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**A ONE-STEP AMBIENT TEMPERATURE FERRITE PROCESS
FOR TREATMENT OF ACID MINE DRAINAGE WATERS**

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**Thesis presented for the
degree of Doctor of Philosophy**

**In the Department of Civil Engineering
University of Cape Town**

**Supervisor
Professor RE Loewenthal**

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I hereby declare that apart from the normal guidance from my supervisor, this thesis is my own unaided work, both in concept and execution. Neither the substance nor any part of the above thesis has been submitted in the past, or is being, or is to be submitted for a degree at this University or at any other university.

Signed by candidate

Barak Eli Morgan

7th October 2005

University of Cape Town

Abstract

Acid mine drainage (AMD) waters are low in pH, very high in dissolved iron, high in non-ferrous (mainly heavy) metals and very high in sulphate salinity. As such, AMD waters present a serious environmental problem in the mining regions of South Africa and elsewhere in the world. Treatment of AMD therefore requires pH neutralisation, removal of ferrous and non-ferrous metals and sulphate removal. This thesis addresses the problem of metals removal from AMD. The approach involves pH elevation and partial oxidation of ferrous iron present in AMD so as to precipitate the ferrite magnetite (Fe_3O_4). Magnetite in turn has the property of incorporating non-ferrous metals into its crystal lattice by cation substitution. Magnetite has several other properties which make its formation an ideal means of metals removal from AMD. Magnetite settles and dewateres extremely well and it is also stable at low pH, making remobilisation of metals into the environment unlikely.

Ferrite formation at elevated temperatures ($>65^\circ\text{C}$) is well established and has been successfully used in Japan to remove dissolved metals from laboratory wastes. The challenge insofar as massive volumes of AMD are concerned is to form ferrites at ambient temperatures. A second challenge is to form ferrites at ambient temperature in the presence of calcium, as lime ($\text{Ca}(\text{OH})_2$) is the most economical agent available for raising pH, but calcium is known to interfere with magnetite formation. To this end a series of batch and steady-state experiments have been performed in order to establish ambient temperature conditions for ferrite formation from AMD-like waters in both the presence and absence of calcium; as well as in the presence of both calcium and some non-ferrous metals commonly found in AMD (Co, Ni, Zn, Mn). The results represent the first well-described proven demonstration of a continuous flow, steady-state ambient temperature ferrite process which works successfully in the presence of calcium.

The process relies upon (1) the property of magnetite/ferrite seed to channel the end-products of oxidation of ferrous solutions in the presence of calcium towards magnetite/ferrite formation; and (2) upon a *contact stabilisation reactor – settler sequence* which serves to enhance the ferrous intermediate : dissolved calcium ratio in

the oxidation reactor so as to overcome the problem of calcium interference in ferrite formation. The feasibility of the process for metals removal from AMD is borne out by a number of robust results pertaining to the quality of the effluent and the density and stability of the resulting sludge.

There are several features of the process described here which render it economically attractive in comparison with existing technologies. Salient among these is the role of the contact stabilisation reactor – settler sequence in separating all the metals in the AMD from ~70% of the bulk AMD volume during the first stage of the process. Thus only ~30% of the bulk AMD volume requires further processing resulting in significantly reduced energy, infrastructure and chemical costs. Another feature of economic significance is the production of a commercially valuable end-product.

For my parents

University of Cape Town

Acknowledgements

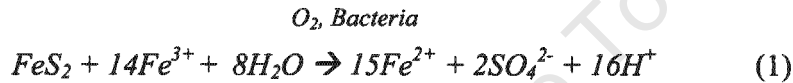
I wish to thank Professor Dick Loewenthal for his expert supervision and unfailing support throughout the duration of this thesis. Ori Lahav is warmly thanked for his guidance in the laboratory during the first two years of this project and for his assistance and support thereafter. Giovanni Hearne performed and interpreted all of the Mössbauer measurements without which this work would not have been possible. The Water Research Commission is thanked for their generous financial support and Greg Steenveld and the other Steering Committee members are thanked for their guidance. Professor George Ekama, Professor Mark Wentzel and Taliep Lakay from the Water Research Laboratory were always available and generous when help was required. Eike von Gerard, Charles Nicholas and Theo Moyana in the workshop are thanked for their technical contribution. Hector Maphungwa and Charles May are thanked for always being available for transporting gas cylinders up to the lab. Stephney Payne and Helen Divey are thanked for performing the atomic absorption measurements and Terry Davies is thanked for help with using the XRD apparatus. The Inter-Library Loans staff are thanked for their efficient service. Special thanks are due to Professor Jenny Day for introducing me to aquatic chemistry and Prof Loewenthal in the first place. Finally I thank Jos Thorne for much too many things to mention.

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Chapter 1 Introduction

Acid mine drainage (AMD) impacts negatively on freshwater resources in the mining areas of South Africa and many other parts of the world. AMD waters are characterised by low pH, very high iron concentrations, significantly high concentrations of non-ferrous (mainly heavy) metals, and very high salinity, principally in the form of sulphate. The chemical makeup of AMD is directly explicable in terms of the biogeochemical process whereby AMD arises: mining activities allow atmospheric oxygen and water to come into contact with rock and, together with the action of aerobic bacteria, cause the oxidation of iron pyrite (FeS_2) present in the rock. This oxidation of pyrite is given by Equation 1.



This reaction releases sulphate, protons and iron into underground water making it strongly acidic, causing leaching of non-ferrous metals from the rock (Kleinmann et al. 1981). The type and concentration of these other metals varies with the local geology.

A comprehensive solution to AMD pollution requires pH neutralisation and both metal and sulphate removal. The latter can be effected by either biological or membrane-based methods. The common approach to the removal of dissolved metals from AMD is to oxidise the ferrous iron to ferric oxide/oxo-hydroxide end-products, which then precipitate and settle. The products of iron oxidation may vary from amorphous non-crystalline ferrihydrite ($\text{Fe}(\text{OH})_3$) to crystalline ferric oxides/oxo-hydroxides such as goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-FeOOH}$), hematite ($\alpha\text{-Fe}_2\text{O}_3$), or the partially oxidised ferrous-ferric crystalline compound magnetite (Fe_3O_4). In general, the precise end-products of oxidation of ferrous solutions depends upon environmental conditions such as pH, redox potential, temperature, concentration of reagents, presence of seed, etc. (Blesa and Matijevic 1989, Cornell and Schwertmann 1996). Characterisation and quantification of individual end-product components is complex and often impossible.

There are three criteria which the sludge of an AMD metals removal treatment process should meet:

- Efficient settling.
- Rapid and extensive dewatering properties in order to achieve a high density at the time of disposal.
- Stability of the sludge at low pH, to avoid possible remobilisation of dissolved metals in the environment at the disposal site.

Crystallised end-products settle and dewater more efficiently than does poorly-crystalline/amorphous ferrihydrite. In the event of a fall in pH, ferrous and non-ferrous metal release from crystallised end-products is less than for amorphous products of oxidation. Achievement of crystallised end-products is, however, not straightforward. In the currently deployed high-density sludge (HDS) process, a relatively high investment is required in order to attain crystallised end-products (Figure 1.1).

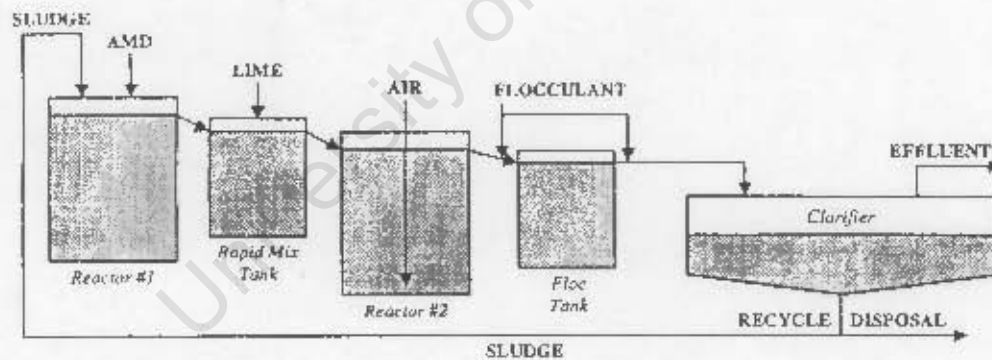


Figure 1.1 Schematic diagram of an example of the High Density Sludge (HDS) process for the treatment of AMD. Notable disadvantages of the HDS process are (1) that the entire AMD volume must pass through the entire reactor system, (2) the need for a flocculation tank and (3) the need for extensive recycling of a relatively low-density sludge. (from Aube and Zinck 1999).

In its various manifestations, the HDS process employs a sludge recycle system during the oxidation of ferrous iron present in AMD (Aube and Zinck 1999, Zinck and Griffith 2000). The end-products of oxidation are a diverse and often poorly defined mixture of iron and non-ferrous compounds. The iron component varies from non-crystalline amorphous ferrihydrite ($\text{Fe}(\text{OH})_3$) to crystallised ferric oxides such as lepidocrocite ($\gamma\text{-FeOOH}$). The crystallinity and density of the end-products are in direct proportion to the investment in reactors (multistage neutralisation), energy (extensive recycling of low-density sludge), chemicals (flocculating polymer and in some instances, insertion of oxygen) and control technology. Non-ferrous metal ions dissolved in the AMD either precipitate as their own hydroxides, are adsorbed by amorphous iron oxy-hydroxides, or become incorporated into crystallised end-products (Aube and Zinck 1999, Zinck and Griffith 2000). A noteworthy disadvantage of the HDS process is that the entire AMD volume must pass through the entire reactor system prior to sludge - effluent separation (Figure 1.1), necessitating extremely large reactors. Despite all these efforts to attain efficient liquid-solid separation, in its most efficient instances, the HDS process is only able to deliver sludges of relatively low density. For example, the Geco HDS process described by Aube and Zinck (1999) produces fresh sludge of only 27.8% solids. After aging for one year on a dry tailings beach, the density reached 60%. These last two limitations of the HDS process, ie. that the entire AMD volume must pass through reactor and the low sludge densities obtained, coupled with the magnitude of the AMD problem (some mining basins pump up to 60 megalitres of water per day (Scott 1995)), underscore the need for improved cost-effective methods of AMD treatment.

In recent years, an ambient temperature ferrite process has been developed for the treatment of AMD (Mckinnon et al. 2000, Morgan et al. 2001, Lahav et al. 2003). The ambient temperature ferrite process approach to metals removal from AMD is centred on the iron oxide magnetite which can be formed by the partial oxidation of ferrous solutions. Magnetite has several key properties which make it an ideal end-product of oxidation for metals removal from AMD or from industrial wastes: it has excellent settling properties, forms a high-density, rapidly dewatering sludge which is very stable at low pH values, and moreover, it has the capacity, shared with several other iron oxides, to effect non-ferrous metal removal and stabilisation via cation

substitution. It can thus be used to remove both dissolved ferrous and non-ferrous metals from an AMD stream. Indeed, in nature iron oxides act as sinks for otherwise toxic heavy metals (Cornell and Schwertmann 1996). Moreover, there are markets for magnetite (Radovenchik et al. 1996) and particularly good markets for high quality magnetite (ie. magnetite with an iron content of greater than 68%) (Guilinger - personal communication, Lines - personal communication).

Magnetite is a partially oxidised iron oxide with the formula Fe_3O_4 (ie. $\text{Fe}^{3+}_2\text{Fe}^{2+}\text{O}_4$). It thus conforms to the general formula $\text{Fe}^{3+}_2\text{M}^{2+}\text{O}_4$ for ferrites. Ferrites are iron oxides conforming to the structure of an inverse spinel ($\text{Mg}^{2+}_2\text{Al}^{3+}\text{O}_4$), where M stands for any of a number of possible metal or non-metal ions with an unhydrated ionic radius of between 0.60 and 1.00 angstrom (Smit and Wijn 1959).

The ferrite structure is built of oxygen atoms in cubic close packing giving rise to octahedral and mixed tetrahedral/octahedral layers (Cornell and Schwertmann 1996). Figures 1.2a, 1.2b and 1.2c illustrate how tetrahedral and octahedral holes lie between the oxygen atoms which make up the crystal lattice framework. FeII ions occupy only octahedral sites while FeIII ions are equally distributed between octahedral and tetrahedral sites. Magnetite is an inverse spinel because in a spinel MII ions occupy the tetrahedral sites and MIII ions occupy the octahedral sites.

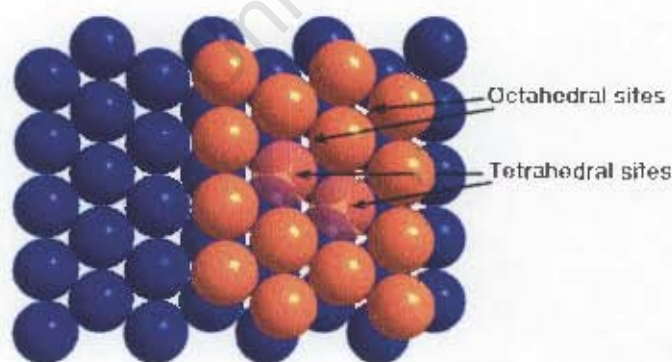


Figure 1.2a Spinel crystal structure showing cubic close packing with octahedral and tetrahedral interstitial sites between layers of oxygen atoms. (from Sauls and Sauls 1998).

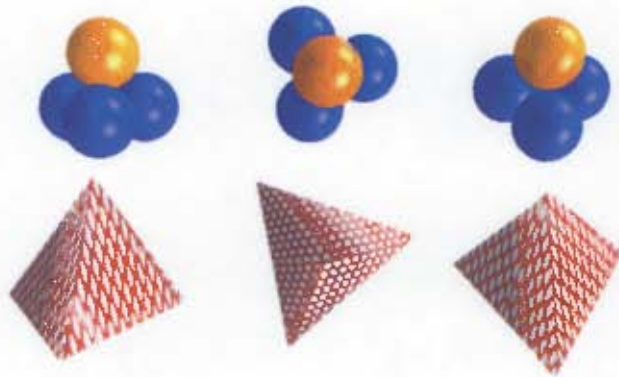


Figure 1.2b Illustration showing how four oxygen atoms make up a tetrahedral site.
(from Sauls and Sauls 1998)

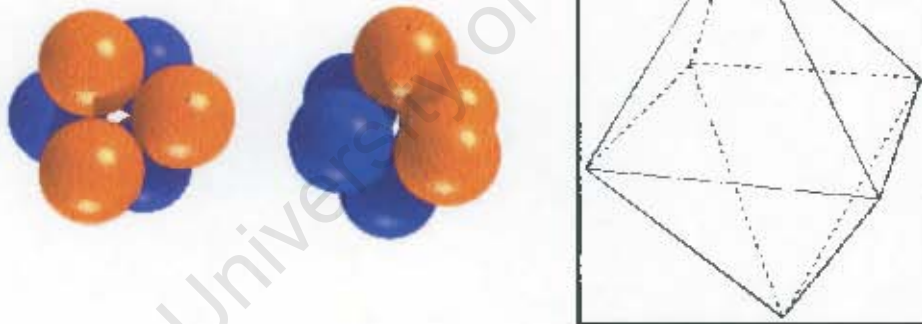


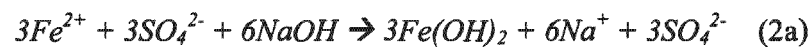
Figure 1.2c Illustration showing how six oxygen atoms make up an octahedral site.
(from Sauls and Sauls 1998)

Cation substitution with non-ferrous ions is made possible by the flexibility of the oxygen framework which accommodates cations which differ in size from Fe^{II} or Fe^{III} . Substitute ions do not necessarily occupy the same position as the displaced ion but will find the octahedral or tetrahedral site which provides the greatest stability for

its particular nature. Magnetite often exists in the non-stoichiometric state: stoichiometric magnetite has a FeII : FeIII ratio of 0.5 whereas in non-stoichiometric magnetite the ratio is < 0.5. Non-stoichiometric magnetite can arise through oxidation of FeII cations which would result in a net positive charge. This positive charge is compensated for by cation vacancies. Maghemite (*magnetite – hematite*) represents the extreme case where all the FeII has oxidised to FeIII and the formula is now $\gamma\text{-Fe}_2\text{O}_3$ where γ distinguishes it from $\alpha\text{-Fe}_2\text{O}_3$ (hematite). The difference is that maghemite retains the cubic close packing (ccp) crystal structure of magnetite whereas hematite has hexagonal close packing (hcp). Like magnetite, maghemite is also strongly magnetic.

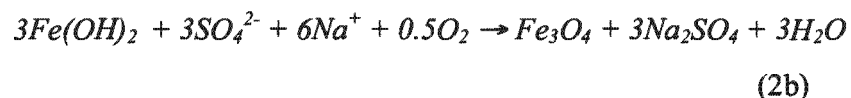
Magnetite is therefore a ferrite in which the metal component is made up purely of iron. If a solution dominated by iron but containing smaller concentrations of other metal ions (such as are found in AMD) is transformed into ferrite, then the resulting precipitant will be dominated by magnetite but some of the iron atoms will be replaced by non-ferrous cations, making for ‘substituted’ magnetite or ‘mixed-species’ ferrites. These properties account for the metal-removing capabilities of magnetite which have been successfully deployed in a high temperature ferrite process for the treatment of laboratory wastes (Katsura et al. 1977, Tamaura et al. 1991a, 1991b).

The first step in the oxidation of dissolved ferrous iron present in AMD (Equation 1) is to elevate the pH in order to precipitate the iron. Using NaOH to raise pH, this hydrolysis reaction is described by Equation 2a:



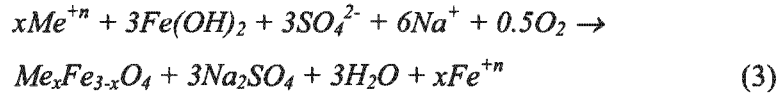
Barrado et al. (1998) proposed the following stoichiometric reactions for ferrite formation from ferrous at pH > 10.5.

In the absence of heavy metals and with a slow oxidation rate:



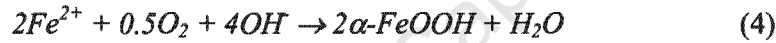
Equation 2b shows that alkalinity is neither produced nor consumed during the formation of magnetite from ferrous hydroxide¹, and that 10.47 mg/L of magnetite (as Fe) are formed for every 1 mg/L of oxygen consumed.

In the presence of heavy metals (*Me*) and with a slow oxidation rate:



In Equation 3 Fe^{+n} represents the total concentration of iron replaced by metal cations in the ferrite structure.

However it is to be noted that with excess oxidising agent goethite is formed instead of magnetite:



The formation of relatively pure precipitates of magnetite from ferrous solutions was until recently only thought to be possible at temperatures greater than 90 °C (Kiyama 1974, Cornell and Schwertmann 1996). Nevertheless, the capacity of magnetite to absorb non-ferrous metals by cation substitution, plus the advantageous settling properties of magnetite, have resulted in the exploitation of magnetite formation as a means to remove metal ions from waste streams. The 'Ferrite Process' refers to a high temperature process (65 °C) developed in Japan for the treatment of laboratory wastes containing heavy metals (Katsura et al. 1977, Tamaura et al. 1991a, 1991b). However during the last two decades, developments in the field of ambient temperature ferrite

¹ In the course of this thesis, the terms 'ferrous hydroxide' and 'ferrous solution' are frequently used in the following way '...magnetite formation from ferrous hydroxide' or 'magnetite formation from ferrous solution...'. These statements are inaccurate for two reasons. Firstly, as will be discussed in detail in Chapter 4, Fe^{2+} does not precipitate solely as $Fe(OH)_2$ but forms other solid ferrous compounds which contain SO_4^{2-} as well. Secondly, once precipitation has occurred the ferrous exists in suspension and not in solution. The above two terms should therefore be regarded as shorthand denoting a suspension of solid Fe^{2+} species. The term 'ferrous intermediate' is therefore introduced below to denote all ferrous precipitates at this stage. The term 'intermediate' is used because these precipitates are unstable and will ultimately turn into end-products.

chemistry have occurred which appear to be opening the way to treating large volumes of water such as AMD.

Topkin et al. (1990) formed ferrites at ambient temperature in a 1-step reaction where Cr(VI) was the oxidising agent for Fe(II) in the redox couple: Fe(II) – Fe(III)/Cr(VI) – Cr(III). In this reaction, ferric ions precipitate together (coprecipitation) with ferrous ions as magnetite.

This can be distinguished from a 2-step reaction where separate ferric and ferrous solutions are combined and ferric and ferrous ions then coprecipitate as magnetite. This is called a 2-step reaction because if one begins with only a ferrous solution, as may commonly occur with AMD, part of it would first need to be separately oxidised to create a ferric solution (step 1). The two solutions are then recombined whereupon ferric and ferrous ions can coprecipitate as magnetite (step 2). As may be expected, the optimum ferric : ferrous ratio for 2-step ambient temperature magnetite formation was found to resemble the stoichiometric ratio (ie. 2 : 1) of these ions in magnetite (Wang et al. 1996).

Navratil (1986) described the removal, via 2-step ambient temperature ferrite formation, of americium and plutonium present in nuclear reactor radioactive wastewater. The following ions were also removed: Al(III), Ba(II), Cd(II), Ca(II), Cs(I), Cr(III), Co(II), Cu(II), Er(III), Ga(III), Pb(II), Mg(II), Mn(II), Hg(II), Ni(II), Rb(I), Ag(I), Sr(II), Sn(IV), Ti(III), UO_2^{2+} , VO_2^+ , Zn(II), ZrO^{2+} . Tamaura et al. (1991b) appear to be the first to have applied a 2-step ferrite process at ambient temperature to a real AMD stream.

Only a limited number of further studies reporting the incorporation of metal or non-metal ions into ferrites at ambient temperature have been published. The following have been identified:

- Schwertmann and Murad (1990): Al incorporation by 1-step slow passive aerial oxidation.

- Yang et al. (1994): Zn, Mn, Al, Cd, Pb, Mg and Cu removal by 1-step active aeration.
- Topkin et al. (1990): Cr(III) via Cr(VI), Zn(II) and Cd(II) incorporation. Both by:
 - (a) Coprecipitation of ferric and ferrous ions (ie. simulating 2-steps).
 - (b) By a 1-step reaction where Cr(VI) acts as the oxidising agent for Fe(II) as described above.
- Kampeis et al. (1996): Zn(II) incorporation by 1-step active aeration.
- Mandaokar et al. (1994): Cu(II), Cr(III), Pb(II) incorporation by 1-step slow aerial oxidation.
- Wang et al. (1996): Zn, Al, Pb by coprecipitation simulating 2-steps.
- Perales Perez et al. (1999): Zn by 1-step aerial oxidation.
- Radovenchik et al. (1995) reviews the Russian literature on the ferrite method. Of the four studies mentioned only one by Topkin et al. (1990), already mentioned above, has been confirmed as being at ambient temperature.

Navratil (1986) comments on ions which are notable for their inability to be incorporated into ferrites. Examples are the alkali metals sodium and potassium, and other species such as Tl^+ and Th^{4+} , all of which, he observes, remain soluble in aqueous solution, even at high pH. Navratil suggests that ions may need to be in the solid phase in order to be included into the crystal lattice.

Several investigations describe an interference effect of certain ions on ambient temperature ferrite formation (Kampeis et al. 1996, Wang et al. 1996, McKinnon et al. 2000). These ions, when present in sufficient concentration, steer the end-products of oxidation towards the formation of non-ferrite iron oxides, presumably by interfering with ferrite formation in some way. A similar interference effect occurs at higher temperatures (eg. Mandaokar et al. 1994). As lime ($Ca(OH)_2$) is the cheapest chemical pH elevating agent available, the question of calcium interference is of particular relevance to AMD. Calcium has been reported to become incorporated into the crystal lattice of magnetite in at least two cases (Desillier et al. 1977, Cornell and Schwertmann 1996). Other authors have reported the exclusion of calcium ions from the lattice during magnetite formation (Yang et al. 1994, Radovenchik 1995). Still others, (Wang et al. 1996, Perales Perez et al. 1998, McKinnon et al. 2000), describe

a pronounced inhibitory effect of calcium on ambient temperature ferrite formation. From these studies it can be concluded that in the presence of significant concentrations of calcium, the end-products of ambient temperature ferrite formation comprise large amounts of non-ferrite iron compounds. One reason cited for the inhibitory effect is that calcium ions, being of larger diameter (1.14 angstrom, Shannon 1976) as compared with ferrous (0.75 angstrom) and ferric (0.69 angstrom), do not easily fit into the ferrite crystal lattice, and so disrupt ferrite formation (Wang et al. 1996, Perales Perez et al. 1998). Navratil (1986) on the other hand, arguing in the same vein as above regarding ions which are not incorporated into ferrites, suggests that dissolved ions are unable to interfere in ferrite formation. He interprets his data for both the alkali and alkali earth metals as supporting this interpretation: eg. successively lower molar concentrations of beryllium, magnesium and calcium ions interfere. Still others (Choung et al. 1999) suggest that calcium forms a hydrated calcium-ferric complex which resists dehydration during crystallisation. Since the mechanism of ferrite formation itself is not well understood (Radovenchik 1995, Cornell and Schwertmann 1996), it is difficult to comment on the mechanism of calcium interference.

Whatever the reason for the interference effect, in an effort to overcome the calcium problem, both Perales Perez et al. (1998) and McKinnon et al. (2000) investigated the effects of magnetite seed on ambient temperature ferrite formation. Perales Perez et al. (1998) found that recycling of magnetic precipitates formed during (ie. a 1-step process) the oxidation of ferrous sulphate solutions in the presence of calcium had a positive effect on ferrite formation at ambient temperature. McKinnon et al. (2000), using a batch test procedure in which ferric and ferrous ions were simultaneously combined simulating a 2-step process, reported that magnetite seed restored the capacity for ferrite formation at ambient temperature in the presence of calcium.

It thus appears from these two studies that in the presence of calcium, through the use of magnetite seed, ambient temperature ferrite formation is indeed possible. This appears feasible as either a 1-step, in-line oxidation procedure or as a 2-step, stoichiometric combination procedure. At the start of the research reported in this thesis there was no indication that either of these two methods is superior. Indeed, the above two studies included, the sparse literature on ambient temperature ferrite

formation reflects the infancy of this field and in particular there is little published information, of a fundamental or systematic nature, with respect to key process parameters such as kinetics, heavy metal substitution, effect of calcium, settling behaviour, and sludge stability. The sole exception to this state of affairs is the review by Perales Perez et al. (2001a) which will be discussed in Chapter 4.

In the light of the great potential for metals removal, and of the studies reporting the use of seed to facilitate ferrite formation in the presence of calcium, it seemed worthwhile to pursue a better understanding, from an engineering perspective, of this reaction. Consequently, on the basis of a hint favouring a 1-step approach (Radovenchik et al. 1995), a preliminary study quickly confirmed the feasibility of the 1-step approach to ambient temperature ferrite formation in the absence of calcium (Morgan et al. 2001). On the strength of this, plus the cost advantages of a 1-step process, a systematic investigation into the fundamentals of 1-step ambient temperature ferrite formation for treatment of AMD was initiated.

Initial investigations conducted under batch conditions are described in Chapter 5 below. These begin with a 'proof of concept' study establishing the viability of 1-step ambient temperature ferrite formation using magnetite seed. Under identical conditions but in the absence of magnetite seed, ferrite formation is negligible.

It became evident at this early stage that the ferrite sludge formed in the presence of seed possessed extremely favourable settling properties and that the total iron concentration in the raw effluent was less than 1 mg/L. The latter represents an iron removal efficiency of greater than 99.9%. Furthermore, in initial stability tests performed at pH 2, the precipitant showed only gradual dissolution amounting to 10% (w/w as Fe) over a period of 53 days.

Given these encouraging results a further set of batch experiments was performed in order to systematically investigate the effects of four fundamental parameters on ambient temperature ferrite formation. These four parameters are seed concentration, rate of oxidation, pH and temperature. The results, based on sludge characterisation studies involving Mössbauer spectroscopy (MS), X-ray diffraction (XRD), and scanning electron microscopy (SEM), show that controlled oxidation of ferrous

solutions under controlled pH conditions at ambient temperature, in the presence of magnetite seed, yields almost pure structural magnetite.

These investigations yielded valuable information with respect to the optimum conditions for ferrite formation. Mössbauer spectroscopy (MS) proved to be an essential tool in the analysis of these results because it enabled, not only identification of the end-products as magnetite, but also precise measurement of the degree of oxidation of the magnetite end-products from these batch experiments. Partially oxidised magnetite has a lower molar percentage ferrous component than stoichiometric magnetite in which the molar percentage ferrous is 33.33%. Within a certain domain, varying combinations of the above four parameters all resulted in solely magnetite end-products. However, Mössbauer spectroscopy revealed subtle, yet systematic, differences in the degree of oxidation of the magnetite produced within a general domain of magnetite formation.

It was found that airflow rate but not seed concentration had an effect on the rate of oxidation, airflow rate being the rate-limiting parameter at all times. From a process perspective, the kinetics of magnetite formation under the above conditions are very favourable. The hydraulic retention time (RT) required for the complete removal of a typical AMD iron concentration (1200 mg/L) varied between 0.3–1.6 hours.

On the basis of these studies it was apparent that many parameters relevant to processing AMD on a large scale were favourable: low oxygen requirement, low retention time, excellent settling properties, excellent iron removal efficiency and substantial sludge stability. However these batch experiments also demonstrated, as previously described by others (Wang et al. 1996, Perales Perez et al. 1998, McKinnon et al. 2000), the profound inhibitory effect of calcium on ferrite formation (Lahav et al. 2003). This is problematic as not only is calcium often present in considerable concentrations in AMD, but lime is the most economical agent for elevating pH.

Chapter 6 below describes investigations aimed at overcoming the negative effect of calcium. These investigations were conducted under conditions of continuous flow (of simulated AMD influent) and constant magnetite seed and ferrous concentrations

(dynamic steady-state conditions). Whereas under batch conditions the ferrous concentration began at an initial value of 1200 mg/L and proceeded linearly to zero, under steady-state conditions the ferrous concentration could be kept constant at any desired value. The effect of the ferrous concentration on ferrite formation could therefore be investigated, leading to the discovery of a threshold effect below which minimal or no ferrite formation occurs, and above which solely ferrites are produced.

This proved to be a key finding as it stimulated the development of a sequence designed to increase the ferrous concentration (see Figure 8.1). This functions by initially combining the raw AMD with magnetite seed at pH 10.5 in a 'contact stabilisation' reactor without any active aeration. In this reactor, Fe^{2+} present in the AMD precipitates at pH 10.5 to form a metastable 'ferrous *intermediate*' (as distinct from a stable 'ferrous-ferric *end-product*'). Upon precipitation, the ferrous intermediate (FI) instantly and completely adsorbs to the magnetite seed. The mix consisting of seed and adsorbed ferrous intermediate (plus any other precipitated non-ferrous metal intermediates) then flows into a gravitational settler where the magnetite seed and all precipitated components adsorbed to it are concentrated prior to oxidation. The bulk AMD water volume (~70% of the total), now devoid of all metals, is drawn off and the concentrated seed and precipitated components are pumped to an oxidation reactor. Here the precipitated components are transformed into ferrites (ie. more seed) which flows into a second settling chamber where the bulk (~90%) of the water is drawn off. The remaining solids comprising original ferrite seed, fresh ferrite seed and ferrous intermediate (the latter at a given supra-threshold concentration) is then allowed to age for a given amount of time. After the aging period, a fraction of the solids is recycled to the contact stabilisation reactor and the remainder is transferred to a second oxidation reactor in which all remaining ferrous/metal intermediates are transformed into stable ferrite prior to final disposal. Through this configuration, it can be seen that the hydraulic retention time of the bulk AMD flow is independent of the rate-limiting step in the ferrite process, ie. the aging step. It is limited only by the very much faster settling step occurring in the first settler. Similarly, the fraction of AMD water reaching the first oxidation reactor is drawn off prior to the next two steps in the sequence, viz. aging and either recycling or exhaustive oxidation. As a consequence of these two separations, the volume of AMD being treated is rapidly diminished to a fraction of the original volume. That is,

contact stabilisation reactor – settler sequence separates all the incoming dissolved metals, as precipitated solids, from the bulk AMD flow prior to oxidation, as does the second settling step separate the solid contents of the first oxidation reactor from the water phase. This allows for much smaller oxidation reactors than would otherwise be necessary.

By virtue of the contact stabilisation reactor – settler sequence, the ferrous intermediate concentration could be rapidly, and indefinitely, increased to any desired value prior to the commencement of oxidation. Thereafter, by matching the incoming ferrous load in the AMD to the rate of ferrite formation (ie. ferrous removal), the ferrous intermediate concentration could be easily maintained at steady-state.

A second effect of the contact stabilisation reactor – settler sequence is to increase the concentration of the solid components relative to the dissolved components. When dissolved calcium is present in the mixture, the settling of all solid components, ie. seed and ferrous intermediate adsorbed to it, via the contact stabilisation reactor – settler sequence, serves to increase the ferrous intermediate (as Fe) : dissolved calcium (as Ca) ratio. This is due to the fact that during settling, the concentration of the solids is increased whereas that of the dissolved substances, ie. calcium, is not. By manipulating this ratio, it was found that a ferrous intermediate (as Fe) : calcium (as Ca) ratio of ~ 3 : 1 serves to overcome the inhibitory effect of calcium on ferrite formation.

Manganese is present in high concentrations in many South African AMD waters (for example up to 438 mg/L, Wittman and Förster 1977). Manganese presents a different problem to calcium in that manganese has a much higher solubility in water than does iron and most other metals². This is problematic because manganese must be precipitated in order to settle during the contact stabilisation – settler sequence. Any manganese in solution will pass out with the effluent from the settler. During the course of this research, it was indeed found that at pH 10.5, ~40% of the manganese

²The K_{sp} of manganese is three orders of magnitude higher than that of iron (see Table 2.2 in Chapter 2).

did not precipitate. However, raising the pH to 12 caused total manganese precipitation.

In conclusion, the key challenges in developing an ambient temperature ferrite process for the removal of metals from AMD are fourfold:

- To achieve ferrite formation at ambient temperature,
- to do so at adequate reaction and settling rates, and
- to do so in the presence of calcium which is known to inhibit ferrite formation (Lahav et al. 2003, Wang et al. 1996).
- To remove non-ferrous metals, including manganese, by cation substitution in the presence of calcium.

The results of the investigations described in Chapters 5, 6 and 7 demonstrate that these four criteria have been met. On the basis of these findings, a detailed semi-quantitative description of an ambient temperature ferrite process is derived. It must be emphasised that the focus of this research has been to explore the feasibility of 1-step ambient temperature ferrite formation in the presence of calcium for the removal of iron and non-ferrous metals from AMD. In so doing, all of the pertinent major factors have been examined and at least semi-quantified. In the light of the many parameters involved it has not been possible in the time available to address or optimise every aspect of the process. Nonetheless, the investigations reported here constitute the first comprehensive proof that a 1-step ambient temperature ferrite process for removal of metals from AMD in the presence of calcium is feasible and moreover that it has significant advantages over the HDS process. On the basis of this demonstration, further studies aimed at optimising the process appear to be warranted.

Chapters 5, 6 and 7 are preceded by three preliminary chapters covering theoretical topics of direct relevance to ambient temperature ferrite formation. Chapter 2 discusses the equilibrium chemistry of metal ions in aqueous solution and Chapter 3 discusses the kinetics of ferrous iron oxidation. In Chapter 4 pathways and mechanisms of ferrite formation are examined.

Chapter 2 The theoretical chemistry of metal ions in AMD waters

Introduction

In the treatment of AMD, iron and heavy metals may be precipitated as hydroxides, oxo-hydroxides, oxides, carbonates (rarely), sulphides and sometimes sulphates. The species that precipitate in any scenario will depend on the nature and concentrations of precipitation ions and *inter alia* on pH, pe (pe = negative log of electron concentration, ie. an index of redox potential) and rates of chemical addition (ie. mixing configuration). In this chapter pH-dependant and pe-dependent equilibrium chemistry is used to examine some aspects of metal hydroxide and metal sulphide mineral precipitation in the context of metals removal from AMD waters. In this respect equilibrium chemistry forms the ideal framework for enquiry – in particular, utilisation of graphical description forms an extremely useful didactic mechanism. Once completed, the more general engineering implications are addressed in later chapters.

2.1 pH-dependant equilibria

In this section pH versus log (of the) species concentration equilibria of metal hydroxides and metal sulphides are considered. In each case aqueous phase and aqueous – solid phase equilibria are dealt with.

Metal hydroxides: aqueous phase equilibrium

All the metals encountered in AMD waters form complexes (and/or ion pairs) with hydroxide species. Such complexing affects the solubility of the mineral as will be shown later. Considering the generic divalent metal ion M^{2+} , up to three hydroxide complexes have been noted ie. MOH , $M(OH)_2^0$, and $M(OH)_3^-$. Though the first (MOH) has meaning considering the aqueous phase alone, the remaining two usually

two-phase equilibrium considerations. In Table 2.1 below are listed data reported for various M^{2+} -hydroxide complexes.

Metal ion	Complex	Divalent log dissociation constant
Fe^{2+}	$Fe(OH)^+$	-4,5
	$Fe(OH)_2^0$	-7,4
	$Fe(OH)_3^-$	-11,0
Mn^{2+}	$Mn(OH)^+$	-3,4
	$Mn(OH)_2^0$	-5,8
	$Mn(OH)_3^-$	-7,2
Zn^{2+}	$Zn(OH)^+$	-5,0
	$Zn(OH)_2^0$	-11,1
	$Zn(OH)_3^-$	-13,6
Ni^{2+}	$Ni(OH)^+$	-4,1
	$Ni(OH)_2^0$	-9,0
	$Ni(OH)_3^-$	-12,0
Pb^{2+}	$Pb(OH)^+$	-6,3
	$Pb(OH)_2^0$	-10,9
	$Pb(OH)_3^-$	-12,0

Table 2.1 Log of dissociation constants for various divalent metal hydroxide complexes (Stumm and Morgan 1996).

The relevant generic reactions and equations for aqueous phase equilibrium are thus:



For each of these reactions there is a corresponding equilibrium equation:

$$[M^{2+}] [OH] / [MOH^+] = K_{b1}' \quad (4)$$

$$[M^{2+}] [OH]^2 / [M(OH)_2^0] = K_{b2}' \quad (5)$$

$$[M^{2+}] [OH]^3 / [M(OH)_3^-] = K_{b3}' \quad (6)$$

Where K' = apparent equilibrium constant including Debye-Hückel effects.

In the practical scenario, the dependant variable of interest is pH and the equilibrium equations should be transformed into this form. Recognising that water is the solvent, Equation 4 becomes:

$$\{[M^{2+}] K_w\} / \{[MOH^+] [H^+]\} = K_{b1}' \quad (7)$$

and

$$[MOH^+] [H^+] / [M^{2+}] = K_w / K_{b1}' = K_{a1}' \quad (8)$$

Such transformation allows presentation of aqueous phase equilibrium as shown, for example, in Figure 2.1 for the divalent iron hydroxide system with Fe_T (total dissolved ferrous) of 2×10^{-2} M.

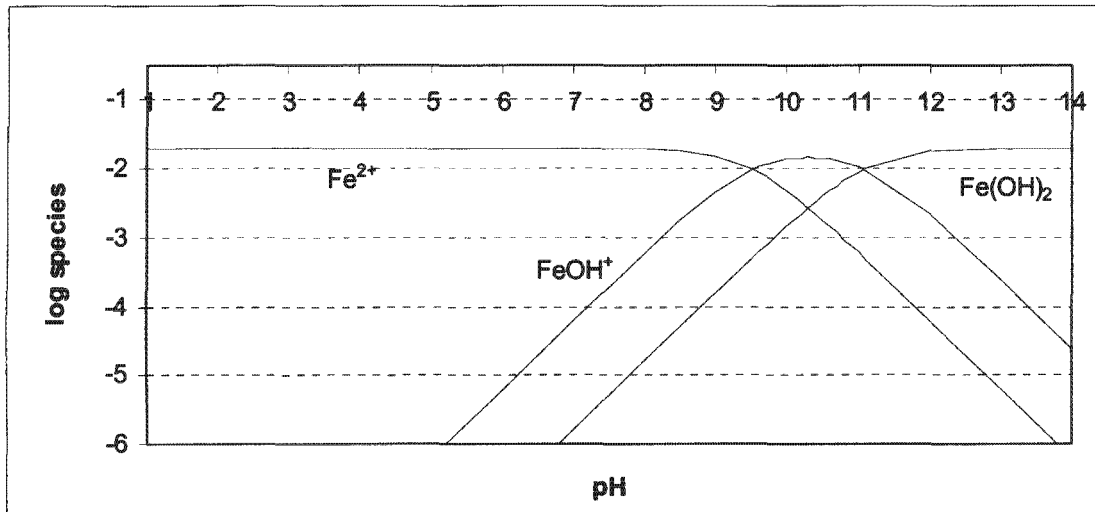


Figure 2.1 Aqueous phase pH versus log species concentration (mol/L) equilibrium diagram for ferrous iron at infinite dilution.

In practice, the diagram has little meaning in the higher pH values (above ~ 8.5) as $\text{Fe(OH)}_{2(s)}$ will precipitate and thus it is never possible to have dissolved Fe^{2+} species ions at the level shown. A more realistic approach is to visualise the system from an aqueous – solid phase equilibrium standpoint.

Metal hydroxides: aqueous – solid phase equilibrium

The maximum concentration of free metal ions is established via the metal's solubility product equation, ie. in the case of metal hydroxides:

$$[\text{M}^{2+}] [\text{OH}]^2 = K_{sp}' \quad (9)$$

Where K_{sp}' = apparent solubility product including Debye-Hückel effects.

However, the concentration $[\text{M}^{2+}]$ in the above equation does not give the total dissolved metal ion species concentration in solution. This arises because M^{2+} forms complexes (dissolved species) as shown in the previous section and the relative concentration of these depends on pH. The total dissolved metal species in solution

will be given by the sum of the free and metal hydroxide complex species concentrations.

The concentration of each of the metal hydroxide complexes at aqueous – solid phase equilibrium (Equations 4 to 6) are determined by linking each of the complex formation equations to the solubility product equation (Equation 9). For example, for the concentration of the complex MOH^+ , at saturation, solving for $[M^{2+}]$ from Equation 4 and substituting into Equation 9 gives:

$$[MOH^+] [OH^-] K_{b1}' = K_{sp}' \quad (10)$$

$$\text{ie. } [MOH^+] = K_{sp}' / ([OH^-] K_{b1}') \quad (11)$$

and similarly for the other complexes:

$$[M(OH)_2^0] = K_{sp}' / K_{b2}' \quad (12)$$

$$[M(OH)_3^-] = K_{sp}' [OH^-] / K_{b3}' \quad (13)$$

and so on for higher order hydroxy complexes. The total dissolved metal species in solution at saturation is thus:

$$M_T = [M^{2+}] + [MOH^+] + [M(OH)_2^0] + [M(OH)_3^-] \quad (14)$$

Such total concentrations of dissolved metal are represented most clearly by taking the logarithms of Equations 9, 11, 12 and 13, transforming $\log [OH^-]$ to pH and plotting a log species versus pH diagram ie.:

$$\log [M^{2+}] = \log (K_{sp}') - 2\log(K_w') - 2pH \quad (15)$$

$$\log [MOH^+] = \log (K_{sp}') - \log(K_{b1}') - \log(K_w') - pH \quad (16)$$

$$\log [M(OH)_2^0] = \log (K_{sp}') - \log(K_{b2}') \quad (17)$$

$$\log [M(OH)_3] = \log (K_{sp}) - \log(K_{b3}) + \log(K_w) + pH \quad (18)$$

In Figures 2.2 to 2.4 are shown plots of log metal species solubility versus pH for the ferrous, nickel and manganese species in water. The various log K_b values are those listed in Table 2.1 and solubility product values are listed below in Table 2.2.

Referring to Figures 2.2 to 2.4, the total dissolved species concentration at any pH is closely equal to the principal species and 0.301 log units above an intercept point. Furthermore, for ferrous, nickel and manganese hydroxide species, the minimum dissolved total metal species concentrations are approximately 10^{-7} M at pH 11 for ferrous, 10^{-8} M at pH 10.5 for nickel and 10^{-7} M at pH 12 for the manganese system.

Precipitant	Log Ksp	Reference
Fe(OH) ₂	-15,1	Stumm and Morgan (1996)
Mn(OH) ₂	-12,8	
Zn(OH) ₂	-16,0	
Ni(OH) ₂	-14,7	

Table 2.2 Solubility product constants for various metal hydroxides.

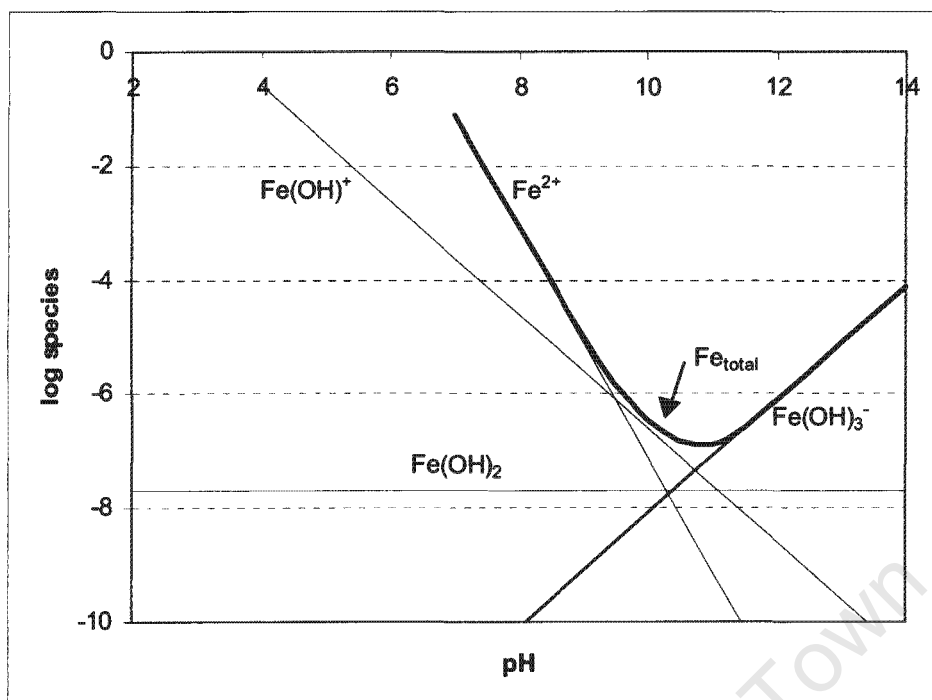


Figure 2.2 Aqueous – solid phase pH versus log species concentration (mol/L) equilibrium diagram for ferrous hydroxide at infinite dilution.

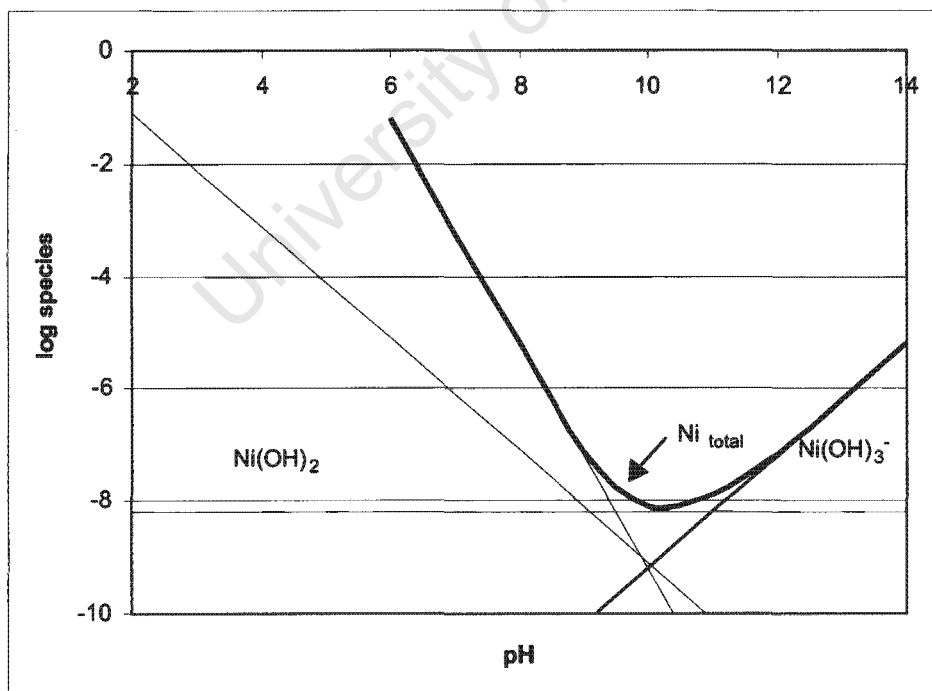


Figure 2.3 Aqueous – solid phase pH versus log species concentration (mol/L) equilibrium diagram for nickel hydroxide at infinite dilution.

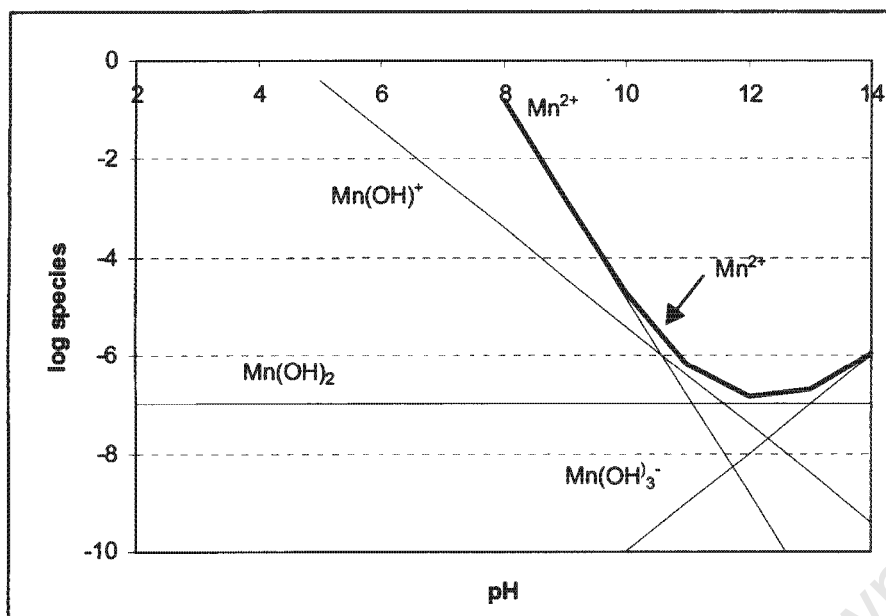


Figure 2.4 Aqueous – solid phase pH versus log species concentration (mol/L) equilibrium diagram for manganese hydroxide at infinite dilution.

Metal sulphides: aqueous phase

The sulphide system comprises a diprotic weak acid system in aqueous solution, H_2S , HS^- and S^{2-} (Figure 2.5).

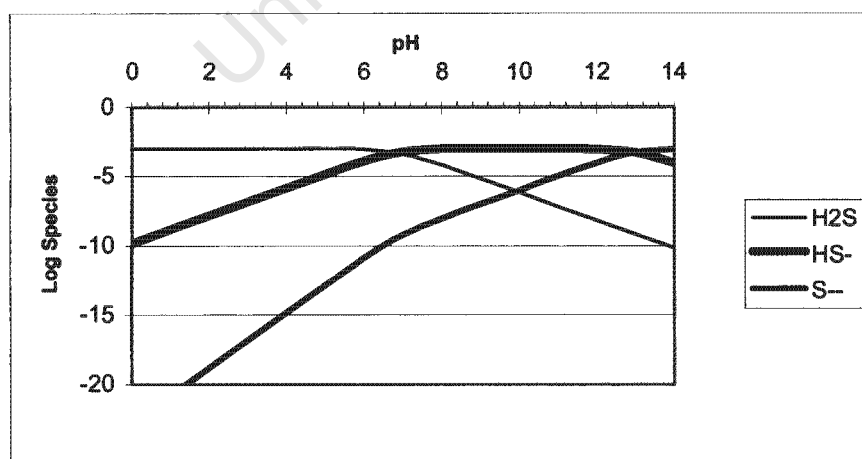


Figure 2.5 Aqueous phase pH versus log species concentration (mol/L) equilibrium diagram of sulphide species.

However, reported data on the dissociation between HS^- and S^{2-} is so variable ($12 < \text{pK}_a < 19$) that direct use of the species S^{2-} is not feasible. Consequently, only weak acid equilibrium between HS^- and H_2S species are normally considered, and solubility products are measured and reported relative to the HS^- species. Considering equilibrium in the aqueous phase $\text{H}_2\text{S} \rightleftharpoons \text{H}^+ + \text{HS}^-$ giving:

$$[\text{H}^+] [\text{HS}^-] / [\text{H}_2\text{S}] = K_a \quad (19)$$

where $\text{pK}_a \sim 7.1$ at 20°C .

The mass balance equation for the sulphide species neglecting S^{2-} is

$$S_T = [\text{H}_2\text{S}] + [\text{HS}^-]_T \quad (20)$$

where S_T = total dissolved sulphide species concentration and $[\text{HS}^-]_T$ = free and metal complexed HS^- species.

Examining the above two equations shows that the species of interest HS^- and H_2S vary with both pH and S_T . This makes solubility computation more difficult than for the hydroxide species discussed previously where the precipitating ligand OH^- varies directly with pH.

For most of the metal species of significant concentration in AMD waters, metal sulphide complexing is not reported, an exception being cadmium. These two scenarios (with and without complexing) require different treatment in determining expected dissolved metal ion concentration and are consequently dealt with separately.

