatic representations of (A) goethite, (B) lepidocrocite and (C) the double chain unit from these structures. (D) is the structure of hematite and (E) depicts the kinked double chains in the hematite and ferrhydrite structures. For (C) and (E), the open circles represent oxygen, while the solid circles represent the iron (III) atoms. From Johnston and Lewis (1986).
Cornell et al. (1987, 1989) state that ferrihydrite consists of spheres 2-5 nm in diameter. Eggleton and Fitzpatrick (1988) used high resolution TEM and XRD to show that 2-XRD line ferrihydrite consisted of spherical particles 2 nm in diameter, while the 6-XRD line ferrihydrite particles were 3.5 nm in diameter. As a result, most researchers now call the gelatinous small chain polymeric material, ferrihydrite.

One explanation of when these spheres change from polycations to ferrihydrite is offered by Dousma and De Bruyn (1976, 1978). They used pH relaxation techniques to show that the formation of small chain polymers is not only fast, but also readily reversible (see Figure 3.1). This material would constitute the polycation stage.

Dousma and De Bruyn (1976, 1978) then postulated that when the polymers become "large", oxolation takes place forming a structure which is slow to react with acid. Misawa et al. (1974) state that the formation of the oxo-bridge may result from deprotonation of the ol-bridge, hence elevated pH could assist in the oxolation process. This material is thought to be the emergence of ferrihydrite.
3.2 FORMATION OF FERRIHYDRITE

As described in the preceding section, the formation of ferrihydrite is closely linked to the formation of the polycations. The structure of ferrihydrite is probably a mixture of oxo and ol bridging.

The name ferrihydrite covers a range of poorly ordered compounds, which change with formation conditions (Cornell et al. 1989). Dependent upon the number of X-ray diffraction lines present, it is possible to have 0, 2, 4, and 6 XRD line ferrihydrite.

Murad and Johnston (1987) have reserved the term ferrihydrite for material which exhibits the 4-6 XRD line spectra. They use the term proto-ferrihydrite for the extremely poorly ordered form which has only two very broad X-ray peaks at 0.25 and 0.15 nm.

Ferrihydrite is usually a dark red colour, but can change to a yellow-brown depending upon the polymer or particle size and its method of formation (Newman 1987). The chemical formula ascribed to ferrihydrite is still to be established and varies between researchers, but \( (5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}) \) as reported by Schwertmann and Cornell (1991) will be used here.
Ferrihydrite is thermodynamically unstable, hence will slowly transformation by dissolution and then precipitation into the thermodynamically favoured crystalline iron oxides (Lewis and Schwertrimann 1979, Cornell and Giovanoli 1985, Newman 1987, Manceau and Combes 1988).

The aging process is very slow at ambient temperatures and takes years to complete at neutral to acidic pH (Schwertmann and Murad 1983). However, an elevated temperature and a high pH promote the transformation via internal rearrangement into hematite.

Tamura et al. (1981a) claim that at pH 11 and 65°C, their X-ray amorphous iron (III) oxyhydroxide rapidly transformed into magnetite in the presence of Fe$^{2+}$ from an Fe(OH)$_2$ source.

In summary, ferrihydrite is usually a red colloidal gelatinous material (Matijevic and Scheiner 1978) which is slow to settle and difficult to filter. Ferrihydrite has been found to consist of spherical particles up to 10 nm diameter, explaining its very poor dewatering ability (Cornell et al. 1989).
3.3 FORMATION OF GOETHITE

Goethite (α-FeOOH) has a needle like structure and is highly crystalline (Sada et al. 1988). Goethite is the thermodynamically stable polymorph of FeOOH and hence is the product favoured by time (Schwertmann and Taylor 1972).

Ferrihydrite (Misawa et al. 1974) and lepidocrocite (Carlson and Schwertmann 1990) are kinetically favoured, but being thermodynamically unstable will slowly transform into goethite and hematite in the presence of nitrate ions (Cornell et al. 1989). The presence of other anions can block or eliminate these paths. The transformation is slow at room temperature, ranging from hours in strongly alkaline solution to years in acidic solution (Misawa et al. 1974).

Dousma and De Bruyn (1979) have studied an apparent induction period for the formation of goethite in acidic solutions. They state that the induction period was a characteristic feature of the aging process, during which neither the pH nor the optical density of the solution were observed to change. The induction period was unaffected by stirring, but was dramatically reduced by seeding. They discussed the relative merits of two growth models based on reaction control by heterogeneous nucleation.
Murphy et al. (1976a, 1976b, 1976c) followed the formation of goethite in partially neutralised iron (III) nitrate solutions using electron microscopy. They found small polycation spheres (1.5-3.0 nm diameter) which had formed after 4 hours of aging. These spheres underwent hydrolysis resulting in a fall in pH. This can be ascribed to the oxolation of the bridging oxygen, eventually resulting in the spheres transforming into colloidal goethite. However, as the spheres hydrolyse their surface charge decreases and the spheres begin to aggregate in a linear fashion. The spheres in the rod-like structure appear to coalesce with time.

Dousma and De Bruyn (1978) also observed formation of rods from polycation spheres. The rods grow mainly in length, but slightly in width and combined with other rods to form rafts of precipitate. These rafts have been identified as goethite (Murphy et al. 1976a, Dousma and De Bruyn 1978).

Misawa et al. (1974) proposed that in strongly alkaline solutions, the polycation ol-bonding is attacked and oxolation occurs. The deprotonation is probably accompanied by the removal of counter anions and associated water. They state that as both the polycations and goethite consist of a hexagonal close packed oxygen framework, the conversion is probably a solid state crystallisation process. This supports the observations of coalesced spheres made by Murphy et al. (1976a, 1976b, 1976c) and Dousma and De Bruyn (1978).
Knight and Sylva (1974) reported that goethite nucleates in solution from the small polymeric species which are released from larger blocks of material (probably polycation spheres or poorly ordered ferrihydrite). Cornell et al. (1989) describe this process as more feasible, noting that the transformation of ferrihydrite to goethite is reconstructive with ferrihydrite dissolving then precipitating as goethite. The mechanism for this process is the same as that given in Figure 3.1 above.

Johnston and Lewis (1986) supported the dissolution and reprecipitation process with evidence from an investigation using Mossbauer spectroscopy. They developed the theory that dimers are the building blocks of double chains which form all the iron oxyhydroxide polymorphs. They stated that ferrihydrite is not a precursor to goethite but may be a precursor to hematite.

In conclusion, it may be said that the dissolution and reprecipitation model has become more generally accepted as the probable mechanism for the formation of goethite from the polymeric material (Figure 3.1).
3.4 FORMATION OF HEMATITE

Hematite (α-Fe₂O₃) has been detected in the hydrolysis products from most iron (III) solutions. There is some speculation as to the reaction path leading to its formation (Flynn 1984, Cornell et al. 1989).

Flynn (1984) stated that hematite does not share the double chains of polycations found in other oxyhydroxide polymorphs, but kinked chains may play a role in its formation. In a well developed theory based on Mossbauer spectroscopy, Johnston and Lewis (1986) suggested that dimers could easily link to form the hexagonal structure of hematite (see Figure 3.3). Van der Woude et al. (1983) were able to show that hematite and polycations formed competitively in solution at pH 1 above 80°C. The addition of seed promoted the formation of hematite supporting the mechanism "from solution".

Johnson and Lewis (1986) used TEM, XRD and Mossbauer techniques to show that hematite forms within the polycation nucleus by internal rearrangement. These polycations were probably ferrihydrite which has a defect hematite structure. The solid state transformation was possible because both materials possess a structure in which oxygen is hexagonal close packed. Aggregation of the ferrihydrite into dense masses promotes ordering, and from this ordered region, the hematite nucleates (Fischer and Schwertmann 1975).
Internal nucleation and growth of hematite involves the dehydration and condensation of water from the structure (Music et al. 1982, Cornell et al. 1989). Any charge imbalances are counteracted by redistribution of the cations within the lattice. Thus temperature is the crucial factor in the formation of hematite, due to the energy required to dehydrate the polynuclear species (Kauffman and Hazel 1975, Cornell and Giovanoli 1985, Dutrizac 1987).

Under the right conditions, the iron oxyhydroxides of goethite and akaganeite can also be converted into hematite (Matijevic and Scheiner 1978, Music et al. 1982, Cornell et al. 1989). These conditions usually involve long reaction times at elevated temperatures (>80°C).

In summary, hematite can form from the aggregation and dehydration of well ordered ferrihydrite with temperature (>80°C), or can nucleate directly from solution given sufficient time and elevated temperature (>80°C).

3.5 FORMATION OF AKAGANEITE

Akaganeite (β-FeOOH) is usually formed in the presence of a high concentration of chloride (Weiser and Milligan 1935, Murphy et al. 1975a, Davey and Scott 1976). At high Fe/Cl ratios (about 3:1 reported by Dousma et al. 1978), hydrolysis follows a path similar to that followed in the presence of nitrate ions. There are two mechanisms proposed for the formation of akaganeite. The first
involves solid state transformation by the penetration of chloride ions. The second is the direct nucleation and precipitation of akaganeite from solution. These mechanisms are described below.

Murphy et al. (1976b, 1976c) have found that partially neutralised iron chloride solutions contained small polycation spheres previously observed in related studies (Murphy et al. 1976a). These spheres joined to form short rods of 2-4 units, which grow in length and width. The growth in width did not appear to involve the addition of more spheres, so they postulated that subsequent growth occurred using unpolymserised material. As the concentration of unpolymserised material remained constant during the experiment, it was postulated that some of the polycationic spheres had to dissolve.

Murphy et al. (1976c) formed polycations in a nitrate solution then isolated them before aging could take place. Half the polycations were returned to the nitrate solution for aging and the other half were aged in a chloride solution. Aging was observed to follow the path it would have taken, had the polycations been formed in situ. They postulated that the original spherical polycations possessed a structure which was independent of the anions present during formation. When placed in a chloride solution, the chloride penetrated the polycation altering the internal arrangement and leading to the formation of akaganeite.
The above results could also be explained by the dissolution/reprecipitation model (i.e. nucleation from solution). The separated polycation spheres eventually all dissolve in the chloride medium and reprecipitate with the chloride altered structural arrangement. This is supported by Schneider and Schwyn (1987), who used Mossbauer and XRD to show that polynuclear species grown in chloride media possess the akaganeite structure as soon as they are formed.

Dousma et al. (1978) suggested that the presence of chloride results in the precipitation of akaganeite by forming a bridge between iron cations. This view is supported by Music et al. (1982), who speculate that while these chloride bridges are rapidly converted to ol and oxo-bonds in the presence of hydroxide, the conversion may be imperfect.

Ellis et al. (1976) described chloride ions as being specifically absorbed within the structure. Schneider and Schwyn (1987) present a growth model where the chloride ion imposes a structure upon the polymer rather than being incorporated into the polymer sequence itself. This is consistent with the structure preposed in Figure 3.3 where the oxyhydroxide is formed by the condensation of twin octahedral iron chains around the chloride containing channels (Murad and Johnston 1987).
In conclusion, the formation akaganeite has been reported to occur via two mechanisms. Firstly there is the formation of polycationic spheres which coalesced to form akaganeite, along with a dissolution and reprecipitation process.

Secondly there is the mechanism of direct nucleation and precipitation from solution, with any initially formed polycationic material completely dissolving and being reprecipitated as akaganeite.

This second view has become more dominant and seems to be receiving wide support (Schneider and Schwyn 1987, Cornell et al. 1989).

3.6 FORMATION OF GREEN COMPLEXES

Little information is available regarding the formation and structure of the green complexes. What is known is that green coloured complexes have long been considered intermediates during the iron (II) oxidation process (Misawa et al. 1974). They form during aeration of neutral iron (II) solutions and are converted to magnetite, lepidocrocite, or the associated green rusts according to aeration rates and solution pH.
3.7 FORMATION OF GREEN RUSTS

The green rusts can be precipitated from green complexes, or from the direct aerial oxidation of Fe(OH)$_2$ (Misawa et al. 1974).

The anions in solution affect the nature of the green rust precipitates. Aeration of neutral iron (II) solutions in a chloride medium will produce "green rust I" while "green rust II" is produced by a sulphate medium (Dasgupta and Mackay 1959).

Associated with both the green rusts, are the possible formation of green complexes depending on the reaction path. Like the green complexes, the green rusts are intermediates and are transformed into magnetite (Tamura et al. 1984), or the iron oxyhydroxides lepidocrocite (Misawa et al. 1974) and goethite (Detournay et al. 1975).

Even with this transient tendency, green rusts have been found in nature and characterised by Mössbauer spectroscopy (Koch and Morup 1991). Natural green rusts were found to rapidly oxidise once exposed to air.
3.8 FORMATION OF MAGNETITE

Magnetite (Fe₃O₄) is well known industrially for its high crystallinity, rapid settling rate and ease of filtration. The formation of magnetite was therefore comprehensively reviewed. Magnetite can be obtained by the aerial oxidation of iron (II) solutions, however the formation conditions depend upon many parameters which are discussed below.

3.8.1 TEMPERATURE

The reaction temperature is one of the most important variables in the formation of magnetite. Most studies have been conducted at a given temperature while focussing on some other parameter. These temperatures are typically within the range of 60 to 100°C (Tamura et al. 1981a, 1984, Sada et al. 1989).

Some researchers have studied several temperatures and generally conclude that the higher the temperature, the more crystalline the product. Kunda and Hitesman (1977) investigated magnetite formation over an extensive range of experimental conditions. They found that under their specified conditions of oxidation rate, concentration etc and a temperature of 75°C; high quality magnetite could be precipitated / transformed within five minutes from a sulphate solution.
Kiyama (1974) carried out an extensive study of the effect of temperature upon reaction products. He found that under the correct conditions of $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio, pH etc, magnetite could be produced at as low a temperature as 40°C. However, at this temperature the other formation conditions must be tightly controlled. A safe working temperature at which conditions become more flexible is 70°C.

Regazzoni et al. (1981) also investigated the effect of temperature on magnetite formation. They were able to produce magnetite at room temperature, but it contained some degree of amorphous material and took two weeks to form.

### 3.8.2 EFFECT OF pH

Another factor influencing the formation conditions of magnetite is the solution pH at precipitation. It has been proposed that magnetite can be synthesised at a pH in the range of 7 to 12 and at temperatures of 65 to 80°C (Tamura et al. 1981a, 1990). While magnetite could form at a neutral pH (Tamura et al. 1983, 1984), it was generally accepted that an alkaline solution was required. Typically a pH in the range of 9-10 was suitable for the formation of magnetite (Misawa et al. 1974, Tamura et al. 1981a, Sada et al. 1989). It has been suggested that an elevated pH of 11-12 may benefit the process, but Tamura et al. (1976a) reported that elevated pH increased the oxidation rate, which complicated the process.
3.8.3 EFFECT OF CATIONS

Impurities can also play a role in the formation of magnetite through the incorporation of various cations into the structure.

The inclusion of cations such as copper (II), cadmium (II), zinc (II), lead (II), manganese (II) and vanadium (IV) have been studied extensively (Inouye et al. 1976, Tamaura and Katsura 1980, Tamaura et al. 1981b, Ito et al. 1983, Krishnamurti and Huang 1988, Djafer et al. 1989). The inclusion of such cations typically leads to crystal defects and associated structural transformations.

3.8.4 EFFECT OF ANIONS

While cation inclusion into a crystal structure can alter the size and shape of the resulting particles, anions have the effect of blocking or enhancing a mechanistic pathway. That is, anions can alter the formation process in such a way that a totally different precipitate is produced (e.g. the production of lepidocrocite rather than magnetite).

Tamura et al. (1976b) reported that some anions (\(F^-, \text{H}_2\text{PO}_4^-\)) enhanced the oxidation rate of iron (II) while others (\(\text{SO}_4^{2-}\)) retarded it.
3.8.4.1 THE SULPHATE SYSTEM

There have been many investigations into the oxidation of iron (II) sulphate solutions. Most have been conducted under conditions where the conversion of iron (II) to iron (III) resulted in the formation of magnetite (Kiyama 1974, Kunda and Hitesman 1977, Sada et al. 1989).

The formation of green rust II has been reported as an intermediate in the process (Misawa et al. 1974, Detournay et al. 1975, Tamaura et al. 1984).

Apart from green rust II, other products such as goethite, lepidocrocite, maghemite and ferrihydrite have been observed, with variations of pH and temperature (Misawa et al. 1974, Solcova et al. 1981, Sada et al. 1988).

The concentration of the sulphate ions also appears to be important. Tamaura et al. (1981a) report that at lower concentrations of sulphate (0.03 M, pH 11 and 65°C), magnetite is formed in three stages. However when the sulphate concentration rose to 0.6 mol dm³, goethite was formed along with what was termed amorphous lepidocrocite. Tamaura et al. (1981a) provided evidence of amorphous lepidocrocite with infra red spectroscopic data.
3.8.4.2 THE CHLORIDE SYSTEM

Tamaura *et al.* (1983) studied the oxidation of iron (II) chloride solutions. At pH 5 the iron (II) was oxidised to iron (III) which then precipitated out as lepidocrocite. Tamaura *et al.* (1983, 1990) found that by elevating the pH to 9, residual iron (II) absorbed onto the surface of the lepidocrocite transforming it into magnetite. The process was very slow as a consequence of the low temperature used.

Regazzoni *et al.* (1981) investigated both the chloride and sulphate systems. They suggested that the precursor for the formation of magnetite is hydrous iron (II) oxide (Fe(OH)$_2$), usually called iron (II) hydroxide. They stated that iron (II) hydroxide is more stable in a chloride medium and shows greater resistance to oxidation than in the sulphate medium. Kiyama (1974) offers supporting evidence, stating that a chloride medium actually facilitates the formation of magnetite compared with a sulphate containing medium.

To produce magnetite, specific control of the oxidation rate is required to maintain the optimum ratio of Fe$^{2+}$ to Fe$^{3+}$ (Kunda and Hitesman 1977). The use of a chloride containing medium to slow the oxidation of the iron (II) system can be beneficial because it provides stability, giving greater control of the oxidation process.
3.8.5 THE OXIDATION OF IRON (II) TO IRON (III)

The ratio of iron (II) to iron (III) plays an important role in the formation of magnetite (Jolivet et al. 1992). Magnetite is a combination of both species in the ratio of 1:2. (Misawa et al. 1974). Kunda and Hitesman (1977) studied the effect of the Fe$^{2+}$/Fe$^{3+}$ ratio upon the magnetic properties of the magnetite formed. They found that the most magnetic magnetite was produced when the ratio was 1:1. Deviation caused a rapid decline in the Satmagan value (a magnetic property) and an associated decrease in the crystallinity.

Sada et al. (1989) reported that the rate determining step for the oxidation of iron (II) was controlled by the dissolution of oxygen. It is well established that iron (III) oxyhydroxides are catalytic to the oxidation process, by surface absorption of oxygen facilitating its dissolution (Tamura et al. 1976b, 1980). Tamura et al. (1976b) found that the oxidation process then proceeded homogeneously (in solution) and heterogeneously (on the iron (III) oxyhydroxide surface). It appears that the pH of the solution is also critical to this process (Misawa 1973).

Magnetite formation can proceed on the surface of iron oxyhydroxide complexes (Kiyama 1974, Tamaura et al. 1981a, Sada et al. 1989) and also via a solid state transformation of green rusts during slow aerial oxidation (Misawa et al. 1974). This is presumably related to the oxidation sites as discussed above.
Tamura et al. (1990) stated that magnetite forms when Fe\(^{2+}\) is absorbed into a lepidocrocite structure. This would make lepidocrocite an intermediate and explain the frequency of mixed products.

### 3.8.6 CONCLUSION

To summarise, the formation of magnetite depends upon temperature, the level of oxygenation and the pH of the solution. The reaction is favoured by slow aerial oxidation (Misawa et al. 1974), a relatively high pH ~9 and a temperature above 65°C (Tamura et al. 1981c).

### 3.9 FORMATION OF MAGHEMITE

Maghemite (\(\gamma\)-Fe\(_2\)O\(_3\)) is not a common mineral, however it has been found in some soils (Taylor and Schwertmann 1974). The occurrence of maghemite as a corrosion product may be more common than thought due to its difficulty to be distinguished from the XRD diffraction pattern of magnetite (Swaddle and Oltmann 1980).

Maghemite is formed through the slow controlled oxidation of iron (II) solutions at ambient temperature via the green rust intermediates (Kiyama 1974, Swaddle and Oltmann 1980). There have been reports of maghemite formation, where the green rust intermediate have not been observed (Newman 1987, Jolivet et al. 1992). However these conditions can produce distorted or mixed products.
According to Schwertmann and Cornell (1991), maghemite is produced from the aerial oxidation of iron (II) solutions and usually contains a few percent of the original iron (II) within the structure. This material was referred to as "magnetic maghemite". Maghemite can also be produced by aerial oxidation of finely divided magnetite (Wells 1962, Tamaura et al. 1981c).

Maghemite is thermodynamically unstable with respect to hematite and will transform to this compound with time. It has been shown (Giovanoli and Brutsch 1975) that the presence of water promotes this conversion. The presence of water also appears to be essential to the formation of maghemite with most synthetic and natural samples containing bound water (Johnson and Merrill 1972).

The formation of maghemite can be inhibited by the inclusion of small amounts of cations such as aluminium and chromium, while low temperature synthesis can lead to a distorted structure (Newman 1987).

In conclusion, the formation of maghemite proceeds via the green rust intermediates by the slow oxidation of iron (II) solutions at ambient temperature and at neutral pH.
3.10 FORMATION OF LEPIDOCROCITE

Lepidocrocite ($\gamma$-FeOOH) is usually formed from the rapid aerial oxidation of iron (II) solutions, along with maghemite ($\gamma$-Fe$_2$O$_3$) and occasionally synthetic feroxyhite ($\delta$-FeOOH) (Misawa et al. 1974, Matijevic and Scheiner 1978). Synthetic structures of lepidocrocite have also been formed from hydrolysis reactions of iron (III) solutions containing either nitrate ions or perchlorate ions (Flynn 1984).

Murphy et al. (1975a, 1976c) found that lepidocrocite formed during the earliest stages of the aging process, prior to the appearance of the dominant form, goethite. Murphy et al. (1976c) concluded that lepidocrocite formed from unpolymerised iron (III) ions in solution. Once an equilibrium quantity of lepidocrocite had formed, no further precipitation took place.

Murphy et al. (1975a) and Flynn (1984) noted that increasing the ionic strength of the solution, accelerated the formation of goethite and suppressed the formation of lepidocrocite.

Naono and Nakai (1989) synthesised lepidocrocite in a solution containing HPO$_4^{2-}$ and Cl$^-$ ions. They believe that the phosphate ions block the formation of goethite allowing the growth of lepidocrocite under appropriate conditions. They used electron microscopy to reveal the crystal growth sequence. It was found that fine needles begin to grow along the c axis from a lepidocrocite nucleus, to give the shape of a double sided comb. As aging progresses these needles loose their
identity and the crystal takes on its flat acicular appearance. Newman (1987) reported that lepidocrocite can have a plate like structure as well as resemble needles.

To summarise for an iron (III) solution, rapid elevation of pH gives rise to the kinetically favoured amorphous ferrihydrite. However, for the iron (II) solution, rapid oxidation and elevation of pH gives the kinetically favoured lepidocrocite. Lepidocrocite like ferrihydrite, is thermodynamically unstable and will, with time, transform via dissolution and reprecipitation into the more stable goethite (Misawa et al. 1974, Sung and Morgan 1980, Newman 1987). With the absorption of free iron (II) ions, lepidocrocite will also transform into magnetite (Tamaura et al. 1983, 1990).

3.11 FORMATION OF ZETA FeOOH, (FEROXYHITE)

The occurrence of this material is rare, being shown to form synthetically during the violent oxidation (via hydrogen peroxide) of green rusts (Misawa et al. 1974) or alkaline Fe(OH)$_2$ suspensions (Pollard et al. 1992).

Feroxyhite is thought to form in nature by the rapid oxidation of iron (II) solutions, favoured by the presence of silica (Newman 1987). The silica is presumably an aid for rapid oxidation of the surface absorbed iron (II) cations. Jimenez-Mateos et al. (1988) have shown that feroxyhite can transform by thermal and mechano-chemical decomposition into hematite.
3.12 SUMMARY

It has been demonstrated that the formation conditions for iron precipitation heavily influence the composition and morphology of the resulting product. Factors such as ions in solution, pH and temperature all influence the precipitation process.

Upon initial hydrolysis, monomer iron (III) species join via OH bridges to form the iron dimer $\text{Fe}_2(\text{OH})_2^{4+}$. The iron dimer links with other dimer units to form double chains. The structure of iron oxides and oxyhydroxides show a similarity in the use of double chains of iron $\text{Fe(O,OH)}_6$ octahedra, suggesting they are fundamental to the formation process (Johnston and Lewis 1986).

The formation of double chains and their subsequent linking to form the various iron oxyhydroxides is summarised diagrammatically in Figure 3./ $\varepsilon$ 3·3.
CHAPTER 4
TECHNIQUES FOR CHARACTERISATION OF IRON OXYHYDROXIDES

A variety of analytical techniques have been reported as useful in the characterisation of the iron (III) oxyhydroxide group of minerals. This not only reflects the importance of these minerals, but is also due to the range of iron oxides and oxyhydroxides that can form by varying precipitation conditions.

There is often a difficulty comparing results between different studies, as precipitation and formation conditions can have a dramatic effect upon product outcome. Not only is there variation in the type of iron oxide or oxyhydroxide that can be produced; but each mineral has the potential to exist anywhere along a continuum, ranging from the X-ray amorphous to the crystalline state. Full characterisation is very important to enable authoritative identification of such precipitates.

An evaluation of the reported characterisation techniques for iron (III) oxyhydroxides is given below. Back-ground theory is reviewed along with the application of these techniques to the iron oxyhydroxide group of minerals.
4.1 X-RAY DIFFRACTION

X-ray diffraction (XRD) is the most commonly used technique for the identification of iron oxides and oxyhydroxides. XRD can provide information regarding the crystal size and degree of order, as well as structural information about unit cell dimensions (Schwertmann and Cornell 1991).

While Mössbauer spectroscopy can achieve identification, separation and proportionation of the iron polymorphs (see section 4.2); it is restricted to a crystal size of approximately 20 nm or larger at room temperature. Yet a crystal of 2-3 nm can diffract X-rays for detection by the XRD technique. A brief account of the XRD technique is given below.

4.1.1 BACKGROUND THEORY

Crystals contain atoms in regular geometric arrays. The size of the atoms and their spatial arrangements influence the spacings between repeating units, termed unit cells. The array of atoms and repeating cells, eludes to the fact that atoms exist in planes and are symmetrical about axes. The positioning of a plane of atoms can be described by the intercepts it has with the symmetry axes, expressed as a reciprocal and termed the Miller indices (h, k and l).
When X-rays are passed through a crystal the atoms scatter the waves in a uniform yet distinctive manner. The uniform intensity of X-rays passing through a crystal is altered giving regions of increased intensity (constructive interference) and decreased intensity (destructive interference). This is caused by the atoms scattering the X-rays in such a manner that phase shifts between waves extinguishes them, but in defined directions the waves combine enhancing intensity. The direction of the regions of enhanced intensity are influenced by the spaces of the atomic planes (termed $d$ values) and the angle of incidence of the X-rays. The relationship between these factors is provided by the Bragg equation below.

$$ n \lambda = 2 d_{hkl} \sin \Theta \quad \text{Equation 4.1} $$

Where

$n$ is the order of the reflection.

$\lambda$ is the wavelength of the X-rays.

$d_{hkl}$ is the lattice spacing.

$\Theta$ is the angle of incidence of X-rays which gives the maximum constructive interference intensity.
The term $d_{hkl}$ derived from the Bragg equation, can be used to determine the unit cell dimensions of a crystal. The position that the $d_{hkl}$ values have and their relative intensities are characteristic and unique to particular crystal structures, hence they can be used for sample identification.

The intensity of a peak can also be used to estimate the relative proportions of a mineral by comparison to that of a pure sample. A calibration curve is made using pure samples mixed in known proportions (X for the first component and Y for the second component, both expressed as wt%).

The area under the first component peak ($A_x$) and the area under the second component peak ($A_y$) are used with the weight percent for each component to plot $A_x / (A_x + A_y)$ against $X / (X + Y)$. Using this standard curve and the area under the component peaks of the unknown, the relative proportions can be established. This procedure assumes that the physical properties of the unknown (eg particle size) are identical to those of the pure sample used in the standard mixtures.

Peak width can be used as an estimation of the degree of crystal order and relative degree of crystal strain due to inherent defects. Peak positioning can be used to find unit cell dimensions and peak shift can give information about cation substitution.
4.1.2 APPLICATION TO IRON OXYHYDROXIDES

Cornell and Giovanoli (1991) used XRD to observe the transformation of akaganeite into goethite and hematite while in the presence of manganese. Goldberg and Glaubig (1985) used XRD to follow boron adsorption on iron oxides, while Cornell et al. (1992) used XRD to observe the substitution of iron with nickel during the transformation of amorphous iron (III) hydroxide into crystalline products. The use of XRD to identify iron oxides and oxyhydroxides has been covered by Schwertmann and Cornell (1991).

4.1.3 CONCLUSIONS

The use of XRD for iron oxide and oxyhydroxide identification is both varied and widespread. A line chart is given below in Figure 4.1 showing the major lines used for iron oxide and oxyhydroxide identification, as well as their relative intensities. The data for this figure was taken from Schwertmann and Cornell (1991) and McClune (1980).
Figure 4.1. Major XRD peaks for the iron oxides and oxyhydroxides. Data taken from McClune (1980).
4.2 MöSSBAUER SPECTROSCOPY

A number of comprehensive reviews on the technique of Mössbauer spectroscopy are available (Bancroft 1973, Fairhurst and Sutcliffe 1978, St Pierre et al. 1989), with many papers focussing on iron oxides and oxyhydroxides (Johnston and Lewis 1986, Murad and Johnston 1987).

Mössbauer Spectroscopy involves the measurement of a spectrum of gamma (γ) ray photons as they pass through a sample. When a nuclei emits a γ-ray photon, momentum conservation results in a recoil energy being transferred to that nuclei (Bancroft 1973, Parish 1985).

The same is true for a nuclei that absorbs a γ-ray photon. This recoil will lower the energy of the emitted photon, while raising the energy requirement for absorption of a photon. The result being that the probability of a γ-ray photon emitted from a source having the energy requirement for absorption by a sample is quite small.

The recoil energy is inversely proportional to the mass of the nuclei (Bancroft 1973, Fairhurst and Sutcliffe 1978, St Pierre et al. 1989). If the nuclei were part of a solid sample, the effective mass would be the mass of the whole sample and the recoil energy would become negligible. This statement holds true because the chemical binding energy of a nucleus in a lattice is much larger than the recoil energy experienced by the nuclei. Hence the recoil energy is effectively transferred to the whole sample becoming negligible as the sample weight rises.
If the source and sample are in solids, a γ-ray photon can be recoil free emitted from the source and resonantly absorbed by the sample without the creation of another photon, (i.e. recoil free) then this is what is termed "The Mössbauer Effect" (Bancroft 1973, Parish 1985).

