

BIO-MEDIATED SYNTHESIS OF MONODISPERSE HEMATITE NANOPARTICLES FROM PYRITE

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A dissertation submitted to the Faculty of Engineering and the Built Environment,
University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for
the Degree of Master of Science in Engineering.

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DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted to the University of the Witwatersrand, Johannesburg for the Degree of Master of Science in Engineering. It has not been submitted before for any degree or examination in any other University.

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..... day of 2010

ABSTRACT

Acidianus spp. a thermophilic bacteria which can oxidize sulphide minerals was used to oxidize pyrite, FeS_2 resulting in the production of acidic ferric sulphate solutions. The ferric sulphate solutions were aged through a forced hydrolysis process at different pH conditions to yield a variety of iron oxide and basic sulphate precipitates. The precipitates were characterized by XRD, SEM and BET analysis. Potassium jarosite was formed as the main phase under acidic conditions whilst maghemite $\gamma\text{-Fe}_2\text{O}_3$ was precipitated as the main phase at a pH of 6-7. Magnetite Fe_3O_4 was formed as the main phase at a pH of 7-8 as well as a pH of 8-9. Spherical globular aggregates of magnetite nanoparticles of high purity and a surface area of $20.77\text{m}^2/\text{g}$ were precipitated at a pH of 7-8. Hematite $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles were then produced via an oxidative transformation of the precursor magnetite nanoparticles at 600°C . The spherical hematite nanoparticles had a surface area of $18.69\text{m}^2/\text{g}$ and a pore volume of $0.0698\text{cm}^3/\text{g}$. This process can thus provide a cheaper alternative for the production of hematite nanoparticles. Hematite nanoparticles have a wide range of uses in fields such as electronics, optics and biomedicine. The findings can be used in acid mine drainage treatment and other systems where iron removal is problematic.

PUBLICATIONS AND PRESENTATIONS

Some of the findings from this research have been published in the following journals and/or presented at the following conference sessions.

Journal Publications

1. **Mchibwa, K. A.**, Ndlovu, S. and Iyuke, S. Precipitation of iron oxyhydroxides and basic sulphates from bioleach liquors generated by thermophilic micro-organisms. *Advanced Materials Research Vols. 71-73 (2009) pp 453-456*
2. **Mchibwa, K. A.**, Ndlovu, S. and Iyuke, S. Characterization of biogenic precipitates formed from the forced hydrolysis of bioleach liquors under different pH conditions. *Submitted.*

Conference Proceedings

- 1 **Mchibwa, K. A.**, Ndlovu, S. and Iyuke, S. Precipitation of iron oxyhydroxides and basic sulphates from bioleach liquors generated by thermophilic micro-organisms. IBS 2009 18th International Biohydrometallurgy Symposium. Bariloche, Argentina, 13-17 September 2009.

DEDICATION

To my family; Tecla, Farai, Tatenda, Tapiwa
&
The loving memory of my father
Munyaradzi Martin.

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Chapter 1

Introduction

1.1 Background

In hydrometallurgical extraction processes, the classic sequence involves extraction of the ore from the mine followed by size reduction where the ore is ground and milled to a size amenable to subsequent processing stages. Usually a lixiviant is used to dissolve the valuables during the leaching process. The leach liquor is then filtered to separate the solid residue remaining from the leach solution. The valuables are recovered from either the solid residues or the filtrate depending on the nature of the particular extractive process for the metal in question. In most cases where the metal is recovered in the solid form, an intermediate production step has to be set up by the client to facilitate reprocessing into a form which can be used by the end market. This intermediate production step allows reprocessing of the solid metal into a new product structure which easily undergoes material development and thus becomes functional for the end user.

In most present industrial setups, this stage generally involves melting or redissolving the solid metal phase followed by material synthesis, mostly to generate micro and nanoparticles that can be worked with or applied to different scientific fields. However, working with high temperatures can have high capital and operational costs and also impact negatively on the environment. A gap therefore usually exists in most processing systems between the metal extraction process and the final end product manufacturing. If, however, this gap could be bridged by the creation of a hydrometallurgical extraction and refining technique that can generate micro and nanoparticles directly from the process solutions, a lot of these concerns can be alleviated. In addition, the sustainability of hydrometallurgical processes can be given a new meaning.

The term *iron oxides* is a group name for iron oxyhydroxides and oxides (Gotic & Music, 2007). Altogether, there are 16 known iron oxides which include the oxides wustite, FeO; magnetite, Fe₃O₄; hematite, α -Fe₂O₃; maghemite, γ -Fe₂O₃, the oxyhydroxides goethite, α -FeOOH; akaganeite, β -FeOOH and the hydroxide, bernalite Fe(OH)₃. Iron oxides are very vital basic materials whose preparation has been studied extensively by many workers (Kandori et al., 2008). The preparation of ferric or iron oxides has generated a lot of interest in research principally due to two reasons. The first reason being of an academic nature, since iron oxide systems can be used as model systems in the study of surface and colloidal properties of metal oxides. Secondly, iron oxides themselves are of prime importance as chemical materials which find extensive applications in various fields (Liu et al., 2005). The preparation of iron oxide sols is one example of a process whose potential gap-bridging benefits could be studied. The possibility of forming iron oxide nanoparticles directly in process solutions without melting or redissolving the solid metal phase will be explored in this study.

Most of the work which has been carried out by researchers on the preparation of ferric oxides and ferric hydroxides, has been done with the starting material for the preparation being a dilute solution of ferric salt, mostly FeCl₃ (Matijevic & Scheiner, 1978; Masataka et al., 1984; Meyer et al., 2000). Matijevic and Scheiner, (1978) and Masataka et al., (1984) for instance, have prepared hematite particles from the forced hydrolysis of highly acidic dilute solutions of ferric chloride salts at elevated temperatures. However, because of the extremely dilute systems (mostly of the order 10⁻³ -10⁻²M FeCl₃) used to avoid tremendous coagulation, when these particles are now produced as ideal materials on an industrial scale, exceedingly low productivity or high cost becomes a big factor. The adoption of this process at industrial scale has therefore been negated.

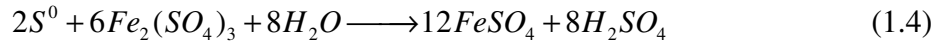
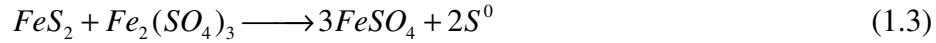
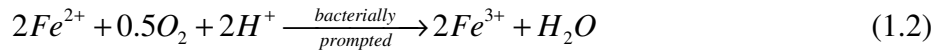
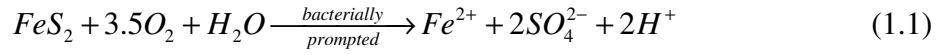
The interactions between microorganisms and metals have been well documented in literature (Beveridge et al., 1997, Crundwell 2003, Rawlings 2004) and the ability of microorganisms to extract and or accumulate metals is already exploited in

biotechnological processes such as bioleaching and bioremediation (Berry & Murr, 1978; Bennet & Tributsch, 1978; Kargi & Robinson, 1985; Keller & Murr, 1978; Edwards, 1998; Evangelou & Zang, 1994; Ndlovu & Monhemius, 2003). The chief process in biooxidation of metal sulphides is the mobilization of metal constituents accomplished through microbially prompted oxidation of the metal sulphide. Microorganism extraction is becoming increasingly important since it is generally more environmentally friendly and less energy intensive than most conventional physicochemical extraction processes. Whenever a mineral is amenable to bioleaching it becomes possible to extract it even from very low grade ores. Pyrite, FeS_2 is the most common sulphide ore and forms under almost all known conditions of mineral deposition. It is cheap and widely available and the bioleaching of pyritic ores to produce iron sulphate solutions is well established. The biologically generated iron sulphate solutions exist in concentrations relatively higher than those used in the conventional methods of ferric oxide sols generation. Thus the problems associated with the chemical synthesis of hematite production (dilute solutions and high costs) can be alleviated if the ferric salt used as the precursor for hematite production is obtained through the bioleaching of pyrite.

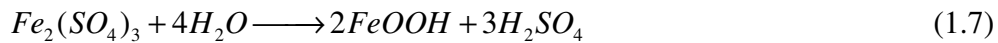
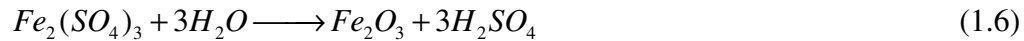
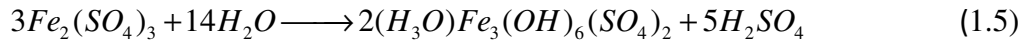
Ferric sulphate solutions generated economically through the bioleaching process can be used as a precursor material to form ferric oxyhydroxides and subsequently hematite nanoparticles. The generation of such sols through ferric salts generated in part or wholly through bacterial oxidation is a relatively new area of research (Wang et al., 2007; Gramp et al., 2008). These workers studied the precipitate sols formed when ferrous sulphate solutions, prepared from reagent-grade chemicals were inoculated with *Acidithiobacillus ferrooxidans* and *Sulfolobus* microorganisms. This study differs from their work in that the iron sulphate solutions used here were generated from pyrite ore biooxidation. The iron oxide sols were also formed from the iron sulphate solutions in a separate aging stage via a forced hydrolysis process. As alluded to earlier, the concentrations of the ferric salt solutions generated in this

work, were of relatively higher concentrations than those used by most workers who have studied the preparation of iron oxide sols from mostly reagent grade chemicals.

In literature, (Rossi, 1990) pyrite oxidation has been described by the following equations



The ferric ion formed during pyrite oxidation is easily hydrolysable and when subjected to forced hydrolysis, the ferric sulphate solutions form ferric oxyhydroxide precipitates (Equation 1.5 to 1.7). In their studies on the forced hydrolysis of ferric sulphate, Umetsu, et al, (1977) showed that a variety of iron hydroxy-sulphates and oxides such as hydronium jarosite, hematite and goethite could be precipitated. The extent of hydrolysis depends on a number of factors, with the pH, ferric ion concentration and temperature being the most influential (Umetsu et al., 1977, Grishin et al., 1988, Kandori et al., 2004).



Thus leach liquors produced from the bacterial oxidation of pyrite can be used as the precursor ferric salt, from which ferric oxyhydroxides can be generated. These ferric oxyhydroxides can then be used as the intermediaries for hematite nanoparticles formation. Nanotechnology is revolutionizing the design of materials in numerous fields of industrial application since the properties of nanostructures are distinct from

the properties exhibited as the bulk-material. Nanoparticles have attracted considerable attention in the recent past due to their interesting size-dependent properties and versatile uses attributed to their smallness. Properties of materials change as their size approaches the nano-scale due to aspects of the surface of the material dominating the properties in lieu of the bulk properties. The synthesis of monodispersed nanoparticles is the ultimate goal for general advanced particulate materials. Hematite nanoparticles which are the ultimate product of interest have a wide range of potential applications in fields such as biomedicine, optics and electronics. Hematite nanoparticles can be used as electromagnetic devices, modern ceramics, catalysts, pigments, photosensitive materials and cosmetics as the properties of these materials critically depend on their size, shape and structure.

1.2 Problem Statement

Most of the work which has been carried out by researchers on the preparation of monodisperse hematite, has been done with the starting material for the preparation being a dilute solution of ferric salt, mostly FeCl_3 (Matijevic & Scheiner, 1978, Masataka et al., 1984, Meyer et al., 2000). These production methods have proved largely unsuccessful for the adoption of hematite production on industrial scale due to their low productivity and high costs. If however the ferric salt can be prepared at a high concentration from an easily available and cheap material under conditions which favour the subsequent nucleation stage, then the low productivity and high costs which negate the successful production of monodisperse hematite at industrial scale can be avoided. This work investigates the feasibility of pyrite to hematite transformation via the bio-production of a ferric salt which can then be used as a precursor material.

1.3 Objectives of the Study

The preparation of monodisperse hematite from dilute ferric salts, particularly FeCl_3 has been studied extensively by researchers in this field. In this study, however we

propose to prepare hematite from the bacterial oxidation of pyrite. Initially pyrite will be biologically leached using *Acidianus spp.*, a thermophilic bacteria to produce a leach liquor. The leach liquor, mainly ferric sulphate, obtained from this bacterial oxidation will then be filtered and aged under conditions which will promote the production of ferric oxyhydroxides. These oxyhydroxides will then be converted ultimately to hematite nanoparticles. The specific aims of this work are to

- Investigate the feasibility of bacteria accelerated pyrite to hematite transformation.
- Establish the conditions (pH and concentration of ferric ions) under which the forced hydrolysis/aging of ferric sulphate yields ferric hydrous sols which can be used as precursor materials for hematite nanoparticle production.
- Investigate the conditions necessary for the phase transformation of the generated ferric hydrous sols to hematite nanoparticles.

1.4 Hypothesis

The development of a process which uses thermophilic bacteria to solubilize pyrite with the subsequent production of hematite nanoparticles from the resulting leach liquor.

1.5 Dissertation Layout

The introduction and background to the research is outlined in chapter 1. In chapter 2 a survey of literature is presented. Here the uses of hematite nanoparticles, the end-

product of interest in this research are explored, and the biological backdrop of the research is delved into. This includes the mechanisms of bacterial leaching, the various micro-organisms used in biohydrometallurgy, pyrite oxidation and factors which affect this process and the phase transformations diagrams showing the stability regions for the various iron oxides. The survey will also cover the main preparation methods which have been used to form hematite from ferric salts, and include such aspects as the theory on precipitation and hydrolysis as well as the forced hydrolysis of ferric salts at elevated temperatures. Chapter 3 will include the materials, methods, experimental procedures and analytical techniques used in the biooxidation of pyrite, aging of leach liquors to form iron oxyhydroxides as well as the transformation of these oxyhydroxides to ultimately form hematite nanoparticles.

Chemical aging tests were done on acidic $\text{Fe}_2(\text{SO}_4)_3$ systems and formed the basis on which the biogenic studies were conducted. The results and discussion on the chemical aging tests will be given in the fourth chapter. The findings from the biogenic studies are presented in Chapter 5.

The focus in chapter 6 is mainly on the optimization of the crucial factors which affect the hydrolysis reaction during aging. In this chapter, a detailed account of the optimization of the pH and iron concentration and their effects on the nature of precursor precipitate formed during aging was given. An account of the solid state transformation of the precursor bioprecipitates to hematite is presented in Chapter 7. This penultimate chapter will also include the optimization of the hematite nanoparticle production stage and size control. Finally, the main conclusions drawn from the research, future work and recommendations will be laid out in Chapter 8. A list of references and appendices is given at the end of the dissertation.

Chapter 2

Literature Review

2.1 General Introduction

The ultimate aim of this study is to produce α -Fe₂O₃ hematite nanoparticles. In nanotechnology, a nanoparticle is defined as a minute object which acts as a complete unit in terms of its properties. Many authors have defined a nanoparticle as a particle having at least one dimension $< 1\mu\text{m}$ (Borm et al., 2006). Nanotechnology has been dubbed the manufacturing technology of the future. As particles approach the nano-scale their surface material properties become more dominant than the bulk material properties and they begin to exhibit unusual and fascinating properties. Iron oxide nanoparticles have a wide range of applications and their synthesis is the ultimate goal for general advanced particulate systems.

This literature review will include information on pyrite oxidation and factors affecting it. Pyrite biooxidation is a well established process and yields mainly acidic ferric sulphate solutions. This biogenic leach liquor which will be primarily acidic ferric sulphate will then be aged under certain conditions to yield a precursor material for hematite nanoparticle production. The preparation methods which have been used to precipitate hematite particles from ferric salt (mainly ferric chloride, FeCl₃) solutions will be reviewed. It is crucial to note that in these cases the ferric salts were prepared mostly from reagent grade chemicals and there are very few cases where biogenic precipitates have been generated. A review of the precipitation processes done on ferric sulphate Fe₂(SO₄)₃ solutions will be included. The factors affecting the precipitation process during aging will be studied. Possible transformation methods to convert the precursor precipitate formed during aging into the desired hematite product will be highlighted. The literature review is expected to provide information that will help in elucidating a possible production route of

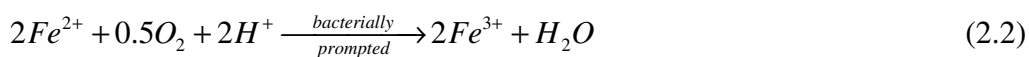
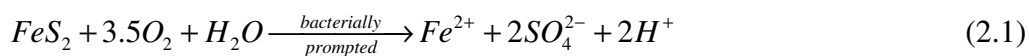
hematite nanoparticles from pyrite biooxidation. The literature review will provide useful guidelines in the methodology and test conditions to be investigated in the experimental work.

2.2 Pyrite Oxidation and Factors Affecting It

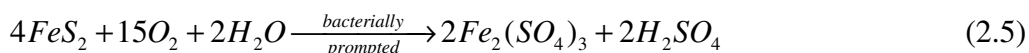
2.2.1 Overview

The dissolution of metals from sulphide ores was initially thought to be a purely chemical process involving reactions between acidic water, atmospheric oxygen and chemical dissolution brought about by sulphuric acid and the ferric ion (Hutchins et al., 1986). The basis of this thinking was questioned following the discovery of acidophilic, iron-oxidizing bacterium in the acid mine drainage of a number of coal mines (Colmer & Hinkle, 1947). This marked the conception of bacterial leaching and its role in the dissolution of sulphidic metal ores. Bacterial leaching is the dissolution of insoluble metal ores, such as metal sulphides by specialized lithoautotrophic bacteria to solutions containing sulphuric acid and other dissolved heavy metals (Ehrlich, 1990). In this section, pyrite oxidation and the various factors affecting it such as microorganisms used in bioleaching and culture medium composition are reviewed.

Iron and sulphur form a wide variety of compounds of the formula Fe_xS_y , the most common being marcasite, pyrrhotite and pyrite. These iron sulphides are characterized by varying extents of chemical stability and solubility depending on their crystal system and the actual ratio of iron to sulphur within the given sulphide. Pyrite, FeS_2 , is cheap and the most abundant sulphidic ore which occurs naturally. Generally, dissolved oxygen or iron (III) ions are oxidizing agents for pyrite in leaching operations and in the environment. Singer and Stumm (1970) have reported that the ferric ion, Fe^{3+} is the major oxidant in the acidic pH region whilst O_2 becomes the primary oxidant at neutral to alkaline pH. In literature, chemical or biological pyrite oxidation by molecular oxygen or by iron (III) ions can be described by the following equations (Rossi, 1990)



The microbial reaction of pyrite results mainly in the production of acidic ferric sulphate and this reaction can be expressed as



2.2.2 Microorganisms Used in Pyrite Oxidation

Bacteria can be generally classified according to the temperature ranges in which they operate most optimally (Barrett et al., 1993) as shown in Table 2.1. Both mesophilic and thermophilic bacteria have been used in pyrite oxidation.

Table 2.1 Classification of chemolithotrophic bacteria according to temperature

Bacterial class	Optimum temperature range/°C
Cyrophiles	<20
Mesophiles	20 – 40
Moderate thermophiles	40 -55
Extreme thermophiles	>55

2.2.2.1 Mesophilic iron and sulphur oxidizing bacteria

The bacteria which are involved in metal sulphide oxidation are sulphur and/or iron oxidizers. They thrive in low pH or acidic conditions and also have the ability to oxidize reduced sulphur compounds (Tuovinen & Kelly 1972). Mesophiles which have been widely studied in pyrite oxidation include *Acidithiobacillus ferrooxidans*, *Acidithiobacillus thiooxidans* and *Leptospirillum ferrooxidans*. These bacteria are obligate chemolithoautotrophs, meaning that they are strictly chemolithoautotrophs. Chemolithoautotrophs are bacteria that have the ability to derive energy via the oxidation of inorganic materials such as minerals.

***Acidithiobacillus ferrooxidans*.** This is an acidophilic chemolithotrophic bacterium which is prevalent in pyrite containing areas (Nordstrom, 1982a). It is a motile, non-sporulating, Gram-negative, rod-shaped bacterium. *A. ferrooxidans* range in size from 0.3 to 0.8µm diameter and in length from 0.9 to 2.0 µm (Barrett et al., 1993). Each bacterium cell achieves motility by means of a single polar flagellum. *A. ferrooxidans* was formerly known as *Thiobacillus ferrooxidans* (Kelly & Wood, 2000). It grows using CO₂ as the sole carbon source and obtains energy from the oxidation of sulphur and reduced sulphur compounds as well as the oxidation of the ferrous ion. This bacterium thrives in an aerobic environment, although it is still able to grow anaerobically with the ferric iron as the terminal electron acceptor and reduced sulphur or metal sulphides or formate as electron donors (Pronk et al., 1991, 1992; Drobner et al., 1990).

***Acidithiobacillus thiooxidans*.** This is a chemolithotrophic acidophilic bacterium. In its morphology it consists of Gram-negative rods (0.4×2.0µm). *A. thiooxidans* is more acid resistant than *A. ferrooxidans* (Kelly & Wood, 2000). It is motile by means of a polar flagellum (Doetsch *et al.*, 1967). *A. thiooxidans* was formerly known as *Thiobacillus thiooxidans* (Kelly & Wood, 2000). It grows in liquid medium on elemental sulfur, thiosulphate or tetrathionate. *A. thiooxidans* cannot oxidize iron or

pyrite but has been shown to grow on a passivating layer of sulphur formed from pyrite leaching in mixed cultures with *Leptospirillum ferrooxidans* (Kelly & Wood, 2000).

***Leptospirillum ferrooxidans*.** These are obligately chemolithotrophic, strictly aerobic, Gram-negative motile bacteria. They are characterized by varying morphology, forming vibrios, spirals, or pseudococci ranging in size from 0.2-0.4 diameter x 0.9-1.1µm length (Rossi, 1990). These bacteria are more acid resistant (Norris, 1983) and more tolerant of high temperatures (20-45°C) than *Acidithiobacillus ferrooxidans* (Rawlings et al., 1999). They obtain energy from the oxidation of reduced iron containing compounds (Rawlings et al., 1999).

2.2.2.2 Thermophilic iron and sulphur oxidizing bacteria

It had been erroneously thought for a long time that *A. ferrooxidans* was the only bacterium capable of sulphide oxidation. This thinking was discounted following the observation that sulphide leaching persisted in copper sulphide and pyrite leach and waste dumps at temperatures well above the active growth range of *A. ferrooxidans* (Lyalikova, 1960). This realization ultimately led to Brock et al., (1972) reporting the existence of a thermophilic bacterium of the genus *Sulfolobus*. There are four genera of thermophilic archaebacteria which can oxidize compounds of sulphur, namely *Sulfolobus*, *Acidianus*, *Metallosphaera* and *Sulfurococcus*. Of these only *Sulfolobus* and *Acidianus* are of importance in biohydrometallurgy (Rossi, 1990).

Acidianus is a genus of thermophilic bacteria and a strain of this archaebacteria will be used in this study. It is aerobic and in its morphological structure consists of coccoid cells 1µm in diameter. The cells are immotile and possess no flagella. *Acidianus* is acidophilic and thrives at an optimum pH of 2 -3. It is extremely thermophilic and grows within a temperature range of 55 to 80°C with optimum growth occurring at 70 to 75°C. *Acidianus* are facultative chemolithoautotrophs and

can grow under autotrophic, mixotrophic or heterotrophic conditions (Barrett et al., 1993). However, they grow more rapidly in mixotrophic conditions in the presence of 0.01-0.02% yeast extract or some other organic compound. *Acidianus brierleyi* has been used extensively in pyrite and chalcopyrite bioleaching (Rossi, 1990). Thermophiles can enhance the solubilization of several metal sulphide ores with varying effectiveness mainly depending on the composition of the growth medium as well as the mineralogy of the solid substrate (Rossi, 1990). Norris and Parrott (1986) successfully utilized *Sulfolobus acidocaldarius*, *Acidianus brierleyi*, and *Sulfolobus solfataricus* in pyrite bioleaching.

The interest shown by many researchers in using thermophilic microorganisms for enhancing the dissolution of sulphide minerals is justified because of a number of reasons. Firstly, in keeping with kinetic principles, sulphide minerals have been leached at higher rates by thermophilic bacteria operating at their optimum temperatures when compared to leaching using mesophilic bacteria. The use of thermophilic bacteria has also resolved some of the operational problems experienced when mesophilic bacteria were utilized in bioprocess operations. A case in point being the temperature increases experienced during the bioleaching of metal sulphide flotation concentrates in stirred tank reactors. In these setups, pronounced increases in temperature have been frequently observed. Mesophilic microbial activity is inhibited at high temperatures and as the temperature increases the mesophiles become prone to being denatured. A possible remedy to this drawback is the installation of cooling coils in the reactors (Parkinson, 1985). The use of thermophilic bacteria eliminates all these operational difficulties and nullifies the extra cooling costs incurred (Rossi, 1990). However, there are a few disadvantages associated with the use of thermophilic microorganisms over mesophiles. These include the extra costs incurred to reach the higher optimum temperatures required for thermophilic activity as well as condensation costs borne to prevent loss of the culture medium due to the greater evaporation rates experienced at the higher temperatures.

2.2.3 Culture Medium

It has already been stated in the preceding section that the culture medium is a key component which determines the effectiveness of sulphide ore biooxidation. A culture medium is a mixture, usually in the form of an aqueous solution of chemical compounds which satisfies all the elemental requirements for cell mass and products of the microorganism. It supplies adequate energy for biosynthesis and maintenance and meets any other specific requirements of the microorganism such as trace elements and vitamins (Rossi, 1990). The culture medium thus constitutes a mineral base, which is the source of all nutrients in inorganic form. These are usually in the form of salts and are referred to as basal salts. Additional supplements which meet the required carbon, energy, nitrogen sources and growth factors are added as required (Rossi, 1990).

The most common medium which has been used in the bacterial oxidation of sulphide minerals has been the 9K Medium (Silverman & Lundgren, 1959). See Appendix A. One of its major drawbacks has been the precipitation of jarosite and sulphates on mineral surfaces during bioleaching. In this study the composition of the medium may also affect the composition of the precipitates formed in the subsequent stage of aging. In the 9K medium the precipitates formed during bioleaching resulted in the formation of encrustations on mineral surfaces which retarded or even inhibited further leaching (Rossi, 1990). Their formation is due to exceedingly high concentrations of K_2HPO_4 and $(NH_4)_2SO_4$ in the 9K medium. A balance has to be struck therefore, in finding a medium whose composition meets the requirements for the bacteria's growth and other physiological requirements whilst simultaneously not providing an environment which is conducive for the formation of inhibitory encrustations. Brock et al., (1972) developed a new culture medium, Medium 88 for thermophilic archaebacteria such as *Acidianus* (Appendix B). The concentrations of the K_2HPO_4 and $(NH_4)_2SO_4$ salts in this medium were significantly lower than in the 9K medium.

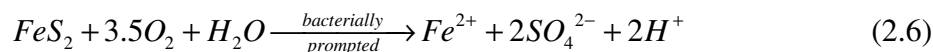
A slightly modified form of this nutrient medium, Medium 88 will be used in this study. This medium has been recommended for thermophilic biooxidation in the Deutsche Sammlung Von Microorganismen and Zellkulturen (DSMZ) catalogue, Braunschweig, Germany which is one of the most extensive databases on microbial studies.