Metal sulphides: aqueous – solid phase equilibrium (no metal sulphide complexing)

Current convention is to report metal sulphide solubility products in terms of HS^- because of the uncertainty associated with the $\text{HS}^-/\text{S}^{2-}$ dissociation constant, ie. in terms of the reaction $\text{MS} + \text{H}^+ \rightleftharpoons \text{M}^{2+} + \text{HS}^-$ with the corresponding solubility product equation:

$$[\text{M}^{2+}] [\text{HS}^-] / [\text{H}^+] = K_{sp}' \quad (21)$$

Note that when solubility product data are to be used relative to S^{2-} , the user should always ensure that the $\text{HS}^-/\text{S}^{2-}$ dissociation constant used comes from the same source as the corresponding K_{sp} value.

The precipitating ligand, HS^- , depends on S_T and pH as follows (derived from Equations 20 and 21):

$$[\text{HS}^-] = S_T K_a' / \{K_a' + [\text{H}^+]\} \quad (22)$$

Substituting this equation into the solubility product expression and simplifying gives the dependence of M^{2+} on pH and S_T at two-phase equilibrium:

$$[\text{M}^{2+}] = K_{sp}' [\text{H}^+] \{K_a' + [\text{H}^+]\} / (S_T K_a') \quad (23)$$

Taking logarithms yields:

$$\log [\text{M}^{2+}] = pK_a' - \log S_T - pK_{sp}' - pH + \log \{K_a' + [\text{H}^+]\} \quad (24)$$

Graphical presentation is now easily effected as follows:

In the region $\text{pH} < \text{pK}_a$ (ie. $[\text{H}^+] \gg K_a$):

$$\log [M^{2+}] = \text{pK}_a' - \log S_T - \text{pK}_{sp}' - 2 \text{pH} \quad (25)$$

In the region where $\text{pH} = \text{pK}_a$ (ie. $[\text{H}^+] = K_a$):

$$\log [M^{2+}] = -\log S_T - \text{pK}_{sp}' - \text{pH} + \log 2 \quad (26)$$

And where $\text{pH} > \text{pK}_a$ (ie. $[\text{H}^+] \ll K_a$):

$$\log [M^{2+}] = -\log S_T - \text{pK}_{sp}' - \text{pH} \quad (27)$$

In Figure 2.6 is shown plotted $\log [\text{Fe}^{2+}]$ solubility with pH for FeS precipitation and values of S_T of 10^{-6} , 10^{-5} and 10^{-4} M. Using pK values listed in Table 2.3.

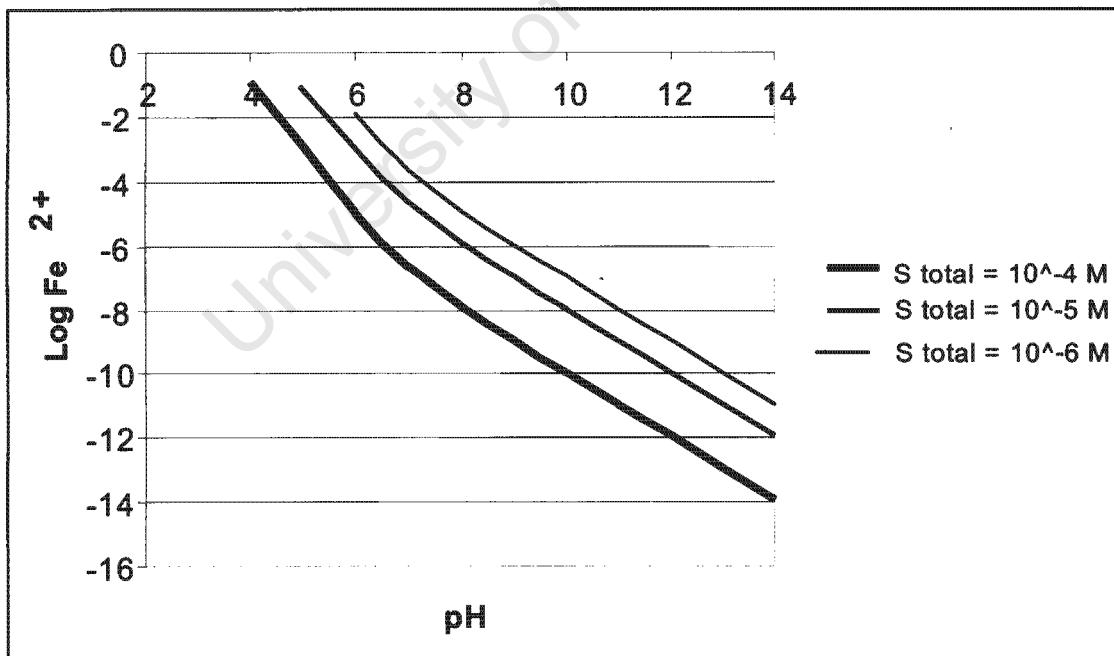


Figure 2.6 Plots of residual Fe^{2+} concentration (mol/L) in solution versus pH for various S_T values

A comparison of various metal ion solubilities can be effected using the above approach. From Figure 2.6 it is apparent that at relatively low pH values, for example pH 6 and S_T of 10^{-4} M, the total dissolved Fe^{2+} concentration is as low as 10^{-5} M. In comparison, for $Fe(OH)_{2(s)}$ governing solubility, at pH 6 the solution would have an extraordinarily high Fe_T value (see Figure 2.2).

Precipitant	log K_s (source: Dryssen and Kremling 1990)
FeS (amorphous)	-2.95
NiS	-5.6
MnS	-3.34

Table 2.3 Metal sulphide solubility products for iron, nickel and manganese.

In Figure 2.7 is shown metal ion in solution with pH for the metal species Fe^{2+} , Ni^{2+} and Mn^{2+} and a total sulphide in solution of 10^{-5} M.

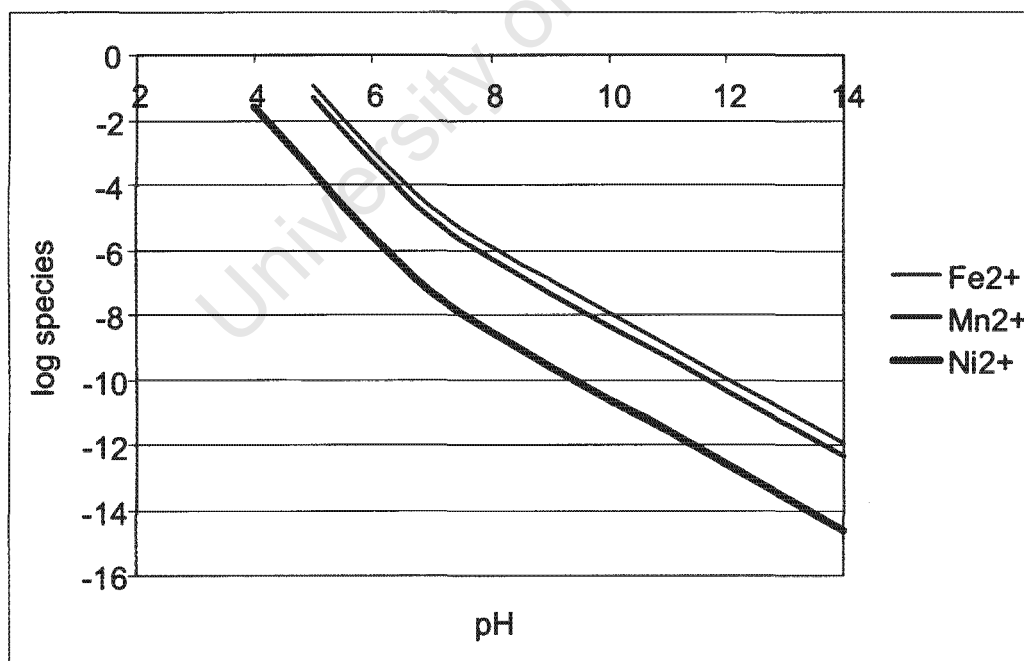


Figure 2.7 Solubility in mol/L of various metal ion species with pH for $S_T = 10^{-5}$ M.

Equations 25 to 27 can easily be used to obtain further insight into the metal sulphide solubilities, for example keeping pH constant and plotting $\log [M^{2+}]$ versus S_T as shown in Figure 2.8.

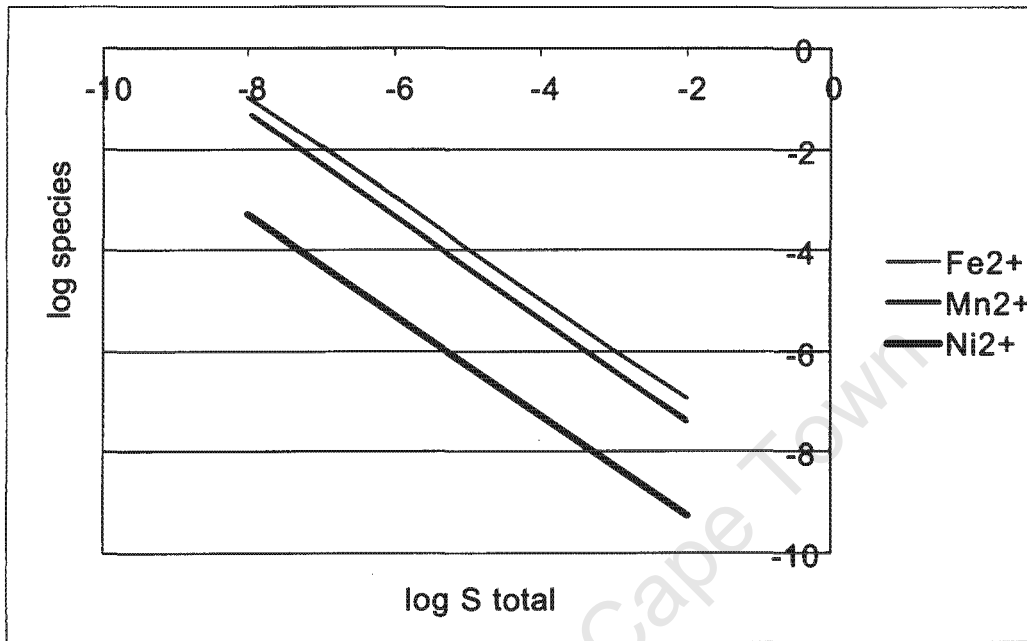


Figure 2.8 Solubility of various metal ion species at pH 6 for various total sulphide concentrations.

Metal sulphides: aqueous – solid equilibrium with metal ion complexing

For aqueous – solid phase equilibrium of metal sulphides where sulphide complexing is reported (together with the solubility product) the approach is to formulate equations for the solid mineral in terms of each of the metal sulphide complexes, $[H^+]$ and S_T . This is achieved by combining the solubility product and complex formation equations. For example, if a metal sulphide complex MHS^+ is reported, the equilibrium dissociation equation is:

$$[M^{2+}] [HS^-] / [MHS^+] = K_{cl} \quad (28)$$

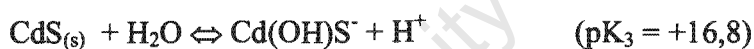
and the solubility product equation is

$$[M^{2+}] [HS^-] / [H^+] = K_{sp}' \quad (29)$$

The equation and equilibrium constant for the complex in the cadmium form is $MS_{(s)} + H^+ \rightleftharpoons CdHS^+$ with some K_x value. Rearranging (28) and (29) above gives the appropriate equilibrium equation:

$$[MHS^+] / [H^+] = K_s' / K_{cl}' = K_x' \quad (30)$$

As an example, consider the metal Cd^{2+} , for which the sulphide complexes $Cd(HS)^+$, $Cd(HS)_2^0$, and $Cd(OH)S^-$ are reported in conjunction with a solubility product for $CdS_{(s)}$ (Daskalakis and Heltz, 1992). The appropriate forms for depicting the system (and the corresponding adjusted equilibrium constants) are:



Taking logarithms of the equilibrium equations for the above reactions and solving for the logarithm of each of the complex species concentrations at aqueous phase equilibrium gives:

$$\log [Cd(HS)^+] = -pK_1 - pH \quad (31)$$

$$\log [Cd(HS)_2^0] = -pK_2 - pH + \log [HS^-] \quad (32)$$

$$\log [Cd(OH)S^-] = -pK_3 + pH \quad (33)$$

Referring to Equation 32 above, the species concentration $[HS^-]$ varies with pH and S_T (as explained earlier) ie. $[HS^-] = S_T K_a' / (K_a' + [H^+]) \sim S_T K_a' / [H^+]$ at $pH < pK_a'$. Consequently, at $pH < pK_a'$, Equation 32 becomes:

$$\log [Cd(HS)_2^0] = -pK_2' + \log S_T - pK_a' \quad (34)$$

And similarly for $\log [Cd^{2+}]$ where $pH < pK_a'$:

$$\log [Cd^{2+}] = -pK_s' - \log S_T + pK_a' \quad (35)$$

Equations 31, 33 and 35 allow a very simple graphical depiction of aqueous – solid phase equilibrium at a particular pH as shown in Figure 2.9 for pH 4, or alternatively at a total dissolved sulphide species concentration across the full pH range.

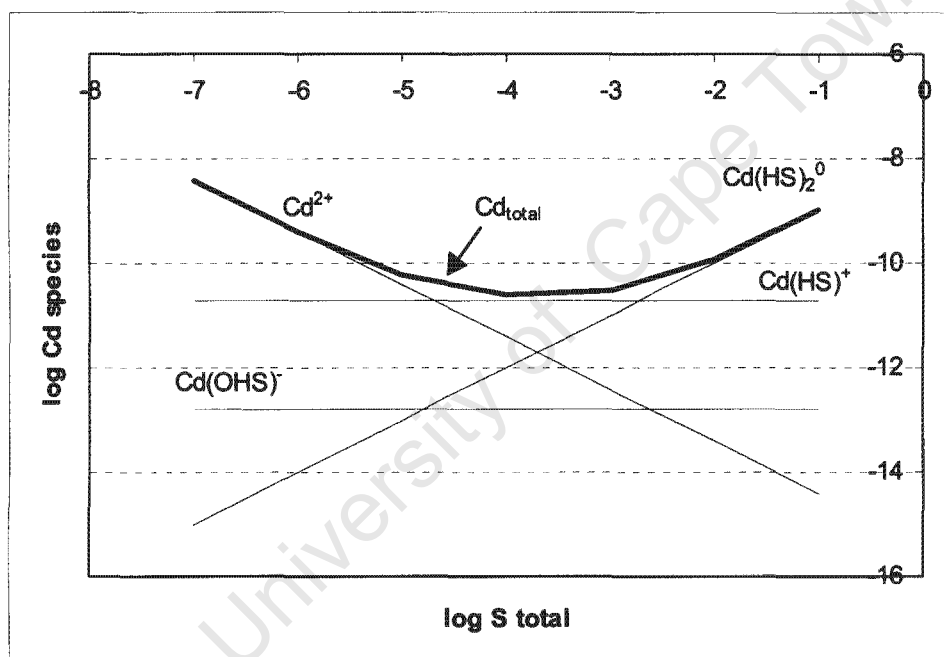


Figure 2.9 Aqueous – solid phase equilibrium diagram for cadmium sulphide species concentration (mol/L) at pH 4 and variable dissolved total sulphide concentrations (mol/L).

2.2 pe-dependant equilibria

The pH-dependant single and two-phase equilibria discussed above assume conditions of fixed low pe (ie. reducing conditions) in order that the oxidation state of participating species may be considered to be stable as pH varies. This however ignores the diversity of metal oxide/hydroxide species which may form under wider redox conditions. In this section therefore pe-dependant (redox) equilibrium dynamics are combined with pH-dependant dynamics in the form of the Pourbaix diagram.

The equation for the half-reaction of the reduction of ferric iron is:

$$K = \frac{[Fe^{2+}]}{[Fe^{3+}][e^-]} \quad (36)$$

The equation for the half-reaction of the reduction of oxygen is:

$$K = \frac{1}{pO_2[H^+]^4[e^-]^4} \quad (37)$$

These relations can be depicted in a Pourbaix diagram where the master variables are pH and pe as shown in Figure 2.10. Instead of having log species concentration on the y-axis, the Pourbaix diagram shows domains of stability for each species as a function of pH and pe. A line representing dissolved O_2 in equilibrium with the air ($pO_2 = 0.21 \text{ atm.}$) is also shown in this plot.

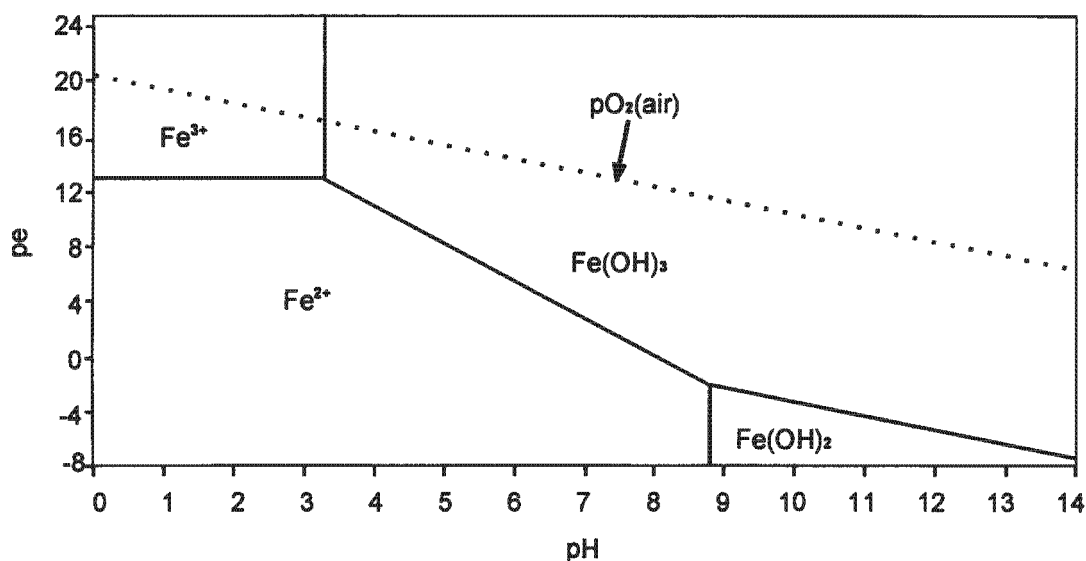


Figure 2.10 Pourbaix diagram showing dissolved Fe ions and solid iron hydroxide species for a maximum dissolved Fe^{3+} species concentration of 10^{-4} M. A more detailed Pourbaix diagram showing additional iron oxides and iron oxyhydroxides is presented in the following chapter.

Consequences for iron and heavy metals removal from AMD waters

Most AMD waters, for example those in the Gauteng region of South Africa, contain *inter alia* a Fe^{2+} concentration of above 1200 mg/L, $\text{Mn}^{2+} > 30$ mg/L, $\text{Ni}^{2+} > 15$ mg/L, $\text{Al}^{3+} > 60$ mg/L accompanied with high SO_4^{2-} concentrations (> 4000 mg/L). For these waters neither of the precipitants $\text{M}(\text{OH})_2$ nor MS are useful *per se* in a treatment process. The metal hydroxides are too voluminous with poor liquid – solid separation properties. Furthermore, the metals are easily leached from the solid phase at a relatively high pH value creating problems of disposal. To effect permanent fixing of the metals, further costly sludge treatment is required.

On the other hand, problems also arise with a metal sulphide removal process because the principal metal sulphide species FeS forms a colloidal precipitant with poor settling properties. In light of the above, oxidation of ferrous iron present in AMD to precipitate ferrite end-products is here considered as a means of complete removal of iron and heavy metals in a single process, without the necessity for further sludge

treatment. Prior to entering the sphere of ferrite formation however, in the next chapter, the pH and pe equilibrium dynamics discussed above provide the basis for an analysis of the kinetics of oxidation of ferrous iron.

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Chapter 3 The kinetics of oxidation of ferrous iron in aqueous solution

Before considering ferrite formation from AMD-like waters it is necessary to consider the oxidation of ferrous (Fe(II)) to ferric (Fe(III)) iron in general. The theory underlying the kinetics of oxidation of Fe(II) in aqueous solution begins with a consideration of empirical observations of the rate in relation to pH. Stumm and Morgan (1996) give the following kinetic equation for the oxidation of Fe^{2+} to Fe^{3+}

$$\frac{-d[Fe^{2+}]}{dt} = k[Fe^{2+}][OH^-]^2 PO_2 \quad (1)$$

This equation was derived from the oxidation of ferrous solutions of no more than 0.5 mM/L (5×10^{-4} M) and at pH values between ~ 4 and 6. In Figure 3.1 it can be seen that below pH ~ 4 the rate of oxidation is independent of pH. Millero (1985) presents data for the rate of oxidation of Fe(II) in solution which includes observations at higher pH values as well (Figure 3.2). This graph shows that at pH values greater than ~8 the rate is independent of pH. At pH values less than ~8 Figure 3.2 is in agreement with Figure 3.1. Thus the overall Fe(II) oxidation rate versus pH graph shows a central region where the rate is strongly pH dependent flanked by regions on either side where the rate is not pH dependent.

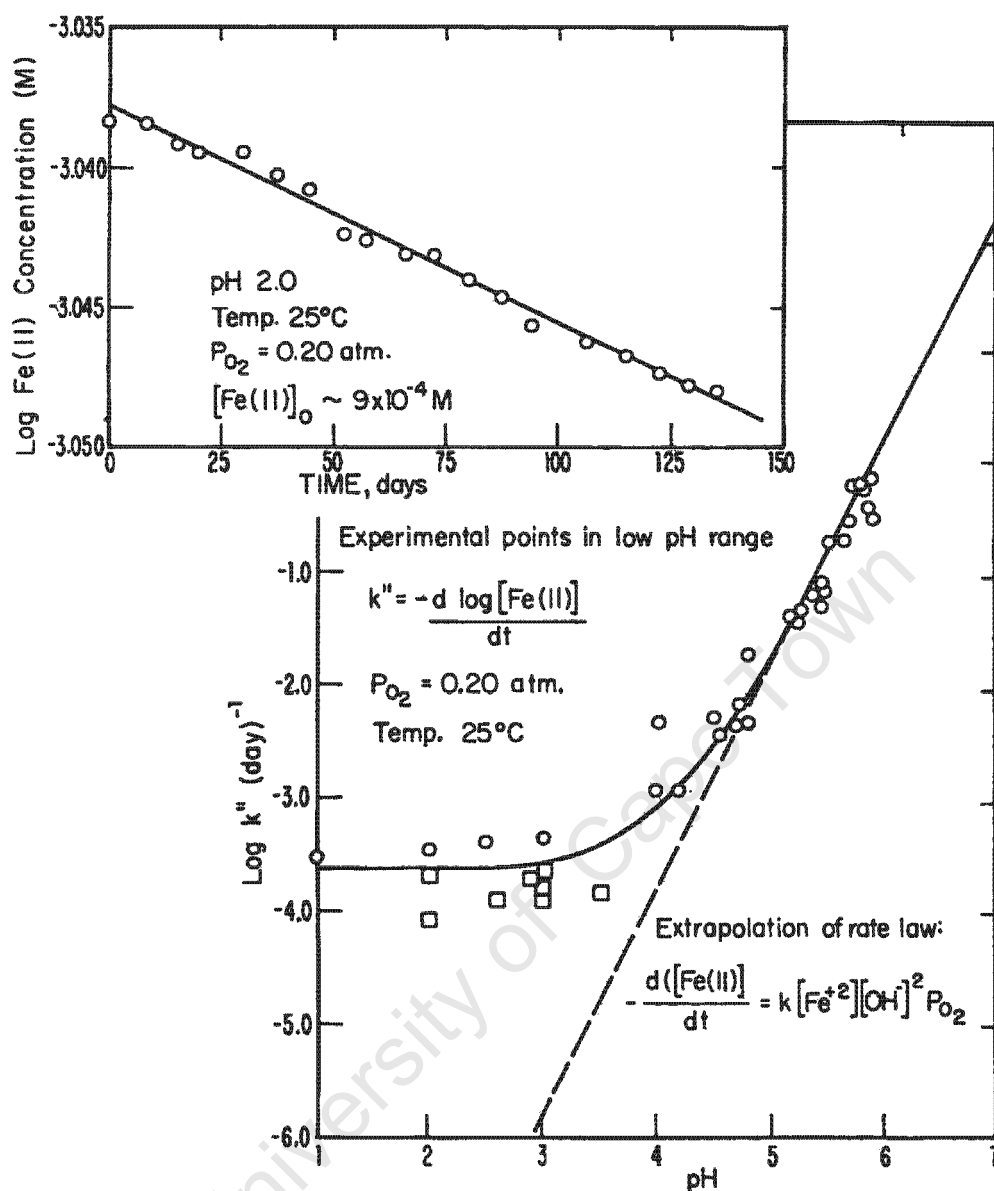


Figure 3.1 Oxidation rate of ferrous iron as a function of pH. At low pH the oxidation rate is independent of pH, while at higher pH values (> 5) the second order dependence on $[\text{OH}^-]$ as required by Equation 1 is fulfilled. Insert: Data for oxidation at pH 2.0 (from Stumm and Morgan 1970).

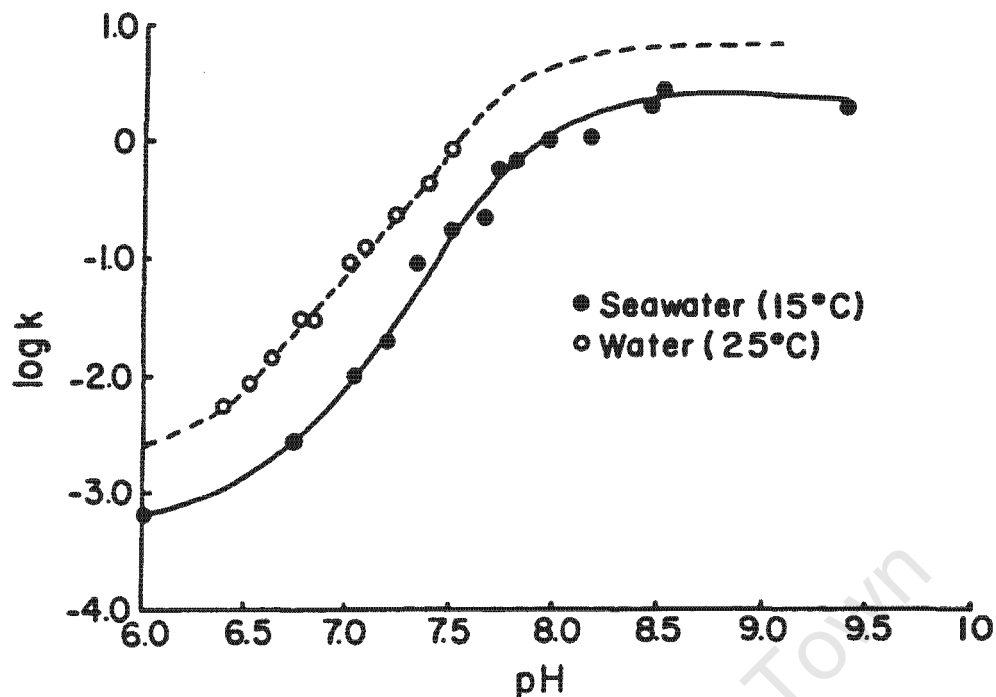


Figure 3.2 Rate constants for oxidation of Fe(II) in water as a function of pH (from Millero 1985).

All of these observations can be explained in terms of the equilibrium chemistry of Fe(II) in aqueous solution. Figure 3.3 is a log species – pH diagram for Fe(II) in single phase liquid equilibrium and Figure 3.4 is a log species – pH diagram for Fe(II) in two phase liquid – solid equilibrium. Inspection of Figure 3.4 shows that in order to reach saturation at pH values below ~8, the total Fe(II) concentration must be orders of magnitude above that used to construct Figure 3.1. In other words, below pH ~8, Fe(II) is effectively infinitely soluble in water and all Fe(II) solutions below this pH region will be non-saturated solutions. The equilibrium chemistry of Fe(II) solutions below ~pH 8 is therefore described by Figure 3.3, ie. single phase liquid equilibrium while for solutions above ~pH 8 Figure 3.4 applies.

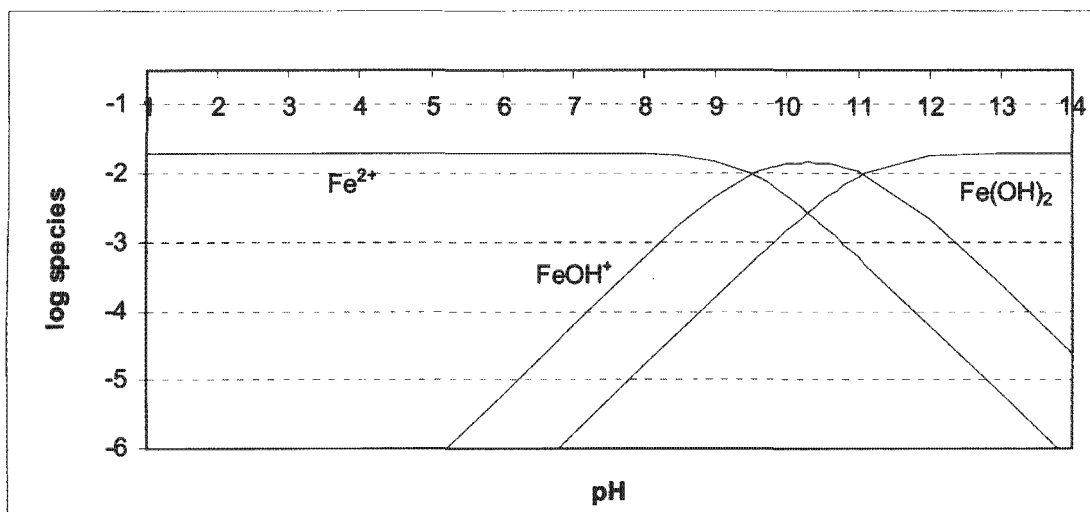


Figure 3.3 Aqueous phase equilibrium for ferrous hydroxide at infinite dilution (Loewenthal et al. 2000).

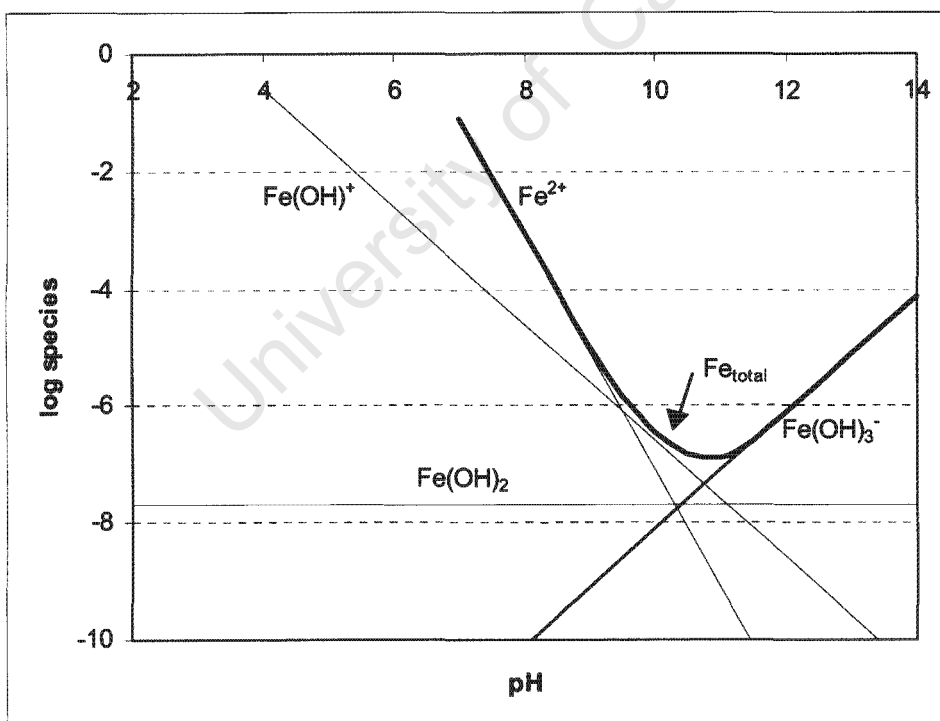
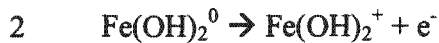
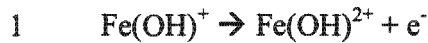
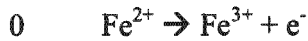


Figure 3.4 Aqueous – solid phase equilibrium for ferrous hydroxide at infinite dilution (Loewenthal et al. 2000).

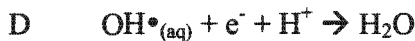
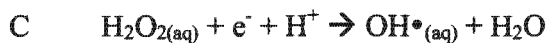
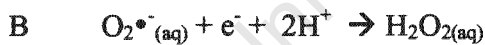
Returning to Equation 1 the oxidation rate is thus first order with respect to PO_2 and $[Fe^{2+}]$ and second order for $[OH^-]$. The following rate equation given by Millero (1985) which separates the individual species found in aqueous Fe(II) solution is useful for the purposes of understanding the oxidation rate in relation to pH¹.

$$\frac{-d[Fe^{2+}]}{dt} = (k_o([Fe^{2+}] + k_1[Fe(OH)^+] + k_2[Fe(OH)_2^0(aq)]))DO \quad (2)$$

From Equation 2 it is clear that more than one oxidation reaction is involved (Stumm and Morgan 1996), viz.



Stumm and Morgan (1996) also provide one-electron steps for the reduction of $O_{2(aq)}$:



Combining sets of equations (0,1,2) with (A,B,C,D), Stumm and Morgan (1996) show that the free energy changes which occur during the oxidation of Fe(II) by oxygen are

¹ In Equation 2 dissolved oxygen concentration (DO) is used instead of PO_2 since it is in fact DO which participates in the oxidation reaction and the DO concentration will vary for a given PO_2 for a variety of reasons such as pH, temperature, ionic strength etc. (Millero 1987).

more negative for the oxidation of $\text{Fe}(\text{OH})_2^0_{(\text{aq})}$ than for either $\text{Fe}(\text{OH})^+$ and Fe^{2+} . In all three reactions 0, 1, 2 step A is endergonic but is least endergonic for reaction 2; and for all three reactions 0, 1, 2 steps B, C, D are all exergonic but in each case reaction 2 is the most exergonic (Figure 3.5a).

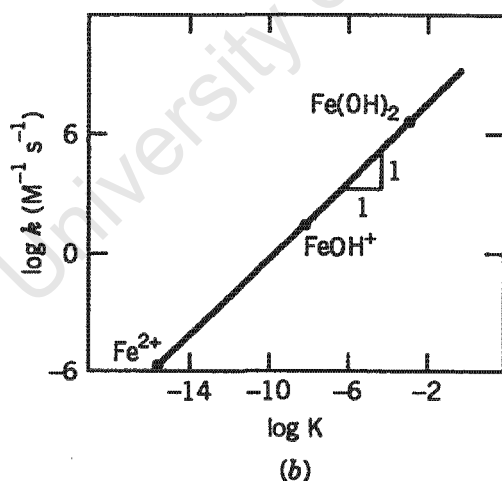
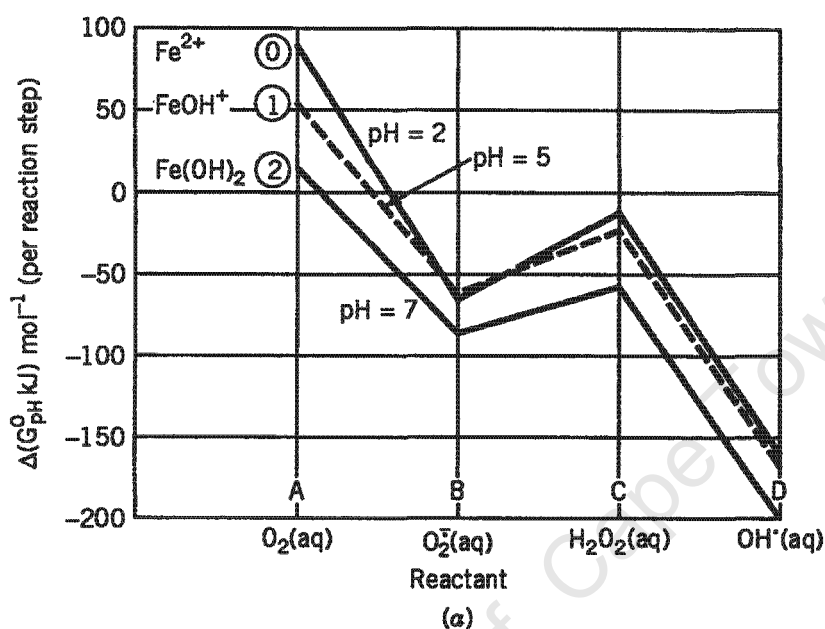
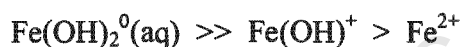


Figure 3.5 a Free energy of the redox reaction steps of the oxidation of Fe(II) to Fe(III) coupled with the one-electron reduction of $\text{O}_{2(\text{aq})}$, $\text{O}_2^{\bullet-}(\text{aq})$, $\text{H}_2\text{O}_{2(\text{aq})}$, and $\text{OH}^\bullet(\text{aq})$ respectively. At pH 2 the oxidation is $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$; at pH 5 $\text{FeOH}^+ \rightarrow \text{Fe}(\text{OH})^{2+}$ and at pH 7 $\text{Fe}(\text{OH})_2^0_{(\text{aq})} \rightarrow \text{Fe}(\text{OH})_2^+$. Reaction A, corresponding to equation A, is endergonic for all three species but least endergonic for $\text{Fe}(\text{OH})_2^0_{(\text{aq})}$. Reactions B, C and D are all exergonic and again most exergonic for the oxidation of $\text{Fe}(\text{OH})_2(\text{aq})$. **b** Plot of reaction rates $\log k$ (from Figure 1) for the oxidation of different Fe(II) species with O_2 (from Stumm and Morgan 1996).

endergonic for all three species but least endergonic for $\text{Fe(OH)}_2^0(\text{aq})$. Reactions B, C and D are all exergonic and again most exergonic for the oxidation of $\text{Fe(OH)}_2^0(\text{aq})$. **b** Plot of reaction rates $\log k$ (from Figure 1) for the oxidation of different Fe(II) species with O_2 (from Stumm and Morgan 1996).

Thus by explicitly making a kinetic argument from thermodynamic data, Stumm and Morgan deduce that step A is the slowest step in each case (because it is most endergonic) and is therefore rate-limiting; and that step A is fastest for reaction 2 (because, of the three, it is least endergonic). Similarly, they deduce that since reaction 2 is most exergonic for steps B, C, D, all in all $\text{Fe(OH)}_2^0(\text{aq})$ produces the fastest oxidation sequence. This conclusion is backed up by two other sources. Firstly 'hydrolysed' ferrous species are more readily oxidised than non-hydrolysed ferrous species:



because OH^- ligands donate electron density through both the σ and π systems to the reduced metal ion which increases reducing power and stabilises the Fe^{3+} formed on oxidation (Stumm and Morgan 1996). Millero (1985) found experimental evidence in support of this. Secondly, Wehrli (1990) has shown a linear free energy relationship between the free energy of the reaction ($\log K$) and the rate ($\log k$) of the reaction for the oxidation of Fe^{2+} , FeOH^+ and $\text{Fe(OH)}_2^0(\text{aq})$ (Figure 3.5b).

Having established the relative rates of oxidation of Fe(II) species one can now easily explain the oxidation rate curve seen in Figures 3.1 and 3.2. It has already been established that Figure 3.3 applies to Fe(II) solutions at $\text{pH} < \sim 8$. Examination of Figure 3.3 shows that in this pH range the concentrations of FeOH^+ and Fe(OH)_2^0 rise steeply with pH. Since these species (especially Fe(OH)_2^0) are far more readily oxidised than Fe^{2+} is, this explains the pH-dependence of the oxidation rate between $\text{pH} \sim 4$ –8. Indeed, above $\text{pH} \sim 5$ both the first two terms on the right hand side of Equation 2 fall away (Stumm and Morgan 1996), which accounts for the second order dependence of the rate law shown in Equation 1 for this pH region. Below $\text{pH} \sim 4$ the concentrations of FeOH^+ and Fe(OH)_2^0 are so low as to be negligible and Fe^{2+}

dominates. Since the oxidation of Fe^{2+} is independent of hydroxyl groups, the oxidation rate is no longer pH dependent.

As already established for all pH values above ~ 8 , all Fe(II) solutions of the order of at least 10^{-3} molar concentration will be saturated solutions. Figure 3.4 shows the speciation of Fe(II) in two phase liquid – solid equilibrium. Here at pH ~ 8 although Fe^{2+} exceeds both FeOH^+ and FeOH_2^0 in concentration, the latter two species are far more easily oxidised due to the presence of hydroxyl groups (Figure 3.5b shows the relative pH dependent rates because pH is built into the value of $\log K$). As one moves from pH ~ 8 to the right in Figure 3.4, both the Fe^{2+} and FeOH^+ concentrations drop steeply whilst the FeOH_2^0 concentration is constant. As the pH increases above 8 the oxidation rate (Equation 2) therefore becomes dominated by FeOH_2^0 . Since this species is constant with respect to pH ‘throughout’² the range, the rate above pH ~ 8 becomes independent of pH.

In conclusion, the arguments above summarise the explanations for the shape of the rate of oxidation of Fe(II) in solution versus pH plot. Taken together, this suggests a sigmoid-shaped curve for the Fe(II) oxidation rate against pH. This is because:

- At pH values below ~ 4 , Fe^{2+} dominates in Equation 2 (Figure 3.2).
- At pH $> \sim 5$, Fe(OH)_2^0 dominates in Equation 2 because it is far more readily oxidised than Fe^{2+} and FeOH^+ .
- Between pH 5 and 8 the Fe(OH)_2^0 concentration rises strongly with pH (Figure 3.3).
- At pH values $> \sim 8$ Fe(OH)_2^0 dominates in Equation 2 and its concentration does not vary with pH.

² Although Figure 3.4 shows the FeOH_2^0 concentration as constant below pH ~ 8 , in practise this never arises for the reasons stated above, ie. all Fe(II) solutions of concentrations of the order of 10^{-3} M/L are unsaturated below pH ~ 8 and single phase liquid equilibrium (Figure 3.3) rather than two phase liquid-solid equilibrium (Figure 3.4) applies. As the pH moves below ~ 8 the threshold for saturation rises logarithmically so that in practise saturated Fe(II) solutions never occur at pH $< \sim 8$.

In saturated Fe(II) solutions Equation 2 reduces to:

$$\frac{-d[Fe^{2+}]}{dt} = kDO \quad (3)$$

because the $[Fe(OH)_2^0]$ is constant (or in Equation 1 the solubility product is a constant). Thus at $pH < \sim 7-8$ the rate limiting factor governing the oxidation rate appears to be pH whereas at high pH values, the DO concentration is the rate-limiting factor.

Finally various other factors which influence the rate of oxidation are noted:

- The rate is both thermodynamically and kinetically enhanced by adsorption of dissolved iron species to hydrous oxide surfaces. This is also because of the association with OH^- (Stumm and Morgan 1970).
- Catalysts such as Co^{2+} and Cu^{2+} enhance the oxidation rate (Stumm and Morgan 1970).
- Anions such as Cl^- and SO_4^{2-} retard the oxidation rate (Millero 1985).
- High ionic strength retards the oxidation rate (Stumm and Morgan 1970, Millero 1985).

It will nevertheless become apparent below that the oxidation rate is not the rate-limiting factor in magnetite formation.

Chapter 4 Pathways and mechanisms of ambient temperature ferrite formation

In recent years interest in ambient temperature magnetite formation has grown largely because of the opportunities it affords for metals removal from large volumes of AMD. However, as Perales Perez et al. (2001a) who provided the first review of the subject observed, the literature regarding the pathways and mechanisms of ferrite formation in aqueous solution at ambient temperature is poorly developed. Cornell and Schwertmann (1996), in their authoritative book on the iron oxides, also note that the precise mechanism of magnetite formation from ferrous hydroxide has not been determined¹. A major reason for this situation stems from the inherent complexity of the processes which occur during magnetite formation. This complexity is highlighted, for example, by the fact that in general under a single set of oxidising conditions two different iron oxide end-products tend to be produced (Cornell and Schwertmann 1996) and conditions must be precisely controlled if a predominance of one end-product over the other is to be achieved. Nevertheless the following discussion aims to integrate that information which is available into an overall picture of ambient temperature ferrite formation in a manner useful to the purposes of this research.

¹ Table 14.1 on page 350 in Cornell and Schwertmann (1996) lists all the interconversions among the iron oxides. For each interconversion the type of transformation is given, eg. thermal dehydroxylation, oxidation, reduction-dissolution etc. Out of all 27 transformations given, the transformation from ferrous hydroxide to magnetite is the only transformation for which the type is “not determined”.

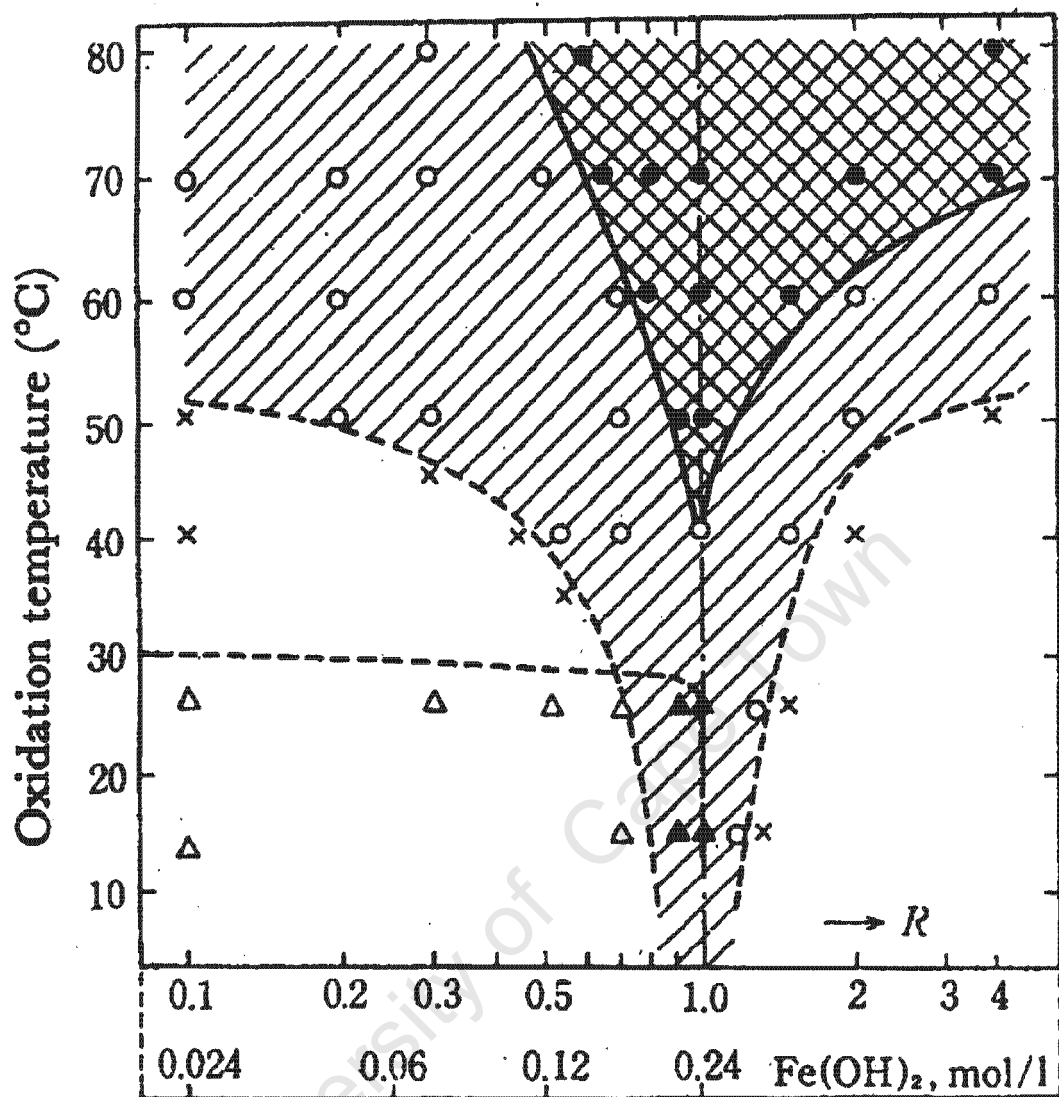


Figure 4.1 Conditions for the formation of Fe_3O_4 by the air oxidation of $\text{Fe}(\text{OH})_2$ suspensions. Airflow = 200L/hr. X-axis: $R = \text{Fe} : (\text{OH})_2$ ratio, Y-axis: Temperature (from Kiyama 1974)

- Fe_3O_4
- x $\alpha\text{-FeOOH}$
- Mixture of Fe_3O_4 and $\alpha\text{-FeOOH}$
- Mixture of Fe_3O_4 , $\alpha\text{-FeOOH}$ and $\gamma\text{-FeOOH}$
- Δ Mixture of $\alpha\text{-FeOOH}$ and $\gamma\text{-FeOOH}$

It has long been well-established that magnetite can be precipitated by oxidising aqueous ferrous solutions at temperatures $> \sim 50\text{ }^{\circ}\text{C}$ and as high as $100\text{ }^{\circ}\text{C}$ (Sidhu et al. 1978, Regazzoni et al. 1981, Blesa and Matijevic 1989, Tamaura et al. 1991a, Mandaokar et al. 1994, Cornell and Schwertmann 1996). This fact is well-illustrated in Figure 4.1 which indicates that magnetite will not ordinarily form at temperatures below $40\text{--}50\text{ }^{\circ}\text{C}$. At temperatures above $40\text{--}50\text{ }^{\circ}\text{C}$ magnetite appears to form via a dissolution re-precipitation pathway (Perales Perez et al. 2001a, Sagumoto and Matijevic 1980, Kiyama 1974) but further details on the reaction mechanism are not known. More recently it has been established that magnetite can be formed via the oxidation of aqueous ferrous solutions at ambient temperatures ($\sim 25\text{ }^{\circ}\text{C}$) if oxidation conditions are controlled (ie. oxidation rate not too high) (Misawa et al. 1974, Tamaura et al. 1984, Cornell and Schwertmann 1996, Perales Perez et al. 1999, Perales Perez and Umetsu 2000). As discussed below, magnetite formation from ferrous solutions depends upon there being a correct balance between the rate of oxidation of FeII and the rate of crystallisation of magnetite. If oxidation outstrips crystallisation the rate of formation of ferric-only oxo-hydroxide (FeOOH) end-products becomes significant.

Perales Perez and Umetsu (2000) provide the following steps and equations to illustrate the mechanism of magnetite formation from the oxidation of aqueous ferrous solutions at pH 11 at ambient temperature:

(a) Hydrolysis of ferrous ion:



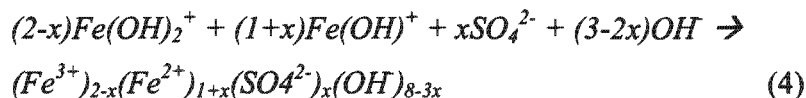
(b) Oxygen transfer:



(c) Oxidation of ferrous ion:

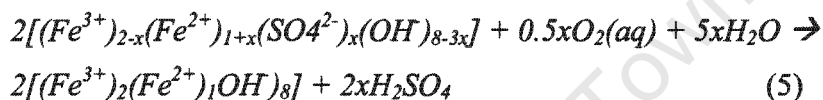


(d) Precipitation of a partially oxidised intermediate (green rust 2):



where x = the number of moles of Fe^{2+} which still need to be oxidised in order to bring the Fe(III) : Fe(II) ratio to 2 : 1 which is the ratio of these ions in magnetite.

(e) Further oxidation of ferrous iron in the green rust 2 intermediate and subsequent hydrolysis of the produced ferric species:



(f) Dehydroxylation/dehydration² and magnetite formation:



Dehydroxylation results in the replacement of hydroxy-bonds with oxo-bonds which enables face-sharing between octahedra and a subsequent increase in crystal density (Cornell and Schwertmann 1996, p. 351).

Green rust

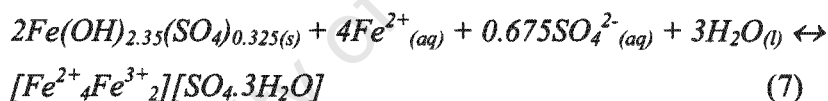
Green rusts (GR), first described by Keller in 1948 (Cuttler et al. 1990), are double-layer hydroxide salts in which positively charged octahedral Fe^{2+} – Fe^{3+} hydroxy layers are linked by interlayer Cl^- , SO_4^{2-} or CO_3^{2-} anions (Hansen et al. 1994, Cornell and Schwertmann 1996). If chloride anions form the interlayer the solid compound is

² The terms dehydration and dehydroxylation are both frequently and interchangeably used to refer to the transformations which occur in Equation 6 because in this instance as OH^- groups disappear from the left-hand side of the equation, H_2O groups appear on the right-hand side. Cornell and Schwertmann (1996, p. 351) for example refer to the following reaction as a dehydration transformation: $2FeOOH \rightarrow Fe_2O_3 + 2H_2O$.

designated Green Rust 1 and if sulphate anions form the interlayer it is designated Green Rust 2. Where carbonate anions form the interlayer, some authors (eg. Drissi et al. 1995) use the designation Green Rust 1 but in order to distinguish it from chloride GR1 it is usually referred to as carbonate GR. Green rusts are only stable at low redox potential, ie. in a reducing environment and appear green in solution. Structurally green rusts have a cubic closed pack crystal structure and belong to the sjogrenite-pyroaurite class of hydroxides (Perales Perez et al. 2001a, Schwertmann and Fechter 1994). The chemical formula for GR2 is $[\text{Fe}^{2+}_4\text{Fe}^{3+}_2(\text{OH})_{12}]^{2+}[\text{SO}_4^{2-} \cdot 3\text{H}_2\text{O}]^{2-}_{(s)}$ (Hansen et al. 1994, Genin et al. 1996).