By moving the source with respect to the sample, the Doppler effect will cause a variation in the γ-ray energies experienced by the sample. When the energy of the photon corresponds to the resonant absorption line of the sample, absorption takes place and the counter will register a minimum of transmitted intensity.

The extreme sharpness of the 14.4 KeV iron line has the advantage that any small changes to the resonant absorption energy, caused by magnetic or chemical electronic interactions, can be detected and quantified (Bancroft 1973, Fairhurst and Sutcliffe 1978). This gives information as to the chemical environment of the iron in the sample.

If the absorbing nuclei does not experience any electronic interactions, then the Mössbauer spectra would consist of a single absorption line at velocity zero (see Figure 4.2). For convenience and convention, the Mössbauer plot counts the number of γ-ray photons transmitted over a range of instantaneous relative velocities between the source and absorbing sample.
The main features and assumptions of the Mössbauer technique (Bancroft 1973) are:

1) The first step in the identification of a mixture of iron minerals by Mössbauer spectra, is to assign different lines to individual mineral phases. This is easy until lines begin to overlap. When overlap occurs the error associated with computed data will be magnified. It is fortunate that the spectra for ferrihydrite, goethite and hematite do not overlap and are readily identifiable at room temperature.

2) The area under each assigned peak is assumed to be directly proportional to the number of Fe$^{3+}$ species present in each mineral, allowing analytical determinations.

3) For point 2 to be valid, the assumption also implies that each mineral contains the same distribution of $^{57}$Fe within the iron population.

4) Component peaks of a quadrupole doublet must be assumed to be of equal intensity and the component peak areas of a magnetic hyperfine interaction are assumed to be in the ratio 3:2:1:1:2:3.

There are a variety of factors which can influence the shape of a Mössbauer spectra. These include chemical shifts, electronic quadruple interactions and magnetic hyperfine interactions. Other factors such as particle size and cationic substitution are also discussed below.
4.2.1 CHEMICAL SHIFTS

The chemical shift (sometimes termed isomer or centroid shift) reflects the electron density surrounding the nuclei. When the sample contains nuclei in different environments to the source, the nuclear size will differ to some degree and hence the electron densities will vary also. This is true for both the excited state and the ground state as seen in Figure 4.3. It will also cause a displacement of the resonance line, but as the chemical isomer shift is not an absolute quantity it must be compared to a zero velocity standard, usually iron foil by convention.

Fairhurst and Sutcliffe (1978) discussed some of the factors affecting the $s$ electron density surrounding the nuclei. These were the population of electrons, the shielding effects of the $p$, $d$ and $f$ electrons and lattice bonding. Temperature and pressure were also important but to a lesser extent. These factors produce distinguishing features in the Mössbauer spectra can reveal a great deal of information about a sample's chemical environment and can distinguish closely related materials (e.g. iron polymorphs).
Figure 4.2. Nuclear energy levels and the isomer shift. (A) Source and absorber nuclear energy levels, (B) resultant Mössbauer spectrum. From Bancroft (1973).

Figure 4.3. Nuclear energy levels and the quadrupole splitting. (A) Absorber nuclear energy levels, excited level (I=3/2) split into two by quadrupole interaction. (B) Resultant Mössbauer spectrum. From Bancroft (1973).
4.2.2 QUADRUPOLE INTERACTIONS

Nuclei with non-spherical charge distribution will have an electric quadrupole moment. This occurs when the nucleus has a spin quantum number (I) larger than 1/2. The excited $^{57}$Fe state has a spin of 3/2 and is split into two levels. The ground state has a spin of 1/2 therefore does not have a quadrupole and is not split. The result of the split energy levels is to produce doublet absorption resonance lines of equal intensity as can be seen in Figure 4.3.

The electron field quadrupole can arise from the oxidation state of the nucleus where electrons occupy different orbits, some symmetrical, some not (Bancroft 1973, St Pierre et al. 1989). It can also arise from the position of neighbouring ions within the lattice. Shielding or antishielding arises if the electrons rearrange their position due to neighbouring ions. Even so, useful information can be obtained regarding the oxidation state and chemical environment.

4.2.3 MAGNETIC HYPERFINE INTERACTIONS

When a magnetic field from either the nucleus itself or an external source is applied, degeneracy of the energy levels is lifted allowing both the ground state and the excited energy levels to split (Bancroft 1973, St Pierre et al. 1989). This results in a series of six possible transitions, as seen in Figure 4.4.
Figure 4.4. Magnetic and quadrupole splitting in $^{57}$Fe. (A) Energy level diagram for combined magnetic and quadrupole splitting. (B) Resultant Mössbauer spectrum. The circled numbers in (A) are the expected intensities for a random sample and also refer to lines in (B). From Bancroft (1973).
4.2.4 OTHER FACTORS

Davey and Scott (1976) highlighted that problems exist for phase identification by Mössbauer spectroscopy of iron (III) oxyhydroxides of small particle size. While Mössbauer spectra identified their sample as akaganeite, XRD and DTA identified it as goethite. The problem was believed to involve the small particle size distribution of the goethite (c.a. 20 nm), as well as structural flaws within the crystals. The small particle size was able to reduce the Neel Temperature (magnetic ordering temperature, see section 4.2.5), hiding the characteristic six line spectra of goethite and produce the doublet of akaganeite. Morup et al. (1983) also found that particle size influenced line broadening.

Murad and Johnston (1987) discuss the ability of reduced particle size to produce supermagnetic relaxation. The energy required to flip an electron's spin is proportional to the volume of the particle. As the particle size decreases to a critical value, thermal energy can cause spontaneous spin flipping at a greater rate than the nucleus can emulate. The nucleus therefore experiences a diminishing magnetic field and the Mössbauer spectra alters accordingly. When the temperature is reduced, there will be a threshold limit reached where the thermal excitation will no longer generate the spontaneous flipping. This temperature is termed the Blocking Temperature, below which supermagnetic behaviour is alleviated and particles become ordered.
Cation substitution has been shown to cause deviations in the magnetic properties of samples, allowing for identification and monitoring of such circumstances (Fysh and Clark 1982).

Murad and Johnston (1987) state that sample identification should be supported by another analytical method (e.g. XRD), as was the finding of Davey and Scott (1976).

4.2.5 CHARACTERISTIC MÖSSBAUER DATA FOR IRON OXYHYDROXIDES

The sharp γ-ray emission as the isotope $^{57}$Co decays to the isotope $^{57}$Fe makes the Mössbauer technique ideal for characterisation of iron containing compounds. The isotope $^{57}$Fe also has a high natural abundance of 2.2 %, which further enhances the attraction of this system.

Murad and Johnston (1987) compiled Mössbauer data on a variety of iron oxides and oxyhydroxides, as have Schwertmann and Cornell (1991). Details of Mössbauer data for the major oxides and oxyhydroxides are summarised below.
4.2.5.1 FERRIHYDRITE

There are a range of ferrihydrites which are classified by the number of lines found in the XRD spectra. The 6-XRD line material is the most ordered, resembling defect hematite in structure (room temperature doublet has quadrupole splitting of 0.7 or less). The 2 or less XRD line material is very poorly ordered and has been labelled proto-ferrihydrite by Murad and Johnston (1987). Spectra for ferrihydrite are shown below in Figure 4.5. The structure of ferrihydrite is represented as a distribution between the 2 and 6-XRD line materials, therefore the Mössbauer spectra must be considered likewise.

Ferrihydrite particles are usually spherical of about 5 nm diameter, hence the room temperature spectra of 2-XRD line and 6-XRD line ferrihydrite are both super-paramagnetic. Due to the continuous distribution of structural iron sites, a single doublet fit is of poor representation, however two doublets will usually suffice (Murad and Johnston 1987).

Webb and Gray (1974) used Mössbauer spectroscopy to observe ferritin cores (ferritin is an iron storage protein) and polymerised iron products. The spectra were comparable suggesting the Fe\(^{3+}\) sites were identical in the materials studied and predominately octahedral. Yang et al. (1986) and St Pierre et al. (1987) conducted similar studies on ferritin.
Figure 4.5A. The Mössbauer spectrum of a natural 2 XRD line ferrihydrite at room temperature, fitted with a distribution of Lorentzian doublets. From Murad and Johnston (1987).

Figure 4.5B. The Mössbauer spectrum of natural 6 XRD line (top) and 2 XRD line (bottom) ferrihydrites at 4.2 K, fitted with hyperfine field distributions. From Murad and Johnston (1987).
4.2.5.2 GOETHITE

The paramagnetic goethite doublet has quadrupole splitting of 0.48 mm s\(^{-1}\), however this value has varied between papers as reviewed by Murad and Johnston (1987). They ascribe this variation to the relative close vicinity of the Neel Temperature (\(\approx 400\) K) and to the crystals being sensitive to element substitution and crystalline defect. The Neel Temperature is the magnetic ordering temperature at which the forces holding the electron spins anti-ferromagnetic, are overcome (Jiles 1991). A typical Mössbauer spectra of goethite is given below in Figure 4.6.

Particle size plays a significant role with goethite samples. Particles of 200 nm can significantly lower the magnetic ordering temperature (Neel Temperature) from 400 K to 365 K, and particles below 20 nm become super-paramagnetic (Murad and Johnston 1987).
4.2.5.3 HEMATITE

Hematite can be divided into three regions to assist classification of the magnetic behaviour as described by Murad and Johnston (1987). These regions are:

1) Paramagnetic above the Curie Temperature \((T_c \approx 955 \text{ K} \text{ for pure, bulk hematite})\) with the doublet having quadrupole splitting of \(0.46 \text{ mm s}^{-1}\). The Curie Temperature is the magnetic ordering temperature where ferromagnetic material becomes paramagnetic (Jiles 1991).

2) Weakly ferromagnetic between the Curie Temperature and the Morin Transition \((T_m \approx 260 \text{ K} \text{ for pure bulk hematite})\), having quadrupole splitting of about \(0.2 \text{ mm s}^{-1}\). The Morin Transition \((T_m)\) is another magnetic ordering temperature peculiar to hematite.

3) Genuinely anti-ferromagnetic below the Morin transition.

Hematite is super-paramagnetic at room temperature if the particle size is less than 8 nm. A typical spectra is given in Figure 4.7 below.
Figure 4.6. The Mössbauer spectrum of goethite from an iron (II) system, recorded at 4.2 K. From Schwertmann and Cornell (1991).

Figure 4.7. The Mössbauer spectrum of hematite recorded at 293 K. From Schwertmann and Cornell (1991).
4.2.5.4 AKAGANEITE

Murad and Johnston (1987) suggest that the spectrum for akaganeite is almost as controversial as its structure. The Neel Temperature has been shown to range from 249 K to 299 K, depending upon the level of incorporated water; but generally a value of 295 K is used. Below the Neel Temperature, akaganeite is anti-ferromagnetic with the spectra comprising of at least three sextets.

At room temperature, the paramagnetic akaganeite consists of a broad doublet with large quadrupole splitting of about 0.7 mm s$^{-1}$. See Figure 4.8 below.

The spectrum is usually fitted with two components having identical isomer shifts but different quadrupole splitting. Johnston and Logan (1979) were able to resolve the spectra into two closely overlapping doublets. They believed that at 77 K, the magnetic hyperfine splitting sextet suggested the presence of two non equivalent iron sites. They have assigned the inner doublet to Fe$^{3+}$ located within the lattice, partly due to that doublet being sharp, hence representing ions in a well defined structure. The second doublet is assigned to Fe$^{3+}$ in the channel sites of akaganeite. These channel sites have a choice of balancing ions therefore the peaks are expected to be broader showing a range of electronic field strengths.
Figure 4.8A. The Mössbauer spectrum of somatoidal akaganeite recorded at 293 K and at 77 K. From Murad (1979).

Figure 4.8B. The Mössbauer spectrum of synthetic akaganeite recorded at 4.2 K showing the three component sextets. From Murad and Johnston (1987).
4.2.5.5 GREEN RUSTS

Cuttler et al. (1990) recorded a spectrum of green rust formed from sulphate solutions, stating that at 77 K, the spectrum was fitted with one iron (II) doublet and one iron (III) doublet. He reported that the iron (II) doublet is marginally different to those found originating from a chloride or carbonate background, but could not support the findings of Olowe (1989), who resolved three iron (II) doublets and two iron (III) doublets. The Mössbauer spectrum of green rust II is given below in Figure 4.9.

4.2.5.6 MAGNETITE

Murad and Johnston (1987) reported magnetite as having a Curie Temperature of about 850 K. The iron in magnetite has two distinctive sites which have an antiparallel spin arrangement below the Curie Temperature. The magnitude of the spins differ resulting in magnetite showing ferrimagnetic behaviour. A typical spectrum for magnetite is given in Figure 4.10.
Figure 4.9. The Mössbauer spectrum of green rust (Fe(II,III) hydroxy carbonate) recorded at 120 K, fitted with two Fe (III) and two Fe (II) doublets. From Murad and Taylor (1984).

Figure 4.10. The Mössbauer spectrum of magnetite recorded at 298 K. From Schwertmann and Cornell (1991).
4.2.5.7 MAGHEMITE

Maghemite (see Figure 4.11) is converted to hematite at a relatively low temperature. This makes the measurement of the Curie Temperature difficult. Murad and Johnston (1987) list data ranging from 820 K to 985 K, reporting that at room temperature well crystalline maghemite is magnetically ordered consisting of a broad line sextet.

4.2.5.8 LEPIDOCROCITE

Lepidocrocite is paramagnetic at room temperature with a Neel Temperature of 77 K (Murad and Johnston 1987). The doublet spectrum has quadrupole splitting of 0.5 mm s$^{-1}$ increasing with decreasing particle size. The doublet is usually fitted with a two component spectra. A typical spectra is given in Figure 4.12.

Pollard et al. (1992) has shown lepidocrocite to be anti-ferromagnetic at 4.2 K. Even with elemental substitution, lepidocrocite can easily be distinguished from ferrihydrite at 4.2 K (Childs et al. 1984). De Grave et al. (1986) were able to isolate the proportion of iron species located on the outer surface layers and found it corresponded with such proportionation by surface area measurements.
Figure 4.11. The Mössbauer spectrum of maghemite produced by heating magnetite at 250°C. Spectra recorded at 298 K, from Schwertmann and Cornell (1991).

Figure 4.12. The Mössbauer spectrum of lepidocrocite recorded at 294 K and at 4.2 K. From Schwertmann and Cornell (1991).
4.2.5.9 ZETA (δ FeOOH) AND FEROXYHITE (δ'FeOOH)

Feroxyhite (δ'FeOOH) is a rare mineral found in nature. The synthetic version has no name but will be called here zeta FeOOH (see Figure 4.13). Murad and Johnston (1987) report feroxyhite as a disordered modification of zeta FeOOH. They report zeta FeOOH to be (ferri)-magnetically ordered at room temperature with an estimated Neel Temperature of about 440 K. Due to its poor crystallinity and varying particle size, the material may show differing degrees of super-paramagnetic behaviour. Pollard et al. (1992) states that feroxyhite is ferrimagnetic forming a doublet at ambient temperatures.

4.2.5.10 POLYMERIC IRON OXYHYDROXIDE

Johnston and Lewis (1986) used Mössbauer spectroscopy to study the formation of iron oxyhydroxides. They demonstrated that a spectral singlet arose from the monomer coordinated octahedrally to six water molecules and that the doublet was likewise octahedrally coordinated. The doublet had large quadrupole splitting suggesting asymmetry in the lattice structure and the peak line widths were narrow suggesting a well defined molecular structure. They concluded that the iron (III) dimer (Fe₂(OH)₂⁴⁺) was responsible for the spectral doublet, as only it provides each iron atom with identical strong electric field gradients consistent with both the narrow band width as well as the large quadrupole splitting.
Figure 4.13. The Mössbauer spectrum of synthetic feroxyhite recorded at 4.2 K and fitted with two sextets. From Murad and Johnston (1987).
By conducting in situ Mössbauer spectra, Johnston and Lewis (1986) were able to follow the aging process. They believe that the monomer is consumed to form the relatively stable dimer, which then polymerises forming chains. The dimers can polymerise to form singular long chains, or they can link together while flanking each other to form double chains. These double chains then can link in various ways to form different iron oxyhydroxides depending upon the hydrolysis rate and other species present.

This is consistent with Nalovic and Janot (1979), who state that even the very small particles (10 linked atoms) possess typical iron oxyhydroxide structure.
4.3 DISSOLUTION TECHNIQUES

The selective chemical dissolution of various forms of iron oxides and hydroxides has been widely used in the field of soil science to assist definition of boundaries between soil types.

There has been a range of extraction techniques reported in the literature, however the most commonly reported have been acid ammonium oxalate (Tamm 1922), or a solution of sodium dithionite as proposed by Deb (1950) and modified by Mehra and Jackson (1960) to include bicarbonate as a buffer. Hydroxylamine has been suggested as an alternative to the acid ammonium oxalate (Ross et al. 1985).

4.3.1 ACID AMMONIUM OXALATE

It has been reported that the acid ammonium oxalate extraction process dissolves the X-ray amorphous iron oxyhydroxide material termed "active", "free" and "short range order" (Schwertmann 1973, Walker 1983, Parfitt et al. 1988).
It has been suggested that acid ammonium oxalate also dissolves some crystalline iron oxyhydroxides, but the degree of dissolution is comparatively small (McKeague and Day 1966, Borggaard 1981 and Ibanga et al. 1983).

Schwertmann (1973) states that as lepidocrocite is considered to be less stable than goethite, it will be extracted to a greater degree. As the crystallinity of lepidocrocite decreases, it would be expected that the dissolution would increase. Tabulated results, in fact show increased dissolution associated with increased surface areas and XRD peak widening. Also, the dissolution of goethite is always less than that for lepidocrocite.

Others have found that the dissolution of crystalline goethite (Borggaard 1979, Fordham et al. 1984, Arduino et al. 1989), lepidocrocite (Borggaard 1979, Ibanga et al. 1983), and hematite (Borggaard 1976, 1981) to be quite small compared to the high levels of extraction from the so called "amorphous" iron oxyhydroxides. Hence it was claimed that the extraction process is capable of discriminatory dissolution.

De Endredy (1963) found hematite was readily dissolved by acid ammonium oxalate while being irradiated by a mercury lamp. To prevent this photochemical reaction it is recommended that extractions be conducted in the dark.
Detailed studies into the parameters effecting acid ammonium oxalate extractions have been conducted. Parfitt (1989) conducted identical extractions over a range of pH values between 3 and 5. He demonstrated that the rate of dissolution increased as the pH decreased until pH 3.5 was reached. As the pH was lowered to 3.0, only a marginal increase in dissolution was detected. He recommended the use of pH 3.0 for increased dissolution rate and to take solution conditions to the more highly buffered region as suggested by McKeague and Day (1966).

Parfitt (1989) conducted experiments covering a range of ammonium oxalate concentrations and was able to show no additional extraction occurred beyond a concentration of 0.15 mol dm$^{-3}$. He recommended a concentration of 0.20 mol dm$^{-3}$ for samples containing greater than 5% extractable iron.

The sample to solution ratios are another factor influencing the efficient dissolution of X-ray amorphous iron. Many have used a ratio of 1:40 (McKeague and Day 1966, Walker 1983, Ross et al. 1985). Parfitt et al. (1988) then Parfitt and Childs (1988) used a ratio of 1:100, whilst Arduino et al. (1989) employed a value of 1:20. Parfitt (1989) observed that for samples containing less than 5% extractable iron, no improvement was obtained using sample to solution ratios larger than 1:100. A ratio of 1:200 was recommended for samples containing greater than 5% extractable iron.
McKeague and Day (1966) investigated the effect of extraction time upon degree of dissolution. They found that the majority of samples released their extractable iron within the first hour of treatment, with only a few samples continuing to be slowly extracted. Since the rate of dissolution was shown to decrease rapidly with time, an extraction time of 4 hours was chosen as stated "somewhat arbitrarily". Parfitt (1989) found samples which had largely completed extraction within 2 hours, as well as other samples which continued to dissolve after 16 hours. These samples contained ferrihydrite and hematite with the explanation suggesting that ferrihydrite being poorly crystalline would dissolve rapidly, while crystalline hematite would dissolve slowly.

Graphical methods were used to locate the point where the dissolution of ferrihydrite was largely complete, yet hematite had hardly been attacked. Parfitt (1989) constructed a plot of \( [(\text{Fe}_t - \text{Fe}_o) / \text{Fe}_t] \) versus log time (\( \text{Fe}_t = \text{total iron}. \text{Fe}_o = \text{oxalate extracted iron}. \)), reconstructed below in Figure 4.14. The plot consisted of two intersecting lines representing the dissolution of firstly ferrihydrite and secondly hematite. The point of inflection was where the best separation occurred at the 4 hour extraction limit.

Clearly the extraction rate is dependant on the degree of crystallinity and particle size. In any one sample there is a continuum of sites being leached at different rates, thus dissolution methods can only give a semi-quantitative determination.
Figure 4.14. \( \frac{\text{Fe}_t - \text{Fe}_o}{\text{Fe}_t} \) plotted against time for a sample from Parfitt (1989). \( \text{Fe}_t \) is the total iron in the sample, while \( \text{Fe}_o \) is the oxalate soluble portion of iron.
4.3.2 DITHIONITE CITRATE BICARBONATE

Dithionite citrate bicarbonate reagent has been widely used to extract iron from soils to assist with classification (Parfitt and Childs 1988).

Dithionite citrate bicarbonate reagent does not distinguish between X-ray amorphous and crystalline iron oxyhydroxides (McKeague and Day 1966) and the dissolution of various crystalline minerals has been widely reported (Farmer et al. 1983).

Parfitt and Childs (1988) comment that the particle size can influence the result. Walker (1983) expressed concern that the use of dithionite citrate bicarbonate reagent for the estimation of total iron in magnetic minerals may give erroneous results. She demonstrated that the dithionite citrate bicarbonate reagent did not attack crystalline magnetite.

Borggaard (1982) reported the extraction process usually required 15 minutes at 80°C, however Parfitt et al. (1988) as well as Parfitt and Childs (1988) demonstrated that extractions for 16 hours at room temperature gave comparable results.
4.3.3 HYDROXYLAMINE

Ross *et al.* (1985) and later Lee *et al.* (1989) suggest that hydroxylamine provides a reasonable alternative to the acid ammonium oxalate method. While hydroxylamine extractions consistently gave slightly lower values for iron than did the acid ammonium oxalate reagent, it tended to be more precise and reproducible. Furthermore, hydroxylamine does not attack crystalline magnetite.

4.3.4 OTHERS

EDTA has been used for the selective removal of organically complexed iron from soils to assist with classification (Farmer *et al.* 1983, McBride *et al.* 1983). X-ray amorphous iron (probably ferrihydrite) can also be selectively dissolved by EDTA (Parfitt and Childs 1988), but extractions can take months to complete (Borggaard 1976, 1979, 1981 and 1982). These extractions have been shown to be comparable to the accepted acid ammonium oxalate standard and is proposed as a suitable replacement, should the presence of oxalate be undesirable.

Farmer *et al.* (1983) used sodium pyrophosphate to assess the levels of organically complexed iron, thus assisting with soil characterisation and classification. McKeague and Sheldrick (1977) emphasise that all dissolution processes are "useful approximations", rather than analytical methods.
4.4 SURFACE AREA

Surface area is generally measured using the adsorption of a gas upon the solid to be characterised. Samples are held in a pure gas atmosphere (e.g. nitrogen) at a temperature near the gas condensation point. At this temperature the gas begins to adsorb onto the surface of the sample by specific forces such as chemical bonds (termed chemisorption), or by weak non specific forces such as van der Waals (termed physical adsorption). The relationship that exists between the relative pressure and volume of adsorbed gas (at standard temperature and pressure) is given by the Brunauer, Emmett and Teller (BET) equation.

\[
\frac{P}{V(P_o - P)} = \frac{1}{V_m c} + \frac{(c - 1) P}{V_m c \cdot P_o}
\]

Equation 4.2

Where ...

\( P \) is the measured pressure.

\( P_o \) is the saturation vapour pressure.

\( V \) is the volume of gas absorbed at the pressure \( P \)

\( V_m \) is the volume of gas required for monolayer coverage of a unit mass of sample.
The value for $c$ is approximated from the equation below.

$$c \approx \exp \left[ (\Delta H_1 - \Delta H_m) / R \, T \right]$$  \hspace{1cm} \text{Equation 4.3}

Where ...

$\Delta H_m$ is the heat of adsorption of the gas monolayer.

$\Delta H_1$ is the heat of liquidification of gas for the second and subsequent layers of adsorption.

$R$ is the gas constant.

$T$ is the temperature in degrees kelvin.

A plot of $P / [V (P_o - P)]$ against $P / P_o$ should give a straight line of slope $(c - 1) / V_m \, c$ and have an intercept of $1 / V_m \, c$. i.e.,

$$V_m = 1 / (\text{slope} + \text{intercept})$$  \hspace{1cm} \text{Equation 4.4}

The monolayer volume gives the area of the sample because the area of each gas molecule is known. Comprehensive reviews of the principles behind the BET equation are given by Shaw (1980) and Hiemenz (1986). Table 4.1 below contains the measured specific surface areas for various iron oxides and oxyhydroxides reported by Schwertmann and Cornell (1991).
**TABLE 4.1: REPORTED SPECIFIC SURFACE AREAS FOR IRON OXIDES AND OXYHYDROXIDES**

<table>
<thead>
<tr>
<th>IRON OXIDE / OXYHYDROXIDE</th>
<th>SURFACE AREA m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>FERRIHYDRITE</td>
<td>180 - 200</td>
</tr>
<tr>
<td>GOETHITE</td>
<td>20 - 90</td>
</tr>
<tr>
<td>HEMATITE</td>
<td>20 - 90</td>
</tr>
<tr>
<td>AKAGANEITE</td>
<td>30 - 100</td>
</tr>
<tr>
<td>GREEN RUST II</td>
<td>250</td>
</tr>
<tr>
<td>MAGNETITE</td>
<td>4</td>
</tr>
<tr>
<td>MAGHEMITE</td>
<td>130</td>
</tr>
<tr>
<td>LEPIDOCROCITE</td>
<td>70 - 80</td>
</tr>
<tr>
<td>FEROXYHITE</td>
<td>200</td>
</tr>
</tbody>
</table>

The data contained in Table 4.1 should be taken as a guide only. For example, Gast *et al.* (1974) reported a surface area of 320 m² g⁻¹ for an X-ray amorphous iron oxyhydroxide, while Eggleton and Fitzpatrick (1988) reported the surface area of 2-XRD line ferrihydrite was 340 m² g⁻¹ and 6-XRD line ferrihydrite was 225 m² g⁻¹. Madrid and De Arambarri (1985) reported lepidocrocite as having a surface area of 116 m² g⁻¹, while Schwertmann *et al.* (1985) reported goethite ranging from 9 to 153 m² g⁻¹. Such variation in the surface area and presumably the crystallinity is usually associated with different methods of sample preparation.
4.5 TRANSMISSION ELECTRON MICROSCOPY

Transmission electron microscopy (TEM) is a very powerful technique for the direct measurement of crystal dimensions. Crystal morphology and phase identification can also be determined. Schwertmann and Cornell (1991) claimed that TEM detected the presence of some iron oxides where XRD was unable to.

TEM can achieve a very high magnification up to 250 000 times, though typical magnifications are about 100 000 times. Samples for TEM analysis are mounted on a polymer coated copper grid. A beam of electrons is focused upon the sample and the transmitted electrons form an image upon a fluorescent screen. Measurements must be conducted at very low pressures to prevent residual vapours distorting the electron beam. By the very definition of TEM, electrons must pass through the sample for it to be illuminated, otherwise only a silhouette will be produced. Images can be captured using photographic techniques. A detailed description of the TEM technique is reported by Slayter and Slayter (1992).

TEM has been used for a wide variety of applications. Cornell and Giovanoli (1988a) used TEM to identify hollow crystalline tubes when akaganeite was attacked by acid. They also found that twinned akaganeite crystals were preferentially attacked at the twinning boundary.
Cornell *et al.* (1991) were able to observe the effect cysteine had upon goethite formation and were able to identify changes to the crystalline shapes. Cornell and Giovanoli (1987a) used TEM to observe the formation of twinned goethite crystals under the influence of silicate species. TEM has been used to follow the formation of goethite in the presence of cations such as manganese (Cornell and Giovanoli 1987b) and cobalt (Cornell and Giovanoli 1988b, Cornell and Giovanoli 1989).

Schwertmann *et al.* (1989) employed TEM to observe the effect of cation exchange as chromium replaced iron in synthetic goethite samples. The extremely high magnification power of this technique has proven invaluable for identification of crystal shapes, defect recognition and direct crystal measurements.

While individual crystals can be easily measured, Schwertmann and Cornell (1991) have reported that between 600 and 800 individual particles over several grids must be statistically measured to obtain an accurate particle size distribution. This highlights the danger of misrepresentation that can occur with this or any microscopy technique. Another problem that can arise is that the particle under observation can be charged or even damaged by the electron beam used to illuminate it. This was the case with the early work on akaganeite, where a "supercell" structure was proposed on the basis of TEM (see section 2.4).
4.6 THERMOGRAVIMETRY

Thermal methods of analysis are some of the oldest techniques used for the study of clay minerals, in which the iron oxyhydroxides can be grouped. Paterson and Swaffield (1980) stated that while XRD is used to find similarities between samples, thermal analysis tends to reveal differences.

Thermogravimetry measures the sample mass as a function of the sample temperature. High sensitivity is achieved by using an accurate balance and calibrating the instrument with a known sample under identical conditions to those used experimentally (Schwarz 1991). Precise weight changes at well defined temperatures characterise iron oxyhydroxide samples as chemically bound water is lost or it undergoes decomposition. Loss of water occurs when the equilibrium water vapour pressure of the sample exceeds the water vapour pressure in the carrier gas at a given temperature.

It is important to note that thermogravimetry is influenced by several factors which must be taken into account when comparing results. These factors can affect the shape and appearance of shoulders within the thermograph and can even change the products formed from the process. These factors are described below.
1) The porosity of a precipitate can remarkably influence thermogravimetry. Foldvari et al. (1988) states that surface water can reside within capillaries of less than 2 nm and results in only a gradual weight loss with increasing temperature. Such broad temperature dehydrations tend to mask other weight loss events.

2) It has been reported that the particle size of a sample has enormous effect upon the weight loss temperature range (Mackenzie 1957). As the particle size increases the temperature for dehydration also increases and with greater definition.

3) Aging of a sample has been shown to influence the crystallinity and proportion of defects found in a precipitate. Goni-Elizalde and Garcia-Clavel (1988a) have shown both to influence thermogravimetric spectra.