2.2.4 Mechanisms of Leaching

Traditionally there have been two models postulated to explain the mechanisms of microbial action during the oxidation of sulphidic ores; the direct attack mechanism and the indirect attack mechanism. In the direct attack mechanism, it was proposed that the solubilization of the ore occurred via enzyme catalyzed chemical reactions involving physical contact between the ore and microorganism. In the indirect mechanism on the other hand, the solubilization is effected through enzymic or non-enzymic chemical reactions without any physical contact between the microorganism and the mineral ore (Rossi, 1990).

Direct Attack Mechanism

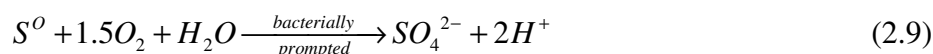
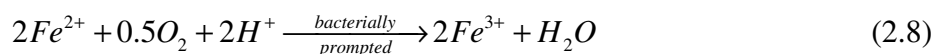
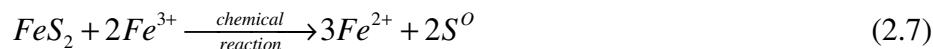
In this mechanism it is proposed that bacteria attach themselves to the ore surface and then subsequently oxidize the sulphur and iron moieties directly through biological means thereby releasing metal ions into solution (Equation 2.6)



Indirect Attack Mechanism

In the indirect mechanism it is assumed that the actual solubilization of the sulphide is brought about by the chemical action of the ferric ion. Ferrous ions serve as the substrate for the iron-oxidizing bacteria, which then regenerates the ferric ion. The

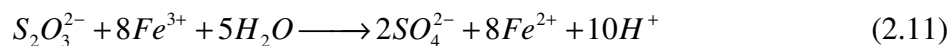
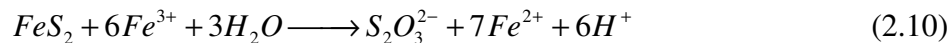
bacteria also oxidize elemental sulphur to sulphate ions. In this mechanism it is therefore not necessary for the bacteria to attach to the mineral surface. The reactions involved are stated in the following equations



Integrated Indirect Model - Thiosulphate and Polythionate Mechanisms

The relevance of the traditional direct and indirect mechanisms has however been called into question following the detection of intermediary sulphur compounds such as sulphite, tetrathionate and thiosulphate during chemical studies of pyrite oxidation (Goldhaber, 1983). The main feature of this integral model is that iron (III) ions and/or protons are the only chemical agents that attack the metal sulphide. Thus, this model is basically ‘indirect’ and the core functions of the bacteria are to i) regenerate the ferric ions and/or protons and ii) concentrate these at mineral/water interface or the mineral/bacterial cell so as to promote the degradation attack (Sand, 2001). Thus cells excrete an exopolymer layer, within which the chemical processes occur. These two indirect mechanisms are the thiosulphate and polysulphide mechanisms (Schippers & Sand, 1999; Sand et al., 2001).

The acid-insoluble metal sulphides namely FeS_2 , MoS_2 and WS_2 , are attacked according to the thiosulphate mechanism. Here, the ferric ion attacks the pyrite producing the thiosulphate. Thiosulphate is however unstable in acidic solutions and undergoes a series of reactions being oxidized to tetrathionate $S_4O_6^{2-}$, disulfane – monosulphonic acid ($HSSO_3^-$), to form sulphate (SO_4^{2-}) and traces of tri- and pentathionate (Schippers et al., 1996). These reactions are summarized in Equations (2.10) and (2.11).



The acid-soluble metal sulphides are degraded via the polysulphide mechanism. Initially the metal sulphide is attacked by protons to form the free metal ions and hydrogen sulphide. A number of reactions then occur resulting in the chain elongation of the polysulphides (Steudel, 1996). These polysulphides then decompose in acidic solutions liberating mainly elemental sulphur rings, S₈. The sulphur remains stable and is only biooxidized to sulphuric acid in the presence of sulphur-oxidizing bacteria such as *Acidithiobacillus thiooxidans* or *Acidianus* (Schippers & Sand, 1999).

2.2.5 Factors Affecting Pyrite Biooxidation

2.2.5.1 Hydrogen Ion Concentration (pH)

Hydrogen ions play an important role in the energy supply mechanism of acidophilic microorganisms such as *Thiobacillus ferrooxidans* and *Acidianus* (Rossi, 1990). The hydrogen ion concentration affects the bacterially prompted oxidation of ferrous ions (Equation 2.2). Pyrite biooxidation as illustrated in Equation 2.5 involves electron transfer and the movement of hydrogen ions. The pH used in the liquid culture media affects both the microbial activity and the associated hydrometallurgical processes. *Acidianus* microorganisms thrive at an optimum pH of 2.0 to 3.0. The pH also affects the precipitation of jarosite-type compounds which have a detrimental effect on bioleaching. Several researchers have identified the best conditions for jarosite precipitation as temperature; 95 to 100 °C, a pH of around 2, vigorous agitation and the presence of seed material (jarosite). The rate of jarosite formation is greatly affected by the presence of jarosite seeds. Seeding is critical for jarosite precipitation

since conditions for jarosite formation can exist in bioleaching without jarosite precipitation actually occurring (Klauber, 2008). In this study the rate of jarosite formation is therefore expected to be minimal during leaching although the formation of jarosite-type precipitates could occur in the subsequent aging/forced hydrolysis stage.

2.2.5.2 Temperature

Each microbial genus is characterized by a defined temperature range within which its microorganisms can thrive and at which growth and reproduction rates are at their peak (See Table 2.1). It is apparent therefore that biohydrometallurgical processes are temperature dependent. It is well known from reaction kinetics principles that an increase in temperature enhances the reaction rate. The increase in temperature is generally accompanied by a decrease in the microbial activity. This conflict is of particular concern when mesophilic bacteria such as *Thiobacillus ferrooxidans* are used in pyrite oxidation. A compromise has to be struck between a temperature that allows the attainment of relatively high mineral dissolution rates and optimum microbial growth. The use of *Acidianus* spp. eliminates the need for any tradeoffs as significant sulphide mineral bioleaching has been reported at 70°C (Norris & Parrott, 1986) and at these temperatures *Acidianus* is well within its temperature tolerance limits. *Acidianus* grows optimally within a temperature range of 70-75°C and its use during bioleaching eliminates the operational difficulties encountered when mesophilic bacteria are used.

2.2.5.3 Particle Size

The rate of bioleaching as is the case with conventional leaching, increases with a decrease in particle size. This is because as the particle size decreases, a greater surface area per unit weight of the particle is exposed for bioleaching at the solid/liquid interface resulting in better mass transfer (Rossi, 1990). This has been confirmed for a number of sulphide minerals, where high solubilisation rates were

attained using the smallest particle size fractions (Bryner & Andersen, 1957; Malouf & Prater, 1961; Torma & Guay, 1976; Mikkelsen et al., 2007). However a particle size which is too small can slow down the leaching rates as diffusion pathways are blocked and solid/liquid interaction hindered. Nemati et al., (2000) in their studies on particle size effects on pyrite bioleaching by *Sulfolobus metallicus*, a thermophilic archaeobacteria found that decreasing the particle size generally increased leaching rates until a critical size ($\sim 25\mu\text{m}$) was reached. They reported that cell activity was adversely affected below this critical size fraction. The authors suggested that the reduction in the particle sizes increased the extent of particle- particle collisions and imposed severe attrition on the bacterial cells. This would ultimately lead to cell structure damage and make the cells unable to oxidise pyrite. Valencia & Acevedo (2009) have suggested that difficulties in cell attachment to small particles and metabolic stress rather than the denaturisation of the cells result in this phenomenon. Grinding costs also increase as the particle size decreases. A concession has to be made between the costs borne when grinding to a smaller particle size and the profits generated due to the enhanced solubilization rates and recoveries.

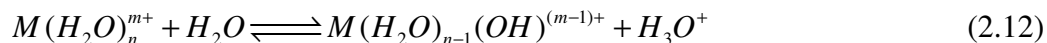
2.3 Hydrolysis

Overview

The leach liquor generated during pyrite bioleaching is predominantly acidic ferric sulphate. This leach liquor will be aged to yield various iron oxyhydroxides, oxides and basic sulphates through a forced hydrolysis reaction. The biogenic precipitate will be used as the precursor material for hematite nanoparticle synthesis. This section contains the theory on hydrolysis and the factors affecting it.

2.3.1 Hydrolysis of Aqueous Metal Ions & Factors Affecting the Process

Hydrolysis is a chemical process where a molecule is cleaved into two parts through the addition of water. A fragment of the parent molecule gains a hydrogen ion (H^+) from the water molecule whilst the other part collects the remaining hydroxyl (OH^-) part. However, there are only a few reactions where hydrolysis occurs under normal conditions and a strong base or acid is usually used to catalyze this reaction between the compound and water. Metal ions form aqua ions of the general formula, $M(H_2O)_n^{m+}$ in aqueous solutions. These metal ions are hydrolyzed to varying extents with the first step in this hydrolysis reaction being generally given as



The aqua ion behaves as an acid according to the Brønsted-Lowry acid-base theory. Here, the positive charge on the metal ion weakens the O-H bond of the attached water molecule through an inductive effect, resulting in the release of a proton (Burgess, 1978). The dissociation constant, pK_a of this reaction is more or less linearly dependent on the charge-size ratio of the metal ions (Baes & Mesmer, 1976). Ions with low charges such as Na^+ are very weak acids and as such hydrolysis is barely noticeable. Systems with large divalent cations such as Ca^{2+} , Pb^{2+} , Sn^{2+} and Zn^{2+} have high pK_a values of around 6 meaning very little hydrolysis occurs whilst small divalent ions such as Be^{2+} are extensively hydrolyzed. Trivalent ions such as Fe^{3+} and Al^{3+} are weak acids (pK_a values around 4.5) and solutions of their salts in water such as $FeCl_3$ and $Al(NO_3)_3$ are noticeably acidic. The addition of acids such as nitric acid to such system suppresses hydrolysis (Baes & Mesmer, 1976).

Equation (2.12) illustrates the initial step involved in hydrolysis. In most cases hydrolysis proceeds beyond this first step leading to the formation of polynuclear species (Baes & Mesmer, 1976). Hydrolysis tends to increase as the pH increases leading to the precipitation of hydroxides (Baes & Mesmer, 1976; Umetsu et al.,

1977). The precipitation of a metal hydroxide is an advanced, though not a final stage of metal ion hydrolysis. This precipitation is easily accomplished through the addition of a base. In certain cases where the metal ion is easily hydrolyzable, metal hydrous oxides may form even without raising the pH by forced hydroxylation at elevated temperatures. The ferric ion amongst its other properties possesses an extraordinary hydrolyzability. At room temperature its water complex readily undergoes deprotonation in acidic solutions, ultimately resulting in the formation of solid phases. The rate of this solid precipitation may also be greatly enhanced by heating the ferric salt. Matijevic & Scheiner, (1978) proposed three basic procedures which can be used in the preparation of ferric hydrous oxide dispersions;

- i) Addition of a base to a ferric salt solution
- ii) Heating of ferric salt solutions in either the presence or absence of a base
- iii) Addition of an oxidizing agent to a ferrous salt solution, followed by subsequent precipitation with a base or heating or both.

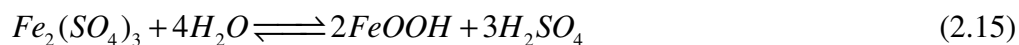
The term ‘forced hydrolysis’ therefore refers to the enhancement of the hydrolysis reaction through either heating, the addition of a base or both.

Metal hydrous sols undergo various phase transformations in aqueous media and/or in the solid state. The hydrolysis reaction and the dissolution/reprecipitation mechanisms are more dominant in the aqueous media whilst topotatic rearrangements are more common in the solid-state reactions. The precipitation of the hydrous oxide sols during hydrolysis in aqueous media usually occurs in two main stages. Initially the solid phase is formed through the nucleation process leading to the growth of these nuclei through diffusional and/or aggregative pathways in the ensuing stage (Matijevic et al., 2000). Nucleation is the creation of crystalline bodies within a supersaturated fluid and is often described as either primary or secondary nucleation. Primary nucleation occurs in the absence of crystals whilst secondary nucleation occurs in their presence. Primary nucleation can be initiated by suspensions of

foreign particles in which case it is referred to as heterogeneous nucleation. Homogeneous nucleation occurs when the critical values of the supersaturation ratio and crystal size are exceeded. Many researchers have studied the formation of hematite from the forced hydrolysis of dilute $\text{FeCl}_3\text{-HCl}$ systems (Matijevic & Scheiner, 1978; Masataka et al., 1984; Hamada et al., 1986). These investigators have shown that the nature of the precipitate particles depends on a number of factors such as the pH, concentration of ferric ions, presence of additives, types of vessels used, temperature and the duration of the precipitation. A small change in any of the reaction conditions can lead to the precipitation of an entirely different product (Matijevic & Scheiner, 1978). The effects of some of these crucial factors are discussed in the following section.

Temperature

The rate of precipitation during hydrolysis increases as the temperature increases, in agreement with reaction kinetics principles. Nucleation rates and crystal growth rates increase during hydrolysis (Wang et al., 1999; Bakardjieva et al., 2005). Workers studying the hydrolysis of different systems have aged their systems at different aging temperatures ranging from room temperature to the boiling temperatures of the system. The rate of solid precipitation is thus greatly increased by an increase in temperature. Umetsu et al., (1977) have lauded hydrolysis as the perfect technique to remove ferric ions from process solutions economically and expressed the hydrolysis of ferric ions in aqueous ferric sulphate solutions in Equations (2.13 to 2.14)



Umetsu et al., (1977) found that the iron oxide phase (jarosite, hematite, goethite) strongly depended on the treatment temperature and they employed hydrothermal temperatures up to 200°C.

Aging Time

The precipitation of a metal hydroxide is an advanced though not final stage in the hydrolysis reaction (Matijevic et al., 1979). Different solid precipitates can be obtained at any given time during aging since the hydrolysis process occurs in a number of stages. Sugimoto et al., (1993) for instance in their studies on the formation mechanism of hematite particles using the gel-sol process found that in the initial hours of aging an amorphous $\text{Fe}(\text{OH})_3$ gel had formed. After 6 hours of aging at 100°C this gel was converted completely into fibrous akagenite, $\beta\text{-FeOOH}$ crystals. Extremely fine $\alpha\text{-Fe}_2\text{O}_3$ particles began to appear within the huge $\beta\text{-FeOOH}$ crystal network after 1 day. As aging progressed the $\alpha\text{-Fe}_2\text{O}_3$ particles continued to grow whilst the $\beta\text{-FeOOH}$ crystal network became progressively smaller. After 8 days of aging only $\alpha\text{-Fe}_2\text{O}_3$ particles remained in the system. It is apparent that precursor materials (such as ferric hydroxides) form during the early stages of aging and complete iron oxide precipitation from aqueous ferric solutions is to be expected after 7-8 days of aging at elevated temperatures.

Effect of Agitation

Agitation is known to affect the morphology of the precipitate particles (Wang et al., 1999; Bakardjieva et al., 2005). Wang et al., (1999) showed in their studies that both the particle size and morphology of precipitate particle altered when magnetic stirring was used during aging. Sugimoto et al., (1993) studied the effect of agitation on the formation of hematite from a condensed ferric hydroxide gel during aging. They used a mechanical stirrer set at 400rpm. Their product particles were extremely polydispersed and they attributed this to renucleation induced by agitation. However, in industrial operations the installation of agitators in crystallizers yields smaller and

more uniform precipitate crystals and reduced batch times. Although agitation may degrade the monodispersity of a system, it is a useful parameter which can be used in the size control of the precipitate particles.

Concentration of Ferric Ions

The concentration of ferric ions has been identified as a factor which affects the precipitate product formed during the hydrolysis reaction (Matijevic & Scheiner, 1978; Music et al., 1994; Kandori et al., 2004). Music et al., (1994) determined the concentration regions for the precipitation of goethite, α -FeOOH and hydronium jarosite, $\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$ as single phases from $\text{Fe}_2(\text{SO}_4)_3$ solutions. α -FeOOH was precipitated from 0.005M and 0.03M $\text{Fe}_2(\text{SO}_4)_3$ solutions upon aging for up to 72 hours at 90°C whilst $\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$ was precipitated after aging 0.1M and 0.5M $\text{Fe}_2(\text{SO}_4)_3$ solutions for periods reaching 72 hours at 90°C and 120°C. The study by Kandori et al., (2004) on the forced hydrolysis of acidic $\text{Fe}_2(\text{SO}_4)_3$ shows a similar trend where α -FeOOH particles were formed from the relatively lower $\text{Fe}_2(\text{SO}_4)_3$ concentration of 0.00316 whilst hydronium jarosite was formed from 0.01M $\text{Fe}_2(\text{SO}_4)_3$. At low concentrations the Fe^{3+} ions readily undergo hydrolysis due to their fairly high charge size ratio. The aqua ions easily undergo deprotonation leading to polymerization and the formation of the goethite oxyhydroxide. At the higher Fe^{3+} concentrations however, the formation of the FeSO_4^+ strongly suppresses the polymerization of the hydroxy complexes yielding $\text{H}_3\text{OFe}_3(\text{OH})_6(\text{SO}_4)_2$. A similar trend was observed in FeCl_3 solutions. Hydrolysis of Fe^{3+} is relatively fast in dilute FeCl_3 solutions leading to the precipitation of β -FeOOH even at room temperatures. Hematite particles have been prepared from acidic dilute FeCl_3 solutions by the phase transformation of β -FeOOH through a dissolution-recrystallization process (Hamada & Matijevic, 1981). However, in more concentrated solutions of 2-4M FeCl_3 , the chloride complexes of Fe^{3+} are dominant and there is a strong suppression of hydrolysis reaction. The biogenic leach liquors generated in this study are expected to be of relatively high concentrations. The survey shows that iron oxyhydroxides or hydroxides could only be precipitated from the hydrolysis of dilute, acidic ferric salt

solutions. Hydrolysis tended to be suppressed in the highly concentrated ferric salt systems. The addition of a base to such systems will be investigated to determine its effect on polymerization in the hydrolysis reaction.

Effect of pH

It has already been seen throughout this section that the pH conditions in a ferric salt system can either suppress or enhance the polymerization process during hydrolysis. Matijevic & Scheiner, (1978) stated that one of the procedures which could be used in the preparation of ferric hydrous oxide sols was the addition of a base to a ferric salt. It is known that the pH used during aging affects the nature of the precipitate.

A useful tool which can be used to study the stability of specific phases under particular restrictions is the Pourbaix diagram. Pourbaix diagrams which are commonly known as E^θ -pH diagrams are used to map out the regions of possible equilibrium or stability which can exist within an aqueous electrochemical system. The vertical axis, E^θ , denotes the electrode potential or voltage with respect to the standard hydrogen as given by the Nernst Equation.

The Nernst equation states

$$E = E^\theta - \frac{RT}{nF} \ln Q \quad (2.16)$$

Where E - cell potential, electromotive force

E^θ - standard cell potential

R – Universal gas constant, $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$

T- absolute temperature in Kelvins

Z- number of electrons transferred in a cell reaction / half reaction

F – Faraday's constant, number of coulombs per mol of electrons, $96\,485 \text{ Cmol}^{-1}$

Q- reaction quotient

The horizontal axis denotes the pH, which is the negative log function of the H^+ ion concentration.

$$pH = -\log[H^+] \quad (2.17)$$

The Pourbaix diagram for iron is given in Figure 2.1. The lines on the diagram represent the major boundaries between the various species.

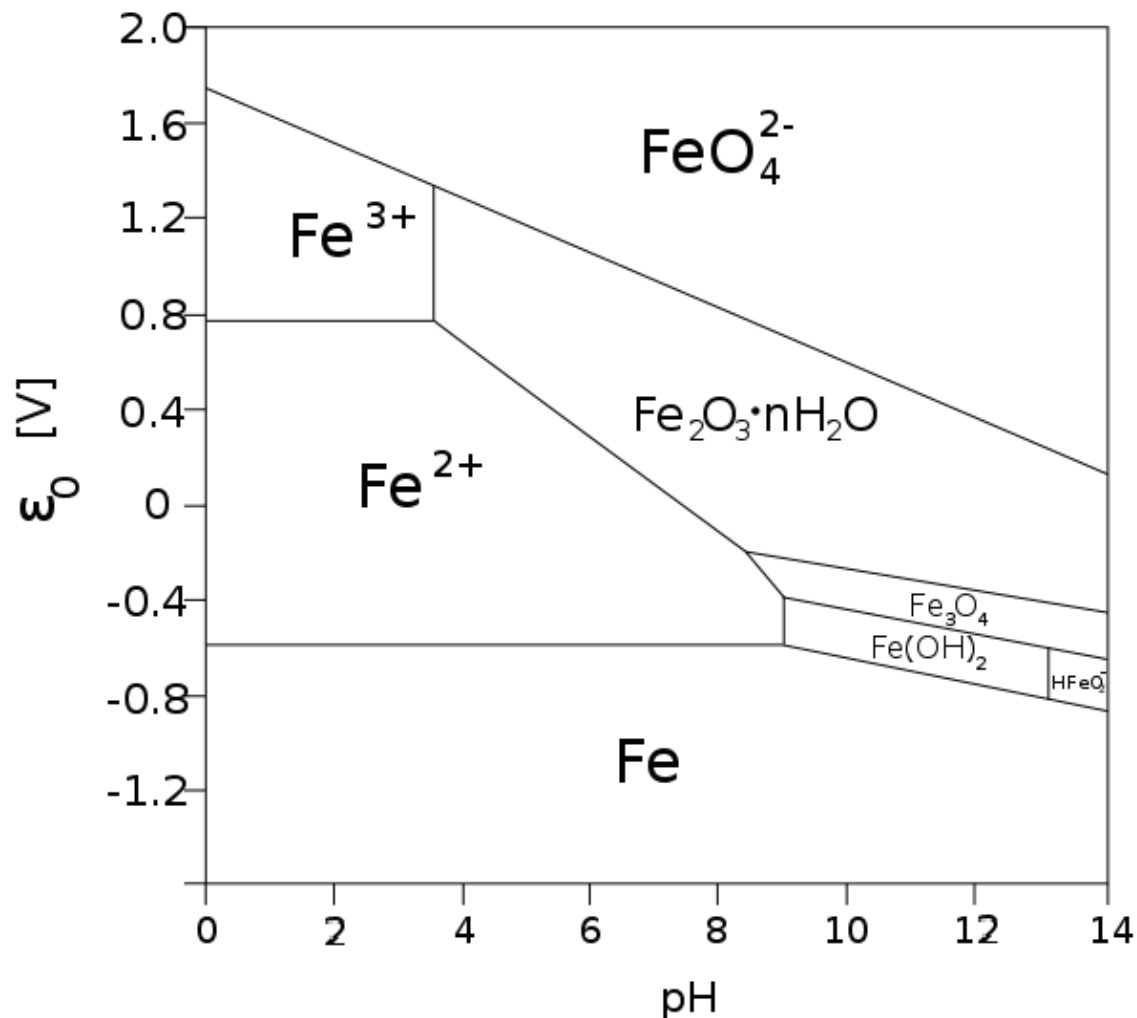


Figure 2.1 Pourbaix diagram for iron at 25°C and 1M ion concentrations for all ionic species.

Source: http://commons.wikimedia.org/wiki/File:Pourbaix_Diagram_of_Iron.svg

The Pourbaix diagram shows that different iron oxides can be formed under different pH conditions. The effect of pH on the precipitation of the precursor iron oxides and iron oxyhydroxides will therefore be investigated during the experimental research.

Effect of Anions

The biogenic leach liquor generated from pyrite oxidation will be aged under varying conditions in the quest to precipitate a precursor material for hematite particle synthesis. The leach liquor will be predominantly acidic $\text{Fe}_2(\text{SO}_4)_3$ but will contain other ions. Most of these ions will be remnants from the salts in the nutrient culture medium. These impurities may affect the nucleation stage during hydrolysis leading to heterogeneous nucleation occurring in the system. Other ions may be precipitated out of the system and form impurities in the hydrolysis product. Matijevic & Scheiner (1978) precipitated various ferric hydrous sols from ferric chloride, ferric nitrate and ferric perchlorate solutions. The dominant particles precipitated from the hydrolysis were $\alpha\text{-Fe}_2\text{O}_3$ particles. They found that the shape of these $\alpha\text{-Fe}_2\text{O}_3$ particles varied greatly and depended on the anion present in the aging solutions. It is therefore likely that the anions present in an aging system have a shape modifying effect on the precipitates.

2.4 Preparation of Iron Oxyhydroxides and Oxides from the Forced Hydrolysis of Ferric Salts

The study of the forced hydrolysis of $\text{Fe}_2(\text{SO}_4)_3 - \text{H}_2\text{SO}_4$ systems has not been as extensive as that of $\text{FeCl}_3\text{-HCl}$ systems which are known to yield hematite precipitates. The precipitation products which have been obtained from aging acidic ferric sulphate solutions are mainly jarosites, alunites and schwertmannite (Kandori et al., 2004; Wang et al., 2007; Gramp et al., 2008; Liao et al., 2008). This system will be more pertinent to this study since the leach liquor generated will be mainly acidic ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4$. In most of the studies which have been done on the

hydrolysis of acidic ferric sulphate systems, the ferric salts used have been prepared from reagent grade chemicals. Thus the aging of biogenic ferric sulphate solutions to produce iron oxyhydroxides and basic sulphates, presents a new dimension in this research area. These bioprecipitates (in the form of iron oxyhydroxides) will become the precursor materials for hematite production, which is the final desired product.

2.4.1 Forced Hydrolysis of Acidic Ferric Sulphate Solutions

A number of workers have studied the forced hydrolysis of acidic ferric sulphate systems (Kiyama & Takada, 1973; Matijevic et al., 1975; Kandori et al., 2004; Wang et al., 2007; Gramp et al., 2008; Liao et al., 2008). Kiyama and Takada, (1973) showed that polymeric complexes of $\text{Fe}_2(\text{SO}_4)_{3/2}(\text{OH})_3$ and $\text{Fe}_3(\text{SO}_4)_{7/2}(\text{OH})_2$ produced by hydrolysing $\text{Fe}_2(\text{SO}_4)_3$ at temperatures below 70°C formed $\text{RFe}_3(\text{SO}_4)_2(\text{OH})_6$ (where R is H_3O , Na, K or NH_4) jarosites. Matijevic et al., (1975) formed monodisperse basic ferric sulphate sols after aging acidic ferric sulphate solutions at elevated temperatures ($80\text{--}90^\circ\text{C}$) for up to 21 hours. They defined conditions for the precipitation of the basic iron sulphates $\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot 2\text{H}_2\text{O}$ and $\text{Fe}_4(\text{SO}_4)(\text{OH})_{10}$. $\text{Fe}_3(\text{SO}_4)_2(\text{OH})_5 \cdot 2\text{H}_2\text{O}$ is the basic structural formula for the alunite mineral group. In this research Matijevic et al., (1975) emphasized the role of FeSO_4^+ complex which is prevalent in acidic solutions. It is crucial in the formation of basic iron sulphates. Sapieszko et al., (1977) showed that this FeSO_4^+ complex suppresses the formation of iron oxyhydroxides and oxides.