Green Rust 2 has been reported to form in at least two different pathways:

1. Aerial oxidation of Fe^{2+} ions, $\text{Fe}(\text{OH})^+$ or $\text{Fe}(\text{OH})_2$ to a hydrous, poorly ordered ferrihydrite ('ferric hydroxide') at ~pH 7. Ferrihydrite in turn reacts with dissolved Fe^{2+} ions at neutral pH values to form GR through the following reaction (Fox 1988, Hansen et al. 1994):



2. Direct precipitation of GR from an initial mixture of ferric and ferrous ions at neutral/slightly basic pH values through the same reaction (Hansen, 1994).

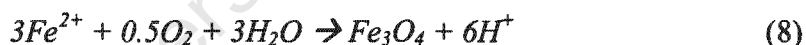
It is noted that an aqueous solution of ferrous iron, from which all oxygen is excluded, when raised to above pH ~7–8, appears whitish in colour. That is, aqueous ferrous hydroxide in aqueous suspension is *white*. Invariably when a ferrous solution is made using a ferrous salt such as ferrous sulphate or ferrous chloride and distilled water, and the pH is raised above pH ~7–8, the resulting suspension is *green* in appearance. The reason for this is that oxygen already dissolved in the water rapidly oxidises some ferrous iron to ferric iron and some of the solid which forms as the iron precipitates out of solution is not ferrous hydroxide but green rust, the green colour of which dominates over the milky-white ferrous hydroxide.

Green rusts containing cations other than iron are also well-known. For example Tamaura (1985, 1986) produced Ni-bearing and Zn-bearing green rusts where divalent ferrous ions are partially replaced by divalent Ni or Zn ions. These non-ferrous metal-bearing GRs can spontaneously transform into ferrites, albeit slowly, at near-ambient temperature (30–70°C) in the pH range 7.6 to 10.6. This transformation reaction occurs via a *dissolution* (of GR) – *precipitation* (of ferrite) process, as evidenced for example by the fact that it does not occur if the GR is first dehydrated (Cornell and Schwertmann 1996).

Because of the preference for divalent over monovalent anions in the interlayer (Miyata, 1983), GR2 and carbonated GR will prevail over GR1 in acid mine drainage. Moreover, because the SO_4^{2-} concentration is much higher than the carbonate system concentration in such waters, GR2 will be the dominant species.

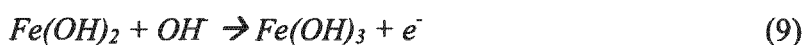
Alkalinity changes during oxidation of ferrous solutions

The following equation shows that two moles of alkalinity are required for every mole of Fe^{2+} oxidised by oxygen to magnetite (Lahav et al. 2003):



This OH^- demand can be thought of as the $\text{Fe}^{2+} : \text{OH}^- = 1 : 2$ ratio required to form $\text{Fe}(\text{OH})_{2(s)}$ from Fe^{2+} (hydrolysis).

The following half-reactions of the redox exchanges between oxygen and $\text{Fe}(\text{OH})_2$ illustrate that once $\text{Fe}(\text{OH})_2$ is formed no further net OH^- is required during the $\text{FeII}(\text{OH})_2 \rightarrow \text{FeIII}(\text{OH})_3$ *oxidation-hydrolysis reaction* which occurs during the formation of magnetite from $\text{Fe}(\text{OH})_2$:



(oxidation-hydrolysis consumes $\text{OH}^- : \text{Fe}^{2+} = 1:1$)



(reduction of O_2 generates $OH^- : Fe^{2+} = 1:1$)

Summing the half-reactions:



(overall no net OH^- alkalinity change)

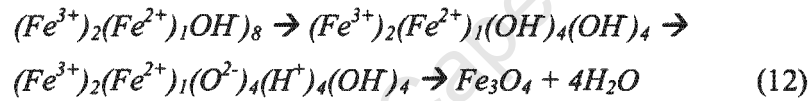
Indeed in general, from a stoichiometric perspective the $FeII(OH)_2 \rightarrow FeIII(OH)_3$ oxidation-hydrolysis reaction involves no net alkalinity change *irrespective* of whether the end-product of oxidation is magnetite or any other iron oxide or oxyhydroxide such as Fe_2O_3 or $FeOOH$.

However what does differ among the various possible end-products of oxidation-hydrolysis of aqueous $Fe(OH)_2$ solutions is the rate at which oxidation-hydrolysis occurs. Perales Perez and Umetsu (2000) studied the rate patterns of oxidation-hydrolysis of $Fe(OH)_2$ solutions at ambient temperature by recording the volume of KOH solution needed to maintain a constant pH (pH 11) during the reaction (Figure 4.2b below).

Given that the overall OH^- requirement is the stoichiometric $Fe : OH^- = 1 : 2$ required to hydrolyse Fe^{2+} , and that as explained above no further net OH^- addition is needed, the need to add KOH during the reaction reflects the fact that *not all the Fe^{2+} is immediately hydrolysed at the beginning of the reaction* when the bulk of the total OH^- demand is added so as to bring the solution to pH 11. Equations 1–6 in this chapter together with steps (a) to (f) are useful in explaining this observation.

In step (a) Fe^{2+} is only partially hydrolysed to $Fe(OH)_2$, the rest being $FeOH^+$. This means that the OH^- demand is initially less than the stoichiometric $Fe^{2+} : OH^- = 1 : 2$ ratio found in $Fe(OH)_2$. During the initial oxidation of ferrous iron in step (c), $Fe(II)OH^+$ undergoes oxidation and only partial hydrolysis to $Fe(III)OH^{2+}$ which accounts for continued sub-stoichiometric OH^- demand. The rate at which OH^- is consumed in this step depends on the rate of oxidation of ferrous iron. In step (d) the formation of the sulphated ferrous-ferric intermediate green rust 2 (GR2) compound

occurs, *only* to the extent that ferric ions created in step (c) are present . As step (c) is continually generating ferric ions, a continual alkalinity demand is exerted during step (d). This demand which contributes to the total negative charge which balances the total positive charge made up by Fe^{2+} and Fe^{3+} in GR2 *is met not only by OH⁻ ions but also by SO₄²⁻ ions present in the medium* (step e). During the formation of GR2, the Fe ‘acidity’ is thus neutralised by both OH⁻ and SO₄²⁻ ‘alkalinity’ which further advances the sub-stoichiometric phase. When the oxidation of ferrous ions has proceeded to the point where the FeII : FeIII ratio = 1 : 2 (ie. the ratio of these ions in magnetite), SO₄²⁻ ions in GR2 are replaced by OH⁻ ions thereby transforming the GR-like intermediate into hydrated magnetite (step f). This replacement of sulphate ions in the ferrous-ferric intermediate compound with OH⁻ *finally brings the OH demand to its stoichiometric Fe : OH = 1 : 2 value*. In the final step depicted by the following stepwise dehydration process:



no additional OH⁻ demand is exerted. Thus in the transformation of $\text{Fe}(\text{OH})_2$ into magnetite Fe_3O_4 , no net alkalinity/acidity is created or destroyed.

Aging

This final step of dehydration-crystallisation may be the rate-limiting step in magnetite formation (Cornell and Schwertmann 1996), although it is also thought that the transformation from GR to magnetite proceeds via a dissolution-precipitation route where dissolution is considered the rate-limiting step (Perales Perez et al. 2001a). A distinction should thus be made between the rate-limiting step in the transformation of $\text{Fe}(\text{OH})_2$ into fresh hydrated magnetite (Equations 1–5) and the rate-limiting step in the transformation of fresh hydrated magnetite into mature well-crystallised magnetite. ‘Aging’ describes the time taken for freshly formed hydrated

magnetite to mature into dehydrated³ well-crystallised magnetite. Two distinct simultaneously-occurring processes can nonetheless be identified during aging: sulphate expulsion and replacement with OH⁻ (proton release) and dehydration-crystallisation (no proton release) (Perales Perez et al. 1999).

In conclusion the overall pattern of KOH consumption during ambient temperature ferrite formation depends upon the rates of oxidation of ferrous ions, the rates of formation of sulphated intermediates and the rates of subsequent substitution of OH⁻ for SO₄²⁻ in the ferrous-ferric compound during the reaction.

Figure 4.2 shows (a) changes in oxidation–reduction potential (ORP) and (b) rate of proton release with duration of oxidation of ferrous sulphate solutions at ambient temperature with the aim of producing magnetite as end-product (Perales Perez and Umetsu 2000). The ‘conditioning stage’ refers to the period during which the pH is raised from ~ pH 4 to pH 11. Thereafter the ‘contact stage’ refers to aerial oxidation of the solution, the pH of which is maintained at 11 by the addition of known amounts of a KOH solution. The pattern of KOH consumption was found to differ during different ‘zones’ during the contact stage as follows:

³ ie. as mentioned above dehydration/dehydroxylation → replacement of hydroxy-bonds with oxo-bonds → face-sharing between octahedral → increased crystal density.

Contact stage zones:

- **< 10 mins contact:** Voluminous weakly magnetic green (GR2) precipitate. **Mechanism:** Minimal proton release, insufficient oxidation, $\text{Fe}^{3+} : \text{Fe}^{2+}$ ratio too low for magnetite formation to occur.
- **Zone 1:** ~ 10 minutes oxidation time, initially no change then rapid oxidation-hydrolysis. The rate of proton release = $1.6 \times 10^{-4} \text{ mol H}^+/\text{Lmin}$ (the range of proton release in which magnetite is produced = $0.4\text{--}1.6 \times 10^{-4} \text{ mol/Lmin}$). Oxidation-hydrolysis $\rightarrow$ initial green precipitate $\rightarrow$ black after ~ 10 minutes of contact stage (hydrated magnetite). **Mechanism:** sufficient oxidation, $\text{Fe}^{3+} : \text{Fe}^{2+}$ ratio ~ 2 : 1 which is the correct stoichiometry for magnetite formation to occur. (ORP = -120mV).
- **Zone 2:** Less rapid oxidation-hydrolysis. Proton release rate is less than $0.4 \times 10^{-4} \text{ mol H}^+/\text{Lmin}$, ie. outside of magnetite producing range, and black mixture turns brown. **Mechanism:** Overoxidised, $\text{Fe}^{3+} : \text{Fe}^{2+}$ ratio $\gg 2 : 1$, too much ferric $\rightarrow$ ferric-only end-products. (ORP close to zero).
- **Zone 3:** Negligible H^+ release. **Mechanism:** In addition to primary ferric-only end-products, secondary oxidation of formerly produced magnetite occurs (ORP = 0).

After Zone 1 further oxidation produces an excess of ferric iron and significant amounts of purely ferric end-products result. As to be expected, the creation of more ferric will result in more hydrolysis and more OH^- demand/ H^+ release, albeit at a lower rate (see Zones 2 and 3 in Figure 4.2b). However this 'extra' proton release does not however represent a different stoichiometry from the case where the reaction stops when magnetite is predominantly produced. This is because for every H^+ released during hydrolysis, during oxidation another H^+ is consumed (Equation 10).

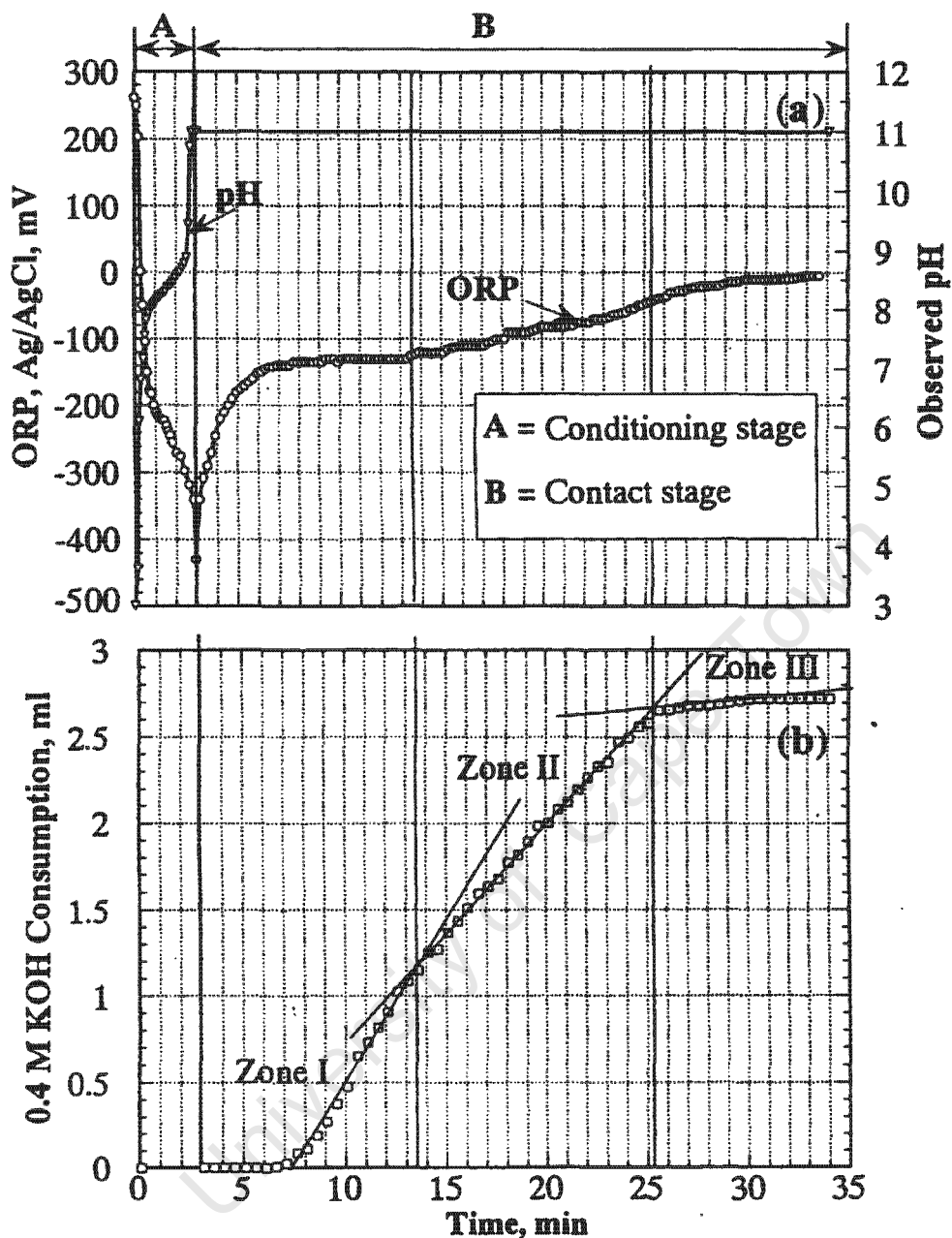


Figure 4.2 (a) Changes in redox potential (ORP) and (b) rate of proton release with duration of oxidation at ambient temperature (from Perales Perez and Umetsu 2000).

Thus according to the scheme of Perales Perez and Umetsu (2000) given above (Equations 1–6, steps a–f), proton release comes from two sources in the magnetite formation reaction:

- a) $\text{Fe}^{2+} \rightarrow \text{Fe}(\text{OH})_2$ hydrolysis reaction (OH^- consumption)
- b) SO_4^{2-} expulsion during aging (Cornell and Schwertmann 1996, p. 342, Perales Perez et al. 1999, p. 133, Figure 5)

Perales Perez et al. (2001a) show that at 55 °C proton release is non-linear suggesting that the mechanism of ferrite formation may be different from that at ambient temperatures where proton release follows a linear pattern.

Oxidation versus dehydration-crystallisation

Ambient temperature magnetite formation requires that the rate of oxidation of ferrous species is not too high so that a right balance between the rate of oxidation of FeII and the rate of dehydration-crystallisation occurs. If oxidation outstrips dehydration-crystallisation the rate of formation of ferric-only oxo-hydroxides (FeOOH) becomes significant. Cornell and Schwertmann (1996, p. 343) attribute this to ‘competition’ between the oxidation and dehydroxylation reaction steps. This refers to the fact that dehydroxylation is the rate-limiting step in magnetite formation. They state:

“Magnetite formation probably requires slow oxidation because complete dehydroxylation of the precursor (green rust) prior to complete oxidation is only possible if sufficient time is available...”

Blesa and Matijevic (1989, p. 214, 216) similarly state that:

“formation of magnetite requires that available Fe(II) behaves as an effective scavenger for Fe(III) ions preventing the formation of solids containing ferric ions only.... The formation of magnetite depends crucially on the fate of Fe(III) ions generated by oxidation; if the rate of oxidation is enhanced by adding oxygen, the rate of nucleation of magnetite around a given Fe(III) center becomes comparable to the rate of oxidation of neighbouring Fe(II) ions; eventually, only ferric (hydrous) oxides [FeOOH] may nucleate”

In contrast Misawa et al. (1974), noting that magnetite formation requires the removal of two oxygen ions per three molecules of $\text{Fe}(\text{OH})_2$, attribute the need for controlled oxidation to the time needed for the removal of oxygen and rearrangement of oxygen and iron in the crystal lattice. The formation of FeOOH on the other hand, they say, requires only the removal of a proton from $\text{Fe}(\text{OH})_2$.

Liquid or solid phase transformation

There is a similar lack of consensus as to whether the oxidation of $\text{Fe}(\text{OH})_2$ via an intermediate into magnetite occurs as a liquid or solid phase transformation. On the basis of thermodynamic and structural considerations Misawa et al. (1974) describe a topotactic phase⁴ transformation (a solid state rearrangement of atoms in a single crystal) from $\text{Fe}(\text{OH})_2$ via GR to magnetite. The essence of their analysis pertains to the differences in close-packing of oxygen between $\text{Fe}(\text{OH})_2$ which has hexagonal close-packing and magnetite which has cubic close-packing. They suggest that GR which they say has *both* hexagonal and cubic close-packing of oxygen provides a structural pathway from $\text{Fe}(\text{OH})_2$ to magnetite. Feitknecht (1959) used TEM to track magnetite formation via GR from $\text{Fe}(\text{OH})_2$ in strongly alkaline media and also concluded a topotactic transformation was involved. However under strongly alkaline conditions Sugimoto and Matijevic (1980) using a variety of investigative techniques including radioactive ^{59}Fe isotope tracing and transmission electron microscopy (TEM), deduced a dissolution re-crystallisation pathway. These authors showed the growth of small primary nuclei near the surface of platy $\text{Fe}(\text{OH})_2$ crystals. This growth involved soluble species and the small primary magnetite particles then aggregated and underwent contact recrystallisation to form single crystals. On the basis of electron microscopy and oxidation kinetics, Kiyama (1974) also concluded that a reconstructive liquid state transformation involving $\text{Fe}(\text{OH})_2$ or green rust 2 dissolution $\rightarrow$ ferrous oxidation $\rightarrow$ magnetite precipitation occurs. To put the question into perspective, in their review Perales Perez et al. (2001a) note both the structural arguments of Misawa (1974) for the solid state phase transformation via GR and SEM evidence for the dissolution – precipitation mechanism.

⁴ In this context the term 'phase' refers not to gas/liquid/solid phases but to a species of iron oxide.

Intermediate and end-products of oxidation of ferrous sulphate solutions: effect of pH

Cornell and Schwertmann (1996) review the effect of pH on the oxidation of ferrous solutions. They divide their discussion as follows:

Acid media: Intermediate GR phases do not form and ferric oxide/hydroxide end-products precipitate directly from soluble FeIII. At pH < 5 and at ambient temperature ferrihydrite forms and at pH 2.74 goethite (α FeOOH) forms.

Slightly acid to slightly alkaline media: At pH 6–7 GR precipitates and at slightly lower pH soluble GR complexes form. Further oxidation at ambient temperature $\rightarrow$ goethite (α FeOOH) and/or lepidocrocite (γ FeOOH).

Moderately alkaline media: At pH > 8 $\text{Fe}(\text{OH})_2 \rightarrow$ magnetite.

Strongly alkaline: $\text{Fe}(\text{OH})_2 \rightarrow \text{GR} \rightarrow$ magnetite.

The number of studies on oxidation of ferrous solutions at ambient temperature are few and the results are not always in agreement. Moreover, comparison is difficult because conditions differ in such ways as pH, concentration of Fe solution, oxidising agent, presence of seed and so on. For example, the following results of Kiyama (1974) contrast with those reported by Cornell and Schwertmann (1996) given above in that GR was not found to be present at high pH (Table 4.1):

R (2NaOH : FeSO₄)	Initial pH	Final pH	Intermediate	End-product*
0.5	7.2	6.5–3.7	GR2	Fe ₃ O ₄ >> α FeOOH
0.6	6		GR2	Fe ₃ O ₄ / γ FeOOH
0.6–1.0	7-9	4.5	GR2, Fe(OH) ₂	Fe ₃ O ₄ / γ FeOOH
1.0	9-10		Fe(OH) ₂	Fe ₃ O ₄
> 1.0	>10		Fe(OH) ₂	Fe ₃ O ₄

Table 4.1 Intermediate and end-products of oxidation of ferrous sulphate solutions (Kiyama 1974). *See Figure 4.1: Fe₃O₄ formed at higher temperatures, FeOOH at lower temperatures.

Perales Perez et al. (1998) present data which is very similar to that of Kiyama's shown above (Table 4.2).

pH	7	8	10	12
Fe phase(s)	GR L	GR L	M	M

Table 4.2 Intermediate and final Fe phases present during ambient temperature magnetite formation from ferrous solutions at various pH values. GR = green rust, L = lepidocrocite (γ FeOOH), M = magnetite. XRD was used to determine Fe phases. Data from Perales Perez et al. (1998).

From the data of Kiyama (1974) and Perales Perez et al. (1998) there appears to be a transition point in the region of pH ~8 where $\text{Fe}(\text{OH})_2$ replaces GR as the intermediate species during magnetite formation from ferrous solutions. It is nonetheless often reported that GR⁵ is the intermediate during ambient temperature ferrite formation from ferrous solutions at high pH (Kiyama 1974, Tamaura et al. 1991, Perales Perez et al. 1998, 2001a); and as seen in Equations 1–6 of Perales Perez and Umetsu (2000) given above, these authors include GR2 as the intermediate ferrous-ferric state of iron during ambient temperature ferrite formation at pH 11, despite their own data shown in Table 4.2. To confuse matters further Tamaura et al. (1991) state that ferrite formation can follow two pathways depending on pH. At pH values ranging from 7 to 10 ferrites form through the GR path whilst at a pH of 10.5 to 11 ferrites form from lepidocrocite (γ - FeOOH)⁶. There are thus inconsistencies in the literature on the exact role of GR and other intermediates during ferrite formation.

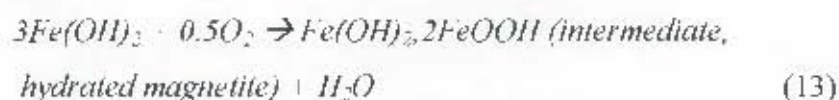
Olowe and Genin (1991) studied the mechanisms of oxidation of ferrous hydroxide in the presence of sulphate ions at ambient temperature. Their results are in conflict with those of Cornell and Schwertmann (1996) and the scheme given by Perales Perez et al. (2001a) given above, and resemble the results reported by Kiyama (1974) shown in Table 4.1 insofar that above ~ pH 8, GR does not play an intermediate role. These investigators studied the initial, intermediate and end-products of oxidation of ferrous hydroxide in the presence of sulphate ions according to varying ratios of Fe : OH at ambient temperature. This latter ratio which they called R⁷ has a determining effect on the reaction (Table 4.3). From this table it can be seen that sulphated intermediates only occur at values of R greater than 0.5 (so-called ‘acidic’ values). At R = 0.5 the intermediate is hydrated magnetite which contains no sulphate but also being green in appearance may be superficially confused with green rust.

Based on their earlier work, Olowe et al. (1991) conclude that the pathway of oxidation of ferrous hydroxide at $9 < \text{pH} < 11$ is as follows:

⁵ GR2 in the case of ferrous sulphate solutions and GR1 in the case of ferrous chloride solutions.

⁶ In the latter case they state that oxidation of the Fe(II) ions takes place on the surface of ferrite particles onto which the Fe(II) ions have been adsorbed. The initial source of these ferrite particles is not made clear.

⁷ R in Figure 4.3 is defined differently to R in Table 4.1.



They emphasise that following the oxidation of ferrous hydroxide, hydrated magnetite contains ferrous and ferric ions in the same ratio as they occur in magnetite:



Description	R (Fe:OH)	pH	Intermediate compound	End-product
Acidic R > 0.5 Sulphated intermediates	4/7	< 8.5	GR2	Goethite (α -FeOOH)
	7/12		(4Fe(OH) ₂ ·2FeOOH, FeSO ₄ ·nH ₂ O)	Lepidocrocite (γ -FeOOH)
	5/8		Sulphated ferrous hydroxide* / GR2	α and γ FeOOH
Stoichiometric R = 0.5	0.5	9–11	Hydrated magnetite (Fe(OH) ₂ ·FeOOH)	Magnetite (Fe ₃ O ₄)
Basic R < 0.5	1/3	< 11	Amorphous active α' - FeOOH	Goethite (α -FeOOH)
No sulphated intermediates	5/12		Basic compound (3Fe(OH) ₂ ·2Fe(OH) ₃)	Basic compound and δ -FeOOH?

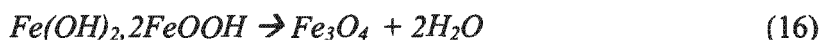
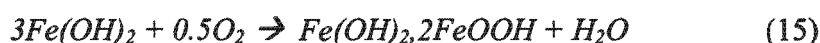
Table 4.3 The initial, intermediate and end-products of oxidation of ferrous hydroxide in the presence of sulphate ions according to varying ratios of Fe : OH. Sulphated intermediates (ie. GR2) were only found at Fe : OH ratios of greater than 0.5.

*Sulphated ferrous hydroxide is an *initial* (non-oxidised) product; the true intermediate (ie. partially oxidised) product at this value of R is still GR2. Compiled using data from Olowe and Genin (1991).

The work of Olowe and Genin (1991) and of Olowe et al. (1988) on the oxidation of ferrous solutions is noteworthy for its conceptual and experimental simplicity. It has therefore been decided here to concentrate on these investigations rather than attempt to unravel the apparent inconsistencies reported from other studies where conditions are difficult to compare.

Olowe and colleagues investigated the effect of varying the Fe : OH ratio during oxidation. All experiments were carried out at 25°C making these studies directly relevant to ambient temperature ferrite formation. Mössbauer spectroscopy was utilised to identify the intermediate and end-products of oxidation produced for different Fe : OH ratios. The notable finding, echoing the results of Kiyama and others above, is that at pH values above pH 9 no intermediate products of oxidation containing sulphate were formed. In other words in this pH range, GR was not formed.

In Figure 4.3 from Olowe and Genin (1991) the near-vertical region of the pH curve corresponds to an R value of 0.5 ($R = \text{Fe} : \text{OH}$) and spans the pH range of 9–11. As these authors point out this is precisely the pH range commonly reported to favour magnetite formation (eg. Kiyama 1974, Tamaura et al. 1991a, Yang et al. 1994). Noting that there is no consensus on the mechanism of magnetite formation Olowe and Genin (1991) venture their conclusion that the intermediate species at point B is the compound $\text{Fe}(\text{OH})_2 \cdot 2\text{FeOOH}$, *also green in colour* but devoid of sulphate ions and designated ‘hydrated magnetite’. They provide the following mechanism of oxidation of ferrous hydroxide in the pH region 9–11:



Indeed from their data Olowe and Genin (1991) conclude that no end-product can be formed simultaneously with GR2 in the region of its existence! Since the region of

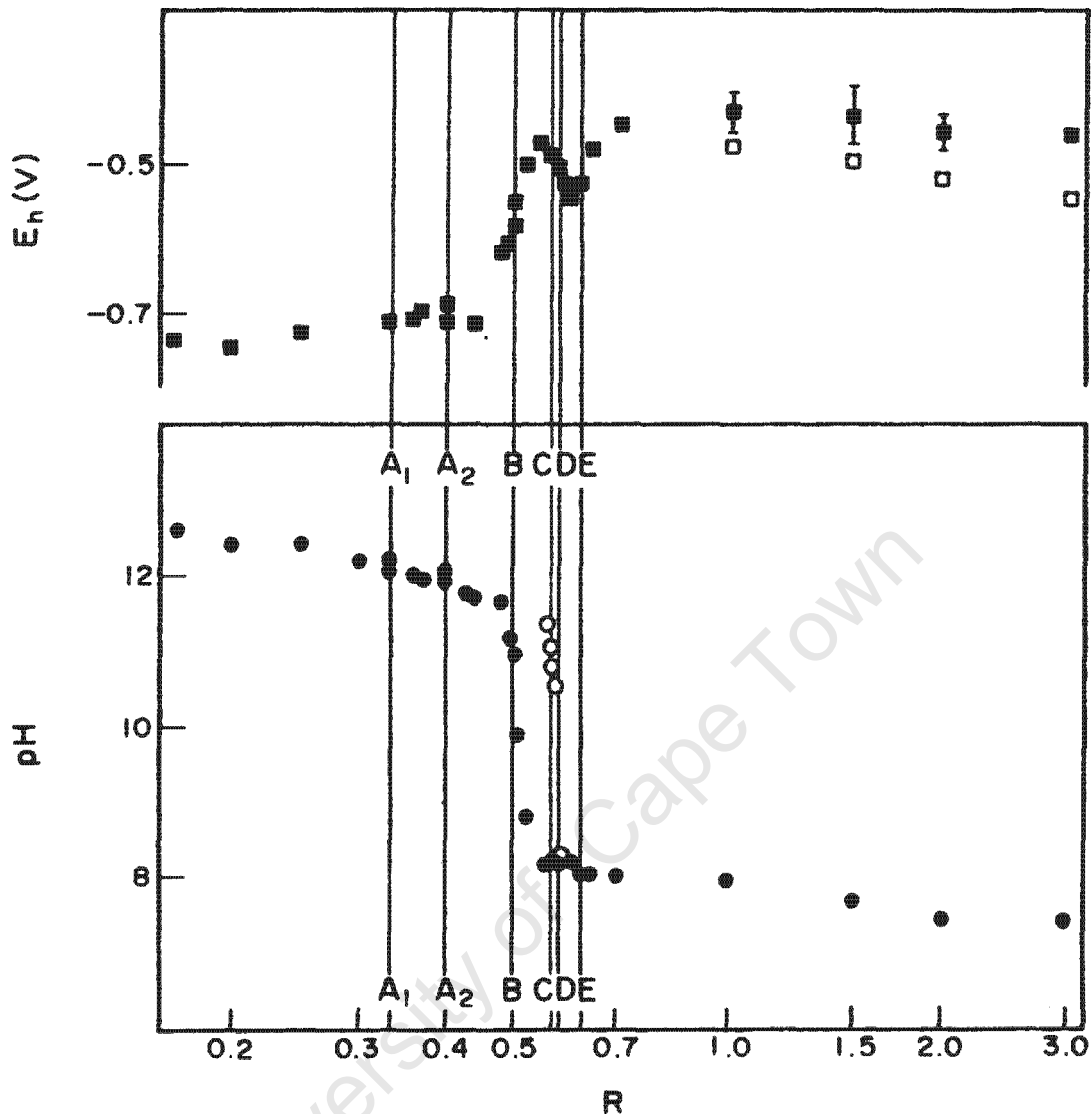


Figure 4.3 pH and E_h (redox potential) plots against R where R = Fe : OH ratio. Solid squares and solid circles refer, respectively, to E_h and pH at the start of the reaction. Each point refers to a separate experiment in which a ferrous solution is neutralised with the correct amount of NaOH for a given value of R. The solution is then stirred in the presence of air. Initial, intermediate and end-products were analysed using X-Ray diffraction (XRD), Mössbauer Spectroscopy (MS) and TEM – see Table 4.3. (from Olwe and Genin 1991).

stability of GR2 is generally agreed to be in the pH range between 7 and 10 (Figure 4.4, Genin et al. 1996), this implies that no end-product formation, including ferrite formation, can occur in this pH range. At first glance this is paradoxical since ferrite formation is well known to occur between pH 9 and 11. This apparent contradiction is however resolvable because the ORP of point B (pH 9-11) is between -0.5 and -0.7 V (Figure 4.3, top) which falls outside of the region of GR2 stability as shown in Figure 4.4 (Olowe and Genin 1991, Genin et al. 1996). It should however be borne in mind that at high pH (pH 12.6) SEM and XRD observations show GR adsorbed to magnetite particles (Perales Perez et al. 1998).

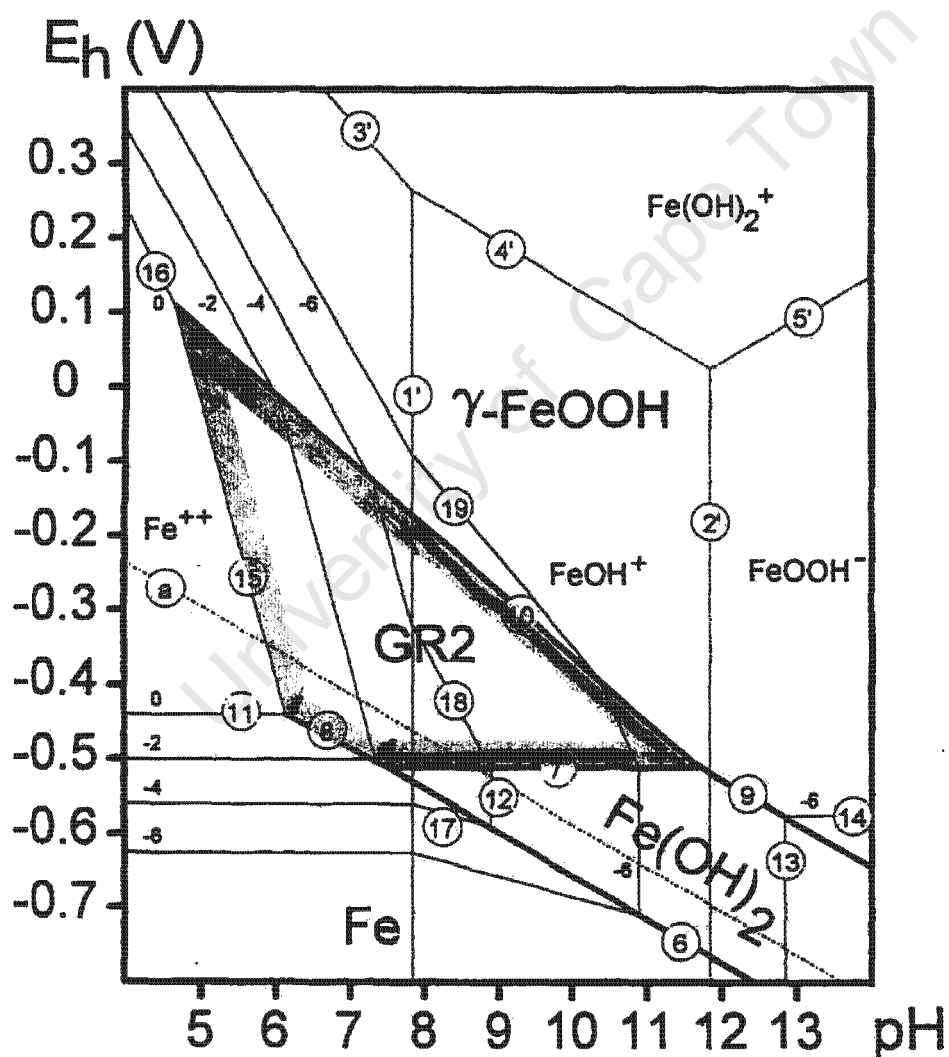


Figure 4.4 Pourbaix diagram showing the region of stability of GR2 (from Genin et al. 1996).

In conclusion the reasons for the discrepancy in the results between Olowe and Genin (1991) and Pereles Perez et al. (2001a) are not apparent, and the nature of the intermediate products of oxidation of ferrous sulphate solutions remains confused.

Effect of pH: water treatment process considerations

Several authors, including the writer have observed that ferrite formation through the GR2 pathway ($\text{pH} < 10$) results in relatively high residual iron and heavy metals concentrations, and inferior sludge settling properties (Kiyama, 1974, Perales Perez et al. 1998). Conversely, ferrite formation at $\text{pH} > 10$ results in excellent Fe removal ($> 99.9\%$) and improved sludge settling properties (Lahav et al. 2003).

Effect of cations and anions

The presence of certain non-ferrous cations and anions can decisively influence the end-products of oxidation of ferrous solutions. Cornell and Schwertmann (1996) emphasise the fact that the stability of the green rust precursor depends upon the interlayer cation and increases in the order $\text{Cl}^- < \text{SO}_4^{2-} < \text{CO}_3^{2-}$. That is GR1 is less stable than GR2 which is less stable than carbonate GR.

Chlorides and other halogenides exert a particularly strong retarding effect on magnetite formation in favour of lepidocrocite formation, possibly by inhibiting the condensation of neighbouring OH^- groups (dehydroxylation) to form Fe-O-Fe bonds. Sulphate on the other hand at concentrations in the order of 0.1M has a goethite promoting effect (Cornell and Schwertmann 1996). Xu and colleagues (Choung et al. 1999, McKinnon et al. 2000) found that the presence of carbonates does not interfere with magnetite formation.

Effect of magnetite seed

As previously discussed, calcium poses a particular challenge to the development of an ambient temperature ferrite process which uses lime for treating AMD. However Perales Perez et al. (1998) were the first to show that magnetite can be formed in the presence of calcium if magnetite seed also is present. In these investigations done at pH 12.6, scanning electron microscopy (SEM) and XRD analyses showed magnetite seed particles partially covered by GR2. Magnetite formation in the presence of calcium and seed has subsequently been confirmed by others (McKinnon et al. 2000, Morgan et al. 2001).

It is therefore of interest to enquire into the role of magnetite seed in ferrite formation from a mechanistic point of view. The mechanism whereby magnetite seed steers the reaction in the presence of calcium towards ferrite formation has not however been elucidated. The closest relevant information is given by Tronc et al. (1984) who provide evidence for the mechanism whereby magnetite seed might steer the reaction which would otherwise, even with no calcium present, produce FeOOH species, towards magnetite, at ambient temperature and high pH. A solution of ferrous iron alone and a solution of ferrous iron in a cationic colloidal suspension of spherical magnetite particles approximately 90nm in diameter were brought to a pH value of about 2.5 (making a protonated cationic colloid) whereafter the pH was raised by the addition of base. The titration plot for the non-colloid solution is shown in curve *c* in Figure 4.5. A region of buffering occurs at about pH 8 and corresponds to the precipitation of Fe(OH)₂ (curve *c* in Figure. 4.5). In contrast the region of buffering seen in the titration curve for ferrous iron in the presence of colloidal magnetite occurs at about pH 6 (curve *a* in Figure 4.5). The explanation given for this asymmetry is that as the pH rises, the free Fe²⁺ ions instead of precipitating as ferrous hydroxide, are adsorbed onto the surface of the colloid particles. When this occurs, for every Fe²⁺ adsorbed two H⁺ ions are released by the colloid particles into solution, thereby preventing the pH from increasing (buffering effect). During the back-titration the process reverses but as a result of differences in the kinetics of adsorption and desorption, the forward and backward titrations differ (Figure 4.6).

Jolivet and Tronc (1988, p. 699) comment that this

“peculiar behaviour results from easy electron delocalization, from few structural changes between reduced (Fe_3O_4) and oxidized ($\gamma\text{Fe}_2\text{O}_3$)⁸ forms, and from adequate particle size which allows the electron reservoir, which the colloid is, to empty and refill in a reasonable time”.

For sake of simplicity Tronc et al. (1984) refer to the colloid in its initial cationic form at pH 2.5 as ‘protonated’ and in its form in alkaline medium as ‘exchanged’.

These authors (Tronc et al. 1984) also investigated the titration curves for different colloidal- Fe^{2+} sols made up by adding various concentration of $\text{Fe}(\text{Cl})_2$ to a magnetite sol otherwise devoid of free, adsorbed or precipitated Fe (Figure 4.7).

⁸ Maghemite.

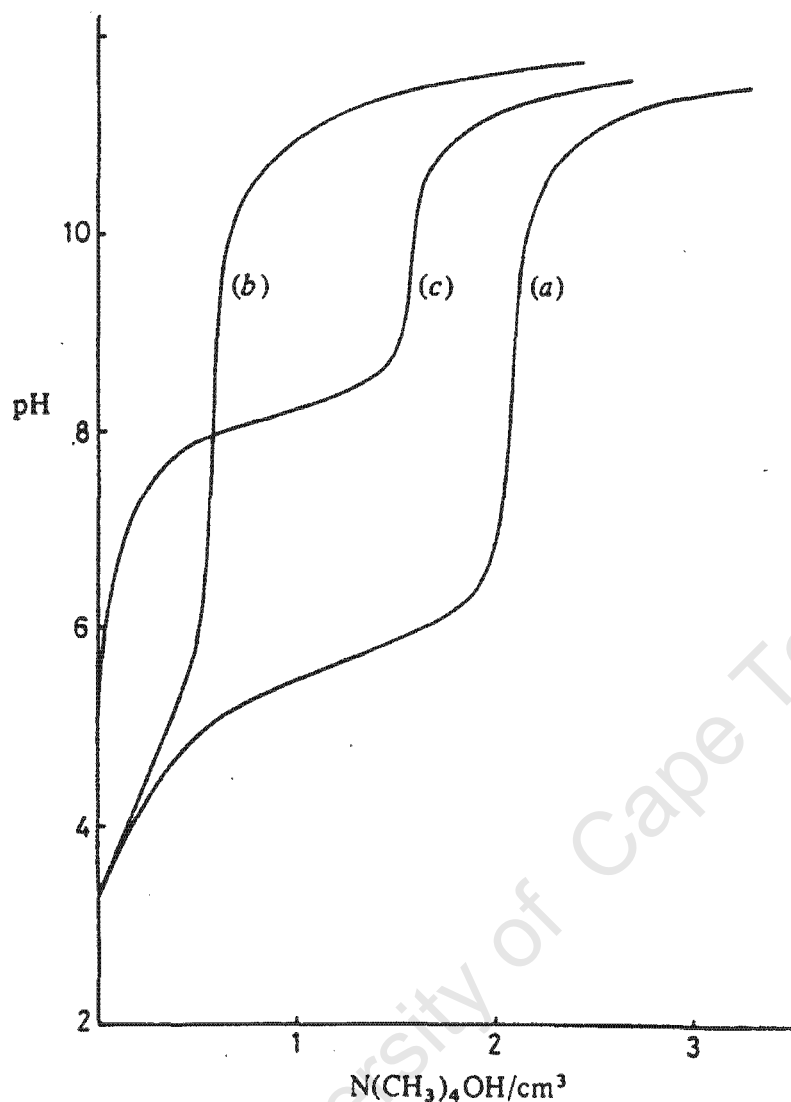


Figure 4.5 Titration plots for a solution of ferrous iron alone (curve c) and a solution of ferrous iron in a cationic colloidal suspension of spherical magnetite particles approximately 90nm in diameter (curve a). Both solutions were brought to a pH of about 2.5 whereafter the pH was raised by the addition of base. For the ferrous solution alone a region of buffering occurs at about pH 8 and corresponds to the precipitation of $\text{Fe}(\text{OH})_2$ (curve c). In contrast the region of buffering seen in the titration curve for ferrous iron in the presence of colloidal magnetite occurs at about pH 6 (curve a) as a result of adsorption onto the colloidal magnetite particles in exchange for H^+ . Curve b plots the titration of the suspension in curve a after ultrafiltration. (from Tronc et al. 1984).

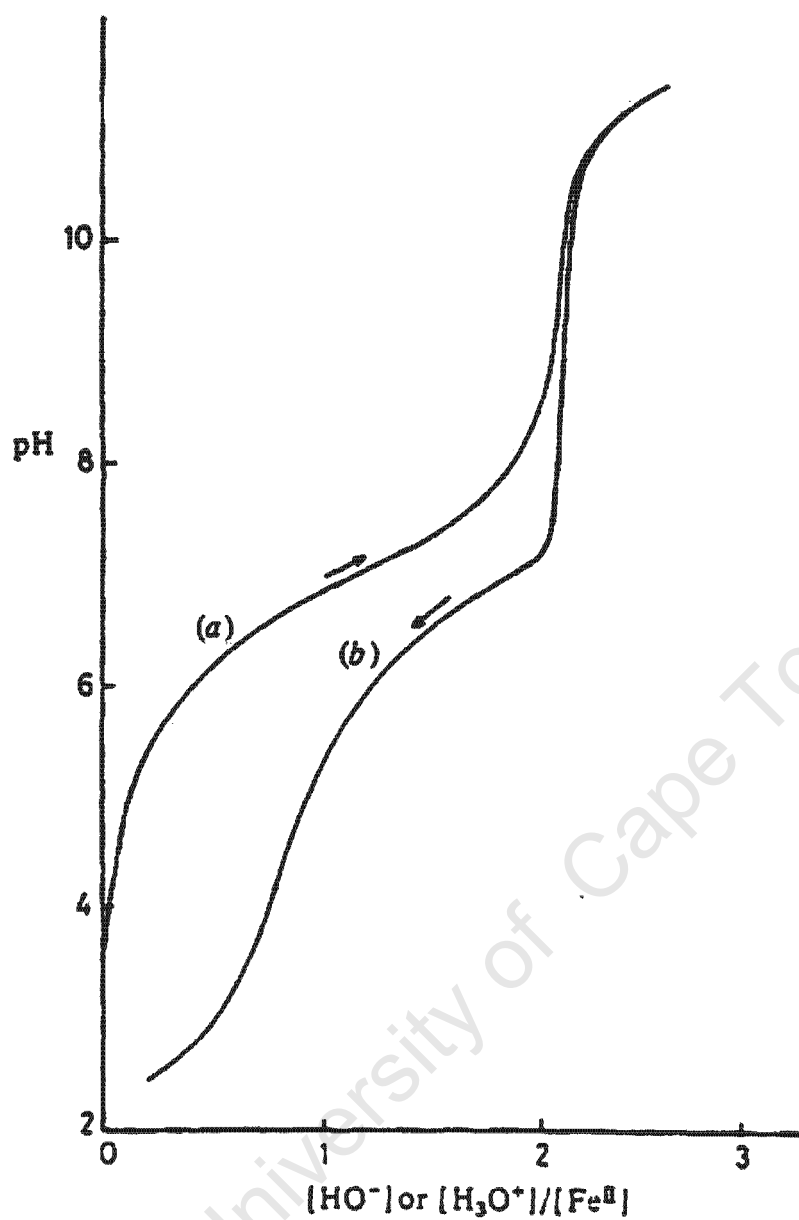


Figure 4.6 Forwards and backwards titrations of magnetite colloid follow different paths (from Tronc et al. 1984)

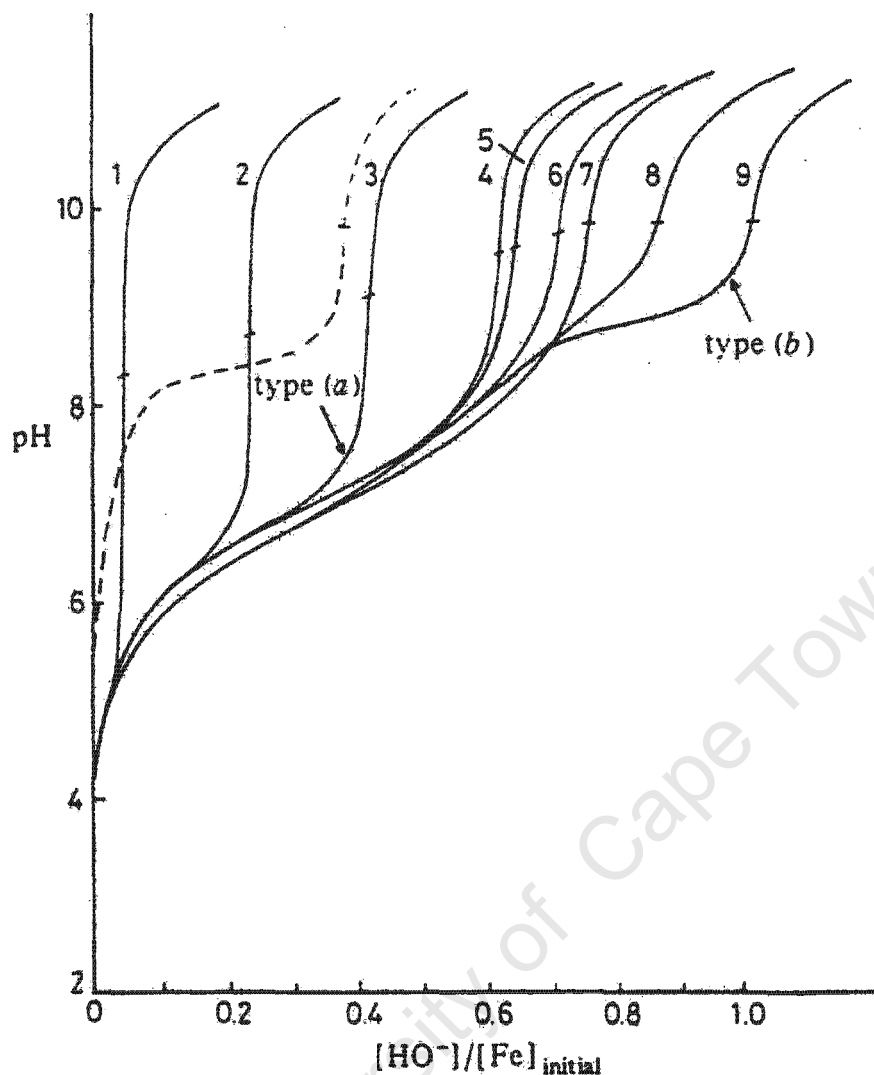


Figure 4.7 Base titrations of magnetite colloid suspensions in the presence of different concentrations of dissolved ferrous iron. Dotted line = Fe^{2+} without colloid; Type *a* = Fe^{2+} concentration not exceeding the Fe^{2+} adsorbing capacity of the colloid; Type *b* = Fe^{2+} concentration exceeding the Fe^{2+} adsorbing capacity of the colloid (from Tronc et al. 1984).

From these investigations Tronc and colleagues found evidence of possible pertinence to the magnetite promoting effect of magnetite seed. Curve type (*a*) in Figure 4.7 resembles curve *a* in Figure 4.5, ie. region of buffering at a pH well below that for a pure ferrous solution without magnetite colloid (dotted line in Figure 4.7). Curve type (*b*) shows the same region of buffering as curve type (*a*) but in addition shows a second region of buffering in the same pH range as the dotted line where colloidal magnetite was not present. In Figure 4.7 the difference between type (*a*) and type (*b*)

titration curves was found to depend upon the dissolved/adsorbed⁹ Fe^{2+} : total Fe (colloidal and dissolved/adsorbed) concentration ratio. When this ratio exceeded ~ 0.33 type (b) curves occurred and when the ratio was less than 0.33 type (a) curves occurred. Significantly, a concentration ratio of 0.33 is equivalent to an overall Fe^{2+} : Fe^{3+} concentration ratio of 1 : 2 which happens to be the ratio of these ions in stoichiometric magnetite. In other words as base is added, the colloidal magnetite seed is able to adsorb Fe^{2+} ions (in exchange for H^+) up to the point where the overall Fe^{2+} : Fe^{3+} concentration ratio equals the 1 : 2 stoichiometry of magnetite. This adsorption accounts for the region of buffering shown in curve type (a) in Figure 4.7. As further base is added, ferrous ions in excess of the stoichiometric amount of 1 : 2 cannot be adsorbed and therefore precipitate as ferrous hydroxide, accounting for the second region of buffering as seen in curve type (b) in Figure 4.7.

From these and other structural investigations Tronc et al. (1984) propose that the colloid particles grow by the formation of an outer magnetite shell derived from adsorbed hydrolysed Fe^{2+} species¹⁰. Electrons from the partial oxidation of adsorbed ferrous ions are pumped into the colloid core causing the reduction of Fe^{3+} in octahedral sites, up to the final Fe^{2+} : Fe^{3+} equipopulation of these sites. This equilibrium, given the initial amount of Fe^{2+} in these sites, determines the degree of electron transfer and therefore the Fe^{2+} uptake capacity. These authors also investigated the capacity of colloidal magnetite to adsorb other metal ions. Co^{2+} but not Ni^{2+} , Fe^{3+} or Al^{3+} was found to readily exchange (adsorb-desorb). However Co^{2+} uptake was three times less than Fe^{2+} uptake and Ni^{2+} , Fe^{3+} and Al^{3+} all precipitated as hydroxides with little or no adsorption occurring.

Noting the strong tendency of both Co^{2+} and Ni^{2+} to occupy octahedral sites to form inverse-spinel ferrites, Tronc et al. (1984) observe that the slight differences in ionic radius between these ions and Fe^{2+} are unlikely to account for the vast differences in uptake observed. On the other hand the oxidisability of these ions does parallel their diminishing uptake behaviour and these authors suggest that the observed uptake of Co^{2+} is governed by a Co^{2+} : Fe^{3+} redox couple. They further suggest two reasons for

⁹ Dissolved at low pH, adsorbed at high pH.

¹⁰ That is, over and above adsorbing free Fe^{2+} ions, colloidal magnetite adsorbs $\text{Fe}(\text{OH})_{2(s)}$ (see chapters 5–7).

the one-third capacity of Co^{2+} relative to Fe^{2+} uptake: (1) Co^{2+} only occupies octahedral sites and (2) Co^{2+} is a less powerful reducing agent compared to Fe^{2+} . This in conjunction with Ni^{2+} , Fe^{3+} and Al^{3+} all being even weaker reducing agents and all being very weakly adsorbed, leads Tronc et al. (1984) to conclude that $\text{Fe}^{2+} - \text{Fe}^{3+}$ electron transfer is indeed the driving force behind magnetite outer shell growth under these conditions. Since the magnetite particles produced at ambient temperature (as described in Chapters 5–7 below) are in a size range for which the above behaviour is described (Figure 5.2b, Chapter 5), and all other conditions are broadly similar, it is possible that these mechanisms play a role in magnetite formation in this context as well.