4) Anion inclusion and entrapment during precipitation has been shown to influence thermogravimetry. The anions NO$_3^-$ and SO$_4^{2-}$ in particular have been reported to decompose or be eliminated at higher temperatures during thermogravimetry, resulting in the addition of an extra weight loss shoulder (Paterson and Swaffield 1980).
5) Thermogravimetry can also be influenced by the sample preparation. If the drying temperature is too high then structural water may be lost. Koch et al. (1986) using XRD, electron microscopy and Mössbauer spectroscopy, have reported that a drying temperature of up to 100°C does not influence the thermograph of goethite.

6) Paterson et al. (1982) reported that different carrier gasses used during thermogravimetric analysis resulted in the formation of different products at various temperatures. It appears that a carrier gas can catalyse or inhibit transformation and dehydration reactions resulting in quite different thermographs. The carrier gas flow rate is important, as is humidity which can strongly influence dehydration.

7) The rate of temperature elevation can also greatly alter the definition achieved from thermogravimetry. Most data is quoted as a temperature range while the temperature is still rising. If isothermal conditions were applied at the start of each peak the range would be narrowed considerably. That is, as the temperature rises the activation energy for dehydration is reached. Once reached, the dehydration reaction will proceed without the further elevation of temperature. Hence if the temperature was held each time there was a mass loss, then the resolution of data would greatly improve.
It has been suggested that thermogravimetry may provide a method for analytical
determination of mixtures of iron oxyhydroxides (Weissenborn 1993). The
various iron oxyhydroxides are discussed below. Hematite is not considered as it
is the end product of all the thermal transformations.

4.6.1 GOETHITE

Goethite undergoes a two step dehydration when heated. The first weight loss is
associated with surface moisture and is reported between the ranges of room
temperature and 100°C (Foldvari et al. 1988, Schwarz 1991). The second weight
loss occurs from the decomposition of goethite to hematite as below.

\[ 2 \text{FeOOH}_{(s)} \rightarrow \alpha \text{Fe}_2\text{O}_3_{(s)} + \text{H}_2\text{O}_{(g)} \]  

Equation 4.5

This reaction has a theoretical weight loss of 10.1 % (Paterson and Swaffield
up to 12 % are frequently reported. This discrepancy has been explained as
excess hydroxyl groups absorbed due to protonation of the surface oxide ions
and coordinated water at exposed iron III sites along crystal edges (Paterson and
Swaffield 1980, Goni-Elizalde and Garcia-Clavel 1988a). Reported dehydration
temperature ranges are listed in Table 4.2.
### TABLE 4.2: REPORTED DEHYDRATION RANGES FOR GOETHITE

<table>
<thead>
<tr>
<th>Reference</th>
<th>Wt loss %</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schwarz (1991)</td>
<td>9.8 %</td>
<td>200 - 300°C</td>
</tr>
<tr>
<td>Weissenborn (1993)</td>
<td>—</td>
<td>285 - 350°C</td>
</tr>
<tr>
<td>Foldvari et al. (1988)</td>
<td>10-15 %</td>
<td>300 - 410°C</td>
</tr>
<tr>
<td>Goni-Elizalde and Garcia-Clavel (1988a)</td>
<td>11.1 %</td>
<td>170 - 470°C</td>
</tr>
<tr>
<td>Goni-Elizalde and Garcia-Clavel (1988a)</td>
<td>11.6 %</td>
<td>150 - 530°C</td>
</tr>
<tr>
<td>Paterson and Swaffield (1980)</td>
<td>11.8 %</td>
<td>250 - 400°C</td>
</tr>
</tbody>
</table>

As can be seen in Table 4.2, the reported dehydration temperatures for goethite span a wide range. This can be accounted for by differences in the samples (e.g. particle size and crystallinity defects) and differences in the analytical procedure (e.g. sample preparation, instrumental conditions, carrier gas composition and flow rate). Derie et al. (1976) state that the range in reported dehydration temperature is due to variation in crystal particle size, but other factors such as heating rate, humidity etc could also be involved.
4.6.2 AKAGANEITE

Thermogravimetry of akaganeite, like its structure, has been quite difficult to resolve. Akaganeite has the hollandite structure and as a consequence is very porous. Foldvari et al. (1988) has shown that the existence of a porous system promotes broadening of dehydration temperatures. Thermogravimetry of akaganeite in a nitrogen atmosphere produces a continuous weight loss between room temperature and 800°C. Points of inflection are observed but are difficult to resolve (Paterson et al. 1982).

Paterson et al. (1982) reported that different carrier gasses resulted in different products being formed. Under a stream of nitrogen, akaganeite transformed at high temperatures via a poorly crystalline pseudomorphous hematite to the plate like crystals of hematite. This was also supported by the work of Chambaere and De Grave (1985). Paterson et al. (1982) report that under a stream of oxygen, the transition was complicated by the possible formation of dehydroxylate akaganeite namely $\beta$Fe$_2$O$_3$. Braun and Gallagher (1972) and Howe and Gallagher (1975) reported $\beta$Fe$_2$O$_3$ also formed as an intermediate under vacuum. However Gonzalez-Calbet et al. (1981) then Gonzalez-Calbet and Alario-Franco (1982) found that heating akaganeite in a vacuum formed maghemite ($\gamma$Fe$_2$O$_3$) as an intermediary to hematite.
Goni-Elizalde and Garcia-Clavel (1988b) used differential scanning calorimetry and thermogravimetry to investigate the above confusion. They found three steps to the thermal dehydration. The first loss of surface water was 2.9 % up to 110°C. The second was between 110 and 190°C, with a total 4.1 % w/w which was water absorbed into the structural tunnels. Between 190 and 350°C the water from hydroxyl groups is removed representing 11.5 % of the original weight. This equates to 12.4 % of the supposed dry weight and is consistent with other workers (Braun and Gallagher 1972, Howe and Gallagher 1975). From 350 to 550°C, a further weight loss of 3.2 % was recorded representing the elimination of HCl.

Goni-Elizalde and Garcia-Clavel (1988b) followed the dehydration reactions using X-ray diffraction and transmission electron microscopy. After the elimination of the adsorbed water in the structural tunnels and prior to the elimination of structural water, the X-ray diffraction patterns showed a broadening of the akaganeite line widths with a loss of intensity. They claim that this proves internally absorbed water plays a role in the stability of the akaganeite structure. Goni-Elizalde and Garcia-Clavel (1988b) state that the sample, on elimination of structural water, then transforms to a phase which has similarities to akaganeite and hematite.
The role of structural water was also investigated by Chambaere and De Grave (1985) who concluded...

"the more crystal water akaganeite contains, the lower the heating temperatures are at which magnetic and structural variations start to take place, and the higher the temperature of the final recrystallisation to hematite".

Variation in the dehydration temperatures was also explained by Fromming (1974) who states that precipitate aging has a pronounced effect upon the thermogram of akaganeite. He states that aging improves crystallinity, elevates dehydration temperatures and possibly causes shoulder broadening.

4.6.3 LEPIDOCROCITE

Mackenzie (1957) reported that lepidocrocite looses structural water at a slightly higher temperature than that of synthetic goethite. He indicated that lepidocrocite transforms into maghemite as an intermediary, before exothermically recrystallising to form hematite. Formation of maghemite was also reported by Naono and Nakai (1989) as well as Giovanoli and Brutsch (1974).
Mackenzie (1957) states that the final exothermic recrystallisation to form hematite can only be observed by differential scanning calorimetry (DSC), since there is no associated weight loss.

De Bakker et al. (1991) using thermogravimetry (TG), DSC and differential thermal analysis (DTA), demonstrated that the transition temperature and the resulting maghemite particle size were not influenced by the original particle size of lepidocrocite. In contrast, they were able to show that the transition temperature for the further conversion of maghemite to hematite was dependant upon the amount of excess water found in the original lepidocrocite structure.

4.6.4 MAGNETITE

Mackenzie (1957) used differential thermal analysis to show that synthetic magnetite oxidises in air to form maghemite between 275 and 375°C. The maghemite then transformed into hematite between 590 to 650°C. The presence of water vapour acted as a catalyst dramatically reducing transformation temperature, emphasising the importance of the atmospheric conditions.
4.6.5 IRON (III) OXIDE GELS "AMORPHOUS MATERIALS"

Mackenzie (1957) has shown that the final precipitation pH of these amorphous species can influence the thermogravimetric data. The higher the pH of formation (up to pH 8.5), the poorer the definition of data. It appears that the higher pH promotes the oxolation of the bridging oxygen within the polymeric chains, producing a more ordered structure and a wider range of crystallinities. The wider spectrum of crystallinities would broaden any shoulders on a thermogravimetric curve, thereby reducing definition.

Elevated precipitation temperature could also result in an elevation of transformation temperatures. This is presumably due to the promotion of a more crystalline structure.

Due to the above influences, fresh preparations of iron (III) oxide gels have a broad weight loss anywhere between 250 and 500°C, making comparisons between products difficult.
4.7 SETTLING RATE

The settling rate of a slurry can be used to differentiate between samples. When used in conjunction with the sediment volume, the technique becomes pseudo-analytical, giving an indication of changes in particle size. This is an important tool when dealing with particles too small for light scattering techniques.

When a slurry of particles suspended in a fluid settles under the influence of gravity, termed sedimentation, several distinctive processes take place due to changes in the solids concentration in the lower regions. For the purpose of this discussion, the processes are described below simply in terms of the effect of solids concentration on the settling rate.

4.7.1 FREE SETTLING ZONE

At very low solids concentration, free settling of individual particles can occur. The precise concentration at which this occurs is a function of the particle number or concentration, as well as the particle size and shape.

In the free settling zone, particles settle at their own velocity under the influence of gravity. The particles do not experience hindrance from collisions or through the effect of fluid displaced by other particles. The settling rate of individual particles depends upon the particle's size, density and shape; as well as the nature of the liquid such as fluid density and viscosity.
It is generally accepted that the free settling zone extends to a solids concentration of approximately 0.2 wt %. However, the precise solids concentration limit depends upon the particle morphology and size distribution. Below this concentration, the sedimentation of individual particles can be described by Stokes Law, as reported by Clift et al. (1978).

\[
U = \frac{d^2 g (P_s - P_l)}{18 \eta} \quad \text{Equation 4.6}
\]

Where:

- **U** = terminal settling velocity (m s\(^{-1}\))
- **d** = particle diameter (m)
- **g** = gravity constant (m s\(^{-2}\))
- **P_s** = density of particle (kg m\(^{-3}\))
- **P_l** = density of liquid (kg m\(^{-3}\))
- \(\eta\) = viscosity of fluid (N s m\(^{-2}\))

Stokes law assumes that the particle is spherical and the liquid is infinite compared to the radius of the particle (ie no other particles are present).
4.7.2 HINDERED SETTLING ZONE

The hindered settling zone is where the settling rate of the particle or agglomerate, is slower than its free settling velocity due to transient interference from other particles. This transient interference can be due to collisions between agglomerates or to the up-flow of displaced supernatant caused by the settling of other particles.

Hindered settling generally occurs with a moderate solids concentration ranging from about 0.2 to 2 wt% for very fine precipitates. Again these concentrations are dependent upon the particle morphology and the nature of the fluid.

Under these conditions it is possible for individual particles to have at different times, either faster or slower settling rates than that particle's free settling velocity. Larger particles would generally have a slower settling velocity due to hindering effects as mentioned, however smaller particles can be drawn down by the larger particles, effectively increasing their settling velocity.
4.7.3 NETWORK SETTLING ZONE

The network settling zone is closely related to the hindered settling zone with the exception that in the network settling zone, the particles all settle collectively with the same settling velocity due to continual rather than transient interactions between particles. The larger particles have decreased settling velocity due to significant hindrance from other particles, to a rate equal to that of the smaller particles. Typically this occurs at solids concentration of above about 2 wt%, but the precise concentration depends upon particle size and morphology.

Under these conditions, the mudline becomes very distinctive and the supernatant liquid is relatively free of residual particles. It is under conditions of essentially network settling that the initial linear settling rate can be measured, shown as the linear portion of the settling plot in Figure 4.15 below.

Figure 4.15 represents a plot of the position of the boundary between supernatant and the settling solids or "mudline", as a function of time. The changing height of the mudline does not follow a uniform interval, but indicates the various zones where different settling processes occur.
Figure 4.15. A standard settling curve where the volume of sediment is measured against time.
Information from such plots can be used to estimate the aggregate or particle size (Farrow and Warren 1993). It should be pointed out that the same settling rate can be achieved by small particles of high density, or by large particles of lower density. If small particles aggregate together, the settling rate increases due to the increase in size, despite the associated decrease in the effective density (Farrow and Warren 1993).

When aggregation processes occur within a suspension, there is typically an induction period preceding the onset of the linear settling rate region. At this time, very small particles do not settle under gravity due to the relatively high forces of diffusion or Brownian motion. Some have suggested such aggregation as a diffusion limited process (Witten and Sander 1981, Kolb et al. 1983, Meakin 1983).

The aggregation of particles are mostly controlled by the balance between van der Waals attraction and electrical repulsions. Other factors such as interfacial reactions including ion exchange, surface coordination and chemisorption can also have an influence (Matijevic 1973).

Aggregation of particles can also be induced by the addition of high molecular weight polyelectrolytes (Thomas and McCorkle 1971, Van De Ven 1988, Baumgartner and Mijalchik 1991), humic substances (Jekel 1986) and polyacrylamides (Moody 1990), as a process termed flocculation. Comprehensive reviews on the theory of flocculation are given by Melik and Fogler (1984a, 1984b), Gregory (1981, 1989) and Svarovsky (1990).
These factors become important when dealing with the iron oxide and oxyhydroxide group of minerals. Depending on formation conditions, different crystal structures are formed with varying densities, surface properties and particle sizes. While such variation is desirable for differentiation between experimental products, care must be taken to ensure which variable is responsible for fluctuations in settling rates.

4.7.4 GEL STRUCTURE ZONE

The gel structure zone is when the particles or agglomerates have settled to a point where a self supporting, three dimensional structure is formed. In this zone no further settling takes place and the maximum solids concentration is reached. This is termed the equilibrium sediment volume, from which the related density of the sediment (pulp density) can be calculated if the initial mass of the settled solids is known.

The solids concentration at which the gel structure forms is influenced by the particle size, morphology and the particle interactions (Zrinyi et al. 1988).
4.7.5 CONCLUSION

The settling rate and equilibrium sediment volume data can provide information regarding the particle size distribution. This is important in the case of iron oxyhydroxides where laser light scattering techniques are ineffective.

The combination of a slow settling rate and a low sediment volume is indicative of small, dispersed particles.
A fast settling rate coupled with a high sediment volume is indicative of agglomerated particles. The settling rate is fast due to the increased particle size, however agglomerated particles tend to trap liquor within the structure resulting in a relatively high sediment volume.
A fast settling rate coupled with a low sediment volume indicates a relatively large, dense particle, such as a highly crystalline precipitate.

However, it must be recognised that the interpretation of settling rate / sediment volume data requires considerable caution due to the number of different parameters which can affect the settling characteristics.

4.8 SUMMARY

This chapter has sought to identify the strengths and weaknesses of current instrumental techniques for the characterisation of iron (III) oxyhydroxides. The polymeric to crystalline nature of these compounds varies with formation conditions and a detailed study of the relationship between techniques was required before the complex precipitation conditions could be adequately studied.
CHAPTER 5
EXPERIMENTAL

Conditions used for the precipitation of the synthetic iron oxide and oxyhydroxide samples are described, along with procedures adopted for the various characterisation techniques.

5.1 CHEMICALS

All chemicals used throughout this study were of AR grade or equivalent. All solutions were prepared using B grade glassware and deionised water.

5.2 REACTOR DESIGN

It has been shown that mixing of reagents can be crucial to the product outcome. Tosun (1988) demonstrated that for a fast reaction, the mixing process influences the particle size distribution. Factors that influence the rate and efficiency of mixing include the tank geometry, the type of turbine, the turbine speed and the position of the feed inlet. A brief review is given below including the conditions selected for experimentation in this study. However, a detailed investigation into the effect of reactor design upon product morphology was outside the scope of this study.
5.2.1 TANK GEOMETRY

The geometry of reaction vessels has been extensively investigated (Sweeney 1978). The inclusion of baffles to a tank is one of the most important aids to mixing. Baffles restrict the circular flow around the tank walls without hindering the radial or axial flows. These baffles are typically flat strips installed vertically in the tank, perpendicular to the wall.

Typically four baffles are attached to the tank wall in a cross hair type manner (Baldi et al. 1978, Barresi and Baldi 1987), although one variation is to place the baffle a short distance off the wall (Armstrong and Ruszkowski 1988, Hemrajani et al. 1988).

Other variations include three larger baffles (Tosun 1988), a cruciform baffle on the tank bottom (Sweeney 1978) and finger baffles descending into the solution (Hemrajani et al. 1988). Baffles can range in size considerably, the most common being about 10 percent of the tank diameter.

While smaller baffles have been shown to produce superior mixing (Hemrajani et al. 1988), these and finger baffles have been discounted due to promotion of air entrainment.
Reactor tanks can have a flat bottom or a curved base. Magni et al. (1988) compared the effect of this upon the mixing performance. They concluded that mixing was more efficient in a flat bottom vessel with normal baffling.

For this study it was decided to use a flat bottom vessel, fitted with four baffles in a cross hair manner. The dimensions of the reactor are shown in Figure 5.1.

5.2.2 TYPE OF IMPELLER

Impellers come in a variety of shapes and sizes, hence a clear definition of requirements must be made.

Generally, each impeller has a region of high shear and turbulent mixing. This region is close to the blades, where the high velocity stream, meets the low velocity bulk solution. In this stream, turbulent eddies and vortices exist, causing rapid mixing and bulk convection currents.

The two mechanisms facilitating mixing are the bulk circulation and the existence of a turbulent zone (Sweeney 1978). Each impeller design has a different combination of these two mechanisms, ranging from high flow (eg typical marine type propeller) through to high shear (eg Sawtooth impeller and bar turbine).
Figure 5.1.
Dimensions for reaction vessel and turbine.
To facilitate the introduction of an alkali into an acidic iron III solution, a reasonable bulk flow is desirable, along with a large turbulent zone for the feed inlet. Experiments in this study were therefore conducted using a Rushton flat blade disc turbine, as favoured by others (Armstrong and Ruszkowski 1988, Magni et al. 1988, Wong and Huang 1988). Figure 5.1 shows the design and dimensions of the turbine used. The relative merit of various turbines is given elsewhere (Sweeney 1978, Weetman and Oldshue 1988, Kubera and Oldshue 1992).

5.2.3 TURBINE SPEED.

Turbine speed strongly influences the mixing efficiency. Van't Riet et al. (1976) claim to have previously shown that the maximum circumferential velocity of a fluid is of the same order of magnitude to the stirrer tip velocity. They state that the discharge is closely followed by strong vortices, which break up into turbulent eddies on hitting the tank walls and baffles. The flow from the turbine splits up and down on hitting the walls and the eddies pass on the turbulent motion to the whole system. This view is supported by Bowen (1986).

The turbine velocity is critical to the turbulence of the system and has been used in modelling the suspension of particles, power dissipation rates and mathematical estimation of mixing times (Kuboi et al. 1974, Brucato and Rizzuti 1988, Geisler and Mersmann 1988, Voit and Mersmann 1988).
Rieger *et al.* (1988) reported that suspension homogeneity increases significantly with turbine speed to a limiting value, beyond which increases in speed have only a marginal effect. This limiting value is dependant upon the particle size and mass.

Tosun (1988) investigated the effect of stirring speed upon the particle size distribution of barium sulphate crystals grown from solution. He observed a curved plot for particle size against rotational speed. To explain these observations, he postulated that as the speed increases, a higher level of supersaturation occurs at the micro-mixing level. This produces more nuclei and hence a lowering of the particle size distribution. Concurrently, as the turbine speed and bulk momentum is increased, the nuclei are transported back to the growth zone (supersaturation zone) and the particle size increases through growth. The interaction of these two mechanisms results in a minimum in the plot of particle size against turbine speed.

Experiments were conducted using a dye in this study to determine the mixing characteristics at different turbine speeds (see section 7.1). It was found that the optimal mixing occurred with a turbine speed of 250 rpm, producing a high level of mixing with a large turbulent zone and did not entrain air into the system.
5.2.4 FEED POSITION

Tosun (1988) experimented with feed positions and observed the effect upon particle size distribution, for a barium sulphate precipitation reaction. He argues that mixing influences all three processes involved in precipitation from a homogeneous solution. These processes are the introduction of the reaction molecules causing supersaturation and nucleation, the transport of the nuclei throughout the system and the introduction of nuclei to new regions of supersaturation. He demonstrated that a feed position located under the impeller, produced a particle half the size of that grown when the feed is located directly in the turbine discharge. Positioning of the feed at the solution surface produced an intermediate size particle with a wider size distribution.

Bowen (1986) reported that for radial turbines, the best point of feed entry for rapid mixing would be in the shear zone (ie on or above the turbine).

For this study, the position of highest shear and mixing, was determined experimentally using a dye (see section 7.1). The feed position selected for all experimentation was located just above the turbine blades, as this produced the most rapid dispersion of material.
5.3 STANDARD PRECIPITATION METHOD

The standard method for the precipitation of iron oxyhydroxides was as follows. A 60 % w/w iron (III) chloride solution was added to 2 l of deionised water to make 0.1 mol dm$^{-3}$ iron and the pH lowered to pH 2 using concentrated hydrochloric acid. The reactor was stirred by a 6 blade Rushton turbine, rotating at 250 rpm, powered by a Caframo Wiarton CSA RZR1-64 motor. The sample was heated to the desired temperature using a water jacket, thermostatically controlled within 2°C.

The solution pH was monitored by a Radiometer PHM29 type meter using an Activon BJ412 glass electrode. The pH was slowly elevated by pumping 5 mol dm$^{-3}$ sodium hydroxide solution using a Cole-Palmer peristaltic pump at a rate of 10 ml per minute into the reactor, emerging just above the turbine blades, at a position of maximum turbulence.

The elevation of pH occurred in two steps. The first elevation was to a set neutralisation point about pH 3 and the solution allowed to age for three hours, prior to the complete caustic addition to a pH of 9.5. The second step allowed the precipitates to mature in solution, with the overall experiment being conducted over a period of 24 hours.
At the completion of the experiment, 200 ml samples of slurry were syphoned from the position of maximum turbulence above the turbine blades for settling experiments. The remaining slurry was filtered through a Whatman # 50 filter paper under vacuum and washed with deionised water. The filtrate was tested for the presence of iron (III) or iron (II) using potassium thiocyanate or 1,10-phenanthroline monohydrate respectively, to ensure complete precipitation had taken place.

The washed iron oxyhydroxide precipitate was oven dried at 60°C. Dry filter cakes were then broken to a powder using a mortar and pestle for further analysis. The sample from each experiment was assigned an arbitrary identity number.

5.4 SETTLING RATE

The 200 ml sample of slurry was syphoned from the turbulent mixing zone, then placed into a 200 ml measuring cylinder. The height of the interface between the supernatant and settling solids (mud-line) was recorded as a function of time. The settling rate was estimated from the initial linear section of the plot of mud-line against time (see section 4.7). Due to the slow intrinsic settling ability of the precipitates, the settling rate has been expressed in this work in the non-SI units of metres per hour (m h⁻¹).
5.5 X-RAY DIFFRACTION

Standard XRD measurements were conducted at a medium scan rate on a Siemens M34007 Diffractometer with an cobalt target, a Philips detector and a Philips PM8203 recorder. Conditions were 30 mA, 35 kV, 2 Θ min\(^{-1}\) and a full scale deflection of 10 000 counts s\(^{-1}\).

High resolution XRD were conducted using a Philips PW 1820 Goniometer, a PW 1830 generator, a cobalt fine focus tube and associated software incorporating TADD by JCPDS.

5.6 MöSSBAUER SPECTROSCOPY

Approximately 100 mg of iron oxide or oxyhydroxide, was ground to a fine powder in a boron carbide mortar and pestle. The iron concentration was reduced by mixing the powder with about 200 mg of sucrose powder. This mixture was evenly spread in a 25 mm diameter circular nylon sample holder for analysis.

Mössbauer spectra were recorded in constant acceleration mode, with a symmetric double ramp waveform and were subsequently folded to eliminate the parabolic background associated with the variation in solid angle between the source and absorber during the scans. The folded spectra consist of 250 channels with about 4x10\(^6\) counts per channel. An approximately 20 mCi \(^{57}\)Co in rhodium source was used.
The velocity scale was calibrated with reference to the spectrum of an iron foil at room temperature, the centre of the six line pattern being taken as zero velocity. All spectra were recorded with samples at room temperature.

Each Mossbauer spectrum was fitted with a doublet and/or a sextet of Lorentzian absorption peaks using a sum of squares minimisation routine. During the fitting procedure the areas and widths of each line of the doublet components were constrained to be equal.

For the sextet components the area ratio of the outer to middle to inner pair of lines was constrained to be 3:2:1. Spectra that exhibited a sextet of peaks with asymmetric line broadening were fitted with a model proposed by Bocquet et al. (1992). In this model, magnetic ordering occurs in clusters which have moments that slowly relax thus producing a Boltzmann distribution in the z component of the magnetisation. Values of the chemical isomer shift, the quadrupole splitting, magnetic hyperfine field splitting, line width and spectral area of each component were allowed to vary freely during the fitting procedure.
5.7 DISSOLUTION TECHNIQUES

Dissolution extraction techniques were performed at ambient temperatures and are described below.

Optimum conditions for the extraction of the synthetic samples were determined with the use of transmission electron microscopy. Parameters such as reagent concentration, sample to solution ratios and extraction time were varied with the resultant filtrate being viewed under TEM. Operational parameters were selected within ranges where visual evidence suggested that the gelatinous material had dissolved but the crystalline phases had not yet been attacked. The extraction conditions settled upon are detailed below.

Samples and extractant were agitated on a bottle roller, then portions of the extract were centrifuged prior to dilution and analysis of iron by atomic absorption spectroscopy (AAS). The AAS was a Scientific Equipment Pty Ltd model GBC 901, using an iron Photon Australia hollow cathode lamp. A lean air-acetylene mixture was used with a lamp current of 7 amp, a slit width of 0.2 μm at a wave length of 248.3 μm.
5.7.1 ACID AMMONIUM OXALATE (AAO)

The 100 mg samples were extracted for three hours in the dark with 300 ml of reagent containing 0.2 mol dm$^{-3}$ ammonium oxalate / oxalic acid buffered to pH 3.0. The method was adapted from that reported by Parfitt and Childs (1988).

5.7.2 DITHIONITE CITRATE BICARBONATE (DCB)

The 100 mg samples were extracted in 100 ml of reagent (1 g sodium dithionite, in 50 ml of 22 wt% sodium citrate, buffered to pH 7.3 with sodium bicarbonate) for 16 hours (Mehra and Jackson 1960, Parfitt and Childs 1988).

5.7.3 HYDROXYLAMINE (HA)

Samples of 100 mg were extracted with 100 ml of hydroxylamine hydrochloride - hydrochloric acid reagent (0.25 mol dm$^{-3}$ NH$_2$OH.HCl - 0.25 mol dm$^{-3}$ HCl) for three hours (Ross et al. 1985).

5.7.4 TOTAL IRON

Samples of 100 mg were dissolved with 20 ml of concentrated hydrochloric acid then made to 1000 ml in volume.
5.8 SURFACE AREA

Surface areas were analysed on a Quantachrome Autosorb-1 multipoint BET surface area analyser, using nitrogen as the adsorbing gas.

5.9 TRANSMISSION ELECTRON MICROSCOPY

Transmission electron micrographs were taken on a Philips 301 electron microscope while operating at 80 KV. Samples were suspended upon a polymer coated copper grid.

5.10 THERMAL GRAVIMETRY

Thermal analysis (TG) was conducted on a Perkin Elmer TGS-2 Thermogravimetric Analyser, with a FDC-1 first derivative computer. A Perkin Elmer heat controller, gas selector, TGS-2 balance control and System 4 thermal analysis microprocessor controller, were linked to a Rikadenki RO2 chart recorder. A temperature ramp of 20 K min\(^{-1}\) was used under a dry argon atmosphere.
CHAPTER 6
EVALUATION OF CHARACTERISATION TECHNIQUES

The investigation of precipitation and formation processes for the various iron oxides and oxyhydroxides, requires an understanding of the nature of the material being formed. In turn, there needs to be a comprehension of the relative abilities and reliability of the characterisation techniques and their interpretation.

To assist this investigation into the precipitation and dewatering of iron oxides and oxyhydroxides, a comprehensive assessment has been made of the relative merit of instrumental and chemical characterisation techniques. This involved the use of 14 samples reflecting the amorphous to crystalline continuum, to highlight the advantages and disadvantages of each technique. The samples were precipitated by varying formation conditions such as solution temperature and rate of hydrolysis (see Chapter 7).

The characterisation techniques used to assess the samples were XRD, Mössbauer spectroscopy, chemical dissolution, surface area, transmission electron microscopy (TEM), thermogravimetry (TG) and settling rate. The application of each technique to the 14 samples is considered below, including a discussion and comparison of results between the techniques.
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6.1 X-RAY DIFFRACTION

X-ray diffraction identified crystalline components to be present in six of the fourteen samples as shown in Table 6.1. These were: Sample 2 (goethite), sample 3 (goethite and hematite), sample 4 (goethite and hematite), sample 10 (goethite), sample 11 (magnetite or maghemite) and sample 12 (magnetite or maghemite). The spectra from some of these samples are shown in Figure 6.1.

The spectra for samples 3 and 10 were quite weak indicating relatively small proportions. Samples 11 and 12 gave spectra consistent with magnetite or maghemite. The broad peaks make it difficult to distinguish between these two oxides and reflects a rather small particle size. All other samples were determined to be 4 to 6 XRD line ferrihydrite. Other crystalline phases present were salts from the precipitation process.

An important finding was that instrumentation can influence the interpretation of data. In the case of XRD, the majority of samples precipitated during this investigation have been shown to be X-ray amorphous by a Siemens M34007 Diffractometer. Yet the same samples tested on a Philips PW 1820 Goniometer revealed 4-6 line ferrihydrite. The explanation for these differences was not pursued.
### TABLE 6.1: SAMPLE CHARACTERISATION TECHNIQUES

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<thead>
<tr>
<th>No</th>
<th>XRD</th>
<th>TEM Crystals</th>
<th>SA m² g⁻¹</th>
<th>TGA % Wt LOSS</th>
<th>SED VOL dm³</th>
<th>SET RATE m h⁻¹</th>
<th>Mössbauer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ferricydrite</td>
<td>nil</td>
<td>205</td>
<td>10% 20-270°C</td>
<td>0.070</td>
<td>0.05</td>
<td>100% Ferricydrite</td>
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<td>2</td>
<td>Goethite</td>
<td>needles 0.2µm</td>
<td>60</td>
<td>5% 20-95°C 10% 110-270°C</td>
<td>0.025</td>
<td>0.20</td>
<td>3% Ferricydrite 97% Goethite</td>
</tr>
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<td>Goethite</td>
<td>needles 0.03µm</td>
<td>200</td>
<td>19% 20-310°C</td>
<td>0.045</td>
<td>0.17</td>
<td>78% Ferricydrite 6% Goethite 16% Hematite</td>
</tr>
<tr>
<td>4</td>
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<td>needles 0.2µm plates 0.2µm</td>
<td>85</td>
<td>6% 20-130°C 6% 130-305°C</td>
<td>0.025</td>
<td>1.20</td>
<td>31% Ferricydrite 32% Goethite 37% Hematite</td>
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<td>0.07</td>
<td>100% Ferricydrite</td>
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</tr>
<tr>
<td>8</td>
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<td>200</td>
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</tr>
<tr>
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<tr>
<td>11</td>
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<td>40</td>
<td>3% 20-200°C</td>
<td>0.020</td>
<td>1.43</td>
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<td>Maghemite or Magnetite</td>
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</table>
Figure 6.1A. XRD of sample 1, ferrihydrite.