Walter-Levy et al., (1964) and Music et al., (1994) studied the hydrolysis of Fe^{3+} ions in $\text{Fe}_2(\text{SO}_4)_3$ solutions. They defined the iron concentration regions for the formation of goethite, $\alpha\text{-FeOOH}$ and hydronium jarosite $\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6$ as single phases. Music et al., (1994) precipitated $\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6$ and a basic sulphate $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$ from the hydrolysis of Fe^{3+} in 0.1M $\text{Fe}_2(\text{SO}_4)_3$ at 120°C whilst hydrolysis of the same system at 90°C led to the precipitation of $\alpha\text{-FeOOH}$. Kandori et al, (2004) also studied the forced hydrolysis of $\text{Fe}_2(\text{SO}_4)_3 - \text{HCl}$ systems. The

shape and size of the precipitates they produced depended greatly on the initial $\text{Fe}_2(\text{SO}_4)_3$ concentration, whilst the nature of the precipitate was pH dependent. Acicular goethite particles were produced at $\text{pH} \geq 1.6$ whilst irregularly shaped hydronium jarosite particles were formed at $\text{pH} \leq 1.5$. In most of these studies the hydrolysis was carried out in 30ml Pyrex vials which were tightly stoppered with Teflon-lined screwcaps. The vials were then placed in constant temperature laboratory ovens for aging periods lasting up to 8 days.

The hydrolysis of solutions prepared in part or wholly from bacterial oxidation is a recent development (Wang et al., 2007; Gramp et al., 2008; Liao et al., 2008). Wang et al., (2007) studied the synthesis and properties of ammoniojarosites prepared using iron oxidizing acidophilic microorganisms between 22 and 65°C. They carried out microbiological oxidation of ferrous sulphate solutions prepared from reagent-grade chemicals at a pH of 2.0 to 3.0 over a range of NH_4^+ concentrations. They defined the ammonium concentrations where schwertmannite, $[\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)]$ and ammoniojarosite, $[(\text{NH}_4, \text{H}_3\text{O})\text{Fe}_3(\text{OH})_6(\text{SO}_4)_2]$ were formed both as single products and as a mixed product. These workers also reported that the use of thermophilic microorganisms at 45 and 65°C in these systems accelerated the formation of ammoniojarosites.

Gramp et al., (2008) synthesized and characterized the jarosites formed in ferrous sulphate solutions inoculated with iron-oxidizing acidophiles. They studied the effect of cation concentrations on the precipitates and concluded that the monovalent cation concentrations determined the type of Fe(III) hydroxysulphate precipitate formed in the biosolutions. The cultures were incubated at $22 \pm 2^\circ\text{C}$ for between 2 and 6 weeks. They concluded that the concentrations of ammonium NH_4^+ , potassium K^+ and sodium Na^+ required for jarosite formation differed according to the jarosite type. Potassium jarosite required the lowest level of monovalent cation to form whilst high levels of NH_4^+ and Na^+ ions were required to form ammoniojarosite and natrojarosite. Schwertmannite was present even at the highest levels of Na^+ and NH_4^+ ion

concentrations. Liao et al., (2008) investigated the oxidation of ferrous sulphate solutions using *Acidithiobacillus ferrooxidans* cell suspensions within an initial pH range of 1.40 to 3.51 and then subsequent precipitation of the resulting Fe(III). The initial pH ultimately influenced the nature of precipitate produced. Precipitates consisting of natrojarosite and schwertmannite were formed when the initial pH was 3.51, whilst only schwertmannite was produced when the initial pH ranged from 1.60 to 3.44. No precipitates were formed when the pH was ≤ 1.40 .

The hydrolysis of acidic ferric sulphate solutions has yielded mainly basic iron sulphates and oxyhydroxides such as jarosites, alunites, goethite and schwertmannite. The literature survey has shown that the presence of the FeSO_4^+ complex in these systems suppressed the formation of iron oxyhydroxides and oxides, which are of prime interest in this work. In the next section established hydrolysis methods used to precipitate hematite from other ferric salt systems will be discussed.

2.4.2 Preparation methods of monodisperse hematite from ferric salts.

A survey of literature suggests that the aging of acidic $\text{Fe}_2(\text{SO}_4)_3$ generates precipitates such as schwertmannite, alunites, jarosites and goethite (Kiyama & Takada, 1973; Matijevic et al., 1975; Kandori et al., 2004; Wang et al., 2007; Gramp et al., 2008; Liao et al., 2008). Hematite nanoparticles have been generated from aging mainly acidic ferric chloride systems (Matijevic and Scheiner 1978; Masataka et al., 1984; Meyer et al., 2000). These methods will be studied to provide elucidation on the treatment of acidic ferric sulphate systems, in the quest to form hematite, Fe_2O_3 .

As outlined earlier the precipitation of a metal hydroxide is an advanced, though not a final stage of metal ion hydrolysis which can be effected by the addition of a base. Monodisperse particles of hematite of different shapes and sizes have been prepared from the forced hydrolysis at elevated temperatures of highly acidic dilute solutions of ferric salts (Matijevic & Scheiner 1978; Masataka et al., 1984; Meyer et al., 2000).

Matijevic and Scheiner, (1978) prepared ferric hydrous oxide sols by aging acidic solutions containing ferric ions and nitrate, perchlorate or chloride ions, at elevated temperatures for periods ranging from a few hours to a few weeks. The solids which were precipitated from solutions containing chloride ions consisted of akagnetite, β -FeOOH or hematite, α -Fe₂O₃ depending on the concentration of the ferric and chloride ions. Hematite, α -Fe₂O₃ solids were precipitated from solutions containing nitrate or perchlorate ions. Masataka et al., (1984) formed spindle-type monodisperse hematite particles from the forced hydrolysis of dilute ferric salts at elevated temperatures using two different procedures. They aged ethanol/water solutions containing ferric chloride and phosphate or hypophospite ions aged at 100°C for 2 to 7 days. In the second method, they initially added sodium hydroxide to ferric nitrate solutions to firstly form ferric hydroxide; then added HCl and NaH₂PO₄ and aged the resulting system at 100°C in an air oven.

2.4.3 The Gel-sol Method

The forced hydrolysis methods used to precipitate hematite from ferric salt systems have been mainly done using dilute ferric salt solutions. This has served a practical purpose since the use of these extremely dilute systems (mostly of the order 10^{-3} - 10^{-2} M) allows tremendous coagulation of the particles to be avoided. However, when these particles are now produced as ideal materials on an industrial scale the dilute systems result in exceedingly low productivity or high cost.

Recent work by Sugimoto et al., (1998), has indicated that hematite particles of various shapes and sizes can be obtained in large quantities starting from an inexpensive ferric salt, ferric chloride, through a two-step phase transformation process from highly condensed Fe(OH)₃ gel to α -Fe₂O₃ via β -FeOOH. This process was termed the gel-sol process and in this method NaOH solution was slowly added to 2.0M FeCl₃ in pyrex bottles to form the highly condensed gel. Borrowing on these studies, the work done by Lui and Osseo-Asare, (2000), has shown that it is possible

to obtain monodisperse hematite particles of interesting shapes spanning nano to micrometer size in large quantities using relatively high $\text{FeCl}_3/\text{NaOH}$ concentrations, unlike conventional methods which have relied mostly on dilute solutions ($\approx 10^{-2}\text{M}$ FeCl_3). Sugimoto et al., (1998) have also shown that adjusting the temperature of formation of the gel, seeding using nanosized hematite seed particles and the addition of other anions allows for the systematic control of the morphology, size and internal structure of the hematite particles formed in the gel-sol process. The underlying principle in this process rests on the premise outlined in section 2.3.1, that hydrolysis can be accomplished by heating the ferric salt in the presence of a base.

2.5 Review of Industrial Iron Removal Processes

A number of precipitation processes have been used to remove iron from solution in industrial practice. Most of these processes have been used in the treatment of metallurgical waste and in the electrolytic industries (Davey & Scott, 1976; Langova et al., 2007). A comparison of the main iron precipitation processes is given in Table 2.2.

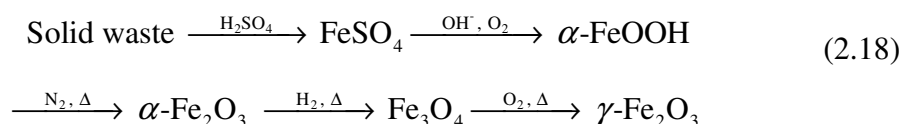
The operating conditions for these three main processes will provide useful test conditions to be studied in our system. A common feature in all of these precipitation processes however is the low iron concentration in solution. The goethite process which removes iron from mainly sulphate and chloride systems however, requires a systematic control of the ferric ion concentration in solution for successful execution (Allen et al., 1970; Andre & Masson 1973). This iron concentration is to be kept at no more than 1g/L during precipitation (Davey & Scott, 1976). The bioleach liquors used in this study however contain ferric ions in significantly higher concentrations. The hematite process produces particles with few impurities but requires the use of hydrothermal temperatures of up to 200°C and will therefore not be easily adapted to our system (Umestu et al., 1977). The transformation of goethite into hematite will therefore need to be considered.

Table 2.2 Comparison of the main industrial iron precipitation processes. (Davey & Scott, 1976).

Operating Conditions	PROCESS		
	Goethite	Jarosite	Hematite
pH	2 - 3.5	< 1.5	Up to 2% H ₂ SO ₄
Temperature (°C)	70 -90	90 – 100	≈200
Anion	Any	SO ₄ ²⁻ only	SO ₄ ²⁻ only
Added cations required	Nil	R where R is Na ⁺ , K ⁺ , NH ₄ ⁺	Nil
Product Compound formed	α- and β-FeOOH α-Fe ₂ O ₃	RFe ₃ (SO ₄) ₂ (OH) ₆	α-Fe ₂ O ₃
Cationic impurities	Medium	Low (apart from "R")	Low
Anionic impurities	Medium	High	Medium
Filterability	V. good	V. good	V. good
Fe in filtrate	< 1g/L often < 0.05g/L	1 - 5 g/L	≈ 3g/L

2.6 Transformation of Precursor Iron Oxides to Hematite, α -Fe₂O₃

The preparation of iron oxide pigments from the industrial waste generated from chemical, metallurgical, and mechanical engineering plants has been studied by researchers (Epikhin & Krylova, 2003; Legodi & de Waal, 2007). Epikhin and Krylova, (2003) studied the preparation of various iron oxide pigments via the synthesis of goethite. They leached the waste with sulphuric acid solutions to form iron sulphate. Goethite, α -FeOOH was synthesized from the ferrous sulphate and subsequently converted to various iron oxides as illustrated in Equation 2.18 (Epikhin & Krylova, 2003)



Epikhin and Krylova synthesized the goethite pigment using a method of nucleus free precipitation with KOH alkali at pH > 13. The yellow goethite pigment was then successively transformed to red hematite, (α -Fe₂O₃), black magnetite, (Fe₃O₄) and reddish brown maghemite, (γ -Fe₂O₃).

Legodi & de Waal, (2007) prepared various iron oxides from mill scale iron waste. They precipitated magnetite in aqueous media using a modified method described by Ueda et al., (1996). Basic conditions of pH between 11 and 12 were used during the precipitation. Legodi & de Waal, (2007) also precipitated goethite at a pH between 5 and 7, employing a modified method of procedures described by Thiebeau et al., (1978). They formed hematite by calcining the goethite precipitate at temperatures ranging from 600 to 900°C.

Since magnetite, Fe_3O_4 is one of the iron oxides which can be formed as a precipitate from the aging of the bioleach liquors, its transformation into hematite, $\alpha \text{Fe}_2\text{O}_3$, is also considered. The transformation of magnetite to hematite is readily achieved through an oxidation reaction.



However at the particle sizes which will be used in this study, the oxidation kinetics no longer remains simple as the magnetite crystal size has a marked impact on the oxidation kinetics and reaction products (Feitknecht, 1964; Gallagher et al., 1968; Gillot et al., 1978; Jolivet & Tronc, 1988). Schwertmann and Cornell, (2003) reported on the influence of temperature and crystal size on the oxidation product. They reported that at temperatures between 200 and 250°C, magnetite crystals smaller than 300nm were transformed via the mixed phase into maghemite which was transformed into hematite at temperatures above 500°C. In larger crystals (>300nm), the complete transformation of magnetite was retarded due to the long diffusion pathways and for the transformation to occur completely, the temperature had to be raised above 500°C (Schwertmann & Cornell, 2003). The iron oxides and/or iron oxyhydroxides generated as precipitates from the hydrolysis of the ferric sulphate systems can therefore be transformed into the hematite nanoparticles.

2.7 Hematite Nanoparticles – Their Nature & Uses

In nanotechnology, a nanoparticle is defined as a particle which has at least one dimension ranging in size between 1 and 100nm (Buzea et al., 2007). Borm et al., (2006) have stated however, that many authors have defined it as a particle having at least one dimension < 1µm and potentially reaching atomic and molecular length scales as small as 0.2nm. Properties of materials change as their size approaches the nano-scale due to aspects of the material surface now dominating the properties in

lieu of the bulk properties. Iron oxides are very important chemical materials that can be applied extensively in many fields (Liu et al., 2005).

The synthesis of metal oxide nanoparticles is an area of research which is receiving a lot of attention from researchers worldwide due to the applications and unusual properties exhibited by these particles (Rao et al., 2004). Magnetic nanoparticles display superparamagnetic behaviour and their magnetic polarizations can be completely reversed when their magnetization is rotated uniformly (Bonet et al., 1999).

Iron oxide nanoparticles have been synthesized and assembled for magnetic data storage (Sun & Zeng, 2002). Data can be stored and recorded in devices such as hard disks, cartridges and cassettes. Magnetic Ink Character Recognition (MICR) is another important field where the magnetic properties of iron oxide nanoparticles are exploited. MICR is a technique that allows special characters which are printed in magnetic ink to be read and inputted automatically into a computer. This character recognition technology is widely used in the banking sector to process cheques with an accuracy far greater than human accuracy or that of other optical recognition systems. The MICR characters have a unique font and are printed with a magnetic ink/toner which contains iron oxides.

Magnetic nanoparticles have found a novel application in Nuclear Magnetic Resonance (NMR) imaging where they are used as intracellular magnetic labels. The operation of NMR imaging is founded on the concept of magnetic relaxation. The presence of magnetic nanoparticles results in the protons within their vicinity relaxing at a much faster rate and thereby inducing a noticeable contrast (Rao et al., 2004). The NMR imaging of target cells has been found to improve significantly when dextran-coated biocompatible nanoparticles have been conjugated with peptides, as the conjugation improves their uptake into the target cells (Josephson et al., 1999). The conjugation of certain oligonucleotide sequences to magnetic nanoparticles has also enabled DNA sequences to be rapidly detected (Josephson et al., 2001). Dextran

coated magnetite nanoparticles have been used to enhance the contrast in Rhesus brain experiments where the photic responses were studied (Dubowitz et al., 2001). Functional NMR imaging techniques have been used in brain mapping studies. In these experiments, humans and primates are exposed to external stimuli while the brain is imaged, facilitating studies where the link between brain region and function is explored. These NMR techniques all rely on the use of iron oxide nanoparticles.

Magnetic nanoparticles have a range of other uses, for instance they are used in cosmetics, as catalyst support, magnetic drug delivery and in localized thermotherapy. Iron pigments are non-toxic and moisture resistant. There is a lot of contemporary research in this field where the formulation of transparent sunscreens prepared from nanoparticulate oxide materials is ongoing. Traditional sunscreens are opaque creams and the interest is in generating a material which can be sprayed and yet invisible. In magnetic drug delivery the pharmacoactive molecules are bound to the magnetic nanoparticles which are then guided in vivo to the target cells through the application of magnetic fields. In localized thermotherapy which is used mainly in cancer therapy, magnetic nanoparticles are guided to the cancerous cells and the particles are then coupled to a strong radio-frequency magnetic field. This results in the local dissipation of large amounts of heat which eventually destroy the tumour. Iron oxide nanoparticles are also used as catalyst support. In heterogeneous catalysis, metal oxide nanoparticles have been built in situ in diesel vehicles to improve fuel efficiency and also reduce particulate emissions.

The synthesis of monodispersed nanoparticles is the ultimate goal for general advanced particulate materials. Hematite nanoparticles are biocompatible, non-toxic, magnetic and chemically active on their surfaces. Thus, hematite nanoparticles have a wide range of potential applications in fields such as biomedicine, optics and electronics.

2.8 Summary

The bio-oxidation of pyrite is well established and yields mainly acidic ferric sulphate solutions. The literature survey showed that various iron oxides and oxyhydroxides could be precipitated from the aging of ferric salt systems, through a forced hydrolysis process depending on the reaction conditions. Hematite particles can be generated from the hydrolysis of mainly dilute acidic FeCl_3 systems whilst the hydrolysis of dilute acidic $\text{Fe}_2(\text{SO}_4)_3$ systems yielded a variety of iron oxides and hydroxides such as jarosites, alunites and schwertmannite. The difficulty in generating iron oxides from such systems stems from the presence of the FeSO_4^+ complex, which suppresses the formation of iron oxides in acidic ferric sulphate solutions.

The nature of the precipitate generated in ferric salt systems after aging is influenced by a number of factors such as pH, concentration of ferric ions, presence of additives, types of vessels used, temperature and the duration of the precipitation. It was revealed that the hydrolysis of the ferric ion could be achieved in a number of ways and heating of such systems in both the presence and absence of a base will be investigated. The biogenic precipitates obtained after aging are expected to be in the form of iron oxyhydroxides which will be the precursor materials for hematite particle formation. The various methods of transforming different iron oxides and oxyhydroxides into hematite were reviewed. In this review, the potential of using a bio-mediated process in the production of hematite nanoparticles *via* the production of precursor bio-iron oxyhydroxides was investigated.

Chapter 3

Materials & Methods

3.1 Materials

3.1.1 Pyrite, FeS_2

The pyrite used in this study was sourced from African Gems and Minerals, Johannesburg, South Africa. The pyrite was crushed and finely milled in a ball mill. The milled pyrite was then classified using standard sieve plates into various class size fractions ranging from $-125\mu m + 38\mu m$. Inductively Coupled Plasma (ICP) analysis revealed that the ore contained 57.4% Fe and 42.4% S and 0.2% other elements.

3.2 Bacterial Growth

Acidianus spp. the thermophilic archaeobacteria used in this study was sourced from Copahue Provincial Park, Argentina and cultured in a modified basal salt medium, Medium 88 (See Section 3.3.3). The medium pH was adjusted to a pH of 2.0 using concentrated H_2SO_4 and sterilised in an autoclave at $121^\circ C$ for 20 minutes. *Acidianus* use sulphur as an energy source and a suitable amount of sterilised sulphur was added to the medium in the form of either elemental sulphur S_8 or $K_2S_4O_6$ to reach a concentration in the medium equivalent to a sulphur content of 10g/L. The medium was inoculated with 10% v/v of the micro-organism and incubated at a temperature of $70^\circ C$ at a pH of 2.0 in a platform shaker. The bacterial growth was monitored using UV-Visible Spectrophotometry.

3.2.1 *Regeneration of Cultures*

Acidianus are facultative chemolithoautotrophs and can grow under autotrophic, mixotrophic as well as heterotrophic conditions (Barrett et al., 1993). As autotrophs these bacterial species are capable of catalyzing the oxidation of elemental sulphur, iron (II) or sulphide minerals gaining energy during this process. These archaeobacteria however, grow more rapidly under mixotrophic conditions in the presence of 0.01 to 0.02% yeast or other organic compounds such as peptone or tryptone (Barrett et al., 1993).

3.2.2 *Adaptation*

The basal salt medium was adjusted to pH 2.0 before autoclaving. A 1% w/v sterile pyrite ore was then added to the medium which was subsequently inoculated with a 10% v/v regenerated culture (Silverman & Lundgren, 1959). The cultures were incubated at 70 °C whilst being agitated at 150rpm. After 5 days the sample was centrifuged at 10 000rpm for 10 minutes and resuspended in fresh medium and incubated again until sufficient adaptation had occurred. Adaptation was indicated by the stabilization of the total iron concentration value in solution. The steady value showed that equilibrium had been reached and maximum iron in the pyrite had been leached into solution. For a 1% w/v pulp density this was usually attained after 2 transfers (10 days).

3.2.3 *Maintenance*

The culture was maintained on a basal salt medium, Medium 88 developed by Brock et al. (1972). The composition of the medium is as given in Table 3.1

Table 3.1 Composition of Modified Medium 88 for *Acidianus* spp.

Medium Salt	Concentration (g/L)
$(\text{NH}_4)_2\text{SO}_4$	1.30
KH_2PO_4	0.28
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.07
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.02

In addition to these main medium salts, the culture medium also contained trace elements in the following concentrations (mg/L) $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 1.80; $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 4.50; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.22; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.05; $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 0.03; $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$, 0.03 and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 0.01. Sulphur was also added to the medium as either elemental sulphur, S_8 or potassium tetrathionate, $\text{K}_2\text{S}_4\text{O}_6$, to reach equivalent concentrations of 10g/L of sulphur. This solution is as recommended in the Deutsche Sammlung Von Microorganismen and Zellkulturen, DSMZ catalogue, Braunschweig, Germany.

The prepared modified basal salt medium 88 was then inoculated with a 10% v/v of the adapted culture. These inoculated cultures were incubated at 70°C and agitated at 150rpm in a platform shaker for 24 hours to provide sufficient aeration. After 24 hours, agitation was stopped and the culture was incubated as a static culture at 65 °C for 7-10 days (Silverman & Lundgren, 1959). After static incubation a 10% v/v inoculum was then subcultured to fresh pyrite medium and the incubation procedure was repeated.

3.2.4 Subculturing Procedures

The subculturing procedures are based on the method developed by Silverman and Lundgren, (1959). After maximum growth of the culture was achieved, the cellular suspension was filtered using Whatman no. 1 filter paper to remove any precipitates. The filtrate was centrifuged at 4200rpm for 30 minutes after which the resulting pellet was resuspended in a sulphuric acid solution at a pH of 2.0 and refrigerated to settle out any precipitates. The supernatant was then centrifuged again and washed with sulphuric acid until the cells were free from iron. The cells were then suspended in 10ml of acid solution at pH of 2.0 and stored at 4°C. Under these conditions the cells remained active for at least one month and were used as inoculum in fresh medium when needed.

3.2.5 Determination of Bacterial Growth using UV-Visible Spectrophotometer

The bacterial growth was determined by measuring turbidity or optical density of the bacterial suspension using UV-Visible double beam spectrophotometer (Model 4802). A bacterial culture acts as colloid suspension and has the ability to block and reflect the light passing through it. Since turbidity is directly proportional to the number of cells present in a culture, this property can be used as an indicator for bacterial concentration. The transmittance which is the percentage of light transmitted is inversely proportional to the bacterial concentration. The absorbance on the other hand is an inverse of transmittance and gives a measure of the optical density and is directly proportional to the bacterial cell concentration. The cells suspended in the suspension interrupt the passage of light allowing less light to reach the photoelectric cell and the amount of light transmitted through the suspension was measured as percentage transmission (or %T). The turbidity for cell suspension was measured at 440nm against clear water as a reference.

Note that the relationships among absorbance (A), transmittance (T) and optical density (OD) are as follows; $T = \frac{I}{I_0}$, where I is the light passing through the sample and I_0 is the light hitting the sample.

$$A = -\log_{10} T.$$

Optical density is a measure of absorbance and is related to transmittance by the following expression;

$$OD = 2 - \log (\%T).$$

This method of determining the bacterial growth however measures both the dead and active bacteria as it does not differentiate between the two states.

3.2.6 Determination of Bacterial Concentration – Plate Count

The number of bacteria in a given sample is usually too great to quantify directly. The sample thus has to be serially diluted and plated on an agar surface so as to allow single isolated bacterium to form visible isolated colonies. These colonies can then be used as an indicator of the number of living (viable) cells within a given sample. Thus during plate counting, the number of colony forming units (CFUs) within a given dilution is determined. The number of CFUs in the original sample is thus determined, through extrapolation. During the plating process, serial dilutions were made in a dilution range from 10^{-1} to 10^{-6} in sterile saline solutions. The plates were done in duplicate. After incubation, plates having between 30 and 300 colonies were chosen, as this range represents the statistically significant range. Conventional streaking of thermophilic micro-organisms on agar media on either petri dishes or roll tubes is not possible because agar melts and water evaporates in the temperature ranges within which these micro-organisms grow (Rakhely & Kovacs, 1996). Lindstrom and Sehlin (1989) developed a procedure for plating *Sulfolobus acidocaldarius* using Gelrite as the gelling agent. Rakhely and Kovacs, (1996) consolidated on this work and used a mixture of Phytigel and alginate as the gelling

agent. Their procedures for modifying the solid surface used for thermophilic bacterial plating were used in this study. The incubation was done in a Labcon platform shaker at 70°C for 5 days. The number of CFUs per ml of sample was calculated by multiplying the number of plates which had between 30 and 300 colonies per plate by the dilution factor of the plate counted.

3.3 Pyrite Leaching

The bio-oxidation of pyrite was done in sterilized 2Litre glass reactors which were fitted with an external circulating waterjacket for heating as shown in Figure 3.1. Leaching was done in 1500 ml of the media inoculated with a cell suspension to give 10%v/v concentration. Pyrite was then added to the solution to give an overall concentration of 3% w/v (Ngubane, 1991). The leaching was done at a temperature of 70°C and the reactor contents were agitated using an overhead stirrer at 150rpm. The initial pH of the solution was adjusted to 2 using concentrated H₂SO₄ and leaching was usually done for 14 days unless as stated in a particular set of experimental runs. The pH was not controlled, but was just monitored during the leaching. Samples were taken from the leach reactors at regular intervals and analysed for pH and iron concentration.