Beyond these reports the mechanism of ferrite formation in the presence of magnetite seed has not been characterised. Furthermore ambient temperature ferrite formation in the presence of seed involves two major transformations, viz. oxidation and aging (dehydration-crystallisation). If the scheme of Tronc et al. (1984) is relevant it remains to be explained exactly how oxidation and dehydration-crystallisation fit into it. Nevertheless from a practical perspective, magnetite seed provides both a way of stabilising magnetite formation when calcium is not present and a way of circumventing the negative effect which calcium exerts on ferrite formation.

Non-ferrous metals removal

In both the high and ambient temperature ferrite processes, cation substitution is the basis of non-ferrous metals removal. Goethite ($\alpha\text{-FeOOH}$), lepidocrocite ($\gamma\text{-AlOOH}$), hematite and magnetite are all known to have isostructural natural mineral equivalents in which cations other than Fe occupy the interstices of the oxygen framework (Cornell and Schwertmann 1996). For example:

Goethite:	$\alpha\text{-AlOOH}$, $\alpha\text{-MnOOH}$, $\alpha\text{-CrOOH}$, VOOH
Lepidocrocite:	$\gamma\text{-AlOOH}$
Hematite:	$\alpha\text{-Al}_2\text{O}_3$, $\alpha\text{-Cr}_2\text{O}_3$ and $\alpha\text{-V}_2\text{O}_3$
Magnetite:	Pb_3O_4 , Co_3O_4 and Mn_3O_4

M^{2+} and M^{4+} cations are also known to enter Fe^{3+} oxides but the uptake is usually less than 0.1 mol/mol. Substitution depends mainly upon similarity of ionic radius of the cations and a linear relationship exists between unit cell volume and ionic radius for several substituted Fe^{3+} oxides. Charge valency is the next important factor but crystal field stabilisation energy (CFSE) and lattice energy also exert an influence. Where the valency of the substituting cation does not match that of the substituted cation, a proportional uptake or release of protons is assumed to restore charge balance. In some cases adsorption of anions may balance the excessive positive charge of substituting M^{4+} cations (Cornell and Schwertmann 1996).

Substitution is not always isomorphous as evidenced by changes in unit cell dimension and various other parameters as measured by Mössbauer spectroscopy, chemical analysis, infrared spectroscopy and so on. Congruent dissolution, meaning equal rate of release of host and guest cations, indicates isomorphic substitution. Incongruent dissolution is an indication of either a separate phase (with a different dissolution rate) or that the substituting ions are concentrated in either the core or periphery of the crystals (Cornell and Schwertmann 1996). Figure 4.8 shows dissolution plots for six different substituted magnetites.

Magnetite and maghemite can both be induced to accept a large variety of cations. Sidhu et al. (1978) synthesised magnetites at 90 °C which contained as much as 0.1 mol/mol of substituted cations. Co, Ni and Zn substituted for octahedral Fe^{2+} and were randomly distributed (congruent dissolution, Figure 4.8) while Cu, Mn and Cd were distributed near the surface (incongruent dissolution, Figure 4.8). Conversion of these magnetites to maghemite caused an outer ferric zone which was devoid of non-ferrous metals, the latter becoming concentrated in the core. When substituted magnetite was converted to hematite, divalent non-ferrous metals were expelled due to charge and size incompatibility and became concentrated near the oxide surface. Cr and Mn however, being compatible with the corundum ($\alpha-Al_2O_3$) structure, remained within the hematite (Sidhu et al. 1980). Al-substituted magnetites in which Al replaces tetrahedral Fe^{2+} have been prepared (Schwertmann and Murad 1990) and magnetite synthesised by Ardizzone et al. (1983) in solution containing sodium acetate buffer contained 2.3 mg/g Na. Similarly and significantly, De Sillier et al.

(1977) produced magnetite containing 0.19mol/mol calcium. Tamaura et al. (1991) quoting Gorter (1954) state that metal ions with charge valencies from I to V can substitute for Fe in the spinel structure of ferrites.

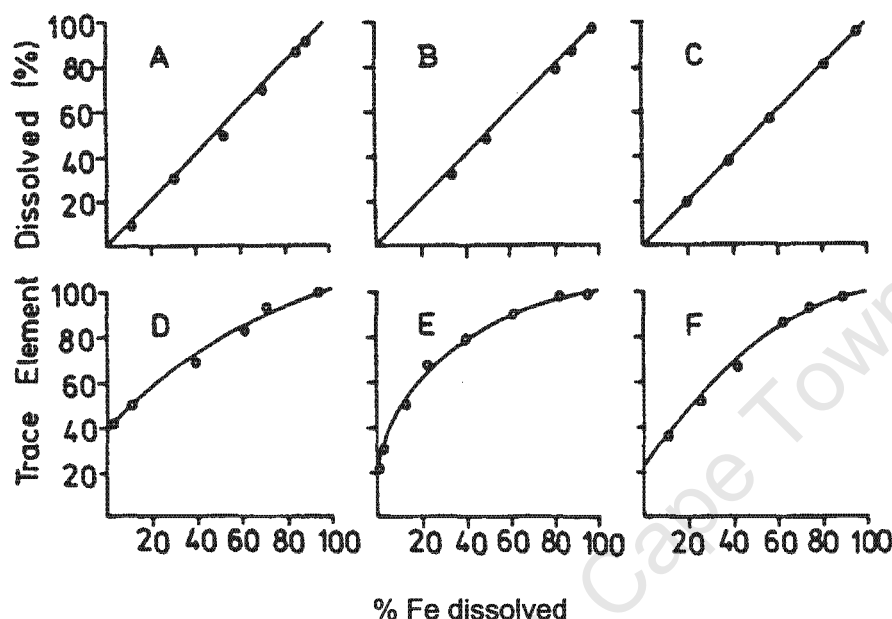


Figure 4.8 Dissolution plots for six different substituted magnetites (from Cornell and Schwertmann 1996, originally described by Sidhu et al. 1978). A cobalt, B nickel, C zinc, D copper, E manganese, F cadmium.

Cation substitution during magnetite formation can be expressed by the following equations (18–23) of Perales Perez et al. (2001a), which closely resemble equations 1–6 above, where M^{2+} represents one or more species of non-ferrous divalent cation:

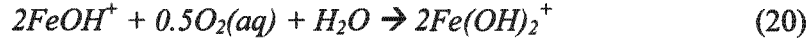
- (a) Hydrolysis of ferrous ion:



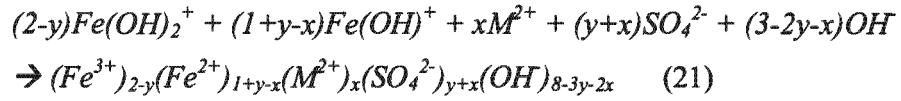
- (b) Oxygen transfer:



(c) Oxidation of ferrous ion:

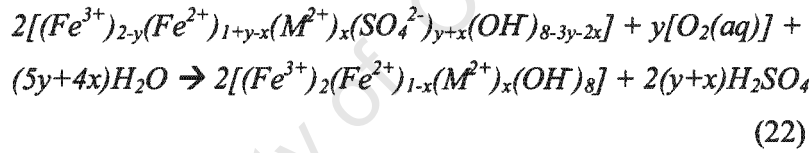


(d) Precipitation of partially oxidised M^{2+} – bearing intermediate (green rust 2):

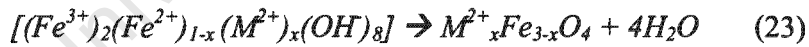


where x = the molar amount of M^{2+} ions which replace Fe^{2+} in the product and y = the number of moles of Fe^{2+} which still need to be oxidised in order to bring the Fe^{3+} : Fe^{2+} ratio to 2 : 1.

(e) Further oxidation of ferrous iron in the M^{2+} – bearing intermediate and subsequent hydrolysis of the produced ferric species:

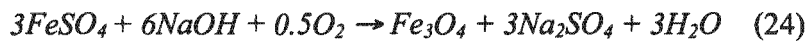


(f) Dehydroxylation/dehydration and partially substituted magnetite formation:

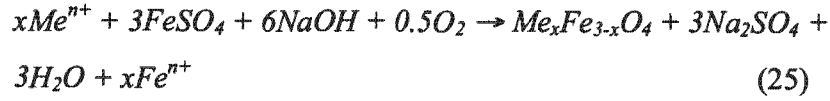


Barrado et al. (1998) proposed the following non-mechanistic reactions for ferrite formation from a ferrous solution raised to pH 10.5:

In the absence of non-ferrous metals (Me):



In the presence of non-ferrous metals:



The term Fe^{+n} in Equation 25 represents the total concentration of iron whose precipitation as ferrite is impeded by the other metal cations present in the water. The displaced iron can appear as ferrous or ferric depending on the valency of the displacing cation. These ferrous and ferric ions will react again to form further ferrite.

Cation substitution during ambient temperature magnetite formation in the context of removing non-ferrous metals from AMD has not been well studied (Perales Perez et al. 2001a) and the ignorance is even greater for the case where calcium is present. Since for AMD treatment we are concerned with calcium derived from the use of lime as a pH elevating agent, the following discussion limits itself to the little that is known in this area.

McKinnon et al. (2000) investigated the removal of non-ferrous metals from AMD at ambient temperature. In these experiments ferrite was formed by adding ferric and ferrous salts together in the ratio of 2 : 1 respectively in the same solution (ie. no oxidation was required). Whilst the mixture was stirred NaOH or lime was used to raise the pH to 7.8. After 17 minutes of agitation the solids were left to age for 2 hours without being agitated. In order to investigate cation substitution, certain divalent or trivalent non-ferrous metals were added to the solutions as well. In these cases the overall trivalent : divalent molar ratio was maintained at 2 : 1. The concentration of the non-ferrous metal was either X for divalent or Y for trivalent where X is defined according to the molar ratio of $Fe^{3+}/Fe^{2+}/M^{2+} = 2/1-X/X$ and Y is defined according to the molar ratio $Fe^{3+}/M^{3+}/Fe^{2+} = 2-Y/Y/1$. In these experiments no magnetite seed was present. The results are shown in Figure 4.9a and 4.9b for divalent and trivalent ions respectively.

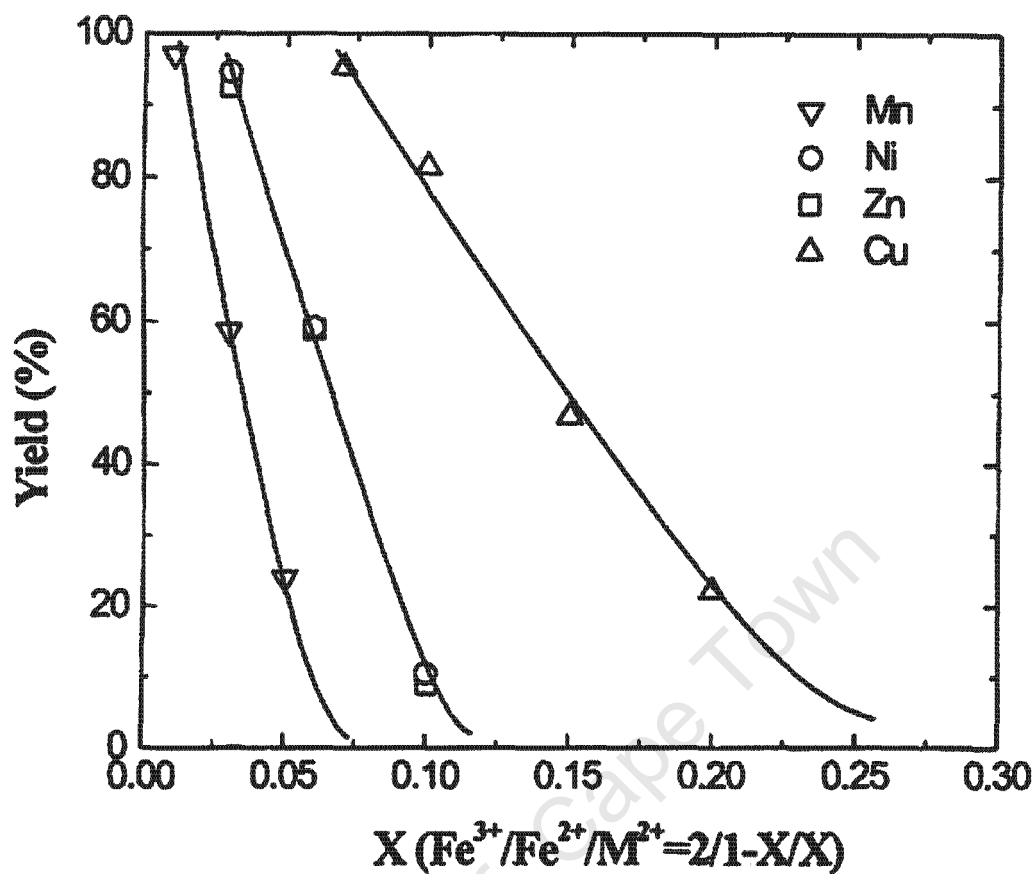


Figure 4.9a Plots showing the percentage yield of magnetic precipitates from various $\text{Fe}^{3+} / \text{Fe}^{2+}$ solution mixtures containing divalent non-ferrous metals and no magnetite seed. X equals the concentration of the divalent non-ferrous metal. The total ratio of trivalent : divalent metal ions was always 2 : 1 and lime was used to increase the pH. In each case as X increases the magnetic yield is markedly diminished. (from McKinnon et al. 2000.)

TABLE 2. Minimum Levels of Interference of Ferrite Formation by Nonferrous Metal Ions (X or Y), at Which Precipitates Are Magnetically Unrecoverable

interference species	Cu	Ni	Zn	Mn	Al
neutralizer					
NaOH	0.32	0.34	0.52	0.52	0.20
CaO	0.24	0.11	0.11	0.06	0.06

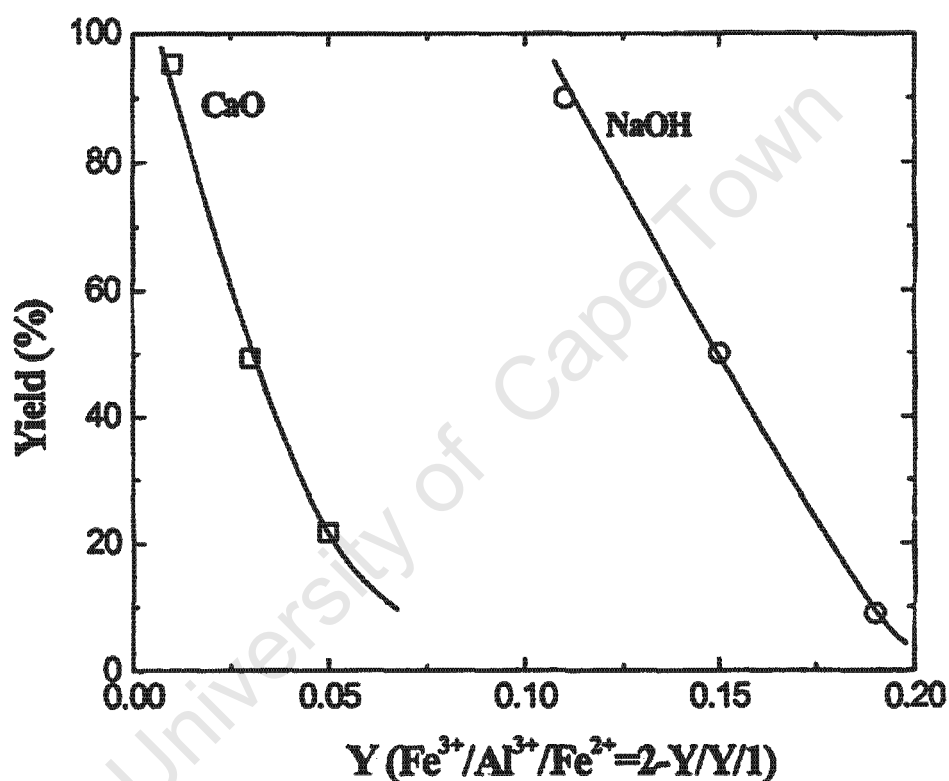


Figure 4.9b Plots showing the percentage yield of magnetic precipitates from $\text{Fe}^{3+} / \text{Fe}^{2+}$ solution mixtures containing aluminium and no magnetite seed. Y equals the concentration of aluminium. The total ratio of trivalent : divalent metal ions was always 2 : 1. Both lime (CaO) and NaOH were used as pH neutralising agents. In each case as Y increases the magnetic yield is markedly diminished but it is diminished much more for lime than for NaOH. (from McKinnon et al. 2000).

These results reveal two main behaviours when non-ferrous ions are present. Firstly in both cases the percentage yield of magnetic ferrite end-products decreases as X or Y increase and this decrease varies for each non-ferrous metal. Secondly, for both X and Y the percentage yield of magnetic ferrite end-products decreases substantially when lime as opposed to NaOH¹¹ is used. Table 2 in Figure 4.9b shows, for both lime and NaOH, the minimum concentrations at which some non-ferrous metals completely inhibit ferrite formation. From Table 2 in Figure 4.9b it can be seen that when lime was used the order of interfering concentrations was $\text{Cu} > \text{Ni} \cong \text{Zn} > \text{Mn}$ whereas with NaOH the order is reversed. Furthermore, noting that the concentration producing interference for Al is much less than that of the divalent metals, (ie. $X \gg Y$), McKinnon et al. (2000) conclude that in general the interference by trivalent metals is greater than that of divalent metals. They do not however provide evidence to substantiate that this is true for all/other trivalent metals.

McKinnon et al. (2000) then repeated the above experiments with magnetite seed present and using lime to elevate pH. The values of X and Y were increased to $0.4 < X < 0.6$ and $Y = 0.2$ which are higher than the minimum concentrations causing total interference when seed was not present. Figure 4.10 illustrates a yield of up to 100% magnetic precipitates depending upon the seed : precipitate weight ratio. As all the data points in Figure 4.10 follow the same trendline the type and concentration of non-ferrous metal did not seem to make a difference, indicating that the seed effect is generic. The authors note that the surface area of seed available seems to be the limiting parameter. It was also found that increasing the aging time, significantly increased the percentage yield.

¹¹ In this respect data for X is not shown in Figure 4.9b but this point is corroborated in the text of the article.

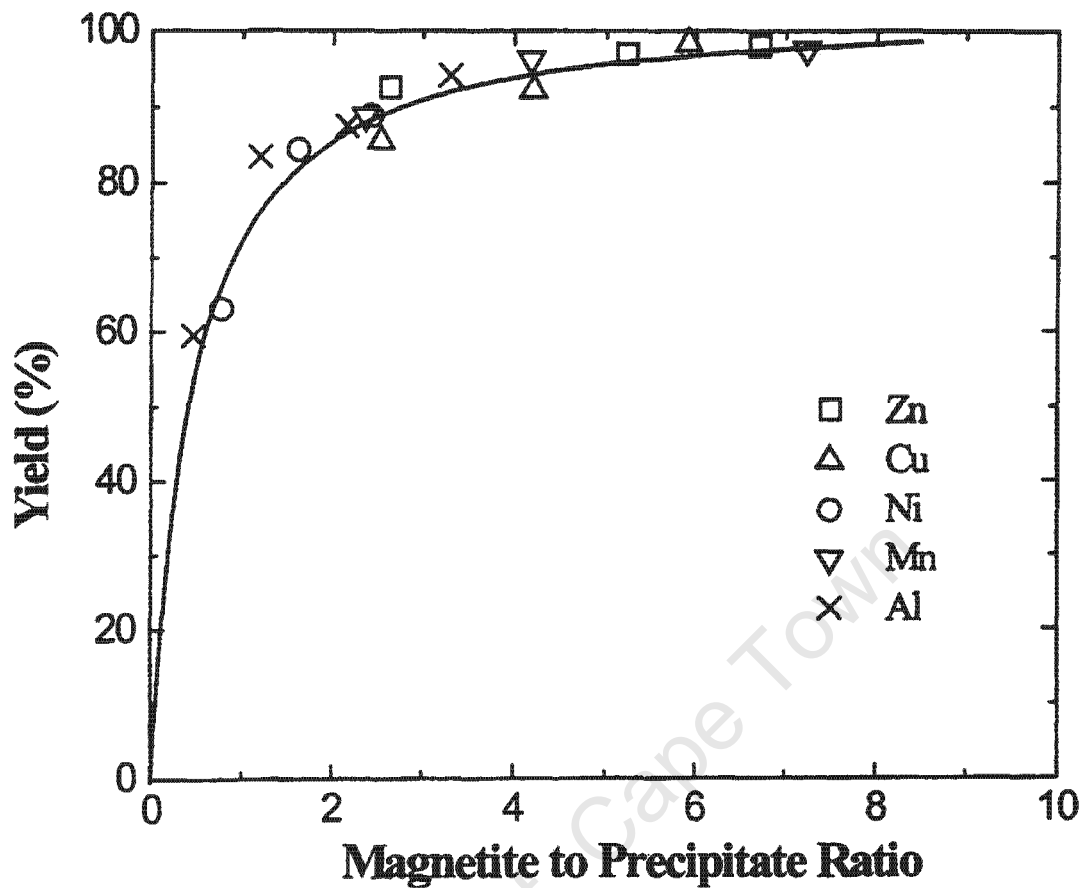


Figure 4.10 Effect of the magnetite seed : precipitate ratio (w/w) on ferrite recovery for different non-ferrous metals using lime to elevate pH (from McKinnon et al. 2000).

Choung et al. (1999) utilised ambient temperature ferrite formation at pH 10.5 to treat simulated AMD using lime without using seed. The rationale in their study was to use CO_2 gas, at low pH (below the pH at which ferrihydrite precipitates) to precipitate calcium as calcium carbonate (CaCO_3) and in this way circumvent the calcium interference problem. Choung et al. (2000) claimed to overcome the inhibitory effect of calcium on ferrite formation by bubbling CO_2 gas through separate calcium-containing ferric and ferrous solutions in order to precipitate CaCO_3 . The difficulty with this study is that at the pH values at which the CO_2 was introduced ($2.5 < \text{pH} < 5$) CO_3^{2-} concentrations are several orders of magnitude lower than the calcium concentrations in question and precipitation of calcium carbonate does not occur (Figure 4.11).

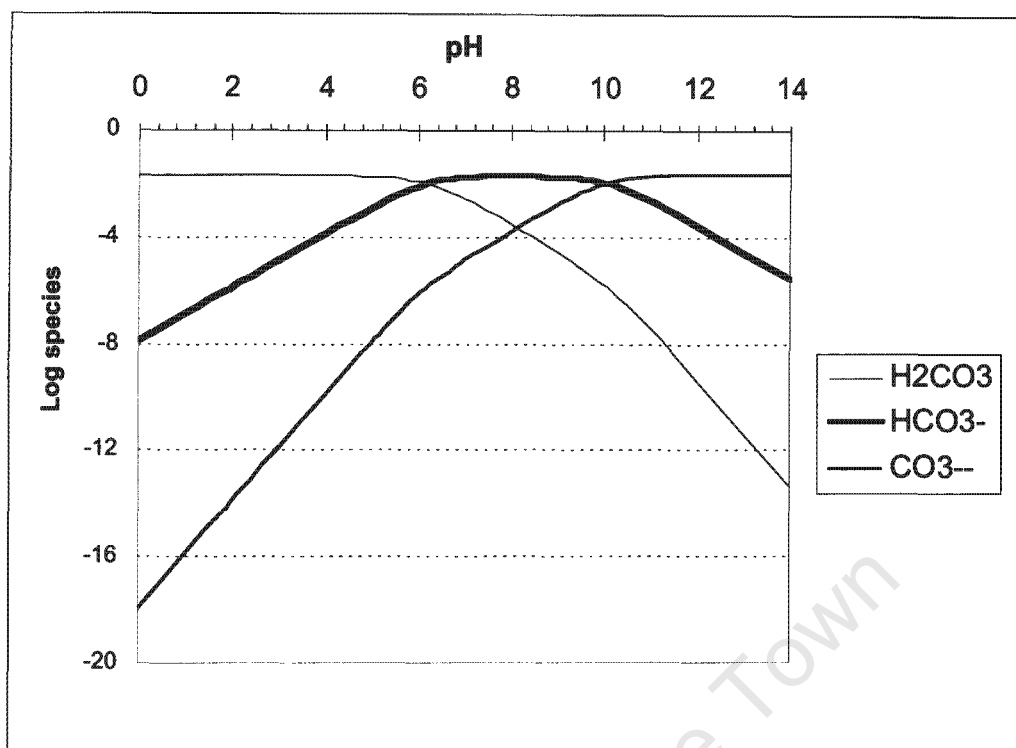


Figure 4.11 A log species concentration versus pH equilibrium diagram for the carbonate system in aqueous solution showing negligible concentrations of CO_3^{2-} at pH values below ~pH 5, thus precluding the formation of calcium carbonate in this region.

Nonetheless Choung et al. (1999) do report an interesting finding which is independent of calcium carbonate formation. It was found that when the pH of separate ferric and ferrous solutions was raised with NaOH and lime respectively, and the solutions subsequently combined, the percentage yield of magnetic ferrite was 100%. The inverse scenario however, where the ferric solution was treated with lime and the ferrous with NaOH (or lime), only resulted in a magnetic ferrite yield of 60% (or 39% when lime was used). The authors conclude that the component interfering with ferrite formation is a $\text{CaFe}_3(\text{OH})_7(\text{SO}_4)_2$ type complex. They go on to suggest that the strongly hydrated nature of this complex hinders the dehydration between ferric and ferrous hydroxides during crystallisation. The results of Choung et al. (1999), in respect of non-ferrous metal removal are nonetheless shown in Table 4.4.

Element mg/L	Fe	Zn	Mn	Al	Mg	Ca
Original AMD	286.2	125.5	79.9	13.2	226.7	354.9
Treated Effluent	<0.1	<0.1	<0.2	<2	15	15

Table 4.4 Results of treatment of a simulated AMD by ambient temperature ferrite formation in the absence of seed using lime to elevate the pH to 10.5. (from Choung et al. 1999).

Several other suggestions of the mechanism of calcium interference have been proposed, the most common being that the unhydrated ionic radius of calcium is slightly too large to stably fit into the ferrite lattice and so disrupts crystal growth (Cornell and Schwertman 1996, Wang et al. 1996). The ionic radius of 6-coordinate $\text{Ca}^{2+} = 114 \text{ pm}$ which exceeds the stated upper limit of $\sim 100 \text{ pm}$ for fitting into the lattice ($60 < \sim \text{range} < 100 \text{ pm}$) (Smit and Wijn 1959). The ionic radius of 6-coordinate $\text{Fe}^{2+} = 75 \text{ pm}$ (low spin) / 92 pm (high spin) and $\text{Fe}^{3+} = 69 \text{ pm}$ (low spin) / 78.5 pm (high spin) (Shannon 1976). However it has already been mentioned in this chapter that magnetite containing 19% calcium has been produced (De Sillier et al. 1977). Thus the fact remains that the inhibitory effect of calcium on ambient temperature magnetite formation is not understood.

Manganese

Manganese warrants some attention because it is far more soluble in aqueous solution than other transition metals. The solubility product for $\text{Mn}(\text{OH})_2$ is for example, 2–3 orders of magnitude higher than that of iron, nickel and zinc (Table 2.2, Chapter 2). It has been shown that ferrites in which iron is substituted by manganese can be prepared at both ambient (Choung et al. 1999, McKinnon et al. 2000) and supra-ambient temperature (eg. 65°C , Kanzaki et al. 1996). McKinnon et al. (2000) and

Choung et al. (1999) found however, that the pH of the precipitation reaction needed to be at least 10.5 in order for the effluent to be free of manganese. Below pH 10.0 more than 40% of manganese ions remained in solution and thus were present in the effluent. Solution conditions therefore need to be taken into consideration to ensure that total or near total precipitation of manganese occurs prior to ferrite formation.

Conclusion

In this section various factors such as temperature, oxidation rate, pH, aging, the presence or absence of seed, anions and cations including calcium and non-ferrous metals, all of which impact upon the pathways and mechanisms of ambient temperature ferrite formation, have been reviewed. From this review numerous insights are gained, not least of which is the role of magnetite seed in circumventing calcium inhibition. At the same time it has become apparent that no adequate theoretical description of the mechanisms whereby ambient temperature ferrite formation occurs which makes it impossible to move forward in any way other than an empirical one. Furthermore with one exception, Perales Perez et al. (1998), all of the results discussed above involved ferrite formation by combining separate ferric and ferrous solutions. AMD on the other hand generally contains ferrous and no ferric iron (Equation 1 in Chapter 1) and an oxidation step is required for ferrite formation to occur. In the light of these facts, it was decided to initiate a systematic experimental study of ambient temperature ferrite formation from purely ferrous-containing solutions, with an oxidising step included. The remainder of this thesis therefore reports on laboratory investigations aimed at the development and application of an ambient temperature ferrite process to AMD waters such as those found in South Africa (Table 4.5).

Parameter	units	value/range	'average'
Aluminium	mg/L	48–90	60–70
Ammonia		0.3	low
Barium		<0.1	
Boron		0.4	
Bromide		0.9	
Calcium (as Calcium)		439	450
Chloride		56	
Copper		<0.1	very low
Fluoride		0.5	
Iodide			
Iron		680–1760	1200
Lithium		<0.1	
Magnesium		203	230
Manganese		18–43	35
Nitrate		3–48	
Potassium		3.5	
Sodium		56–150	
Sulfate		3391–5330	5000
Hydrogen sulfide			
Zinc		1.4–3.2	
Silicon			
Silica			
Radium226	mBq/L		
Uranium	µg/L	297–500	300
Tritium	Bq/L		
Alkalinity	mg/L CaCO ₃	0	0
EC	mS/m	527	
Dissolved organic C	mg/L	3.2	
pH		3.5–4.	
Turbidity	NTU	22	(raw water is clear but ferrous oxidises → turbidity)
Cobalt	mg/L	2–5	
Nickel		5–28	
Mercury	µg/L	1–7	
Vanadium	µg/L	400–1500	

Table 4.5 Example of AMD from a West Rand gold mine in Gauteng Province, South Africa (data supplied by mine).

Addendum to Chapter 4

Precipitation, nucleation and crystallisation theory

The factors governing the precipitation, nucleation and crystallisation of particles from supersaturated solutions are multiple and vary from one case to another (Mullin 2001, Söhnel and Garside 1992). Both endogenous factors specific to the solute and resulting crystalline solids, and exogenous factors such as solvent(s), temperature, seed, pH, mixing conditions, redox potential etc. bear upon the outcome. Despite this enormous complexity, some general principles do apply (Söhnel and Garside 1992).

In the context of ambient temperature ferrite formation, the main factors influencing particle size are pH, seed size and concentration and degree of supersaturation. pH effects particle charge which in turn effects electrostatic inter-particle forces. The zero point charge of magnetite is around pH 5 (Cornell and Schwertmann 1996). Strongly charged particles repel one another more intensely which inhibits coagulation into bigger aggregates and so inhibits particle size. Seed size, geometry and concentration together determine seed surface area. Where particle growth is divided between nucleation (resulting in smaller particles) and secondary growth on seed crystals (making bigger particles), seed surface area will strongly influence particle size distribution. Lastly, the degree of supersaturation effects particle size by influencing the rate of nucleation: the higher the supersaturation, the higher the rate of nucleation.

Nevertheless, the application of precipitation/crystallisation theory to the current research turns out to be less important than might be anticipated. This is because, as will become apparent in chapters five and six, all of the main factors which influence particle size viz. pH, seed concentration and degree of supersaturation, are all already constrained to within narrow ranges by the conditions necessary for the formation of magnetite at ambient temperature in the first place. pH is limited to values of no less than ~ pH 9 below which one-step ambient temperature magnetite formation is seriously compromised. Seed concentration is primarily determined by its relationship with the maximal oxidation rate compatible with ambient temperature ferrite formation. Thirdly, the minimum level of ferrous supersaturation is a function of the level needed to suppress calcium interference. Finally, the optimisation of these

factors according to the criteria of magnetite formation results in a particle size with excellent settling properties. Thus while there is no doubt some room for fine-tuning, the need for an in-depth consideration of precipitation, nucleation and crystallisation theory is beyond the scope of this thesis.

University of Cape Town

Chapter 5 Ambient temperature ferrite formation under batch conditions

Introduction

The initial aim of these investigations into ambient temperature ferrite formation was to test, under clearly defined conditions, the feasibility of using seed to facilitate the formation of magnetite by the aerial oxidation of AMD waters (Morgan et al. 2001). This 'proof of concept' stage was therefore confined to the investigation of magnetite formation using seed at ambient temperature via the oxidation of pure ferrous sulphate solutions under batch conditions; and did not address the issues of calcium or non-ferrous metals. Once the concept of ambient temperature magnetite formation using seed was successfully proven, systematic investigations under batch conditions into the effects of four major operational parameters were effected. These parameters were airflow rate, seed concentration, pH and temperature. The emphasis was to properly understand, quantify and optimise the chemistry underlying ferrite formation as applied to AMD in order to design and implement a treatment process. Other aspects relevant to a magnetite seed-based process, such as kinetics of oxidation, presence of calcium, sludge settlement, sludge impurities and sludge stability were also considered. The experimental studies performed for each of these two batch stage investigations are now separately described below.

5.1 Proof of concept

Materials and methods

Reagents

The following analytical grade reagents (Sigma-Aldrich, Kimix) were used as received: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Na_2SO_4 , NaOH , KOH , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, hydrazine sulphate, KNO_3 , NaHCO_3 , 32% HCl , 1,10-phenanthroline monohydrate, glacial acetic acid, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

Instrumentation and methods of measurement

pH was measured with a Metrohm pH probe-temperature transducer coupled to a Metrohm 744 meter. Dissolved oxygen was measured with a YSI 5739 DO probe coupled to a Hitec Micro Systems (Cape Town, SA) meter. Bottled air and nitrogen, fed through rigid gas tubing, were passed sequentially via an adjustable pressure regulator and a rotameter flowmeter to the reactor. At the reactor soft flexible tubing conveyed the gases to a stone diffuser fixed to the middle of the reactor floor. Ferrous iron was measured by the phenanthroline method (APHA, 1998). Total iron was determined by atomic absorption using a Varian SpectrAA 30 spectrometer. During a cycle, total iron was measured using a bench-top Spectroquant (Merck) system. Magnetite which served as the initial seed to start up each experiment was made according to the method suggested by Regazzoni et al. (1981).

All experiments were performed in a clear perspex reactor with internal dimensions of $18.75 \times 11.5 \times 11.5 \text{ cm}^3$ (height x width x width) capable of holding 2.62 litres. The reactor lid was fitted with a large centrally positioned circular port and four smaller ports positioned in each corner. The central port accommodated the shaft of the mixing paddle ($7.5 \times 2.5 \text{ cm}^2$, width x height) which rotated through a bearing fixed above the reactor. The top of the paddle was located 7cm above the reactor floor and was centrally positioned directly above the diffuser through which air/N₂ were released. The large central port was also used to add reagents to and take samples from the reactor and also accommodated the DO probe.

Experimental procedure

Each experiment consisted of a sequence of repeated batch cycles. The procedure for each cycle was identical: the premix consisted of distilled water containing approximately 8.4 g/L of seed which was stirred continuously at 187 rpm. Prior to the addition of ferrous sulphate, N₂ gas was bubbled liberally for 10 minutes from the bottom of the reactor in order to deoxygenate the premix which was maintained at a pH below 4 at this stage. 0.0215 M/L of FeSO₄·7H₂O (giving an initial ferrous concentration of 1200 mg/L) was then added to the reactor. This established a seed: ferrous (Fe:Fe) starting ratio of 7:1. NaSO₄ was then added to establish a SO₄²⁻ : dissolved Fe ratio of 2 : 1 characteristic of AMD. The pH was then raised to 10.5 by

the addition of 5 M NaOH and aeration commenced at 0.05 L/min (air pressure upstream of the flowmeter = 100kPa). 1 ml samples were taken at regular intervals until the end of the cycle. During the course of the cycle the pH was maintained at 10.5 by the addition of small volumes of 1M NaOH . The amount and time of addition of each dose of NaOH was recorded. Changes in the DO value were also recorded. A cycle ended when the DO had risen to and remained stable at ~8 mg/L. Prior to the commencement of the next cycle a calculated amount of seed was removed from the reactor in order to restore the seed concentration to 8.4 g/L. The supernatant was also removed and replaced twice with distilled water between cycles in order to prevent salinity accumulating in the reactor. A minimum period of two hours was maintained between successive cycles. Two or three cycles were performed during the daytime in every 24 hour period.

Experiments without seed: Experiments were conducted in an identical fashion to that described above, the only differences being that no seed was present in the premix and no recycling was performed.

Experiments with calcium: Experiments were conducted in an identical fashion to that described above, the only difference being that Ca^{2+} was present in the premix in the molar ratio $\text{Ca}^{2+} : \text{Fe}^{2+} = 1 : 1$.

Sludge settling tests: At the end of the cycle mixing was stopped and the suspended solids were allowed to settle. After 30 minutes of settling time the volume of the settled solids was measured. Settlement results are depicted as Sludge Volume Index (SVI) (APHA, 1998), expressed as ml/g-Fe.

Supernatant measurements: 2 hours after the end of a cycle a 5 ml sample of raw supernatant was taken, and without further processing, assayed for total iron concentration.

Sampling procedure during cycle: 1ml samples were taken during each cycle from approximately halfway down the depth of the reactor. Each 1 ml sample of reactor contents was diluted immediately to 100 ml in a volumetric flask with 0.01M HCl pH 2). The sample was briefly mixed by shaking and allowed to stand for 5 minutes. The

sample was then vacuum filtered through a 0.45 μm membrane filter and 50 ml of the filtrate were set aside for later analyses of total iron and ferrous iron concentrations. The remaining filtrate was used to monitor total iron concentration during the course of a cycle. The membrane filter used to process the final sample of any cycle was retained and allowed to dry at room temperature overnight. The residue of seed and precipitated solids on the filter was then subjected to XRD and SEM analysis.

Characterisation of precipitant: The precipitant was characterised using X-ray diffraction (XRD), scanning electron microscopy (SEM) and by measuring the ferrous : total iron ratio (Fe^{2+} : Fe_T).

Scanning electron microscopy (SEM): The precipitated material deposited on the membrane filter of the final sample of each cycle was examined by SEM.

X-Ray Diffraction: A section of the same filter from each cycle used for SEM was subjected to XRD analysis using a Phillips PW3710 XR diffractometer with a copper tube.

Fe^{2+} : Fe_T ratio in sludge: Two 20 ml samples taken from high and middle zones of the mixed reactor were dissolved in 30 ml of 32% HCl. Complete dissolution takes about 15 minutes whereafter the pH of the solutions was raised immediately to 1.3 by addition of a well deoxygenated 5M NaHCO_3 solution. The sample was then diluted further with distilled water to a concentration suitable for total iron and ferrous measurements.

Results and discussion

Reaction pathways followed and intermediate and end-products generated during the oxidation of ferrous solutions vary according to conditions of pH, temperature, concentration of reactants, presence and type of anions, mixing conditions, etc. in ways which are complex and poorly understood (Sugimoto and Matijevic 1980, Blesa and Matijevic 1989, Cornell and Schwertmann 1996). By and large, conditions

conducive to magnetite formation from ferrous solutions are slow oxidation, strongly alkaline pH, high ferrous concentrations and high temperature (Cornell and Schwertmann 1996).

In this work, pure ferrous solutions (1200 mg/L as Fe) were oxidised at low airflow rate (0.05 L air/ min), pH 10.5, high sulphate concentration, rapid mixing conditions and ambient temperature. The experiments were carried out in batch fashion in the presence and absence of magnetite seed. Experiments without seed comprised a single batch test whereas those with seed consisted of a sequence of repeated identical batch tests with recycling of the seed from one cycle to the next. With respect to the latter, the results presented below were taken from the eighth cycle of such an experiment by which time the chemical composition of the seed had reached steady state.

Formation of magnetite at ambient temperature with in-line aerial oxidation

Experiments conducted with and without magnetite seed showed clearly that seed strongly channels the reaction towards magnetite formation. Experiments without seed produced a yellow-orange precipitant consisting of a mixture of iron oxide species. This precipitant displayed poor settling characteristics and a relatively weak response to a hand magnet. SEM examination revealed a partially crystallised, partially amorphous structure with no apparent magnetite particles (Figure 5.2a). The XRD pattern consisted of a few clear peaks (which did not match magnetite) and high background noise. A search-match analysis suggested that gypsum and $\text{Fe}_6(\text{OH})_{12}\text{CO}_3$ were present (data not shown). Ferrous : total iron ratio in this precipitant was 5.7% indicative of a maximum presence of magnetite of around 17% of the total iron. Further characterisation of the species present in this precipitant was not pursued.

Experiments with seed produced a precipitant that was charcoal-black in colour, settled very well ($\text{SVI} \cong 8 \text{ ml/g-Fe}$), and reacted strongly to a hand magnet. XRD analysis indicated the presence of magnetite with no other peaks occurring (Figure 5.1). SEM shows small cuboid particles consistent with the appearance and size ($\sim 0.1 \text{ micron}$) of magnetite (Figure 5.2b). Ferrous : total iron ratio in this precipitant was $\sim 30\%$. The stoichiometric ratio being 33.3%, this value is well within the range

reported for magnetite in the literature (Kiyama 1974, Cornell and Schwertmann 1996).

Magnetite formation occurred at a rate of 12.8 mg-Fe/L/min during the linear phase of the reaction (Figure 5.3). During this phase the measured dissolved oxygen concentration was zero and the oxygen utilisation efficiency was around 22%. After settling of the precipitant, the concentration of dissolved iron in the supernatant was always below 1 mg/L.

Tests of precipitant stability at pH 3 (0.001 M HCl solution) revealed that only 1.1% (mass/mass) of the precipitant dissolved after 120 hours. These leaching results are in keeping with those reported by Wang et al. (1996).

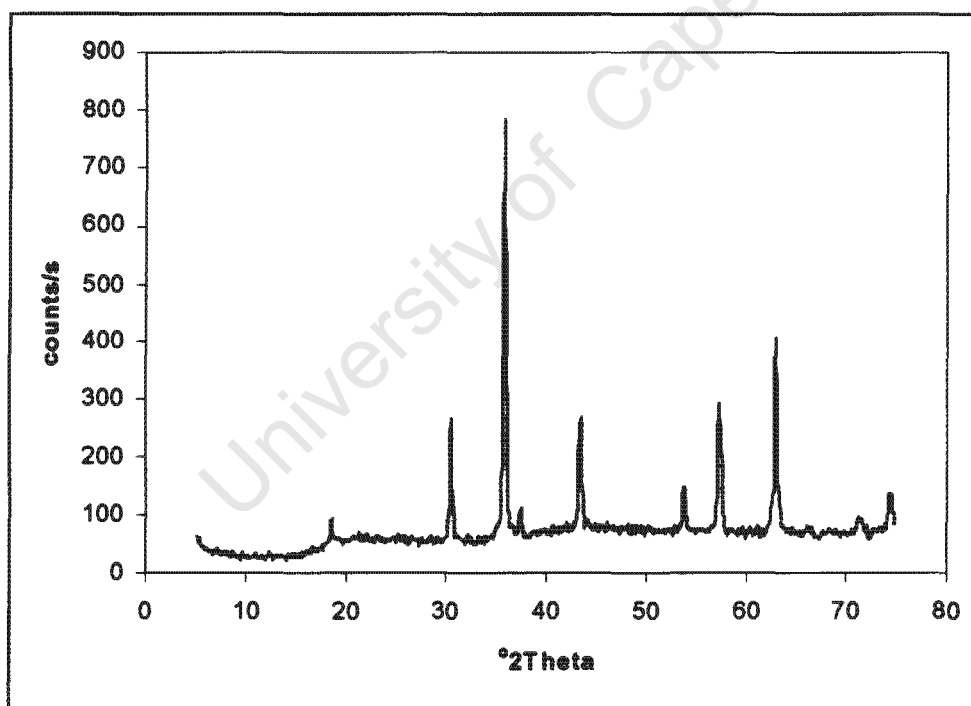


Figure 5.1 XRD pattern of the precipitant from the experiment with seed (8th cycle). See Figure 7.3b in Chapter 7 for a standard XRD pattern of magnetite.

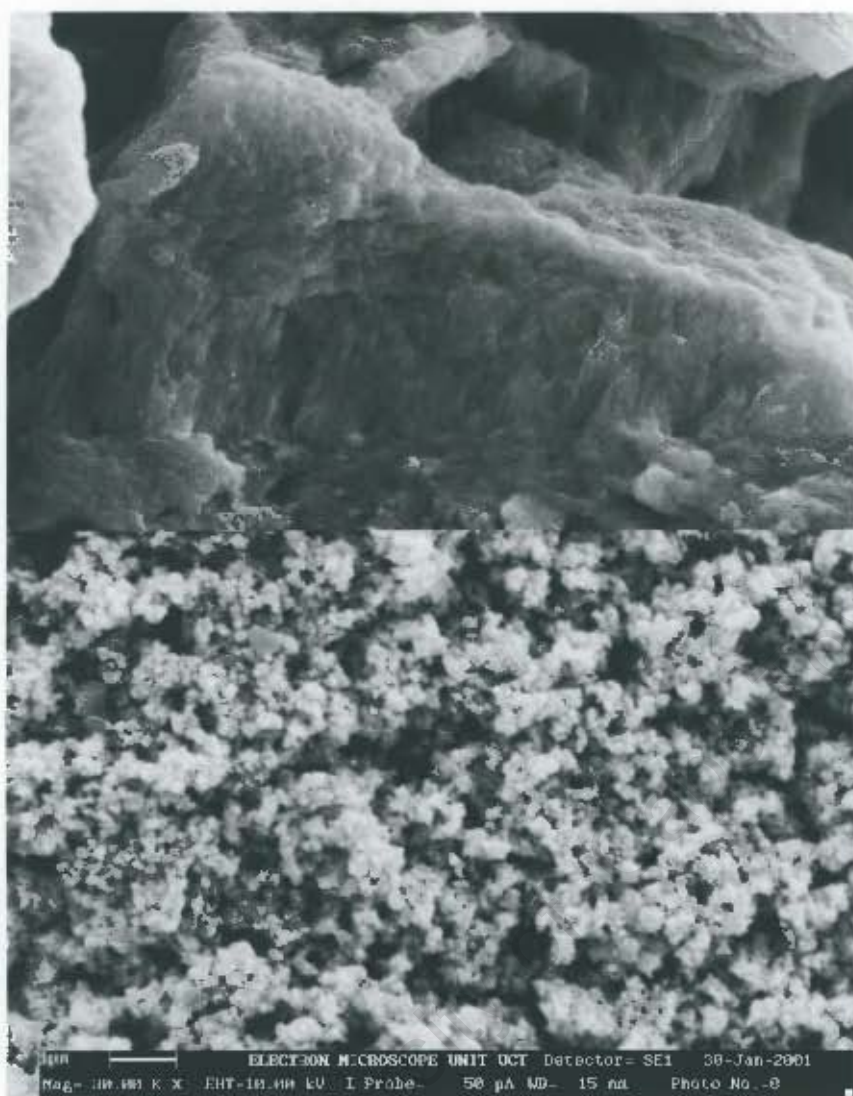


Figure 5.2 Scanning electron micrographs of precipitants. **a.** (top) experiment without seed. **b.** (bottom) experiment with seed. Each cuboidal magnetite crystal is about 100nm in dimension. Magnification x30 000.

Kinetics

Figure 5.3 shows results from a typical batch test with seed following the sampling procedure described in materials and methods. Results were taken from the eighth cycle to ensure that the solids in the reactor were predominantly endogenous. Results of the two previous cycles were identical to the results shown and discussed here, indicating that the system had reached steady state with respect to the precipitated solids. In this section the term 'ferrous (or ferric) intermediate' (FI) represents the

fraction of the mixed sludge that is soluble as ferrous (or ferric) after 5 minutes at pH 2. Ferrous intermediate, ferric intermediate, and oxygen concentrations shown in Figure 5.3 are measured values while magnetite values are calculated on the basis that magnetite is the sole end-product stable at pH 2 as supported by the XRD, SEM and dissolution results given above.

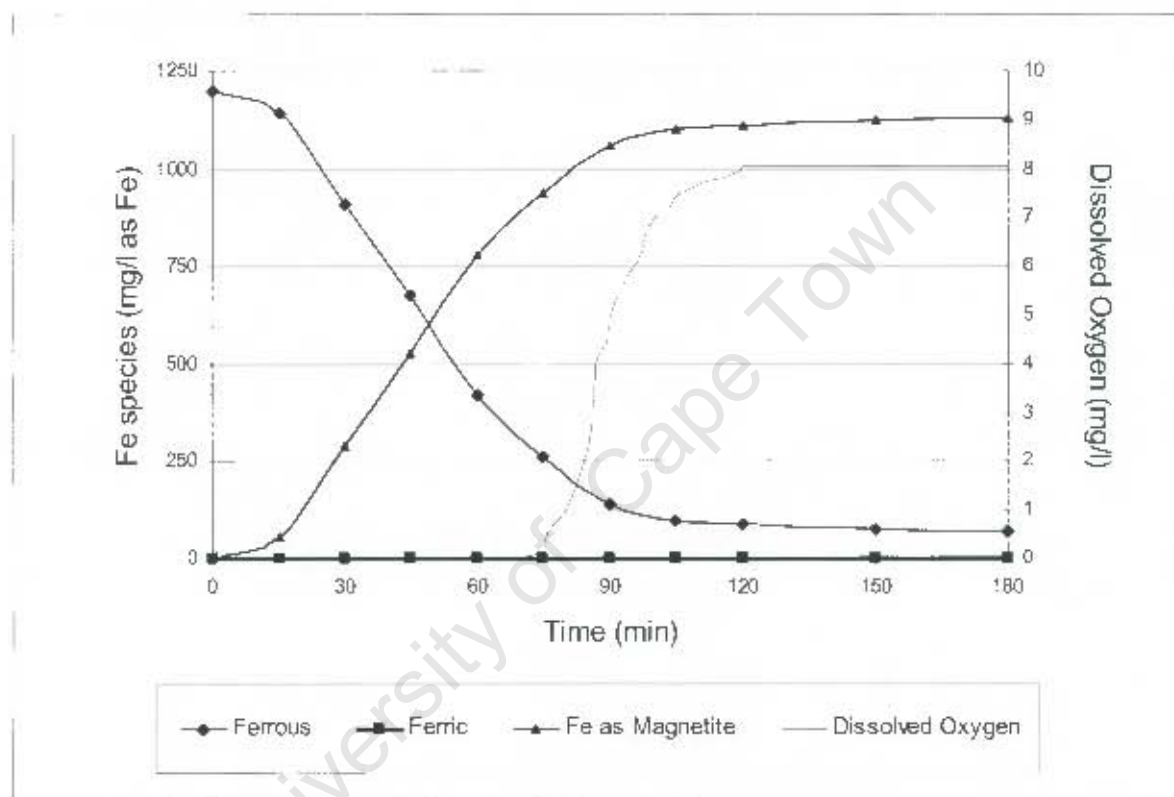


Figure 5.3 Changes in concentration of iron species and oxygen with time during a typical batch cycle with seed.

Figure 5.3 illustrates that the ferric intermediate concentration remains at zero throughout the cycle. Since ferrihydrite is rapidly soluble at pH 2 and would contribute to a ferric measurement, and noting that ferrous iron is being oxidised, one concludes that ferric iron is being incorporated into magnetite. This situation contrasts with that observed at higher air flow rates where significant concentrations of ferric iron were measured (see Figure 5.5).

Figure 5.3 reveals that the pattern of disappearance of ferrous intermediate (oxidation to ferric plus incorporation of ferrous into magnetite) appears to occur in two distinct phases. For the first 75 minutes oxidation is essentially linear at a rate of $\sim 12.8 \text{ mg-Fe}^{2+}/\text{L}/\text{min}$. Throughout this initial phase the DO concentration was zero, indicating that the oxygen transfer was the rate limiting step with respect to ferrous disappearance. After 75 minutes an abrupt steep increase in the DO concentration occurred at which time the rate of ferrous intermediate oxidation declined rapidly (DO concentration increased to 4 mg/L at 90 minutes) and the ferrous intermediate curve followed an asymptotic shape at a value of $\sim 75 \text{ mg-Fe}^{2+}/\text{L}$. Taken together these results allow calculation of the magnetite concentration at time_t; $[\text{magnetite}]_t = [\text{initial ferrous}] - ([\text{ferrous intermediate}]_t + [\text{ferric intermediate}]_t)$; which is, in this case, an almost mirror image of the ferrous curve.

Referring to Figure 5.3, at the end of the linear phase, the ferrous intermediate curve assumes an asymptotic shape. This observation is explained, as discussed in Chapter 4, by the property of magnetite to selectively release ferrous iron at low pH values such as that at which the samples were processed, i.e. pH 2 (Tronc et al. 1984). At low pH this fraction of the ferrous iron in magnetite is replaced by hydrogen ions. This substitution is reversible (Jolivet and Tronc 1988). The asymptotic portion of the curve is therefore an artefact of measurement, and the reaction should be considered to be complete at the time of the increase in the dissolved oxygen concentration. Indeed, the increase in the DO concentration correlates with the exhaustion of ferrous intermediate at pH 10.5. In this respect it must also be emphasised that from a total iron concentration of 1200 mg/L at the beginning of a cycle, the supernatant at the end of a cycle contained less than 1 mg/L of iron (removal efficiency of 99.9%).