Figure 6.1B. XRD of sample 2, goethite.
Figure 6.1C. XRD of sample 3, hematite, goethite and ferrihydrite.

Figure 6.1D. XRD of sample 11, magnetite or maghemite.
6.2 MöSSBAUER SPECTROSCOPY

Mössbauer Spectroscopy is a principle technique for the characterisation of iron oxyhydroxides. This is due to many of the iron oxides and oxyhydroxides having different and distinctive Mössbauer spectra at room temperature.

However below a particle size of 20 nm, the various minerals lose their magnetic-hyperfine-field-splitting sextet of peaks due to superparamagnetic behaviour. The resulting single quadrupole-splitting doublet is more difficult to resolve, as the range of the spectral differentiation for each mineral is less than that for spectra with magnetic-hyperfine-field-splitting. For example, it can be difficult to resolve ultra fine (<20 nm) goethite and ferrihydrite at ambient temperature. Often these difficulties can be resolved by measuring the spectra at liquid nitrogen or liquid helium temperatures. While being effective in the separation of the iron oxyhydroxide forms, the analysis time is greatly extended and the cost increases accordingly.

Sample identification and spectral area (representative of the relative oxyhydroxide proportions) are listed in Table 6.1, while the various spectral parameters are listed in Table 6.2. Examples of typical Mössbauer spectra (samples 1, 2, 3, 4 and 11) are shown in Figure 6.2. Samples 2, 3, 4, and 10 were determined to contain crystalline goethite, while samples 3 and 4 also contained crystalline hematite. All samples contained ferrihydrite except 11 and 12 which were solely maghemite.
<table>
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<tbody>
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</tr>
<tr>
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</tr>
<tr>
<td></td>
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<tr>
<td></td>
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<td>Ferrilydrite</td>
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<tr>
<td></td>
<td>Maghemite</td>
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</tr>
<tr>
<td></td>
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<tr>
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<tr>
<td></td>
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<tr>
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<tr>
<td></td>
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<tr>
<td></td>
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</tr>
<tr>
<td>10</td>
<td>Ferrilydrite</td>
<td>0.33</td>
</tr>
</tbody>
</table>
Footnotes to Table 6.2:

(a) Mössbauer spectral parameters derived from fitting Lorentzian absorption peaks to the data with a sum of squares minimisation routine. For spectra with symmetrically broadened lines, the data was fitted using the model of slowly relaxing clusters (Bocquet 1992). Spectra were measured at room temperature.

(b) $\delta$ is the chemical shift (mm s$^{-1}$)

(c) $\Delta E_Q$ is the quadrupole splitting, or the quadrupole perturbation on the magnetic hyperfine field splitting (mm s$^{-1}$).

(d) $\Gamma$ is the linewidth (mm s$^{-1}$) (for the outer lines in the case of a sextet)

(e) %A is the percentage spectral area for each component.

(f) $B_{hf}$ is the magnetic hyperfine field splitting (T)

(g) Errors are at least $\pm 0.02$ mm s$^{-1}$ for $\delta$, $\pm 0.03$ mm s$^{-1}$ for $\Delta E_Q$, $\pm 0.5$T for $B_{hf}$, $\pm 0.02$ mm s$^{-1}$ for $\Gamma$ and $\pm 1$ for %A. Errors will tend to be larger for components with smaller values of %A and where significant overlapping of peaks occurs.

(h) The assignments of the different mineral forms to each signal are based partly on the spectral parameters and partly on evidence from XRD and TEM measurements.
Figure 6.2. Mossbauer spectra of (A) sample 1 ferrihydrite, (B) sample 2 goethite and ferrihydrite, (C) sample 3 hematite, goethite and ferrihydrite, (D) sample 4 hematite, goethite and ferrihydrite, (E) maghemite.
6.3 DISSOLUTION TECHNIQUES

Chemical dissolution techniques have been proposed as a method for determining the proportion of ferrihydrite present in an iron oxyhydroxide sample (see Section 4.3). Mössbauer spectroscopy is the only reliable method for the accurate determination of the ferrihydrite in each sample, so this data was used to evaluate the reliability of the chemical dissolution techniques.

6.3.1 THE ACID AMMONIUM OXALATE REAGENT

It has been suggested that Acid Ammonium Oxalate (AAO) primarily extracts short order iron oxyhydroxides such as ferrihydrite and can be used as a direct estimate (McKeague and Day 1966). Others suggest that ferrihydrite is underestimated by the AAO technique and require the AAO figure to be multiplied by 1.7 to estimate the true ferrihydrite content (Parfitt and Childs 1988, Parfitt 1989). These claims were investigated and are discussed below.

Results from the chemical dissolution of iron using AAO are given in Table 6.3. It was found that AAO extracted 80 to 100% of the iron determined to be ferrihydrite by Mössbauer spectroscopy, for most samples listed in Table 6.3. These results indicate the suggestion of determining ferrihydrite by multiplying the AAO figure by 1.7, clearly to be in error.
TABLE 6.3: ESTIMATION OF FERRIHYDRITE BY CHEMICAL DISSOLUTION

<table>
<thead>
<tr>
<th>Exp N</th>
<th>AAO % of Fe</th>
<th>HA % of Fe</th>
<th>DCB % of Fe</th>
<th>Mössbauer % of Fe</th>
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<td>1</td>
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<td>14</td>
<td>76</td>
<td>66</td>
<td>34</td>
<td>100</td>
</tr>
</tbody>
</table>

KEY:

- AAO % of Fe: The percentage of iron that was extracted by acid ammonium oxalate and hence believed to be in the ferrihydrite form.
- HA % of Fe: The percentage of iron that was extracted by hydroxylamine and hence believed to be in the ferrihydrite form.
- DCB % of Fe: The percentage of iron that was extracted by dithionite citrate bicarbonate and hence believed to be in the ferrihydrite form.
- Mössbauer % of Fe: The percentage of iron that was determined to be ferrihydrite by Mössbauer spectroscopy.
The AAO data also indicated that while most chemical extractions compared favourably to the Mössbauer spectroscopic data, some were clearly understated.

This suggested that AAO had difficulty extracting well ordered ferrihydrite as determined by low Mössbauer quadrupole splitting (<0.7 mm s⁻¹) or high resolution XRD (4 or more peaks). At the same time, AAO completely extracted crystalline maghemite.

While it is expected that AAO would attack maghemite (Borregaard 1982), the inability to extract iron from the well ordered form of ferrihydrite cannot be explained by present extraction theories. Hence while AAO extractions give a reasonable approximation for ferrihydrite, it is not an authoritative technique.

6.3.2 THE DITHIONITE CITRATE BICARBONATE REAGENT

The Dithionite Citrate Bicarbonate (DCB) extraction technique (Deb 1950) was suggested as a method of estimating the total iron present in soils. Yet results tabulated in Table 6.3 show that it did not extract all of the iron, even from samples known to be ferrihydrite.
It has been suggested that several extractions are required for complete dissolution (Parfitt and Childs 1988). However McKeague and Day (1966) state that several DCB extractions did not remove all crystalline iron from their samples and suggest that others who have been able to extract all the iron must have ground their sample extremely fine. The fine particle size explanation does not hold for these results, as most samples had a very small particle size (see Section 6.5).

Taylor and Schwertmann (1974) report that maghemite was not susceptible to DCB attack, supporting the results for samples 11 and 12 (Table 6.3).

In most samples, the AAO reagent extracted higher quantities of iron than did the DCB. Clearly not all is understood about the dissolution mechanisms of these reagents.

6.3.3 THE HYDROXYLAMINE REAGENT

The Hydroxylamine (HA) extraction data listed in Table 6.3 has highlighted several points of interest. Firstly there is a general correlation between HA and AAO extractions, but there is also a high degree of individual point variation. Such variation has been dismissed in the past due to the overall magnitude of the differences being small (Lee et al. 1989). However, in this case up to a 20% difference in extractions have been found.
Secondly HA gave both higher and lower extractions for iron than AAO. This is consistent with the work of Ross et al. (1985) and suggests that the work of Lee et al. (1989), which showed most extractions to be lower than AAO, was dominated by the presence of magnetite.

In this study, the HA reagent did not appreciably dissolve the micro-crystalline maghemite, suggesting it be used in place of AAO when magnetite or maghemite are present.

Finally the HA extractions have also yielded results higher than the DCB reagent. Clearly the DCB technique appears to have problems and should be used with caution.

6.3.4 DISCUSSION

The results shown in Table 6.3 highlight the inconsistency and dangers involved with using dissolution techniques without comparison to other techniques, especially Mössbauer spectroscopy.

While extraction techniques generally follow the trend observed by Mössbauer spectroscopy, exceptions occur. For example, characterisation techniques determined sample 1 to be 4-6 line ferrihydrite. Mössbauer spectroscopy indicated this sample to be particularly well ordered ferrihydrite having quadrupole splitting of 0.65 mm s\(^{-1}\), which is at the lower end of the ferrihydrite range. Even being well ordered, this sample should have been easily extracted
for iron. However quite a varied analysis was found. Both AAO and HA failed
to extract any appreciable ferrihydrate from sample 1, while DCB was able to
extract the iron without any difficulties.

In contrast DCB failed to extract appreciable quantities of iron from samples 13
and 14 (both ferrihydrate) while both AAO and HA achieved a reasonable
extraction.

While dissolution techniques appear ineffective as a quantitative determination
for the forms of iron, they are still very useful for qualitative comparisons. This
is in agreement with Schwertmann (1973) who explains that all dissolution
methods are largely empirical because the X-ray amorphous and crystalline states
represent extremes of a continuum. No technique will perfectly cut the continuum
at any particular point, yielding a quantitative answer.

6.4 SURFACE AREA

The specific surface area (BET method) of the samples are tabulated in Table 6.1
above. The technique was found to be complicated by the adsorbed water
associated with ferrihydrate. The inability to heat the samples above 80°C to
prevent thermal decomposition, resulted in out-gassing of the instrument taking
up to 24 hours. Results show that the surface area for samples determined as
ferrihydrate (using Mössbauer spectroscopy), ranged from 120 to 200 m² g⁻¹. This
range could initially be interpreted as an indication of crystallinity, however no
trend has been substantiated.
Ferrihydrite has been reported with a surface area as low as 122 m² g⁻¹ by Stanjek and Weidler (1992) and as high as 328 m² g⁻¹ by Borggaard (1991). Typically, ferrihydrite has been reported with a surface area of 200 m² g⁻¹ (Schwertmann and Cornell 1991). Hence if an iron oxyhydroxide sample had a surface area of 200 m² g⁻¹, then it is probable the sample was ferrihydrite. Likewise if a sample of iron oxyhydroxide had a surface area of 20 m² g⁻¹, then it was likely to be highly crystalline. For example the surface area of goethite ranges from 20 to 60 m² g⁻¹ (Schwertmann and Cornell 1991).

The problems become apparent between these extremities. For example, sample 2 had a surface area of 60 m² g⁻¹ which is consistent with goethite of small particle size (Koch and Moller 1987). This result suggests that the proportion of ferrihydrite present is quite small if any is present at all. The goethite could be of small particle size contributing entirely to the total surface area, or the particle size could be large with a small proportion of the high surface area ferrihydrite present.

The surface area of sample 4 was 86 m² g⁻¹, which is consistent with well crystalline hematite (Schwertmann and Cornell 1991). However this value could also represent very fine goethite, or a combination of goethite hematite and ferrihydrite. The measured value being in the expected range of hematite is entirely coincidental and in no way determines the proportion or identity of any iron oxides and oxyhydroxides present.
6.5 TRANSMISSION ELECTRON MICROSCOPY

Transmission Electron Microscopy (TEM) has proven invaluable for the identification of crystalline iron oxyhydroxides and determining the crystal particle size. The technique is relatively fast in operation, with several samples being processed within an hour.

Results given in Table 6.1 above, have proven very helpful in determining differences in crystallinity between samples. For example, samples 3 and 4 were shown to differ in crystal size. In sample 3, goethite consisted of 0.01 μm needles (Figure 6.3B), whereas in sample 4 the goethite consisted of 0.2 μm needles (Figure 6.3C). Hexagonal plates of hematite 0.2 μm in diameter, were also identified in sample 4 (Figure 6.3C).

The gelatinous material observed as a dark non-uniform shadow in Figure 6.3B (sample 3) was ferrihydrite. Figure 6.3D shows the crystals present in sample 11 with no indication of ferrihydrite being present.

This ability to identify the presence or absence of ferrihydrite is very important, as ferrihydrite has a large bearing upon other characterisation techniques such as surface area, TG and settling rate. Knowledge of the presence of ferrihydrite could alter the interpretation of such data.
Figure 6.3. TEM photographs of (A) sample 2 goethite needles and gelatinous ferrihydrite, (B) sample 3 fine goethite needles and ferrihydrite, (C) sample 4 Hexagonal hematite platelets, goethite needles and gelatinous ferrihydrite, (D) sample 11 acicular maghemite. BAR = 0.1 μm.
The results given in Table 6.1 were taken from samples of pure iron oxides and oxyhydroxides, hence the identification of phases is relatively simple. However, Cornell and Giovanoli (1987a, 1987b, 1988b) have shown that the incorporation of impurities results in the formation a wide variety of shapes and malformed crystals making identification difficult. Hence care should be taken to confirm results using another characterisation technique.

Associated with the power of using a technique that magnifies the subject in excess of 100 000 times, comes the problem of representation. Schwertmann and Cornell (1991) have reported that over 600 individual particles must be measured to gain an accurate particle size distribution.

6.6 THERMOGRAVIMETRY

Thermogravimetry (TG) was able to distinguish between the relatively pure iron oxides and oxyhydroxides, but had limited success with mixed products. Results are listed in Table 6.1 and are discussed below.

Most samples (e.g. sample 1) gave a one step weight loss between ambient and 300 °C (Figure 6.4A). This is consistent with the range of crystallinity and site hindrances expected to be found in an amorphous polymeric substance like ferrihydrite (Foldvari et al., 1988).
Figure 6.4. Thermogravimetry. (A) sample 1 ferrihydrite, (B) sample 2 goethite and ferrihydrite, (C) sample 4 hematite, goethite and ferrihydrite.
The TG of sample 2 (Figure 6.4B) gave a two step weight loss between ambient and 100 °C, then between 200 and 290 °C, consistent with goethite as reported by Schwertmann et al. (1985).

A two step weight loss (ambient to 130 °C, 220 to 310 °C) was also observed with sample 4 (Figure 6.4C). However, this was not as well defined reflecting a combination of iron oxyhydroxides.

6.7 SETTLING RATE AND SEDIMENT VOLUME

The initial linear settling rate for samples 1 to 14 are listed in Table 6.1 above. While the initial linear settling rate was unable to differentiate between the iron oxide and oxyhydroxide forms, it proved invaluable in determining subtle changes in crystallinity and particle size.

The precipitates formed in samples 4, 11 and 12 had settling rates about 1 m h\(^{-1}\) while most others usually had settling rates around 0.05 m h\(^{-1}\). Such variation in the settling rate is of enormous benefit, indicating substantial differences in the character of iron oxide and oxyhydroxide samples. The precise nature of these differences can only be determined through other analytical techniques.

The equilibrium sediment volume also gives an indication of the nature of the iron oxyhydroxides. The sediment volumes are listed in Table 6.1 above and like the settling rate, show large differences between samples.
6.8 COMPARISON AND DISCUSSION

Results from Mössbauer spectroscopy were treated as authoritative and the data from each other technique then sequentially compared to it. Comparisons were made on a sample by sample basis.

Mössbauer spectroscopy has determined sample 1 to be 100% ferrihydrite with quadrupole splitting of 0.65 mm s⁻¹. This indicated that the ferrihydrite is of exceptional good order. This was confirmed by high resolution XRD, which identified the sample to be 6 XRD line ferrihydrite (see Figure 6.1). The surface area, TEM, TG, settling rate and sediment volumes were all consistent with the 100% ferrihydrite determination.

Mössbauer spectroscopy indicated sample 2 to contain about 97% goethite and 3% of either ferrihydrite or microcrystalline goethite (Table 6.1), consistent with XRD. The surface area of 60 m² g⁻¹ and the two step TG (Figure 6.4a) were consistent with this determination. The chemical dissolution techniques gave the ferrihydrite estimation of 6% for AAO and 2% for HA, again consistent with the Mössbauer data. The settling rate of 0.26 m h⁻¹ and sediment volume of 0.025 dm³ indicated a degree of crystallinity also consistent with the Mössbauer data. The TEM of sample 2 (Figure 6.3a) indicated large quantities of a gelatinous phase typical of ferrihydrite. This is inconsistent with all the other characterisation techniques, suggesting that visual estimation of the proportion of ferrihydrite by TEM is unreliable.
The Mössbauer spectra of sample 3 indicated 8% goethite, 16% hematite and 78% ferrihydrite. This separation and determination of phase composition was consistent with XRD, surface area, TEM, TG settling rates and sediment volume data.

The Mössbauer spectra of sample 4 yielded 32% goethite, 37% hematite and 31% ferrihydrite, again consistent with all other characterisation techniques.

Sample 10 was shown by Mössbauer spectroscopy to contain 10% goethite with the balance being ferrihydrite. This was consistent with the weak goethite signal observed in the XRD analysis. Surface area, TEM and TG were unable to detect the change in crystallinity when compared to other samples of pure ferrihydrite, while settling rate and the sediment volume were marginally different.

The Mössbauer spectra of samples 11 and 12 (see Figure 6.2e) both gave a single sextet of peaks indicating maghemite rather than the characteristic double sextet associated with magnetite. The absence of a central doublet also suggests very little ferrihydrite is present, consistent with the surface area measurements and TEM observations. XRD was unable to differentiate between magnetite and maghemite for these two samples. The settling rate and sediment volume of these samples was consistent with the TEM and Mössbauer data, indicating a very high degree of crystallinity.
Mössbauer spectroscopy and XRD indicated all other samples to be 100% ferrihydrite, consistent with surface area, TEM and TG. The Mössbauer spectra of these samples were noted to have low quadrupole splitting in the range of 0.65 to 0.70 mm s\(^{-1}\), indicating a relatively high degree of order as proposed by Murad and Johnston (1987). They state that 6-XRD line ferrihydrite has a quadrupole splitting of 0.70 mm s\(^{-1}\) or less, while 2-XRD line ferrihydrite has a quadrupole splitting up to 0.90 mm s\(^{-1}\). The slow settling rates and the high sediment volumes indicate poor dewatering ability, consistent with what is known about ferrihydrite.

6.9 CONCLUSIONS

XRD has proven reliable in identification of iron oxyhydroxides and gives an indication of the crystallinity. It is also a rapid and inexpensive technique allowing it to be used for all samples.

Mössbauer spectroscopy is the authoritative technique for the characterisation of iron oxides and oxyhydroxides. However the time and cost constraints prevent its use for all but a select few samples.

Chemical dissolution techniques while inexpensive and much faster than Mössbauer spectroscopy, are not as reliable. More investigation is required before these techniques can be considered quantitative. However qualitative information is easily obtained.
The inability to differentiate mixed samples prevents surface area measurements and thermogravimetry being used as a primary or first up characterisation technique. However, these methods are beneficial supporting the findings of other instrumental and chemical techniques.

Transmission Electron Microscopy (TEM) has proven invaluable for the identification of crystalline iron oxyhydroxides and can give an indication of particle size. However statistical problems cause accurate particle distributions to be time consuming, while the gelatinous nature of ferrihydrite prevents its estimation.

Finally, the settling rate and sediment volume are rapid and simple techniques. They have proven to be reliable for distinguishing between closely related samples and their data could prove valuable to industrial applications.

The techniques of choice for blanket application as characterisation techniques for iron oxides and oxyhydroxides are XRD and settling rate / sediment volume.
CHAPTER 7
PRECIPITATION OF IRON (III) OXIDES AND OXYHYDROXIDES
WITH CAUSTIC (NaOH)

Current industrial practice for the precipitation of metal hydroxides is to elevate
the pH of solution using one of three basic techniques. These techniques are:

i) Use a solution of caustic.

ii) Use a slurry of slaked lime or magnesia.

iii) Use direct addition of solid lime or magnesia.

These three options vary in their chemical complexity. For example, the
precipitation of iron oxides and oxyhydroxides from a chloride media using
slowly dissolving solid particles of alkali, would involve the following processes.

i) The hydration process of the solid particle.

ii) The dissolution and dissociation of ions.

iii) The initial hydrolysis of iron (III) monomers.

iv) The formation of short chain polymeric species.

v) The precipitation of iron oxides and oxyhydroxides.

The use of slurried alkali species would eliminate the first of these processes,
while soluble caustic would eliminate the first two. In addition, a sulphate
medium would precipitate gypsum (CaSO₄·2H₂O) with the use of lime, whereas
Na₂SO₄ and MgSO₄ are soluble.
This chapter deals with the simplest system, the use of a soluble caustic (NaOH) solution. The alternatives are dealt with in Chapter 8 (lime) and Chapter 9 (magnesia).

An iron (III) chloride solution precipitated with sodium hydroxide was used to represent a simple system. This enabled the investigation of some of the variables which may influence the precipitation process, such as rate of precipitation (including mixing), temperature and the influence of other anions, cations and ligands in solution.

7.1 MIXING CRITERIA

Since the speciation and precipitation of iron (III) is dependant upon the solution pH, experiments were conducted to investigate whether the initial mixing of the caustic played a role in heterogeneous precipitation and the effect of this on the overall product. The term "heterogeneous precipitation" is used here to refer to the localised addition of concentrated caustic leading to regions of high pH. This would result in different intermediate iron species being formed to those that would result had the caustic been added evenly throughout the system; that is "homogeneous precipitation".

The experiment called for comparison of the products formed from "poor" and "good" mixing. To facilitate this experiment the location of an alkali dispensing point in the reactor needed to be determined which enabled "good" mixing.
7.1.1 DETERMINATION OF FLOW CHARACTERISTICS WITH MIXING

Observation of the flow characteristics of a solution under turbine influence was followed by using purple potassium permanganate solution as a tracer. The tracer was added to the reaction vessel at several locations under different agitation conditions (high and low) and the mixing efficiency was visually assessed.

The turbine speeds were 150 rpm and 250 rpm. The location of injection points and subsequent flow patterns are shown in Figures 7.1, 7.2 & 7.3 and are described below.

The first injection point for the tracer was on top of the solution surface. The resulting flow pattern is shown in Figure 7.1. As the tracer was added to the reaction chamber under the slower mixing conditions, the vast majority formed a concentrated cone descending towards the turbine centre. This was then spun out and dispersed against the tank wall and baffles. A smaller high concentration zone was observed under faster mixing conditions, with more material initially being buffeted and dispersed by the tank baffles.

The observed flow patterns suggested that the addition of caustic at this point would form a high concentration gradient. It was considered that this would lead to irreversible heterogeneous precipitation in this region of the solution.
Figure 7.1.
Dispersal of dye within reactor vessel. Dye added at solution - air interface.
The second injection point was located on the bottom of the turbine disc. The tracer was pumped down the turbine shaft, mixing with the solution directly below the turbine. The observed flow pattern is shown in Figure 7.2 and is described below. When the tracer was injected below the turbine, a cone was formed with its base on the bottom of the turbine disc and the apex pointing down. This cone was much smaller and appeared less defined than that observed at the first injection point. The effect of turbine speed was minimal with the cone being broader and more concentrated at the lower speed. The overall mixing was much faster with the tracer finally being thrown against the tank wall, pushed upward and dispersing against the baffles. This injection point was far superior to injection at the top of the solution.

The third injection point was directly above the turbine blades. This position caused maximum dispersal and mixing within the shortest time. The flow pattern is shown in Figure 7.3 and discussed below. As soon as the tracer was released it was thrashed by the action of the turbine. Some of the tracer was buffeted up and down into rapidly dispersing turbulent eddies. The majority was thrown against the tank wall and baffles where it was dispersed rapidly through the bulk solution. A small amount of tracer was observed flowing up the tank wall where it rapidly collapsed towards the turbine shaft being dispersed. The effect of turbine speed was minimal under these conditions. It was concluded that a caustic solution would be best introduced into the reaction chamber by injection just above the spinning turbine blades.
Figure 7.2.
Dispersal of dye within reactor vessel. Dye added by injection through shaft at base of turbine.
Figure 7.3.
Dispersal of dye within reactor vessel. Dye added by injection just above turbine blades.
7.1.2 HETEROGENEOUS AND HOMOGENEOUS PRECIPITATION

The observations from the tracer experiments in Section 7.1.1, were used to facilitate heterogeneous and homogeneous precipitation. Sufficient caustic to raise the pH to 2.3 was introduced into an iron (III) chloride solution at two designated injection points. In one case, caustic was injected on top of the solution, while in the second case caustic was injected above the turbine blades. These first two experiments (Numbers 15 and 16) were otherwise treated identically as shown in Table 7.1 below. Caustic was added via a peristaltic pump in a standard two step process.

The two step process involved partial addition of the alkali, followed by a three hour intermediate aging step. Further alkali was then added for complete precipitation and to raise the pH to between 9 and 10. The slurry was then allowed to age for a total of 24 hours (see Section 5.3).

Upon initial mixing, both solutions (experiments 15 and 16) immediately turned red. This is believed to be due to the formation of the very short chain polymeric iron hydroxide, possibly even the iron dimer (Johnston and Lewis 1986).

The precipitates formed upon further addition of caustic were aged to 24 hours, then sampled and characterised. Results of the characterisation (Table 7.1), indicate the precipitates to be identical within experimental error.
As the red colloid is an indication of homogeneous precipitation, it was concluded that heterogeneous precipitation can be avoided by the slow addition of caustic by a peristaltic pump, or by injecting the caustic into a zone of high turbulence.

**TABLE 7.1: THE EFFECT OF CAUSTIC ADDITION LOCATION AND RATE UPON IRON (III) OXYHYDROXIDE CHARACTERISTICS**

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<tr>
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<td>2.2</td>
<td>2.2</td>
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<td>FINAL pH</td>
<td>8.1</td>
<td>8.3</td>
<td>9.5</td>
<td>9.6</td>
<td>9.6</td>
<td>10.2</td>
</tr>
<tr>
<td>pH AFTER 24 h⁻¹</td>
<td>7.4</td>
<td>7.8</td>
<td>9.1</td>
<td>9.3</td>
<td>9.0</td>
<td>10.0</td>
</tr>
<tr>
<td>COLOUR</td>
<td>red brown</td>
<td>red</td>
<td>red</td>
<td>red</td>
<td>red</td>
<td>red</td>
</tr>
<tr>
<td>SETTLE RATE m h⁻¹</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.05</td>
<td>0.03</td>
</tr>
<tr>
<td>XRD</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
</tr>
<tr>
<td>AAO</td>
<td>82 %</td>
<td>81 %</td>
<td>78 %</td>
<td>76 %</td>
<td>87 %</td>
<td>86 %</td>
</tr>
<tr>
<td>SURFACE AREA m²g⁻¹</td>
<td>140</td>
<td>170</td>
<td>120</td>
<td>150</td>
<td>140</td>
<td>120</td>
</tr>
<tr>
<td>TG</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
</tr>
<tr>
<td>MøSS-BAUER</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
<td>Ferrhydrite</td>
</tr>
</tbody>
</table>
To further investigate the matter, another two pairs of experiments were conducted (Numbers 13 and 17; 14 and 18) in which the caustic was added rapidly in a two step process. When the required amount of caustic was poured into the reaction chamber from a pipette on top of the solution surface (14 and 18), there was immediate formation of the brown-red heterogeneous precipitate which took hours to re-equilibrate and dissolve back to the red polymeric material. When the caustic was poured into the vessel above the turbine blades (experiments 13 and 17), only a small quantity of the heterogeneous precipitate formed, which was observed to rapidly dissolve.

The data shown in Table 7.1 demonstrates that the products of experiments 13 to 18 were ferrihydrite and identical within experimental error. All precipitates had slow settling rates, high surface areas and were poorly crystalline as indicated by the high chemical extraction values by the acid ammonium oxalate (AAO) method. It was concluded that the red polymeric material formed immediately from the well mixed solution and the red polymeric material eventually formed from the dissolution of the heterogeneous precipitate from the poorly mixed solution, are identical.

It was observed during these experiments that the higher the pH in the first step of neutralisation, the slower the dissolution of heterogeneous precipitate and hence formation of the red colloidal material.
Experiments 17 and 18 had 90 % of the caustic required for stoichiometric precipitation added in the first step which elevated the pH 3.1; whereas samples 13 and 14 received 50 % in the first step raising the pH to 2.2. The three hour intermediate aging period appears to be long enough to allow for reversal of the initial heterogeneous precipitation.

7.2 TEMPERATURE

It is well documented that temperature plays a large role in the product outcome from iron (III) precipitation (Christensen et al. 1980). At ambient temperature, iron (III) precipitation results in a gelatinous polymeric material which is slow to settle and difficult to filter. At high temperatures (80 °C), crystalline iron oxides and oxyhydroxides are produced.

To define the effect of temperature more quantitatively, identical experiments were carried out at 21 °C, 40 °C and 60 °C. Using a two step precipitation process, 75 % of the total caustic was added to the iron (III) chloride solution in the first step to raise the pH to 3, then the precipitates were allowed to age for a period of three hours. The rest of the caustic was added to complete precipitation and to raise the pH to about 9. In this case, the resulting precipitates varied in their physical and chemical characteristics with several points of interest.
Firstly, associated with the elevation of precipitation temperature was an increase in the product crystallinity and a change in the composition of the iron oxyhydroxide produced. Sample 19, precipitated at 21°C, consisted of ferrihydrite. Sample 10 (40°C) consisted of ferrihydrite and poorly crystalline goethite, while sample 20 (60°C) contained ferrihydrite, goethite and crystalline hematite. Broad XRD lines suggest crystalline phases are of small particle size.

Although the solution contained a chloride concentration of 0.27 mol dm⁻³, XRD did not detect the presence of akaganeite. Cornell and Giovanoli (1988a) reported that 0.5 mol dm⁻³ chloride, was required to promote the formation of akaganeite. Thus it appears that the concentration of chloride used here was below a limiting factor where akaganeite was not produced.