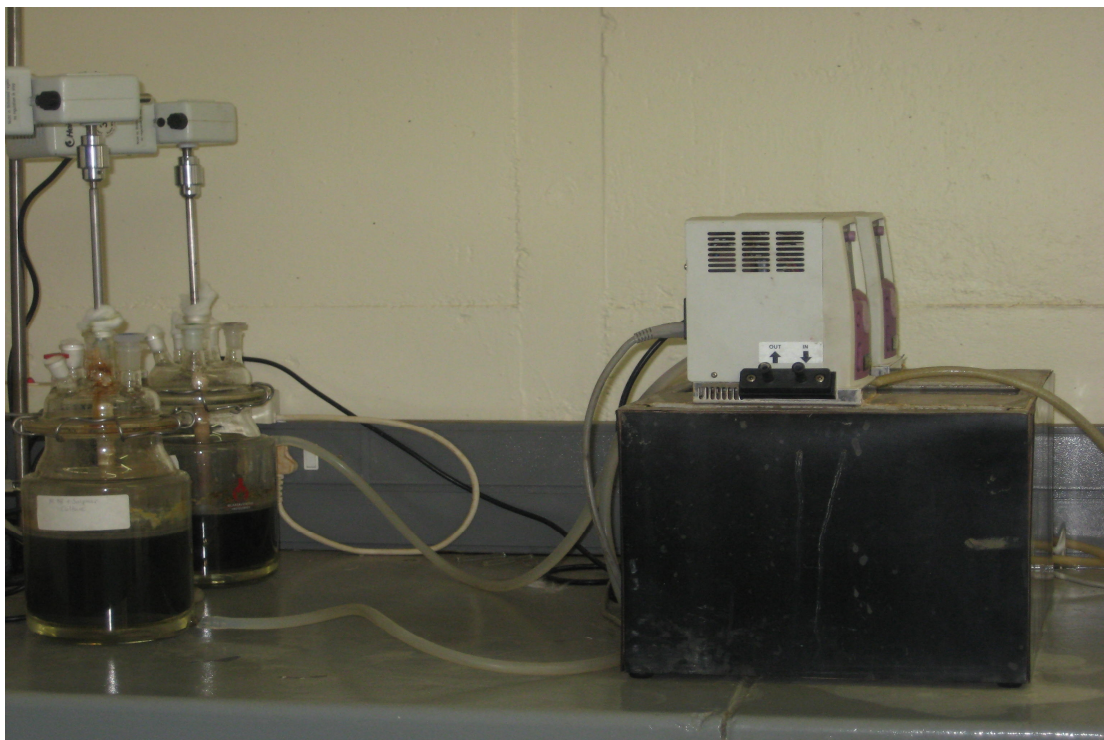


Figure 3.1 Experimental setup for pyrite bio-oxidation

3.4 Aging/Forced Hydrolysis

Upon completion of leaching, the reactor contents were filtered using gravity filtration. The filtrate was aged in a closed vessel which was fitted with condenser system under reflux at a temperature of 85°C to 90°C for 8 days (Matijevic et al., 1978; Kandori et al., 2004). The pH was regulated according to the experimental conditions being investigated in the specific experimental run. Upon completion of aging, the vessel contents were filtered and the solid precipitates air-dried. The dried precipitate particles were then characterized by X-Ray Diffractrometry (XRD) and Scanning Electron Microscopy (SEM).

3.5 Phase Transformation

The biogenic iron oxyhydroxides and oxides were transformed into the final product, hematite via an oxidation/reduction transformation. A BRF16/5-2416 Muffle furnace supplied by Elite Thermal Systems Limited, USA was used for the phase transformation. The furnace was equipped with a Eurotherm 2416 programmer. The precursor precipitates generated from aging the biogenic leach liquors were spread on an alumina crucible and placed in the furnace, where oxidation in air occurred. The heating cycle employed allowed the temperature to be raised from ambient temperature to the required oxidation temperature, T_1 °C at a rate of 10°C/minute, after which it was held constant at T_1 °C for 12 hours.

3.6 Analytical Techniques

3.6.1 Iron Concentration

The iron concentration was determined using the Varian SpectrAA-55B atomic absorption spectrophotometer (AAS) with an air/acetylene flame. The conditions used during the analysis were as stated in Table 3.2 (Varian Techtron (Pvt) Ltd., 1989).

Table 3.2 Operating conditions for iron determination by Varian (AAS)

Metal	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Working Range (ppm)
Iron	372	0.2	5	1 - 100

Aqueous metal standards were prepared using distilled water from a stock solution of 1000 ppm obtained from Associated Chemicals Enterprises Ltd, South Africa and diluted to the required concentrations of 20, 40, 60 and 80 ppm for calibration of the atomic absorption spectrophotometer (AAS). Fresh standards were prepared every

week. All samples analysed were diluted to the correct concentration range and were measured in triplicate.

3.6.2 pH and Redox Potential Measurements

A 744 Metrohm model pH meter was used for all pH and redox potential measurements. The pH meter was calibrated before use by using standard buffer solutions of pH 4, 7 and 10. The Ag/AgCl electrode was stored in 3M KCl solution to prevent desiccation. After use, the electrode was washed with distilled water and then dried.

3.6.3 Characterization of the aging precipitates

3.6.3.1 X-Ray powder Diffractometry (XRD)

The precipitates obtained during aging/forced hydrolysis were characterized by X-Ray powder diffraction (XRD) using a Philips PW1710 with a PW1830 diffractometer. A monochromatic $\text{CuK}\alpha$ radiation operated at 40kV and 20mA at 1°divergence slit was used to scan all samples from over a 2θ angle of 10° to 80°. A step interval of 0.04 and a counting time of 1 second were used. The patterns were collected and the phase identification of the precipitates was done using X'Pert HighScore software loaded with International Centre for Diffraction Data (ICDD) data files for comparison and matching.

3.6.3.2 Scanning Electron Microscopy (SEM)

The morphology of the precipitated particles was revealed using scanning electron microscopy (SEM). All samples were mounted on aluminium stubs and treated with carbon and gold palladium sputter treatment. Images were taken using a JEOL 840 scanning electron microscope operated with an accelerating voltage of 20kV.

3.6.3.3 Branauer-Emmett- Teller (BET) Analysis

Branauer-Emmett-Teller (BET) is a technique that is used to measure the surface area and pore volume of a sample. These parameters are important, for example, when studying adsorption properties of materials since they provide an indication of a material's adsorption efficiency. BET analysis of the biogenic precipitates was performed using an automated gas adsorption analyzer (Trister 3000 V6.05). Samples were degassed with N₂ gas using Micromeritics Degassing System at 150⁰ C prior to the determination of their surface areas and pore volumes. Degassing was done for twelve hours at the N₂ flow rate of 60cm³ /min. The analysis was performed under liquid nitrogen.

Chapter 4

Chemical Aging Tests

4.1 Introduction

The literature survey in Chapter 2 has shown that hematite is formed from the forced hydrolysis of $\text{FeCl}_3\text{-HCl}$ systems whilst the forced hydrolysis of $\text{Fe}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4$ has yielded jarosites, alunites and schwermannite (Matijevic & Scheiner, 1978; Masataka et al., 1984; Meyer et al., 2000; Kandori et al., 2004; Wang et al., 2007; Gramp et al., 2008). The bioleach liquor generated during pyrite oxidation is expected to be mainly acidic $\text{Fe}_2(\text{SO}_4)_3$. The acid generated is expected to be principally H_2SO_4 . Therefore in this chapter, the forced hydrolysis of $\text{Fe}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4$ systems will be studied. Although reagent grade chemicals will be used in these tests, the results will provide a useful benchmark for the test conditions to be used during the aging of the biogenic leach liquors.

Aging was done on 0.045M and 0.154M $\text{Fe}_2(\text{SO}_4)_3$ in 0.1M H_2SO_4 . The higher $\text{Fe}_2(\text{SO}_4)_3$ concentration of 0.154M corresponds to an iron equivalent of 17.22g/L, which is the maximum possible iron content which can be leached into solution, assuming 100% dissolution of the Fe in pyrite, FeS_2 (Appendix C). The lower concentration of 0.045M $\text{Fe}_2(\text{SO}_4)_3$ corresponds to 5g/L of Fe and was chosen arbitrarily as a lower iron concentration value (See Appendix C). Kandori et al., (2004) aged $\text{Fe}_2(\text{SO}_4)_3\text{-HCl}$ systems in 30ml glass vials for periods up to 8 days and found that the shape and size of the precipitate produced depended greatly on the initial $\text{Fe}_2(\text{SO}_4)_3$ concentration, whilst the nature of the precipitate was pH dependent. The influence of the pH and $\text{Fe}_2(\text{SO}_4)_3$ concentration on the precipitates will thus be elucidated during these studies. The results should

provide useful pointers on the parameters to be investigated in the quest to generate a precursor iron oxide for hematite production.

4.2 Materials and Methods

4.2.1 Materials

Chemicals used were of reagent grade and sourced from Merck Chemicals, South Africa. Anhydrous ferric sulphate, $\text{Fe}_2(\text{SO}_4)_3$ and 98% H_2SO_4 were used as received.

4.2.2 Preparation

The aging vessel, a round-bottomed flask fitted with a condenser system was charged with 300ml of 0.045M $\text{Fe}_2(\text{SO}_4)_3$ (equivalent to 5g/L of iron in solution; see Appendix C) at a temperature between 30°C and 40°C. An equivalent volume of 0.1M H_2SO_4 was then added slowly to the vessel. The vessel ports were closed and the condensation system was fitted and run. The vessel was placed on a heating mantle which allowed the temperature to be controlled. The system was refluxed and aged at a temperature of 85 - 90°C for 8 days. The same procedure was repeated at a higher iron concentration of 0.154M $\text{Fe}_2(\text{SO}_4)_3$ (equivalent to the theoretical maximum possible iron concentration in solution of 17.22g/L of iron). All tests were done in triplicate.

4.2.3 Sampling

A small sample volume (between 2 and 5ml) was withdrawn at regular intervals from the vessel. The sample was allowed to cool to room temperature and the pH and iron concentration were determined.

4.2.4 Precipitate

At the end of the 8 day aging period, the vessel contents were filtered under gravity. The precipitate was air dried and characterized by XRD.

4.2.5 Determination of the change in iron concentration and pH

The concentration of iron in the solution was determined by Atomic Absorption Spectrophotometry using a Varian Spectr AA-55B as described in section 3.6.1. A Metrohm 744 pH meter was used to measure the pH, see section 3.6.2.

4.3 Results and Discussion

Aging under acidic conditions – no pH control

The initial pH of the acidic 0.045M $\text{Fe}_2(\text{SO}_4)_3$ system was 1.39, which then dropped to a pH value of 1.05 at the end of the aging process. Similarly, a decrease in pH was also observed in the acidic 0.154M $\text{Fe}_2(\text{SO}_4)_3$ system where the initial pH was 1.53 at the commencement of aging and dropped to a pH value of 0.95 at the end of the aging period. See Figure 4.3

4.3.1 Phase Characterisation- XRD

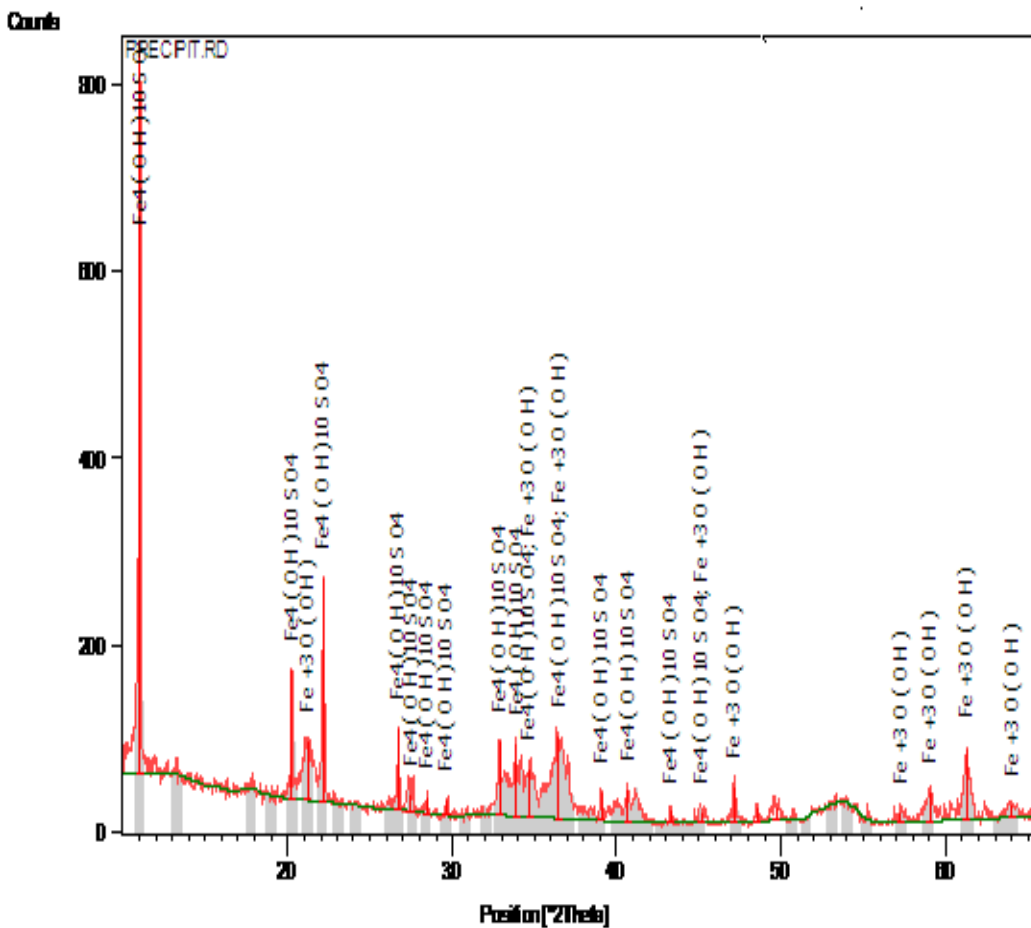


Figure 4.1 X-ray Diffractogram of the precipitate obtained when 0.045M ferric sulphate/ 0.1M H₂SO₄ was aged without pH control.

The X-ray diffractogram in Figure 4.1 shows that the precipitate obtained when the acidic 0.045M $\text{Fe}_2(\text{SO}_4)_3$ was aged under acidic conditions. The precipitate was a mixed product of iron sulphate hydroxide, $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$ and goethite, $\text{FeO}(\text{OH})$; $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$ was identified as the main phase.

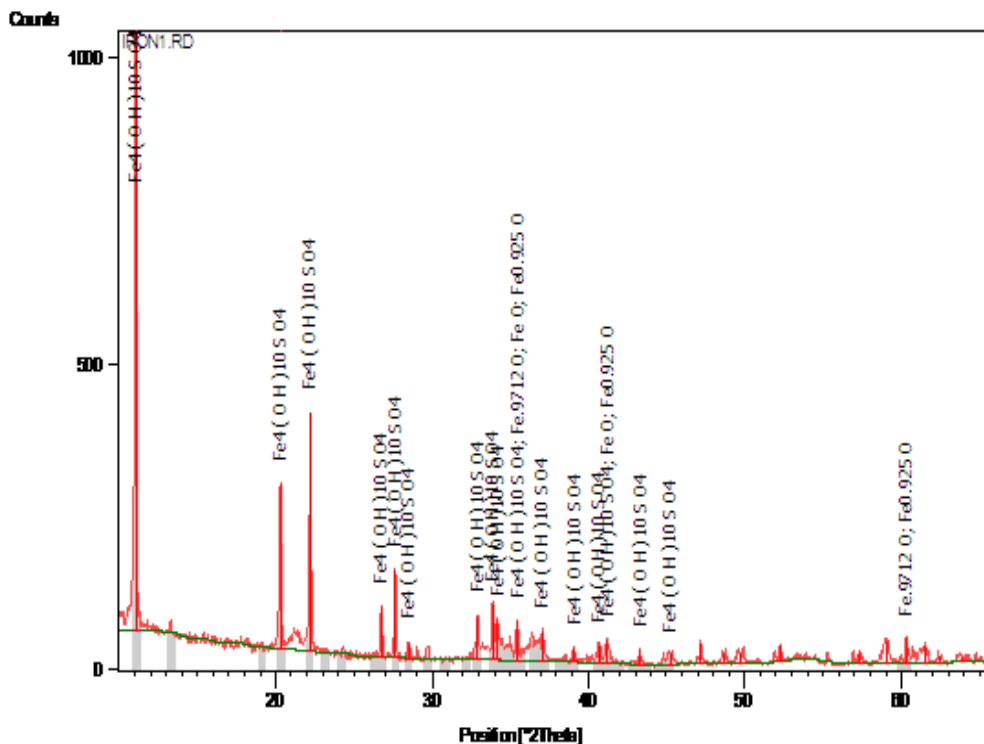


Figure 4.2 X-ray Diffractogram of the precipitate obtained when 0.154M ferric sulphate/ 0.1M H₂SO₄ was aged without pH control.

Figure 4.2 shows the X-ray diffraction pattern generated for the precipitate obtained when the 0.154M ferric sulphate system was aged with no pH control (acidic conditions). The precipitate was a mixture of iron sulphate hydroxide, Fe₄(OH)₁₀SO₄ and iron oxides, FeO, which contained iron and oxygen in varying proportions. Here, as in the previous case of the 0.045M ferric sulphate system, iron sulphate hydroxide, Fe₄(OH)₁₀SO₄ was the principal phase. In both the 0.045M and 0.154M ferric sulphate systems the main precipitate was iron sulphate hydroxide Fe₄(OH)₁₀SO₄. This is in agreement with the findings of Music et al., (1994) who in their studies on the hydrolysis of Fe³⁺ ions in 0.1 M Fe₂(SO₄)₃ solutions at 120°C produced H₃OFe₃(OH)₆(SO₄)₂ and basic sulphate, Fe₄(OH)₁₀SO₄. Wills and Harrison, (1999) also established that jarosite precipitates are formed by the hydrolysis of strongly

acidic solutions ~pH 0.5–2 of Fe^{3+} ions, sulfate ions and the relevant cations. They found that amorphous iron hydroxysulfates such as $\text{Fe}_4\text{OH}_{10}\text{SO}_4$ were precipitated at the higher end of this pH range (0.5-2). The forced hydrolysis of the ferric sulphate systems under acidic conditions therefore, yielded iron sulphate hydroxide. The concentration of the initial ferric sulphate in solution did not seem to affect the nature of the precipitation product except for the composition of the iron oxide and oxyhydroxides which made up the minor component of the precipitates.

4.3.2 Total iron concentration & pH evolution during aging

During the aging of both the 0.045M and 0.154M ferric sulphate systems, the pH was monitored but not controlled. Aging therefore occurred under acidic conditions during the aging period.

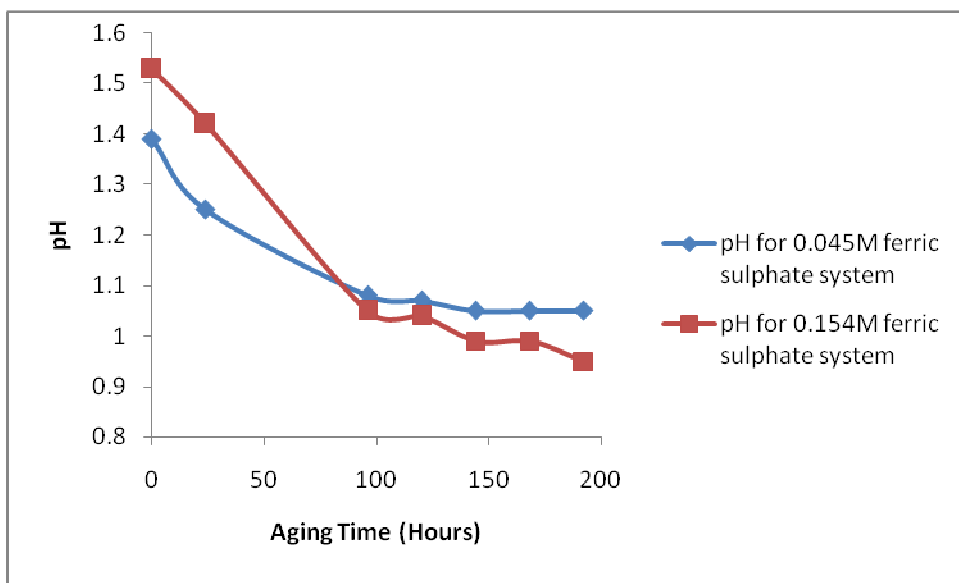
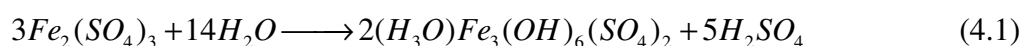


Figure 4.3 pH evolution during aging for the 0.045M and 0.154M ferric sulphate systems

Figure 4.3 shows the pH profile during the course of aging for both the 0.045M and 0.154M ferric sulphate systems. It is clear that aging occurred under acidic conditions in both systems. The profile shows that there is a general decrease in pH in the two ferric sulphate systems. The precipitation of iron-oxyhydroxides from aging $Fe_2(SO_4)_3$ is quite complex and influenced by a number of factors. Umetsu et al., (1977) studied the hydrolysis of ferric ions in sulphate systems, the associated processes are represented in Equations (4.1) to (4.3).



Umetsu et al., (1977) found that various iron oxides were produced under different reaction conditions such as the concentration of the ferric ions and temperature. Hydrothermal temperatures of up to 200°C were sometimes employed and the component of the iron oxide phase was found to be strongly dependent upon the treatment temperature (Umetsu et al., 1977).

It is apparent from Equations (4.1) to (4.3) that the hydrolysis of the ferric ion, which occurs during aging, leads to the precipitation of an iron oxide or basic sulphate and the simultaneous release of sulphuric acid. The drop in pH is therefore due to the release of H^+ (as H_2SO_4) which happens during the hydrolysis. Figure 4.3 shows that the pH of the two systems decreased from initial values of about 1.5 and 1.4 to final approximate values of 1 and 0.95.

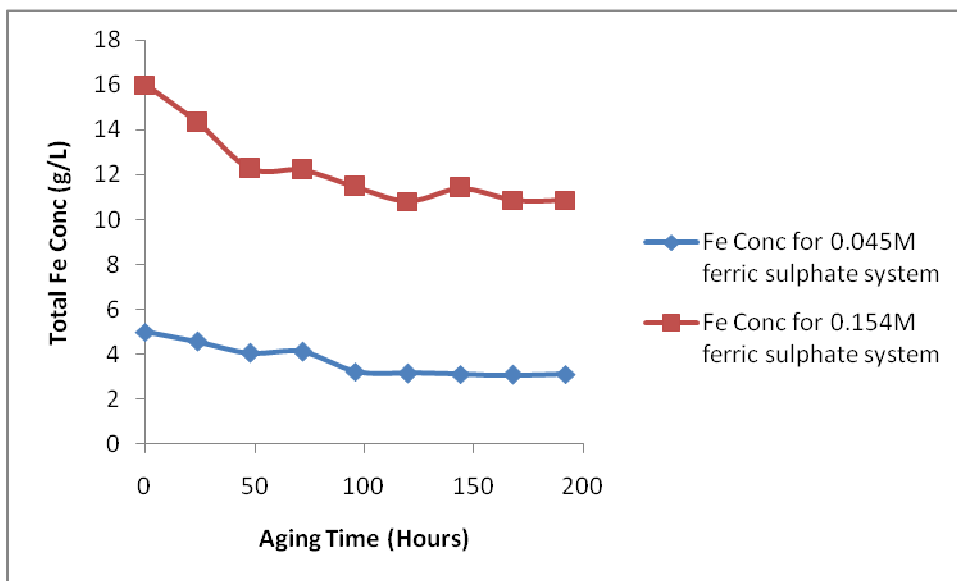


Figure 4.4 Total iron concentration (g/L) in solution during aging for the 0.045M and 0.154M ferric sulphate systems.

Figure 4.4 shows the iron profile for the 0.045M and 0.154M ferric sulphate systems during aging. The total iron concentration decreases from about 5 g/L to 3g/L and from about 16g/L to 11g/L for the 0.045M and 0.154M systems respectively. It is observed that the initial iron concentration value measured at the beginning of aging is slightly lower (16g/L) than the expected value (17.22g/L) for the acidic 0.154M $\text{Fe}_2(\text{SO}_4)_3$ system. This anomaly is probably due to the fact that hydrolysis of the ferric ion starts to occur during preparation of the system, leading to slight precipitation of the iron oxyhydroxides and/or sulphates. This phenomenon is not uncommon and has been reported by Matijevic and Scheiner (1978). This hydrolysis which occurs early at the beginning of the aging process is more pronounced in the 0.154M $\text{Fe}_2(\text{SO}_4)_3$ than in the 0.045M system because of the relatively higher ferric ion concentration. The general decrease in the total iron concentration in solution observed in both systems during the course of aging is due to the fact that various iron oxides and basic iron sulphates are precipitated when the ferric ion hydrolyzes during the aging period (Equation 4.1 to 4.3). These oxides and basic sulphates are precipitated as solids leading to a depletion of the ions available in solution.

However, there are few instances, such as between 120 and 144 hours for the 0.154M $\text{Fe}_2(\text{SO}_4)_3$ system where there is a momentary increase in the iron concentration in solution before it eventually reverts to the prevailing decreasing trend. This trend was observed and confirmed during the duplicate aging testworks and can be attributed to the porous structure of alunite and jarosite compounds. Jarosite-type compounds have the ability to scavenge unwanted elements from hydrometallurgical ore processing solutions (Dutrillac, 1983). During the course of aging, it is possible that the mainly $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$ precipitate will absorb some of the aqueous iron ions into its porous structure momentarily, then release these aqueous iron ions into the solution until equilibrium is established when ferric ion hydrolysis ceases and the iron concentration in solution falls to a stable value.

The XRD analyses (Figure 4.1 and 4.2) show that the precipitate produced in the two systems was mainly a basic iron sulphate $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$ and FeOOH and FeO in minor proportions. Matijevic et al., (1975) reported that these basic iron sulphates, $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$ are similar to the jarosite group, $[\text{MFe}_3(\text{SO}_4)_2(\text{OH})_6]$. The results therefore are in line with findings from workers who have studied the hydrolysis reaction of ferric ions in sulphate systems. The FeSO_4^+ complex is prevalent in acidic ferric sulphate systems. Matijevic et al., (1975) reported that the presence of this complex suppresses the polymerization process and formation of iron oxyhydroxides and oxides. The validity of this assertion was tested by increasing the pH of the ferric sulphate systems in an attempt to see if this had an effect on iron oxide and oxyhydroxide formation. Since aging under acidic conditions produced mainly iron basic sulphates, the pH value during aging was subsequently increased to a neutral to basic pH range of 6 and 9, to determine if the pH conditions employed during aging had any significant effect on iron oxide formation.

4.4 Aging under neutral to basic conditions –pH controlled between 6 and 9

To determine if the pH had an influence on the nature of the precipitate formed during aging, both the 0.045M and 0.154M ferric sulphate systems were aged under neutral to basic conditions. In these tests the pH of these acidic ferric sulphate systems was adjusted through the addition of concentrated NaOH solution. The pH was adjusted daily and kept in the pH range between 6 and 9.

4.4.1 Phase Characterization- XRD

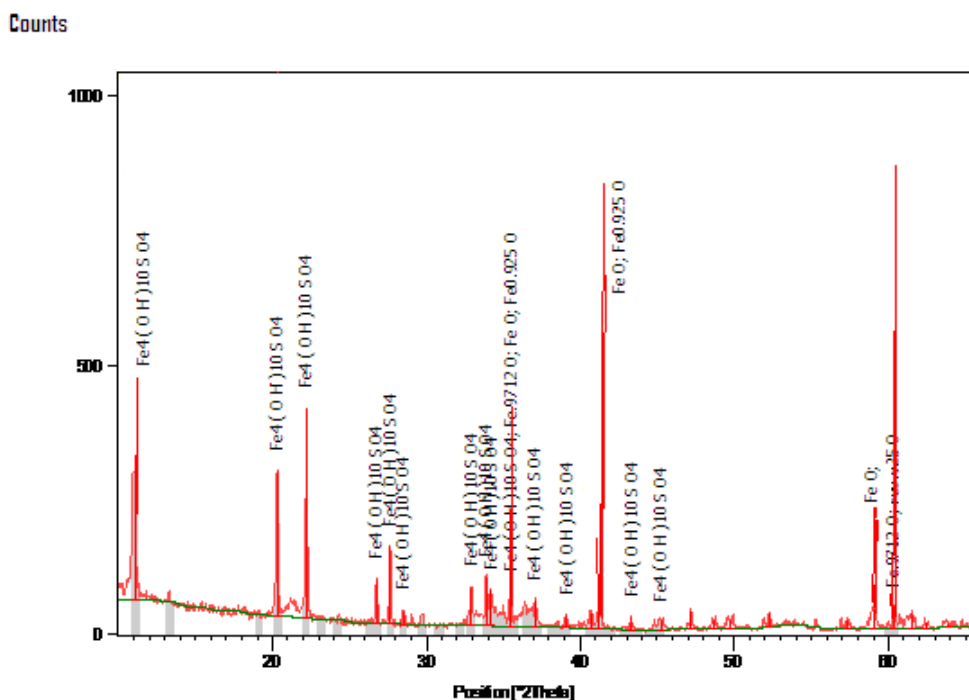


Figure 4.5 X-ray Diffractogram of the precipitate obtained when 0.045M ferric sulphate/ 0.1M H₂SO₄ was aged within a pH range of 6-9.