Summary and conclusions of 'proof of concept' investigations

Sludge characterisation studies (XRD, SEM and dissolution tests) show that oxidation of ferrous solutions under controlled pH and oxidation conditions (pH 10.5, air flow rate = 0.05 l/min) in the presence of magnetite seed (initial seed : ferrous ratio = 7:1) yields almost pure magnetite at ambient temperature. Under identical conditions, but in the absence of magnetite seed, a poorly characterised mixture of largely amorphous

iron oxides are formed with magnetite comprising not more than 17% of the total iron. From a process perspective, the kinetics of magnetite formation under the above conditions (rate = 12.8 mg as Fe/L/min) are very favourable.

Under the batch test conditions reported here, the kinetics of ferrous intermediate removal appear to change from approximately zero order kinetics to markedly slower rates. This is an apparent rather than a real change and is attributable to an artefact of measurement, ie. the selective release of ferrous iron from magnetite at the low pH values required for sample processing.

The total iron concentration in the effluent was always less than 1 mg/L in all the experiments with seed, representing an iron removal efficiency of 99.9%. The precipitant settled well (SVI $\cong$ 8 ml/g-Fe) and showed substantial stability at pH 3 (dissolution of 1.1% after 120 hours).

5.2 Systematic investigations under batch conditions

Materials and methods

Reagents

The following analytical grade reagents (Sigma-Aldrich, Kimix) were used as received: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, Na_2SO_4 , NaOH , KOH , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, hydrazine sulphate, KNO_3 , NaHCO_3 , 32% HCl , 1,10-phenanthroline monohydrate, glacial acetic acid, $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$.

Instrumentation and methods of measurements

pH was measured with a Metrohm pH probe-temperature transducer coupled to a Metrohm 744 meter. Dissolved oxygen was measured with a YSI D55 DO meter. Bottled air and nitrogen, fed through rigid gas tubing, were passed sequentially via an adjustable pressure regulator and a rotameter flow meter to the reactor. At the reactor soft flexible tubing conveyed the gases to a stone bubbler fixed to the middle of the reactor floor. Ferrous iron was measured by the phenanthroline method (APHA, 1998). Total iron was determined by atomic absorption using a Varian SpectrAA 30 spectrometer. During a cycle total iron was measured using a bench-top Spectroquant (Merck) system. Magnetite which served as the initial seed to start up the first experiment was made according to the method suggested by Regazzoni et al. (1981). Intrinsic magnetite, formed by the ensuing ambient temperature method was used in all experiments thereafter.

All experiments were performed in a clear perspex reactor with internal dimensions of $18.75 \times 11.5 \times 11.5 \text{ cm}^3$ (height x width x width) capable of holding 2.62 litres. The reactor was fitted with a lid which has a large centrally positioned circular port and four smaller ports positioned in each corner. The central port accommodated the shaft of the mixing paddle ($7.5 \times 2.5 \text{ cm}^2$, width x height) which rotated through a bearing fixed above the reactor. The top of the paddle was located 7cm above the reactor floor and was centrally positioned directly above the bubbler through which air/ N_2 were released.

Experimental procedure

Each experiment consisted of a sequence of repeated batch cycles. The procedure for each cycle was identical: a premix of distilled water containing a given concentration of seed which was stirred continuously at 187 rpm. Prior to addition of ferrous sulphate, N_2 gas was liberally bubbled for 10 minutes from the bottom of the reactor in order to deoxygenate the premix that was maintained at a pH below 4 at this stage. 0.0215 M/L of $FeSO_4 \cdot 7H_2O$ (giving an initial ferrous concentration of 1200 mg/L) was then added to the reactor. To establish a $SO_4^{2-} : Fe$ ratio of 2:1 characteristic of AMD, $NaSO_4$ was added. The pH was then raised to 10.5 (or 9.0) by the addition of 5 M NaOH and aeration commenced (air pressure upstream of the flowmeter = 100KPa). 1 ml samples were then taken at regular intervals until the end of the cycle. During the course of the cycle the pH was maintained at 10.5 (or 9.0) by the addition of small volumes of 1M NaOH. The amount and time of addition of each dose of NaOH was recorded. Changes in the DO value were also recorded. Prior to the commencement of the next cycle a calculated amount of seed was removed from the reactor in order to restore the seed concentration to the desired initial concentration. The supernatant was also removed and replaced twice with distilled water between cycles in order to prevent salinity accumulating in the reactor. A minimum period of two hours was maintained between successive cycles. Two or three cycles were performed during the daytime in every 24 hour period.

In each experiment recycling continued until the chemical composition of the freshly made seed had reached steady state, here defined as no change in the ferrous : total iron ratio of the precipitated mineral for a minimum of three cycles. Unless otherwise stated the experiments were effected under the following conditions: initial Fe^{2+} concentration = 1200 mg/L as Fe, mixing velocity = 187 RPM, pH = 10.5 and temperature = $23 \pm 1^\circ C$.

Sludge settling tests: At the end of the cycle mixing was stopped and the suspended solids were allowed to settle. After 30 minutes of settling time the volume of the settled solids is measured. Settlement results are depicted as Sludge Volume Index (SVI) (APHA, 1998), expressed as ml/g-Fe.

Supernatant measurements: 2 hours after the end of a cycle, 200 ml of supernatant was taken from 3 cm below the top and filtered. The filter was then immersed in 32% HCl and the dissolved iron was then measured for residual iron oxide fines.

Sampling procedure during cycle: The 1 ml samples taken during each cycle were taken from approximately halfway down the depth of the reactor. Each 1 ml sample of reactor contents was immediately diluted to 100 ml in a volumetric flask with 0.01M HCl (pH 2). The sample was mixed briefly by shaking and allowed to stand for 5 minutes. The sample was then vacuum filtered through a 0.45 micron membrane filter and 50 ml of the filtrate were set aside for later analysis of total iron and ferrous iron concentrations. The remaining filtrate was used to monitor total iron concentration during the course of a cycle. At the end of each experiment, a membrane filter was used to process a sample diluted in distilled water rather than 0.01M HCl and dried at room temperature overnight. The residue of seed and precipitated solids on the filter was then subjected to XRD analysis. Finally, an undiluted sample of settled sludge was taken for Mössbauer spectroscopy.

Characterisation of precipitant: Characterisation of the precipitant was performed by Mössbauer and XRD analysis as well as by complete dissolution in 32% HCl to obtain the ferrous : total iron ratio.

⁵⁷Fe Mössbauer spectroscopy (MS): Samples were sent to Dr Giovanni Hearn at the School of Physics, University of the Witwatersrand, for Mössbauer spectroscopy. All further discussion, figures and tables in this chapter pertaining to Mössbauer analysis are drawn from his report. MS in conventional transmission geometry was used to detect Fe-bearing phases within the sample. As an atomic-scale local probe it is equally effective in the analysis of poorly crystallised or amorphous materials where conventional macroscopic-type probes like XRD have considerable limitations.

X-Ray Diffraction: A filtered sample from each cycle was subjected to XRD analysis using a Phillips PW3710 XR diffractometer with a copper tube.

Fe²⁺/Fe_T ratio in sludge: Two 1 ml samples taken from the middle zone of the mixed reactor were dissolved in 4 ml of 32% HCl (~pH -1). Complete dissolution takes up to

15 minutes. Thereafter the sample was diluted with distilled water to attain a concentration suitable for total iron and ferrous measurements which were performed without delay in order to avoid any possible oxidation of ferrous iron.

Experiments with calcium: These experiments were conducted in the same way as described above but with the addition of 21.5 mmol/L of CaCl_2 to the reactor premix prior to the commencement of each cycle. Such addition simulates the use of lime to obtain an operational pH of ~ 10.5 in practice for AMD water with a Fe^{2+} concentration of 1200 mg/L.

Results and discussion

Effect of seed concentration

To assess the seed concentration affect, experiments were conducted at a fixed air flow rate of 0.05 L/min and at varying concentrations of magnetite seed. Results are given in Column 1 of Table 5.1 and are presented as the ferrous : total iron ratio expressed in percent. Table 5.1 shows clearly that the presence of seed even at relatively low concentrations of 1.2 g/L as Fe strongly channels the reaction towards a final product with the stoichiometry of magnetite, ie. ferrous : total iron ratio close to 33%. These experiments all produced a precipitant that was charcoal-black in colour, settled very well, and reacted strongly to a hand magnet. XRD analysis indicated the presence of magnetite with no other peaks occurring.

Initial seed concentration g-Fe / L (initial seed : Fe ²⁺ ratio)	Airflow rate L/min			
	0.05	0.085	0.12	0.6
0	5.7	—	—	—
1.2 (1 : 1)	32.15 ± 0.42	28.86 ± 0.24	27.42 ± 1.70	17.36 ± 0.74
4.8 (4 : 1)	32.03 ± 0.72	30.86 ± 0.01	29.61 ± 0.73	21.49 ± 1.59
8.4 (7 : 1)	30.52 ± 0.51	—	—	27.60 ± 1.54

Table 5.1 Effect of initial seed concentration and airflow rate on the ferrous to total iron ratio (shown in percent) in the sludge. Results are given as average ± one standard deviation.

Effect of airflow rate on magnetite formation

In the absence of seed, higher oxidation rates tend to inhibit magnetite formation (Cornell and Schwertmann 1996). To assess the effect of airflow rate, experiments were conducted at seed concentrations of 1.2 g/L and 4.8 g/L and varying airflow rates. Ferrous : total iron ratio results for these experiments are shown in rows 2 and 3 of Table 5.1. The results show a clear trend: the higher the airflow rate (increased oxidation rate), the lower the ferrous content of the final precipitate. These results are most clear when comparing an airflow rate of 0.05 L/min to one of 0.6 L/min at initial seed concentrations of both 1.2 and 4.8 g/L (a decrease from 32.15% to 17.36% and 32.03% to 21.49% respectively). However, an increase from 0.05 L/min to 0.12 L/min

caused only a small decrease in the ferrous content of the sludge, especially at the higher seed ratio of 4.8 g/L.

Mössbauer, XRD and SEM analyses showed that all of the precipitants from rows 2—4 in Table 5.1 had the structural characteristics of magnetite, with no evidence of any other crystalline or amorphous phases. For example, Figure 5.4 shows the Mössbauer spectra of steady-state precipitants made at 0.12 L/min (Figure 5.4, top) and 0.6 L/min (Figure 5.4, bottom). Both spectra show the two partially overlapping sextets (representing the tetrahedral and octahedral sites) typical of magnetite (Vandenberghe et al. 1990). The heavy solid line represents the overall theoretical fit.

Mössbauer analysis of the sample made at 0.12 L/min (Figure 5.4, top) found the ferrous : total iron ratio to be $28 \pm 1.0 \%$ (as calculated from the integrated area under the sub-spectrum) which accords well with the dissolution value of 29.61 %. For this same sample an additional $6 \pm 1.0 \%$ ferric was found in the octahedral B-site over and above the $33 \pm 1.0 \%$ expected and indeed found in this same site. These 6 % are interpreted as ferrous which has oxidised to ferric in the octahedral B-site. The measured value of only $28 \pm 1.0 \%$ octahedral B-site ferrous accords with this interpretation. Therefore despite this partial oxidation (also detected as a decrease in the ferrous : total iron ratio), Mössbauer analysis in conjunction with the XRD and SEM findings, indicates that the typical magnetite crystal structure is maintained. In this sample however, the Mössbauer results indicate that the downward deviations from stoichiometry are nevertheless accompanied by some disruption of the crystal order in the form of cation vacancies, as evidenced by line-width broadening of the octahedral sextet.

At the relatively high airflow rate of 0.6 L/min and in the presence of a low concentration of initial seed (1.2 g/L as Fe) the sludge formed contained on average only 17.36% of ferrous. Again the structural data (MS, XRD, SEM) indicate that even such a large deviation from stoichiometry appears to be ordered within the crystalline structure of magnetite, albeit Fe in magnetite with a distribution of local atomic environments and severely disrupted neighbourhoods from charge compensating vacancies as a result of the oxidation. The evidence for such a distribution of Fe local

environments is deduced from both the spectral line-broadening and collapsed magnetic fields evident as a distortion in the centre of the Mössbauer spectrum (Figure 5.4, bottom).

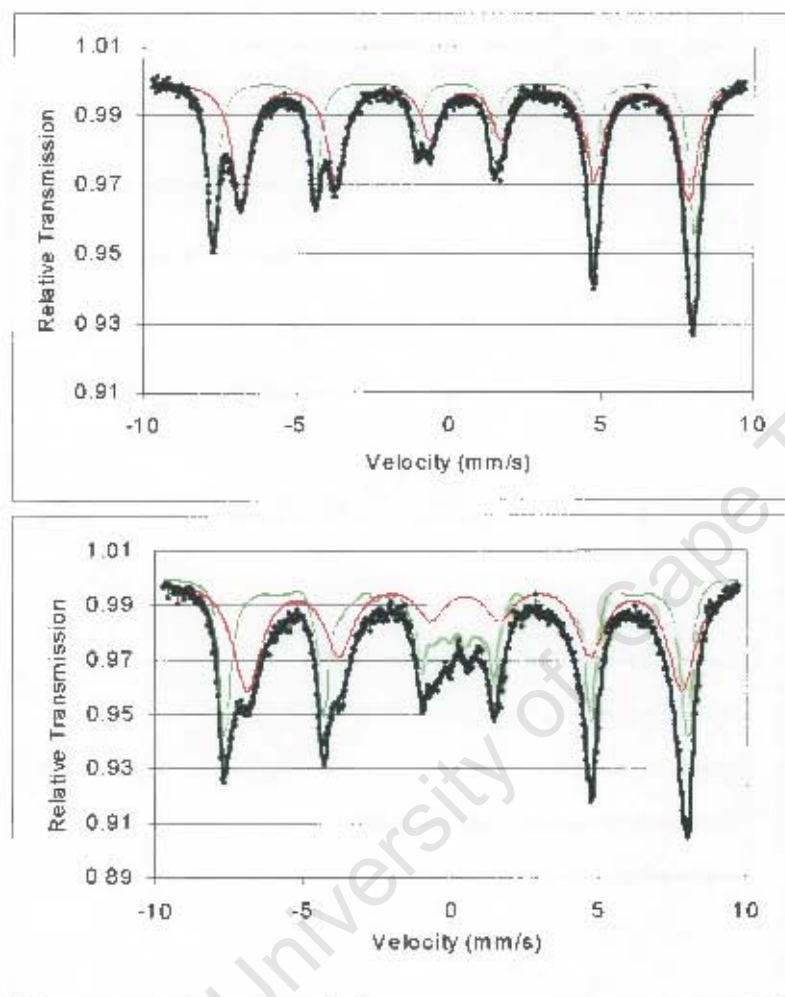


Figure 5.4 Mössbauer spectra for two samples at varying airflow rates and seed concentrations. pH = 10.5. **Top** Airflow rate = 0.12 L/min, seed concentration = 4.8 g/L. **Bottom** Airflow rate = 0.6 L/min (bottom), seed concentration = 1.2 g/L. In each case the heavy solid line represents the theoretical fit of the two sub-spectra indicated by lighter lines. (from reports compiled by Dr G Hearne).

Notably however, as shown in Table 5.1, increasing the seed concentration to 8.4 g/L as Fe resulted in a shift back towards stoichiometric magnetite (ferrous : total iron ratio of $27.6 \pm 1.54\%$). This again highlights the role of seed in channeling the reaction towards magnetite despite the high airflow rate.

Effect of airflow rate and seed concentration on ferrous removal kinetics

Figure 5.5 shows results from a typical batch test with seed concentration = 4.8 g/L, pH = 10.5, air flow rate = 0.12 L/min. Results of the two previous cycles were identical to the results shown and discussed here, indicating that the system had reached steady state with respect to the precipitated solids.

Ferrous intermediate, ferric intermediate, and oxygen concentrations shown in Figure 5.5 are measured values while the 'stoichiometric magnetite' values are calculated as the concentration of stoichiometric magnetite (given in mg-Fe/L) which could form according to the amount of ferrous intermediate which disappears.

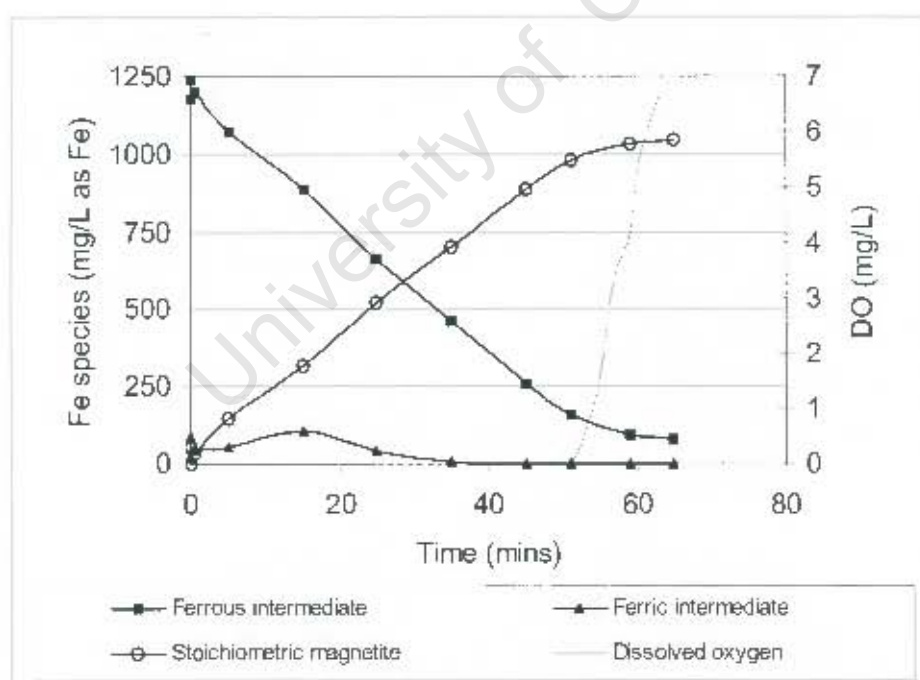


Figure 5.5 Changes in concentration of iron species and oxygen with time during a typical cycle with seed. Results are those for pH = 10.5, seed concentration = 4.8 g/L, airflow rate = 0.12 L/min.

Figure 5.5 illustrates that after an initial transient rise the ferric intermediate concentration remains close to zero throughout the cycle. As in Figure 5.3 and for the same reasons mentioned there (i.e. measurement artefact) the pattern of disappearance of ferrous intermediate (oxidation to ferric plus incorporation of ferrous into magnetite) appears to occur in two distinct temporal phases. For the first 50 minutes the rate of ferrous intermediate removal is linear (in this case at a rate of $\sim 20.4 \text{ mg-Fe}^{2+}/\text{L}/\text{min}$). Throughout this initial phase the DO concentration was zero, indicating that oxygen transfer was the rate limiting step in the transformation of ferrous iron into *fresh* precipitate. After 50 minutes an abrupt steep increase in the DO concentration occurred at which time the rate of ferrous intermediate removal appears to decline rapidly to an asymptotic concentration of $\sim 80 \text{ mg/L Fe}^{2+}$. As already explained the residual concentration of soluble ferrous forming the asymptotic portion of the plot does not constitute ferrous intermediate which has not been converted to magnetite. Rather, it is a measurement artefact stemming from the selective partial release of ferrous iron from magnetite (now present as original plus newly formed seed) at the low pH values at which samples were processed (Jolivet and Tronc 1988). This interpretation is supported by the observation that the residual ferrous concentration increases with seed mass (eg. at 0.05 L/min airflow rate; no seed = 18 mg/L residual ferrous, 1.2 g/L seed = 28 mg/L residual ferrous, 4.8 g/L seed = 88 mg/L residual ferrous). This artefactual residual FI concentration is therefore a seed as opposed to a substrate effect. The shape of the ferrous intermediate curve is therefore misleading and under reactor conditions of high pH, linear kinetics would continue to lower solid ferrous intermediate concentrations.

The effect of airflow rate on the ferrous removal rate is given in Figure 5.6 for a seed ratio of 4.8 g/L. The results are calculated for the part of the reaction required to reduce the solid ferrous intermediate concentration from 1200 to 100 mg/L (below 100 mg/L the calculation is hindered by the measurement artefact discussed above). As shown, the rate of ferrous removal was linear with airflow rate. This result concurs with the observation that in all experiments the dissolved oxygen concentration was zero until all ferrous had been oxidised or incorporated into magnetite as Fe^{2+} . Taken together these facts confirm that oxygen supply (mass transfer) was rate-limiting. Under these conditions, the retention times (RT) needed to remove 1200 mg/L of

ferrous to a final product predominantly composed of magnetite varied between 0.3–1.6 hours. It should be noted that the seed concentration did not affect the rate of ferrous removal. Under otherwise uniform conditions the latter depends exclusively on the airflow rate. This was indicated by the closely similar ferrous removal rates obtained at particular airflow rates at widely differing seed concentrations (data not shown).

From Figure 5.6 it is evident that the retention time does not, as it may be expected to, vary in a linear fashion with the ferrous removal rate. The main reason for this can be found in Table 5.1 which shows that the percentage ferrous in the end-product decreases as the airflow rate increases. This means that more ferrous is oxidised as the airflow rate increases and this requires a longer retention time. This interpretation is supported by data, presented in Figure 6.12 in the next chapter, which shows a linear relationship between retention time and percentage ferrous.

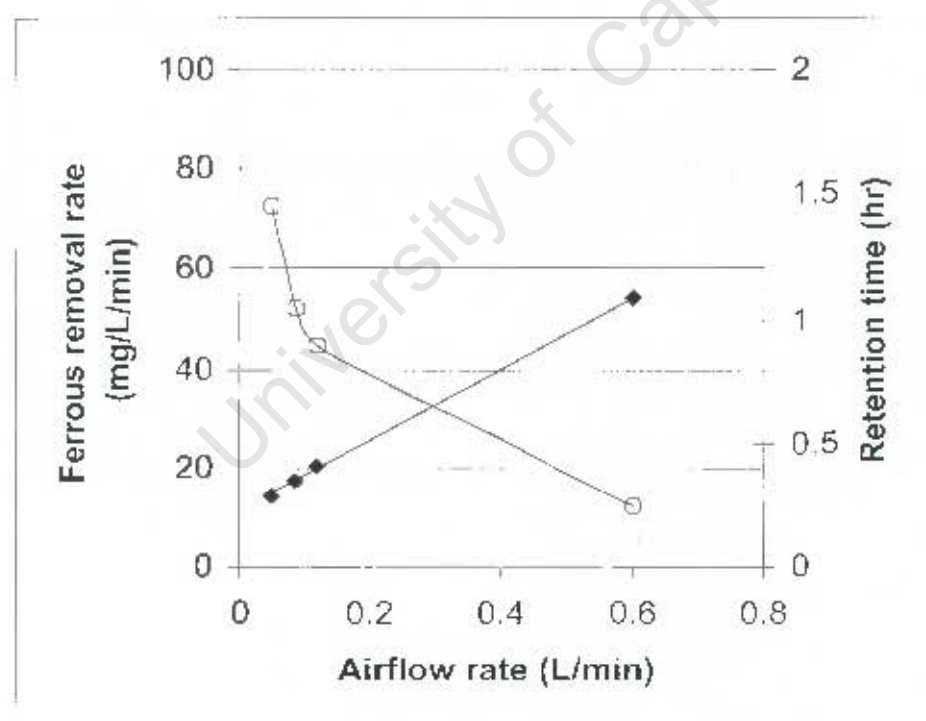


Figure 5.6 Ferrous removal rate (diamonds) and reaction retention time (circles) as a function of airflow rate (initial seed concentration 4.8 g/L as Fe).

Effect of pH

Experiments were conducted at pH 9 for airflow rates of 0.05, 0.085 and 0.12 L/min at an initial seed concentration of 4.8 g/L as Fe. Results are shown in comparison with those at pH 10.5 (Table 5.2). The same trend of decreasing percentage ferrous with increasing airflow rate is apparent.

Airflow (L/min)	% ferrous	
	pH 9	pH 10.5
0.05	27.7	32.03
0.085	25.77	30.86
0.12	21.34	29.61

Table 5.2 Percentage ferrous results for pH 9 compared to those for pH 10.5 at a seed concentration of 4.8g/L.

Effect of temperature

All experiments reported thus far were conducted at 23 ± 1 °C. The results of experiments investigating the effects of lower temperatures on kinetics and end-products are shown in Table 5.3. As temperature decreases, a clear decrease in the percentage ferrous : total iron in the final product is seen.

Temperature (°C)	23 ± 1	13 ± 1	7 ± 2
% ferrous : total iron	30.86 ± 0.01	24.24 ± 1.77	19.04 ± 0.01

Table 5.3 Affect of temperature on percentage ferrous in the end-product (airflow rate = 0.085 L/min, seed concentration = 4.8 g/L).

Sludge stability: leaching experiments

Dissolution of iron oxides is thought to occur largely through weakening of the Fe-O bond (Cornell and Schwertmann 1996). In addition ferrous ions, by virtue of their larger diameter, are more easily dislodged than ferric ions. Protonation of surface hydroxide groups is the mechanism whereby the Fe-O bond is weakened. Since adsorption is a function of concentration in the aqueous phase, solution pH is a prime factor in determining the rate of dissolution. However complexing ligands and reducing agents interact with pH to influence the dissolution rate, as do structural features of the solid. Dissolution rates therefore vary with multiple parameters of both solid and solution.

Sludge dissolution was tested for 53 days at pH 2 and pH 5 without the addition of complexing or reducing agents. The sludge tested consisted initially of 28% ferrous. Results shown in Figure 5.7 reveal complete sludge stability at pH 5 over time, whereas at pH 2 slow but steady dissolution occurred (~10% after 53 days). Since pH values lower than 5 are unlikely to occur at the site of sludge disposal, these results are promising. Nevertheless, the stability of ferrites made at ambient temperature containing non-ferrous cations remains to be determined.

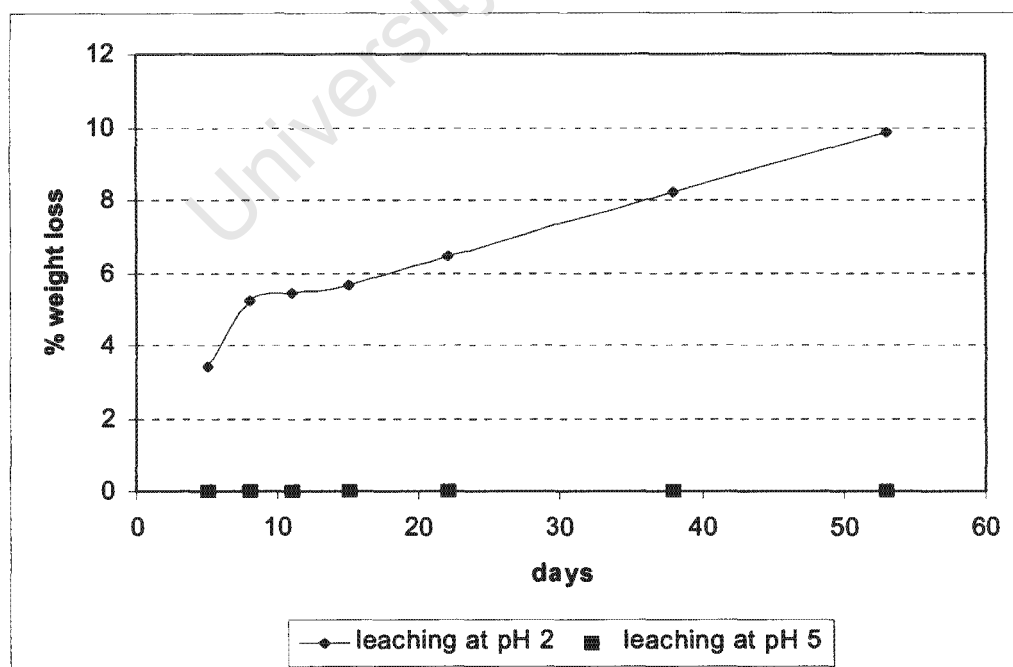
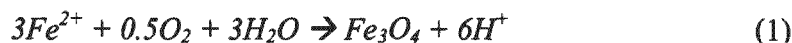


Figure 5.7 Sludge stability at pH 2 and pH 5.

Alkalinity demand

The alkalinity requirement for the formation of magnetite from ferrous is given by Equation 1 and indicates an OH⁻ : ferrous molar ratio of 2:1



In all experiments, around 95% of the alkalinity was added (as NaOH) to precipitate the ferrous intermediate and reach the target pH. The remaining 5% was required during the reaction in order to maintain the pH at the desired value. The final molar ratio of OH⁻ added : ferrous was approximately 2 to 1 in all experiments (experimental values ranged between 1.98 to 2.1), which conforms to the expected stoichiometric value for Fe(OH)₂. The reasons for the observation that only 95% hydroxide was consumed at the beginning of the reaction have been discussed in detail in Chapter 4. Finally, it is worth noting, as discussed in Chapter 3, that all likely final products of the oxidation of ferrous (ie. α-FeOOH, γ-FeOOH, Fe₂O₃, Fe(OH)₃ and Fe₃O₄) will exert the same net OH⁻ : ferrous molar ratio demand, ie. 2:1. The proposed process, operated at pH 10.5, therefore entails no unusually high alkalinity demands.

Sludge settlement and effluent quality

Sludge settlement was quantified using the Sludge Volume Index (SVI) method, SVI being the volume occupied by 1 g-Fe sludge after a settling period of 30 minutes. Results for all experiments are given in Table 5.4. By and large, the settlement was better at the lower airflow rates, but even at 0.6 L/min, the SVI was low (67 ml/g-Fe) and settlement was excellent. Magnetic filtration would enhance these already highly advantageous settling values. Effluent quality was measured by quantifying residual iron fines in the effluent after a settlement period of two hours as described in Material and Methods. Fines concentration in all the experiments was always below 1 mg/L as Fe representing an iron removal efficiency of greater than 99.9%.

Seed concentration (g/L)	Airflow rate (L/min)			
	0.05	0.085	0.12	0.6
1.2	11.39	32.56	32.19	67.61
4.8	7.38	14.41	22.02	28.47
8.4	8.00			16.04

Table 5.4 Sludge density after 30 minutes of settling in ml/g-Fe according to seed concentration and airflow rate.

Ferric intermediate

During a particular cycle, a soluble (at pH 2) ferric intermediate fraction was measured by subtracting the ferrous concentration from the total iron intermediate concentration. In all experiments, the ferric intermediate concentration was very low at the end of the batch cycle. By and large, it was also low throughout the cycle although at higher airflow rates, concentrations of up to ~200 mg/L as Fe formed. As can be seen in Figure 5.5 ferric intermediate accumulated towards the beginning of the cycle only to be largely incorporated into magnetite or other end-products by the end of the cycle.

Aging

No explicit attempt to investigate aging was included in these experiments and indeed the aging period between cycles varied from 2 to ~18 hours. In subsequent experiments described in the next chapter, it became evident that under very similar conditions, no aging period is required. This finding justifies ignoring aging in the batch experiments described above.

Effect of calcium

Calcium (but not magnesium) has been reported to interfere with ambient temperature magnetite formation (Perales Perez et al. 1998, McKinnon et al. 2000). Perales Perez et al. (1998) proved that recycling of seed enhanced magnetite formation in a 1-step process. Seed has also been reported to restore the formation of pure magnetite in the presence of calcium in the context of a two-step process (McKinnon et al. 2000). However no systematic information on the effect of calcium in a one-step (in-line oxidation) process is available. The effect of calcium is of paramount importance since not only do many AMD waters contain high concentrations of calcium, but lime is the most cost-effective source of alkalinity. Experiments were therefore performed in which calcium was added in equimolar amounts with respect to ferrous iron in order to simulate the use of lime. Preliminary results clearly show the inhibitory effect of calcium: at 0.12 L/min airflow rate and a seed concentration of 4.8 g/L, percentage ferrous in the sludge was only ~13%. The corresponding value in the absence of calcium was 29.61%. Furthermore, the macroscopic appearance (colour brown as opposed to charcoal) of the sludge together with XRD and Mössbauer analyses indicated the presence of non-magnetite phases in significant amounts. Increasing the seed concentration to 8.4 g/L in the presence of calcium had the effect of increasing the percentage ferrous to 18.8%.

Summary and conclusions of systematic investigations under batch conditions

A novel approach towards the removal of iron and non-ferrous metals from typical South African AMD waters is presented. This approach is premised on the knowledge that high temperature ferrite formation acts as a medium for both iron and non-ferrous metal removal from waste-streams. The object of the research is to test the applicability of this approach to the ambient temperature conditions appropriate for the treatment of large AMD volumes. The approach involves the controlled oxidation of ferrous-containing AMD water at ambient temperatures in the presence of magnetite seed. The resulting oxidation product is the ferrite ($M1^{3+}_2M2^{2+}O_4$) magnetite (Fe_3O_4) which has the capacity for non-ferrous metal removal by cation substitution. This results in a single, stable and easy to remove ferrite sludge.

Sludge characterisation studies (Mössbauer spectroscopy, XRD, and SEM) show that oxidation of ferrous solutions under controlled pH and oxidation conditions (pH 9 and 10.5, airflow rate = 0.05 to 0.6 L/min) in the presence of magnetite seed (initial seed concentration 0 to 8.4 g/L) yields almost pure structural magnetite at ambient temperature. Dissolution tests however reveal that the ferrous : total iron ratio of this magnetite varied between ~30% and ~17% according to conditions of pH, temperature, airflow rate and seed concentration. Taken together the structural and chemical analyses indicate that magnetite of varying degrees of oxidation is being formed. Under identical conditions, but in the absence of magnetite seed, a poorly characterised mixture of largely amorphous iron oxides are formed with a ferrous : total iron ratio of 5.7%.

Airflow rate and seed concentration independently affected the percentage ferrous in the final precipitant (Table 5.1). A clear trend between airflow rate and percentage ferrous was found with lower airflow rates resulting in higher percentage ferrous. Airflow rates below 0.12 L/min produced percentage ferrous ratios closely approaching that of stoichiometric magnetite (27–32.5 %). Seed concentration also had a marked effect on the percentage ferrous. This is most apparent at high airflow rates. For example, at 0.6 L/min as the seed concentration increased from 1.2 g/L to 8.4 g/L the percentage ferrous increased from 17.36 % to 27.6 %.

Airflow rate but not seed concentration had an effect on the rate of oxidation, airflow rate being the rate-limiting parameter at all times. From a process perspective, the kinetics of magnetite formation under the above conditions are very favourable. The hydraulic retention time required for the complete removal of a typical AMD iron concentration (1200 mg/L) was from 0.3 to 1.6 hours.

The total iron concentration in the raw effluent was always less than 1 mg/L in all the experiments with seed. This represents an iron removal efficiency of greater than 99.9%.

The precipitant settled well (Table 5.4) and showed complete stability at pH 5 (Figure 5.7). At pH 2 gradual dissolution amounting to 10% (w/w as Fe) was observed over a period of 53 days.

Results of experiments conducted at pH 9 parallel those at pH 10.5 but reveal lower percentage ferrous in the final precipitant (Table 5.2). Temperature was found to affect the percentage ferrous in the end-product (Table 5.3).

All of the parameters relevant to processing AMD on a large scale were found to be favourable: low oxygen requirement, low retention time, excellent settling properties, excellent removal efficiency and good sludge stability at pH 5.

In the following chapter, investigations into ambient temperature ferrite formation under continuous flow, steady-state conditions, in the absence and presence of calcium are described.

Chapter 6 Ambient temperature ferrite formation under continuous flow, steady-state conditions, in the absence and presence of calcium

Introduction

The results discussed in Chapter 5 demonstrate the feasibility of ambient temperature magnetite formation from ferrous solutions in the presence of magnetite seed (Morgan et al. 2001, Lahav et al. 2003). The presence of a threshold concentration of magnetite seed was found to channel the end-products exclusively towards magnetite formation. Under the same conditions, in the absence of seed, the end-products consisted of a mixture of iron oxides containing a maximum of ~17 % magnetite. These investigations delineated the effects of airflow rate, seed concentration, pH and temperature on magnetite formation under batch conditions. Significant findings were that oxidation is the rate-limiting step in the domain where pure magnetite is formed, and that magnetite seed concentration does not affect the rate of ferrite formation. The favourable settling properties ($SVI = 8 \text{ ml/g-Fe}$) and pH stability of the magnetite sludge were also documented (Lahav et al. 2003). Furthermore, in line with the results of others (Wang et al. 1996, Perales Perez et al. 1998), calcium was shown to markedly inhibit magnetite formation under batch conditions (Lahav et al. 2003). The question of aging was not addressed in these experiments.

Chapter 6 reports results for seeded ferrite formation from ferrous solutions obtained under steady-state conditions, both in the presence and absence of calcium. Under batch conditions, the ferrous intermediate (FI) concentration diminishes steadily from the initial value to zero, as magnetite is formed. It is therefore clear that the previously investigated batch conditions are heterogeneous over time with respect to ferrous intermediate concentration and ferrous intermediate : seed ratio. Since a high background ferrous intermediate concentration is known to favour magnetite formation, it is desirable to control this parameter. Thus, a reactor system was designed which enabled the ferrous intermediate concentration to be maintained at a constant value (dynamic steady-state conditions). This facilitated easy investigation into the effect of ferrous intermediate concentration on magnetite formation which in

turn lead to the discernment of a threshold effect with respect to the ferrous intermediate concentration during ferrite formation. That is, whereas it was previously well-recognised (Cornell and Schwertmann 1996) that, in the absence of seed, a high ferrous concentration favoured ferrite formation, nowhere has it been suggested or shown that a clear threshold effect exists. The steady-state reactor system reported here, not only elucidated this threshold effect, but also enables it to be easily quantified.

As will be described below, the steady-state reactor system also allowed the incorporation of a 'contact stabilisation' (precipitation) reactor used to increase the ferrous intermediate (as Fe) : dissolved Ca^{2+} (as Ca) ratio prior to oxidation. The ability to amplify this ratio has proven to be the key to overcoming the calcium inhibition effect. Another favourable aspect emanating from the introduction of the contact stabilisation reactor is a significant reduction in the size of the oxidation reactor necessary, because only the settled sludge is subjected to oxidation rather than the entire bulk AMD flow. This feature, together with insight into the ferrous intermediate concentration threshold effect and the ability to amplify the ferrous intermediate : dissolved Ca^{2+} ratio, appears to have paved a clear way to a well-understood, reliable, robust and easily implemented ambient temperature ferrite process.

Steady-state continuous flow conditions

Materials and methods

Experimental set-up: Figures 6.1 and 6.2 show the two reactor configurations investigated. Figure 6.1 shows the configuration used for ferrite formation in the absence of calcium. Magnetite seed is recycled from the settling tank to the main oxidising reactor (5.2L) so as to maintain the total iron concentration in the latter at approximately 20.0 g-Fe/L. A ferrous solution representing the AMD is introduced into the main oxidising reactor which is maintained at pH 10.5, and the ferrous ions precipitate to form solid ferrous intermediate species. Introduction of air causes oxidation of ferrous to ferric in the main reactor allowing for magnetite formation. The fraction of ferrous intermediate in the main oxidising reactor which is not

transformed into magnetite was maintained at a constant concentration (50–100, 150–250 and ~500 mg-Fe/L in the three experiments). Air was introduced into the main oxidising reactor at a controlled flow rate so as to maintain the ferrous intermediate at the three selected concentrations. The effluent of the main oxidising reactor flowed into a settler where solid-liquid separation occurred. The clarified effluent from which all iron has been removed flowed out of the system. The sludge, which is a mixture of crystallised magnetite, freshly precipitated hydrated magnetite and ferrous intermediate species was then returned to the main reactor via a second oxidising reactor (2.5L) designed to complete the oxidation process. The pH of this reactor was also maintained at 10.5. Both oxidation reactors (5.2 and 2.5 L) were constantly mixed from above by a rotating paddle. No aging stage was included.

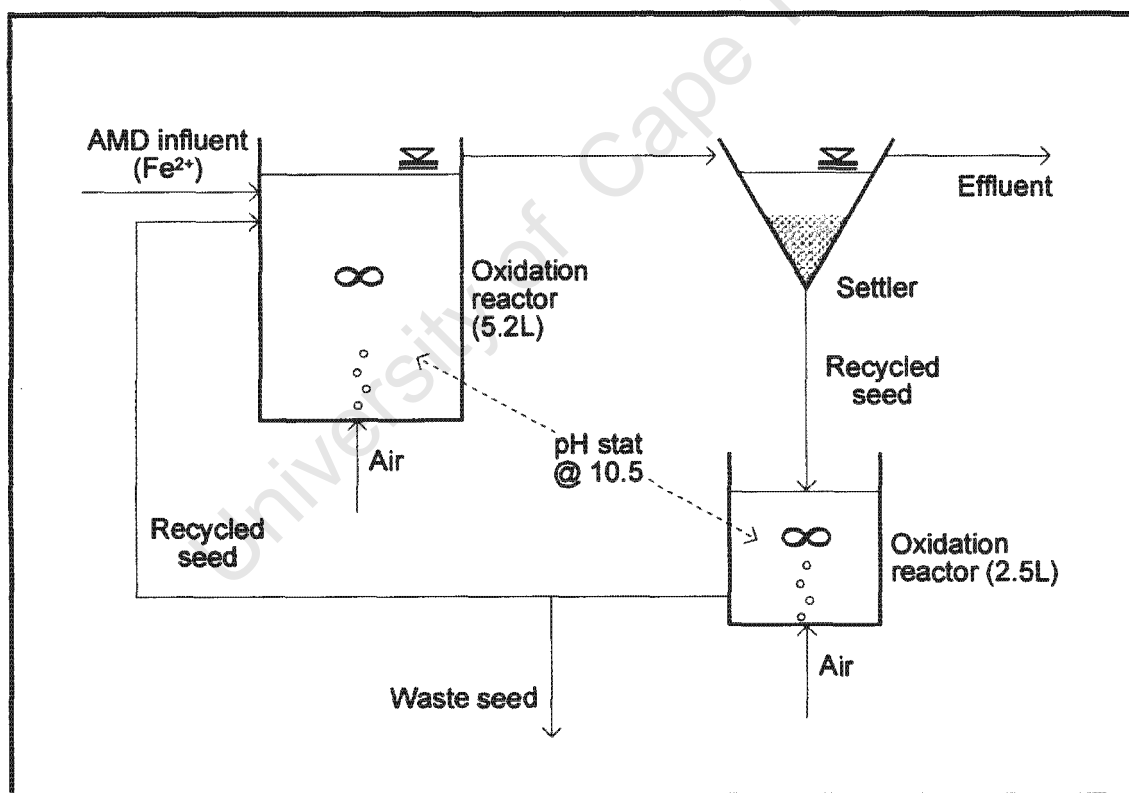


Figure 6.1 Reactor configuration for experiments without calcium.

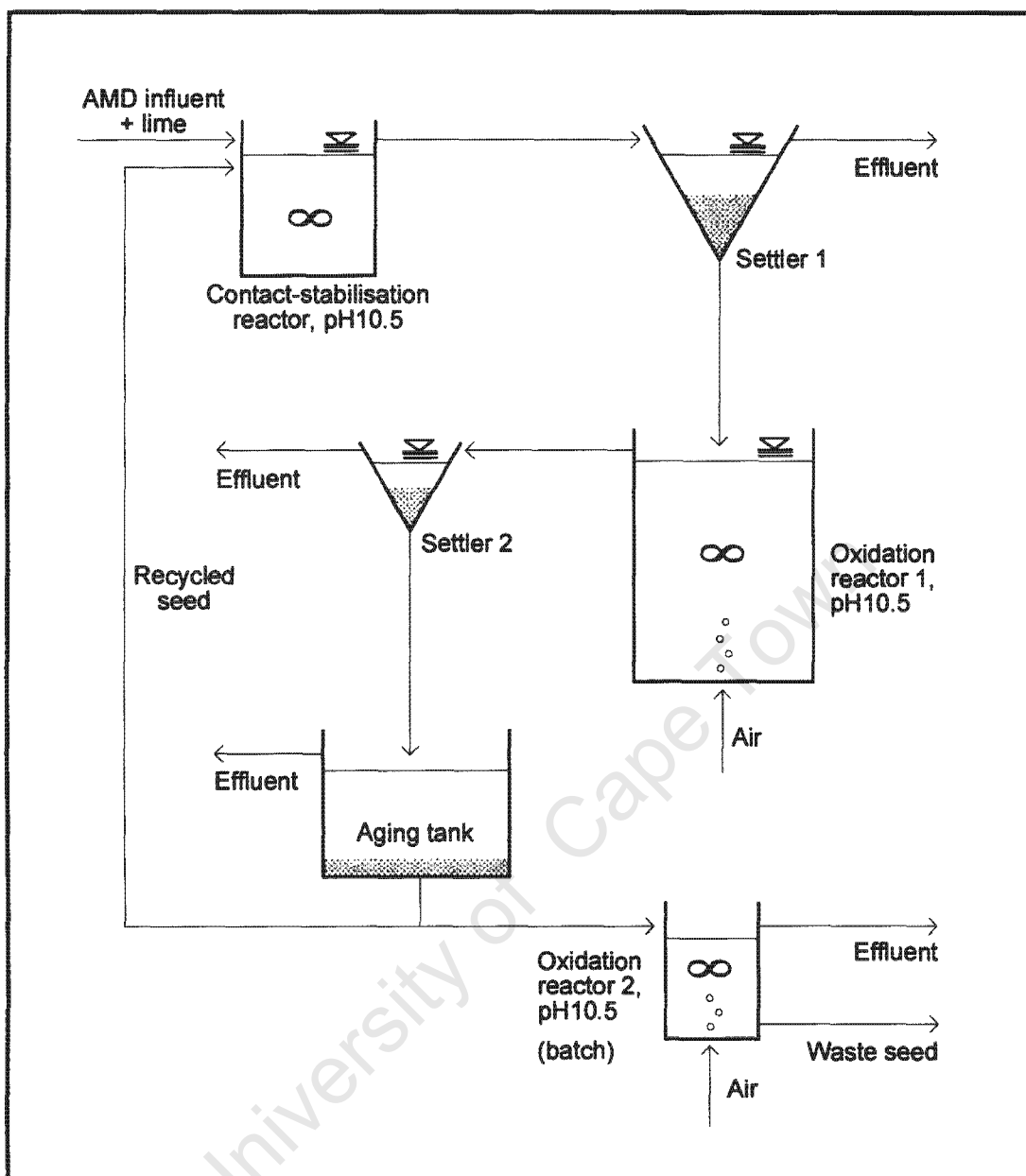


Figure 6.2a Schematic representation of the continuous flow, steady-state reactor system used in the presence of calcium.



Figure 6.2b Photograph of the apparatus depicted in Figure 6.2a which was used for experiments where calcium was present. a. Contact stabilisation reactor. b. Settler 1. c. Oxidation reactor 1. d. Settler 2. e. Tank receiving effluent from Settler 1. f. Source of air. g. pH controllers. h. Rotameter airflow rate controllers. i. Sludge underflow from Settler 2 to Aging tank (Aging tank and Oxidation reactor 2 not shown)

Figure 6.2a shows the configuration used for magnetite formation in the presence of calcium. Figure 6.2b shows the actual apparatus depicted in Figure 6.2a. The seed concentration in the oxidising reactor was again maintained at ~ 20.0 g-Fe/L. In this case however separate equimolar ferrous and calcium solutions, representing the AMD and added lime, were first introduced into a pH 10.5 contact stabilisation reactor. The effluent of this reactor flowed under gravity into the first settler. The clarified effluent left the system while the settled sludge was cycled to the first oxidising reactor. The ferrous intermediate in the underflow was therefore significantly concentrated relative to the concentration in the source AMD whilst the dissolved calcium concentration remained unchanged. In the oxidation reactor the sludge is completely mixed, aerated and maintained at pH 10.5 by the addition of a

The pH, dissolved oxygen, ferrous intermediate and total iron were measured in each compartment at various times. The term 'total iron' (Fe_T) represents the iron in a sample which undergoes complete dissolution in 32% HCl within 15 minutes. This includes magnetite seed and/or other end-products of oxidation but not ferrous intermediates because the sample is diluted in 100 ml of 0.01M HCl (ie. pH 2) before being filtered: end-products remain on the filter but intermediate phases dissolve and leave with the filtrate. End-products are then dissolved in 32% HCl before being diluted to a concentration and pH suitable for total iron and ferrous measurements.

The system was run continuously for at least three sludge ages. Characterisation of the sludge was performed by XRD and Mössbauer modalities as well as by ferrous : total iron ratio determination.

X-ray diffraction: XRD was performed using a Phillips PW3710 XR diffractometer with a copper tube.

^{57}Fe Mössbauer spectroscopy: Samples were sent for Mössbauer spectroscopy to Dr Giovanni Hearne at the School of Physics, University of the Witwatersrand. All of the discussion, figures and tables in this chapter pertaining to Mössbauer analysis are drawn from his report. Mössbauer measurements were performed in conventional transmission geometry. A linear motor driven by a triangular reference wave-form was used to scan the resonance profile. A Kr- CO_2 proportional counter was used to detect the transmitted 14.4 keV resonance radiation from a 10 mCi $^{57}\text{Co}(\text{Rh})$ radioactive source. Each dried powdered sample was mounted in a specially designed powder-clamp holder. Sample quantities were thoroughly mixed with an inorganic buffer material and the mixture of sample and buffer distributed in the sample holder to form a disk of uniform thickness of 20 to 25 mg/cm^2 for transmission Mössbauer measurements. Data acquisition of each spectrum and its mirror-image was for a duration to ensure at least ~100 000 counts in each of 1 024 channels of a PCA-based multi-channel analyser. Prior to analysis each spectrum was folded with its mirror image and adjacent channels subsequently added. This serves to remove geometrical base-line distortions and reduces the $(\sqrt{N})$ statistical scatter in the final data set used for analysis. The fitting program NORMOS (distributed by WISSEL-Germany) has

been used for theoretical fits of the data with Lorentzian line-shapes to de-convolute various sub-components (phases) in the spectrum. A minimum number of subspectra (doublets, sextets and/or distribution of sextets) are used to obtain the best fit to the total spectrum.

Determination of $\text{Fe}^{2+}/\text{Fe}_T$ ratio in sludge: Two 1 ml samples from high and middle zones of the mixed reactor were taken for $\text{Fe}^{2+}/\text{Fe}_T$ ratio determination as described above. That is, a 1 ml sample of mixed liquor from the reactor was diluted in 100 ml of 0.01M (pH 2) HCl in order to dissolve all ferrous intermediate species prior to filtration (0.45 micron). The solid material left on the filter is therefore the end-products of the oxidation reaction which can then be dissolved in concentrated (10M) HCl to allow ferrous (Fe^{2+}) and Fe total (Fe_T) to be measured.

Ferrous iron: Fe^{2+} was measured by the phenanthroline method. Total iron was measured using a bench-top Spectroquant (Merck) system. SVI was determined according to the method given in APHA (1998).

Leach tests: Leach tests involved mixing a sludge sample and then allowing it to settle in 500 ml of a 0.01 M aqueous HCl solution (ie. pH 2). Thereafter, samples of the supernatant were taken at intervals and measured for total iron. At the end of the test, the entire mixture was filtered and the solids were dissolved in 32% HCl in order to determine the remaining sample mass (as Fe). The initial sample mass was calculated by adding total dissolved mass to remaining mass and results were then expressed as percentage mass loss.

Results and discussion

Formation of magnetite at steady-state in the absence of calcium: effect of the ferrous intermediate concentration

The reactor system used for these experiments is shown in Figure 6.1. Figure 6.3 shows the ferrous intermediate (FI) concentration maintained in the oxidising reactors for three different experiments (Exp 6.1, Exp 6.2, and Exp 6.3 corresponding to 50–100, 150–250 and ~500 mg ferrous intermediate per liter, respectively).

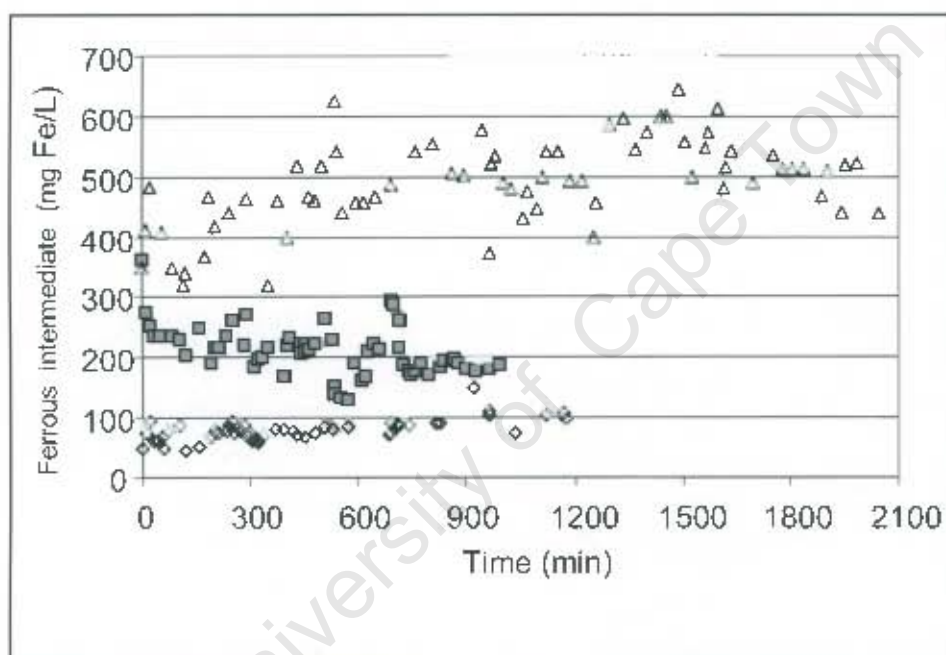


Figure 6.3 Ferrous intermediate concentrations maintained in the oxidation reactors for the three experiments conducted in the absence of calcium.