Surface area measurements (Table 7.2) suggested that all three samples were sub-micron particles. Yet the AAO dissolution data suggested that the 60 °C sample was substantially different to the other two. TEM was unable to identify crystalline phases in samples produced at 21 °C or 40 °C, but identified the presence of hematite in the sample produced at 60 °C, supporting the XRD and AAO data.

The settling rate was able to differentiate the samples quite distinctly, ranging from 0.02 to 0.17 m h⁻¹ (Figure 7.4). However the surface area for all samples was about 200 m² g⁻¹. This probably reflects differences in the aggregation of settling particles (i.e. their effective particle size distribution), even with each sample containing ferrihydrite.
Figure 7.4. Settling curve for samples 19 (20°C), 10 (40°C) and 20 (60°C). Sediment volume is plotted against time.
The settling rate method was simple, fast and reproducible. Therefore it was considered to be an effective method for detecting subtle differences between samples. The equilibrium sediment volume was found to be another useful parameter for discriminating between the samples, in this case ranging from 0.075 to 0.045 dm$^3$(Table 7.2).

The sediment volume when used in conjunction with the mass of iron oxyhydroxide can be used to calculate the sediment density. However because the precipitates differed in composition and degree of polymerisation, density calculations become speculative. For this reason, sediment volumes have been used throughout this thesis for comparative purposes.

**TABLE 7.2: EFFECT OF TEMPERATURE ON THE CHARACTERISTICS OF IRON (III) PRECIPITATES**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>TEMPERATURE °C</th>
<th>XRD</th>
<th>SURFACE AREA m$^2$g$^{-1}$</th>
<th>AAO % Fe EXTRACTED</th>
<th>SETTLING RATE m h$^{-1}$</th>
<th>SEDIMENT VOLUME dm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>21</td>
<td>Ferrihydrite</td>
<td>194 m$^2$g$^{-1}$</td>
<td>77 %</td>
<td>0.02</td>
<td>0.075</td>
</tr>
<tr>
<td>10</td>
<td>40</td>
<td>Ferrihydrite Goethite</td>
<td>199 m$^2$g$^{-1}$</td>
<td>74 %</td>
<td>0.11</td>
<td>0.050</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>Ferrihydrite Goethite Hematite</td>
<td>217 m$^2$g$^{-1}$</td>
<td>54 %</td>
<td>0.17</td>
<td>0.045</td>
</tr>
</tbody>
</table>
7.3 NEUTRALISATION, NUCLEATION AND PRECIPITATION

It has been reported that the formation of iron oxides and oxyhydroxides can be influenced by the rate of precipitation, the presence of an induction period and aging effects (Cornell et al. 1989). The formation process is governed by both kinetic and energetic principles. The rate of neutralisation can determine whether a kinetic or a thermodynamic favoured precipitate will be formed. Induction periods usually allow for nucleation of a crystalline seed upon which crystalline products can grow. Aging increases the crystallinity by further growth as well as by dissolution and reprecipitation processes. By manipulating a two step precipitation process, these factors can be investigated by varying the rate and extent of hydrolysis, as well as the duration of an intermediate aging period where aging and nucleation can take place.

7.3.1 MANIPULATION OF THE TWO STEP PRECIPITATION PROCESS

To study the effects of induction and nucleation, several experiments were conducted comparing a one step and a two step precipitation process. The two step process involved partial addition of the alkali to raise the pH to about 3, followed by a three hour intermediate aging step. Further alkali was then added for complete precipitation and to raise the pH to between 9 and 10. The slurry was then left to age for a further 21 hours. A single or one step process involved complete precipitation and elevation of pH without an intermediate aging step.
The aging step during the course of the precipitation process allowed for induction and nucleation of seed, facilitating observation of these events by characterising the precipitates.

The settling characteristics of the slurry have been shown to be a reliable and rapid method to assess the precipitation process. The settling rate was employed as the primary investigation technique, with other methods used to assist characterisation and promote a better understanding. To investigate the relative advantages between the one step and two step precipitation process, the best conditions for the two step process first needed to be established by varying the percentage of NaOH added in the first step and the aging time.

7.3.1.1 PERCENTAGE OF TOTAL ALKALI ADDED IN FIRST STEP

The first step of the two step process involved the partial hydrolysis of the iron (III) solution. This is reported as a percentage of the total alkali required for stoichiometric precipitation and to elevate the pH to above 9. For example, if it required 0.10 dm$^3$ of alkali to completely precipitate the iron and raise the pH to 9, then a "70 % first step" means that 70 % of the total alkali (i.e. 0.070 dm$^3$) was delivered in the first step of the process. The pH obtained as a function of the alkali delivered is given in Figure 7.5. For example, a 70 % NaOH addition in the first step would result in an intermediate aging period having a pH of about 3.0.
Figure 7.5. Solution pH plotted against % hydrolysis.
For these experiments, the percentage of alkali added in the first step was varied to determine its effect on the product crystallinity, as shown by the settling rate, surface area and the percentage of extractable iron using the AAO method (Table 7.3). Figure 7.6 is a plot of the sediment volume against time for samples 5 and 21, typical of ferrihydrite.

**TABLE 7.3: EFFECT OF PARTIAL NaOH ADDITION UPON IRON (III) PRECIPITATE CHARACTERISTICS**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>% ALKALI in 1st STEP</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm³</th>
<th>SURFACE AREA m² g⁻¹</th>
<th>% AAO EXTRACTED</th>
<th>TEMPERATURE °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>25</td>
<td>0.03</td>
<td>0.065</td>
<td>140</td>
<td>79</td>
<td>26</td>
</tr>
<tr>
<td>5</td>
<td>60</td>
<td>0.08</td>
<td>0.060</td>
<td>130</td>
<td>80</td>
<td>26</td>
</tr>
<tr>
<td>22</td>
<td>74</td>
<td>0.08</td>
<td>0.065</td>
<td>130</td>
<td>75</td>
<td>26</td>
</tr>
<tr>
<td>23</td>
<td>83</td>
<td>0.02</td>
<td>0.075</td>
<td>160</td>
<td>94</td>
<td>27</td>
</tr>
<tr>
<td>24</td>
<td>93</td>
<td>0.03</td>
<td>0.060</td>
<td>180</td>
<td>83</td>
<td>25</td>
</tr>
<tr>
<td>25</td>
<td>100</td>
<td>0.03</td>
<td>0.065</td>
<td>190</td>
<td>87</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>83</td>
<td>0.03</td>
<td>0.070</td>
<td>180</td>
<td>77</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>62</td>
<td>0.08</td>
<td>0.070</td>
<td>200</td>
<td>77</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>92</td>
<td>0.11</td>
<td>0.050</td>
<td>200</td>
<td>74</td>
<td>40</td>
</tr>
</tbody>
</table>

It is apparent from Table 7.3, that the surface area and AAO dissolution data do not show any substantiative trends. XRD determined all samples to be ferrihydrite, with the exception of sample 10, which contained some micro-crystalline goethite.
Figure 7.6. Settling curves for samples 5 and 21 showing the difference between agglomerated and non-agglomerated ferrihydrite. Sediment volume is plotted against time.
The settling rates were within the typical range observed for ferrihydrite, however the shape of the settling curves displayed significant differences. This indicated that while there are no differences in crystallinity, there may be differences in the surface charge of the iron (III) oxyhydroxide particles. The settling curve for sample 5 (Figure 7.6 above) suggested some agglomeration had taken place, when compared to sample 21. It is thought that the surface charge density is linked to the pH and amount of precipitate formed upon addition of the caustic during the second step. This is related to the level and degree of oxolation of short chain polymeric species present during the intermediate aging period. Agglomeration appears to be favoured when 60 % of the caustic is added in the first step.

When the caustic is added in the second step and the pH is raised from 3 to 9, localised pH gradients will exist. Since the point of zero charge for iron (III) oxides and oxyhydroxides is usually between pH 6.6 and 8.2 (Leja 1982), the possibility exists for both positively charged polymeric species in bulk solution and negatively charged oxolated polymer in the high pH regions to coexist for a short period of time. Charge balance would result in pseudo-chemical agglomeration resulting in larger particle sizes. At the final pH of 9, all particles eventually possess a negative charge.

The higher precipitation temperature of sample 10 is believed responsible for the formation of goethite, as reflected by the sediment volume of 0.050 dm$^3$. These results indicate that the temperature of precipitation is the predominant factor influencing the morphology of the iron oxyhydroxides.
7.3.1.2 DURATION OF THE INTERMEDIATE AGING STEP

A two step process was employed with 75% of the caustic added in the first step. The duration of the intermediate aging step was varied and the precipitates characterised to observe the effect of these parameters on the crystallinity of the final product. From the settling rates listed in Table 7.4, there appears to be an advantage using short aging times. This is attributed primarily to how the settling rate is calculated. Most samples commenced settling immediately, however the one and two hour aged samples (samples 26 and 27) had an induction period prior to settling. The settling rate is measured over the area of most rapid free fall and in the case of sample 26 shown below in Figure 7.7, the settling rate is not comparable to other systems.

The shape of the curve indicates some agglomeration and suggests that the surface properties of the product are different (See Section 4.6). This is likened to the mechanism discussed in Section 7.3.1.1, where the rate and level of caustic addition to a two step process also resulted in agglomerated samples. The same process is thought to occur when the samples are only aged for a short time between caustic additions. With a shorter aging period, the reversal of heterogeneously precipitated product is not complete, providing the right conditions for agglomeration of polymeric species upon commencement of the second caustic addition step.
Figure 7.7. The settling curve for sample 26, showing an induction period prior to rapid settling.
The induction period was not observed when the three hour intermediate aging period was used, hence it was chosen for all further experiments. The sediment volume for all three samples was 0.070 dm$^3$, suggesting no variation in particle or aggregate size. The chemical dissolution of poor order iron by AAO indicated a slight trend supporting the use of longer aging periods, however values were still within the expected range for ferrihydrite.

**Table 7.4: DURATION OF INTERMEDIATE AGING AND RESULTING PRECIPITATE CHARACTERISTICS**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>AGING TIME</th>
<th>SETTLING RATE m h$^{-1}$</th>
<th>SEDIMENT VOLUME dm$^3$</th>
<th>XRD</th>
<th>% AAO</th>
<th>TEMPERATURE °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>1 h</td>
<td>0.15</td>
<td>0.070</td>
<td>Ferrihydrite</td>
<td>92 %</td>
<td>23 °C</td>
</tr>
<tr>
<td>27</td>
<td>2 h</td>
<td>0.04</td>
<td>0.070</td>
<td>Ferrihydrite</td>
<td>87 %</td>
<td>23 °C</td>
</tr>
<tr>
<td>6</td>
<td>3 h</td>
<td>0.03</td>
<td>0.070</td>
<td>Ferrihydrite</td>
<td>81 %</td>
<td>26 °C</td>
</tr>
</tbody>
</table>

An intermediate aging step of three hours duration prevented the occurrence of an induction period during precipitate settling, hence it was used for further experimentation. It is thought that incomplete reversal of the heterogenously precipitated product provided conditions suitable for agglomeration of ferrihydrite particles similar to those found in Section 7.3.1.1.
7.3.1.3 TURBINE SPEED

Mixing efficiency has been shown to alter the products that form during hydrolysis and this efficiency is a function of the turbine speed. To investigate this further, the turbine speed was varied in samples 28 (420 rpm) and 29 (225 rpm) to see if it influenced precipitation products.

Results shown in Table 7.5 indicate the composition of precipitates formed at both turbine speeds were identical within experimental error. All other characterisation techniques such as XRD and thermogravimetry were unable to identify any changes in the precipitates.

Experiment 28 was observed to entrapped air into the reactor system during precipitation. To ensure that this had not masked any improvement in precipitate crystallinity due to increased mixing, air was pumped into experiment 30 while operating at the lower turbine speed to see if this reduced precipitate order. No changes in the precipitate were observed due to aeration during this experiment.

**TABLE 7.5: THE EFFECT OF TURBINE SPEED UPON PRECIPITATE CHARACTERISTICS**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>SPEED rpm</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm³</th>
<th>XRD</th>
<th>TEMPERATURE °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>420</td>
<td>0.02</td>
<td>0.080</td>
<td>Ferricydite</td>
<td>26 °C</td>
</tr>
<tr>
<td>29</td>
<td>225</td>
<td>0.03</td>
<td>0.075</td>
<td>Ferricydite</td>
<td>26 °C</td>
</tr>
<tr>
<td>30</td>
<td>240</td>
<td>0.03</td>
<td>0.075</td>
<td>Ferricydite</td>
<td>24 °C</td>
</tr>
</tbody>
</table>
These results apply for samples that have undergone an intermediate aging period, where the heterogeneously precipitated product has equilibrated back to the short chain red polymeric material. It is thought that turbine speed could affect the settling curves by decreasing the polymeric surface charge as a result of improved mixing, decreasing localised pH regions and the formation of heterogeneous polymer.

While a turbulent zone is required to facilitate good mixing, it is possible that very high shear will damage growing polymers and agglomerates, reducing the overall particle size. No breakdown in the particle size distribution was observed for a series of ferrihydrite samples, with turbine speeds up to 420 rpm. For the apparatus used, a turbine speed of 250 rpm provided turbulent mixing with no benefit observed in using a higher speed, hence was used for all further experimentation.

7.3.2 ONE OR TWO STEP PRECIPITATION PROCESS

It has been reported that changing preparation conditions can alter precipitate size and shape (Matijevic and Scheiner 1978). To test these reports, a series of experiments were conducted at various temperatures using both the one and two step precipitation processes to observe any such alterations. Samples of the precipitates were assessed to observe any relative advantage. As shown in Table 7.6, the settling rate and sediment volume of precipitates from the two step process are at least comparable to those from the one step process.
TABLE 7.6: EFFECT OF ONE OR TWO STEP CAUSTIC ADDITION UPON PRECIPITATE CHARACTERISTICS

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>TEMPERATURE °C</th>
<th>Nº OF STEPS</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm³</th>
<th>% AAO EXTRACTION</th>
<th>ALKALI ADDED TO 1° STEP %</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>26</td>
<td>1</td>
<td>0.03</td>
<td>0.065</td>
<td>87</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>26</td>
<td>2</td>
<td>0.08</td>
<td>0.060</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>60</td>
<td>1</td>
<td>0.19</td>
<td>0.045</td>
<td>76</td>
<td>100</td>
</tr>
<tr>
<td>20</td>
<td>60</td>
<td>2</td>
<td>0.17</td>
<td>0.045</td>
<td>54</td>
<td>75</td>
</tr>
</tbody>
</table>

The AAO extraction data favoured the two step process. Generally, it was more difficult to chemically extract iron from the products of the two step process, suggesting they were more ordered or crystalline.

It is postulated that the two step process provided sufficient time to form the red colloidal material observed during the intermediate aging period. As discussed in Section 7.3.1.1, the correct balance of the quantity of red colloid and degree of oxolation of the heterogeneous polymer allows for agglomeration of ferrihydrite particles with elevation of pH to 9.

The red colloidal polymeric material is also essential for the nucleation of seed material and the precipitation of a crystalline product at higher temperature. Without an intermediate aging period, the short chain iron is rapidly hydrolysed with oxolation of the bridging hydroxyl groups.
Dousma and De Bruyn (1979) observed the development of a solid colloidal phase required induction periods when precipitating goethite from acidic solutions at ambient temperature; while Goodman et al. (1988) failed to precipitate goethite without the addition of seed, presumably by not allowing for an induction period. Gelatinous precipitates were the result.

Hsu (1972) and Hsu and Ragone (1972) reported that the initial ratio of nuclei (seed) to monomeric units governed the appearance and stability of the iron (III) hydrolysis. At a low pH, there is plenty of monomer and little nuclei, whereas at high pH there is an abundance of nuclei but little monomer. They were of the impression that the condensation of monomer produced growth, growth is now understood to be via the iron dimer species.

The ratio of caustic to iron addition (when 60 to 70 % of the total alkali has been added), would result in the formation of Fe(OH)$_2^+$ at pH 2-3, however this species is unlikely to exist as the monomer (Johnston and Lewis 1986).

An investigation into these intermediates is given below in Section 7.3.3
7.3.3 Mössbauer Analysis of Intermediates Formed During the Nucleation Process

To further investigate the nature of the intermediate formed during aging, a solution of iron (III) chloride was partially precipitated with caustic as with previous experiments and samples taken at intervals throughout the process.

Three samples (A, B and C) were analysed by Mössbauer spectroscopy as frozen iron (III) solutions at liquid helium temperature.

Sample A was a partially hydrolysed iron (III) solution equivalent to material formed during the intermediate aging period of the standard precipitation method.

Sample B was a rapidly precipitated material with heterogeneous precipitation achieving localised pH of up to 9.

Sample C was material that underwent heterogeneous mixing and hence experienced a high localised pH gradient. This sample was allowed to age at pH 2.5 for three hours prior to being frozen for analysis. During this time the brown precipitate was observed to dissolve back to the red colloidal material present in sample A.
The spectra of sample A (Figure 7.8) shows a sextet of peaks along with a central singlet. The singlet is representative of either the unreacted iron (III) monomer (Chaves and Garg 1975), or polymeric material of exceedingly small particle size to allow super-paramagnetic relaxation even at 5 K (St Pierre, personal communication).

If the singlet were caused by unreacted iron (III) monomer, theoretically there should also be a small sextet of peaks with larger quadrupole splitting than that of the major component observed in Figure 7.8. There is a slight shoulder at the base of the major sextet of peaks that could account for this, though considered unlikely.

The singlet accounted for 45 % of the spectra. The major component sextet had magnetic hyperfine field splitting of a low 46.8 T, indicating very poor order among the polymeric species (a low level of oxolation).

It is important to point out that there was no evidence of the existence of the iron (III) dimer species (FeOH)$_2^{4+}$ in sample A (Note, iron atoms are bridged by oxygen or hydroxide species, see Figure 3.1). Iron dimer in a reasonable concentration would result in a spectral doublet with large quadrupole splitting. The absence of this dimer was surprising as the red colloidal material was thought to indeed be predominantly the iron dimer. These results suggest that while the iron dimer has been shown to be the building block for crystalline iron oxyhydroxides (Johnston and Lewis 1986), its existence may be rapidly transient during the precipitation process.
Figure 7.8. Mössbauer spectra of homogeneous precipitate (Sample A) recorded at 5K.
Sample B, the rapidly precipitated material, had magnetic hyperfine field splitting of 50.1 T. The line widths have narrowed as seen in Figure 7.9, indicating an increase in the degree of oxolation compared to the polymeric material observed in sample A. This is a result of the much higher pH experienced by sample B.

Sample C was the heterogeneously precipitated brown material that was allowed to dissolve back to the red colloidal material present in sample A. The spectra for sample C is shown in Figure 7.10 and clearly indicates differences in the spectral proportions between the singlet and the sextet.

The singlet only accounted for 11 % of the signal compared with 45 % for sample A. The magnetic hyperfine field splitting of the sextet was 47.8 T, indicating it to be part way between the colloid of sample A and the heterogeneous precipitate of sample B. This suggests that the oxolation process that formed the precipitate of sample B has been partially reversed. The process appears to be slow, in accordance with the assumptions of Dousma and De Bruyn (1976).

These results demonstrate several important points. Firstly a spectral doublet with large quadrupole splitting was not evident in any of the samples indicating that the iron dimer is not present in significant quantities.
Figure 7.9. Mössbauer spectra of heterogeneous precipitate (Sample B) recorded at 5K.
Figure 7.10. Mössbauer spectra of a heterogeneous precipitate aged at pH 2.5 for 3 hours (Sample C), recorded at 5K.
Secondly, it is suggested here that the 2-XRD line ferrihydrite or proto-ferrihydrite, is the result of aging (oxolation) of the polymeric material formed upon rapid hydrolysis. With a lower pH (ca 2.5) and time, this material can redisolve back to the short chain red colloidal material by reversal of the oxolation process (see Figure 7.11).

The short chain material can then precipitate into the various iron oxyhydroxides including 4-6 XRD line ferrihydrite via the iron dimer.

Three samples (D, E, and F) were recorded at liquid nitrogen temperature to further investigate the reaction process and confirm or repudiate the absence of iron (III) dimer. Samples D and E were concentrated and dilute iron (III) chloride solutions being about 3.7 mol dm\(^{-3}\) (pH = 0) and 0.1 mol dm\(^{-3}\) (pH = 1) respectively. The Mössbauer spectra for these samples are shown in Figures 7.12 and 7.13.

The spectra of sample D consisted of a singlet at 0.78 mm s\(^{-1}\), having a half height width of 0.99 mm s\(^{-1}\). This is consistent with spin-spin interactions between iron (III) atoms in close proximity to each other, due to the relatively high concentration. The spectra of sample E was a singlet at 0.60 mm s\(^{-1}\), having a half height width of 3.22 mm s\(^{-1}\), being indicative of monomeric iron (III) at low concentrations (St Pierre, personal communication).
Figure 7.11. Model for the growth and formation of polymeric material into ferricydrite.
Figure 7.12. Mössbauer spectra of sample D recorded at 78K.
Figure 7.13. Mössbauer spectra of sample E recorded at 78K.
Sample F was a partially hydrolysed sample at pH 2.5, similar to sample A, except a higher proportion of caustic was added. The spectra (shown in Figure 7.14) indicated a sextet of peaks with magnetic hyperfine field splitting of 44.6 T and a doublet which comprised 55 % of the signal. It is important to note that the magnetic hyperfine field splitting data can not be compared between samples measured at different temperatures.

Magnetic hyperfine field splitting at liquid nitrogen temperature (78 K) indicates that the average particle size would be in excess of 7 nm. This is consistent with the colloidal spheres found by Murad and Johnston (1987) (2-7 nm), as well as Spiro et al. (1966) (7 nm); but slightly larger than those found by Murphy et al. (1976a, 1976b, 1976c) (1.5-3 nm) or Eggleton and Fitzpatrick (1988) (2-3.5 nm).

The variation in results are explained by Von Gunten and Schneider (1991), who described the aggregation of subunits into colloids which grew with time. They explain growth by suggesting as the hydroxyl bridges are converted to oxygen bridges (oxolation), the colloid surface charge decreases causing further aggregation. Particles from 1 to 20 nm were reported. Polycation growth was also observed by Murphy et al. (1975b).
Figure 7.14. Mössbauer spectra of sample F recorded at 78K.
Eggleton and Fitzpatrick (1988) not only reported different particle sizes for 2 and 6-XRD line ferrihydrite (2 and 3.5 nm respectively), but they also gave different formulae. 2-XRD line ferrihydrite being Fe$_4$(O,OH,H$_2$O)$_{12}$ and 6-XRD line material having bulk composition of Fe$_{4.6}$(O,OH,H$_2$O)$_{12}$. Pankhurst and Pollard (1992) found that 2 and 6-XRD line ferrihydrite have different Mössbauer parameters, hence different chemical environments. These reports are consistent with the mechanism proposed above and shown in Figure 7.11.

Again there is no evidence in sample F for the existence of the iron dimer species in appreciable concentrations for detection by Mössbauer spectroscopy.

The absence of dimer does not preclude its importance as the building block of the iron oxyhydroxides, but suggests that upon its release from the polymer, it is rapidly consumed and so is always present at very low concentration. What precipitates upon addition of caustic is a short chain iron (III) polymer of very poor order, having a low level of oxolation.

Johnston and Lewis (1986) were able to show that the initial hydrolysis polymers were dependant upon solution conditions and were not always ferrihydrite in nature. Their short chain polymeric material was determined by Mössbauer spectroscopy at 78 K to have magnetic field strengths significantly greater than ferrihydrite, yet lower than microcrystalline goethite.
Bauminger et al. (1988) stated that the dynamic behaviour of iron in poor order ferritin (akin to ferrihydrite) is different from that in well ordered ferritin, indicating that the iron is bound differently in the two systems. It is suggested here that this would extend to the 2 & 6 XRD line ferrihydrite samples.

This is in contrast to Murad and Johnston (1987), who report that though the two broad XRD line ferrihydrite should be labelled proto-ferrihydrite, the crystallinity of ferrihydrite is practically a continuum, hence "proto" and 6-XRD line ferrihydrite can not be classified as separate minerals.

It is proposed here that the material termed proto-ferrihydrite is indeed a separate mineral. The continuum approach reflects the inability of current XRD techniques to differentiate blended material where some of the weaker ferrihydrite peaks are hidden within the background noise.
7.4 INFLUENCE OF ANIONS UPON THE SIMPLE SYSTEM

It has been widely reported that anions influence the morphology and composition of iron (III) oxyhydroxides (Flynn 1984). Chloride and sulphate were selected for detailed investigation since they are the two major anions associated with hydrometallurgical waste streams.

7.4.1 EFFECT OF HIGH CHLORIDE BACKGROUND CONCENTRATION

The system investigated consisted of a solution 0.1 mol dm$^{-3}$ in iron (III), and 0.3 mol dm$^{-3}$ in chloride. Sodium chloride was added to give a total chloride concentration of 3.3 mol dm$^{-3}$, then the solution was precipitated according to the standard procedure (Section 5.3). Results are tabulated in Table 7.7 below.

The XRD spectra of sample 31 (precipitated at 22°C) identified the sample to be ferrihydrite without any akaganeite being detected. In previous work, Murphy et al. (1976a) were able to isolate akaganeite from a partially neutralised system at only 0.1 mol dm$^{-3}$ chloride. Dousma et al. (1978) isolated akaganeite from an iron (III) nitrate solution where the chloride to iron ratio was only 1:3, while Feitknecht et al. (1975) were unable to detect akaganeite at a Cl:Fe ratio of 3:1.
The formation of ferrihydrite is kinetically favoured over the formation of goethite (Johnston and Lewis 1986) and is also proposed to be favoured over the formation of akaganeite under high chloride conditions. This is predictable as akaganeite is formed by the hindering effect of chloride ions upon goethite formation. Akaganeite should only form at higher temperatures that would normally favour goethite.

It is significant that the settling rate of sample 31 was slower than samples 5, 6 and 22, which had little or no additional chloride. The settling rate was only 0.01 m h\(^{-1}\), compared with 0.03, 0.08 and 0.08 m h\(^{-1}\) respectively.

It appears that the high chloride concentration reduces the settling ability of the poorly ordered ferrihydrite material. This is consistent with the work of Flynn (1990), who suggested that concentrations of chloride over 2 mol dm\(^{-3}\) promoted the conversion of the cationic iron (III) polymer to an anionic form by binding of the Cl\(^{-}\). Presumably this is related to the displacement of the iron chloride equilibrium (to the right as shown below), reducing the activity of iron (III).

\[
\text{FeCl}_2^+ \quad \overset{\rightleftharpoons}{\underset{\rightleftharpoons}{\rightarrow}} \quad \text{FeCl}_3 \quad \overset{\rightleftharpoons}{\underset{\rightleftharpoons}{\rightarrow}} \quad \text{FeCl}_4^-
\]

While the equilibrium level of iron (III) is dependant on the pH, the decreased activity of the iron (III) would result in less hydrolysis and oxolation, hence poorer order.
The surface charge on polymeric particles would also be enhanced by high concentrations of chloride anions, effectively preventing the possibility of polymeric agglomeration. This would result in a very slow settling rate, as was observed for sample 31. This effect upon surface charge should not be confused with the influence of chloride upon the goethite crystallisation process.

It is proposed that akaganeite will only form under conditions normally favouring the crystallisation of goethite. To test this proposition, sample 32 was precipitated at 60°C with 3.3 mol dm⁻³ chloride present. The XRD spectra showed reasonably crystalline akaganeite and a trace of goethite, in confirmation of the proposition.

The crystalline akaganeite in sample 32 had a settling rate of 0.14 m h⁻¹ as opposed to 0.17 m h⁻¹ for the comparable hematite and goethite sample 20.

It appears that the hindering effect of a high chloride concentration upon the crystallisation mechanism not only prevents the formation of goethite, but also prevents the formation of hematite. This is consistent with the theory of iron oxides and oxyhydroxides being formed from double chains. Hematite formation would be blocked in the same way goethite formation would be, as the chloride associated with the double chain would produce steric hindrance altering the crystal structure.
TABLE 7.7: EFFECT OF MIXED CHLORIDE AND SULPHATE IONS UPON PRECIPITATE CHARACTERISTICS

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>CHLORIDE mol dm⁻³</th>
<th>SULPHATE mol dm⁻³</th>
<th>XRD</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm⁻³</th>
<th>TEMPERATURE °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>3.3</td>
<td>----</td>
<td>Ferricydrite</td>
<td>0.01</td>
<td>0.065</td>
<td>22 °C</td>
</tr>
<tr>
<td>32</td>
<td>3.3</td>
<td>----</td>
<td>Akaganeite Ferricydrite</td>
<td>0.14</td>
<td>0.020</td>
<td>60 °C</td>
</tr>
<tr>
<td>33</td>
<td>----</td>
<td>0.15</td>
<td>Goethite Ferricydrite</td>
<td>0.08</td>
<td>0.035</td>
<td>17 °C</td>
</tr>
<tr>
<td>34</td>
<td>----</td>
<td>3.15</td>
<td>Ferricydrite</td>
<td>0.02</td>
<td>0.160</td>
<td>20 °C</td>
</tr>
<tr>
<td>35</td>
<td>0.3</td>
<td>0.07</td>
<td>Ferricydrite Goethite</td>
<td>0.01</td>
<td>0.065</td>
<td>17 °C</td>
</tr>
<tr>
<td>36</td>
<td>0.3</td>
<td>0.25</td>
<td>Ferricydrite</td>
<td>0.01</td>
<td>0.070</td>
<td>17 °C</td>
</tr>
<tr>
<td>37</td>
<td>0.15</td>
<td>0.07</td>
<td>Goethite Ferricydrite</td>
<td>0.01</td>
<td>0.045</td>
<td>18 °C</td>
</tr>
<tr>
<td>38</td>
<td>0.07</td>
<td>0.15</td>
<td>Goethite Ferricydrite</td>
<td>0.01</td>
<td>0.030</td>
<td>18 °C</td>
</tr>
</tbody>
</table>

7.4.2 EFFECT OF SULPHATE ION

The role of sulphate ion during the precipitation of iron (III) solutions has been extensively examined. Magini (1979) used X-ray scattering techniques to prove that the sulphate forms a complex with iron (III). Sapeszko et al. (1977) used spectrophotometric and potentiometric data to suggest that the dominant species present in solution at ambient temperature was FeSO₄⁺. The log of the equilibrium stability constant for FeSO₄⁺ is 2.24, while for FeCl₂⁺ it is 1.30 (Sillen and Martell 1971). This indicates that the iron (III) sulphate complex is stronger than the comparable iron (III) chloride complex, therefore the sulphate ion is more likely to influence the precipitation process.
Dousma *et al.* (1979) used optical density experiments during precipitation to support their proposal that the iron-sulphate complexes catalysed the nucleation and growth of precipitates. They reported that the ratio of sulphate to iron (III) could influence the precipitation product morphology, forming hematite, goethite and an amorphous material. It is thought that the amorphous material was ferrihydrite.