Figure 4.5 shows that in the 0.045M ferric sulphate system, the precipitate formed from aging within a pH range of 6 -9 was a mixture of an iron oxide, FeO; goethite,

FeOOH and basic iron sulphate, $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$. Goethite and the iron oxide were present in greater quantities than the basic iron sulphate.

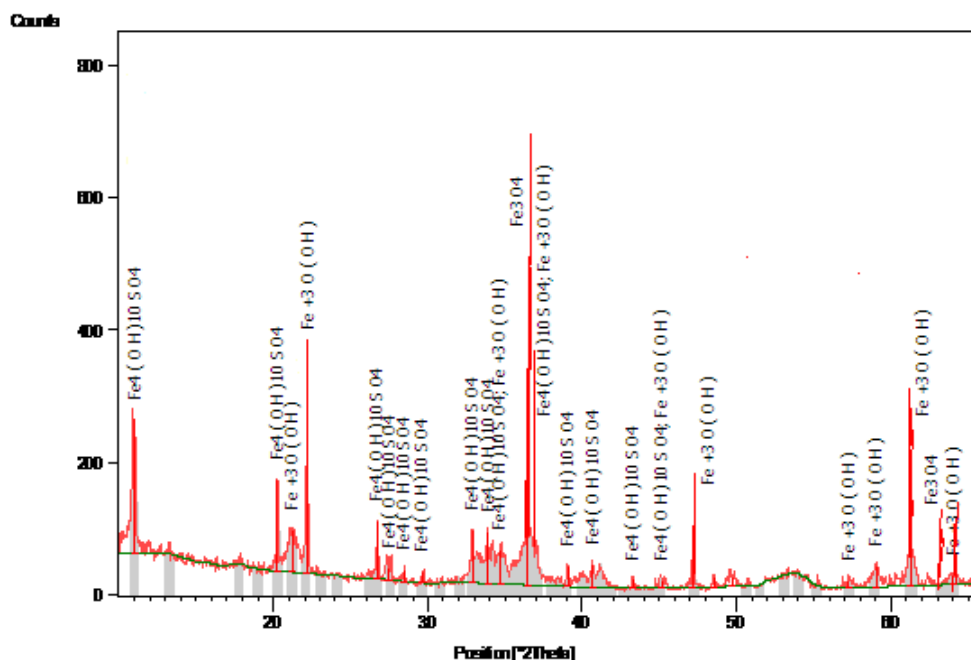


Figure 4.6 X-ray Diffractogram of the precipitate obtained when 0.154M ferric sulphate/ 0.1M H_2SO_4 was aged within a pH range of 6 - 9.

Figure 4.6 shows that the precipitate formed in the 0.154M ferric sulphate system within a pH range of 6-9 comprised a mixture of iron oxide phases and the basic iron sulphate. The phases present were identified as iron oxide, FeO; magnetite, Fe_3O_4 ; goethite, FeOOH and basic iron sulphate, $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$. The iron oxides, FeO, Fe_3O_4 and FeOOH were more abundant than the basic iron sulphate. Therefore it is clear that aging of the acidic 0.045M and 0.154M ferric sulphate systems under neutral to basic conditions (pH 6-9) led to the precipitation of mainly iron oxides and oxyhydroxides. This is unlike the case experienced when aging of these systems was done under acidic conditions, where mainly basic sulphates, $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$ were precipitated. It seems that increasing the pH minimized the formation of the FeSO_4^+ complex, which was identified as being responsible for suppressing iron oxide

formation (Matijevic et al., 1975; Music et al., 1994).

The precipitation process is complex and influenced by a number of factors such as pH, temperature, concentration of ferric ions and nature of anions present, with even the slightest changes in the reaction conditions leading to the formation of a totally different precipitation product (Music et al, 1994). The pH seemed to be the more dominant influential parameter. The precipitation products of aging under neutral to basic conditions produced more iron oxides as compared to the products formed under acidic conditions. The effect of the concentration of initial ferric ions in the systems seems to have been overridden by the pH in determining the nature of the precipitate formed. However at the higher initial concentrations (0.154M) more iron oxides and oxyhydroxides formed in the precipitates when compared to the lower concentrations of 0.045M ferric sulphate.

4.5 Summary & Conclusions

The aging of $\text{Fe}_2(\text{SO}_4)_3$ - H_2SO_4 systems prepared from reagent grade chemicals, under various conditions was studied in this chapter. These chemical aging tests are expected to provide a useful benchmark for the aging of biogenic systems, which will be investigated in this work. When both the 0.045M and 0.154M $\text{Fe}_3(\text{SO}_4)_2$ in 0.1M H_2SO_4 were aged under acidic conditions basic iron sulphates of the general formula $\text{Fe}_4(\text{OH})_{10}\text{SO}_4$ were mainly precipitated through a hydrolysis reaction with iron oxides and oxyhydroxides being a minor constituent. The precipitation process is complex and influenced by a number of factors such as pH, concentration of ferric ions and nature of anions present. The formation of the FeSO_4^+ complex in acidic ferric sulphate solutions was reported to suppress the formation of iron oxides and oxyhydroxides. The pH was therefore subsequently increased during the aging of the ferric sulphate systems to values between 6 and 9. XRD analysis revealed that iron oxyhydroxides and oxides such as FeO, FeOOH and Fe_3O_4 were precipitated as the main phase when both systems (0.045M and 0.31M $\text{Fe}_3(\text{SO}_4)_2$ in 0.1M H_2SO_4) were

aged under neutral to basic conditions. The findings show that the pH influences the nature of the precipitation product significantly. Basic iron sulphates, with the formula $\text{Fe}_4\text{OH}_{10}\text{SO}_4$ were precipitated under acidic aging conditions whilst mainly iron oxides were precipitated under neutral to basic conditions. The higher initial ferric sulphate concentration seemed to encourage the formation of more iron oxides in the precipitates although the concentration of the ferric ions did not seem to have a significant effect on the precipitation product. However, the pH influenced the nature of the precipitate greatly.

Chapter 5

Biogenic Studies

5.1 Introduction

The aging of $\text{Fe}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4$ systems derived from reagent-grade chemicals was studied in Chapter 4. The findings from the chemical aging tests were useful in identifying crucial factors to be studied during the aging of biogenic leach liquors derived from pyrite biooxidation. In this chapter pyrite oxidation using thermophilic *Acidianus* spp. bacteria was studied. The effect of the composition of the culture medium on the rate of bioleaching was investigated. Here, the effect of the sulphur form used in the culture medium, either as elemental sulphur S_8 or potassium tetrathionate $\text{K}_2\text{S}_4\text{O}_6$ was studied. Preliminary aging tests were carried out on the acidic ferric sulphate solutions generated during pyrite bioleaching and the phases present in the biogenic precipitates were characterized by X-ray diffraction. These preliminary biogenic tests were crucial in assessing the viability of generating iron oxyhydroxides and oxides, which could be used as a precursor material for hematite, Fe_2O_3 formation which is the ultimate end product of interest.

5.2 Materials and Methods

5.2.1 Determining the effect of the sulphur form (S_8 or $\text{K}_2\text{S}_4\text{O}_6$) used in the culture medium on the rate of bioleaching

Pyrite bioleaching was carried out as described in Section 3.4. Since *Acidianus* use sulphur as an energy source, the effectiveness of the sulphur form used, as either elemental sulphur or potassium tetrathionate on the biooxidation rates was investigated (See Section 3.3). The total iron concentrations of the leach liquors during the course of bioleaching in both the elemental sulphur and potassium tetrathionate based media were determined using Atomic Absorption Spectroscopy.

5.2.2 Determination of Bacterial Growth using UV-Visible Spectrophotometer

The bacterial growth of *Acidianus* was determined as outlined in section 3.2.5.

5.2.3 Determination of Bacterial Concentration – Plate Count

The actual bacterial concentration of *Acidianus* spp. used as inoculum in the $K_2S_4O_6$ media for the pyrite leaching was determined using the plate counting method described in section 3.2.6. The average viable cell count used in the experimental studies was 4.3×10^7 colonies per ml.

5.2.4 Preliminary Aging Tests of leach liquor obtained during pyrite bioleaching

The biogenic leach liquors generated during pyrite leaching using a $K_2S_4O_6$ media (Section 3.3) were then aged to form various biogenic precipitates via a forced hydrolysis reaction. The aging procedure is outlined in section 3.4. The chemical aging tests done in the preceding chapter, chapter 4 revealed that the pH greatly influenced the nature of the biogenic precipitate. In this work, the biogenic leach liquors will be aged under both acidic and basic pH conditions to determine if this factor, as was the case for the chemical aging tests, is also of essence in affecting the iron oxyhydroxide or basic sulphate formed in biogenic systems.

5.3 Results and Discussion

5.3.1 Determination of Bacterial Growth using UV-Visible Spectrophotometer

The bacterial growth of the *Acidianus* cultures was determined by measuring the optical density of the bacterial suspension using the UV-Visible double beam spectrophotometer. Figure 5.1 shows that higher bacterial concentrations were experienced in the $K_2S_4O_6$ culture medium when compared to the S_8 based medium.

Maximum growth in the $K_2S_4O_6$ based medium was achieved after 5 days. This period was therefore chosen as the optimum period for incubation during culturing.

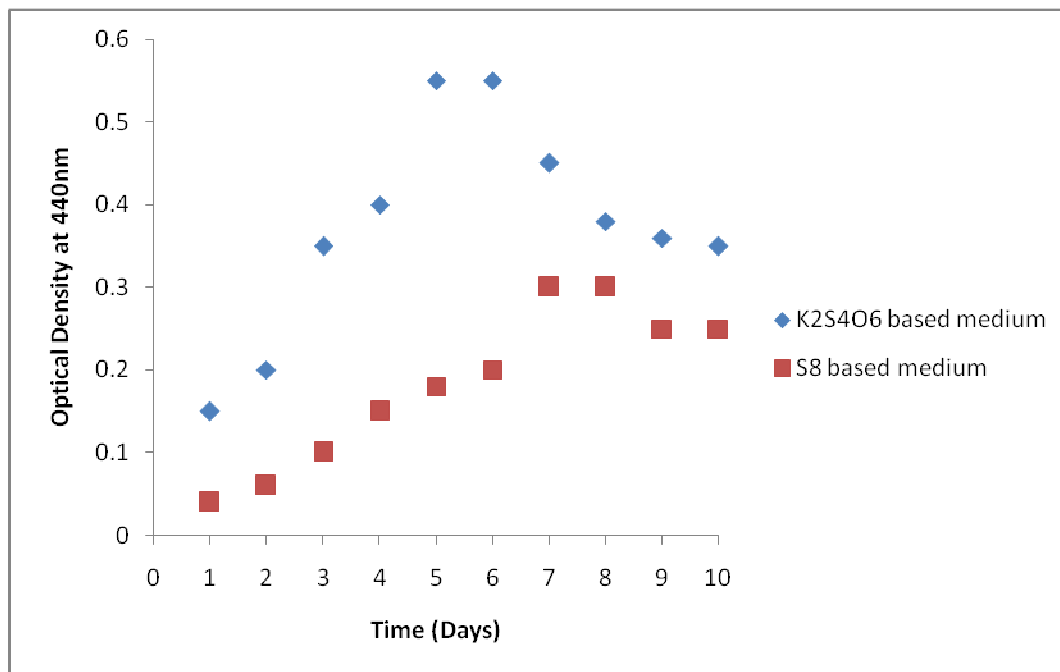


Figure 5.1 Optical density of *Acidianus* cultures measured at 440nm.

5.3.2 Effect of the sulphur form (S_8 or $K_2S_4O_6$) used in the culture medium on the rate of bioleaching.

Figures 5.2 and 5.3 show the total iron concentrations in solution obtained when the bioleaching of pyrite by *Acidianus* spp. was carried out in both the potassium tetrathionate, $K_2S_4O_6$ and elemental sulphur, S_8 based media respectively. At the end of the leaching period, 12.8g/L of iron was leached into solution in the $K_2S_4O_6$ medium as compared to 3.82g/L of total iron in the sulphur based medium, which translates to oxidation rates of 74% and 22% for the potassium tetrathionate and sulphur based media respectively. *Acidianus* derive energy for growth from the

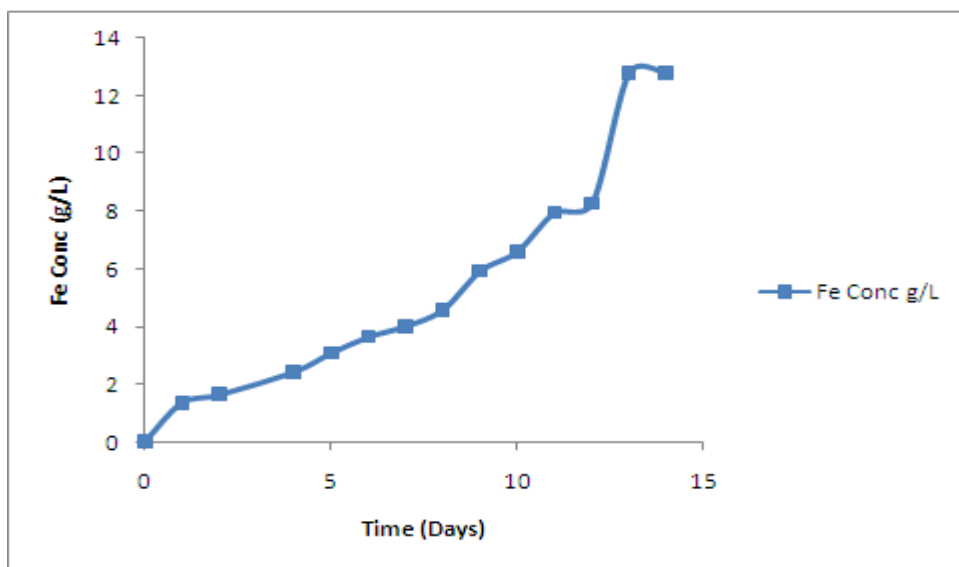


Figure 5.2 Total iron concentration in the potassium tetrathionate, $K_2S_4O_6$ based medium

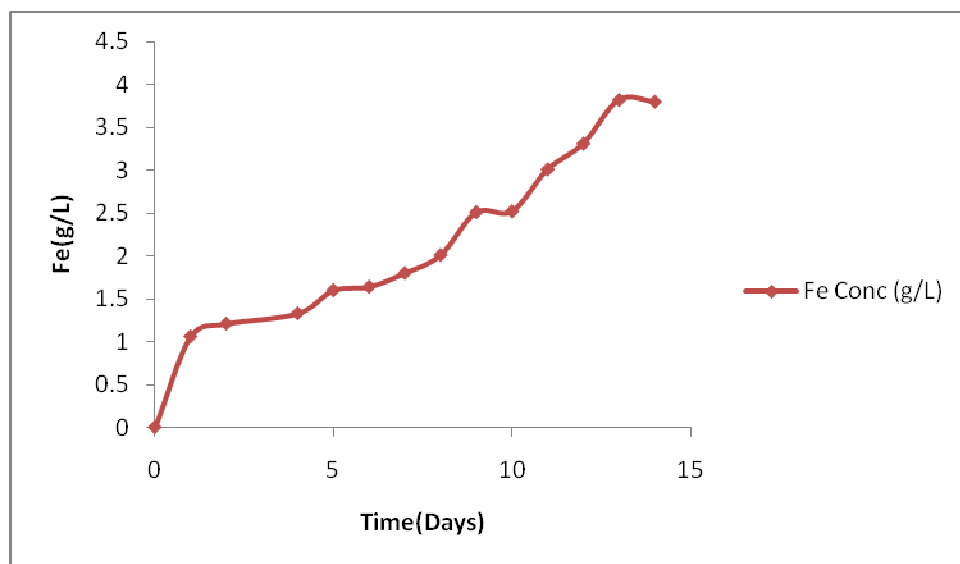


Figure 5.3 Total iron concentration in the elemental sulphur, S_8 based medium

chemical oxidation of inorganic sulphur compounds (Rossi, 1990). It is possible that during the first few days of bioleaching when the archae are still adapting during the lag phase of growth, abiotic reactions are more favourable. The changes in the redox potential during bioleaching in both media are shown in Figure 5.4.

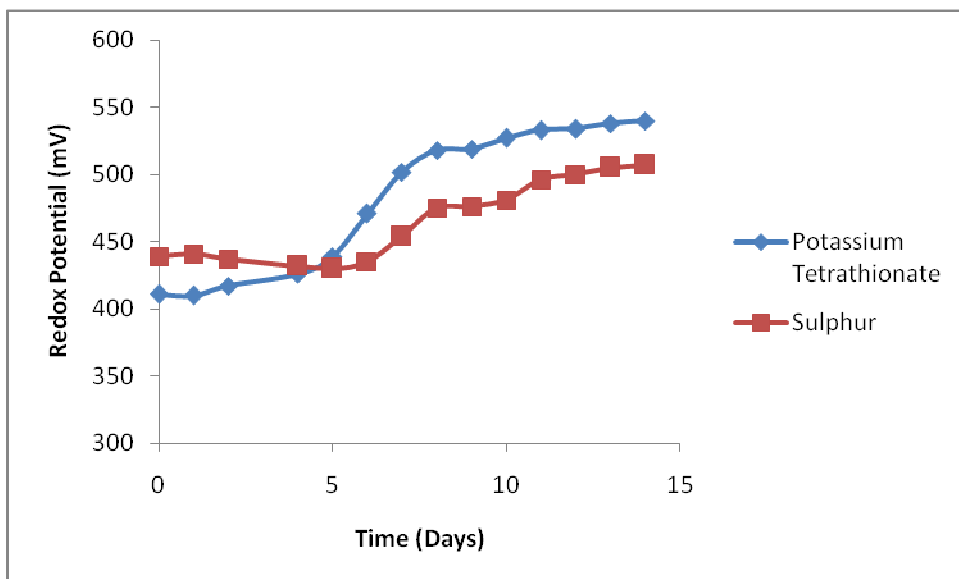
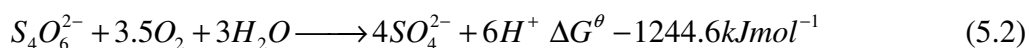


Figure 5.4 Redox potential profiles in the potassium tetrathionate, $K_2S_4O_6$ and elemental sulphur, S_8 based media over the course of bioleaching.

A general increase in the redox potential is observed in both systems during the course of bioleaching. This is expected as the iron in pyrite is oxidized during leaching. Higher redox potential values were observed in the potassium tetrathionate based media compared to the elemental sulphur based media. The higher redox potential measurements imply that greater ionic activity was experienced in the potassium tetrathionate medium compared to the sulphur based medium. Rohwerder et al., (2003) in their review of bacterial metal sulphide oxidation stated that whilst elemental sulphur is inert to abiotic oxidation at acidic pH levels, reduced sulphur compounds such as thiosulphate and tetrathionate are oxidized abiotically to sulphate and protons (Equation 5.2). Kelly (1999) described these oxidation reactions for the sulphur and potassium tetrathionate based media as shown in Equation (5.1) and (5.2) respectively



More H^+ ions are generated in the tetrathionate based media (Equation 5.2) and these ions enable more ferrous ions to be oxidized to ferric ions. Since more ferric ions are generated, attack on pyrite is enhanced and hence pyrite oxidation is greater in the tetrathionate based medium than in the sulphur based medium. This assertion is readily supported by the more acidic pHs observed during the initial stages of bioleaching in the potassium tetrathionate based medium (Appendix D). Equation (5.2) also shows that the oxidation of tetrathionate to sulphate has a more negative Gibbs free energy when compared to the oxidation of sulphur to the sulphate ion (5.1). It is thus possible for more energy to be availed to the microorganisms in the potassium tetrathionate media for cell synthesis, growth and in ATP pathways (Rossi, 1990). Greater bacterial growth is therefore experienced in the potassium tetrathionate medium leading to greater solubilisation rates of 74% in this medium compared to the lower rate of 22% in the sulphur based medium during the leaching period. The potassium tetrathionate, $K_2S_4O_6$ based medium was therefore used in all subsequent experiments.

5.3.3 Phase Characterization of Biogenic Precipitates

The biogenic leach liquor obtained after pyrite biooxidation by *Acidianus* spp. for a leaching duration of 14 days was aged under different pH conditions for 8 days. Hydrolysis of the ferric ion in the leach liquors occurred during aging, leading to the precipitation of various solid phases. Figure 5.5 shows the X-ray diffractogram for the precipitate generated under acidic conditions. The pH dropped from values of 3.5 to 2.1 when the pH was not regulated during aging (Appendix E). The phases which were present in the precipitate were identified as potassium jarosite $KFe_3(SO_4)_2(OH)_6$ and potassium sulphate K_2SO_4 . Figure 5.6 shows that magnetite, Fe_3O_4 , hematite Fe_2O_3 and potassium sulphate K_2SO_4 were the phases identified in the precipitate when aging occurred under neutral to basic conditions (pH 6-9). The hydrolysis of the ferric ion in sulphate systems can be described by Equations (5.1) to (5.3)

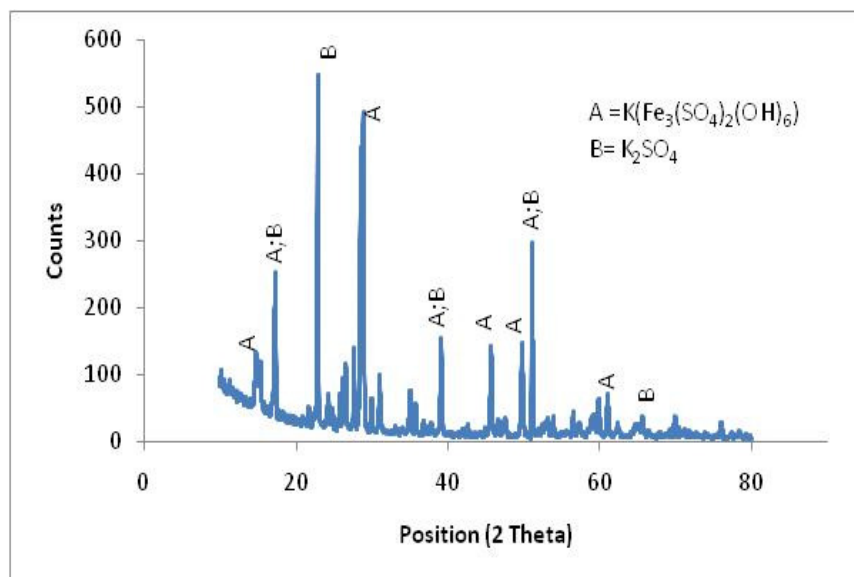


Figure 5.5 X-ray Diffractogram of the precipitate generated upon aging a biogenic $K_2S_4O_6$ leach liquor under acidic conditions (pH not adjusted)

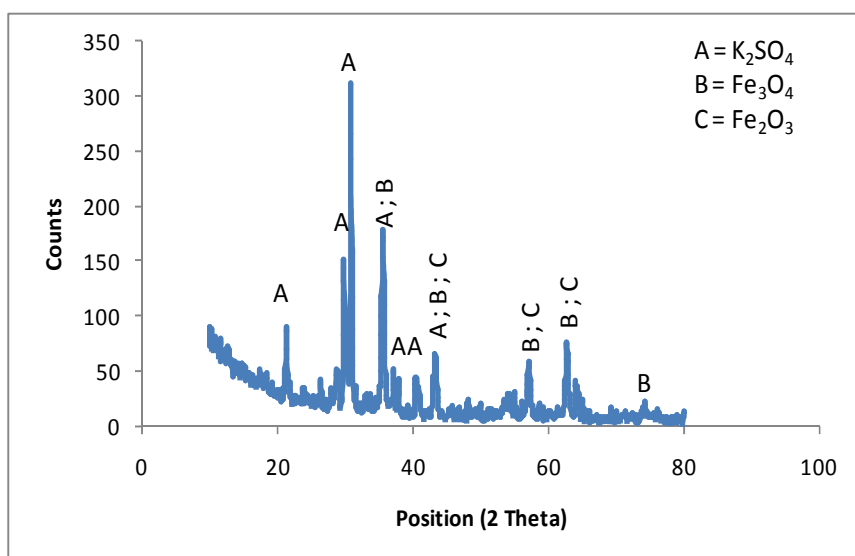
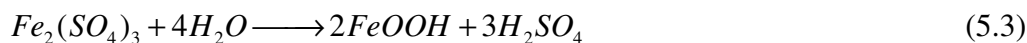
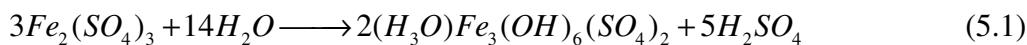


Figure 5.6 X-ray Diffractogram of the precipitate generated upon aging a biogenic $K_2S_4O_6$ leach liquor under neutral to basic pH conditions.

The products of the hydrolysis reaction are dependent on the reaction conditions such as pH, temperature and concentration of ferric ions. Dutrizac (1983) studied the precipitation of jarosite-type compounds in hydrometallurgical circuits. In the zinc industry they found that excesses of sulphate, iron and alkali ions could be removed from zinc sulphate-sulphuric acid solutions through the precipitation of jarosites (Music et al., 1994). Iron jarosites have the general formula $M Fe_3(SO_4)_2(OH)_6$

Where $M = H_3O^+, Na^+, K^+, Rb^+, Ag^+, Ti^+, NH_4^+, \frac{1}{2} Pb^{2+} \text{ or } \frac{1}{2} Hg^{2+}$

In these tests potassium jarosite, $KFe_3(SO_4)_2(OH)_6$ was precipitated during aging under acidic conditions. This is due to the fact that the potassium cation, K^+ was the most abundant cation present in the culture medium as 23.6g/L of $K_2S_4O_6$ and 0.28g/L of KH_2PO_4 . Thus these potassium salts are present in the medium at a factor of almost 20 times the concentration of the next abundant cation, NH_4^+ which is in the form of $(NH_4)_2SO_4$ (See section 3.2.3). Therefore K^+ overrides H_3O^+ and NH_4^+ as the cation of choice in the general jarosite formula. The precipitate also contains potassium sulphate which forms as the excess K^+ ions in the biogenic liquor react with the SO_4^{2-} ions during aging.