, Exp 6.1 (FI = 50–100 mg-Fe/L), % Exp 6.2 (FI = 150–250 mg-Fe/L), Δ Exp 6.3 (FI = ~500 mg-Fe/L)

End-product analysis: When the process was operated with a ferrous intermediate concentration of 50–100 mg-Fe/L the colour of the precipitate produced was green-brown. Since the colour of magnetite is charcoal it was apparent that under these conditions pure magnetite was not being produced.

Figure 6.4a shows the Mössbauer spectrum (MS) for the precipitate formed in Exp 6.1 at a ferrous intermediate concentration in the range 50–100 mg-Fe/L. The spectrum is fitted with three components, two of which are crystalline component sextets representing the A-site and B-site in the magnetite fraction of the sample (compare dashed lines in Figure 6.4a with Figure 6.4c). The third component is modelled as an additional distribution of magnetic fields with Mössbauer parameters typical of poorly crystalline goethite (α -FeOOH) (thin solid line) (Pollard et al. 1992). Therefore the Mössbauer analysis suggests the presence of two Fe-bearing phases, viz. magnetite and goethite. The integrated area under each subspectrum in the Mössbauer analysis makes it possible to ascribe 44% of the iron in the sample to goethite and 56% to magnetite. Chemical analysis of this sample gave a ferrous fraction of $13\% \pm 1\%$ (as compared to $\sim 33\%$ in pure stoichiometric magnetite). The relative areas of the A-site and B-site sextets permit a quantification of the degree of oxidation of the magnetite fraction from the Mössbauer spectrum (Vandenberghe et al. 1990). The Mössbauer spectral analysis also indicates that 14% of the total iron in the sample was in the ferrous form.

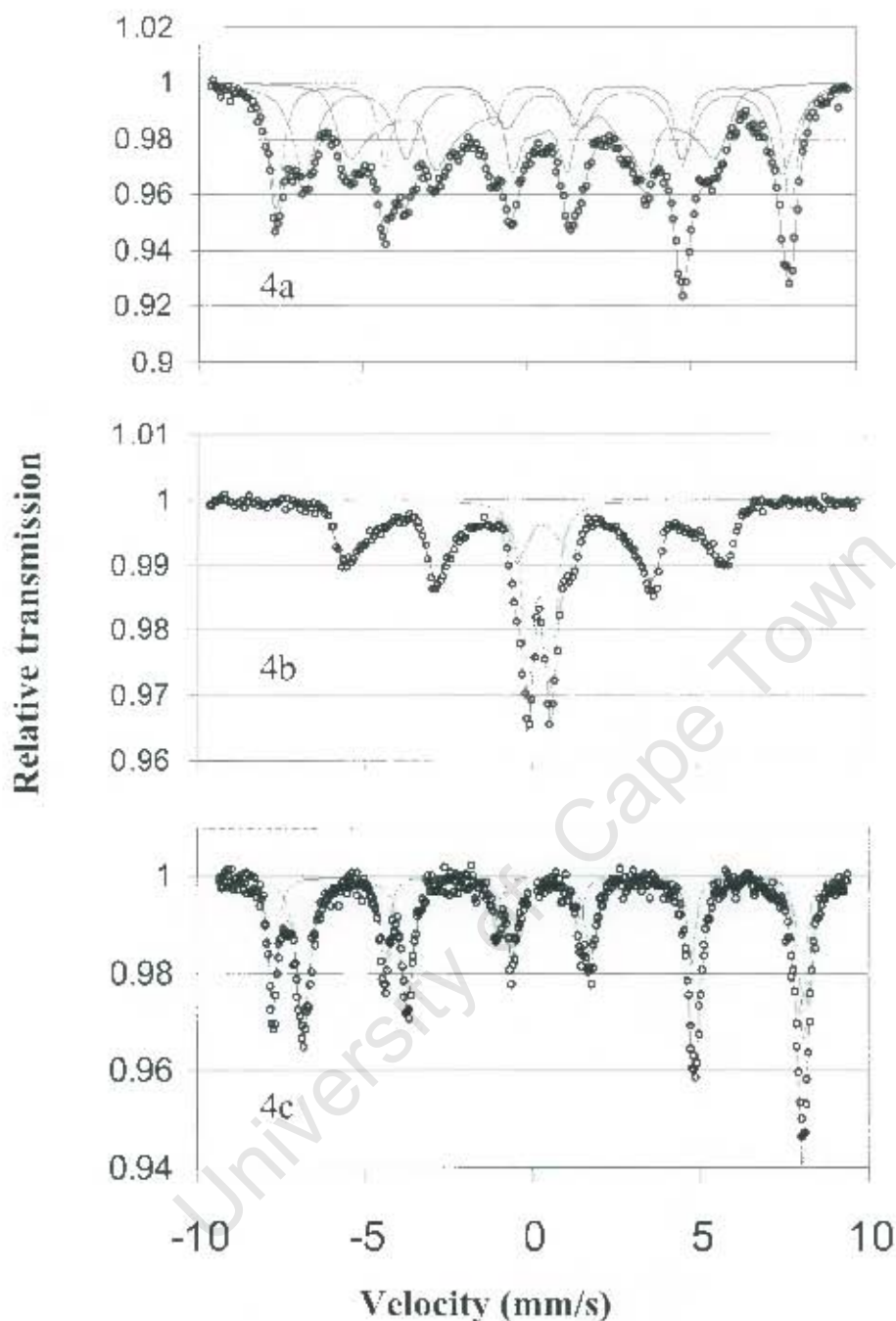


Figure 6.4 a. Mössbauer spectrum for the precipitate from Exp 6.1 (ferrous intermediate concentration = 50–100 mg-Fe/L) **b.** Mössbauer spectrum for the precipitate from Exp 6.1 after treatment with 32% HCl. **c.** Mössbauer spectrum for a sample of near-stoichiometric magnetite which serves as a standard of reference. In all cases open circles represent the raw data, with overall theoretical fit as a solid line through the data points (from reports compiled by Dr G Hearne).

For further assessment, a sample of the same precipitate was dissolved in 32% HCl which dissolves all the magnetite within 15 minutes, leaving a residual yellow-brown suspended solid which was analysed by Mössbauer spectroscopy and XRD. Figure 6.4b shows the MS spectrum for this sample. The overall fit to the spectrum is the solid line through the data points represented as open circles. A dashed line representing a distribution of magnetic fields supposed to be indicative of poorly crystalline bulk goethite phase is discerned, similar to that seen in Figure 6.4a. In addition, a central doublet attributed to (superparamagnetic) nanocrystalline goethite is also present. This component likely arises from the effects of the concentrated HCl on the goethite fraction. The XRD results for this sample are shown in Figure 6.5 and have signatures of crystalline goethite, with no evidence of other iron oxides or oxyhydroxides.

Taken together, these results confirm that the precipitate was not purely magnetite, but that large amounts of another Fe-bearing phase, goethite, were present.

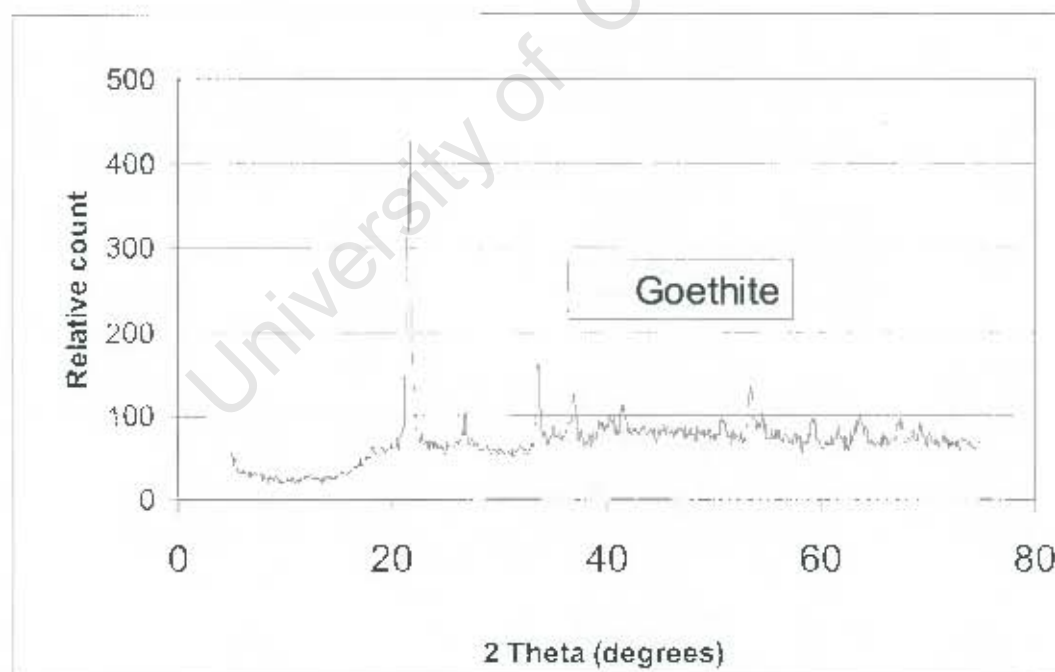


Figure 6.5 XRD pattern for the precipitate from Exp 6.1 (ferrous intermediate concentration = 50–100 mg-Fe/L) after treatment with 32% HCl.

At a ferrous intermediate concentration of 150—250 mg-Fe/L (Exp 6.2 in Figure 6.3) the colour of the precipitate was green-brown as in the previous experiment, again indicating the presence of products of oxidation other than magnetite. Detailed characterisation of this precipitate was not pursued.

At a ferrous intermediate concentration of ~500 mg-Fe/L (Exp 6.3 in Figure 6.3) the precipitate, attained after dynamic steady-state has been reached, was charcoal in colour. Figure 6.6a shows the XRD pattern for this precipitate compared to the reference pattern for stoichiometric magnetite (Figure 6.6b). The pattern is characteristic of magnetite and there is no evidence of non-magnetite phases. The percentage ferrous content for this sample was $28\% \pm 1\%$ by chemical analysis.

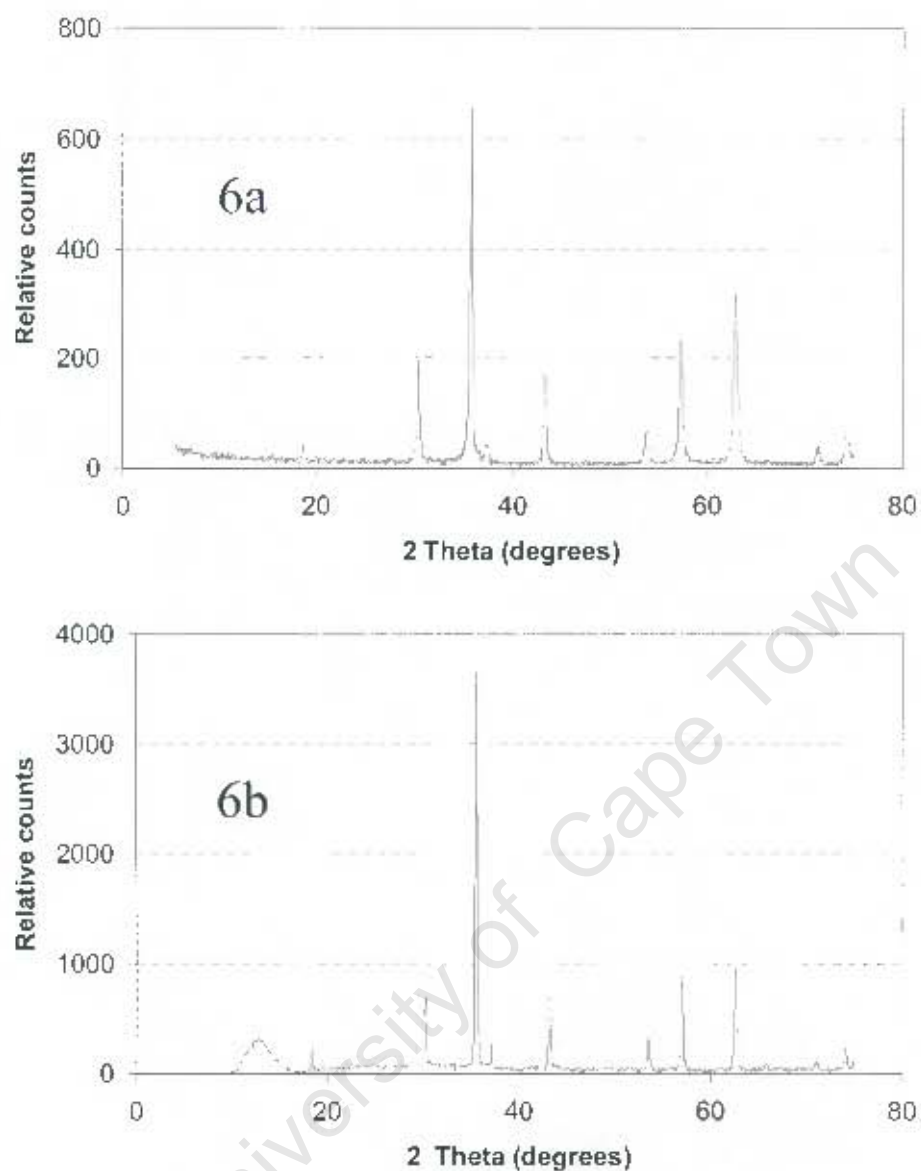


Figure 6.6 a. XRD pattern for the precipitate from Exp 6.3 where the ferrous intermediate concentration was maintained at ~500 mg-Fe/L. **b.** XRD pattern for a reference sample of magnetite (the same sample used for the MS analysis shown in Figure 4c, supplied by Dr G Hearne).

Based on the sludge analysis it was therefore apparent that there is a critical threshold of the ferrous intermediate concentration in order to form substantially pure magnetite. Results of sludge analysis indicated a steady-state ferrous intermediate concentration of approximately 500 mg-Fe/L above which solely magnetite was

produced. Below this threshold, goethite was found to be the main end-product of oxidation. This result is in accord with the literature on magnetite formation in the absence of seed where it is qualitatively stated that a high ferrous concentration favours magnetite as the end-product of the oxidation of ferrous solutions (Cornell and Schwertmann 1996).

Formation of magnetite at steady-state in the presence of calcium: effect of the ferrous intermediate concentration

Figure 6.2a shows the reactor system used for experiments in which calcium was present. This system differs from that when calcium was absent for the following reasons: The problem of calcium inhibition in ambient temperature ferrite formation has already been discussed in Chapter 4. Although the mechanism of inhibition is unknown it was postulated that increasing the *ferrous intermediate : dissolved calcium ratio* in the oxidation reactor would reduce the inhibitory effect of calcium. It was also postulated that allowing the freshly precipitated sludge to age (ie. stand without mixing or aeration) would promote magnetite formation by allowing time for dehydration-crystallisation in the absence of further oxidation to occur (Perales Perez et al. 1999, McKinnon et al. 2000).

In the absence of calcium a concentration of greater than 500 mg-Fe/L was found necessary for magnetite formation. Exp 6.4, in which Ca^{2+} was present in 1 : 1 molar ratio to Fe^{2+} , was therefore performed just above this threshold concentration (ie. in the range 500–800 mg-Fe/L), without allowing any aging period. The percentage ferrous in this experiment was however found to rapidly decline to a value of less than 15% and simultaneously the sludge was observed to turn brown indicating a prevalence of ferric oxide/oxo-hydroxide end-products (data not shown). In an attempt to improve the outcome, in Exp 6.5 the reactor was turned off for 18 out of every 24 hours allowing the freshly formed precipitate to age. Aging improved the ferrous fraction in the sludge to $18\% \pm 1\%$ by chemical analysis at steady-state. In addition no brown discolouration of the sludge occurred. Data for this experiment is shown in Figure 6.7 (Exp 6.5) and Mössbauer and XRD results for this experiment are shown in Figure 6.8. Although features indicative of magnetite are dominant in both

measurements, both modalities also show clear evidence of an additional non-magnetite component in the sample. Mössbauer analysis reveals that this is an additional ferric component (solid line sub-spectrum in Figure 6.8) accounting for ~20% of the total iron in the sample. The derived Mössbauer parameters for this component are not typical of goethite, and this component therefore represents one or more unidentified ferric species. Mössbauer analysis indicates that the percentage ferrous content of the magnetite phase is 25%. This amounts to a net ferrous fraction of 20% of the total iron in the sample, which accords well with the $18\% \pm 1\%$ obtained by chemical analysis.

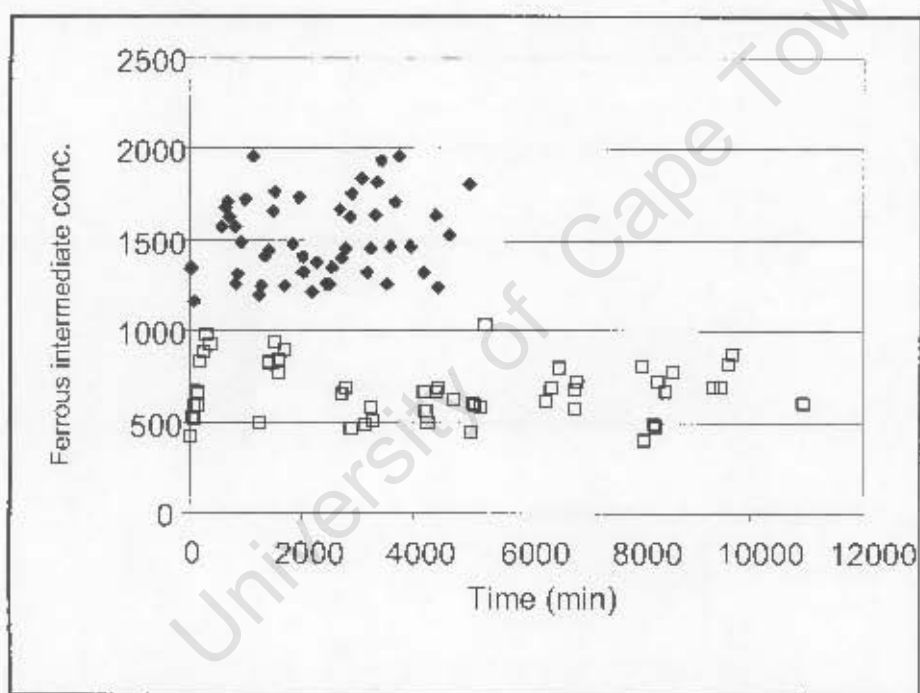


Figure 6.7 Ferrous intermediate concentrations maintained in the oxidation reactors for two experiments conducted in the presence of calcium. $\square$ Exp 6.5 (FI = 500–800 mg-Fe/L, 18 hours aging), $\blacklozenge$ Exp 6.7 (FI = 1200–1700 mg-Fe/L).

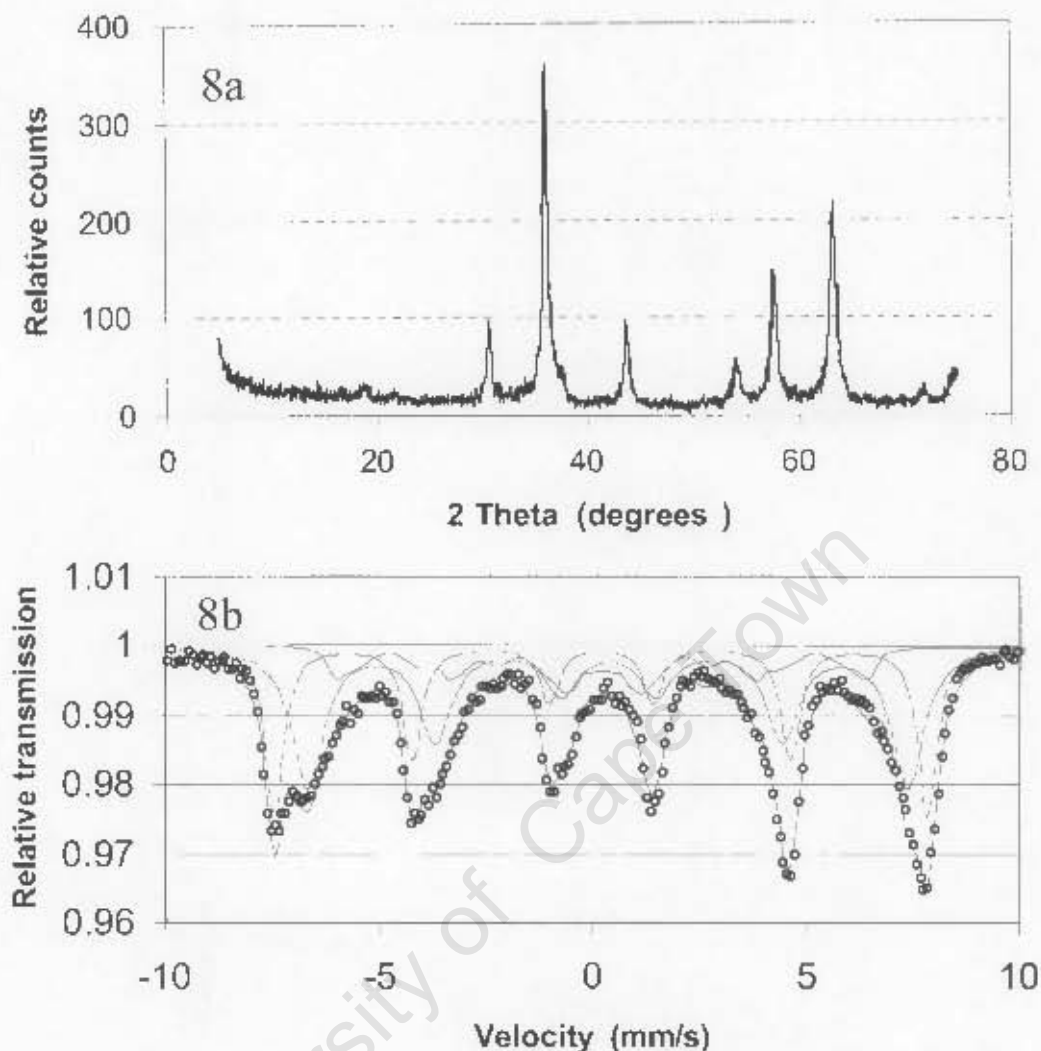


Figure 6. 8 XRD (8a) and MS (8b) for sludge from Exp 6.5 conducted in the presence of calcium (ferrous intermediate concentration of 500–800 mg-Fe/L, 18 hours aging) (from reports compiled by Dr G Hearne).

Raising the ferrous intermediate concentration to between 1 200 and 2000 mg-Fe/L without aging again resulted in a rapid decrease in the ferrous fraction of the sludge (which again began to turn brown) to a value below 22% at which point the experiment was terminated (Exp 6.6, data not shown). In contrast, the sludge of Exp 6.7 performed under the identical conditions to Exp 6.6 but with aging for ~18 out of every 24 hours was found to consist of predominantly (> 95%) magnetite with a ferrous fraction of $30\% \pm 1\%$ by chemical analysis, and $27\% \pm 1\%$ by Mössbauer

analysis (Figure 6.9b). No brown discolouration indicative of non-magnetite ferric phases was observed. This finding was further substantiated by XRD analysis (Figure 6.9a). Data for this experiment is shown in Figure 6.7 (Exp 6.7).

Experiment Exp 6.7 was repeated at a slightly higher ferrous intermediate concentration (~ 2000 mg/L). Data for this experiment (Exp 6.8) is shown in Figure 6.10 and includes measurements of the percentage ferrous in the precipitant which remained at $\sim 30\%$ throughout the course of the experiment, confirming the results obtained in Exp 6.7.

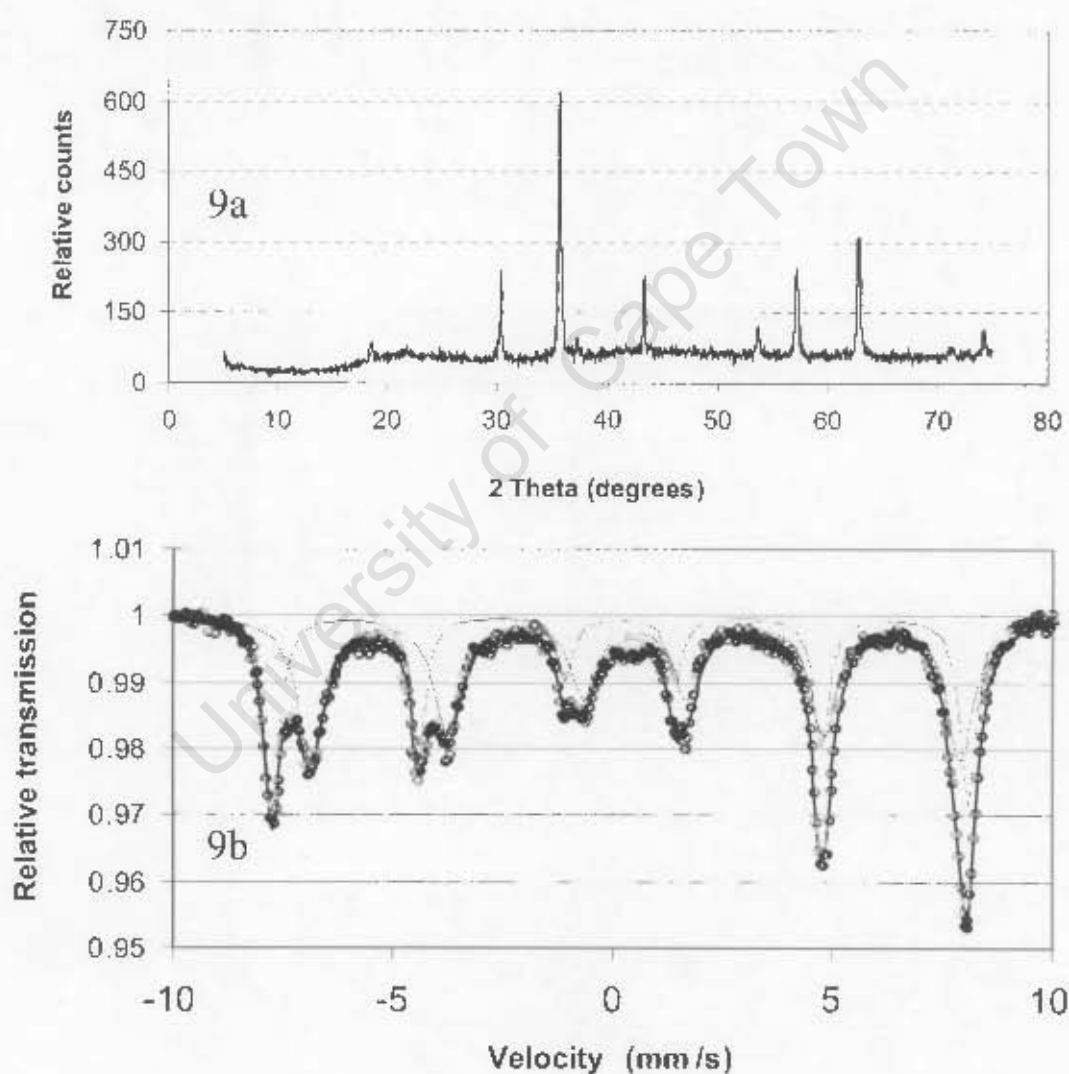


Figure 6.9 XRD (9a) and MS (9b) for sludge from Exp 6.7 conducted in the presence of calcium (ferrous intermediate concentration of 1200–1700 mg-Fe/L) and including an aging period of 18 hours (from reports compiled by Dr G Hearne).

Fe, Ca with aging (4.26 sludge ages)

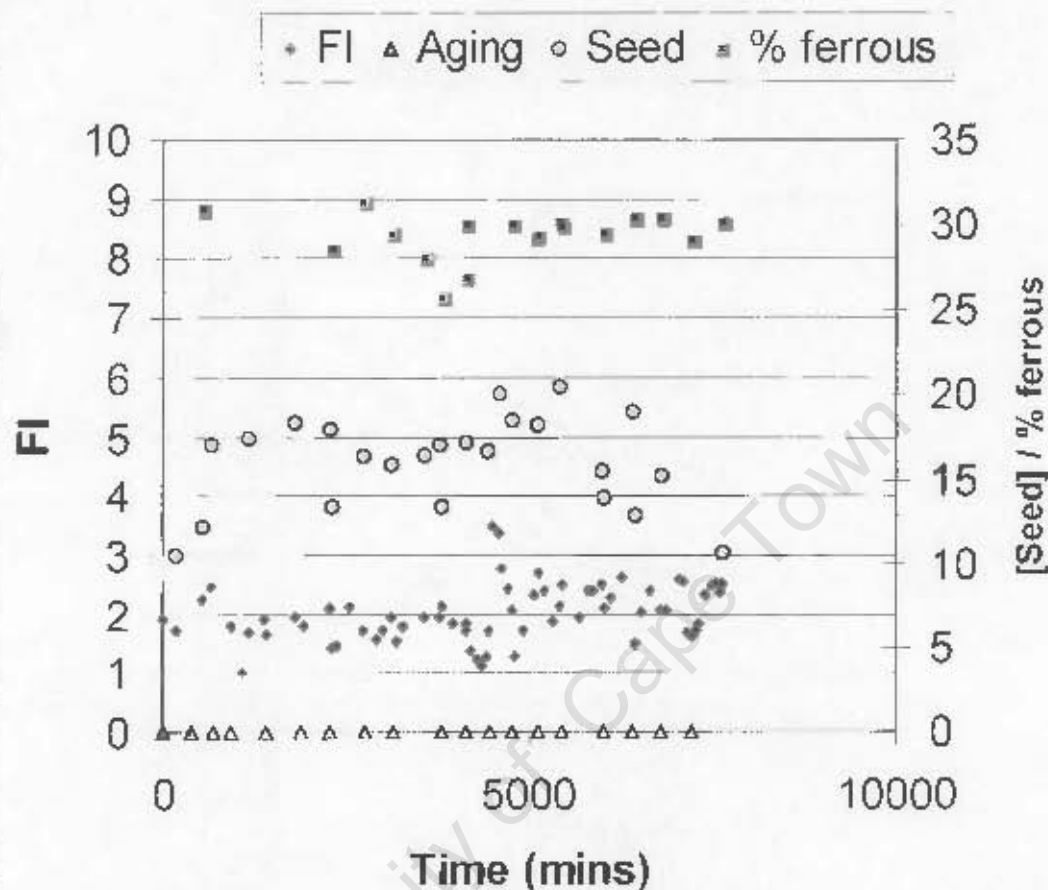


Figure 6.10 Data for Exp 6.8 performed in the presence of calcium with a ferrous intermediate (FI) concentration of 2 ± 0.48 g/L and an aging period of 17.31 ± 1.67 hours. Time along the x-axis represents the accumulated oxidation period in minutes with aging periods cut out. Each aging period is marked along the x-axis with a small triangle. The units for both y-axes are in g/L.

The results presented above appear to link the inhibitory effect of calcium on magnetite formation to the ferrous intermediate : dissolved Ca^{2+} ratio. It was postulated before that an increase in this ratio in conjunction with an aging period might serve to overcome this inhibition. Exp 6.5 (FI = 500—800 mg-Fe/I. and 18 hours aging shows that aging alone does not suffice to overcome calcium inhibition. On the other hand, at higher FI concentrations (accompanied by a constant dissolved

calcium concentration) and with an 18 hour period of aging, substantially pure magnetite can be produced with less than 5% of other iron phases. Further experiments were performed in which the aging period was successively diminished and it was found that a minimum of 3–6 hours aging is required to produce magnetite with a ferrous fraction of greater than 28–30 % (see Table 6.1 below). McKinnon et al. (1999) found a power law relationship between a threshold aging time and calcium concentration. The following relationship was derived under experimental conditions where separate ferric and ferrous solutions were mixed and the pH raised with lime in the absence of seed:

$$\text{Threshold aging time} = 1.17 \times 10^1 [\text{Ca}]^{1.61} \quad (1)$$

The role of the contact stabilisation reactor

As suggested above, enhancing the FI : dissolved Ca^{2+} ratio appears to overcome the inhibitory affect of calcium on magnetite formation. This was achieved by placing a contact stabilisation (CS) reactor before the settler (Figure 6.2a). The pH of the contact stabilisation reactor was maintained at 10.5, as in the oxidation reactor. The dissolved iron present in the raw AMD introduced into the contact stabilisation reactor thus fully precipitates (as FI) and is subsequently adsorbed onto the magnetite seed. The near-instantaneous time required for these steps allows for a relatively small contact stabilisation reactor. The effluent from the contact stabilisation reactor containing magnetite seed coated with ferrous intermediate then reaches the settler. The seed particles greatly enhance the settling of the ferrous intermediate phase which would otherwise, in the absence of seed, form a bulky voluminous floc with poor settling properties. This results in both a concentrated sludge and a short retention time in the settler. The concentration of the ferrous intermediate species in the underflow sludge of the settler is enhanced ~3 times relative to the concentration of dissolved iron in the raw AMD (data not shown). Calcium in the main oxidising reactor is largely in the liquid phase as few or no gypsum crystals were observed in the underflow from the settler. Gypsum growth was however observed on the walls of the settler. During the settling period the concentration of dissolved calcium does not increase. Consequently, the ferrous intermediate : dissolved Ca^{2+} ratio would be elevated by at least the solid-liquid separation factor which was found to be close to

solids : total volume $\cong 1 : 3$ (see below). This factor was also reflected in the ratio of seed concentration in the contact stabilisation reactor : oxidising reactor which was consistently found to be $1 : 2.5-3$ (data not shown). Since Fe^{2+} and Ca^{2+} in the influent were introduced at equimolar concentrations, it would appear that increasing the ratio between the FI and the calcium to ~ 3 has the effect of largely overcoming the calcium inhibition effects.

Another notable effect of the contact stabilisation reactor – settler sequence (see Figure 6.2) is the separation of the metals from the bulk AMD volume prior to oxidation. This means that the bulk AMD volume does not enter the oxidation reactor, allowing for much lower infrastructure costs. The SVI of the contents of the contact stabilisation reactor was found to be 30 ml/g and the separation ratio after 30 minutes of settling time was 35 : 100 (solids : total volume). Extending the settling time beyond 30 minutes does not have a marked effect on the sludge : water ratio. Thus a settling chamber with a retention time (RT) of 30 minutes appears optimal. Since the retention in the contact stabilisation reactor need only be a few minutes, the combined contact stabilisation reactor – settler sequence does not require a large-scale infrastructure.

Effluent and sludge characteristics

Under the experimental conditions shown in Figure 6.7 (Exp 6.7: ferrous intermediate 1200–1700 mg-Fe/L), the total iron concentration in the effluent leaving the settling tank was always less than 1.0 mg/L and the final sludge, composed of essentially pure magnetite, settled exceptionally well (SVI = 3.2 ml/g-Fe). After standing for 14 days, the wasted sludge attained a paste-like consistency with a concentration of 257 g-Fe/L. An indication of the stability of the sludge at pH 2 is demonstrated by the data shown in Figure 6.11. After an initially rapid increase the mass loss began to plateau at 15.6 % after 77 days. Such a limited release of ferrous iron is a documented property of magnetite in acidic aqueous solution (Jolivet and Tronc 1988).

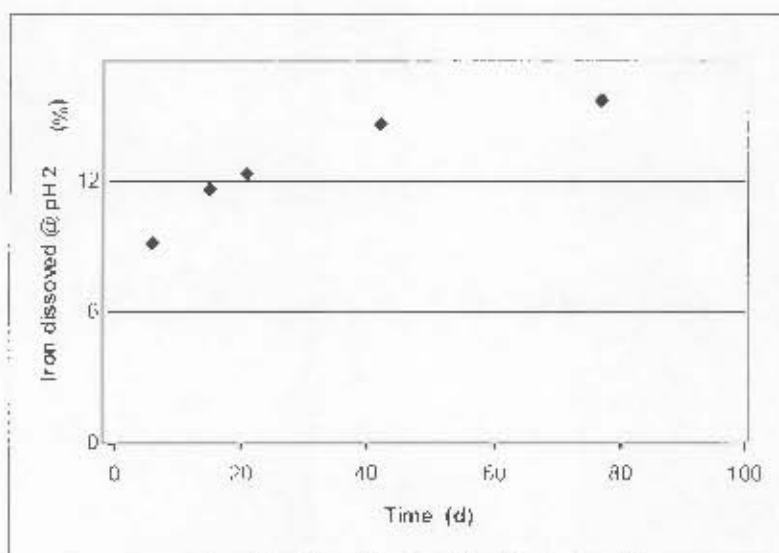


Figure 6.11 Results of a pH 2 leach test conducted with sludge derived from the experiment with calcium (ferrous intermediate concentration = 1200–1700 mg-Fe/L). Units along the y-axis = % dissolved Fe^{2+} / Total Fe.

Influence of retention time and aging on the percentage ferrous of the end-product

As discussed in Chapter 4, Perales Perez and Umetsu (2000) found a marked effect of the duration of oxidation on the nature of the end-product under batch conditions in the absence of seed and calcium. In their experiments duration of oxidation was an independent variable. In Chapter 5, the effect of duration of oxidation on the end-product under batch conditions in the presence of seed was reported (Table 5.1). In this case changes in duration of oxidation were a direct effect of changes in airflow rate.

In Exp 6.9, the duration of oxidation under continuous flow steady-state conditions was investigated. In this case, duration of oxidation, expressed as hydraulic retention time (RT) in the oxidising reactor, was a function of reactor volume because the AMD flow rate was kept constant while the reactor volume was varied¹ (Table 6.1). Varying reactor volume did not however only influence retention time but also effected airflow rate and hence the rate of oxidation. This was because in order to maintain a constant

¹ Hydraulic retention time = reactor volume/AMD flow rate.

supra-threshold ferrous intermediate concentration in the oxidation reactor as retention time was varied, the oxidation rate had to be increased or decreased by adjusting the airflow rate.

Volume oxidation reactor (L.)	RT (Hours)	Aging (Hours)	Fe load (mg/min)	% Ferrous
0.85	0.94	0	50	early failure
1.2	1.33	6	50	19.7
2	2.22	6	50	22.6
5.2	6.1	6	50	28.0
5.2	6.1	3	50	28.1
5.2	6.1	< 3	50	< 25%

Table 6.1 Data showing the effects of duration of oxidation (expressed as retention time, RT). The effect of duration of aging on the percentage ferrous in the final precipitate is also shown. Ferrous intermediate = 2–2.5 g/L.

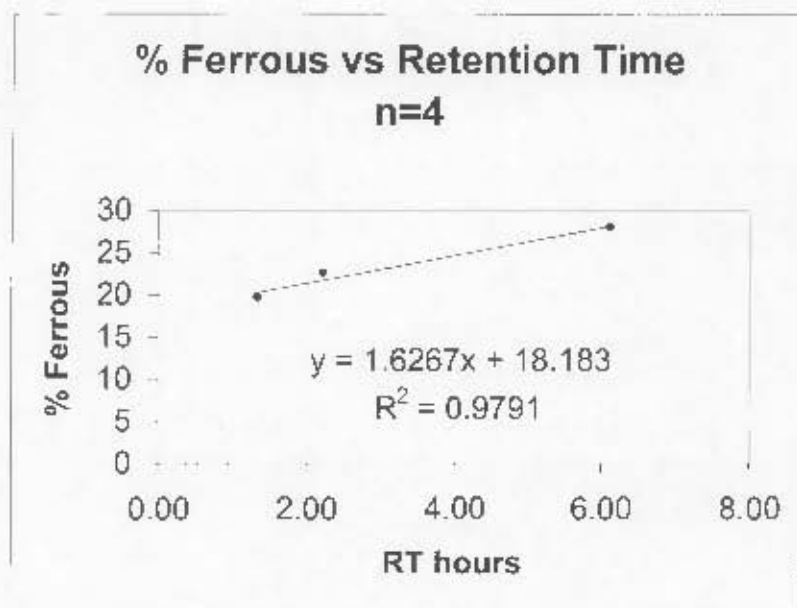


Figure 6.12 Relationship between the duration of oxidation (RT) and the percentage ferrous in the final precipitate for the data in rows 2–5 in Table 6.1.

The results for Exp 6.9 presented in Table 6.1 and Figure 6.12 show that the percentage ferrous in the end-product varies in a linear fashion with retention time. But retention time directly affects oxidation rate and so the percentage ferrous in the end-product is sensitive to the rate of oxidation in a linear fashion. It is also evident from Table 6.1 that decreasing the aging time from 6 hours to 3 hours did not affect the percentage ferrous but an aging time of less than three hours did.

A retention time of 6.1 hours was required to produce magnetite with a percentage ferrous of 28%. This is significantly longer than the retention times reported by Zinck and Griffiths (2000) for the HDS process (Table 6.2). This is not surprising since magnetite formation requires relatively low oxidation rates whereas the HDS process does not. However, as described in Chapter 5, low percentage ferrous values do not mean that the magnetite structure has been lost. Low percentage ferrous end-products produced at shorter retention times (eg. rows 2 and 3 in Table 6.1) are therefore compatible with complete ferrous removal from AMD (Table 5.1, Chapter 5). It has not yet been determined how low percentage ferrous end-products may effect the

removal of non-ferrous metals, but it is possible that retention times of the order of those seen in the HDS process may be achieved for the ambient temperature ferrite process (ATFP) as well.

ATFP	HDS	HDS	HDS	HDS
6.1	2.7	3.1	3.7	4.1

Table 6.2 Comparison of retention times in hours between the ambient temperature ferrite process (ATFP) and four instances of the HDS process (HDS data from Zinck and Griffith 2000).

Oxidation rate

From the data in Table 6.1 the oxidation rate can be calculated: the simulated AMD is introduced into the system at a rate of 11.5 mg-Fe²⁺/L/min (see Experimental procedure at the start of Chapter 6). At steady-state the ferrous disappearance rate in the oxidation reactor is therefore also 11.5 mg-Fe²⁺/L/min. Taking the data in row 5 of Table 6.1 as an example, the percentage ferrous in the end-product was 28.1%. Because ferrous disappearance occurs as a result of both oxidation to Fe³⁺ (71.9% in row 5) and by incorporation of Fe²⁺ into magnetite (28.1%) the actual oxidation rate, in this case, is 0.72 of the ferrous disappearance rate, ie. 8.3 mg-Fe/L/min. This value is less than the values obtained in the batch tests in the absence of calcium (12.5–20 mg-Fe/L/min, Chapter 5). Although, under the steady-state conditions described here, the effect of oxidation rate was not systematically investigated, attempts to increase the oxidation rate under steady-state conditions when calcium was absent presented no problem up to ferrous feed rates of 15–20 mg-Fe/L/min (data not shown). However if calcium was present any increase in the oxidation rate above 8.5–10 mg-Fe/L/min resulted in a decrease in the percentage ferrous in the end-products and in the appearance of brown ferric end-products visible to the eye (data not shown). The presence of calcium therefore seems to limit the maximum ferrous oxidation rate at which magnetite is formed, relative to the case where calcium is absent by a factor of ~0.5.

Summary and conclusions

The conditions under which magnetite can be produced from simulated AMD in a continuously operated ambient temperature ferrite process, both in the absence and presence of calcium, have been described. The presence of calcium simulates the use of lime as a pH elevating agent. The dynamic steady-state conditions required can be easily attained using relatively unsophisticated equipment and methods. Experiments without calcium reveal a threshold ferrous intermediate concentration of approximately 500 mg-Fe/L above which solely magnetite is formed, without any need for aging. Below this concentration, goethite (α -FeOOH) was formed in significant amounts. Experiments in the presence of calcium revealed the formation of substantially pure near-stoichiometric magnetite requires both an aging period of at least 3–6 hours as well as relatively higher (1 200 to 2000 mg-Fe/L) ferrous intermediate concentrations. Such concentrations can be attained and maintained by the introduction of a contact stabilisation reactor - settler sequence upstream of the main oxidising reactor. The elevation of the ferrous intermediate concentration in the oxidising reactor together with the incorporation of a contact stabilisation reactor - settler sequence increases the ferrous intermediate : dissolved calcium ratio in the oxidation reactor by ~3 times. It is proposed that the increased ferrous intermediate : dissolved calcium ratio, in conjunction with a suitable aging period, is the mechanism whereby the inhibitory effect of calcium on magnetite formation is avoided. In all experiments, the iron concentration in the effluent leaving the first settling tank was lower than 1 mg-Fe/L and the final sludge, when composed of essentially pure magnetite, settled extremely well (SVI = 3.2 ml/g-Fc). The proposed reactor design shown in Figure 6.2a results in early separation of a metals-containing AMD stream from the bulk AMD volume, resulting in significantly smaller reactor infrastructure needs. The maximum oxidation rate compatible with magnetite formation under steady-state condition in the presence of calcium is ~8.5 mg-Fe/L/min as compared with 12.5–20 mg-Fe/L/min when calcium is absent. Results reflecting the high stability of sludge made in the presence of calcium have also been presented. The concept has potential to be flexibly applied to non-AMD waste-streams containing dissolved metals.

Chapter 7 Ferrite formation at steady-state in the presence of calcium and non-ferrous metals

The previous chapter described conditions under which magnetite is formed at ambient temperature in the presence of calcium. This chapter describes ferrite formation experiments done in the presence of calcium and non-ferrous metals. Three experiments with the following combinations of Fe and non-ferrous metals were performed:

Exp 7.1 Co : Fe = 1 : 10

Exp 7.2 Co : Ni : Zn : Fe = 2.5 : 2.5 : 2.5 : 100

Exp 7.3 Co : Ni : Zn : Mn : Fe = 2.5 : 10 : 2.5 : 2.5 : 100

The experimental setup was identical to that shown in Figure 6.2 and an influent molar ratio of Ca : Fe of 1:1 was used in all three experiments. Apart from changes in the makeup of the simulated AMD and in the duration of the aging period, the experiments were conducted exactly as for the steady-state experiment presented in Chapter 6 and shown in Figure 6.10. Methods of analysis were also the same.

Results and discussion

Exp 7.1 Ferrite formation in the presence of cobalt and calcium

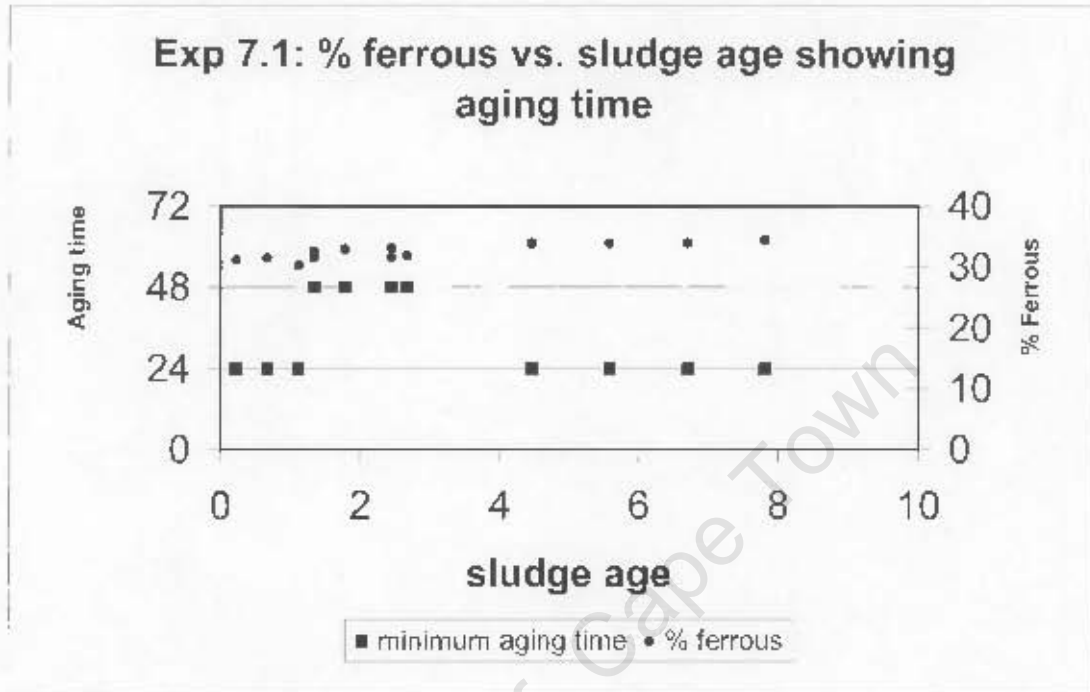


Figure 7.1 Results for Exp 7.1 where calcium and cobalt were present (Co : Fe = 1 : 10, Ca : Fe = 1:1). See text for details.

Results for Exp 7.1 in which both calcium and cobalt were present are shown in Figure 7.1. The seed concentration was maintained at 17.4 ± 2.3 g/L. The percentage ferrous remained stable at an average of 32.61 ± 1.2 % over 8 sludge ages¹. For most of the experiment the aging period was 24 hours. In the period between 1.3 and 2.5 sludge ages the aging period was 48 hours. The increased aging period did not influence the percentage ferrous in the fresh end-product. The XRD pattern for the final product after an aging period of 1 month is shown in Figure 7.2a. This precipitate was identified as the ferrite 'cobalt iron oxide' (CoFe_2O_4) (Phillips Expert Data Analyzer 1996-1999). Figure 7.2b shows the XRD pattern for the same

¹ Sludge age is defined as the time required to produce an amount of new sludge equal to the total sludge mass (in g-Fe) which was present in all compartments of the reactor at the start of the experiment. For these three experiments the starting seed mass was 160 g and one sludge age was 53.3 hours.

precipitate after 3 months of aging. Although some minor changes in the XRD pattern at 3 months aging versus 1 month of aging are apparent, the XRD identification software still identified the sample as cobalt iron oxide. These results confirm the conclusion made from macroscopic observations and chemical analysis that a ferrite with a high percentage ferrous was formed.

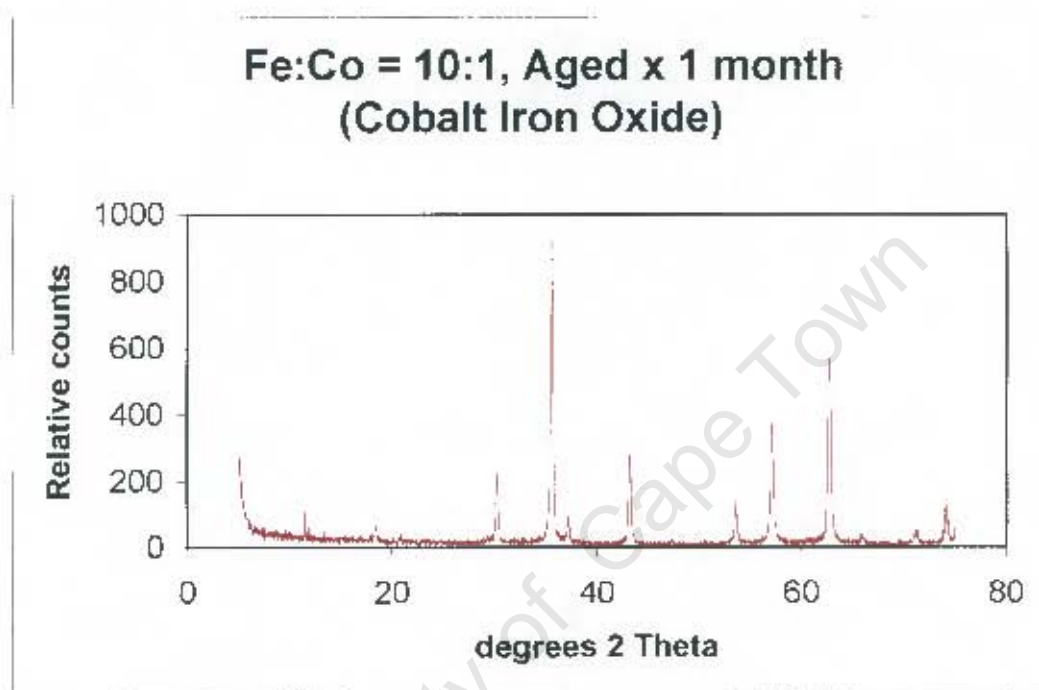


Figure 7.2a XRD tracing for end-product of Exp 7.1 (Co : Fe = 1 : 10, Ca : Fe = 1:1) after 1 month of aging.

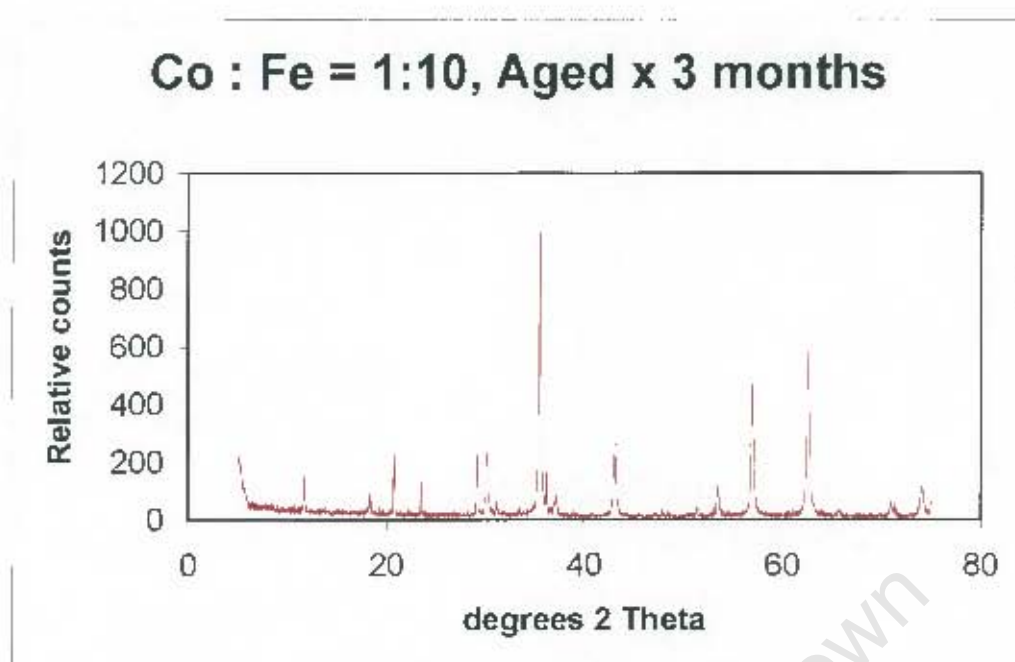


Figure 7.2b XRD tracing for end-product of Exp 7.1 (Co : Fe = 1 : 10, Ca : Fe = 1:1) after 3 months of aging.