To investigate the influence that sulphate has upon the composition and morphology of precipitated iron (III) oxyhydroxides, experimentation was conducted using a pure iron (III) sulphate solution with no chloride present.

The iron (III) sulphate system was precipitated according to the standard method. Sample 33 was precipitated at 17°C with a sulphate to iron ratio of 3:2.

XRD identified the presence of poorly crystalline goethite of very small particle size, consistent with the surface area of 80 m² g⁻¹. Mössbauer spectroscopy determined sample 33 to consist of at least 93 % microcrystalline goethite with up to 7 % ferrihydrite, as confirmed by TEM (Figure 7.15). The ferrihydrite was of good order with quadrupole splitting of 0.62 mm s⁻¹. The settling rate was 0.08 m h⁻¹, comparable to the best precipitates from the chloride system.
Figure 7.15. TEM photograph of sample 33 showing goethite needles. BAR = 0.1 μm.
It is proposed that the modest settling rate is due to the adsorption of sulphate ions onto the red colloid intermediate; which at low sulphate concentrations reduces the cationic surface charge and enhances agglomeration and crystallisation with subsequent elevation of pH.

These results are in accord with the findings of Leskela and Leskela (1984) and Dousma et al. (1979). Brady et al. (1986) found goethite and a ferrihydrite like material when they hydrolysed sulphate contaminated acid mine drainage. At elevated temperatures (>90°C), Matijevic et al. (1975) reported crystalline precipitates of basic iron (III) sulphates \( \text{Fe}_3(\text{SO}_4)_2(\text{OH})_5.2\text{H}_2\text{O} \) and \( \text{Fe}_4(\text{SO}_4)(\text{OH})_{10} \).

Under certain conditions however, Flynn (1990) obtained a product he termed "Dense Amorphous Basic Ferric Sulphate" (DABFS) at ambient temperature, which was given the formula \( \text{Fe}_4(\text{SO}_4)(\text{OH})_{10-x}\text{H}_2\text{O} \) (where \( 2<x<3 \)). DABFS was reported to have excellent intrinsic dewatering ability, with settled sediment densities being between 12 and 22 % solids; however settling rates were not quoted. DABFS is reported to form in solutions where:

1. \( \text{OH}^- / \text{Fe(III)} = 1:2 \) to \( 2:1 \). \( \text{pH about 2.5 - 3} \)
2. \( \text{Fe(III)} \leq 0.2 \text{ mol dm}^{-3} \)
3. \( \text{SO}_4^{2-} \leq 0.2 \text{ mol dm}^{-3} \)
4. \( \text{SO}_4^{2-} : \text{Fe(III)} \geq 1:2 \)
5. Temperature \( \leq 40 \) °C
These conditions were held for the first step of experiment 33 with the exception that the pH was slightly higher than 3. The actual experimental conditions for the first step would place the ratio of hydroxide to iron (III) at about 2.3:1, which increases during the second step of the procedure where the pH was elevated from 3.5 to above 9.

Flynn (1990) reported that departure from ideal DABFS formation conditions would result in the formation of voluminous gelatinous precipitates (presumably ferrihydrite). Also, DABFS will transform into goethite at ambient temperature over a period of months in slightly acidic conditions. However the product obtained from experiment 33 was already converted to microcrystalline goethite upon completion of the experiment. Further investigation using Mössbauer spectroscopy upon frozen partially hydrolysed solutions, may resolve why different products are formed.

Brady et al. (1986) reported that the transformation of jarosite into oxyhydroxides was dependant upon the sulphate to iron (III) ratio. At low sulphate to iron (III) ratios (<1:2), goethite formation is enhanced with respect to ferrihydrite. The ratio used here was 2:3, suggesting that in the use of different systems, the range of ratios whereby sulphate will assist the formation of goethite over ferrihydrite has been greatly extended from that proposed by Brady et al. (1986).
7.4.3 HIGH SULPHATE BACKGROUND CONCENTRATION

The effect of a high sulphate concentration was studied using the hydroxide system in experiment 34. The iron (III) sulphate was bolstered with sodium sulphate to a sulphate concentration in excess of 3 mol dm$^{-3}$. Results are tabulated above in Table 7.7. It was apparent that the increased sulphate concentration was detrimental to the overall precipitate crystallinity, with only ferrihydrite being detected by XRD. The settling rate for sample 34 was only 0.02 m h$^{-1}$ (as with background chloride salts) and the sediment volume was a high 0.160 dm$^3$.

These results are supported by Dousma et al. (1979) who reported an associated decrease in crystallinity with increased concentration of sulphate. They are also supported by Flynn (1990), who report that a sulphate concentration in excess of 0.2 mol dm$^{-3}$ increased the formation of voluminous gelatinous precipitates. Brady et al. (1986) reported that a sulphate to iron (III) ratio in excess of 3:2 would completely inhibit the formation of crystalline goethite, favouring ferrihydrite. This is consistent with results for sample 34.

It is proposed here that the increased concentration of sulphate, with respect to the iron concentration, results in the formation of anionic sulphato complexes $\text{Fe(SO}_4\text{)_2}^-$, whilst excess sulphate ion adsorption onto the short chain iron polymer prevents agglomeration. The surface absorbed anionic sulphato complexes also prevents the formation of crystalline goethite by steric hindrance (cf chloride).
7.4.4 CHLORIDE / SULPHATE MIXTURES

In the absence of high concentrations of background anions, the formation of FeCl$_4^-$ and Fe(SO$_4$)$_2^-$ is limited with the equilibrium favouring FeCl$_2^+$ and FeSO$_4^+$ for the chloride and sulphate environments respectively.

The sulphate environment has been shown to enhance the goethite crystallisation process (Section 7.4.2), by adsorption of the FeSO$_4^+$ complex during precipitation, followed by the expulsion of sulphate from the crystallisation process.

Two sets of experiments were conducted in this system. The first involved the use of 0.1 mol dm$^{-3}$ iron (III) chloride (0.3 mol dm$^{-3}$ Cl$^-$) with added sodium sulphate. Experiments 35 and 36 contained 0.07 mol dm$^{-3}$ and 0.25 mol dm$^{-3}$ sulphate respectively in addition to the 0.3 mol dm$^{-3}$ chloride.

The XRD spectra of sample 35 indicated a trace of poorly crystalline goethite, while sample 36 was shown to consist entirely of ferrihydrite. The settling rate for both samples was only 0.01 m h$^{-1}$.

In the second set of experiments, iron (III) chloride was added to iron (III) sulphate, holding the iron concentration at 0.1 mol dm$^{-3}$. This meant the overall anion concentration was lower than the first experiments.
Sample 37 contained half as much sulphate as chloride, while sample 38 contained twice as much sulphate as chloride. (See Table 7.7)

The XRD spectra of both samples indicated the presence of some crystalline goethite as shown by the narrow XRD lines, but amorphous ferrihydrite (2-XRD line) was the dominant precipitate.

Both the resulting precipitates settled slower than the samples from the chloride only systems. This is a reflection of the strong sulphate ion adsorption, preventing the agglomeration of ferrihydrite polymeric material, while assisting in the crystallisation of microcrystalline goethite.

It is significant that the samples with lower anion concentrations (samples 37 & 38), had a much lower sediment volume, indicating lower levels of polymer and a more crystalline precipitate (supported by XRD).

The sediment appeared to be layered suggesting two distinctive phases, as confirmed by TEM. The crystalline phase would be expected to settle first, followed by the gelatinous ferrihydrite, as more free anions are released during the iron oxide precipitation. The crystalline goethite had a light yellow appearance contrasting to dark red ferrihydrite.
7.5 INFLUENCE OF OTHER CATIONS

During the study of high chloride concentrations, an investigation was conducted into the effect of cations with differing charge. Magnesium chloride (MgCl$_2$.6H$_2$O) and sodium chloride (NaCl) were chosen for these experiments. The chloride concentration was held at 3.3 mol dm$^3$, with 1.5 mol dm$^3$ magnesium being compared to 3 mol dm$^3$ sodium. The systems were precipitated with caustic, according to the standard precipitation method, with results shown in Table 7.8.

Samples 31 (NaCl) and 39 (MgCl$_2$) were both shown to be ferrihydrite by XRD and although both settled slowly (0.01 and 0.03 m h$^{-1}$ respectively), the faster settling rate in the presence of Mg$^{2+}$ appears to be significant. In these high ionic strength solutions, it is predicted that chloride ions occupy the doublelayer around the cationic intermediate polymer and inhibit agglomeration. Co-absorption of Mg$^{2+}$ would neutralise the surface charge and favour agglomeration rather more than Na$^+$.

Samples 32 (NaCl) and 40 (MgCl$_2$) were precipitated at 60°C. Sample 40 exhibited a green tinge to the black brown precipitate observed in sample 32. An XRD of sample 32 showed reasonably crystalline akaganeite and a trace of goethite. Sample 40 was shown to consist of very poorly crystalline akaganeite and ferrihydrite. The settling rate for sample 32 was 0.14 m h$^{-1}$, while sample 40 was 0.03 m h$^{-1}$. 
Thus at elevated temperatures, it appears that the presence of magnesium cations impair the crystallisation process and settling rate, relative to the sodium cation. This is similar to the findings of Cornell and Giovanoli (1988b) who found that copper (II) retarded the transformation of ferrihydrite into goethite by hindering the dissolution of ferrihydrite. Presumably the divalent cation competes with the proton for adsorption onto the oxo bridges of ferrihydrite, thus hindering the cleavage and recrystallisation process.

**TABLE 7.8: THE INFLUENCE OF Mg$^{2+}$ AND Na$^{+}$ BACKGROUND SALTS ON THE TYPE OF IRON OXYHYDROXIDE FORMED**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>Mg$^{2+}$ mol dm$^{-3}$</th>
<th>Na$^{+}$ mol dm$^{-3}$</th>
<th>TEMPERATURE °C</th>
<th>XRD</th>
<th>SEDIMENT VOLUME dm$^3$</th>
<th>SETTLING RATE m h$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>---</td>
<td>3.0</td>
<td>22</td>
<td>Ferrihydrite</td>
<td>0.065</td>
<td>0.01</td>
</tr>
<tr>
<td>39</td>
<td>1.5</td>
<td>---</td>
<td>22</td>
<td>Ferrihydrite</td>
<td>0.060</td>
<td>0.03</td>
</tr>
<tr>
<td>32</td>
<td>---</td>
<td>3.0</td>
<td>60</td>
<td>Akaganeite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Goethite</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ferrihydrite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1.5</td>
<td>---</td>
<td>60</td>
<td>Akaganeite</td>
<td>0.025</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ferrihydrite</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
To ensure that the difference in the observed settling rate was due to the properties of the precipitate and not to the concentration of magnesium, MgCl₂ was added at different concentrations to a sample containing ferrihydrite, goethite and hematite, then the settling rate recorded.

Results are shown below in Figure 7.16, as a plot of slurry volume against time. While the settling rate was observed to change, it is not sufficient to explain the differences described above (i.e. 0.03 - 0.14 m h⁻¹). Therefore, the adsorption of magnesium onto the ferrihydrite surface must be responsible for the hindered crystallisation process, hence the poor settling results obtained in sample 40.

7.6 INFLUENCE OF CITRATE AND OXALATE

Sodium oxalate and sodium citrate are known to effect the iron (III) precipitation process (Cornell et al. 1989). They represent very strong iron (III) complexing ligands and therefore their influence provides a useful comparison with the weaker iron (III) ligands, SO₄²⁻ and Cl⁻.

Cornell et al. (1989) reported an increased level of hematite formation when using these ligands. They demonstrated citric acid prevented the formation of goethite hence increasing the relative proportion of hematite while oxalic acid actually accelerated the nucleation of hematite by holding the iron atoms at an atomic distance suitable for hematite formation.
Figure 7.16. Settling curves for a goethite/ferricydrite sample dosed with different levels of magnesium chloride (mol dm$^{-3}$).
Cornell (1985) reported that $1 \times 10^{-4}$ mol dm$^{-3}$ citric acid completely prevented transformation of ferrihydrite into goethite, by inhibiting the formation of nuclei.

Krishnamurti and Huang (1991) reported that citrate promoted the formation of lepidocrocite at the expense of goethite during the oxidation of iron (II) solutions. They suggest that the complexation, electrostatic and steric effects of citrate in solution, influence the oxygen coordination of the edge shared Fe(O$_2$OH)$_6$ octahedra to promote the formation of lepidocrocite. This is similar to the formation of akaganeite where the chloride blocks formation of other oxyhydroxides and influences the linking of iron octahedra to form the hollandite structure. The difference being that the adsorption of chloride onto the octahedra blocks other polymorph formation, whereas the citrate appears to actively promote the formation of lepidocrocite.

When Krishnamurti and Huang (1991) increased the ligand to iron ratio from 1:1000 to 1:100, both iron (III) oxyhydroxides were inhibited with non crystalline products being produced. Upon increasing the citrate to iron ratio to 1:10, they found that the strong complexation of citrate for the iron (II) actually retarded oxidation and also the formation of iron (III) precipitates.
In this work the ligands were present throughout the precipitation process at a concentration of 0.05 mol dm$^{-3}$. This would yield an additive to iron (III) ratio of 1:2, much higher than 1:1000 and 1:10; suggested by Cornell et al. (1989). The higher concentrations were chosen to amplify any changes that may occur during the hydrolysis and subsequent precipitation of iron (III) oxyhydroxides and to extend the range of conditions reported.

The precipitation procedure was conducted as previous experiments using caustic as the source of alkali. Samples 41 (oxalate) and 42 (citrate) were precipitated at 21°C. Sample 41 was an orange red precipitate while 42 was a dark, red solution from which only a small quantity of solids precipitated at pH 9. XRD verified both samples were ferrihydrite, however it was difficult obtaining enough precipitate from sample 42 for an XRD scan. Sample 41 (oxalate) settled slowly at 0.01 m h$^{-1}$, while sample 42 (citrate) did not settle. Complete precipitation was obtained however at 60°C (samples 43,44).

XRD of sample 43 (oxalate) gave a trace of akaganeite and hematite, with the bulk of the sample being ferrihydrite. Sample 44 (citrate) was shown to consist of ferrihydrite, very poorly crystalline akaganeite and a trace of hematite and goethite.
These results reinforce the proposed mechanism for the iron precipitation process. The ligands inhibit the polymerisation and precipitation of crystalline iron oxides, by complexing with Fe$^{3+}$ and possibly short chain species. This is a reflection of the high equilibrium stability constants for iron (III) citrate and oxalate species (log 17.29 and 7.56 respectively, Sillen and Martell 1971). High concentrations of citrate almost completely prevent the hydrolysis of iron at pH 9 and at ambient temperature.

### TABLE 7.9: THE INFLUENCE OF OXALATE AND CITRATE UPON PRECIPITATION PRODUCTS

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>LIGAND</th>
<th>TEMPERATURE °C</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>OXALATE</td>
<td>21</td>
<td>0.01</td>
<td>0.070</td>
</tr>
<tr>
<td>42</td>
<td>CITRATE</td>
<td>21</td>
<td>0.00</td>
<td>0.200</td>
</tr>
<tr>
<td>43</td>
<td>OXALATE</td>
<td>60</td>
<td>0.07</td>
<td>0.040</td>
</tr>
<tr>
<td>44</td>
<td>CITRATE</td>
<td>60</td>
<td>0.03</td>
<td>0.065</td>
</tr>
</tbody>
</table>
7.7 CONCLUSION

Heterogeneous precipitation was observed to dissolve back to a red polymeric material after mixing for three hours at pH 3.0 or lower. Precipitates from this red polymeric material were identical to those of the red polymeric material formed by homogeneous precipitation.

The shape of the settling curves suggest that surface charge effects play a role in the agglomeration of ferrihydrite particles (c.f. Ca$^{2+}$, Mg$^{2+}$ & SO$_4^{2-}$; Chapters 8 & 9).

Experimentation verified that temperature during precipitation significantly influences the crystallinity and composition of the resulting products. Temperatures above 60 °C are required before significant changes in crystallinity, settling rate and sediment volume are observed; consistent with current industrial practice.

The settling rate and degree of order appear to be improved by the intermediate aging step of the two step process, particularly at higher temperature. This advantage was believed to be due to the aging period allowing red colloidal polymeric material to form. This material influences the surface charge density observed during the second step addition of alkali. At ambient temperature, mild polymeric agglomeration takes place, however at elevated temperature (60°C), such agglomeration assists the formation of crystal nuclei essential for precipitation of an ordered product.
The importance of the intermediate aging step especially at elevated temperature, suggests that the precipitation process is heavily influenced by the presence of the red colloidal material observed during the aging procedure. The red polymeric material was shown by Mössbauer spectroscopy to be a very short chain polymeric iron (III) hydroxide, with no evidence of iron (III) dimers.

High chloride concentrations have a detrimental effect upon precipitate settling rates and crystallinity. The adsorption of chloride ions onto polymeric chains prevented polymer agglomeration as the pH was elevated at low temperature. With temperatures above 60°C, the surface adsorbed chloride on polymer chains blocks goethite and hematite formation. Twinned dimer chains have to crystallise around the strongly absorbed chloride anions to form akaganeite. The akaganeite is crystalline, but has a high degree of associated 2-line ferrihydrite.

The precipitation of goethite from pure iron (III) sulphate solutions at ambient temperature signified a change in the mechanism. This change is believed to be due to the complexation of the iron (III) species by sulphate, apparently facilitating the precipitation of crystalline goethite. It is thought that the sulphate ions hold the iron species in place for crystallisation, or they facilitate the formation of an ordered seed for subsequent precipitation. The former view could be likened to the adsorption of chloride onto polymeric iron chains during the formation of akaganeite. Concentrations of sulphate ions (<0.25 mol dm⁻³), promoted the formation of microcrystalline goethite, even in the presence of up to 0.3 mol dm⁻³ Cl⁻. This improvement in crystallinity did not correspond to a substantial increase in the settling rate.
The presence of high concentrations of background chloride or sulphate, appears to be detrimental to the crystallinity and settling rate of the precipitates formed. It is believed that the anions prevent the agglomeration and crystallisation process by adsorption onto the intermediate polymer and subsequent complexing with iron (III) thus stabilising the short chain polymeric material. This material will hydrolyse into poorly ordered ferrihydrite.

Magnesium cations at ambient temperature appear to partially neutralise surface charge build up on polymeric intermediates and promote the agglomeration of ferrihydrite. At elevated temperature, it is suggested that the magnesium cations hinder the redissolution of ferrihydrite and slow release of the iron dimer essential to the formation of crystalline products.

The presence of high concentrations of either sodium citrate or oxalate block the formation of crystalline precipitates. At higher concentrations these ligands prevent the formation of the polymeric intermediate, but at low concentrations they adsorb onto it hindering the release of iron dimer. Poor order ferrihydrite is therefore precipitated.
CHAPTER 8
PRECIPITATION OF IRON (III) OXIDE AND OXYHYDROXIDE WITH LIME

Current industrial practice for the elevation of pH and the subsequent precipitation of iron compounds is to add slaked lime to the waste stream. In most cases the slaked lime will represent a heterogeneous precipitation system with a relatively high pH gradient surrounding the hydrated calcium oxide surface. The solubility of calcium hydroxide is 1.85 g dm\(^{-3}\) in cold water, which decreases to 0.77 g dm\(^{-3}\) in hot water (Weast 1978).

The use of lime as the source of alkali will also have a bearing upon the composition and physical properties of the final precipitate slurry. This is related to the anions associated in the waste stream. While calcium chloride is highly soluble in cold water, calcium sulphate dihydrate (gypsum) has a solubility of only 2.41 g dm\(^{-3}\) (Weast 1978). Hence gypsum will usually form a precipitate with the high concentrations present in most industrial applications. The inclusion of precipitated gypsum (CaSO\(_4\).2H\(_2\)O), which has a highly acicular morphology, in the final precipitate slurry will naturally influence the settling rate and dewatering ability.

With these considerations in mind, some of the factors influencing the precipitation of iron oxides and oxyhydroxides with lime are discussed below with reference to the simple sodium hydroxide system.
8.1 LIME AND IRON (III) CHLORIDE

To observe any differences between the sodium hydroxide and lime systems, slaked lime (i.e. calcium hydroxide, $\text{Ca(OH)}_2$) and NaOH were delivered into identical reaction chambers, under identical conditions for a standard two step process.

Samples 45, 46 and 47 were precipitated using slaked lime to different first step ratios of alkali to iron. Samples 22 and 23 are included for comparison to the best settling caustic (NaOH) system. Results are listed in Table 8.1 below.

XRD identified all experiments to have precipitated ferrihydrite. The settling rates are all consistent with partially agglomerated ferrihydrite and are higher than those usually obtained with the NaOH system. It is thought that agglomeration occurs at the interface between the high pH surrounding the dissolving lime particle and the low pH of bulk solution. Oxolated polymeric iron (III) species surrounding the lime particle would have a negative surface charge and attract cationic iron (III) species from the bulk solution forming polymeric agglomerates.

The sediment volumes for all samples listed in Table 8.1 randomly ranged from 0.060 to 0.075 dm$^3$, consistent with ferrihydrite. The AAO extraction data indicated that the precipitates from the slaked lime system contained only 20 - 40 % extractable iron, while comparable NaOH samples (e.g. 5, 8 & 22) contained as much as 80 %.
The discrepancy is believed due to the presence of calcium which inhibits the AAO dissolution process by preferentially coordinating with the oxalate, rather than any changes to the precipitate order. This view was supported by XRD, settling rate, sediment volume, TG and TEM which were unable to determine any improvements in crystallinity or order.

**TABLE 8.1: COMPARISON BETWEEN PRECIPITATES FORMED USING SLAKED LIME AND THOSE FROM CAUSTIC**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>ALKALI</th>
<th>% ALKALI IN 1st STEP</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm⁻³</th>
<th>XRD</th>
<th>AAO</th>
</tr>
</thead>
<tbody>
<tr>
<td>23</td>
<td>NaOH</td>
<td>83 %</td>
<td>0.02</td>
<td>0.075</td>
<td>Ferrihydrite</td>
<td>94 %</td>
</tr>
<tr>
<td>22</td>
<td>NaOH</td>
<td>74 %</td>
<td>0.08</td>
<td>0.065</td>
<td>Ferrihydrite</td>
<td>75 %</td>
</tr>
<tr>
<td>45</td>
<td>CaO</td>
<td>75 %</td>
<td>0.07</td>
<td>0.075</td>
<td>Ferrihydrite</td>
<td>24 %</td>
</tr>
<tr>
<td>46</td>
<td>CaO</td>
<td>65 %</td>
<td>0.06</td>
<td>0.060</td>
<td>Ferrihydrite</td>
<td>28 %</td>
</tr>
<tr>
<td>47</td>
<td>CaO</td>
<td>90 %</td>
<td>0.07</td>
<td>0.060</td>
<td>Ferrihydrite</td>
<td>34 %</td>
</tr>
</tbody>
</table>

**8.2 HETEROGENEOUS PRECIPITATION**

Current industrial practice involves the slaking of lime prior to its use as an alkali. It was proposed that the use of dry lime may influence the dewatering ability of the iron precipitation products. The slaking of lime is known to be exothermic and generate heat which should be beneficial for the precipitation of iron (III) at the surface of the particle.
Coinciding with this exothermic reaction would be the relatively slow release of hydroxyl species. While slow hydrolysis has been shown to be beneficial to the precipitation process (Chapter 7), the release would occur at a localised level. Wentzler and Aplan (1992) have shown the existence of a large concentration gradient of alkali surrounding a limestone particle. A pH gradient was eluded to by Giles et al. (1993) using rotating disc experiments to study the dissolution kinetics of slaked lime. These pH gradients result in rapid hydrolysis which is known to be detrimental to the iron (III) precipitate order (Flynn 1990).

To establish the combined effect of the exothermic reaction of dissolution as well as the associated high pH gradient, experiment 48 was performed using the standard two step precipitation processes with dry lime as the source of alkali. Results are tabulated below in Table 8.2. Sample 45 was used to compare the slaked lime equivalent.

**TABLE 8.2: EFFECT OF DRY OR SLAKED CaO UPON PRECIPITATES**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>LIME</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm³</th>
<th>XRD</th>
<th>AAO</th>
<th>TEMPERATURE °C</th>
</tr>
</thead>
</table>
Settling rate, sediment volumes, thermal analysis, chemical extraction and XRD were unable to determine any significant differences between samples 45 and 48, indicating there to be no advantage in the use of dry lime over slaked lime, after intermediate aging for three hours at pH 3.

However, the transmission electron micrograph of sample 48 produced a very interesting result. Figure 8.1 shows a surface reaction product of iron (III) oxyhydroxide surrounding what was a lime particle. The hollow structure is where the calcium oxide has dissolved away through the observed pores.

This is consistent with Wentzler and Aplan (1992) who found iron oxyhydroxide and gypsum coatings surrounded their limestone particles. They reported that large limestone particles were completely covered, with precipitate preventing the dissolution of the core. This variation is believed to be due to the much smaller size particle used in this work and the use of pure calcium oxide as opposed to limestone.

Samples 49 (slaked CaO) and 50 (dry CaO) were precipitated at 60 °C. The XRD spectra have shown the presence of calcite (CaCO₃) in these samples along with ferrihydrite. No other iron oxides or oxyhydroxides were detected suggesting they were hindered in their formation.
Figure 8.1. TEM photograph of sample 48 showing the surface reaction products surrounding what was a lime particle. BAR = 0.1 μm.
Whilst there was no difference in the settling rates between the two samples (0.02 m h⁻¹), they were slower than those precipitated at ambient temperature, but still typical of non-agglomerated ferrihydrite. This is consistent with lower pH gradients or localised high pH regions at elevated temperature. The absence of crystalline goethite and hematite is attributed to the presence of the divalent cations hindering the release of the iron dimer for recrystallisation (see Section 7.5).

However, the sediment volumes of both precipitates were about 0.040 dm⁻³, approximately half that of samples precipitated at ambient temperature. These results are consistent with low molecular weight polymers and very fine particles which are slow to settle, but ultimately pack closely together.

8.3 THE INFLUENCE OF ANIONS UPON THE CaO SYSTEM

The detrimental effect of high chloride concentration has been shown in Section 7.4 as has the possible improvement in crystallinity in the presence of sulphate. The effect of sulphate upon the formation of gypsum in the slaked lime system was therefore further investigated and described below.

8.3.1 SULPHATE

A study of the effect of using iron (III) sulphate (Fe₂(SO₄)₃) in place of iron (III) chloride was conducted to observe the effect of sulphate and hence gypsum formation.
Sample 51 (CaO) was precipitated at 20 °C using the standard precipitation method. XRD detected large quantities of gypsum and an unknown "ettringite like" \([\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_2\cdot 25\text{H}_2\text{O}]\) compound. The lines match up well with this material, assuming the iron substituted for aluminium.

High resolution XRD determined this unknown to be a combination of calcite and aragonite (both are forms of calcium carbonate, \(\text{CaCO}_3\)), emphasising the need to use more than one characterisation technique to confirm composition. Iron was present in the form of 6-XRD line ferrihydrite. A point of interest was the absence of the expected goethite structure, found in the NaOH - iron sulphate system.

Mössbauer spectroscopy determined the iron in sample 51 to be ferrihydrite having quadrupole splitting of 0.68 mm s\(^{-1}\) (see section 6.2). The low value for quadrupole splitting indicates a very high degree of order to the material. This is confirmation as to the presence of 6-XRD line ferrihydrite as determined by high resolution XRD.

The surface area of sample 51 was 30 m\(^2\) g\(^{-1}\), indicating a highly crystalline precipitate as confirmed by the TEM photograph shown below in Figure 8.2. The settling rate of sample 51 (0.28 m h\(^{-1}\)) was four times faster than the slaked lime-chloride system (sample 35 was 0.07 m h\(^{-1}\)) and the hydroxide sulphate system where goethite was formed (sample 33 was 0.08 m h\(^{-1}\)). Results are tabulated in Table 8.3 below.
Figure 8.2. TEM photograph of sample 51 showing the highly crystalline sample morphology. BAR = 0.1 μm.
The rapid settling rate, coupled with a high sediment volume of 0.060 dm$^3$, indicates that the samples settled rapidly as both crystals and agglomerates with a high proportion of encapsulated liquor. This is consistent with the product being well ordered ferrihydrite accompanied by gypsum, calcite and aragonite.

It appears that the co-precipitation of well ordered ferrihydrite with gypsum in the diffusion layer surrounding the dissolving lime particle results in a highly crystalline product. The ferrihydrite in the layer surrounding the lime particle experiences the high localised pH; thus would have a negative surface charge. This would attract positively charged colloid from solution (low bulk solution pH) enhancing agglomeration. The formation of this layer surrounding the lime particle would slow the release of hydroxide groups into solution, resulting in less iron polymer being formed and precipitates having a greater degree of order. Gypsum would also form in this layer as dissolved Ca$^{2+}$ meets the bulk solution SO$_4^{2-}$. The addition of gypsum to this layer would also reduce the migration of hydroxide groups into bulk solution (Wentzler and Aplan 1972); inhibiting extensive polymerisation and providing surface sites for growth of well ordered 6-XRD line ferrihydrite.
8.3.2 CHLORIDE AND SULPHATE MIXTURES

Two sets of experiments were conducted in this system. Both sets were conducted according to the standard two step precipitation process.

The first set of experiments involved the use of iron (III) chloride (0.3 mol dm$^{-3}$ Cl$^-$) with added sodium sulphate. Experiment 52 contained an extra 0.075 mol dm$^{-3}$ sulphate to the 0.3 mol dm$^{-3}$ chloride, while experiment 53 contained an extra 0.25 dm$^{-3}$ sulphate.

There was very little difference between the samples with XRD finding both precipitates contained ferrihydrite, gypsum and bassanite (CaSO$_4$.1/2H$_2$O). The detection of bassanite by XRD is attributed to the conversion of gypsum during the sample drying procedure. Results are tabulated below in Table 8.3.

The settling rates of the two samples (0.11 and 0.09 m h$^{-1}$ for 52 and 53 respectively) were faster than the samples from the comparable lime - chloride only systems (sample 45, 0.07 m h$^{-1}$). The sediment volumes were also much lower being 0.045 and 0.040 dm$^{-3}$ for samples 52 and 53 respectively, as opposed to 0.075 dm$^{-3}$ for sample 45.
The second set of experiments kept the iron concentration to 0.1 mol dm\(^{-3}\) while changing the ratio of iron (III) chloride and iron (III) sulphate. Sample 54 contained half as much sulphate as chloride while sample 55 contained twice as much sulphate as chloride. Concentrations and results are listed in Table 8.3.