Increasing the pH during aging to values between 6 and 9, led to the precipitation of a mixed product of Fe_3O_4 and Fe_2O_3 iron oxides contaminated with K_2SO_4 . As was previously discussed during the chemical aging tests, the presence of the $FeSO_4^+$ complex in biogenic acidic solutions also suppresses the formation of iron oxyhydroxides and oxides (Matijevic et al., 1975; Music et al., 1994; Kandori et al., 2004). However, increasing the pH of the biogenic leach liquor enabled the precipitation of the iron oxyhydroxides and oxides to occur, via the ferric hydrolysis reaction. Magnetite, Fe_3O_4 and hematite, Fe_2O_3 were therefore precipitated when aging was done under neutral to basic conditions.

5.4 Summary & Conclusions

This chapter focused on the preliminary biotests whose findings will be used in mapping a bio-mediated route for hematite nanoparticle formation from leach liquors emanating from pyrite oxidation. Sulphur is used as a substrate for growth by thermophilic *Acidianus* bacteria. The effect of the sulphur form (as either elemental sulphur, S_8 or potassium tetrathionate, $K_2S_4O_6$) on the rate of pyrite bioleaching was studied. Higher leaching rates were obtained in the $K_2S_4O_6$ based medium where 74% of the iron in pyrite was oxidized compared to a lower oxidation value of 22% experienced in the elemental sulphur based medium during the leaching period of 14 days. Optical density measurements also showed that higher bacterial growth of the microorganisms occurred in the $K_2S_4O_6$ based medium compared to the S_8 based medium. The $K_2S_4O_6$ sulphur form was therefore found to be more effective than the S_8 form and subsequently used in all ensuing bioleach experiments.

The leach liquors generated in the $K_2S_4O_6$ based media were subsequently aged under different pH conditions. Aging under acidic conditions led to the precipitation of mainly potassium jarosite, $KFe_3(SO_4)_2(OH)_6$ through the hydrolysis reaction of the ferric ions in the leach liquor. However, as was the case for the chemical aging tests, when the pH was raised to neutral and basic conditions an entirely different product was precipitated. Aging of the biogenic liquors in the pH range 6-9 resulted in the precipitation of mainly magnetite and hematite, which are both iron oxides. The major impurity in the precipitates was K_2SO_4 . The pH seems to be the most influential factor which determines the nature of the iron oxyhydroxides, oxides or basic sulphates formed during the aging process. The subsequent chapter will look at the optimization of pH, since this is such a crucial parameter in the aging process. The effect, if any, of the iron concentration on the precipitation process will also be investigated.

CHAPTER 6

pH and Fe Concentration Optimization Tests

6.1 Introduction

The results obtained from the preliminary aging tests on both the chemical and biological systems (Chapter 4 and 5) show that the pH is an influential factor which determines the nature of the precipitate formed during aging. In the biogenic systems, a mixed product of basic iron hydroxysulphates and potassium sulphate was formed during aging under acidic conditions. Iron oxides containing potassium sulphate as an impurity were precipitated under neutral to basic pH conditions (pH 6 -9). The precipitate formed under a pH range of 6 to 9 was a mixed product of magnetite, Fe_3O_4 and hematite Fe_2O_3 . In these optimization tests, this broad pH range was subsequently narrowed into smaller pH intervals of 1 unit each and the precipitate phase formed in each pH interval was determined. The purity of the solids formed in each pH interval was determined using Inductively Coupled Plasma Emission Spectroscopy (ICP) analysis. These findings from ICP analysis would help to indicate if any pure phases of the iron oxides were formed in these pH intervals.

The formation of a pure phase of the iron oxides is an important process stage in the quest to form hematite nanoparticles, which are the ultimate end product of interest. It is envisaged that the iron oxide produced during these pH optimization tests will either be a suitable precursor material for hematite nanoparticle formation or be the end product hematite itself. The effect of iron concentration on the biogenic precipitate formed during aging is also discussed in this chapter. Leach liquors of different Fe concentrations were obtained by carrying out pyrite biooxidation for varying leach durations. This chapter therefore elaborates on the materials used and methods followed during these pH and Fe concentration optimization tests as well as

the analytical techniques used to characterize the precipitates. The findings at the various pH intervals under investigation namely; pH 6-7; pH 7-8 and pH 8-9 and at different leach liquor Fe concentrations are presented and discussed before summarizing and concluding the chapter.

6.2 Materials and Methods

6.2.1 *Generation of bioleach liquor – Pyrite Bioleaching*

Pyrite oxidation was carried out as described in Section 3.3 to generate bioleach liquors. These liquors were subsequently aged to produce the precursor iron oxides and/or hydroxides which would be used in α -Fe₂O₃ hematite nanoparticle generation. All tests were done in duplicate.

6.2.2 *Optimization of pH – Aging Under Different pH Conditions*

After bioleaching for 14 days, the reactor contents were filtered through a 0.22 μ m nucleopore filter. The filtrate was aged in a closed vessel as described in section 3.5. Aging was done for 8 days. The pH was regulated within the required pH range through the addition of concentrated NaOH. When aging was completed, the vessel contents were filtered and the solids air-dried.

6.2.3 *Optimization of Iron Concentration – Aging of Bioleach Liquors with Different Iron Concentrations*

In these tests, aging was done on biogenic leach liquors which had been generated by leaching for different leaching durations. Different leaching periods result in the production of leach liquors of different iron concentrations. Thus, the effect of aging bioleach liquors of different iron concentrations was studied. Pyrite bioleaching was done as described in Section 3.3, with the leaching duration varied in order to generate leach liquors with different iron concentrations.

6.2.4 Characterization of the biogenic precipitates

The dried biogenic precipitates obtained during aging were characterized by X-ray Diffractometry (XRD), scanning electron microscopy (SEM), and Branauer-Emmett-Teller (BET) Analysis as required. The procedures used in executing these analytical techniques are as outlined in section 3.6.3.

6.3 Results & Discussion

Optimization of pH – Aging Under Different pH Conditions

The biogenic leach liquor generated after 14 days of leaching and of 0.23M Fe concentration was aged under different pH conditions for 8 days.

6.3.1 Aging within a pH range of 6 – 7

During these tests, the pH of the leach liquor was adjusted to a pH range between 6 and 7 using concentrated NaOH. The liquors contained 12.8g/L of total iron. Figure 6.1 and Figure 6.2 show the X-ray diffractogram and peak matching list of the precipitate obtained under these pH conditions respectively. The phases present in the precipitate were identified as a mixture of maghemite, $\gamma\text{-Fe}_2\text{O}_3$, hematite, $\alpha\text{-Fe}_2\text{O}_3$ and potassium sulphide, K_2S_5 . The main phase in the precipitate was maghemite. Potassium sulphide occurred as an impurity and was precipitated from the aqueous potassium and sulphur-containing ions in the liquor.

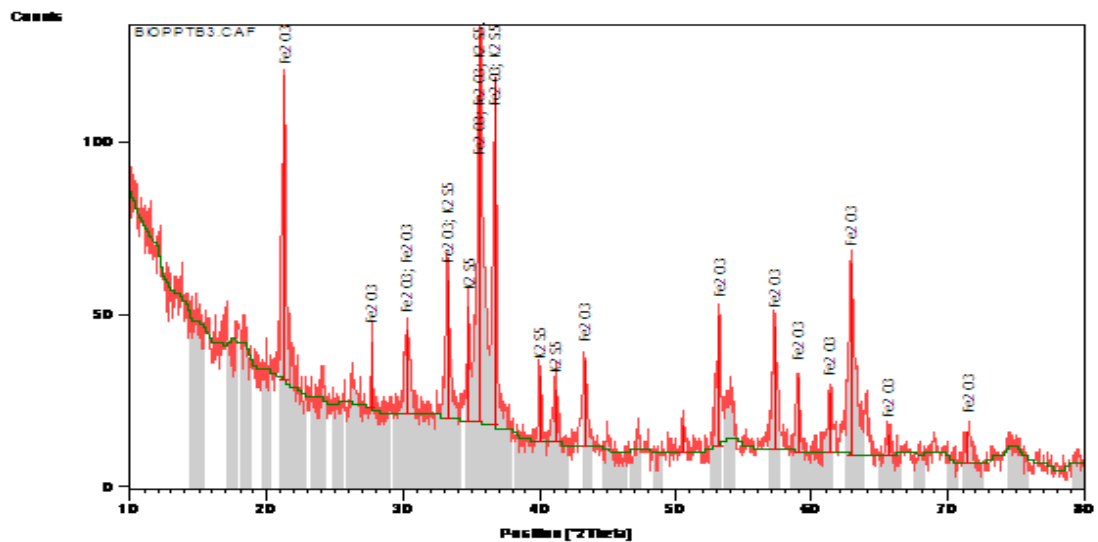


Figure 6.1 X-Ray Diffractogram of the precipitate formed upon aging within a pH range of 6 -7.

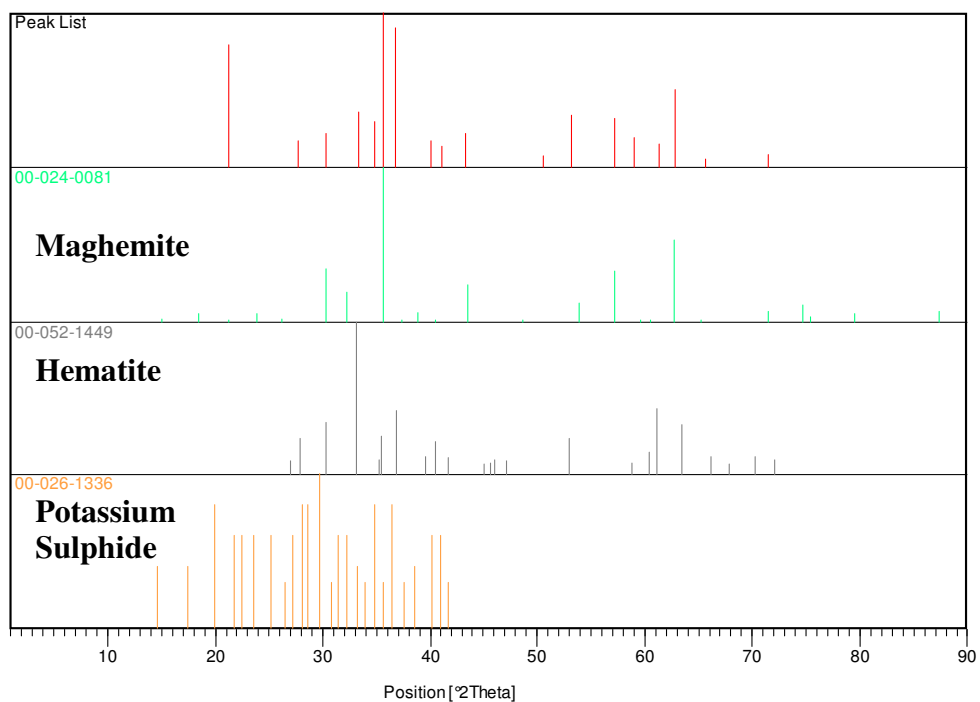


Figure 6.2 Peak matching list of the precipitate formed within a pH range of 6 -7.

Figure 6.3 shows the SEM image of the precipitate. The particles were pseudocubic in shape and occurred as globular agglomerates.

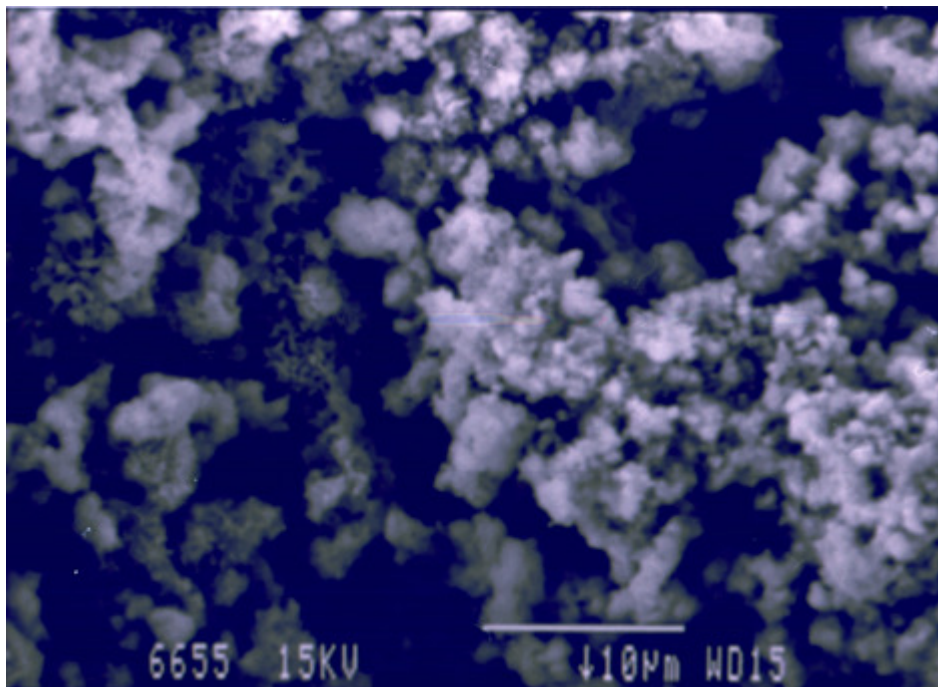


Figure 6.3 SEM image of the precipitate formed within a pH range of 6 -7.

6.3.2 Aging within a pH range of 7 – 8

Figures 6.4 and 6.5 reveal that the precipitate formed within a pH range of 7 and 8 is purely magnetite, Fe_3O_4 . No other phase was detected in the precipitate from X-ray diffractometry. Figure 6.6 shows the SEM image of the biogenic precipitate. The magnetite precipitate consists of spherical globular agglomerates of approximately $20\mu\text{m}$ in diameter. Discrete particles, which form part of the agglomerate can be seen on the image.

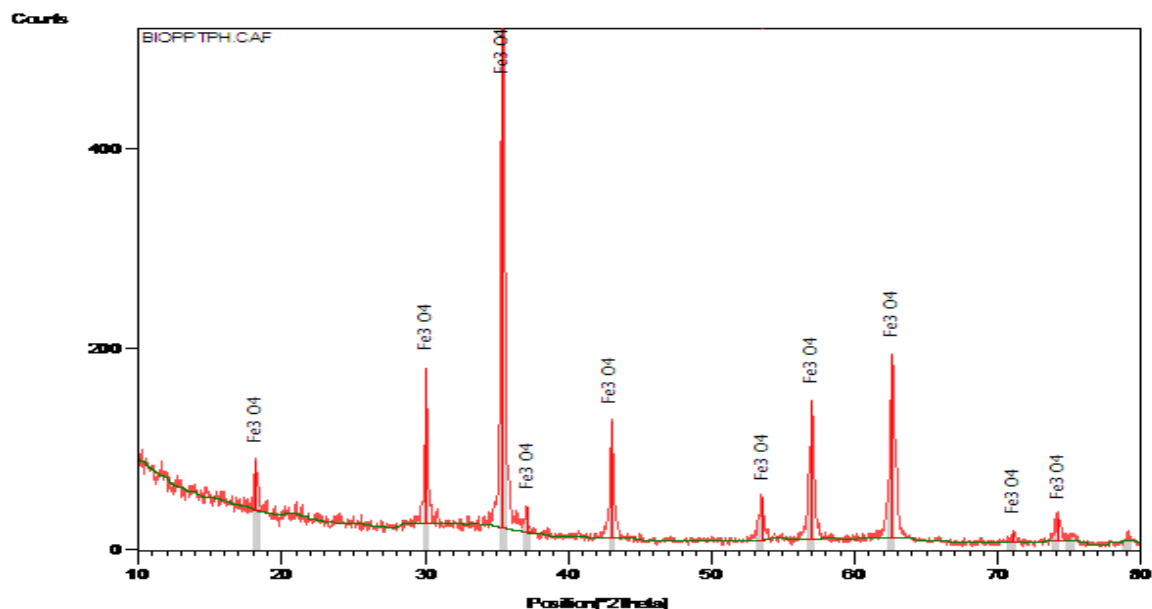


Figure 6.4 X-Ray Diffractogram of the precipitate formed upon aging within a pH range of 7 -8.

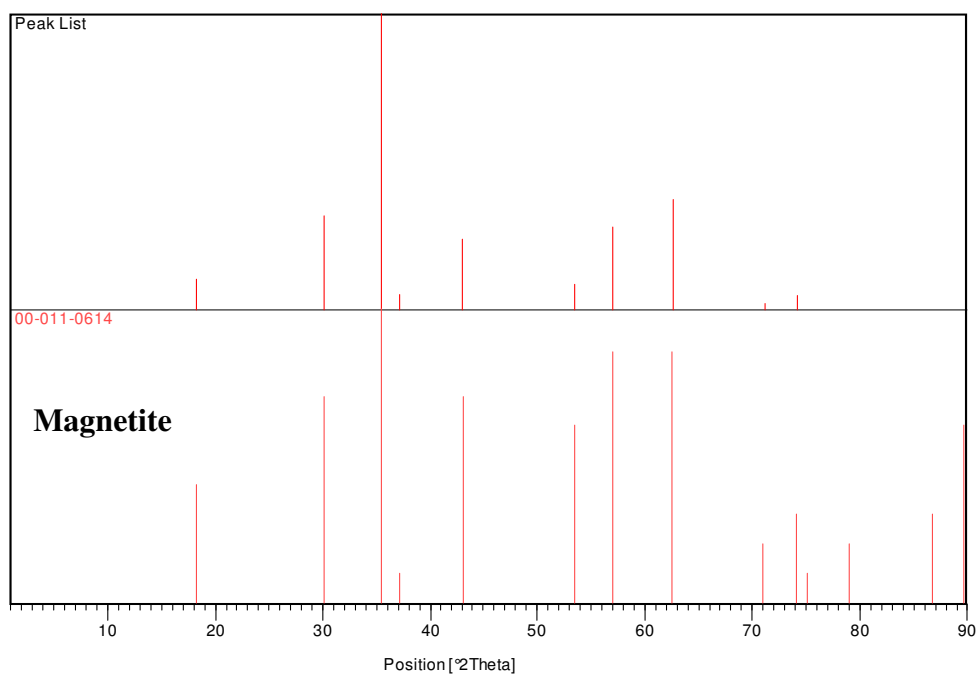


Figure 6.5 Peak matching list of the precipitate formed within a pH range of 7 -8.

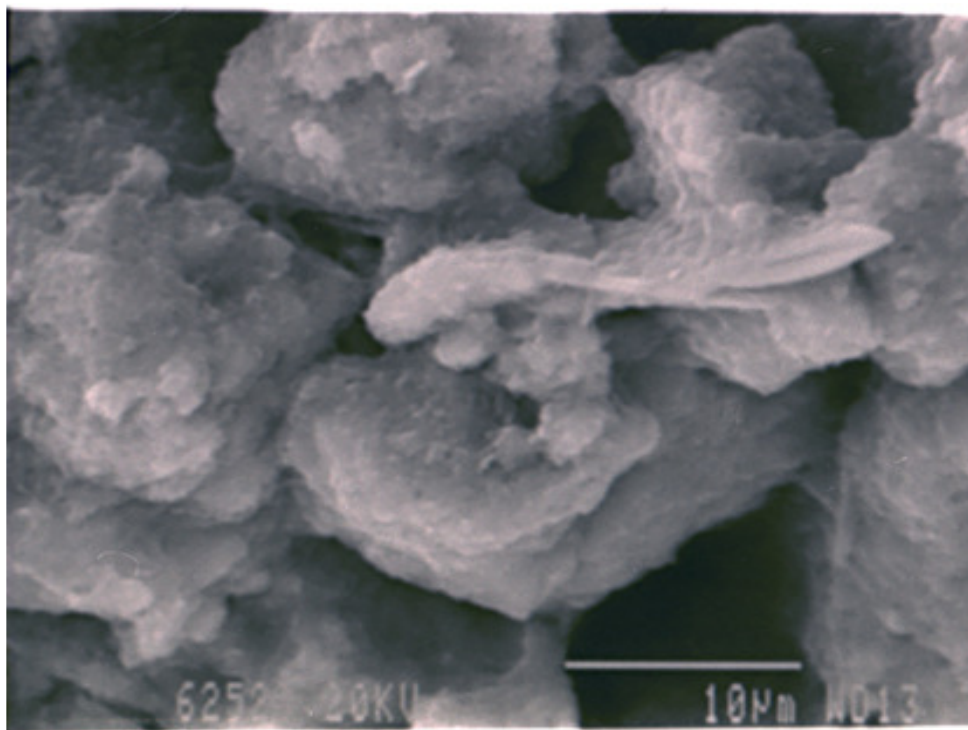


Figure 6.6 SEM image of the precipitate formed within a pH range of 7 -8.

6.3.3 Aging within a pH range of 8 – 9

In these tests, aging was done within a pH range 8 -9 . Figure 6.7 and 6.8 show the X-ray diffractogram and peak matching list of the precipitate. XRD analyses showed that the precipitate was a mixture of magnetite, Fe_3O_4 and goethite, FeOOH . Magnetite was identified as the main phase present in the precipitates. Figure 6.9 shows the SEM image of the precipitate. The electron micrographs show that the precipitate consisted of globular aggregates of spherical particles.

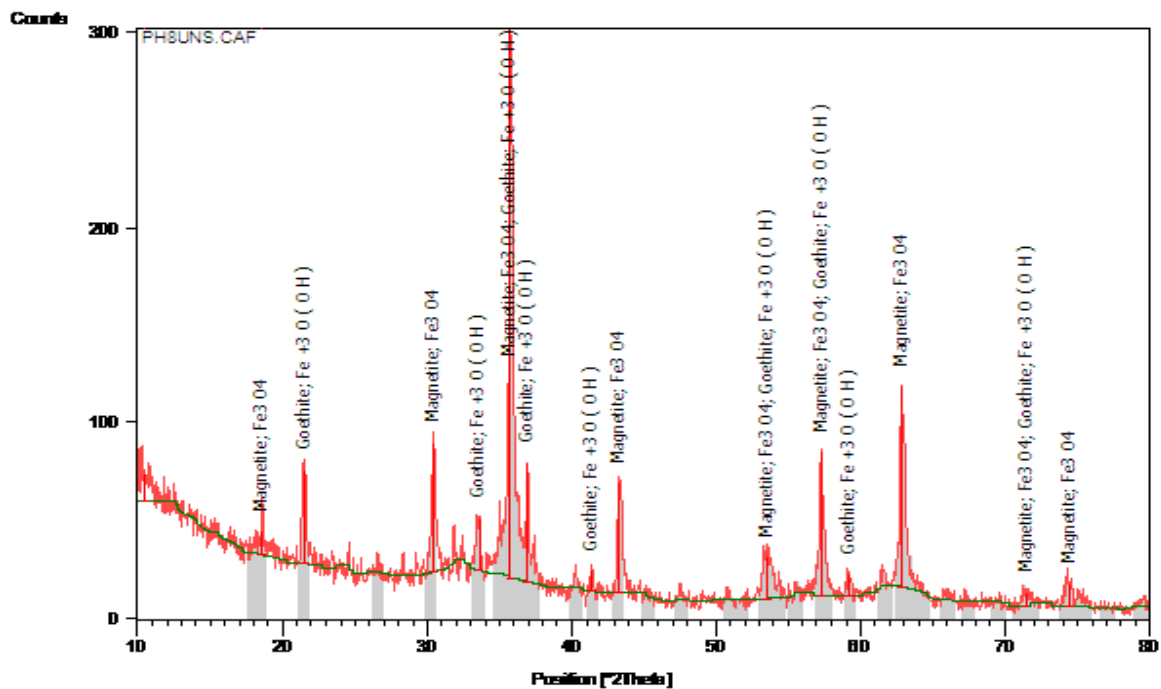


Figure 6.7 X-Ray Diffractogram of the precipitate formed upon aging within a pH range of 8 -9.

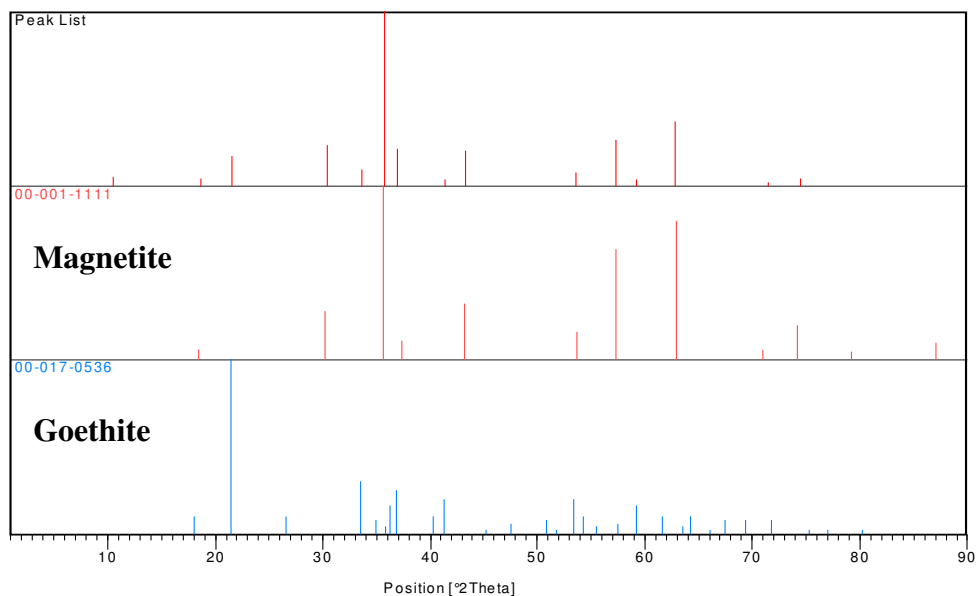


Figure 6.8 Peak matching list of the precipitate formed within a pH range of 8-9.

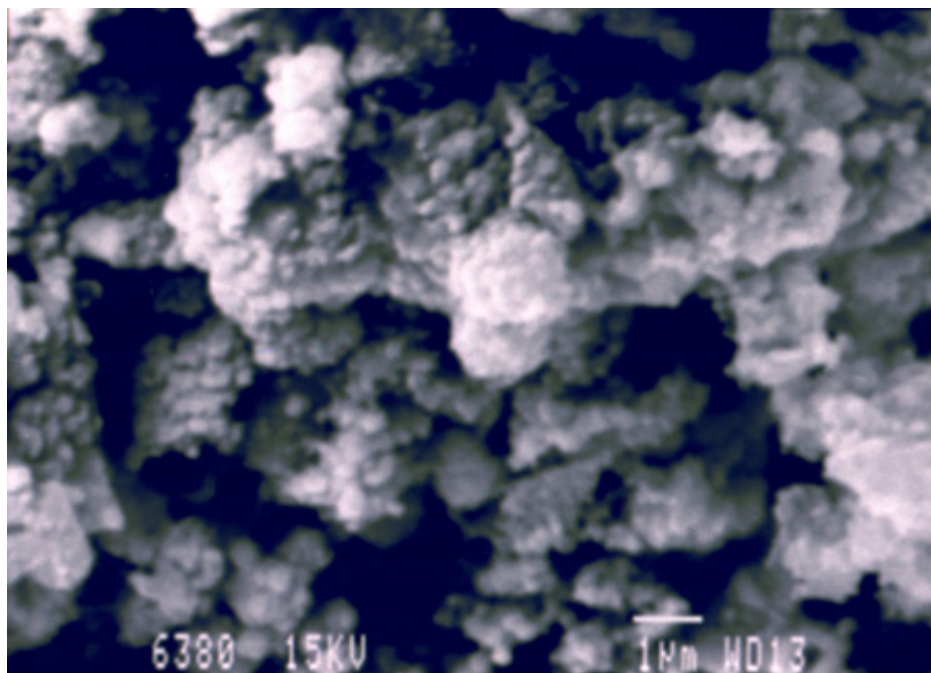


Figure 6.9 SEM image of the precipitate formed within a pH range of 8 -9.