Further data for Exp 7.1 is given in Table 7.1. Although the effluent filtrate is essentially free of iron and cobalt, the concentration of these elements present as 'fines' in the effluent is significant. The reason for the occurrence of fines is unclear and requires further investigation. Notably however, the ratio of Co : Fe in the fines reflects the ratio of these elements in the simulated AMD as would be expected. Similarly the molar ratio in the final precipitate closely reflects the initial concentrations.

Sample	Concentration (mg/L)	Molar %
Influent	Fe 3909 Co 421	10.6%
Effluent: Dissolved fines	Fe 6.22 Co 0.64	10.78%
Effluent: Filtrate	Fe <0.06 Co 0.09	9.7%
Final precipitate $\text{Fe}^{2+} : \text{Fe}_T = 32\%$	Fe 177.6 Co 17.23	9.7%

Table 7.1 Data for the influent, effluent and final precipitate for Exp 7.1 in which cobalt and calcium were present. The molar percentage values of the effluent fines and final precipitate reflect the Co : Fe ratio in the influent. In both cases the molar percentage closely approximates the ~1 : 10 value of the influent.

Exp 7.1 is significant in that it unequivocally proves the formation of a mixed-species ferrite by cation substitution for the case of cobalt under one-step ambient temperature conditions in the presence of calcium (Ca : Fe = 1 : 1). The non-ferrous metal (Co) was present at a significant molar concentration of 10 percent with respect to ferrous iron in the simulated AMD. The initial concept upon which this research was founded is thus substantiated.

Exp 7.2 Ferrite formation in the presence of Co, Ni, Zn and calcium

Figure 7.3a shows results for Exp 7.2 where Co, Ni and Zn were present in concentrations as shown in Table 7.2. The Ca : Fe ratio was 1 : 1, aging period = 24 hours.

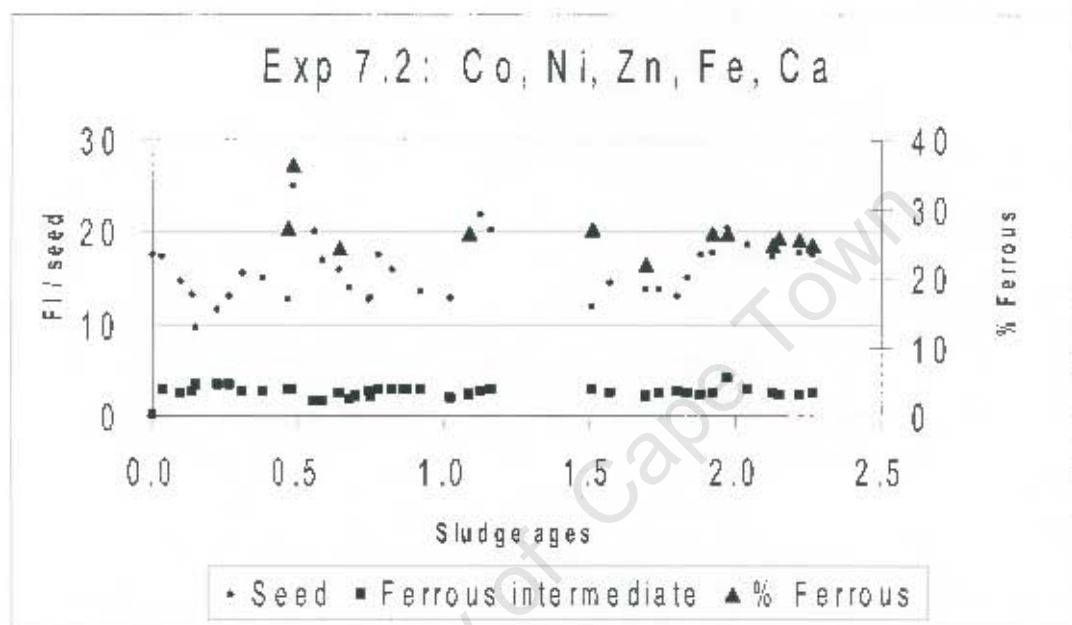


Figure 7.3a Data for Exp 7.2 in which Co, Ni, Zn, Fe and Ca (Ca : Fe = 1 : 1) were present. See text for details.

Simulated AMD	Fe	Co	Ni	Zn
Concentration mg/L	3976	113	104	99
Concentration Mol/L	35.60	0.96	0.89	0.76
Molar % of total iron		2.69	2.49	2.13

Table 7.2 Measured data for simulated AMD for Exp 7.2 ($\text{pH} \leq 3$, Fe : $\text{SO}_4 = 1 : 2$)

Characterisation of the end-product

Referring to Figure 7.3a it can be seen that for Exp 7.2 the percentage ferrous in the fresh precipitate stays relatively constant (at 26.48 % $\pm$ 3.47). It should be borne in mind that when divalent non-ferrous metals are present in the simulated AMD, a decrease in the percentage ferrous of both the fresh precipitate and final end-product is to be expected as a consequence of cation substitution. In these cases the total percentage of non-ferrous metals in the end-product should be borne in mind. Using data from Table 7.5 below, total non-ferrous metals comprised 6.5 % (mol M^{2+} / mol Fe_T) of the total Fe in the end-product. Thus, working from the percentage ferrous of 33.3 % in stoichiometric magnetite, a maximum of 26.8 % ferrous : total iron can be expected to be found in the fresh precipitate of Exp 7.2. It is noteworthy that the result obtained agrees well with this value. It is perhaps for this reason that, as can be seen in Figure 7.3a, an increase in the seed concentration did not result in an increase in the percentage ferrous of the fresh precipitate – it is already at its maximum. After exhaustive oxidation the percentage ferrous decreased to 22.9 % (average of two values in Table 7.4 below) as a consequence of further oxidation.

Structural analysis

A sample of precipitant taken from Exp 7.2 at 2.4 sludge ages was aged for 48 hours post-exhaustive oxidation and subjected to XRD and Mössbauer analysis.

X-ray diffraction: The XRD pattern (Figure 7.3b) illustrates that this precipitate has structural features of ferrite.

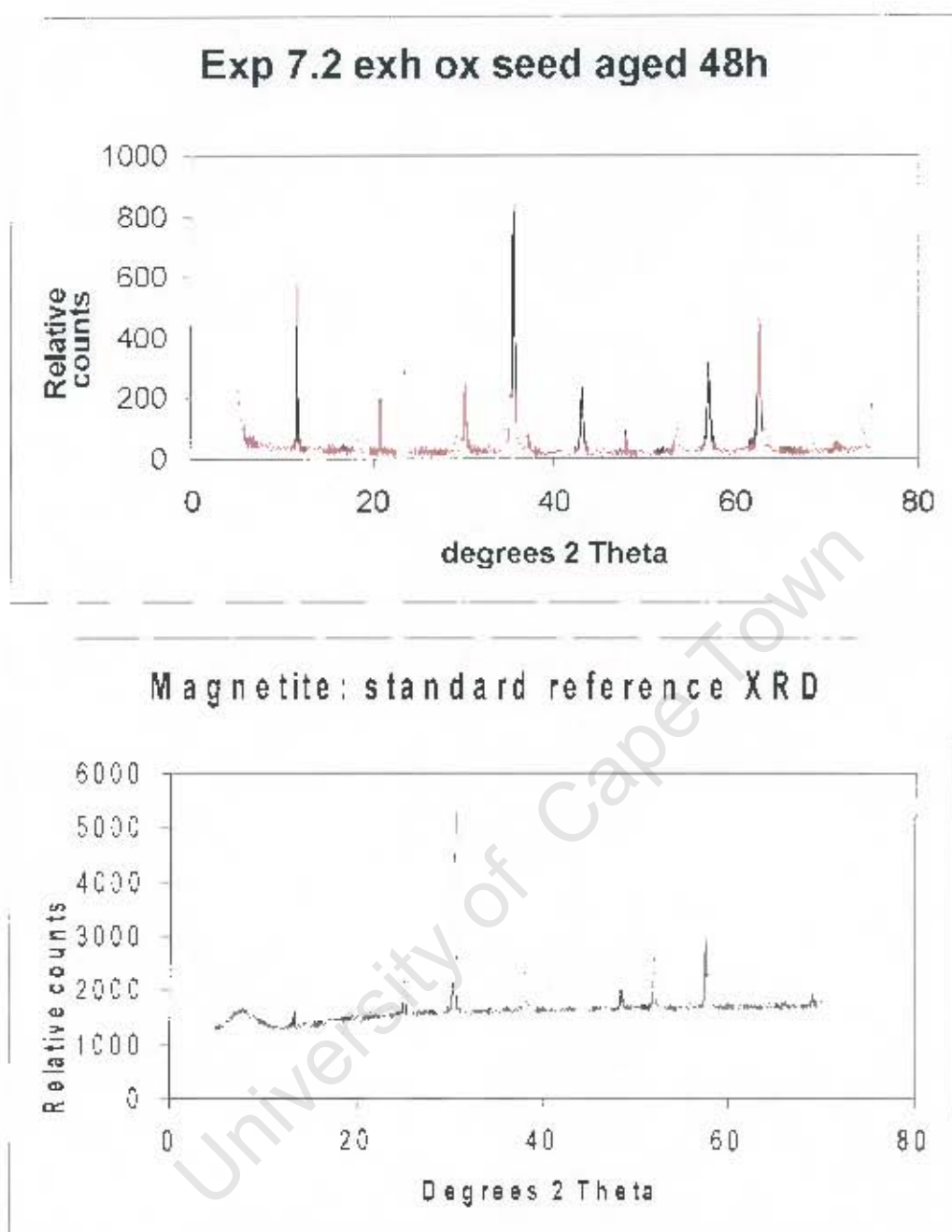


Figure 7.3b Above: XRD tracing for a sample of seed from Exp 7.2 which contained Co, Ni, Zn and calcium after exhaustive oxidation and aging for 48 hours. In addition to the magnetite peaks there are other significant peaks indicating either some deviation from the pure ferrite structure or the presence of other compounds. The nature of these additional peaks was not investigated further. **Below:** Standard reference XRD pattern for magnetite (supplied by Dr G Hearne).

Mössbauer spectroscopy: Mössbauer spectroscopy was performed by Dr Giovanni Hearne in the School of Physics, University of the Witwatersrand. All of the discussion, figures and tables in this chapter pertaining to Mössbauer analysis are drawn from his report. Consistent with the XRD results, the Mössbauer spectrum of the sample of end-product from Exp 7.2 has the characteristic signatures of magnetite (Figure 7.4a), except for a marked difference in the relative intensities of resonance lines close to -7.5 mm/s compared with stoichiometric magnetite. This is indicative of some degree of oxidation, and the results of the spectral analysis indicate the ferrous (Fe^{2+}) content to be $23 \pm 1\%$, in comparison with 33% expected in a stoichiometric compound.

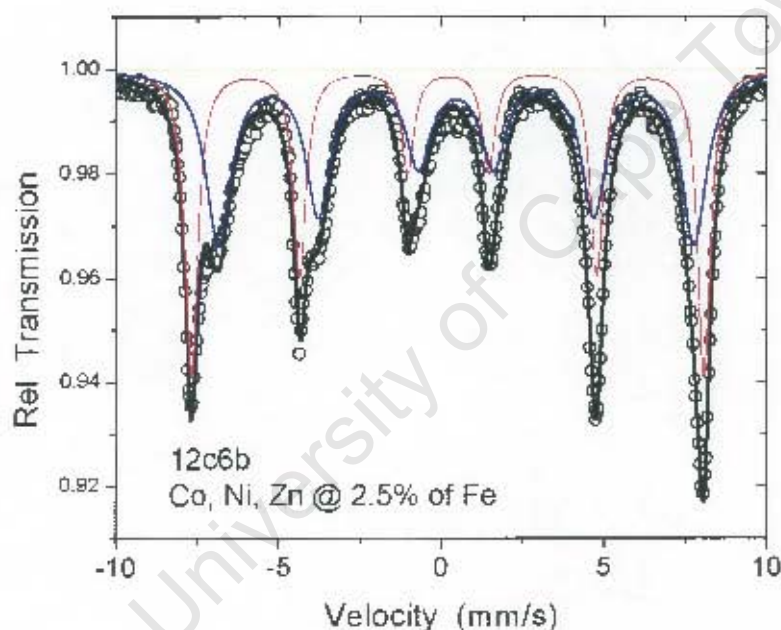


Figure 7.4a Mössbauer spectrum of the same sample from Exp 7.2 used for XRD analysis as shown in Figure 7.3a. The spectrum is fitted with two sextets. The overall theoretical fit is the solid line through the data points represented as open circles (from reports compiled by Dr G Hearne).

SAMPLE	Spectral Component	Γ , Linewidth (mm/s)	δ/Fe (mm/s)	QS (mm/s)	B_{hf} (T)	*Abundance %
Exp 7.2	Tet A-site and oxidised Oct B-site	0.47	0.29	-0.01	49.0	33.3 Fe ³⁺ 10(1) Fe ³⁺
	§ Octahedral B-site	0.94	0.63	-0.01	45.3	33.3 (5) Fe ³⁺ 23.3(5) Fe ²⁺

Table 7.3a Hyperfine interaction parameters of the spectral components in Figure 7.4a. Statistical error indicated in parenthesis. * From the integrated area under the sub-spectrum. § Relative line-intensities of the sextet for the B-site permitted to vary.

Excessive broadening at the octahedral B-site is evident from the ratio of the linewidths of the B-site and A-site, $\Gamma_B / \Gamma_A = 2.0$. This may be compared to the two reference samples shown below: **(1)** The Mössbauer spectrum for sample S1, which is a reference for magnetite made in the presence of calcium with no non-ferrous metals present, is shown in Figure 7.4b. The ratio of the linewidths of the B-site and A-site, $\Gamma_B / \Gamma_A = 1.7$ for this sample (Table 7.3b). **(2)** The Mössbauer spectrum for a sample of stoichiometric magnetite is shown in Figure 7.4c. The ratio of the linewidths of the B-site and A-site, $\Gamma_B / \Gamma_A = 1.5$ for this sample (Table 7.3c).

When compared against stoichiometric magnetite, any broadening in sample S1 is attributable to oxidation on the B-site and also perhaps from the influence of calcium in the mixture. The further line-broadening effects in the sample of end-product from Exp 7.2 which seems to occur mainly on the octahedral B-sites may be ascribed to heavy-metal uptake into the magnetite lattice by substitution into the octahedral sites of the spinel lattice. This substitution has the effect of modifying the iron atomic local environment through the presence of near- and next-nearest neighbour “foreign” cation species. These foreign species will slightly perturb the known hyperfine interaction parameters (IS , QS and B_{hf}) expected for the B-site in magnetite, and as such will be manifested as a line-broadening effect of the B-site spectral component

(Vandenberghe et al. 1990, Schwertmann and Cornell 1991, Pollard et al. 1992, Stevens et al. 1998).

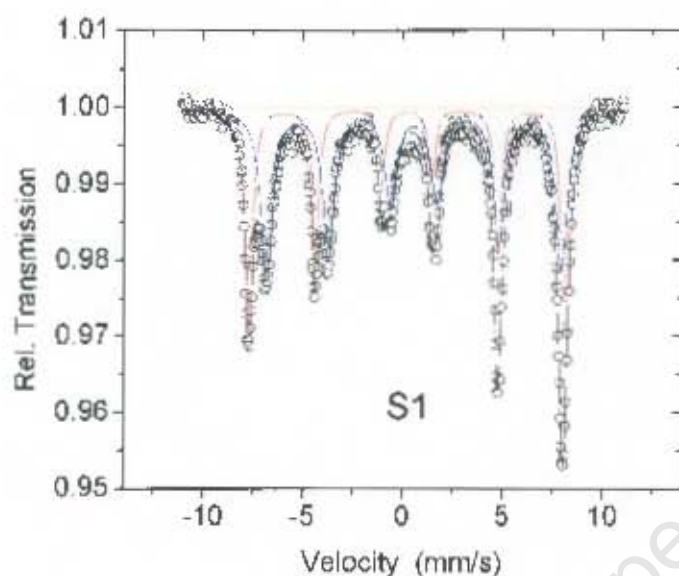


Figure 7.4b Mössbauer spectrum of reference sample S1 (magnetite prepared in the presence of calcium) fitted with two sextets. The overall theoretical fit is the solid line through the data points represented as open circles (from reports compiled by Dr G Hearne).

SAMPLE	Spectral Component	I , Linewidth (mm/s)	δ/Fe (mm/s)	QS (mm/s)	B_{hf} (T)	γ Abundance %
S1	Tet A-site and oxidised Oct B-site	0.43	0.29	-0.01	49.0	$33(1) \text{ Fe}^{3+}$ $7(1) \text{ Fe}^{3+}$
	$\S$ Octahedral B-site	0.74	0.63	-0.01	45.8	$33(1) \text{ Fe}^{3+}$ $27(1) \text{ Fe}^{2+}$

Table 7.3b Hyperfine interaction parameters of the spectral components in Figure 7.4b. Statistical error indicated in parenthesis. γ From the integrated area under the sub-spectrum. $\S$ Relative line-intensities of the sextet for the B-site permitted to vary.

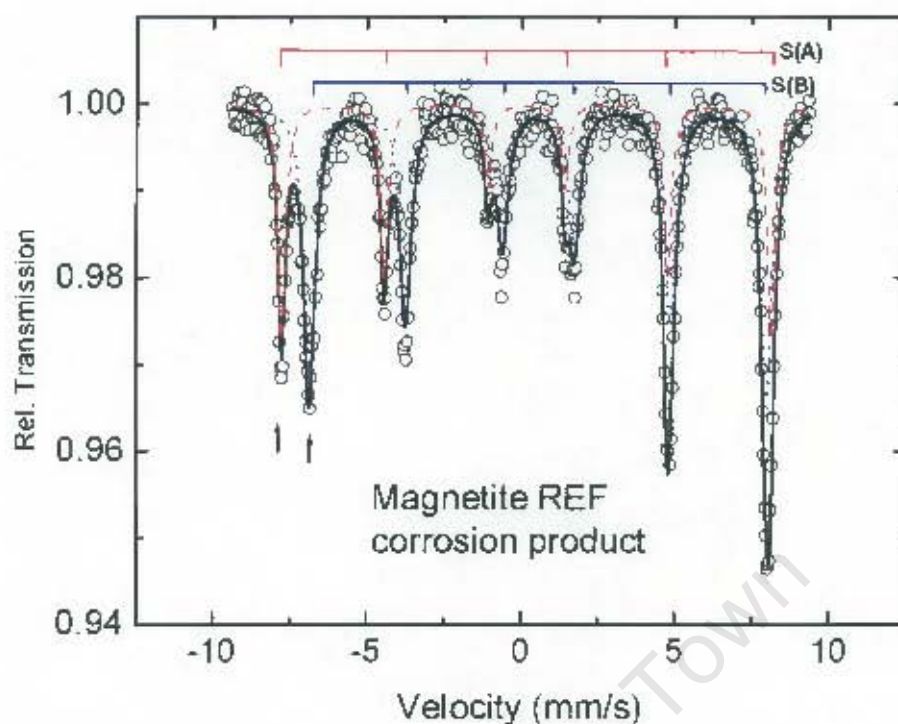


Figure 7.4c Mössbauer spectrum of a reference sample of stoichiometric magnetite (from reports compiled by Dr G Hearne).

SAMPLE	Spectral Component	Γ , Linewidth (mm/s)	δ/Fe (mm/s)	QS (mm/s)	B_{hf} (T)	Abundance %
Magnetite ref	A	0.30	0.28	0	49.2	33.6
	B	0.45	0.66	0	46	66.4

Table 7.3c Hyperfine interaction parameters of the spectral components of stoichiometric magnetite.

In conclusion, the results of chemical analyses, X-ray diffraction and Mössbauer spectroscopy all confirm a substituted magnetite ferrite structure for the end-products of Exp 7.2. Non-ferrous metal removal by cation substitution in Exp 7.2 is examined in further detail in the following section.

Non-ferrous metals removal

Sample	ferrous	Co	Ni	Zn
AMD		2.69	2.49	2.13
End-product 1: 2.1 sludge ages	22.34	2.46	1.99	2.14
End-product 2: 2.2 sludge ages	23.44	2.46	1.95	2.02
Average % uptake		91	79	98

Table 7.4 Chemical analysis of two samples of end-product taken from the penultimate (sample 1) and final (sample 2) batches of exhaustive oxidation of Exp 7.2 (after 2.1 and 2.2 sludge ages respectively). The percentage of each metal (percent mol M^{2+} / mol Fe_T) present in each sample is shown, as is the percentage concentration of each metal in the simulated AMD. The last row in Table 7.4 gives the average percentage uptake (removal) for each non-ferrous metal for the two samples.

The data shown in Table 7.4 confirms a high percentage uptake of all three non-ferrous metals into the end-product of the process. For the two samples, the average percentage uptake relative to the molar ratio of each non-ferrous metal : iron in the simulated AMD is 91%, 79% and 98% for Co, Ni and Zn respectively. The values for Ni and Zn are consistent with those reported by Kanzaki et al. (1998) who found that Zn (93%) was preferentially incorporated into ferrite over Ni (80%) even when the concentration of Ni in the starting solution was greater than the concentration of Zn^{2+} . The data from Table 7.4 is presented in graphical form in Figure 7.5.

² Ferrite formation in Kanzaki et al. (1998) was at 65°C and consisted of a single batch test without any seed being present.

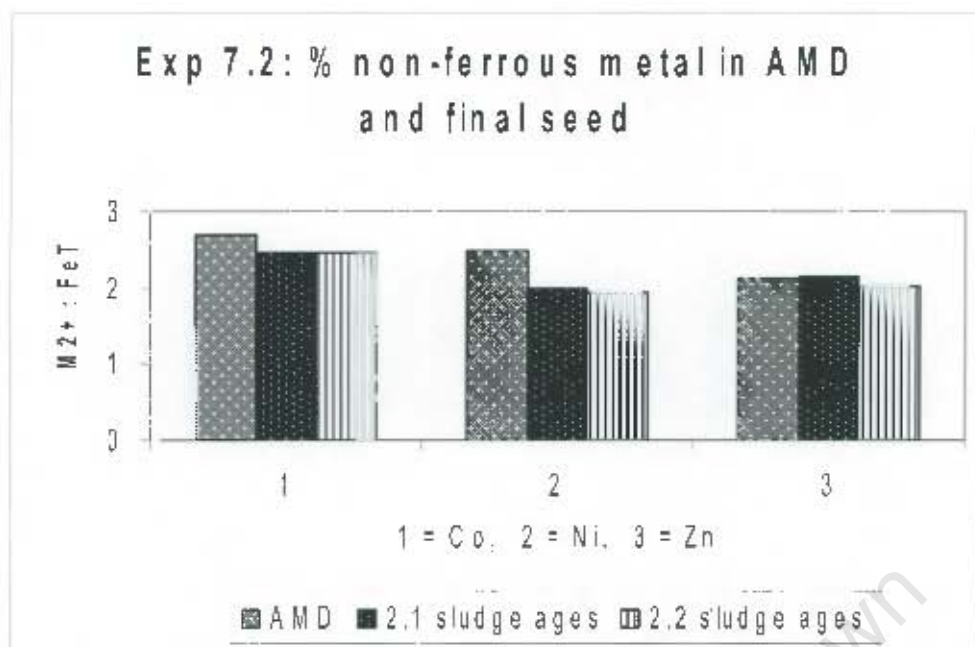


Figure 7.5 Graphical presentation of the data in Table 7.4 showing the average percentage of each non-ferrous metal : Fe (% mol/mol) in the seed of Exp 7.2 after exhaustive oxidation and aging. On the x-axis 1 = Co, 2 = Ni, 3 = Zn. The first series shows the percentage of each of these metals in the simulated AMD for Exp 7.2.

The results shown in Table 7.4 and Figure 7.5 indicate a high degree of incorporation of non-ferrous metals into the final precipitate. However a small discrepancy in the mass balance for each metal is reflected by the deficit between the molar ratio of metal : iron in the initial simulated AMD versus the ratio in the final precipitate. Notwithstanding the congruence with the results of Kanzaki et al. mentioned above, the reasons for this deficit are not immediately clear, but with hindsight of information gained from Exp 7.3 (see below) it seems that the most probable reason is that the system was not yet at steady-state with respect to the complete replacement of original seed.

Effluent

Data for non-ferrous metals in the effluent is shown in Tables 7.5a and 7.5b. The data in these tables was obtained by taking a 50 ml sample from near the top of the first

settler and filtering it through a 0.45 μ filter which separated suspended solids from the solute. The suspended solids ('fines') were then completely dissolved in concentrated HCl before being diluted to 50 ml again and assayed for each metal. Table 7.5a shows the results for the concentration of metals present as fines in the effluent. Table 7.5b shows the concentrations of dissolved metals present as solute in the filtrate of the 50 ml samples discussed above.

Sludge ages	Fe	Co	Ni	Zn
1.7	2.29	0.1	0.04	0.05
1.9	N/A	4.14	1.66	1.86
2.1	N/A	0.07	0.05	0.095

Table 7.5a Concentrations of metals in mg/L present as fines in the effluent for Exp 7.2. Data is for three consecutive samples taken after 1.7, 1.9 and 2.1 sludge ages respectively. On one occasion (1.9 sludge ages) the levels of fines in the effluent were significantly high but returned to acceptable limits by the following day. Such elevations only occurred after a rare blockage or other malfunction of the equipment. The Fe concentrations for the second and third samples are not available as the Fe in these samples precipitated prior to measurement.

Sludge ages	Fe	Co	Ni	Zn
1.9	N/A	0.15	0.09	<0.01
2.1	2.35	0.13	0.055	0.03

Table 7.5b Concentrations of dissolved metals present in the effluent filtrate of Exp 7.2 after 1.9 and 2.1 sludge ages.

Ferrous intermediate : calcium ratio

The role of the contact stabilisation reactor – settler sequence in raising the ferrous intermediate : dissolved calcium ratio has already been discussed in Chapter 6. The calcium concentration in the first oxidation reactor was measured and the results are shown in Table 7.6.

Sludge ages	Ca (mg/L.)
1.9	271
2.2	246
2.3	303

Table 7.6 Concentration of dissolved calcium (mg/L) in the oxidation reactor for Exp 7.2.

The values shown in Table 7.6 accord extremely well with the expected theoretical value of 287.5 mg/L based on the K_{sp} of CaSO_4 (gypsum), taking Debye-Hückel effects into account (calculations not shown). Since the dissolved calcium concentration in the oxidation reactor is less than or equal to the concentration in the contact stabilisation reactor – settler sequence³, these results confirm that the ferrous intermediate : dissolved Ca ratio in the oxidation reactor is indeed greatly enhanced by the contact stabilisation reactor - settler sequence as described above. It is postulated that it is this enhanced ratio which allows for ferrite formation in the presence of calcium which otherwise interferes.

³ Gypsum precipitation in the contact stabilisation reactor reactor – settler sequence indicates that calcium is at saturation or supersaturation with respect to CaSO_4 . The latter therefore governs calcium solubility. No gypsum precipitation is observed in the first oxidation reactor indicating that calcium is at or below saturation in this compartment. It therefore follows that the dissolved calcium concentration in the first oxidation reactor is less than or equal to the concentration in the contact stabilisation reactor – settler sequence.

Redox potential in the oxidising reactor

Perales Perez et al. (1999, 2001a) have shown a definite relationship between the oxidation reduction potential (ORP) and the course of the magnetite-forming reaction under batch conditions in the absence of seed as discussed in Chapter 4. To investigate whether the ORP could serve as a useful control parameter during steady-state ambient temperature ferrite formation as performed in Exp 7.2, the ORP was measured during the course of the reaction. Figure 7.6 shows the relationship between the ferrous intermediate concentration (FI) and ORP over the period from 1.9 to 2.1 sludge ages. Figure 7.6 shows that no algebraic relationship other than a close clustering of points occurs. The reasons for the poor correlation between FI and ORP over time under the conditions of Exp 7.2 are twofold. Firstly the ORP is a function of many parameters including DO, pH, seed concentration, temperature etc. and not purely FI. Secondly, the ORP is far more sensitive than the FI to changes in these parameters. Consequently the ORP does not serve as a reliable immediate indicator of the FI concentration which has been shown to be the most important parameter to monitor during ambient temperature ferrite formation.

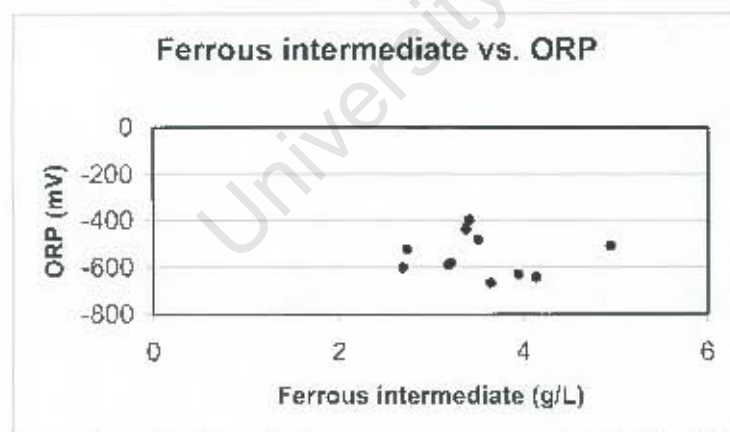


Figure 7.6 Ferrous intermediate versus ORP in the oxidation reactor of Exp 7.2 during the period from 1.9 to 2.1 sludge ages

Stability of the final precipitate

Figure 7.7 shows the percentage loss of Fe from a 60 mg sample of final seed from Exp 7.2 which was submerged in 1L of a 1 : 1 molar mixture of sulphuric and nitric acids diluted with distilled water to pH 5 (Zinck and Griffith 2000). Prior to submersion, the sample had been exhaustively oxidised and left to age for 2 weeks. These data show clearly that the precipitate is highly resistant to dissolution under these conditions. The initial decrease in the percentage mass lost into solution seen in Figure 7.7 is possibly attributable to oxidation followed by precipitation (as $\text{Fe}(\text{OH})_3$) and settling, of an initial release of ferrous iron stemming from the proton-ferrous exchange phenomenon discussed in Chapter 5. This would result in a decrease in the dissolved Fe concentration sampled from near the surface. No visible precipitant was however observed either in suspension or settled on the bottom of the jar but considering the minute amounts involved this is not necessarily surprising. It can nevertheless be concluded that, in respect of iron, the precipitant is indeed very resistant to dissolution under these conditions.

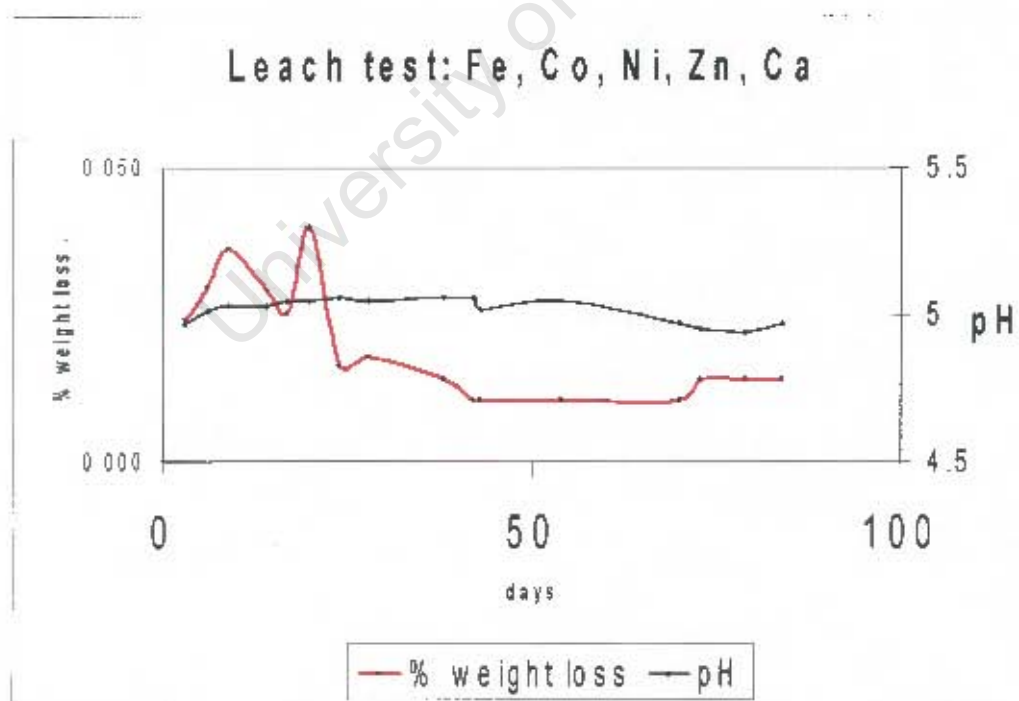


Figure 7.7 Graph showing the percentage loss of iron (mg dissolved Fe / mg total Fe) from a sample of final precipitate for Exp 7.2 subjected to a 1:1 mixture of sulphuric and nitric acid at ~pH 5. After every measurement the contents of the jar

were vigorously swirled for 30 seconds to promote mixing of any leached metal ions prior to the next measurement. Swirling was not done soon before a measurement was taken because of the likelihood of sampling suspended ferrite solids.

Results for iron and non-ferrous metal concentrations in the leachate after 12 weeks for Exp 7.2 are given in Table 7.7. Although very low, the non-ferrous metal concentrations are disproportionately high relative to the Fe concentration which stabilised at 0.018 mg/L, an order of magnitude lower. The reasons for this paradoxical result are not known but are unlikely to be due incongruent dissolution (cf. Figure 4.8).

Exp 7.2	Fe	Co	Ni	Zn
Concentration mg/L	0.018	0.21	0.20	0.13

Table 7.7 Concentrations of iron and non-ferrous metals in the leachate after 12 weeks for the end-product of Exp 7.2.

Settling behaviour

After exhaustive oxidation ($\text{DO} > 2 \text{ mg/L}$) but no interim aging, the SVI of the final precipitant for Experiment 7.2 was 3.9 ml/g, indicative of extremely efficient liquid – solid separation¹.

¹ SVI results in chapters 5 and 6 were expressed in ml/g-Fe. In Chapter 7, g-Fe has been converted into g by multiplying by a factor of 1.38 which is the ratio of the molecular mass of magnetite : molecular mass of Fe^{2+} x 3. In other words, by regarding the iron end-products as 100% magnetite, the SVI can be expressed as mass-magnetite instead of mass-Fe.

Exp 7.3 Ferrite formation in the presence of Co, Ni, Zn, Mn and calcium.

Exp 7.3 was initiated using the seed formed in Exp 7.2 but the concentrations and complement of non-ferrous metals in the influent was changed to those shown in Figure 7.8. In particular Mn, a ubiquitous metal in South African AMD waters, was added and the Ni concentration was increased to 10% of the ferrous concentration. The total non-ferrous metal concentration in this experiment was therefore ~18.5%. Exp 7.3 was otherwise performed in the identical manner to Exp 7.2 (aging – 24 hours).

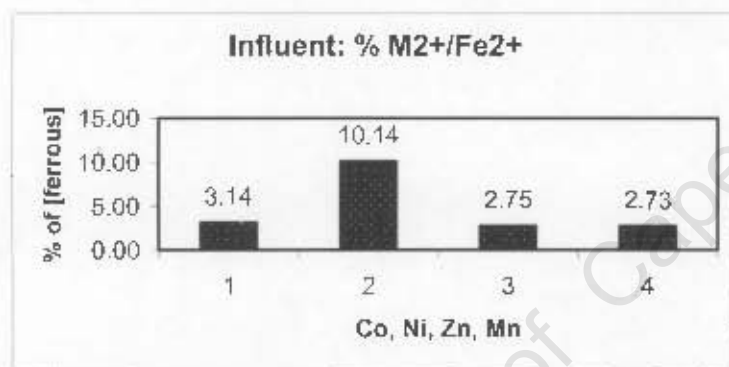


Figure 7.8 Averages of two measurements of concentrations of non-ferrous metals present in the influent for Exp 7.3 expressed as a percent of the total measured ferrous concentration (3933 mg/L) in the influent solution (~pH 3, Fe : SO₄ = 1 : 2). σ: Co=0.094, Ni=0.202, Zn= 0.068 and Mn=0.568.

Early measurements of the effluent of Exp 7.3 revealed dramatically elevated concentrations of iron (> 60 mg/L) and non-ferrous metals (> 1-5 mg/L) in both solid and liquid phases (data not shown). Evidently, the precipitation reaction expected to occur in the contact stabilisation reactor was not working properly. Speciation analysis (Gustafsson 2004) revealed that at pH 10.5 Mn²⁺ was only ~60% hydrolysed. The reason for the presence of iron, Co, Ni and Zn in the effluent could not be explained but from a practical perspective it was clear that the pH needed to be raised in order to ensure complete precipitation of Mn. Inspection of Figure 2.4 in Chapter 2 reveals that Mn solubility reaches a minimum at ~pH 12. The pH of both the contact

stabilisation and oxidation reactors was therefore maintained at this value. Data for Exp 7.3 performed at pH 12 is shown in Figure 7.9a.

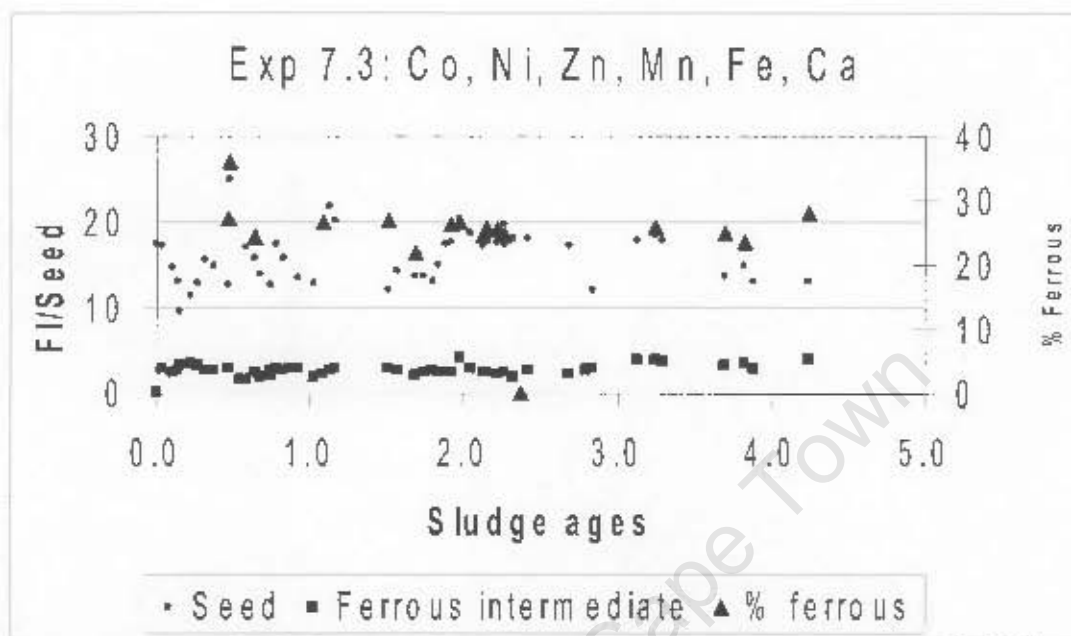


Figure 7.9a Data for Exp 7.3 in which Co, Ni, Zn, Mn and calcium were present and which was performed at pH 12. The graph shown is an extension of the graph shown in Figure 7.3a which pertains to Exp 7.2 because Exp 7.3 was continued from the point where Exp 7.2 was terminated. In Figure 7.9a the small arrow on the x-axis at 2.4 sludge ages marks the beginning of Exp 7.3. The data to the left of the arrow is for Exp 7.2. The arrow on the x-axis also marks the point at which Mn was added to the influent and the Ni concentration was increased to 10% of the ferrous concentration. It was also at this point that the pH was increased from 10.5 to 12.0.

Metal intermediates

Figure 7.9b shows the measured non-ferrous metal intermediate values in the oxidation reactor for Exp 7.3. For each metal the corresponding percentage in the AMD influent solution is given. As expected, the metal intermediate values closely approximate the AMD values indicating that, in this respect, steady-state has been reached. Figure 7.9b also shows that Mn precipitation appears to be complete.

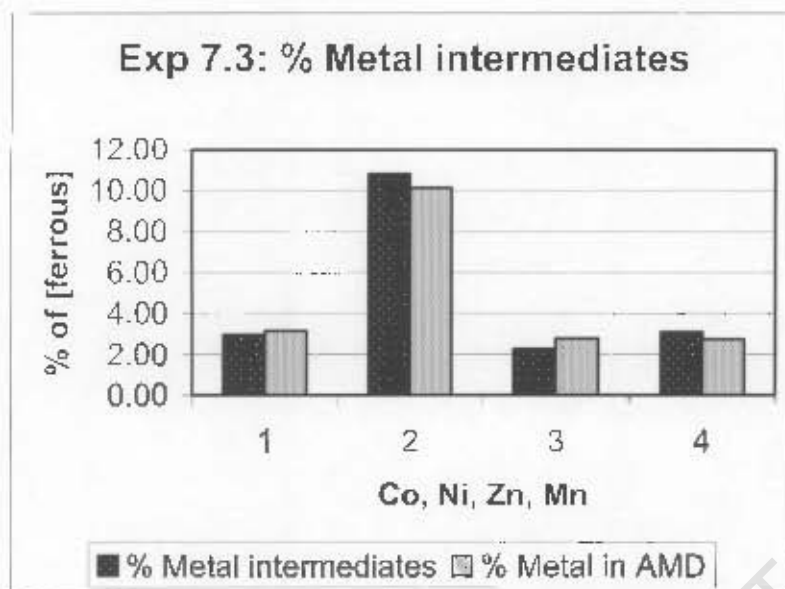


Figure 7.9b Graph showing the average percentage metal intermediate concentrations in the oxidation reactor for Exp 7.3, $n=3$, σ : Co=0.041, Ni=0.725, Zn=0.84 and Mn=0.56.

Characterisation of the end-product

In Figure 7.9a it can be seen that for Exp 7.3 the percentage ferrous in the fresh precipitate stays relatively constant (average = 26.24 ± 2.99). As discussed above in relation to Exp 7.2, when divalent non-ferrous metals are present in the simulated AMD, a decrease in the percentage ferrous of both the fresh precipitate and final end-product is to be expected as a consequence of cation substitution. In the case of Exp 7.3 the theoretical total percentage of non-ferrous metals in the end-product at steady-state is 18.5%. The maximum expected percentage ferrous in the end-product is therefore expected to be $33.3\% - 18.5\% = 14.8\%$ which is clearly much lower than the values seen in Figure 7.9a. One major reason for this discrepancy is that both Ni and Mn had not reached steady-state in the precipitate by the time the percentage ferrous was measured (see Table 7.8 below). Using the data from Table 7.8 the maximum percentage ferrous expected at the time of sampling is $33.5\% - 8.8\% = 24.5\%$ which is in reasonable agreement with the value obtained. After exhaustive

oxidation the percentage ferrous decreased to 22% by chemical analysis (24% by Mössbauer spectroscopy) as a consequence of further oxidation.

Structural analysis

A sample of precipitant taken from Exp 7.3 after 4.2 sludge ages was aged for 48 hours post-exhaustive oxidation and subjected to XRD and Mössbauer analysis.

X-ray diffraction: The XRD pattern (Figure 7.10a) illustrates that this precipitate has structural features of ferrite.

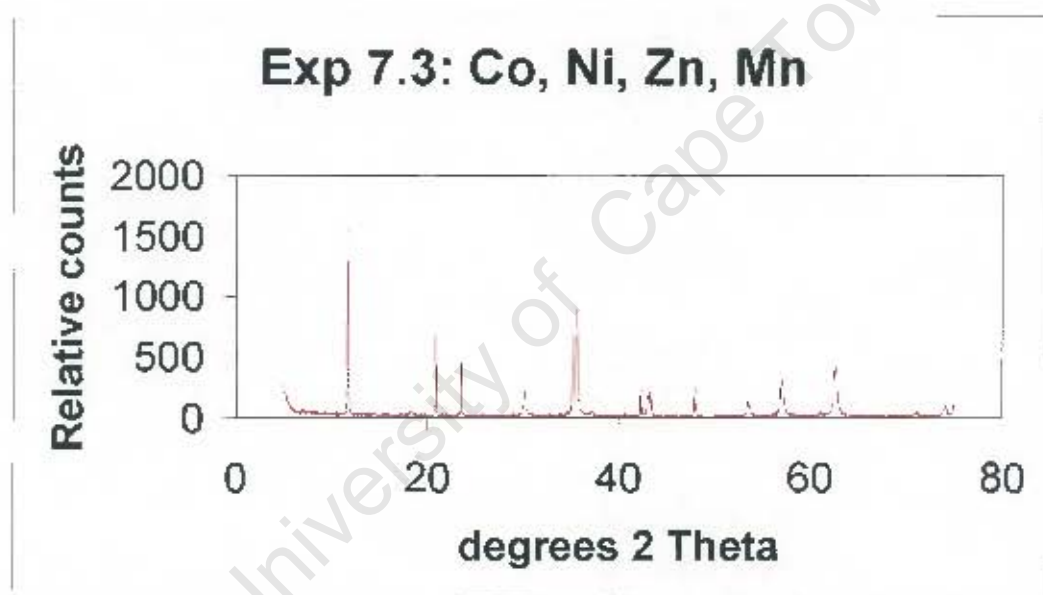


Figure 7.10a XRD result for the final precipitant for Exp 7.3 after exhaustive oxidation and aging for 48 hours. As in the case of Exp 7.2, in addition to the magnetite peaks there are other significant peaks indicating either some deviation from the pure ferrite structure or the presence of other compounds. The nature of these additional peaks was not investigated.

Mössbauer spectroscopy: Consistent with the XRD results, the Mössbauer spectrum of the sample of end-product from Exp 7.3 has the characteristic signatures of magnetite (Figure 7.10b), except for a marked difference in the relative intensities of

resonance lines close to 7.5 mm/s compared with stoichiometric magnetite. This is indicative of some degree of oxidation, and the results of the spectral analysis indicate the ferrous (Fe^{2+}) content to be 24(1)%, in comparison with 33% expected in a stoichiometric compound.

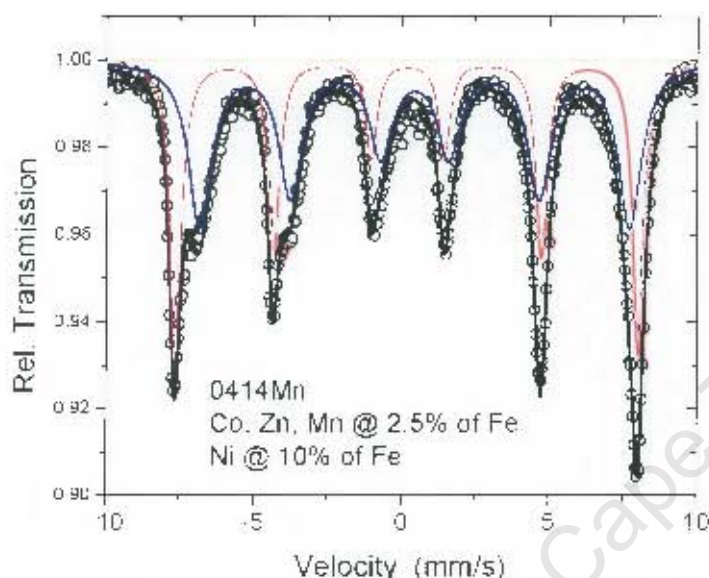


Figure 7.10b Mössbauer spectrum of the same sample of end-product from Exp 7.3 used for XRD analysis as shown in Figure 7.10a in which Co, Ni, Zn, Mn and Ca were present. The spectrum is fitted with two sextets. The overall theoretical fit is the solid line through the data points represented as open circles (from reports compiled by Dr G. Hearne).

SAMPLE	Spectral Component	Γ , Linewidth (mm/s)	δ/Fe (mm/s)	QS (mm/s)	B_{hf} (T)	*Abundance %
Exp 7.3	Tet A-site and oxidised Oct B-site	0.46	0.29	-0.03	49.0	33.3 Fe ³⁺ 9(1) Fe ³⁺
	§ Octahedral B-site	0.94	0.63	-0.03	45.1	33.3 (5) Fe ³⁺ 24 (1) Fe ²⁺

Table 7.9 Hyperfine interaction parameters of the spectral components in Figure 7.10b. Statistical error indicated in parenthesis. * From the integrated area under the sub-spectrum. § Relative line-intensities of the sextet for the B site permitted to vary.

As was the case for Exp 7.2, excessive broadening at the octahedral B-site is evident from the ratio of the linewidths of the B-site and A-site, $\Gamma_B / \Gamma_A = 2.0$. This may be compared to the same two reference samples shown above, ie. (1) the Mössbauer spectrum of magnetite made in the presence of calcium with no non-ferrous metals present (Figure 7.4b). The ratio of the linewidths of the B-site and A-site, $\Gamma_B / \Gamma_A = 1.7$ for this sample (Table 7.3b). (2) The Mössbauer spectrum for a sample of stoichiometric magnetite (Figure 7.4c). The ratio of the linewidths of the B-site and A-site, $\Gamma_B / \Gamma_A = 1.5$ for this sample (Table 7.3c).

When compared against stoichiometric magnetite, any broadening in sample S1 is attributable to oxidation on the B-site and also perhaps from the influence of calcium in the mixture. The further line-broadening effects in the sample of end-product from Exp 7.3 which seems to occur mainly on the octahedral B-sites may be ascribed to heavy-metal uptake into the magnetite lattice by substitution into the octahedral sites of the spinel lattice. This substitution has the effect of modifying the iron atomic local environment through the presence of near- and next-nearest neighbour “foreign” cation species. These foreign species will slightly perturb the known hyperfine interaction parameters (IS , QS and B_{hf}) expected for the B-site in magnetite, and as such will be manifested as a line-broadening effect of the B-site spectral component.

In conclusion, the results of chemical analyses, X-ray diffraction and Mössbauer spectroscopy all confirm a substituted magnetite ferrite structure for the end-products of Exp 7.3. Non-ferrous metal removal by cation substitution in Exp 7.3 is examined in further detail in the following section.

Non-ferrous metals removal

Exp 7.3	Co	Ni	Zn	Mn
Average % M^{2+} in dissolved seed (n = 3)	3.29	2.52	2.75	0.42
σ	0.055	0.090	0.102	0.363
% M^{2+} in simulated AMD	3.14	10.14	2.75	2.73
% uptake	105	25	100	15

Table 7.8 Data showing the percentage and percentage uptake of non-ferrous metals in the fresh precipitate of Exp 7.3.

In Table 7.8 both Co and Zn show 100% uptake while Ni and Mn show only 25% and 15% respectively. These low values are attributable to the fact that the system was not yet at steady-state with respect to these two metals which were only added 1.36 sludge ages prior to first measurement (in the case of Ni the concentration was increased from 2.5% to 10%). In the case of Mn the standard deviation is 85% of the average percentage value so the latter should be treated with caution. Nevertheless, Figure 7.11 illustrates increasing trends in percentage uptake with time (sludge age) for these two metals whereas the graphs for Co and Zn have levelled off.

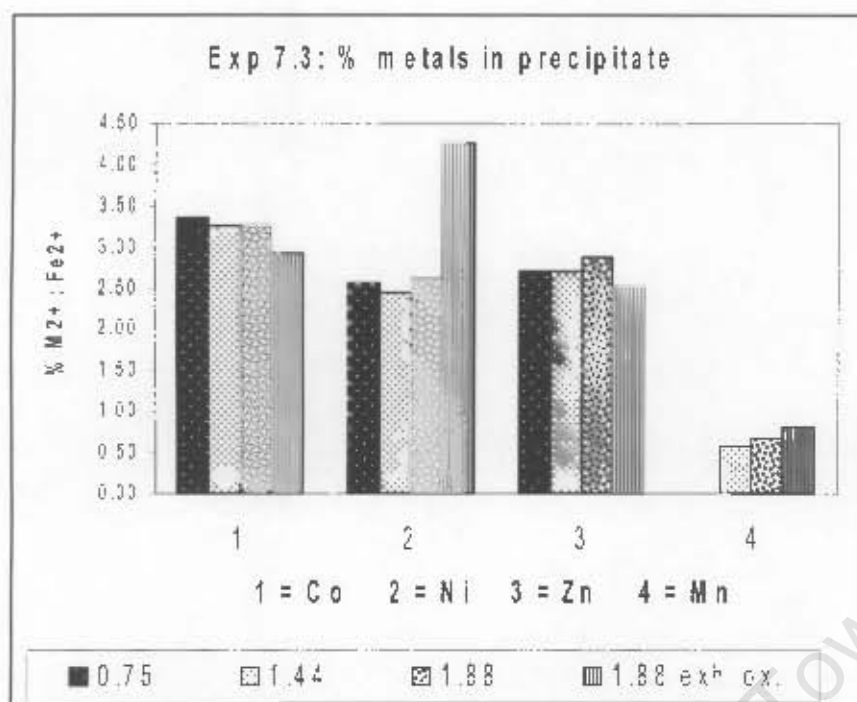


Figure 7.11 Changes in the percentage uptake of non-ferrous metals in the fresh precipitate of Exp 7.3 over time (sludge age) showing increasing trends for both Ni and Mn which are not yet at steady-state in this respect. Numbers on the x-axis represent each metal in the order shown. Patterns corresponding to columns indicate time in sludge ages.

Effluent

Data for metals concentrations in the fines and filtrate of the effluent for Exp 7.3 was obtained in the same manner as for Exp 7.2. Figure 7.12a shows the absolute concentrations found in 3 samples (taken at different times) of the solid fraction of the effluent for each metal as well as for calcium. The concentrations of non-ferrous metals are all well below 0.5 mg/L.