**TABLE 8.3 MIXED CHLORIDE AND SULPHATE SYSTEMS WITH SLAKED LIME**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>ALKALI</th>
<th>[Cl(^{-})] mol dm(^{-3})</th>
<th>[SO(_4^{2-})] mol dm(^{-3})</th>
<th>SETTLING RATE m h(^{-1})</th>
<th>SEDIMENT VOLUME dm(^{-3})</th>
<th>XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>22</td>
<td>NaOH</td>
<td>0.3</td>
<td></td>
<td>0.08</td>
<td>0.065</td>
<td>Ferricydrite</td>
</tr>
<tr>
<td>33</td>
<td>NaOH</td>
<td></td>
<td>0.15</td>
<td>0.04</td>
<td>0.030</td>
<td>Goethite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ferricydrite</td>
</tr>
<tr>
<td>45</td>
<td>CaO</td>
<td>0.3</td>
<td></td>
<td>0.07</td>
<td>0.075</td>
<td>Ferricydrite</td>
</tr>
<tr>
<td>51</td>
<td>CaO</td>
<td></td>
<td>0.15</td>
<td>0.28</td>
<td>0.060</td>
<td>Ferricydrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gypsum</td>
</tr>
<tr>
<td>52</td>
<td>CaO</td>
<td>0.3</td>
<td>0.075</td>
<td>0.11</td>
<td>0.045</td>
<td>Ferricydrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gypsum</td>
</tr>
<tr>
<td>53</td>
<td>CaO</td>
<td>0.3</td>
<td>0.25</td>
<td>0.09</td>
<td>0.040</td>
<td>Ferricydrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gypsum</td>
</tr>
<tr>
<td>54</td>
<td>CaO</td>
<td>0.15</td>
<td>0.075</td>
<td>0.45</td>
<td>0.030</td>
<td>Ferricydrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gypsum</td>
</tr>
<tr>
<td>55</td>
<td>CaO</td>
<td>0.075</td>
<td>0.113</td>
<td>0.90</td>
<td>0.025</td>
<td>Ferricydrite</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Gypsum</td>
</tr>
</tbody>
</table>

The settling rates varied quite dramatically between samples as seen in Table 8.3 and were particularly high for samples 54 and 55. Both these samples had very low sediment volumes of 30 and 25 dm\(^{-3}\) respectively, suggesting they consisted of small dense particles. This is a two to three fold increase in sediment density above that normally experienced for iron (III) oxyhydroxides precipitated from a chloride only or sulphate only system at ambient temperature.
The variation in settling rates does not appear to correlate with the concentration of sulphate in solution, but rather on the ratio of iron to sulphate. As Table 8.4 shows, the maximum settling rate occurs when the ratio is in the order of 1:1.

The presence of excess chloride has a significant effect however (cf samples 52 and 54), presumably due to the background salt altering the surface charge of the iron oxyhydroxide species. Further work is needed to clarify this.

**TABLE 8.4: THE IRON TO SULPHATE RATIO AND RESULTING PRECIPITATE SETTLING RATES**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>RATIO Fe(^{2+}):SO(_4)^{2-}</th>
<th>SETTLING RATE (m h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>53</td>
<td>0.4 : 1</td>
<td>0.09</td>
</tr>
<tr>
<td>51</td>
<td>0.7 : 1</td>
<td>0.28</td>
</tr>
<tr>
<td>55</td>
<td>0.9 : 1</td>
<td>0.90</td>
</tr>
<tr>
<td>54</td>
<td>1.3 : 1</td>
<td>0.45</td>
</tr>
<tr>
<td>52</td>
<td>1.3 : 1</td>
<td>0.11</td>
</tr>
</tbody>
</table>

**8.4 CONCLUSIONS**

The use of slaked lime produced precipitates of ferrihydrite little different from those produced by the caustic system, but with generally slightly higher settling rates. Slaked lime and caustic can therefore be considered interchangeable for the iron (III) chloride system, with no resulting change to the precipitate morphology.
The characterisation techniques were unable to identify significant differences between the crystallinity or settling rates of precipitates from the reaction of iron (III) chloride with dry or slaked lime. TEM was able to observe the formation of a crust of iron oxyhydroxide around the dissolving lime particle.

The use of lime for the precipitation of iron from a sulphate system has produced a highly ordered ferrihydrite that appears to be intimately associated with the co-precipitated gypsum. This is attributed to in part the slow release of OH\(^{-}\) into the bulk solution and to the creation of crystal surfaces suitable for adsorption and growth of a highly ordered product. There appears to be an optimal ratio of iron to sulphate (1:1), that facilitates this co-precipitation.

Enormous improvements in the settling ability and settled sediment densities were achieved with the mixed chloride and sulphate system. This improvement was a result of optimal iron to sulphate ratios, rather than the influence of chloride which was shown to hinder the process. Settling rates were increased ten fold to those from a chloride only system, and three fold over a sulphate only system. Sediment densities were at least doubled over the same comparison, based solely on ferrihydrite formation.
CHAPTER 9

PRECIPITATION OF IRON (III) OXIDE AND OXYHYDROXIDE

WITH MAGNESIA

It has been suggested that the use of slaked magnesia is beneficial to the dewatering process by producing an iron oxyhydroxide precipitate of superior settling ability (Frost et al. 1990), yet no mechanistic explanation for this has been proposed. Therefore the information gained in this work regarding the precipitation process at the molecular level was applied to the magnesia system.

Magnesium oxide has lower solubility than lime (0.006 g dm$^{-3}$ Weast 1978) in cold water, as does slaked magnesia (brucite Mg(OH)$_2$) (0.009 g dm$^{-3}$ Latimer and Hildebrand 1959). Yet the solubility of magnesium sulphate is 260 g dm$^{-3}$ (Weast 1978), which highlights an immediate advantage in using magnesia over slaked lime. That is, unlike gypsum (CaSO$_4$·2H$_2$O), magnesium sulphate is soluble in cold water.

To observe the influence of using magnesium oxide as the source of alkali upon the precipitated iron oxyhydroxides, several sets of experiments were conducted. The results of these experiments are described below.
9.1 MAGNESIA AND IRON (III) CHLORIDE

A study of the effect of using magnesium oxide as the neutralisation media was conducted to test claims that the resultant product was of superior settling ability (Frost et al. 1990). This enhanced settling ability was presumably related to improved agglomeration or crystallinity. Experiments were conducted according to the standard two step precipitation method using slaked magnesia.

Sample 56 was precipitated at 21°C with a first step of 70% alkali addition. The XRD of sample 56 identified the presence of magnesium iron oxide hydroxide chloride hydrate, iowaite (Mg₄Fe₅(OH)₈Cl₆.xH₂O). However, the high ratio of magnesium to iron suggested that only a small proportion of iron was precipitated in this form, the bulk being ferrihydrite.

The settling rate for sample 56 was only 0.02 m h⁻¹ and the sediment volume was 0.080 dm³. These values are similar to poorly ordered ferrihydrite precipitated under conditions of high anion concentrations (samples 31 & 34), or rapid hydrolysis (sample 25). In these cases, the poorly ordered ferrihydrite is the result of hydrolysis of the short chain polymeric material. This indicates that the agglomeration of ferrihydrite in the second step of hydrolysis has not occurred. This is likely to be a result of the slow dissolution of the magnesium oxide and hydroxide particles. With the slow elevation of pH under well stirred conditions, there would be minimal pH gradients for adsorbed polymers to become negatively charged and agglomerate with cationic polymer in the bulk solution at pH < 5.
9.1.1 EFFECT OF VARYING FIRST STEP ADDITION

To explore the optimum conditions for the precipitation of iron oxyhydroxides, experiments were also conducted using different addition rates of dry or slaked magnesia to the first step. Sample 57 was precipitated with 50 % of the slaked magnesia added in the first step, compared to 70% for sample 56. Sample 58 was also precipitated to a first step of 70 %, but using dry magnesium oxide. The products from these experiments were identical, consisting of poorly crystalline iowaite and ferrihydrite.

The settling rates were slow (0.01 - 0.02 m h$^{-1}$) and the sediment volumes ranged from 0.08 to 0.090 dm$^3$. The slow settling rates combined with high sediment volumes suggest the formation of large yet low density particles.

These results demonstrate that the amount of base required to be added in the second step is not as critical as with other systems and the use of dry MgO has no effect upon the settling rate when compared to the slaked system.
TABLE 9.1: PRECIPITATES FROM MAGNESIA AND IRON (III) CHLORIDE

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>MgO TYPE</th>
<th>% HYDROLYSIS</th>
<th>TEMPERATURE °C</th>
<th>XRD</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>slaked</td>
<td>70</td>
<td>21</td>
<td>Ferrihydrite, Iowaite</td>
<td>0.02</td>
<td>0.080</td>
</tr>
<tr>
<td>57</td>
<td>slaked</td>
<td>50</td>
<td>19</td>
<td>Ferrihydrite, Iowaite</td>
<td>0.01</td>
<td>0.090</td>
</tr>
<tr>
<td>58</td>
<td>dry</td>
<td>70</td>
<td>19</td>
<td>Ferrihydrite, Iowaite</td>
<td>0.01</td>
<td>0.085</td>
</tr>
<tr>
<td>59</td>
<td>dry</td>
<td>80</td>
<td>60</td>
<td>Ferrihydrite, Iowaite</td>
<td>0.00</td>
<td>0.20</td>
</tr>
</tbody>
</table>

9.1.2 EFFECT OF HIGHER TEMPERATURE

To observe the effect of elevated temperature, experiment 59 was conducted at 60 °C. Again the XRD of sample 59 identified the presence of poorly crystalline iowaite and ferrihydrite. However, unlike the caustic system, the precipitate was very thick and did not settle at all (see Table 9.1). The settled sediment volume after 24 hours equated to the starting slurry volume (ie it had already reached the gel structure zone). This lack of crystallinity at elevated temperatures in the presence of magnesium ions is surprising. One explanation is that adsorption of magnesium onto the surface of polymeric material hinders acid attack and cleavage of oxo bridges, interrupting the release of iron dimer during the crystallisation period at elevated pH.
9.2 INFLUENCE OF ANIONS

The influence of anions upon the caustic (see section 7.4) and slaked lime (see section 8.3) systems has already shown that chemistry and solution speciation can be modified. These influences were investigated and are discussed below.

9.2.1 SULPHATE

The use of other anions such as sulphate have given encouraging results regarding crystallinity in the caustic system, where microcrystalline goethite was produced at ambient temperature. However due to the small particle size, there was no improvement to the settling rate. When iron (III) sulphate was precipitated with lime, settling rates were improved due to precipitation of highly ordered ferrihydrite with gypsum. The use of magnesium oxide (discussed below) avoids the formation of gypsum and allows the behaviour of iron oxyhydroxide to be studied for comparison.

A solution of 0.1 mol dm$^{-3}$ iron (III) sulphate was precipitated as per previous experiments, but using dry magnesium oxide.

Sample 60 was precipitated at 17°C and the product was identified as very well defined 6-XRD line ferrihydrite and brucite (Mg(OH)$_2$). A high resolution XRD of sample 60 washed with dilute acid is shown in Figure 9.1 below. The very weak lines are marked to assist identification.
Figure 9.1. XRD of sample 60, believed to be 6-line ferrihydrite or DABFS. The weak peaks are marked to assist identification.
Even though sample 60 was precipitated at ambient temperature, the settling rate of the slurry was very rapid (1.14 m h\(^{-1}\)). The settled bed or sediment volume was a very low 0.015 dm\(^3\). Used in conjunction, these results suggest a dense particle of small size. This is not characteristic of ferrihydrite, not even the well ordered 6-XRD line variety.

The settled sediment volume would equate to a solids concentration of about 13 % w/w, using 5Fe\(_2\)O\(_3\).9H\(_2\)O as the formula for ferrihydrite (Schwertmann and Cornell 1991) and not including the presence of brucite. These results indicate very good intrinsic dewatering capabilities and a very high degree of precipitate order.

The surface area of sample 60 was only 10 m\(^2\) g\(^{-1}\), indicating a highly crystalline precipitate unlike typical ferrihydrite which ranges between 120 and 300 m\(^2\) g\(^{-1}\).

Mössbauer spectroscopy has determined the precipitate of sample 60 to be ferrihydrite, however the quadrupole splitting of 0.75 mm s\(^{-1}\) was too high to represent well ordered 6-XRD line ferrihydrite. The spectral doublet is shown below in Figure 9.2. In contrast, the line width of peaks was a low 0.44 mm s\(^{-1}\), indicating a well defined chemical environment.

The TEM photograph of sample 60 (Figure 9.3) shows that the crystalline morphology is completely different to the uneven gelatinous nature expected for ferrihydrite (see Figures 6.3A and 6.3B).
Figure 9.2. Mössbauer spectra of sample 60 recorded at room temperature.
Figure 9.3. TEM photograph of sample 60 showing a highly crystalline morphology. BAR = 0.1 μm.
While the high resolution Philips PW 1820 goniometer indicated 6-XRD line ferrihydrite, the Siemens M34007 diffractometer suggested the product was amorphous. Flynn (1990) proposed that when the concentration of iron was under 0.2 mol dm$^{-3}$ and the sulphate to iron ratio was larger than 0.5, the precipitated material consisted of a "dense amorphous basic ferric sulphate" (DABFS), which had rapid settling characteristics, yet was X-ray amorphous.

The requirements for DABFS formation (see section 7.4.2) were met by the above experimental conditions. Presumably sample 60 is also the product reported as DABFS, which this work has identified as a form of ferrihydrite.

Although results indicate that this precipitate is anomalous to the expected behaviour of 6-XRD line ferrihydrite, they are remarkably similar to ferrihydrite precipitated with gypsum (sample 55, Section 8.3.2).

Clearly sulphate ion must play a role in the process since high crystallinity and fast settling rates were not observed in the chloride media. One possibility is for sulphate ion to adsorb onto cationic iron polymer (pH < 5) and mechanically hold it in place for precipitation (e.g. goethite from the caustic - sulphate system), later being expelled with the elevation of pH.
Another role would be to promote the formation of dense amorphous basic ferric sulphate (DABFS - see Section 7.4.2) upon the surface of the dissolving magnesia particle. A dense DABFS like precipitate would hinder the diffusion of \( \text{OH}^- \), which would inhibit the formation of gelatinous iron polymer. The short chain species that form with slow diffusion of \( \text{OH}^- \), agglomerate with the growing DABFS particle while being assisted in site allocation by specifically absorbed sulphate.

Since goethite was not identified in the precipitates from this system, the presence of magnesium must have hindered the dissolution / reprecipitation process necessary to convert ferrihydrite into goethite, as found in the caustic - sulphate system. This is presumably done by hindering cleavage of oxo-bridging between iron atoms.

### 9.2.2 CHLORIDE AND SULPHATE MIXTURES

Two groups of experiments were conducted in this system. The first group involved the use of iron (III) chloride (0.3 mol dm\(^{-3}\) Cl\(^{-} \)) with added sodium sulphate. Again dry magnesium oxide was used as alkali.

Experiment 61 contained 0.075 mol dm\(^{-3}\) sulphate (from added Na\(_2\)SO\(_4\)), experiment 62 contained 0.25 mol dm\(^{-3}\) sulphate and experiment 63 contained 0.15 mol dm\(^{-3}\) sulphate. The chloride concentration was held at 0.3 mol dm\(^{-3}\). Results are tabulated below in Table 9.2.
TABLE 9.2: PRECIPITATES FROM IRON (III) CHLORIDE AND SULPHATE MIXTURES WITH MgO

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>[SO₄²⁻] mol dm⁻³</th>
<th>[CL⁻] mol dm⁻³</th>
<th>XRD</th>
<th>SEDIMENT VOLUME dm⁻³</th>
<th>SETTLING RATE m h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>56</td>
<td>---</td>
<td>0.3</td>
<td>Iowaite, Ferricydrite</td>
<td>0.080</td>
<td>0.02</td>
</tr>
<tr>
<td>60</td>
<td>0.15</td>
<td>---</td>
<td>Ferricydrite</td>
<td>0.015</td>
<td>1.14</td>
</tr>
<tr>
<td>61</td>
<td>0.075</td>
<td>0.3</td>
<td>Ferricydrite</td>
<td>0.030</td>
<td>1.62</td>
</tr>
<tr>
<td>63</td>
<td>0.15</td>
<td>0.3</td>
<td>Ferricydrite</td>
<td>0.028</td>
<td>0.83</td>
</tr>
<tr>
<td>62</td>
<td>0.25</td>
<td>0.3</td>
<td>Ferricydrite</td>
<td>0.044</td>
<td>0.73</td>
</tr>
<tr>
<td>65</td>
<td>0.113</td>
<td>0.075</td>
<td>Ferricydrite</td>
<td>0.014</td>
<td>1.08</td>
</tr>
<tr>
<td>64</td>
<td>0.075</td>
<td>0.15</td>
<td>Ferricydrite</td>
<td>0.017</td>
<td>1.08</td>
</tr>
<tr>
<td>66</td>
<td>0.04</td>
<td>0.225</td>
<td>Iowaite, Ferricydrite</td>
<td>0.074</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The settling rates for samples 61, 62 and 63 were particularly high, being 1.62, 0.73 and 0.83 m h⁻¹ respectively. The variation in settling rate is best explained in terms of Figure 9.4 below. In the absence of sulphate, the settling rate of the precipitate is very slow. But with the addition of 0.075 mol dm⁻³ sulphate, there is a dramatic improvement in the settling rate. With increased sulphate addition, the settling rate passes through a maximum and falls.

Even at higher sulphate concentrations, the slowest settling rate is 10 to 20 times faster than the comparable magnesium oxide - chloride system. Clearly it is the iron to sulphate ratio, and / or the sulphate concentration itself that influences the precipitation process by adsorption and balancing surface charge.
Figure 9.4. The plot of settling rate against sulphate concentration shows a dramatic rise with the inclusion of 0.075 mol dm$^{-3}$ sulphate, followed by a tapering off as the concentration rises further.
In the second set of experiments, the iron concentration was kept at 0.1 mol dm$^{-3}$ and the ratio of iron (III) chloride to iron (III) sulphate changed (see Table 9.2). The settling rate of sample 66 (Fe$^{3+}$ : SO$_4^{2-}$ was 5:2) was as slow as comparable chloride only systems, reflecting the low level of sulphate present. There appears to be a minimum sulphate concentration around 0.05 mol dm$^{-3}$, below which it is no longer effective. This is consistent with the DABFS formation theory (Flynn 1990), whereby the sulphate concentration must be between 0.05 and 0.2 mol dm$^{-3}$ to facilitate the formation of DABFS at 25 °C. Experiments 62 and 66 were outside the optimum DABFS formation conditions.

The presence of up to 0.3 mol dm$^{-3}$ chloride or ratios of Cl$^{-}$ : SO$_4^{2-}$ up to 4:1 do not hinder the process. Flynn (1990) reported that a chloride concentration in excess of 2 mol dm$^{-3}$ prevented the formation of DABFS, probably by displacing the sulphate complex.

The results from sections 9.2.1 and 9.2.2 suggest that the presence of sulphate is fundamental to the precipitation of highly ordered ferrilydrite (DABFS). As sulphate complexes with Fe$^{3+}$ forming FeSO$_4^{+}$ (Sapiensko et al. 1977 and Magini 1979), it is feasible that the direct influence of the complexed sulphate holds polymeric iron chains in position for growth of the highly ordered ferrilydrite (DABFS). This is consistent with the findings of Flynn (1990) who suggested that the sulphate remained within the final structure; proposing the formula Fe$_4$(OH)$_{16}$SO$_4$.2H$_2$O.
The Mössbauer spectra of sample 60 showed a narrow spectral line width indicating a very well defined chemical environment for the iron. This precludes sulphate being chemically complexed to the iron atom, but rather held within the ferrihydrite lattice by electrostatic forces and are therefore labile. These results are supported by Parfitt and Smart (1977) who have shown that sulphate can adsorb onto goethite surfaces.

Flynn (1990) found DABFS to form only when the rate of release of OH⁻ was controlled using weak alkalis such as ammonium bicarbonate, potassium bicarbonate, sodium bicarbonate and lithium carbonate. When he used strong alkalis such as sodium carbonate, sodium hydroxide or ammonium hydroxide, the gelatinous "hydrous oxide" (probably ferrihydrite). This explains why DABFS and rapidly settling precipitates were not obtained with caustic addition to sulphate or mixed sulphate and chloride systems.

9.3 HIGHER IRON CONCENTRATIONS

As the magnesia - sulphate system precipitated well ordered products of good settling ability, further experimentation was conducted upon it to see if the enormous advantage in settling rates held for higher concentrations of iron. The settling rates were 0.89 m h⁻¹ for 0.2 mol dm⁻³ Fe (sample 67) and 0.22 m h⁻¹ for 0.4 mol dm⁻³ Fe (sample 68). As the solids concentration increased, there was a subsequent decrease in the settling rate as expected. However, the formation of well ordered ferrihydrite (DABFS) was observed at iron concentrations of 0.4 mol dm⁻³, extending the formation range reported by Flynn (1990).
9.4 COMPARISON OF MgO, Mg(OH)₂, MgCO₃

The effect of using dry magnesium oxide (MgO), slaked magnesia (Mg(OH)₂) and magnesium carbonate (MgCO₃) were compared using the mixed chloride and sulphate iron (III) system (see Table 9.3 below). The sulphate concentration was 0.075 mol dm⁻³, while the sulphate to chloride ratio was 1:2.

**TABLE 9.3: PRECIPITATES OF IRON (III) WITH MgO, Mg(OH)₂, MgCO₃**

<table>
<thead>
<tr>
<th>SAMPLE NO</th>
<th>ALKALI</th>
<th>XRD</th>
<th>SEDIMENT VOLUME dm⁻³</th>
<th>SETTLING RATE m h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>MgO</td>
<td>Ferrhydrite</td>
<td>0.017</td>
<td>1.08</td>
</tr>
<tr>
<td>69</td>
<td>Mg(OH)₂</td>
<td>Ferrhydrite</td>
<td>0.016</td>
<td>0.89</td>
</tr>
<tr>
<td>70</td>
<td>MgCO₃</td>
<td>Ferrhydrite</td>
<td>0.040</td>
<td>0.13</td>
</tr>
</tbody>
</table>

These results indicate that the samples from ambient temperature precipitation of iron (III) using powdered magnesium oxide (sample 64) and slaked magnesia (sample 69) are very similar in settling rate and sediment volume.

Magnesium carbonate has a low rate of reaction with acid above pH 3 and its low solubility in the final stages of neutralisation prevented its complete dissolution, allowing the formation of hydromagnesite (Mg₅(CO₃)₄(OH)₂·4H₂O) which was detected in sample 70 by XRD. It is likely that carbonate ion will compete with sulphate ion in the latter stages of neutralisation and interfere with the formation of DABFS. However, the slower settling rate may also be a result of hydromagnesite formation. The precipitates of ferrhydrite and gypsum were slower to settle than DABFS, formed under similar conditions using magnesia.
9.5 CONCLUSIONS

The use of magnesium oxide to hydrolyse the pure iron (III) chloride system has no advantage over caustic and is less effective than lime upon the settling rate and sediment volume. It is felt that the dissolution of magnesia in a well stirred reactor allows the iron oxyhydroxides to equilibrate in solution and does not offer particle surfaces, or regions of high pH to encourage agglomeration and crystallisation.

The precipitates formed in the presence of sulphate ion are rapidly settling and believed to be due to the formation of dense amorphous basic ferric sulphate (DABFS), which is similar in high resolution XRD and Mössbauer spectroscopy to 6-line ferrihydrite. Sulphate ion is believed to absorb onto the red cationic hydrolytic polymer formed at pH 2-3 and is physically rather than chemically incorporated into the ferrihydrite like structure.

The optimum conditions for rapid settling precipitates closely match those for formation of DABFS. At 25°C, these conditions are < 0.2 mol dm⁻³ Fe (III) and 0.05 - 0.20 mol dm⁻³ SO₄²⁻. The presence of up to 0.3 mol dm⁻³ Cl⁻ and mole ratios of Cl⁻ : SO₄²⁻ up to 4:1 have little effect.

There is little difference in the use of dry or slaked magnesia, but slower settling, voluminous precipitates were obtained using MgCO₃.
CHAPTER 10

PRECIPITATION FROM IRON (II) SOLUTIONS USING CAUSTIC, LIME AND MAGNESIA

Not all industrial waste liquors contain iron in the oxidised Fe$^{3+}$ form. Many processes, such as synthetic rutile plants, contain iron (II) in their waste liquors. The presence of iron (II) allows for the precipitation of crystalline magnetite, well known for rapid gravity dewatering. However, formation conditions often involve high temperatures (60 to 100°C), elevated pH (pH 9 - 10), controlled iron (II) to iron (III) ratios (1 : 1) and restricted oxidation rates (see Section 3.7). Some processes deliberately reduce iron (III) liquors to obtain the required iron (II), but where a multitude of contaminant cations and anions are present, highly crystalline magnetite is difficult to produce (Kiyama 1974). Due to the cost of heating waste liquors, a low temperature alternative is attractive.

The iron (II) system was therefore examined to further investigate the precipitation processes where iron oxides and oxyhydroxides can be readily settled and dewatered.
10.1 NUCLEATION OF Fe(OH)$_2$ USING CAUSTIC

The effect of induction and nucleation upon hydrolysis products from the iron (II) chloride system were investigated. Sodium hydroxide was used as the alkali to establish a simple system while the iron concentration was constant at 0.1 mol dm$^{-3}$.

The proportion of alkali added in the first step of the precipitation process was varied as with previous experiments in the iron (III) system. Precipitate identification by XRD and characterisation by settling rate and sediment volume are listed below in Table 10.1.

All experiments were conducted at ambient temperature, around 20°C. X-ray diffraction determined the presence of either magnetite or maghemite in all samples. Samples 71, 72 and 73 also contained some poorly crystalline akaganeite (as suggested by peak width and size) and an amorphous iron component. Samples 74 and 75 were highly crystalline, as determined by the very strong yet narrow XRD peaks. The increased crystallinity resulted in the very high settling rates achieved for samples 74 and 75 (0.53 and 1.42 m h$^{-1}$ respectively), shown in Figure 10.1. The sediment volumes for samples 74 and 75 were 0.012 and 0.015 dm$^{-3}$ respectively, suggesting the crystalline particles to be small yet of relative high density. The sediment volume for samples 74 and 75 would give a sediment density of approximately 11 % w/w.
Figure 10.1. Settling curves for samples 74 and 75.
### TABLE 10.1: EFFECT OF % NaOH IN FIRST STEP UPON PRECIPITATE SETTLING FROM IRON (II) CHLORIDE SOLUTION

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>% NaOH IN FIRST STEP*</th>
<th>pH OF AGING STEP*</th>
<th>XRD</th>
<th>SETTLING RATE $\text{m h}^{-1}$</th>
<th>SEDIMENT VOLUME $\text{dm}^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>72</td>
<td>40 %</td>
<td>7.1</td>
<td>Magnetite or Maghemite Akaganeite</td>
<td>0.06</td>
<td>0.042</td>
</tr>
<tr>
<td>75</td>
<td>50 %</td>
<td>7.2</td>
<td>Magnetite or Maghemite</td>
<td>1.42</td>
<td>0.015</td>
</tr>
<tr>
<td>74</td>
<td>60 %</td>
<td>7.1</td>
<td>Magnetite or Maghemite</td>
<td>0.53</td>
<td>0.012</td>
</tr>
<tr>
<td>73</td>
<td>75 %</td>
<td>7.6</td>
<td>Magnetite or Maghemite Akaganeite</td>
<td>0.01</td>
<td>0.116</td>
</tr>
<tr>
<td>71</td>
<td>85 %</td>
<td>7.7</td>
<td>Magnetite or Maghemite Akaganeite</td>
<td>0.01</td>
<td>0.076</td>
</tr>
</tbody>
</table>

### NOTES

* % of stoichiometric NaOH required to precipitate FeCl$_2$ as Fe$_2$O$_3$ and raise pH to 9.

+ Note that iron (II) hydroxides precipitate between pH 7 and 8, while the iron (III) system precipitates between pH 2 and 3.
A transmission electron micrograph of sample 75 can be seen in Figure 10.2. The shape of the crystals do not differentiate between magnetite (Fe₃O₄) or maghemite (γFe₂O₃), but an absence of amorphous material is evident.

Mössbauer spectroscopy was able to confirm that the precipitates from the above listed experiments were maghemite (see Figure 10.3). While the formation of maghemite has been reported at ambient temperatures (Schwertmann and Cornell 1991), it was unexpected to produce highly crystalline maghemite of rapid settling ability.

The fastest settling rates were achieved with about 50 to 60 % of the total caustic added in the first step of the two step precipitation process. 50 % of the total caustic (ie for Fe³⁺) would result in about 75 % of the iron (II) being precipitated as Fe(OH)₂. It appears that the use of a well mixed / aerated intermediate aging period has assisted with nucleation of a more ordered precipitate, presumably by catalysing the oxidation of the iron (II). Oxidation is known to primarily occur at particle surfaces (Feitknecht 1959, Kiyama 1974) and a certain level of Fe(OH)₂ must be precipitated to optimise the oxygen mass transfer from air.

It is believed that during the well stirred intermediate aging period, oxidation of the iron (II) solution begins with adsorption of Fe²⁺ onto the negatively surface charged Fe(OH)₂ particle at pH 7. Charge neutralisation promotes agglomeration and fast settling precipitates. Contact with dissolved oxygen oxidises the adsorbed species to form FeO·Fe₂O₃ (magnetite).
Figure 10.2. TEM photograph of sample 75 showing a highly crystalline morphology. BAR = 0.1 μm.
Figure 10.3. Mössbauer spectra of sample 75 indicating only maghemite is present.
If too little caustic is present for the intermediate aging step, then the surface area of Fe(OH)_2 particles is limited and oxidation is slow. If too much caustic is added in the first step (>75%), then the precipitation of Fe(OH)_2 reduces the level of Fe^{2+} in solution, preventing surface charge neutralisation and the formation of magnetite. Hence settling rates are low.

When the level of Fe^{2+} is low, absorption of dissolved oxygen would also oxidise the Fe(OH)_2 precipitate. The resulting precipitate is then maghemite, akaganeite or lepidocrocite, according to the ratio of Fe^{2+} to Fe^{3+}, the ratio of Fe^{3+} to Cl^- and the rate of conversion (Feitknecht 1959, Kiyama 1974). The large difference in settling rates according to the % NaOH added in the first step suggests that the charge on the surface of Fe(OH)_2 around pH 7 is sensitive to the concentration of Fe^{2+} present in solution.

It should also be noted that the slow specific absorption of dissolved oxygen, followed by oxidation at that site, fundamentally favours a more crystalline product by the site dependant mechanistic pathway.

10.2 THE OXIDATION PROCESS

To confirm that the oxidation process was in fact via reaction at the particle surface and not directly from solution, samples 11 and 12 were precipitated under different oxygen conditions at 19°C. Sodium hydroxide was added in the first step to a level of 50 %, according to the standard procedure.
Experiment 11 was purged with nitrogen prior to precipitation, but then oxygen was allowed to enter the system by air entrainment due to turbulent mixing. For experiment 12, the system was bubbled with oxygen during precipitation to ensure maximum oxygenation of the solution.