These results do confirm the findings made in the chemical tests and preliminary biotests (Chapter 4 and 5 respectively), that the pH is an influential factor which determines the nature of precipitate formed, since various precipitates were formed at different pH conditions.

6.3.4 Determination of Optimum pH

The optimum pH for the precipitation of a suitable precursor was determined after considering the XRD, BET and elemental analysis of the precipitates. The phases present in the precipitates as identified by X-ray diffraction, under various pH conditions are given in Table 6.1

Table 6.1 Phases present in biogenic precipitates formed under various pH conditions

pH	Major Phase	Minor phases
Acidic(pH)	Potassium jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	Potassium sulphate, $\text{K}_2\text{S}_2\text{O}_6$ Sulphur, S
6 -7	Maghemite, $\gamma\text{-Fe}_2\text{O}_3$	Hematite, $\alpha\text{-Fe}_2\text{O}_3$ Potassium sulphide, K_2S_5
7-8	Magnetite, Fe_3O_4	None
8-9	Magnetite, Fe_3O_4	Goethite, FeOOH

The findings in Table 6.1 show that iron oxides were precipitated only when the pH was raised to a range between 6 and 9. These results are in agreement with Le Chatelier's Principle which states that whenever a system at chemical equilibrium encounters a change in its status quo, equilibrium shifts to counteract the imposed change. It was outlined in the Chapter 2 that aqueous metal ions are hydrolyzed to various extents, with the initial step in the hydrolysis reaction being described by Equation (2.12). It is apparent therefore that the addition of a base during hydrolysis shifts the equilibrium of Equation (2.12) to the right. The OH^- ions react with the H_3O^+ ions and according to Le Chatelier's Principle equilibrium shifts to the right, in order to replace the consumed H_3O^+ ions and re-establish equilibrium. The forward reaction and the polymerization process is therefore enhanced leading to hydroxide and oxide precipitation.

These precipitates were then analysed for their elemental composition using Inductively Coupled Plasma Emission Spectroscopy (ICP) data. The elements analysed were iron, Fe; sulphur, S and potassium, K. These data are shown in Table 6.2

Table 6.2 Inductively coupled plasma emission spectroscopy data on the elemental composition of the biogenic precipitates formed under different pH conditions.

Precipitate	Elemental Composition ICP Value (%)		
	Fe	S	K
Ppt I (Acidic pH)	28.2	14	8.1
Ppt II (pH 6-7)	65.5	5.7	4.1
Ppt III (pH 7-8)	71.2	0.2	0.18
Ppt IV (pH 8-9)	67.8	0.17	0.15

Where Ppt refers to precipitate. Ppt I- precipitate formed under acidic conditions; II at pH 6-7; III at pH 7-8 and IV at pH 8-9.

The results in Table 6.1 show that aging under acidic conditions led to the formation of a precipitate which was mainly potassium jarosite, $\text{KFe}_3(\text{SO}_4)_2\text{OH}_6$ whilst aging done under more basic conditions enhanced the hydrolysis reaction leading mainly to the precipitation of iron oxides. The precipitates formed under acidic conditions and at a pH of 6-7 both contained traces of potassium sulphide impurities. However, at higher basic conditions of pH 7-8 and pH 8-9, no traces of potassium containing impurities were detected and the precipitates generated were wholly comprised of iron oxides. The data in Table 6.2 shows the elemental composition (Fe, S and K) of the precipitates obtained by ICP analysis. This data was used to determine the purity of the precipitates by comparing the theoretical, stoichiometric composition of the precipitates to the actual elemental composition obtained using ICP analysis. The theoretical elemental composition of each of the major phases present in the precipitates (refer to Table 6.1 for major phases) was used in the calculations as shown in Appendix F.

The results from these calculations are presented in Table 6.3 and differences between the theoretical and actual elemental compositions enabled the purity of the precipitates to be determined. For instance, potassium jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ theoretically contains 33.5% Fe, 12.7% S and 7.8% K. The amount of Fe present in

the sample is 84% of the theoretical value whilst the amounts of both S and K in the precipitate are in excess of the theoretical value by 10% and 3.8%, respectively. Whilst the major phase formed from aging under acidic conditions was potassium jarosite, the precipitate also contained potassium sulphate and sulphur as impurities.

Table 6.3 Comparison of theoretical & actual elemental compositions of major phases in precipitates

Precipitate	Elemental Composition					
	Theoretical Value (%)			Actual ICP Value (%)		
	Fe	S	K	Fe	S	K
Ppt I	33.5	12.7	7.8	28.2	14	8.1
Ppt II	70	–	–	65.5	5.7	4.1
Ppt III	72.4	–	–	71.2	0.2	0.18
Ppt IV	72.4	–	–	67.8	0.17	0.15

Where Ppt refers to precipitate. Ppt I- precipitate formed under acidic conditions; II at pH 6-7; III at pH 7-8 and IV at pH 8-9

The deficiency of Fe can be attributed to the presence of the excess of S and K, which led to an overall decrease in the amount of Fe in the biogenic precipitate. X-ray diffraction showed that precipitate II comprised maghemite, $\gamma\text{-Fe}_2\text{O}_3$, iron oxide, Fe_2O_3 and potassium sulphide, K_2S_5 . Maghemite, $\gamma\text{-Fe}_2\text{O}_3$ was identified as the main phase in the precipitate. The precipitate contained 65.5% Fe, 5.7% S and 4.1% K. The amount of Fe in the precipitate was 93.6% of the theoretical value whilst the S and K in the precipitate emanated from potassium sulphide. X-ray diffraction showed that the precipitate formed at a pH of 7-8 was a solitary phase of Fe_3O_4 . No other phase was detected using XRD. ICP analysis showed that precipitate III contained 71.2% Fe, 0.2% S and 0.18% K. Fe was therefore present at 98.3% of the theoretical value and the amounts of S and K were negligible in the sample. The ICP data therefore confirmed that the precipitate formed at a pH of 7-8 was Fe_3O_4 of high purity. Precipitate IV was formed at a pH of 8-9. Magnetite, Fe_3O_4 was identified by X-ray diffraction as the major phase present accompanied by minor amounts of goethite.

The precipitate contained 67.8% Fe and 0.17% S and 0.15% K. The Fe was 93.6% of the theoretical value whilst the impurities, S and K were in negligible quantities.

The surface area and pore volumes of the precipitates were determined using BET analysis and are shown in Table 6.4. The surface area and pore volume are crucial parameters which give an indication of the adsorption characteristics of a sample. The surface area characteristics of a material play an important role in determining its use as a catalyst. It has been mentioned in the literature review chapter that hematite nanoparticles can be used as catalysts for various processes. The adsorption characteristics of the precipitates were determined using Branauer-Emmett-Teller (BET) analysis. The procedure is described in section 3.7.3.3 of Chapter 3. The precipitate number or labelling is the same as that used in Table 6.3 where precipitate I for instance refers to the biogenic precipitate formed under acidic conditions.

Table 6.4 Branauer-Emmett-Teller (BET) data on biogenic precipitates formed under different pH conditions.

Precipitate	Surface area (m²/g)	Pore volume (cm³/g)	Pore Diameter (nm)
I (Potassium jarosite)	1.21	0.0085	28.00
II (Maghemite)	10.57	0.0588	22.26
III (Magnetite)	20.77	0.0765	14.73
IV (Magnetite)	7.77	0.0379	19.54

Where Ppt refers to precipitate. Ppt I- precipitate formed under acidic conditions; II at pH 6-7; III at pH 7-8 and IV at pH 8-9. The major phase in each of the precipitates is shown in brackets.

The surface areas of the precipitates range in size from 1.21m²/g to 20.77m²/g. These are typical values for iron oxides (Crosby et al., 1983). Crosby and his co-workers reported that the natural, iron oxide samples in their studies had surface areas ranging from 6.4 to 164 m²/g. Wang et al., (2007) also reported surface areas below 14m²/g in their characterization of biogenic precipitates. Precipitate I formed under acidic conditions had the lowest surface area of 1.21m²/g whilst precipitate III, which

was pure magnetite had the highest surface area of $20.77\text{m}^2/\text{g}$. The pore diameters of the precipitates ranged from 14nm to 28nm. Precipitate I had the lowest pore volumes of $0.0085\text{cm}^3/\text{g}$ whilst precipitate III had a pore volume of $0.0765\text{cm}^3/\text{g}$.

It can therefore be concluded that the optimum pH is a pH range of 7-8. Magnetite was formed at this pH, and had the highest purity in terms of iron content of 98.3% amongst all the precipitates. The magnetite precipitate exhibited the highest surface area of $20.77\text{m}^2/\text{g}$ amongst all the precipitates. This pH is also optimum since the magnetite precursor formed at this pH occurred as the solitary phase within the precipitates. This is advantageous since the presence of a solitary phase in the precursor material enhances the possibility of forming hematite particles with negligible impurities. Magnetite can be transformed into hematite *via* an oxidative reaction (Gillot et al., 1978).

6.4 Optimization of Iron Concentration – Aging of Bioleach Liquors with Different Iron Concentrations

Biogenic leach liquors of different iron concentrations were produced by leaching pyrite for different leach periods. The total Fe concentration over the extended leach period is shown in Figure 6.10.

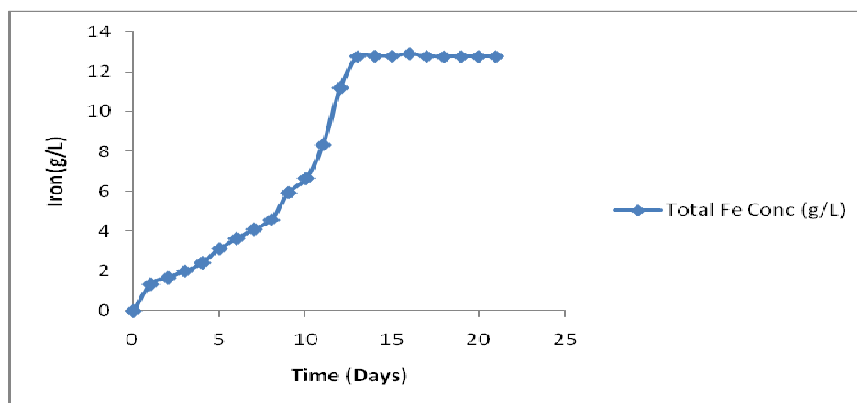


Figure 6.10 Total iron in bioleach liquors used for iron concentration optimization tests

The bioleach liquors generated after leaching for 3 ; 7 ; 10 ; 14 and 21 days were then aged as described in section 3.4. These number of days were chosen arbitrarily, to get liquors with different iron concentrations. Figure 6.10 shows that the total iron concentration plateaus off to a stable value of around 12.8 g/L during the last stage of leaching. A pH of 7 -8 was used during aging in these tests, since this was found to be the optimum pH during the pH optimisation tests (See Section 6.3.4). All tests were done in duplicate. The iron concentrations in the leach liquors after 3, 7, 10, 14 and 21 days of leaching were 2; 4.09; 6.65; 12.8 and 12.78g/L respectively. The corresponding concentrations in molar units are 0.036; 0.073; 0.118; 0.229 and 0.228M respectively given that the molar mass of iron is 56g/mol. The iron concentration obtained after 14 and 21 days is similar and results will be reported at a concentration of 12.8g/L.

6.4.1 Aging of 2g/L Fe (0.036M) system

Figure 6.11 and 6.12 show the X-ray diffractogram and peak matching list respectively, of the biogenic precipitate formed when the bioleach liquor which contained 0.036M Fe was aged through a forced hydrolysis process at a pH of 7-8. The main phase present in the precipitate was potassium jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ with minor quantities of hematite, $\alpha\text{-Fe}_2\text{O}_3$ present.



6.4.2 Aging of 4.09g/L Fe (0.073M) system

The biogenic precipitate formed from aging the 0.073M Fe system contained a mixed product of iron oxide, FeO, goethite, FeOOH and hematite, $\alpha\text{-Fe}_2\text{O}_3$ (Figure 6.13 and 6.14).

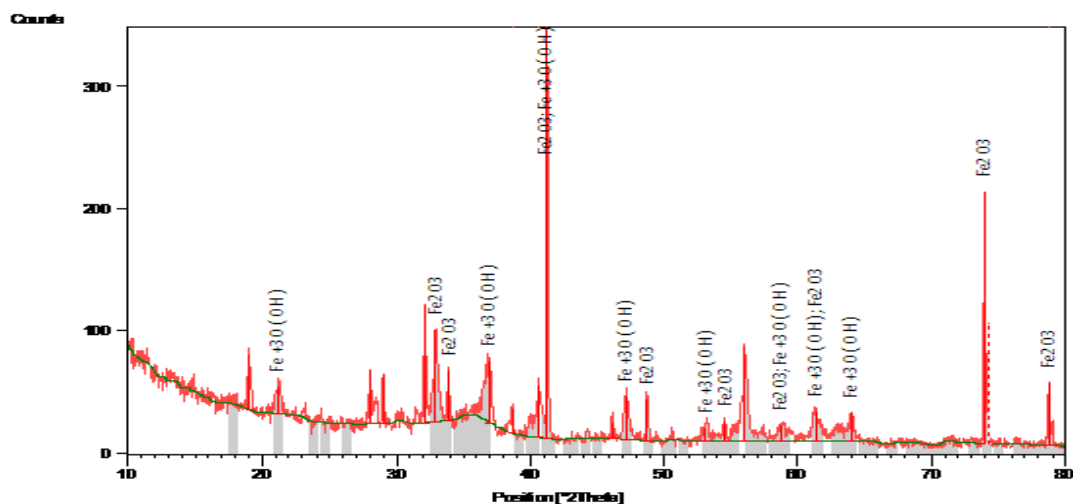


Figure 6.13 X-ray diffractogram of the precipitate formed from the 0.073M Fe system at a pH of 7-8

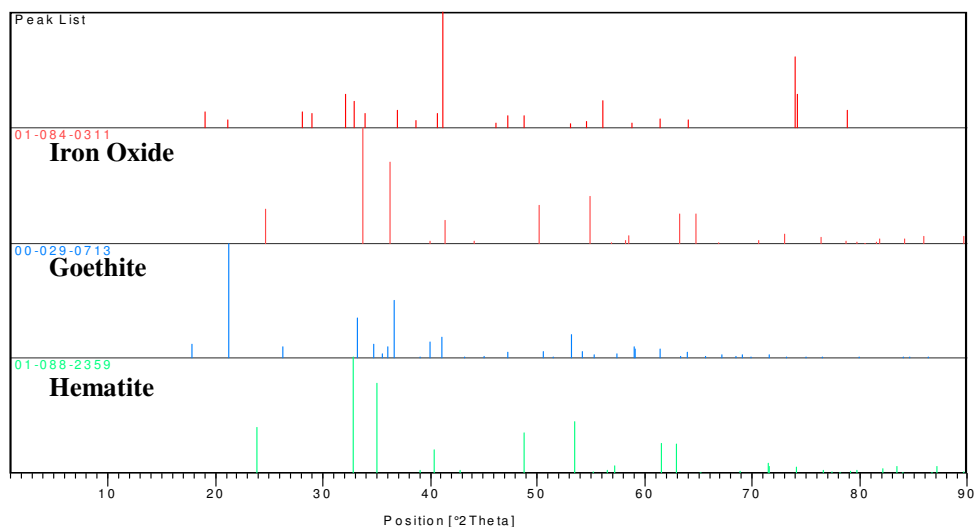


Figure 6.14 Peak matching list of the precipitate formed from the 0.073M Fe system

6.4.3 Aging of 6.65g/L Fe (0.118M) system

Figures 6.15 and 6.16 show the X-ray diffractogram and peak matching list of the precipitate formed from the 0.118M Fe system. The Figures show that magnetite, Fe_3O_4 was the main phase present. Goethite, FeOOH was present in minor quantities.

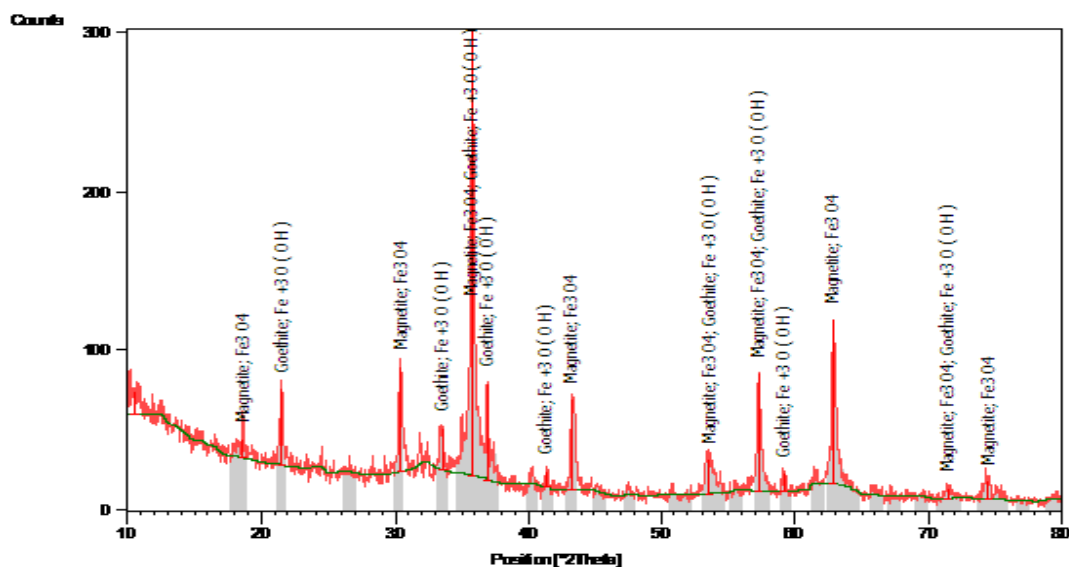


Figure 6.15 X-ray diffractogram of the precipitate formed from the 0.118M Fe system at a pH of 7-8

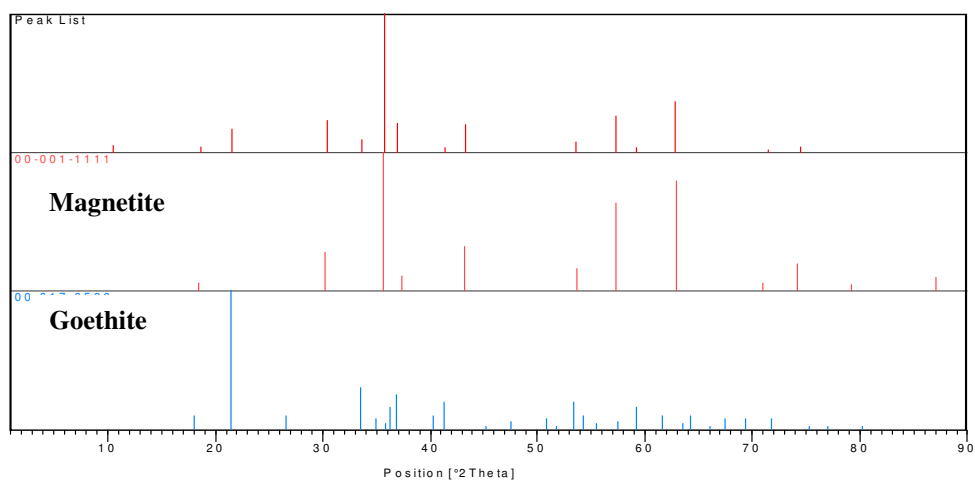


Figure 6.16 Peak matching list of the precipitate formed from the 0.118M Fe system

6.4.4 Aging of 12.8g/L Fe (0.229M) system

Figures 6.17 and 6.18 show the X-ray diffractogram and peak matching list of the precipitate formed from aging the 0.229M Fe system. The precipitate was identified as being purely magnetite, Fe_3O_4 . These findings at the various Fe concentrations are all presented in Table 6.5

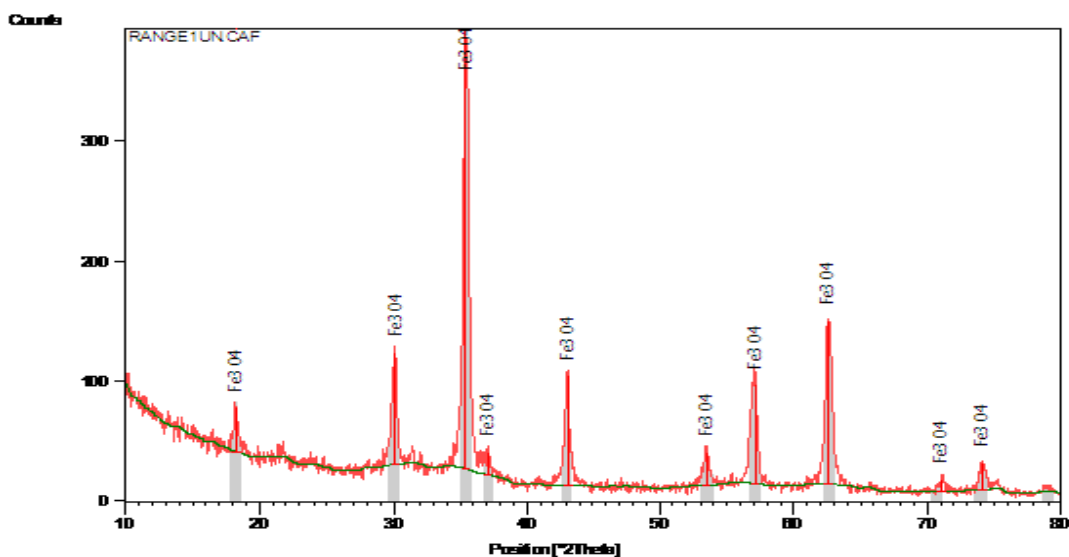


Figure 6.17 X-ray diffractogram of the precipitate formed from the 0.229M Fe system at a pH of 7-8

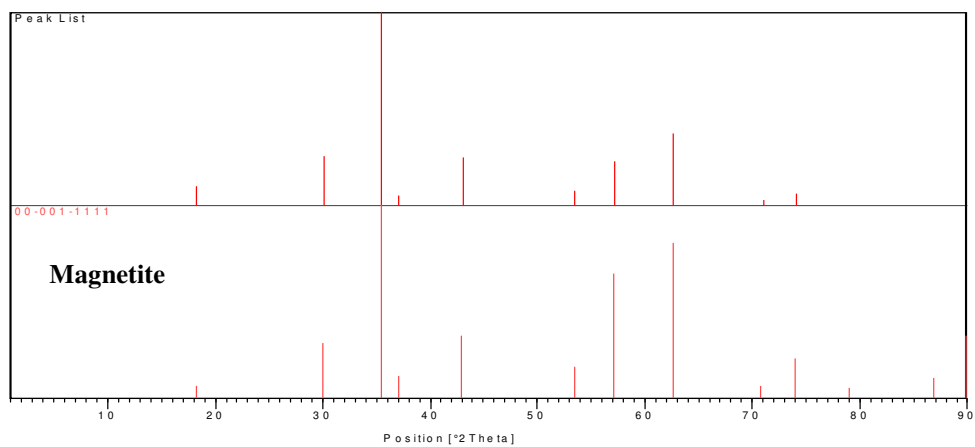


Figure 6.18 Peak matching list of the precipitate formed from the 0.229M Fe system*6.4.5 Determination of Optimum Fe Concentration***Table 6.5 Phases present in biogenic precipitates formed from biogenic leach liquors of various initial Fe concentrations at a pH of 7 -8**

Fe Concentration (M)	Major Phase	Minor phases
0.036	Potassium jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$	Hematite, $\alpha\text{-Fe}_2\text{O}_3$
0.073	Iron oxide, FeO	Goethite, FeOOH Hematite, $\alpha\text{-Fe}_2\text{O}_3$
0.118	Magnetite, Fe_3O_4	Goethite, FeOOH
0.229	Magnetite, Fe_3O_4	None

The findings in Table 6.5 show that potassium jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ was identified as the main precipitate at the lowest Fe concentration of 2g/L (0.036M) whilst mixtures or pure phases of the iron oxides were formed at the higher Fe concentrations. A concentration of 0.073M Fe is the threshold concentration for iron oxide and hydroxide formation. At an iron concentration of 4.09g/L (0.073M) a mixed product of an iron oxide, FeO, goethite, FeOOH and hematite, $\alpha\text{-Fe}_2\text{O}_3$ was precipitated. A mixed precipitate of magnetite, Fe_3O_4 and goethite, FeOOH, with magnetite being the main phase was precipitated from the forced hydrolysis of a 6.65g/L (0.118M) Fe system.

The aging of solutions containing higher Fe concentrations of 12.8g/L (0.229M) resulting from bioleaching durations of 14 days and 21 days, both produced purely magnetite, Fe_3O_4 particles. Mixed phases of the precipitates were obtained from the solutions of lower iron concentrations, with pure phases being obtained from solutions of 0.23M Fe concentration. The aging of bioleach liquors of different initial Fe concentrations at a pH of 7-8, therefore generally resulted in the formation of

various iron oxides, with magnetite being formed from the aging of all bioleach solutions formed from 10 or more days of bioleaching. The findings show that the iron concentration did have an effect on the precipitate formed at a pH of 7 -8, although this effect was not as marked as the effect shown by the pH on the nature of the precipitate. The optimum Fe concentration for the formation of a magnetite (a precursor for hematite formation) was found to be 0.23M Fe.

6.5 The Fe Pourbaix Diagram at Optimum Aging Conditions

Pourbaix diagrams (E- pH) diagrams are used to map out the regions of possible equilibrium or stability which can exist within aqueous electrochemical systems. The actual redox potential values measured during the aging experiments are depicted in Figure 6.19.