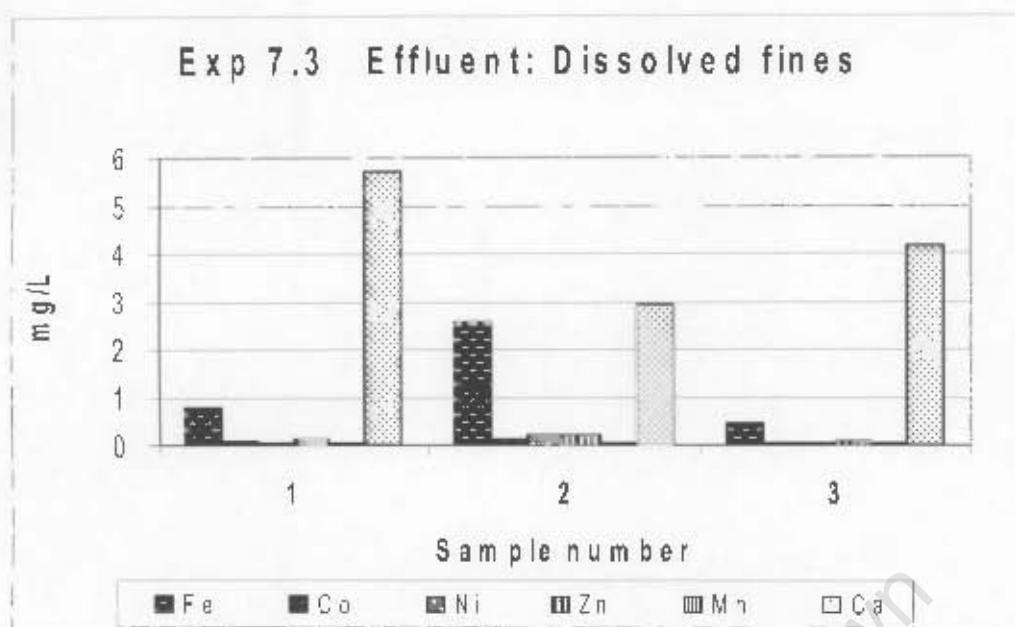


Figure 7.12a Graph showing concentrations of metals and calcium in three separate samples of the filtered fraction (fines) of the raw effluent of Exp 7.3. The concentrations of non-ferrous metals are all well below 0.5 mg/L.

The metal concentrations in the effluent filtrate for Exp 7.3 are shown in Figure 7.12b and are an order of magnitude lower than those found in the solid fraction (fines) of the effluent indicating effectively total removal of dissolved metals from the AMD. But even these amounts can probably be significantly reduced through optimisation of the settling process.

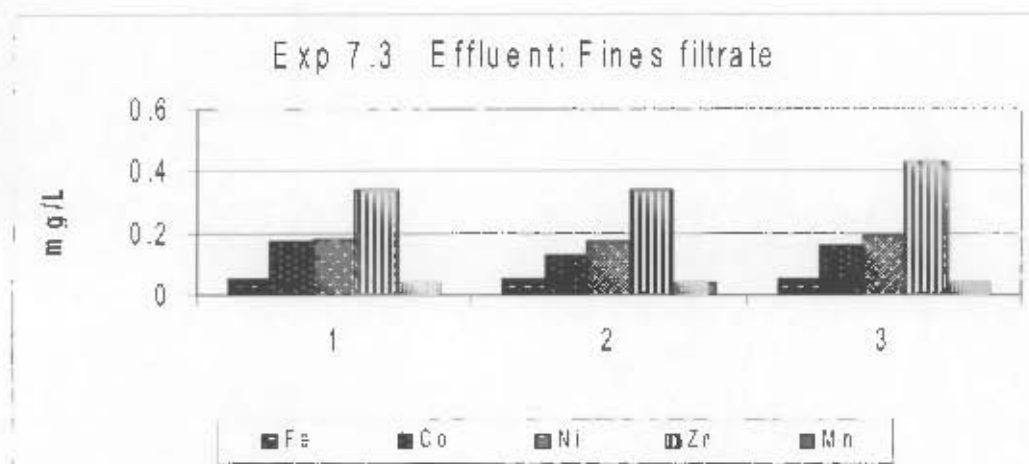


Figure 7.12b Graph showing the very low concentrations of metals in the filtrate fraction of the raw effluent for the same three samples as in Figure 7.12a.

Calcium

A layer of calcite (CaCO_3), identified by XRD (Figure 7.13) approximately 1mm in depth formed on the surface of the effluent waste tank. This was not observed in Exp 7.2 and can be explained by the higher pH of 12 in Exp 7.3 which allows for a higher dissolved CO_3^{2-} concentration (see Figure 4.11 in Chapter 4).

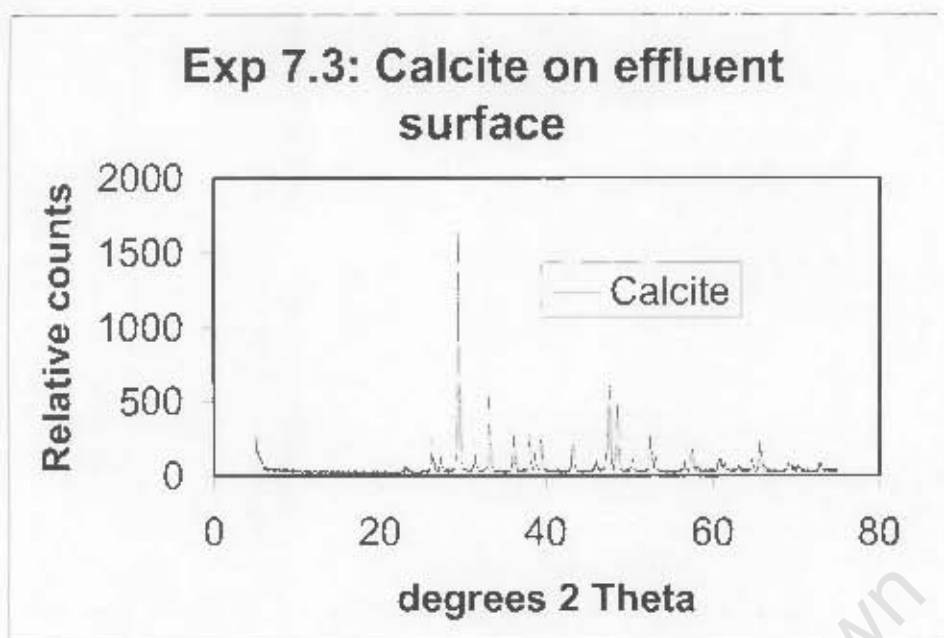


Figure 7.13 XRD tracing of the crystalline material which formed on the surface of the effluent waste tank for Exp 7.3. This was clearly identified as calcite (CaCO_3).

Table 7.10 shows the concentration of calcium in the filtrate fraction of the raw effluent for Exp 7.3. These results exceed the solubility of calcium with respect to CaSO_4 (expected value – 287.5 mg/L although at pH 12 CaCO_3 may also govern calcium solubility⁵) indicating the probability that not all of the calcium passing through the filter is dissolved calcium and that some may be nanocrystalline gypsum or calcite. Table 7.10 shows that the calcium present in the filtrate represents a significant percentage of the total calcium introduced into the AMD influent in order to simulate the use of lime. The alkalinity demands of Exp 7.3 were ~25% higher than those for Exp 7.2 because in addition to the amount of alkalinity needed to precipitate the ferrous and non-ferrous metals, a further ~25% of this amount was needed to reach pH 12. Calculations which take into account the increasing buffering capacity of water between pH 10.5 and pH 12 account for this increased alkalinity demand (data not shown).

⁵Since some calcite did precipitate, calcium solubility is also being governed by the carbonate system. At this stage however, it is impossible to say to what extent calcium solubility is being governed by the sulphate system or by the carbonate system. Theoretical modelling of this problem is complicated by complex formation and should be the subject of future research (Loewenthal, pers. comm.).

Ca mg/L	Ca mol/L	Molar % Ca in influent
553	13.80	39
680	16.97	48
725	18.09	52
486	12.13	35

Table 7.10 Data for amounts of calcium measured in four samples of filtrate of the raw effluent from Exp 7.3. See text for details.

Stability of the final precipitate

Figure 7.14 shows the percentage loss of Fe from a 62.5 mg sample of final seed from Exp 7.3 which was tested for stability in exactly the same manner as described above for Exp 7.2 (i.e. submerged in 1L of a 1 : 1 molar mixture of sulphuric and nitric acids diluted with distilled water to pH 5). These data show clearly that the precipitate is highly resistant to dissolution under these conditions. As seen in the leaching behaviour of the end-product of Exp 7.2, an initial decrease in the percentage mass lost into solution is also seen for Exp 7.3 in Figure 7.14. This decrease was attributed to an oxidation-precipitation ($\text{Fe}^{2+} \rightarrow \text{Fe}(\text{OH})_3$) and settling effect of an initial release of ferrous iron stemming from the proton-ferrous exchange phenomenon discussed in Chapter 5. Once again however, no visible precipitant was observed either in suspension or settled on the bottom of the jar, but again considering the minute amounts involved this is not surprising. It can nevertheless be concluded that with respect to iron, the precipitant from Exp 7.3 is also very resistant to dissolution under these conditions.

Table 7.11 shows the concentrations of iron and non-ferrous metals in the leachate after 7 weeks for the end-product of Exp 7.3. Once again, as in Exp 7.2, the concentrations of the non-ferrous metals are approximately an order of magnitude higher than that of iron.

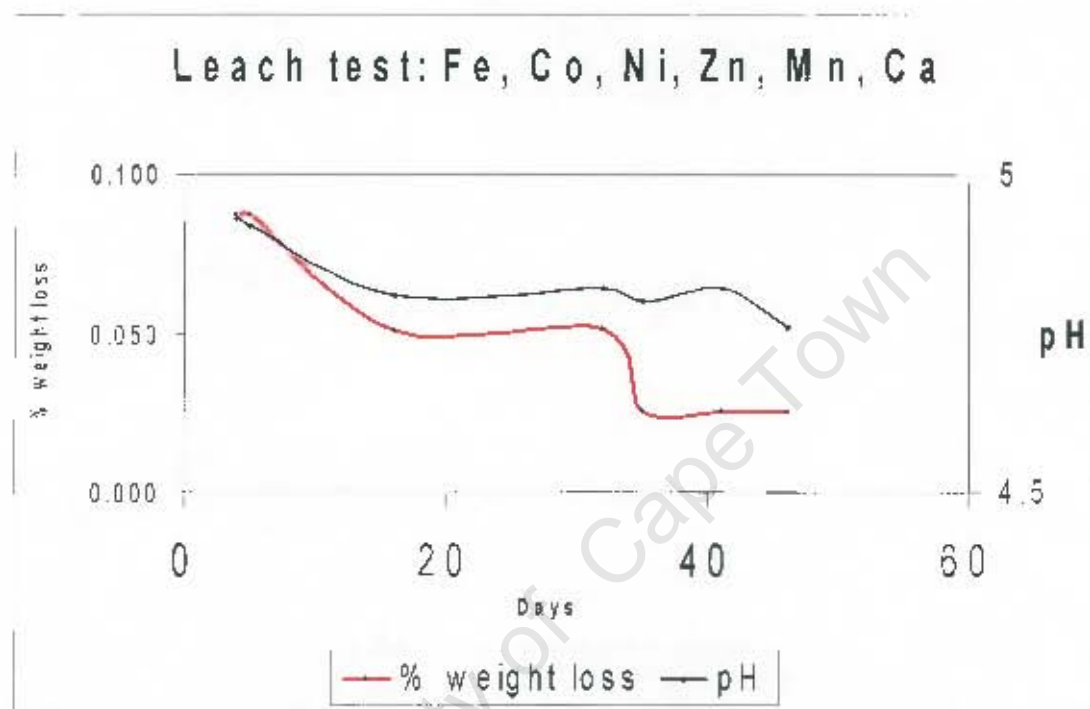


Figure 7.14 Graph showing the percentage loss (mg dissolved Fe / mg total Fe) from a sample of final precipitate for Exp 7.3 subjected to a 1:1 mixture of sulphuric and nitric acid.

Exp 7.3	Fe	Co	Ni	Zn	Mn
Concentration mg/L	0.015	0.09	0.25	0.06	0.05

Table 7.11 Concentrations of iron and non-ferrous metals in the leachate after 7 weeks for the end-product of Exp 7.3.

Settling and dewatering

After exhaustive oxidation but no interim aging, the final precipitant of Exp 7.3 showed a SVI of 12.9 ml/g. The initial 1L sample used to determine the SVI had an iron concentration of 42 g-Fe/L. On the strength of the structural studies discussed above it can be assumed that ~100% of the iron in the sludge was in the ferrite form. Using the molecular weight of magnetite, this ferrite fraction would weigh 57.9 g.

Eleven days after SVI measurement, the supernatant was drawn off and the remaining now paste-like sludge which occupied ~200 ml (Figure 7.15) was left to dry in an open one litre beaker at room temperature. This sludge dried into a hard cake with a total mass of 62.2 g after ~20 days (Figure 7.16). The iron content of this dried sludge was therefore 67.5% (42 g-Fe / 62.2 g total mass) which translates into a ferrite/total dried sludge mass of 93.2%. This leaves 6.8% of the dried sludge mass unaccounted for.

Dissolution of a small fragment of the dried sludge in concentrated HCl took less than five minutes except for a very few barely visible lance-like particles which resisted dissolution. Since the mass of these insoluble particles was negligible it can be concluded that the 6.8% of the mass which is not attributable to ferrites is most likely residual water. The volume of the dried sludge cake was determined to be 26.5ml (by measuring the amount of water it displaced) providing a dry density of 1.58 g-Fe/ml or 2.37 g dried sludge/ml.

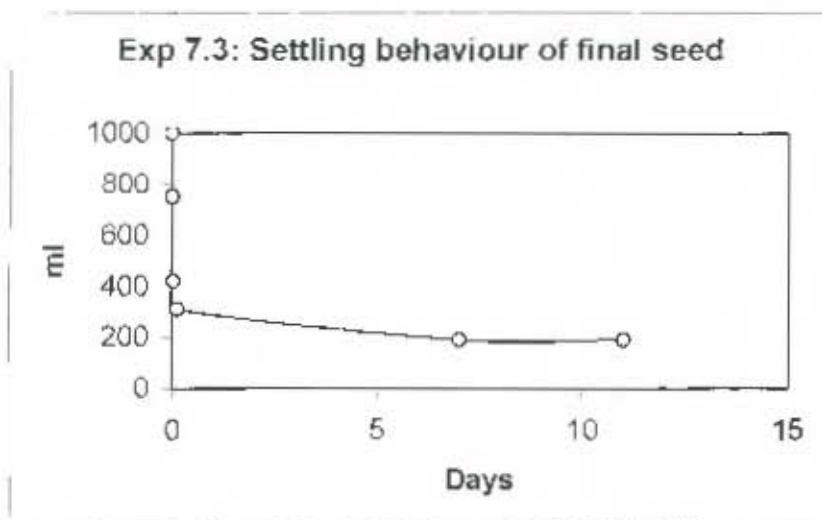


Figure 7.15 Graph showing the settling behaviour of 1l. of the final precipitant of Exp 7.3 after exhaustive oxidation but no interim aging.



Figure 7.16 The sludge obtained from the SVI measurement for Exp 7.3 dried into a hard cake after ~20 days. Scale in cm.

Summary and conclusions

The results of the experiments described in this chapter represent the culmination of a research project which started with a simple batch experiment designed to test the feasibility of magnetite formation by oxidising an aqueous ferrous solution at ambient temperature in the presence of magnetite seed. The rationale was to set the basis for a process whereby dissolved ferrous and non-ferrous metals could be removed from large volumes of AMD through cation substitution in the magnetite ferrite lattice. This initial 'proof of concept' experiment was followed by systematic investigations under batch conditions into the effect of pH, temperature, airflow rate and seed concentration on magnetite formation. These studies established a robust optimal *pH – airflow rate – seed concentration* zone where magnetite could be reliably produced at ambient temperature.

The next challenge was to find a way of overcoming the inhibitory effect of calcium on magnetite formation. To this end a continuous flow, dynamic steady-state reactor system was designed which facilitated the maintenance of an elevated ferrous intermediate concentration in the oxidation reactor. With this tool, the existence of a threshold ferrous intermediate concentration effect, above which solely magnetite was produced despite the presence of high concentrations of calcium was established. In the presence of calcium a minimum aging period was also found to be required for magnetite formation to occur. In order to complete the picture it only remained for non-ferrous metals such as are commonly found in significant concentrations in AMD to be introduced and tested for their removal.

Experiment 7.1 provided clear evidence for the complete removal of Co at a Co : Fe ratio of 1 : 10 and a high quality ferrite end-product (CoFe_2O_4) was produced. In Experiment 7.2 Co, Ni and Zn were all present in the simulated AMD, each at similar concentrations totalling ~7.5% of the Fe concentration. The percentage uptake of these metals into the end-product were 91%, 79% and 98% respectively. In the light of subsequent results it would appear that these less-than 100% uptake rates are attributable to the system not having reached steady-state. Nevertheless the pattern of uptake is consistent with that in the literature where Ni has been shown to be less efficiently incorporated into the ferrite crystal than is Zn (Kanzaki et al. 1998). Sludge

stability at pH 5 for the end-product of experiment 7.2 proved to be excellent with an Fe percentage mass loss of only ~0.02% detectable in the leachate solution at steady-state over a period of more than 12 weeks. The final precipitate generated in experiment 7.2 settled extremely efficiently with an SVI of only 3.9 ml/g.

In experiment 7.3 the Ni concentration in the simulated AMD was increased from 2.5 % to 10 % (Ni : Fe) and Mn was added as an additional non-ferrous metal. Co and Zn concentrations remained unchanged. Mn was added both because it is a ubiquitous metal in South African AMD waters as well as because of the potential difficulties it raises due to its significantly greater solubility ($\log K_{sp} \text{Mn(OH)}_2 = -12.8$ compared with $\log K_{sp} \text{Fe(OH)}_2 = -15.1$, see Table 2.2 in Chapter 2 for $\log K_{sp}$ values of Ni and Zn hydroxide). Although other authors report the successful removal of Mn via ferrite formation at pH 10 (Kanzaki et al. 1996, at 65°C) and pH 10.5 (Choung et al. 1999, McKinnon et al. 2000) it was indeed found that at pH 10.5, a high percentage of the Mn in the simulated AMD remained present in the effluent, having failed to precipitate in the contact stabilisation reactor and therefore settle in the first settler. Speciation analysis predicted a maximum of 95% Mn hydrolysis was possible and that this would happen at pH 12.2. Those studies mentioned in which Mn was totally removed by being incorporated into ferrite were all batch experiments in which no separation of effluent and precipitated solids occurred prior to oxidation. This issue certainly requires further empirical and theoretical investigation. In particular, from a practical perspective the minimum pH at which the effluent can be kept free from Mn needs to be theoretically modelled and empirically determined.

The quality of the AMD effluent from Exp 7.3, performed at pH 12, was determined by filtering and analysing two fractions of an effluent sample: filtered solids and filtrate solutes. At pH 12 no significant Mn or other metals were found in the effluent. In fact the metals content of both effluent fractions was consistently very low (Tables 7.5a and 7.5b). It is noted however that the release into the environment of minute amounts of metals in the form of 'ferrite fines' is unlikely to cause any detrimental ecological effects. Indeed as previously mentioned, iron oxides act as heavy metal sinks in the natural environment.

The final precipitant from experiment 7.3 reflected a 100% uptake of Co and Zn from the simulated AMD as opposed to the 91% and 98% seen in experiment 7.2 which in retrospect had probably not yet attained steady-state. The percentage Ni and Mn uptake in experiment 7.3 was 25% and 15% respectively but neither of these metals had yet reached steady-state in terms of seed replacement at the time the experiment was terminated.

As was the case for experiment 7.2, the final precipitate of experiment 7.3 was extremely stable at $\text{pH} < 5$ (Figure 7.14), losing only $\sim 0.025\%$ of its mass at steady-state over a period of 7 weeks.

The settling behaviour of the final precipitant produced by experiment 7.3 was not as good as that for experiment 7.2 where Mn was not present. The SVI for Exp 7.3 was 12.9 ml/g compared to 3.9 ml/g for Exp 7.2. Nevertheless, the overall settling and dewatering behaviour of the precipitant of experiment 7.3 was favourable, with the solids occupying 20% of the initial volume after 11 days. Thereafter further desiccation of the sludge at room temperature took ~ 20 days and resulted in a hard caked material with a percentage solids density of more than 93%. In contrast, as mentioned in Chapter 1, the Geco HDS process, after one year of drying, produced a sludge with a density of only 60% solids. Similarly the sludge produced by experiment 7.3 had an iron content of 67.5% whereas the iron content of the Geco HDS sludge was only 45%. The absolute densities of the sludge from experiment 7.3 were 1.58 g-Fe/ml or 2.37 g dried sludge/ml.

The results of the experiments described in this chapter indicate that the concept of ferrous and non-ferrous metals removal from AMD by one-step ambient temperature ferrite formation to be both possible as well as technically very feasible. For the combination of the four non-ferrous metals tested (Co, Ni, Zn and Mn), the process yields high quality results in all of the criteria relevant to the treatment of AMD. These results are discussed in the following chapter.

Chapter 8 Conclusion

This study set out to establish the feasibility of ambient temperature ferrite formation using in-line oxidation as a means of metals removal from AMD. In order to establish the feasibility five criteria needed to be met:

1. Acceptable effluent quality
2. Favourable sludge characteristics
3. Successful operation in the presence of calcium
4. Successful non-ferrous metals removal
5. Operational and economic viability

To this end a series of batch and continuous flow, steady-state investigations into ambient temperature ferrite formation with in-line oxidation were performed.

Batch conditions

After proving (without calcium) that the concept of ambient temperature ferrite formation using magnetite seed was feasible, a matrix of batch experiments were performed which quantified the effects of four parameters on magnetite formation, viz. seed concentration, rate of oxidation, pH and temperature. Optimum conditions for ferrite formation were found to be high seed concentration (8.4 g/L), slow oxidation (12.5–20 mg-Fe/L/min), pH = 10.5 and higher ambient temperatures (22 °C versus 13 °C or 7 °C). Under batch conditions, the presence of calcium at concentrations equimolar to ferrous, was found to severely inhibit magnetite formation.

Continuous flow, steady-state conditions

A reactor system was devised which allowed steady-state concentrations of seed and ferrous intermediate to be maintained in the oxidation reactor. This is in contrast with

batch conditions where the seed concentration increases as the ferrous intermediate concentration decreases to zero. Under continuous flow conditions, in the absence of calcium a steady-state ferrous intermediate concentration of greater than 500 mg-Fe/L was found to be necessary for magnetite formation to occur, without the necessity of any aging period. In the presence of calcium a steady-state ferrous intermediate concentration of greater than 1200 mg-Fe/L *as well as an aging period* of three to six hours was found necessary for magnetite formation to occur.

Contact stabilisation reactor – settler sequence

The reactor configuration used for the continuous flow, steady-state experiments included a contact stabilisation reactor – settler sequence which had two significant functions (Figure 8.1):

- Enhancement of the ferrous intermediate : dissolved calcium ratio in the oxidation reactor. This raised ferrous intermediate : dissolved calcium ratio is crucial in overcoming the inhibitory effect of calcium on ferrite formation.
- Early separation of 60–70% of the bulk AMD volume from the treatment process, leaving only precipitated metals and 30–40% of the AMD volume in need of further processing. This reduction in volume at the start of the process translates into reduced infrastructure costs at all points downstream of the contact stabilisation reactor – settler sequence.

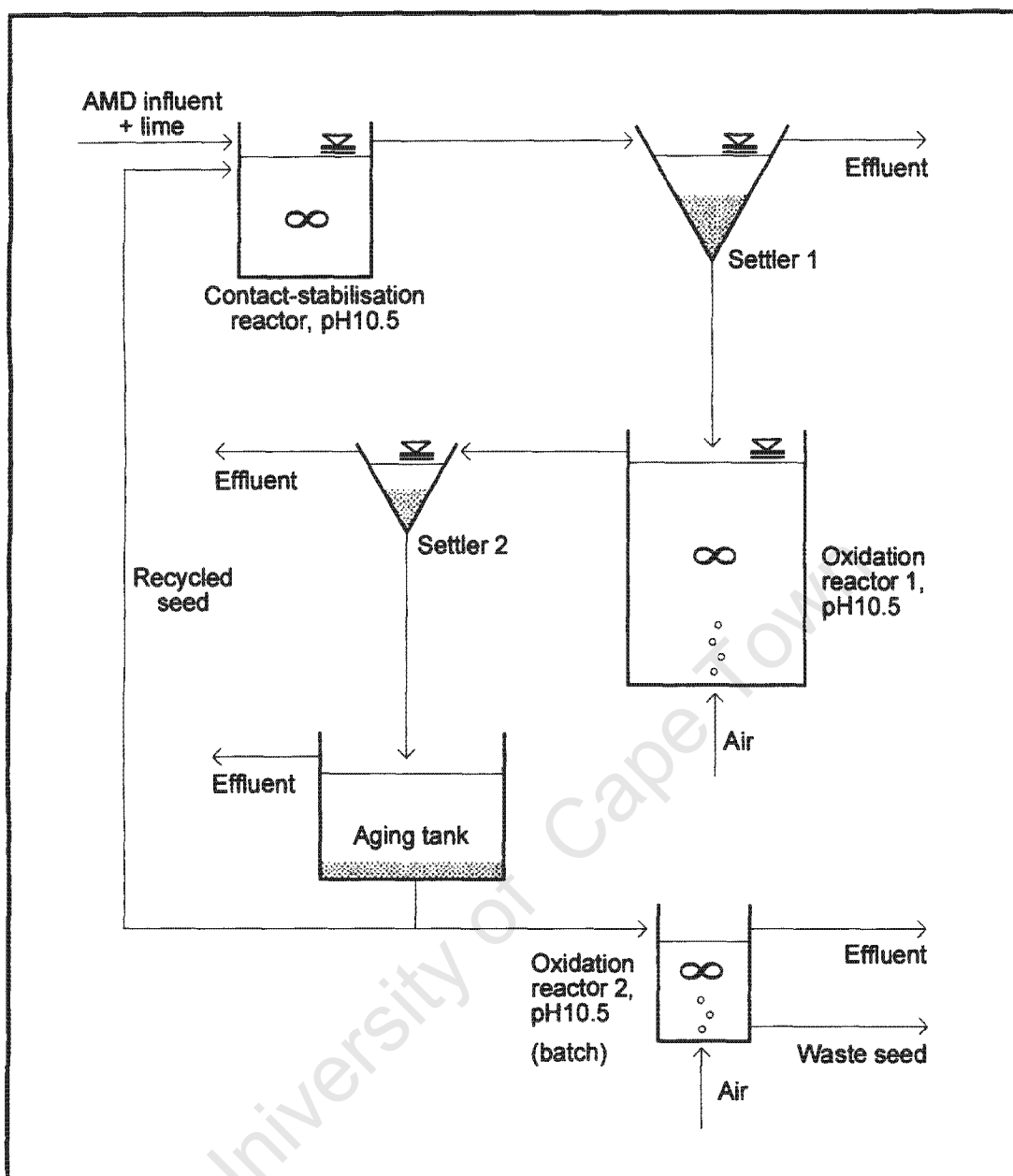


Figure 8.1 Schematic representation of the continuous flow, steady-state reactor system which successfully removed ferrous and non-ferrous metals from simulated AMD in the presence of calcium, simulating the use of lime as the pH elevating agent.

An ambient temperature ferrite process for the removal of ferrous and non-ferrous metals from AMD waters

The investigations described above formed the foundation for the development of the process depicted in Figure 8.1, which meets all of the above five criteria. These five criteria are now used to summarise the details of this process:

Acceptable effluent quality

In all phases of investigation, from batch to continuous operation at steady-state, the effluent (consisting of the clarified supernatant) contained very low concentrations of iron and other metals. The effluent does contain high concentrations of calcium (~600 mg/L) and, as is the case for the influent, high sulphate concentrations. A separate unit process for the removal of sulphate from the effluent has been developed (Ristow et al. 2004). The pH of the effluent equals the operational pH of the contact stabilisation reactor (pH 10.5–12). Since the effluent has no significant buffering capacity, the pH can be easily reduced by carbonation with CO₂ gas prior to entering the next unit process. Carbonation will result in CaCO₃ precipitation, an effect beyond the scope of this thesis.

Favourable sludge characteristics

It was stated in Chapter 1 that the sludge of an AMD treatment process needs to meet three criteria:

- Efficient settling (and therefore low sludge volume).
- Rapid and extensive dewatering properties in order to achieve a high density at the time of disposal.
- Stability of the sludge at low pH to avoid possible remobilisation of dissolved metals in the environment at the site of disposal.

The final sludge resulting from the ambient temperature ferrite process here described meets all these criteria to a very high degree. The SVI of the sludge comprising both

ferrous and non-ferrous metal intermediates adsorbed onto magnetite seed in the first settler varies from ~2.2 ml/g (no calcium present) to ~25 ml/g (calcium present) to ~60 ml/g (calcium and manganese present). In the latter case a retention time of 30 minutes in the first settler is adequate in order to attain complete liquid-solid separation.

The SVI of the sludge (calcium and manganese present) following exhaustive oxidation is 12.9 ml/g. After a few days the sludge reaches a thick paste-like consistency making it possible to remove all of the clarified supernatant above the compacted solids. Thereafter, at ambient temperature (~18–30 °C), the remaining solids took ~20 days for ‘complete’ desiccation to occur, leaving a hard caked material with a dry density of 1.58 g-Fe/ml or 2.37 g dried sludge/ml.

The final sludge proved to be very stable at low pH losing less than 0.025% mass (mass dissolved Fe/mass total Fe). Non-ferrous metal concentrations in the leachate were also very low (Figure 7.14 and Table 7.11).

Successful operation in the presence of calcium

The problem of calcium interference in ferrite formation has been solved through a combination of a high precipitated ferrous intermediate : dissolved calcium ratio in the oxidation reactor and an adequate aging time of greater than ~3 hours. The first of these conditions is achieved through the incorporation of a contact stabilisation reactor – settler sequence upstream of the oxidation reactor which serves to concentrate the ferrous intermediate relative to dissolved calcium by an initial factor of ~3 times. Thereafter the ferrous intermediate concentration in the oxidation reactor can be raised to any desired value if oxidation is withheld. Once the desired concentration is reached, it can be maintained at steady-state by matching the rate of oxidation to the rate of ferrous intermediate entering the oxidation reactor. It has proven easy to maintain a relatively constant ferrous intermediate concentration in this way, which in turn ensures that ferrite formation is not impeded by the presence of calcium. This solution to the calcium problem sheds little light on the mechanism of calcium interference. The hypothesis that calcium, with an ionic radius of 114 pm, disrupts crystal growth by not easily fitting into the lattice has no experimental

support. Moreover, there are reasons to question this hypothesis. Firstly, Choung et al. (1999) showed that interference only arises when calcium and ferric but not ferrous iron are combined which suggests that the formation of calcium-ferric entity underlies the mechanism of interference. Secondly ferrite containing up to 19 percent calcium (moles calcium : moles magnetite) has been produced which proves that calcium has little difficulty entering and remaining in the lattice without disrupting crystal growth (see Chapter 4).

Following oxidation the freshly formed ferrite flows to the second settler where aging begins. If the retention time in the second settler is adequate, aging can be completed there. Alternately the sludge can be transferred to an aging tank from where a fraction of the now well-crystallised ferrite sludge is recycled to the contact stabilisation reactor.

Successful non-ferrous metals removal

The formation of the ferrite magnetite from AMD at ambient temperature was motivated by the known property of magnetite to accept non-ferrous metal ions into its crystal lattice and thereby remove both ferrous and non-ferrous metals from the AMD. The process here described has been successfully tested in this regard, in the presence of calcium, for Co, Ni, Zn and Mn with an aging period of 24 hours. One hundred percent removal of Co and Zn was observed. Ni and Mn removal was seen to steadily increase as the process moved towards steady-state with respect to these metals. McKinnon et al. (2000) produced evidence indicating the generic nature of seeded ambient temperature ferrite formation with respect to non-ferrous metals. In Figure 4.10 in Chapter 4 the percentage yield of magnetic precipitates increase along the same curve irrespective of the identity of the non-ferrous metal present (ie. Zn, Cu, Ni, Mn or Al) (McKinnon et al. 2000).

Operational and economic viability

The ambient temperature ferrite process developed during the course of this research should be relatively simple to put into practice for treatment of AMD streams. The process has several advantages over the currently deployed HDS process. The chief

factor making the ambient temperature ferrite process superior to the HDS process is the ease whereby well-crystallised end-products of oxidation with good settling properties are achieved. Some of the major advantages of the ambient temperature ferrite process are given below:

- Incoming AMD first encounters the contact stabilisation reactor – settler sequence which immediately reduces the volume of AMD requiring treatment by 60–70%, which translates into significantly reduced infrastructure and energy costs. In the HDS process, the entire AMD volume must pass through the entire reactor sequence and precipitated solids are recycled from 10 to 30 times (10 kg to 30 kg solids recycled for every 1 kg newly precipitated solids). Since fresh sludge density is generally less than 20%, this means that large volumes of water must be recycled too (Zinck and Griffith 2000).
- Unlike the HDS process, no polymer flocculating agents are required.
- Unlike the HDS process, where pure oxygen is sometimes required to ensure an adequate oxidation rate such as at Grootvlei Mine in Gauteng, South Africa (own observation), in the ambient temperature ferrite process only air is ever required.
- The final ferrite sludge consisting mainly of high quality magnetite is a valuable product worth more than US\$110/ton (Lines, pers. comm). Coal preparation plants are a major user of magnetite for the washing of coal and the largest and most modern coal preparation plants in the world are in South Africa (Lines, pers. comm). Magnetite is also used as a feed substance in the making of steels.
- The ambient temperature ferrite process described here can operate on any scale and is as applicable to the treatment of a dissolved metals-containing waste stream stemming from an industrial process as it is to AMD.

- If desired the process can be modified such that following the contact stabilisation reactor – settler sequence, the now concentrated adsorbed solid metal intermediates can be re-dissolved and the metals recovered separately by other means.
- Operation of the ambient temperature ferrite process has simple technological requirements. Apart from appropriately designed reactors, settlers, pumps and conduits only a minimum of other process control entities are needed, viz.:
 1. pH control.
 2. Aeration control including dissolved oxygen metering.
 3. On-site ferrous and total iron measuring capability. Apart from a visible light spectrophotometer (costing ~R20 000) these measurements require only very basic laboratory equipment and can be very easily and rapidly performed.
 4. Off-site non-ferrous metals analysis (weekly or monthly or as desired).

Gypsum precipitation (pH 10.5): Initially, the commonest cause of malfunction in the laboratory were blockages caused by small amounts of gypsum (CaSO_4) crystals settling at the base of the first settler and clogging the entrance of the conduit carrying the underflow to the oxidation reactor. This problem was solved by elevating the pick-up pipe a small distance above the bottom of the settler so that the gypsum responsible for the blockages bypassed it and settled below. Build-up of this residue was easily avoided by draining a small amount of liquor from a port at the very bottom of the settler every few days.

As a result of the rapid precipitation kinetics of gypsum, almost all gypsum formation occurred on the walls of the contact-stabilisation reactor and to a lesser extent on the walls of the first settler. No fouling of the main oxidation reactor, second settler, batch (exhaustive oxidation) reactor or any other component occurred. The build-up of

gypsum in the contact stabilisation reactor did not present any problems during the course of these experiments but would have to be dealt with in an operational reactor in the long term. Existing methods of prevention of gypsum build-up as used in the HDS process for example should function equally well in the ambient temperature ferrite process. Implementation of the ambient temperature ferrite process therefore poses no technical difficulties. Furthermore, much of an existing HDS plant infrastructure could be readily converted to ambient temperature ferrite formation.

Calcium carbonate precipitation (pH 12): At pH 10.5 no calcium carbonate precipitation was observed whereas at pH 12 it was macroscopically observed on the surface of the effluent waste tank. This can be ascribed to CO_2 absorption resulting in high concentrations of CO_3^{2-} .

Future research needs

The aim of the investigations described in this report has been to pave the way towards an ambient temperature ferrite process for removal of metals from AMD. As such many details have been overlooked or passed by on the way. The emphasis of this work has been practical rather than theoretical and engineering goals have taken precedence over scientific ones. With this in mind the following factors are identified as priority areas for further research.

Additional studies of non-ferrous metals removal: Al, Mg, Cr and Pb should be prioritised and the question of removal of radioactive uranium found in some South African AMDs should be investigated. Should the ambient temperature ferrite process described here successfully remove uranium species from AMD, safe disposal of the resulting radioactive ferrite sludge will need to be considered.

Optimisation studies: This applies to oxidation rates in both oxidation reactors; to the operational pH in each compartment, especially when Mn is present; to the presence of 'fines' in the effluent, to aging times and to ferrous intermediate and seed concentrations in varying non-ferrous metal contexts. The effect of percentage ferrous of the ferrite end-product on non-ferrous metals removal also requires optimisation.

In addition, the concentrations of iron and non-ferrous metals in the effluents from both settlers and in the supernatant of the second oxidation reactor following exhaustive oxidation, need to be optimised in accordance with the Target Water Quality Ranges (TWQR) set by the South African Department of Water Affairs and Forestry (DWAF 1996). However if the effluents from these sources are all subjected to a sulphate removal process (Ristow et al. 2004) the implications and fate of residual metal concentrations must be considered in this context.

Calcium carbonate and calcium sulphate: Calcium solubility with respect to both sulphate and carbonate should be theoretically modelled, taking complex formation into account. Complete calcium, sulphate and carbonate mass balances should be performed at steady-state at both pH 10.5 and pH 12 so that calcium solubility and precipitation under steady-state conditions can be compared to theoretically derived values.

Additional applications: Applications to specialised industrial waste-waters containing dissolved metals should be investigated. The potential for using the process for the production of specialised ferrites as required by the electronics or nano-industries should be investigated (Chinnasamy et al. 2002, Perales Perez et al. (2001b).

In final conclusion, conditions for ferrite formation from AMD-like waters have been established in both the presence and absence of calcium, as well as in the presence of calcium *and* significant concentrations of non-ferrous transition metals commonly found in AMD (Co, Ni, Zn, Mn). This represents the first well-described proven demonstration of a continuous flow, steady-state ambient temperature ferrite process in which lime can be used as the pH-elevating agent. The process relies on:

- The property of magnetite/ferrite seed to channel the end-products of oxidation of ferrous solutions in the presence of calcium towards magnetite/ferrite formation.
- A contact stabilisation reactor – settler sequence which enhances the ferrous intermediate : dissolved calcium ratio in the oxidation reactor serving, together with aging, to overcome the problem of calcium interference with ferrite formation.

The feasibility of the process for metals removal from AMD is borne out by a number of robust results pertaining to the quality of the effluent and the density and stability of the resulting sludge. Furthermore there are several features of the process as here described which render it economically attractive in comparison with existing technologies. These include significantly reduced energy, infrastructure and chemical costs as well as a commercially valuable end-product.

References

- APHA (1998) *Standard methods for the examination of water and wastewater*, 20th edition.
- Ardizzzone S, Formaro L, Sivieri E, Burriesci N and Petrera M (1983) Preparation and characterization of magnetite samples having different stoichiometric compositions, *J. Chem. Soc. Faraday Trans. I.* **79**, 2449–2456.
- Aube BC and Zinck JM (1999) Comparison of AMD treatment processes and their impact on sludge characteristics. Paper presented at *Mining and the environment II, Sudbury '99*. September 12–16, 1999, at Sudbury, Ontario, Canada.
- Barrado E, Prieto F, Vega M and Fernandez-Polanco F (1998) Optimisation of the operational variables of a medium scale reactor for metal containing wastewater purification by ferrite formation. *Wat. Res.* **32**(10), 3055–2061.
- Blesa MA and Matijevic E (1989) Phase transformations of iron oxides, oxo-hydroxydes, and hydrous oxides in aqueous media. *Advances in colloid and interface science*, **29**, 173–221.
- Chinnasamy CN, Jayedevan B, Perales-Perez O, Shinoda K, Tohji K and Kasuya A (2002) Growth dominant co-precipitation process to achieve high coercivity at room temperature on CoFe_2O_4 nanoparticles, *IEEE transactions on magnetics*, **38**(5).
- Choung JW, Xu Z and Finch JA (1999) Advances in the ambient temperature ferrite process applied to acid mine drainage treatment. *Environmental Technology* **21**, 201–207.
- Cornell RM and Schwertmann U (1996) *The iron oxides: structure, properties, reactions, occurrence and uses*. VCH: Germany.

- Cuttler AH, Cranshaw TE, and Longworth G (1990) A Mössbauer study of green rust precipitates: 1. Preparations from sulphate solutions. *Clay Minerals*, **25**, 289–301.
- Daskalakis KD and Heltz GR (1992) *Environ. Sci. Technol.* **26**, 2462.
- Desillier J, Govaert A, De Grave E, Chambaere D and Robbrecht G A (1977) Mossbauer study of Ca^{++} -containing magnetites. *Phys. Stat. Sol. A* **43**, 619–624.
- Drissi SH, Refait P, Abdelmoula M and Genin JMR (1995). The preparation and thermodynamic properties of Fe(II)-Fe(III) hydroxide carbonate (green rust 1); pourbaix diagram of iron in carbonate-containing media, *Corrosion Science* **37**(12), 2025–2041.
- Dryssen D and Kremling K (1990) Increasing hydrogen sulphide concentration and trace metal behavior in the anoxic baltic waters. *Mar. Chem.* **30**, 193–204.
- DWAF (1996) *South African water quality guidelines, vol. 7, Aquatic ecosystems*. First edition, 1996. Department of water affairs and forestry.
- Fox LE (1988) The solubility of colloidal ferric hydroxide and its relevance to iron concentrations in river water. *Geochim. Cosmochim. Acta* **52**, 771–777.
- Genin JMR, Olowe AA, Refait PH, Simon L (1996) On the stoichiometry and pourbaix diagram of Fe(II)-Fe(III) hydroxyl-sulphate or sulphate-containing green rust 2: an electrochemical and mossbauer study. *Corrosion Science* **38**(10), 1751–1762.
- Gorter EW (1954) Saturation magnetization and crystal chemistry of ferromagnetic oxides. *Philips Res. Rep.* **9**, 295, 321 and 403.
- Gustafsson JP (2004) Visual Minteq, version 2.31, , available from:
<http://www.lwr.kth.se/english/OurSoftware/Vminteq/index.htm>)
- Hansen HCB, Borggaard OK, and Sorensen J (1994) Evaluation of the free energy of formation of Fe(II)-Fe(III) hydroxy-sulphate (green rust) and it's reduction to nitrite. *Geochimica et Cosmochimica Acta* **58**(12), 2599–2608.

- Jolivet J and Tronc E (1988) Interfacial electron transfer in colloidal spinel iron oxide. Conversion of Fe_3O_4 - $\gamma\text{Fe}_2\text{O}_3$ in aqueous medium. *J. of Colloid and Interface Sci.* **125**(2), 688–700.
- Kampeis P, Franzreb M and Eberle SH (1996) Conditions of the formation of zinc-bearing ferrites in regard of heavy metal removal from wastewater by magnetic separation. *Acta hydrochim. hydrobiol.* **24**(2), 61–67.
- Kanzaki T, Kikuchi K, Sato M et al. (1996) Formation of manganese- and manganese,zinc-bearing ferrites by oxidation of aqueous suspensions and analysis of their cation distributions, *J electron spectroscopy and related phenomena* **77**, 221–232.
- Kanzaki T, Doi K et al. (1998) Formation of nickel and nickel, zinc-bearing ferrite in aqueous suspension by air oxidation. *Journal of electron spectroscopy and related phenomena* **97**, 225–234.
- Katsura T, Tamaura Y and Terada H (1977) Treatment of the laboratory wastewaters by the magnetic separation process. *Indust. Water* **233**, 16–21.
- Kiyama M (1974) Conditions for the formation of Fe_3O_4 by the air oxidation of $\text{Fe}(\text{OH})_2$ suspensions. *Bulletin of the chemical society of Japan*, **47**(7), 1646–1650.
- Kleinmann R L P, Crerar D A and Pacelli R R (1981) Biogeochemistry of acid mine drainage and a method to control acid formation. *Mining Engineering* **33**(3), 300–305.
- Lahav O, Morgan BE, Hearne G and Loewenthal RE (2003) One-step ambient temperature ferrite process for treatment of acid mine drainage waters. *Journal of Environ. Eng.*, **129**(2), 155–161.
- Loewenthal RE, Morgan BE, and Lahav O (2000) Iron and heavy metals in acid mine drainage waters – equilibrium and treatment considerations. Proceedings of the WISA Anaerobic Processes Division – Technology Transfer Workshop. August 2000, Pretoria.

- Mandaokar SS, Dharmadhikari DM and Dara SS (1994) Retrieval of heavy metal ions from solution via ferritisation. *Environmental Pollution* **83**, 277–282.
- McKinnon, W, Choung JW, Xu Z and Finch JA (2000) Magnetic seed in ambient temperature ferrite process applied to acid mine drainage treatment. *Env. Sci. Technol.* **34**, 2676–2581.
- Millero FJ (1985) The effect of ionic interactions on the oxidation of metals in natural waters. *Geochimica et cosmochimica acta* **49**, 547–553.
- Misawa T, Hashimoto K and Shimodaira (1974) The mechanism of formation of iron oxide and oxyhydroxides in aqueous solutions at room temperature. *Corrosion Science* **14**, 131–149.
- Miyata S (1983) Anion-exchange properties of hydrotalcite-like compounds. *Clay Minerals* **31**, 305–311.
- Morgan BE, Loewenthal RE and Lahav O (2001) Fundamental study of a one-step ambient temperature ferrite process for treatment of acid mine drainage waters. *Water SA*, **27**(2), 277–282.
- Morgan B, Lahav O, Hearne GR and Loewenthal RE (2003) A seeded ambient temperature ferrite process for treatment of AMD waters: magnetite formation in the presence and absence of calcium ions under steady state operation. *Water SA* **29**(2), 117–124.
- Mullin JW (2001) Crystallisation, 4th edition. Butterworth Heineman, Oxford.
- Navratil JD (1986) Radioactive waste management at rocky flats. In Lc Ainslie (ed.), *Radwaste '86 conference on treatment and containment of radioactive waste and its disposal in arid environments, 1986*. Atomic energy corporation of South Africa, 635–643.
- Olowe AA and Genin MR (1991) The mechanism of oxidation of ferrous hydroxide in sulphated aqueous media: importance of the initial ratio of the reactants. *Corr. Science* **32**(9), 965–984.

- Perales Perez O, Umetsu Y and Sasaki H (1998) Precipitation and densification of magnetic iron compounds from aqueous solutions at room temperature. *Hydrometallurgy* **50**, 223–242.
- Perales Perez O, Tohji K and Umetsu Y (1999) Ambient-temperature synthesis of metal-bearing ferrites: how and why? *Journal of Alloys and Compounds* **290**, 129–136.
- Perales Perez O and Umetsu Y (2000) ORP-monitored magnetite formation from aqueous solutions at low temperatures. *Hydrometallurgy* **55**, 35–56.
- Perales Perez O, Tohji K and Umetsu Y (2001a) Theory and practice of the removal of heavy metal ions by their precipitation as ferrite-type compounds from aqueous solution at ambient temperature. *Metallurgical review of MMIJ, The mining and materials processing institute of Japan*, **17**(2)137–180.
- Perales Perez O, Sasaki H, Jayadevan B, Hihara T, Tohji K, Sumiyama K and Kasuya A (2001b) Production of monodispersed particles by using effective size selection methods at the nanosize level, in *Proc. Int. Symp. Cluster Assembled Materials*, IPAP Conf. Series 3, 101–104.
- Phillips Expert Data Analyzer (1996-1999) Phillips Electronics N.V.
- Pollard RJ, Cardile CM, Lewis DG, and Brown LJ (1992) Characterization of iron oxyhydroxide polymorphs and ferrihydrate using low-temperature, applied-field, Mossbauer spectroscopy. *Clays and Clay Minerals*, **27**(1), 57–71.
- Radovenchik, V M, Shutko, A P, and Gomelya, N D (1995) Water treatment using magnetic fields. *Journal of Water Chemistry and Technology* **17**(5), 23–40.
- Regazzoni AE, Urrutia GA, Blesa MA and Maroto AJG (1981) Some observations on the composition and morphology of synthetic magnetites obtained by different routes. *Inorganic and nuclear chemistry* **43**, 1489–93.

- Ristow NE, Sötemann SW, Wentzel MC, Loewenthal RE and Ekama GA (2004) The effects of hydraulic retention time and feed COD concentration on the rate of hydrolysis of primary sewage sludge. Presented at 10th World congress on anaerobic digestion, Montreal, Canada, 29 Aug. – 2 Sept. 2004.
- Sauls BL and Sauls FC (1998) In Close packed structures: face centered cubic (fcc) or cubic close packed (ccp), www.kings.edu/~chemlab/vrml/clospack.html.
- Schwertmann U and Cornell RM (1991) *Iron Oxides in the Laboratory --Preparation and Characterisation*, VCH, Weinheim-Germany .
- Schwertmann U and Fechter H (1994) The formation of green rust and its transformation to lepidocrocite. *Clays and Clay Minerals* **29**, 87–92.
- Schwertmann U and Murad E (1990) The influence of aluminium on iron oxides: xiv. Al-substituted magnetite synthesized at ambient temperatures. *Clays and Clay Minerals* **38**(2), 196–202.
- Scott (1995) Flooding of central and east rand gold mines: an investigation into controls over inflow rate, water quality and the predicted impacts of flooded mines. *South African Water Research Commission Report No. 486/1/95*.
- Shannon RD (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst. A* **32**, 751–767.
- Sidhu PS, Gilkes RJ and Posner AM (1978) The synthesis and some properties of Co, Ni, Cu, Mn and Cd substituted magnetites. *J. inorg. Nucl. Chem.* **40**, 429–435.
- Sidhu PS, Gilkes RJ and Posner AM (1980), The behaviour of Co, Zn, Ni, Cu, Mn and Cr in magnetite during alteration to maghemite and hematite. *Soil Sci. Soc. Am. J.* **44**, 135–138.
- Smit J and Wijn H P J (1959) *Ferrites: physical properties of ferrimagnetic oxides in relation to their technical applications*. Wiley: New York.

- Söhnel O and Garside J (1992) *Precipitation: basic principles and industrial applications*. Butterworth Heineman, Oxford.
- Stevens JG, Khasanov AM, Miller JW, Pollak H and Li Z (1998) *Mössbauer Mineral Handbook*. Mössbauer Effect Data Center.
- Stumm W and Morgan JJ (1970) *Aquatic chemistry*. Wiley-Interscience: New York.
- Stumm W and Morgan JJ (1996) *Aquatic chemistry*. John Wiley & Sons: New York.
- Sugimoto, T and Matijevic, E (1980) Formation of uniform spherical magnetite particles by crystallization from ferrous hydroxide gels. *Journal of colloid and interface science* **74**(1), 227–243.
- Tamaura Y (1985) Zn(II)-bearing green rust and its spontaneous transformation into Zn(II)-bearing ferrite in aqueous solution. *Bull. Chem. Soc. Jap.* **58**, 2951–2954.
- Tamaura Y (1986) Ni(II)-bearing green rust and its spontaneous transformation into Ni(II)-bearing ferrites. *Bull. Chem. Soc. Jap.* **59**, 1892–1832.
- Tamaura Y, Yoshida, T, Katsura T (1984) The synthesis of green rust II ($\text{Fe}^{\text{III}}_1\text{-Fe}^{\text{II}}_2$) and its spontaneous transformation into Fe_3O_4 . *Bull. Chem. Soc. Jap.* **57**, 2411–2416.
- Tamaura Y, Katsura T, Rojarayanont S, Yosida T, and Abe H (1991a) Ferrite process; heavy metal ions treatment system. *Wat. Sci. Tech.* **23**, 1893–1900.
- Tamaura Y, Tu PQ, Rojarayanont S, and Abe H (1991b), Stabilization of hazardous materials into ferrites. *Wat. Sci. Tech.* **23**, 399–404.
- Topkin Y V, Roda I G, Anfinogenov N V and Prishchep N N (1990) Removal of heavy metal ions from solutions by the ferrite method. *Khimiya I Tekhnologiya*, **12**(10), 895–897.
- Vandenbergh RE, De Grave E, Landuydt C and Bowen LH (1990) Some aspects concerning the characterization of iron oxides and hydroxides in soils and clays. *Hyperfine Interactions* **53**, 175.

- Wang W, Xu Z and Finch (1996) Fundamental study of an ambient temperature ferrite process in the treatment of acid mine drainage. *Env. Sci. Technol.* **30**, 2604–2608.
- Wehrli (1990) Redox reactions of metal ions at mineral surfaces. In W. Stumm (ed.), *Aquatic Chemical Kinetics*. Wiley-Interscience: New York.
- Wittmann GTW and Förster U (1977) Heavy metal enrichment in mine drainage: iv. The orange free state goldfield. *South African Journal of Science* **73**, 374–378.
- Yang K, Misra M and Mehta R (1994) Removal of heavy metal ions from acid mine water by ferrite coprecipitation process. In Misra, M (ed.), *Separation Processes: Heavy Metals, Ions, and Minerals*. The Minerals, Metals and Materials Society.
- Zinck JM and Griffith WF (2000) An assessment of HDS-type lime treatment processes—efficiency and environmental impact. In Proceedings from the fifth international conference on acid rock drainage **II**, 261–270. May 21–24, Denver, Colorado. Society for mining, metallurgy, and exploration, Inc.