It was postulated that if oxidation of Fe$^{2+}$ occurred in solution from the dissolved oxygen, then there would be a large difference in the crystallinity and settling rates between sample 11 and sample 12 due to the relative speed of oxidation and precipitation. However if the process occurred by oxygen adsorption onto particle surfaces, then the crystallinity and settling rates etc would be similar.

XRD detected the presence of either magnetite or maghemite in both samples, while Mössbauer spectra clearly gave a single sextet of peaks conclusively determining both the precipitates to be maghemite.

**TABLE 10.2: EFFECT ON PRECIPITATE SETTLING OF DIFFERING OXIDATION CONDITIONS**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>CONDITIONS</th>
<th>MOSSBAUER / XRD</th>
<th>SETTLING RATE m h$^{-1}$</th>
<th>SEDIMENT VOLUME dm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>N$_2$ purge, air entrainment</td>
<td>Maghemite</td>
<td>1.43</td>
<td>0.019</td>
</tr>
<tr>
<td>12</td>
<td>O$_2$ added</td>
<td>Maghemite</td>
<td>1.43</td>
<td>0.012</td>
</tr>
</tbody>
</table>

The settling rate and sediment volume indicated samples 11 and 12 are identical, consisting of highly crystalline dense small particles.
These results indicate that the oxygen mass transfer into solution is not the rate determining step and is consistent with oxygen adsorption onto a surface followed by iron (II) adsorption and subsequent oxidation. Had the iron (II) been oxidised in solution, then a greater difference in the precipitates of samples 75, 11 and 12 would have been expected.

10.3 EFFECT OF TEMPERATURE

Elevated temperatures have been reported as beneficial to the production of magnetite (Tamura et al. 1981a), while Schwertmann and Cornell (1991) described higher temperatures as favouring the formation of maghemite. Keijama (1974) was able to produce magnetite at 40°C in a highly controlled environment while Regazzoni et al. (1981) produced magnetite and some amorphous material (presumably lepidocrocite or ferrihydrite) at room temperature after two weeks. Tamura et al. (1983) reported the transformation of lepidocrocite into magnetite at ambient temperature required 60 hours in the presence of iron (II).

In an attempt to produce magnetite, experiment 76 was conducted at 70°C using the iron (II) chloride - caustic system, in which 55 % of the total caustic was added during the first step of the two step process.

While XRD determined the precipitate to be either magnetite or maghemite, the Mössbauer spectra shown below in Figure 10.4 indicated that the precipitate was principally maghemite however some magnetite was present.
Figure 10.4. Mössbauer spectra of sample 76 indicating the presence of maghemite and magnetite.
The Mössbauer spectra of magnetite indicated partial oxidation, suggesting over oxidation of the sample. There was also a small central component consisting of 7% of the spectral area representing ferrihydrite, again indicating over oxidation has occurred.

A transmission electron micrograph of sample 76 (Figure 10.5) shows gelatinous ferrihydrite surrounding maghemite crystals. Note that over oxidation would lead to excess or rapid production of iron (III) which would kinetically favour the precipitation of ferrihydrite.

Surprisingly, the overall settling rate for sample 76 was slower than the maghemite produced at ambient temperature in experiment 75. The settling rate for sample 76 was 0.23 m h\(^{-1}\), compared to 1.42 m h\(^{-1}\) for sample 75 (see Table 10.3). This is attributed, in part, to less adsorption of Fe\(^{2+}\) onto Fe(OH)\(_2\) and hence less neutralisation of negative surface charge.

**TABLE 10.3: EFFECT OF TEMPERATURE ON THE PRECIPITATION OF MAGNETITE**

<table>
<thead>
<tr>
<th>SAMPLE NO</th>
<th>TEMPERATURE °C</th>
<th>XRD / Mössbauer</th>
<th>SETTLING RATE m h(^{-1})</th>
<th>SEDIMENT VOLUME dm(^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>76</td>
<td>70</td>
<td>Maghemite, Magnetite &amp; Ferrihydrite</td>
<td>0.23</td>
<td>0.028</td>
</tr>
<tr>
<td>75</td>
<td>18</td>
<td>Maghemite</td>
<td>1.42</td>
<td>0.015</td>
</tr>
</tbody>
</table>

It is clear that whilst elevated temperature assisted the formation of magnetite, it also increased the oxidation rate producing more iron (III) in experiment 76. This resulted in partial oxidation of magnetite and ferrihydrite formation.
Figure 10.5. TEM photograph of sample 76 showing the crystalline precipitate lightly covered with gelatinous material. BAR = 0.1 μm.
Changing the oxidation rate can heavily influence the morphology of the resulting precipitates. Schwertmann and Cornell (1991) report that during the formation of maghemite, increased rates of oxidation lead to the formation of lepidocrocite while higher initial proportions of iron (III) produced ferrihydrite.

The oxidation process relies upon the surface adsorption of Fe$^{2+}$ and oxygen upon the Fe(OH)$_2$ particle (Bertsch et al. 1989). The Fe$^{2+}$ species, which is specifically adsorbed onto the particle, is then oxidised. Elevated temperatures can change this process in several ways. Higher temperature decreases the surface adsorption of oxygen limiting mass transfer. The solubility of oxygen in solution is reduced and the adsorption of Fe$^{2+}$ species onto Fe(OH)$_2$ decreases due to decreased surface area with increased crystallinity.

At the elevated temperature and pH, the oxidation of iron (II) in solution increases even with the reduced solubility of oxygen (Tamura et al., 1976a; Tamaura et al., 1981a; Sada et al., 1988). This allows more Fe(OH)$_3$ polymeric species to develop, which in turn facilitates oxygen transfer into solution via surface adsorption. This would result in the initial pure iron (II) solution taking some time to begin to oxidise (i.e. induction), followed by increasingly rapid activity.
10.4 THE EFFECT OF LIME AND MAGNESIA ON THE IRON (II) CHLORIDE SYSTEM

Experiment 77 was conducted as per the standard experimental method at 19°C, using 60% of the slaked lime in the first step of the two step process. Oxidation was by the introduction of air through turbulent mixing.

The product from this experiment was found to consist of poorly crystalline magnetite or maghemite, as indicated by the broad XRD peaks and ferrihydrite. The settling rate was 0.09 m h⁻¹ and the sediment volume was 0.031 dm³, consistent with a very small particle size. Results are tabulated in Table 10.4.

Sample 78 was precipitated at 70°C and XRD detected either magnetite or maghemite along with calcite (CaCO₃). The Mössbauer spectra shown in Figure 10.6, again indicated the presence of some magnetite along with maghemite.

A central doublet (18%) may be ferrihydrite but could also be associated with a broad featureless component (31%) which is possibly akaganeite. Room temperature Mössbauer spectra make absolute identification and differentiation between these components difficult, as the Neel Temperature of akaganeite is close to ambient (see Section 4.2.5.4). Thus low temperature work would be required to differentiate signals.

Unlike the results using NaOH, the settling rate at 70 °C was faster than at 19°C, but equivalent to that precipitated using caustic (see Table 10.4).
Figure 10.6. Mössbauer spectra of sample 78 indicating the presence of maghemite, magnetite and possibly akaganeite.
### TABLE 10.4: EFFECT OF (Ca(OH)$_2$) ON THE IRON (II) CHLORIDE SYSTEM

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>ALKALI</th>
<th>TEMPERATURE °C</th>
<th>XRD / MOSSBAUER</th>
<th>SETTLING RATE m h$^{-1}$</th>
<th>SEDIMENT VOLUME dm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>77</td>
<td>Ca(OH)$_2$</td>
<td>19</td>
<td>Maghemite, Ferrihydrite</td>
<td>0.09</td>
<td>0.031</td>
</tr>
<tr>
<td>78</td>
<td>Ca(OH)$_2$</td>
<td>70</td>
<td>Maghemite, Magnetite &amp; Akaganeite ?</td>
<td>0.21</td>
<td>0.036</td>
</tr>
<tr>
<td>79</td>
<td>MgO</td>
<td>20</td>
<td>Magnetite / Maghemite</td>
<td>0.10</td>
<td>0.054</td>
</tr>
<tr>
<td>75</td>
<td>NaOH</td>
<td>18</td>
<td>Maghemite</td>
<td>1.42</td>
<td>0.015</td>
</tr>
<tr>
<td>76</td>
<td>NaOH</td>
<td>70</td>
<td>Maghemite, Magnetite &amp; Akaganeite ?</td>
<td>0.23</td>
<td>0.028</td>
</tr>
</tbody>
</table>

With lime, the elevation of precipitation temperature was beneficial to the precipitate crystallinity; as indicated from the improved settling rate. This is in accord with general findings of others (Tamura et al. 1981a, Schwertmann and Cornell 1991). The inferior settling rate compared to caustic at ambient temperature is attributed to the poor crystallinity of the magnetite or maghemite produced and to the presence of ferrihydrite.

It appears that at ambient temperature, the slowly dissolving calcium oxide & hydroxide particles provide additional surface for oxygen and Fe$^{2+}$ adsorption. Therefore a proportion of Fe$^{2+}$ will be adsorbed and oxidised at the surface of the lime particle and neutralisation of surface charge less effective. Furthermore, the rate of oxidation is known to increase with elevated pH (Kiyama 1974), hence the oxidation of iron (II) to iron (III) in the high pH region surrounding the lime particle is likely to be more rapid than in homogeneous solutions using caustic, resulting in the formation of ferrihydrite.
Similar results were obtained when magnesia was substituted for lime. Experiment 79 had 60 % of the dry magnesium oxide added at the first step of the standard two step precipitation process. The product from this experiment consisted of poorly crystalline magnetite or maghemite (as determined by broad XRD peaks) and ferrihydrite or very poor lepidocrocite. The settling rate was 0.10 m h⁻¹ and the sediment volume was 0.054 dm⁻³; comparable to the lime - iron (II) chloride system but inferior to the caustic - iron (II) chloride system.

10.5 MIXED IRON (II)/(III) CHLORIDE SYSTEMS WITH CAUSTIC, LIME AND MAGNESIA

During the preceding experiments it was noted that the slaked lime and magnesia systems produced a bright orange-red precipitate of ferrihydrite about pH 3.5. Ferrihydrite is autocatalytic to the oxidation of iron (II) (Tamura et al. 1976b, 1980); this is known to influence the morphology of the precipitates (Fierro et al. 1987).

To investigate these observations, several sets of experiments were conducted using various initial concentrations of iron (III) mixed with the iron (II) chloride system. Three types of alkali were used; caustic, lime and magnesia.
10.5.1 THE SODIUM HYDROXIDE MIXED IRON (II)/(III) CHLORIDE SYSTEM

Different ratios of iron (II) to iron (III) were investigated, with 55 % of the caustic added in the first step of a standard two step process. The initial quantity of iron (III) chloride present is listed below in Table 10.5.

**TABLE 10.5 THE CAUSTIC - MIXED IRON (II)/(III) CHLORIDE SYSTEM**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>% IRON (III)</th>
<th>pH OF AGING</th>
<th>XRD / MöSSBAUER</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>10 %</td>
<td>7.2</td>
<td>Maghemite, Ferrihydrite</td>
<td>0.71</td>
<td>0.018</td>
</tr>
<tr>
<td>81</td>
<td>25 %</td>
<td>4.3</td>
<td>Maghemite, Akaganeite, Ferrihydrite</td>
<td>0.56</td>
<td>0.016</td>
</tr>
<tr>
<td>82</td>
<td>50 %</td>
<td>2.5</td>
<td>Maghemite, Akaganeite, Ferrihydrite</td>
<td>0.37</td>
<td>0.015</td>
</tr>
<tr>
<td>83</td>
<td>75 %</td>
<td>2.2</td>
<td>Akaganeite, Ferrihydrite</td>
<td>0.07</td>
<td>0.055</td>
</tr>
</tbody>
</table>

Ferrihydrite was detected in all precipitates as confirmed by XRD. The decreasing settling rates are directly related to the proportion of ferrihydrite present and the higher initial level of iron (III) This is in accord with the findings of Schwertmann and Cornell (1991).

When the majority of the iron is initially in the iron (III) form, as in experiment 83, oxidation of iron (II) is catalysed by iron (III) oxyhydroxides. Thus very little iron (II) remains to assist precipitation of magnetite or maghemite and the system behaves like pure FeCl₃.
The settling rates for samples 80, 81 and 82 were quite reasonable. It appears that the production of maghemite can tolerate quite a high initial level of iron (III) in the system but there is a direct relationship between the starting proportion of iron (III) and the settling rate of the resulting precipitates. Presumably there is sufficient Fe(OH)$_2$ with negative surface charge precipitated at pH 7 during the second step addition to facilitate the agglomeration of cationic hydrolytic polymer and subsequent oxidation and precipitation of maghemite.

**10.5.2 THE LIME MIXED IRON (II)/(III) CHLORIDE SYSTEM**

These experiments were conducted according to the standard two step precipitation method, using slaked lime as the alkali. With the lime particles believed to accelerate iron (II) oxidation and ferrihydrite precipitation, the addition of iron (III) to the initial solution is expected to be detrimental to the crystallinity and settling rates. Results listed in Table 10.6 reflect these trends.

**TABLE 10.6: THE EFFECT ON SETTLING RATES OF THE LIME - MIXED IRON (II)/(III) CHLORIDE SYSTEM**

<table>
<thead>
<tr>
<th>SAMPLE N°</th>
<th>% Iron (III)</th>
<th>pH OF AGING</th>
<th>XRD</th>
<th>SETTLING RATE m h$^{-1}$</th>
<th>SEDIMENT VOLUME dm$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>84</td>
<td>10 %</td>
<td>4.6</td>
<td>Akaganeite, Magnetite or Maghemite, Calcite, Ferrihydrite</td>
<td>0.36</td>
<td>0.015</td>
</tr>
<tr>
<td>85</td>
<td>25 %</td>
<td>4.6</td>
<td>Akaganeite, Calcite, Ferrihydrite</td>
<td>0.09</td>
<td>0.028</td>
</tr>
<tr>
<td>86</td>
<td>50 %</td>
<td>3.2</td>
<td>Akaganeite, Calcite, Ferrihydrite</td>
<td>0.06</td>
<td>0.038</td>
</tr>
<tr>
<td>87</td>
<td>75 %</td>
<td>2.3</td>
<td>Akaganeite, Calcite, Ferrihydrite</td>
<td>0.07</td>
<td>0.040</td>
</tr>
</tbody>
</table>
The pH of the intermediate aging period is a reflection of the amount of iron (III) present. Even with only 10-25 % of the initial iron present as iron (III), oxidation of iron (II) during aging with 50 % lime addition is sufficient to maintain the equilibrium pH around 4, rather than 7 associated with the presence of Fe(OH)$_2$.

X-ray diffraction patterns detected the presence of maghemite only in sample 84. Samples containing only ferrihydrite, akaganeite and calcite, were slow to settle. The absence of maghemite in these samples is evidence that the iron (II) was rapidly oxidised during aging, then precipitated as ferrihydrite and akaganeite in the second step lime addition.

It is surprising to see evidence of akaganeite in the XRD, since a chloride concentration of 0.3 mol dm$^{-3}$ is regarded to be too low to produce akaganeite (see Section 7.2). This indicates that it is not the concentration of chloride that is important but rather the adsorption of chloride ion and the ratio of chloride to iron (III).

It appears that the slow oxidation of iron (II) is required for the precipitation of maghemite at ambient temperature using slaked lime.
10.5.3 THE MAGNESIA - MIXED IRON (II)/(III) CHLORIDE SYSTEM

Identical experiments to those above were conducted, but using magnesia as the neutralising media. The results are listed below in Table 10.7.

**TABLE 10.7: THE EFFECT ON SETTLING RATES OF THE MAGNESIA - MIXED IRON (II)/(III) CHLORIDE SYSTEM**

<table>
<thead>
<tr>
<th>SAMPLE NO</th>
<th>% IRON (III)</th>
<th>pH OF AGING</th>
<th>XRD</th>
<th>SETTLING RATE m h⁻¹</th>
<th>SEDIMENT VOLUME dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>88</td>
<td>10 %</td>
<td>4.7</td>
<td>Iowaitte, Ferrihydrite</td>
<td>0.32</td>
<td>0.038</td>
</tr>
<tr>
<td>89</td>
<td>25 %</td>
<td>4.7</td>
<td>Iowaitte, Ferrihydrite</td>
<td>0.23</td>
<td>0.036</td>
</tr>
<tr>
<td>90</td>
<td>50 %</td>
<td>4.5</td>
<td>Iowaitte, Ferrihydrite</td>
<td>0.12</td>
<td>0.047</td>
</tr>
<tr>
<td>91</td>
<td>75 %</td>
<td>4.0</td>
<td>Iowaitte, Ferrihydrite</td>
<td>0.05</td>
<td>0.058</td>
</tr>
</tbody>
</table>

The product from these experiments were identified by XRD as ferrihydrite and iowaitte, a magnesium iron oxyhydroxide hydrate (Mg₄Fe(OH)₈OCl·xH₂O).

Again the trend in the settling rates is quite evident and predictable. The higher the percentage iron (III) originally present, the more ferrihydrite produced, the slower the settling rate and the higher the settled sediment volume.
10.6 CONCLUSIONS

Highly crystalline maghemite of excellent settling ability was precipitated during the aerial oxidation of an iron (II) solution at ambient temperature, when 50% of the total caustic was added in the first step of a two step process. The presence of Fe$^{2+}$ is believed to neutralise negatively surface charged Fe(OH)$_2$. This precipitation of maghemite has potential as an industrial process at ambient temperature, however further work needs to be conducted into the rate of oxidation and whether these conditions can be duplicated in industrial plants.

While the use of elevated temperature assisted the formation of magnetite in the caustic system, it also increased the oxidation rate of iron (II) producing ferrihydrite.

Precipitates from the slaked lime - iron (II) chloride system generally had inferior settling rates to those samples precipitated at ambient temperature from the caustic - iron (II) chloride system. The use of magnesium oxide for hydrolysis of an iron (II) chloride system produced a precipitate that had similar settling characteristics to those from the slaked lime experiments.

When the ratio of iron (III) : iron (II) is < 1:3 in solution, all three neutralisation media produce crystalline maghemite with reasonable settling rates at ambient temperature. Caustic allows an iron (III) to iron (II) ratio of up to 1:1 and produces crystalline maghemite with a fast settling rate. This is due to caustic not catalysing the oxidation of iron (II).
It is believed that the presence of slaked lime and magnesia particles catalyse the oxidation of iron (II) by air in a well stirred reactor and produce a ferrihydrite with slow settling ability. This ferrihydrite acts to catalyse the oxidation of iron (II). The use of caustic minimises iron (II) oxidation during aging and is more suitable for treating iron (II) / iron (III) chloride solutions exposed to air.
CHAPTER 11

CONCLUSIONS FOR INDUSTRIAL APPLICATIONS AND RECOMMENDATIONS FOR FURTHER STUDY

The complexity of the iron oxide and oxyhydroxide precipitation process has often meant that industry has been unable to invest time and funding into finding a chemical solution to the dewatering of iron laden effluent. Consequently the approach that has invariably been taken is to use engineering solutions to overcome inadequate precipitation; usually resulting in major capital expenditure and large dewatering and clarification units.

The information contained within this thesis provides some potential chemical answers for the precipitation and dewatering of iron laden industrial effluent. A summary of findings is given below as a series of applications for various chemical environments. This is followed by recommendations for further investigations.

11.1 THE PURE IRON (III) CHLORIDE SYSTEM

Research has shown that the rate of addition of alkali to well stirred iron (III) solutions at ambient temperature has little effect upon the settling ability of the precipitated products. Mixing efficiency, localised pH gradients, high chloride concentration and step wise elevation of pH at ambient temperature similarly had little effect upon the settling rate or sediment volume.
All samples have been identified as ferrihydrite. The use of lime and magnesia in a well stirred reactor had no significant effect except for possible cost savings over the use of caustic. No difference in the precipitates were observed between the use of dry or slaked lime and magnesia. Results are summarised in Tables 11.1, 11.2 & 11.3 representing the caustic, lime and magnesia media respectively; diagrammatically represented in Figure 11.1. The intermediate formed during aging at pH 3 has been shown by Mössbauer spectroscopy to be short chain cationic hydrolytic polymer. The high surface charge of this polymer inhibits agglomeration and rapid settling.

The only variable to improve the settling rate and sediment volume was the influence of temperature. Temperature in excess of 60°C allowed the precipitation of goethite, hematite and ferrihydrite with reasonable inherent settling rates. These results corroborate current industrial practices such as the high temperature, "goethite", "hematite" and "magnetite" processes.

However, the "pulp recycle" process has been recently investigated by Parekh and Aplan (1988) and offers the potential of a low temperature iron precipitation process. The process termed "pulp recycle" or "high density solids recycle" operates by recycling some of the clarifier underflow back into the process. This recycled underflow is first mixed with the alkali where at high pH, negatively charged surface adsorption sites are created on the mineral surfaces. Once delivered into the precipitation chamber, this "activated pulp" acts as a seed material suitable for adsorption of cationic hydrolytic polymer iron species from the slightly acidic solution, hence encouraging agglomeration and precipitate growth.
### TABLE 11.3: SETTLING RATES FOR IRON OXYHYDROXIDES PRODUCED USING MAGNESIA AS THE ALKALI

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>SETTLING RATE m h⁻¹ (IRON OXYHYDROXIDE PHASE)</th>
<th>SEDIMENT VOLUME dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (III), Chloride, 20°C</td>
<td>0.01 - 0.02 (F,I)</td>
<td>0.080 - 0.095</td>
</tr>
<tr>
<td>Iron (III), Chloride, 60°C</td>
<td>0 (F,I)</td>
<td>0.200</td>
</tr>
<tr>
<td>Iron (III), Sulphate, 20 °C</td>
<td>1.14 (F*)</td>
<td>0.015</td>
</tr>
<tr>
<td>Iron (III), Sulphate / Chloride, 20°C</td>
<td>1.08 (F*)</td>
<td>0.017</td>
</tr>
<tr>
<td>Iron (II), Chloride, 20°C</td>
<td>0.10 (Mh,F)</td>
<td>0.054</td>
</tr>
<tr>
<td>Iron (II) / Iron (III), Chloride, 20°C</td>
<td>0.05 (F,I)</td>
<td>0.058</td>
</tr>
</tbody>
</table>

**KEY:**

- **F** = Ferrihydrite
- **F** = DABFS
- **I** = Iwaite
- **Mh** = Maghemite
<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>
<td>0.02</td>
</tr>
<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>
<td>0.17</td>
</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>
<td>1.42</td>
</tr>
<tr>
<td>7</td>
<td>Fe (II) - Cl - 70°C - NaOH</td>
<td>MAGHEMITE, MAGNETITE</td>
<td>0.23</td>
</tr>
<tr>
<td>8</td>
<td>Fe (II)/Fe(III) - Cl - 20°C - NaOH</td>
<td>FERRIHYDRITE, MAGHEMITE, AKAGANEITE</td>
<td>0.37</td>
</tr>
<tr>
<td>9</td>
<td>Fe (III) - Cl - 20°C - CaO</td>
<td>FERRIHYDRITE</td>
<td>0.05</td>
</tr>
<tr>
<td>10</td>
<td>Fe (III) - Cl - 60°C - CaO</td>
<td>FERRIHYDRITE, CALCITE</td>
<td>0.02</td>
</tr>
<tr>
<td>11</td>
<td>Fe (III) - SO4 - 20°C - CaO</td>
<td>FERRIHYDRITE, GYPSUM</td>
<td>0.28</td>
</tr>
<tr>
<td>12</td>
<td>Fe (III) - SO4 /Cl - 20°C - CaO</td>
<td>FERRIHYDRITE, GYPSUM</td>
<td>0.45</td>
</tr>
<tr>
<td>13</td>
<td>Fe (II) - Cl - 20°C - CaO</td>
<td>FERRIHYDRITE, MAGHEMITE</td>
<td>0.09</td>
</tr>
<tr>
<td>14</td>
<td>Fe (II) - Cl - 70°C - CaO</td>
<td>MAGHEMITE, MAGNETITE</td>
<td>0.21</td>
</tr>
<tr>
<td>15</td>
<td>Fe (II)/Fe(III) - Cl - 20°C - CaO</td>
<td>FERRIHYDRITE, AKAGANEITE, CALCITE</td>
<td>0.06</td>
</tr>
<tr>
<td>16</td>
<td>Fe (III) - Cl - 20°C - MgO</td>
<td>FERRIHYDRITE, IOWAITE</td>
<td>0.01</td>
</tr>
<tr>
<td>17</td>
<td>Fe (III) - Cl - 60°C - MgO</td>
<td>FERRIHYDRITE, IOWAITE</td>
<td>0.01</td>
</tr>
<tr>
<td>18</td>
<td>Fe (III) - SO4 - 20°C - MgO</td>
<td>DABFS</td>
<td>1.14</td>
</tr>
<tr>
<td>19</td>
<td>Fe (III) - SO4 /Cl - 20°C - MgO</td>
<td>DABFS</td>
<td>1.08</td>
</tr>
<tr>
<td>20</td>
<td>Fe (II) - Cl - 20°C - MgO</td>
<td>FERRIHYDRITE, MAGHEMITE</td>
<td>0.1</td>
</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>

![Settling Rate Graph](image)

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).
11.2 THE PURE IRON (III) SULPHATE SYSTEM

The use of caustic gave a precipitate of goethite at ambient temperature, however the very small particle size resulted in a slow settling rate.

Lime produced a highly crystalline product of well ordered ferrihydrite (DABFS ?), co-precipitated with gypsum. The precipitates had rapid settling characteristics, however excess gypsum retarded the process.

Precipitation with magnesia produced a highly crystalline, dense and rapid settling precipitate of well ordered ferrihydrite (DABFS), together with some brucite (Mg(OH)₂). The precipitate was similar to or identical to DABFS reported by Flynn (1990). XRD and Mössbauer studies have shown that incorporated sulphate is not chemically or structurally bound to the iron atoms.

DABFS is favoured when OH⁻ is slowly released into solution containing < 0.2 mol dm⁻³ Fe (III) and < 0.2 mol dm⁻³ SO₄²⁻.

The effect of temperature on this system did not improve the settling characteristics and in some cases (eg magnesia) reduced them.
11.3 THE MIXED IRON (III) CHLORIDE / SULPHATE SYSTEM

The effect of a mixed system was dominated by the influence of sulphate. The caustic system failed to precipitate microcrystalline goethite, apparently requiring a higher ratio of sulphate to iron. The rapidly dispersing caustic also does not favour the production of DABFS (Flynn 1990).

With reduced sulphate levels, less gypsum was precipitated when using the lime system allowing the sample to settle faster. These results suggest lime has an advantage over caustic in sulphate media.

The use of magnesia again precipitated a highly crystalline precipitate (DABFS), provided there was sufficient sulphate present in the system.

11.4 THE PURE IRON (II) CHLORIDE SYSTEM

At ambient temperature the use of a well mixed, aerated caustic system precipitated crystalline maghemite of very rapid settling ability and of very low sediment volume. Poor quality maghemite was produced along with ferrihydrite when using lime and magnesia due to enhanced oxidation of iron (II) on the solid particles. The precipitates had slow settling characteristics. Elevated temperature assisted the formation of magnetite in the caustic system, however the major components were maghemite and slow settling ferrihydrite.
11.5 THE MIXED IRON (II) / IRON (III) CHLORIDE SYSTEM

The higher the initial level of iron (III), the greater the quantity of ferricyanide produced and the slower the settling rate. However, the caustic system still produced a precipitate of fair settling ability even with a 50/50 mixture.

11.6 RECOMMENDATIONS FOR FURTHER INVESTIGATION

Further research is required to apply this information to industrial effluent. In this work the concentration of iron (III) or iron (II) was maintained at 0.1 mol dm\(^{-3}\) and the range and concentration of background salts was limited to keep the system as simple as possible. More work is required to determine the effect of iron (III) concentrations and other background salts as found in industrial applications.

Furthermore the precipitates were formed under fixed conditions of stirring, aging and stepwise addition of alkali. The effect of mixing and aging time needs more examination when using lime or magnesia which are slow to dissolve and give regions of high localised pH around their particles. With iron (II) or mixed iron (II)/(III) solutions, the effect of mixing will determine the aeration and rate of oxidation of iron (II) and can be expected to effect the phase of iron oxyhydroxide precipitated. Time did not permit such investigations to be carried out.
Measurements of the surface charge of these gelatinous precipitates is difficult but warrants further investigation, as fast settling rates are attributed in part to surface charge neutralisation by other ions or species in solution. In this regard, one area to investigate is the effect of using flocculating agents, which were purposely avoided in this work to maintain simplicity. These agents often modify the surface charge of the intermediaries or precipitates and can be tailored to suit the ionic strength or pH of the solution.

Frequently industrial effluent treatment and subsequent dewatering processes mix the waste streams from a wide variety of sources, then try to solve the chemical problems that occur particularly with iron precipitation. The findings of this report have shown that iron chemistry can be manipulated to optimise crystalline structure and settling rate. Such manipulation can take place in as little as three hours and this could be dramatically reduced via temperature elevation.

The use of waste heat is possible as temperatures of only 60 to 80°C are very beneficial to the precipitation process. The waste stream containing the iron contaminants could be diverted to an intermediate processing tank where the precipitation of iron can be manipulated. Several ambient temperature options are possible and should also be trialled.
It is important to divert the iron laden waste stream prior to mixing with other effluent to keep the liquid volume down. This allows for easier heating and keeps the chemistry relatively simple (with respect to the mixed effluent system), giving a greater opportunity to precipitate iron in a readily dewaterable form. The slurry is then fed back into the effluent treatment system. The benefits of such a system where the iron has been precipitated as a rapidly settling solid could include:

1) The efficiency of dewatering solids from the effluent should increase allowing greater throughput.

2) The density of underflow sludge from gravity clarifiers should improve and have improved subsequent filtration.

3) Lower flocculant consumption due to the formation of a crystalline material of lower surface area.

4) The overflow from clarifiers should improve, hence the size requirements of settling ponds could decrease.

Possible savings in cost need to cover the requirement of an intermediate processing tank and associated infrastructure.
Other areas for further investigation should include models of industrial dewatering techniques such as the use of pulp recycle, flocculation and filtration methods. The use of flocculants upon the polymerisation and precipitation process itself should also prove informative.

In particular, the use of pulp recycle (described in Section 11.1) has been shown to dramatically improve the settled sediment density of clarifier underflow while operating at ambient temperature. Parekh and Aplan (1988) have shown that lime is highly suitable as the alkali for this process. This thesis has shown that magnesia can precipitate iron (III) with higher crystallinity than those from lime under sulphate or mixed chloride / sulphate environments. It is suggested that a study of the pulp recycle system using magnesia could result in further improvement to iron oxyhydroxide precipitation.
CHAPTER 12

REFERENCES