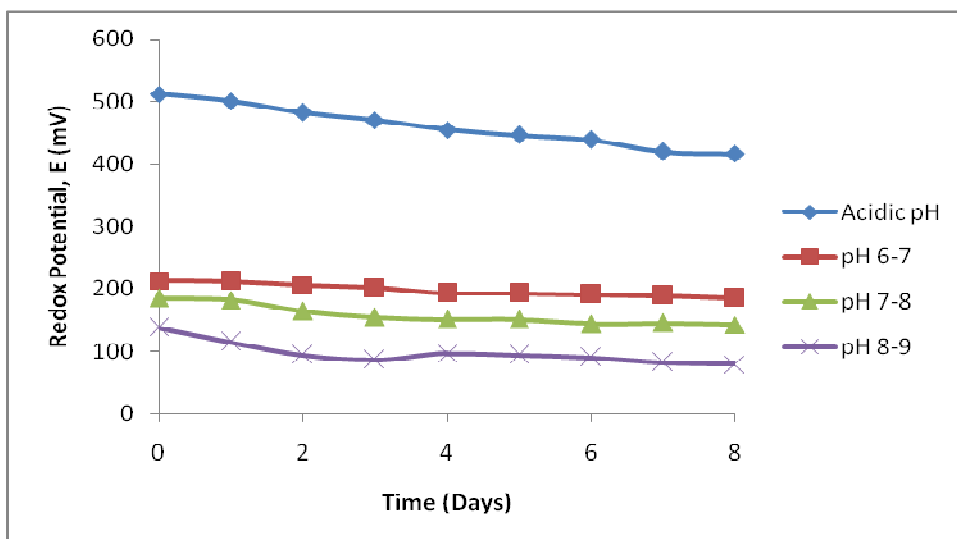


Figure 6.19 Changes in redox potential during aging at various pH conditions

Figure 6.19 shows that a general decrease in the redox potential values occurred during the aging process. This is expected as the predominantly Fe^{3+} , ferric ions in the leach liquors were reduced to various iron oxides.

The Pourbaix diagram was then constructed after identifying all the possible reactions of interest within the system and their associated E-pH relationships at the optimum aging conditions (Refer to Appendix G). Figure 6.20 shows the Pourbaix diagram for the system.

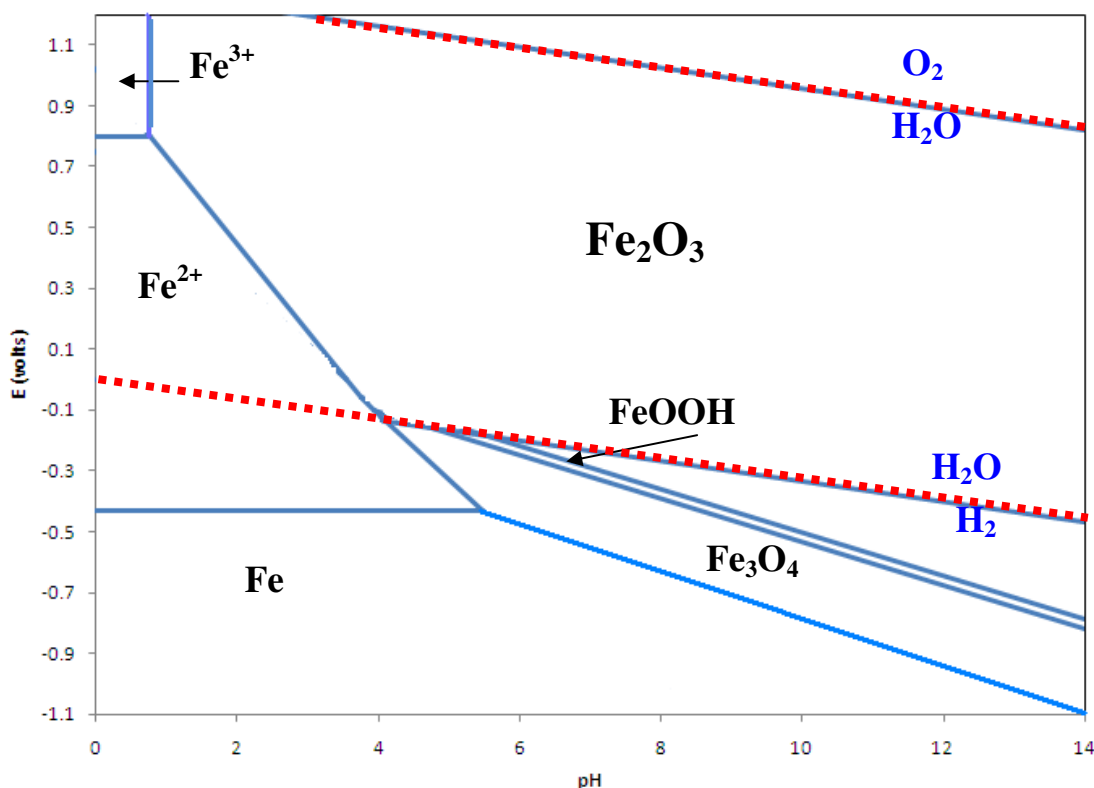


Figure 6.20 E-pH Diagram for Fe-H₂O System at 90°C (363.15K) and [Fe³⁺] = 0.23M

The biogenic leach liquors used as the starting material for the aging process, initially consist of Fe^{2+} and Fe^{3+} ions (Equations 2.1 to 2.5) and have high E values (See Figure 5.4).

Figure 6.20 shows that magnetite, Fe_3O_4 is stable under slightly neutral conditions; $\text{pH} > 6$ and remains stable throughout all basic pH conditions. At these pH conditions, Fe_3O_4 exists at low values of E, which are reducing conditions. The experimental findings in Figure 6.19 show that aging the bioleach liquors at pHs of 6-7; 7-8 and 8-9 resulted in a decrease of the redox potential values. Low redox potential values indicate the presence of reducing conditions and thus reducing conditions were experienced in the system during aging. Figure 6.20 shows that magnetite, Fe_3O_4 can be precipitated as a major phase under reducing conditions and a pH range of 6-14. This is consistent with the experimental findings as magnetite was formed under reducing conditions within a pH range of 7-8.

A study of the Pourbaix diagram in Figure 6.20 shows that hematite, $\alpha\text{-Fe}_2\text{O}_3$ is stable under high E values (oxidizing conditions) and a broad range of pH conditions (pH 1-14). As mentioned previously, Figure 6.19 shows that reducing conditions were experienced during the experimental aging runs within a pH range of 6-9. The reducing conditions prevalent during the aging tests were therefore not conducive for hematite precipitation. This is agreement with our findings as hematite, $\alpha\text{-Fe}_2\text{O}_3$ was never formed as the major phase in any of the biogenic precipitates (Table 6.1).

The Pourbaix diagram shows that goethite, FeOOH is only stable under reducing conditions within a relatively small, restricted region. It is possible to form goethite under the reaction conditions although the Pourbaix diagram suggests it would be fairly difficult to produce it as a major phase. Goethite was identified as a minor phase in the precipitate formed at a pH of 8-9.

The Pourbaix diagram shows a good correlation with the observed results, confirming that magnetite, Fe_3O_4 is the major, stable iron oxide phase that can be precipitated at a temperature of 90°C from a liquor containing 0.23M Fe under reducing conditions and neutral to basic pH.

6.6 Summary & Conclusions

Two of the most important parameters which influence the nature of the precipitate formed during aging have been identified as the pH and the concentration of the iron. This chapter therefore focused on the optimization of these two factors. During the pH optimization tests, bioleach liquors generated after 14 days of thermophilic pyrite oxidation (0.23M Fe) by *Acidianus* microorganisms were aged at various pH conditions namely acidic; pH 6-7; pH 7-8 and pH 8-9.

The main phase precipitated under acidic conditions was identified as potassium jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. Under neutral to basic conditions iron oxides were formed with magnetite, Fe_3O_4 or its intermediaries being formed. Maghemite, $\gamma\text{-Fe}_2\text{O}_3$ was formed as the main phase at a pH of 6-7. Pure magnetite, Fe_3O_4 was precipitate at a pH of 7-8 whilst at a pH of 8-9, magnetite was identified as the main phase from a mixed product of magnetite and goethite. Thus a pH of 7 -8 was identified as the optimum pH for the precipitation of magnetite, Fe_3O_4 , which can be used as a precursor material for hematite, $\alpha\text{-Fe}_2\text{O}_3$ formation.

Bioleach solutions of different iron concentrations were then aged at the optimum pH of 7-8, to determine the effect of iron concentration on the nature of the precipitates formed. At the lowest iron concentration of 2g/L (0.036M) the main phase in the precipitate was identified as potassium jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$. Iron oxides were precipitated at the higher iron concentrations. Pure magnetite, Fe_3O_4 was precipitated at the highest iron concentration of 0.23M Fe obtained after 14 and 21 days of leaching.

The pH was thus identified as the most crucial factor which determined the nature of the precipitate formed. In this chapter the precise conditions to be employed during

aging to produce a precursor iron oxide for hematite production were successfully identified. Magnetite, Fe_3O_4 , which will be used as a precursor material for hematite particle formation was precipitated during the aging of a bioleach liquor generated after 14 days of leaching (0.23M Fe concentration) at a pH of 7-8 through a forced hydrolysis reaction.

Chapter 7

Hematite, $\alpha\text{-Fe}_2\text{O}_3$ Nanoparticle Production

7.1 Introduction

In the preceding chapter, the process parameters which could be employed during aging in order to yield a suitable iron oxide which could be used as the precursor material for hematite nanoparticle production were successfully identified. Pure magnetite, Fe_3O_4 was precipitated from aging bioleach solutions through a forced hydrolysis process. The ultimate aim of this research is to generate hematite nanoparticles. In this chapter the phase transformation of this magnetite precursor into the desired product, hematite was studied. The effect of stirring on the size of the magnetite particles produced during aging was also investigated. If the precursor magnetite particles could be reduced to nanosize, then the phase transformation of these magnetite nanoparticles to hematite nanoparticles could be investigated and established. Profiles of the changes in particle size during aging are also presented in the discussion section on the effect of the stirring. This chapter is therefore dedicated to investigating the formation of hematite nanoparticles from the precursor magnetite iron oxide.

7.2 Materials and Methods

7.2.1 Effect of stirring on the magnetite particle size

Stirring was undertaken during the aging stage in order to investigate its effect on the size of the precipitated particles. A 336 Boeco magnetic stirring hotplate was used during these aging testworks. The process parameters employed during aging were as described previously – namely pH 7-8, aging time of 8 days and an aging temperature of 85-90°C. The magnetic stirring bars used were teflon-coated to prevent

contamination of the biogenic liquors. A stirring speed of 1250rpm was used in all the tests. This speed was chosen because it is the highest setting on the 336 Boeco hotplate and the smallest particle sizes will be generated from this setting.

7.2.2 Phase transformation of magnetite to hematite

The conversion of the precursor iron oxide, magnetite which was generated during aging to hematite was done in a BRF16/5-2416 Muffle furnace. The conversion occurred *via* an oxidative transformation. The experimental procedures and materials used are described in Section 3.5 of Chapter 3.

7.2.3 Characterization of the biogenic precipitates

X-ray diffractometry (XRD) was used for phase identification whilst morphological characterization of the precipitates was done using scanning electron microscopy (SEM) as appropriate. The surface characteristics were determined by BET. The procedures used for these analytical techniques are as described in Section 3.6.3.

7.3 Results & Discussion

7.3.1 Effect of stirring - evolution of Fe_3O_4 particle size during aging

Figure 7.1 shows the SEM image of magnetite particles precipitated from bioleach liquors, without stirring during the process of aging. The image shows that the precipitate consisted of almost spherical globular agglomerates. The agglomerates were up to 20 μ m in diameter. Discrete spherical globules which formed part of the agglomerate could also be identified. These smaller particles were up to 3.5 μ m diameter in size. One such particle is encircled in red on the SEM image.

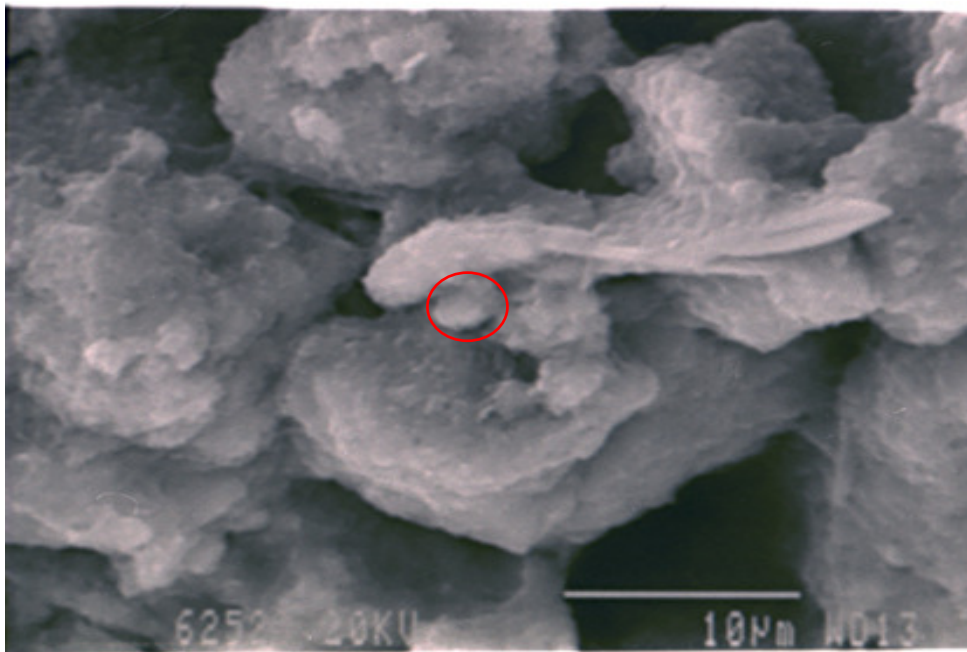


Figure 7.1 SEM image of magnetite particles after 8 days of aging without stirring. A magnetite particle is shown encircled in red.

The effect of stirring on the magnetite particle size during the course of aging was investigated. The Figures depicted in 7.2; 7.3 and 7.4 show the evolution of the particle size during aging after 4, 6 and 8 days respectively.

Figure 7.2 shows that after 4 days of aging with stirring, the magnetite particles appeared as spherical agglomerates. As the precipitation occurs in the presence of stirring some of the magnetite particles through attrition, are removed from the main spherical agglomerates, forming new nucleation sites where more growth of the precipitates can occur again; hence the appearance of ‘uniform’ precipitation and dispersion as opposed to the case of precipitation without stirring shown in Figure 7.1. The image shows the presence of a few relatively large spherical globules consisting of smaller aggregates of spherical particles. An isolated cluster, encircled in red on the image, was approximately 5µm in size.

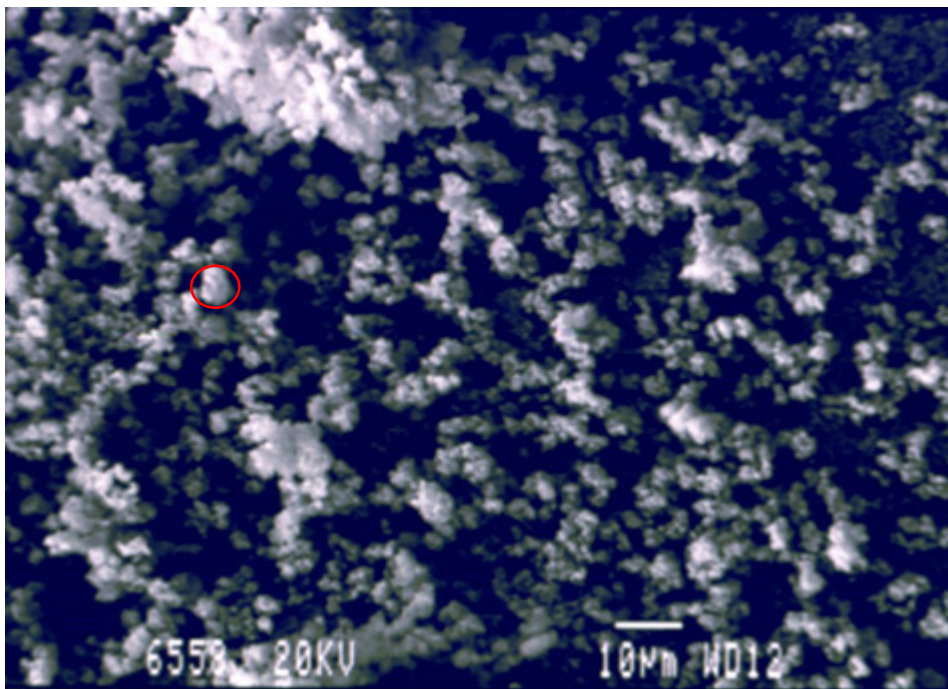


Figure 7.2 SEM image of magnetite particles after 4 days of aging with stirring. A cluster of magnetite particles is encircled in red.

Figures 7.3 and 7.4 show the SEM images which were obtained as aging with stirring progressed for 6 and 8 days respectively. Again, the magnetite particles form spherical globular agglomerates. In this instance the agglomerates are now more closely drawn together and are not as dispersed as observed after 4 days of aging in the SEM micrograph of Figure 7.2. As aging progresses, more of the magnetite particles are precipitated and form globular aggregates. The aggregates in Figure 7.4 appear more densely packed compared to those in Figure 7.3. It is possible that the inter-molecular forces between the aggregates become stronger as aging progresses, leading to the aggregates drawing closer together and becoming more densely packed. Figure 7.3 shows a typical ‘unit’ of this agglomerate (encircled in red). This unit is 0.5µm in diameter and consists of 1 or 2 particles. Stirring, after a period of 6 days, therefore, seems to have the effect of dispersing the agglomerate

particles through an attrition process and encouraging uniformly dispersed and fairly discrete particle and/or particle cluster growth to occur within the precipitate.

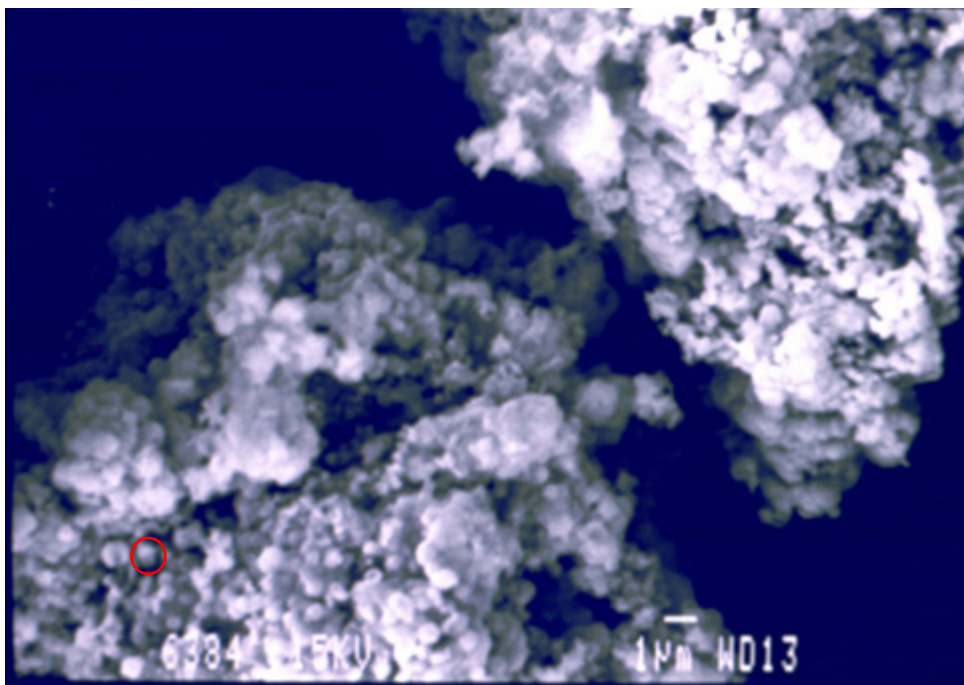


Figure 7.3 SEM image of magnetite particles after 6 days of aging with stirring. A typical unit of the agglomerate cluster is encircled in red.

Figure 7.4 shows the SEM image of the precipitate which was obtained after 8 days of aging accompanied by stirring. It is evident that the magnetite particles are still in clusters of spherical agglomerates. These agglomerates are however not as uniformly dispersed as in earlier stages of the aging process. The particles in Figure 7.3 are more uniformly dispersed than those shown in Figure 7.4. This is possibly due to the fact that a greater mass of magnetite particles is present in the slurry in the aging vessel as aging nears completion compared to earlier times in the aging process. Stirring is therefore relatively less effective at the end of the aging period compared to earlier periods. As aging progresses, the magnetite clusters formed become denser and would thus tend to sediment out of the slurry, and more or less settle out at the

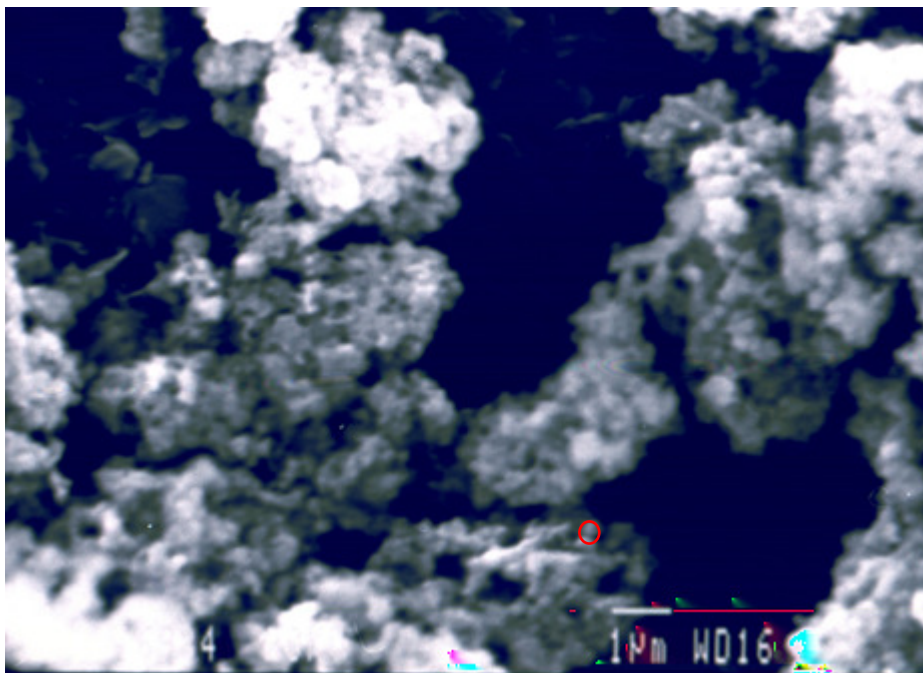


Figure 7.4 SEM image of magnetite particles after 8 days of aging with stirring. A discrete magnetite particle is encircled in red.

bottom of the vessel. Consequently uniform attrition and dispersion of the particle agglomerates would be restricted in accordance with fluid flow principles. A discrete magnetite particle identified as part of a globular agglomerate is shown encircled in red on Figure 7.4. This particle was $0.2\mu\text{m}$ diameter in size, which corresponds to 200nm. A smaller particle diameter size could be possibly obtained through the use of a higher stirring speed (See Section 2.3). The stirring speed used in this work, was the highest that could be set on the magnetic stirring hotplate (Section 7.2.1).

It is therefore apparent that stirring generally has the effect of decreasing the particle sizes. Magnetite particles decreased in diameter from $3.5\mu\text{m}$ (3 500nm) in instances where there was no stirring to $0.2\mu\text{m}$ (200nm) in cases where stirring was employed. The monodispersity of the system was enhanced by stirring, although after a certain critical time of 6 days, there seemed to be no noticeable enhancement of the monodispersity. Thus magnetite nanoparticles which could be used as precursor materials for hematite nanoparticle formation were successfully produced.

7.3.2 Oxidation of magnetite, Fe_3O_4 - Heating Temperature of 520°C.

The precursor magnetite nanoparticles were heated in air in a Muffel furnace at a temperature of 520°C for a holding time of 12 hours. The detailed experimental procedure is given in Section 3.5. Figures 7.5 and 7.6 show the XRD pattern and peak matching list of the product obtained after heating at 520°C, respectively.

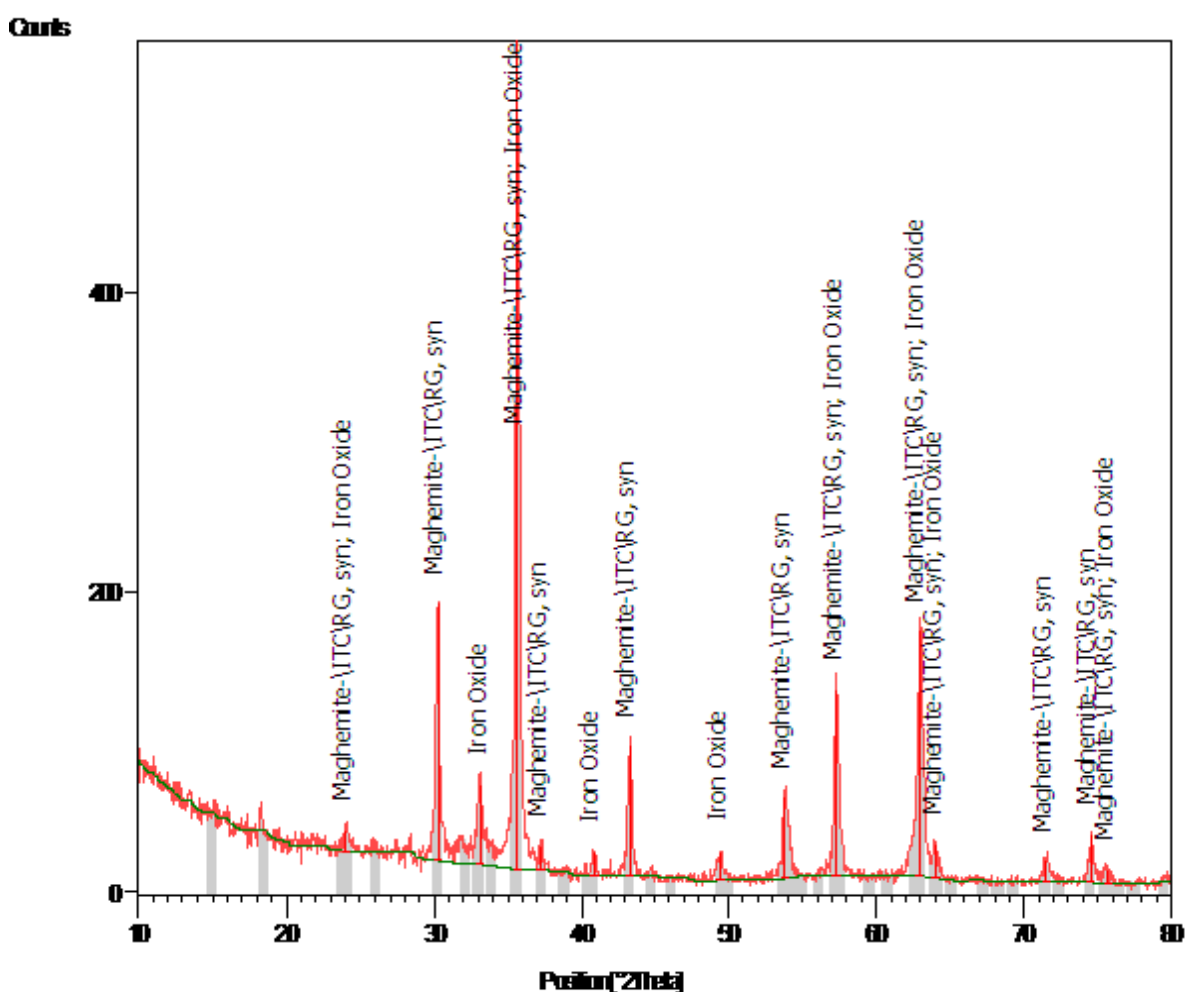


Figure 7.5 X-Ray Diffractogram of the product formed after heating magnetite at 520°C.

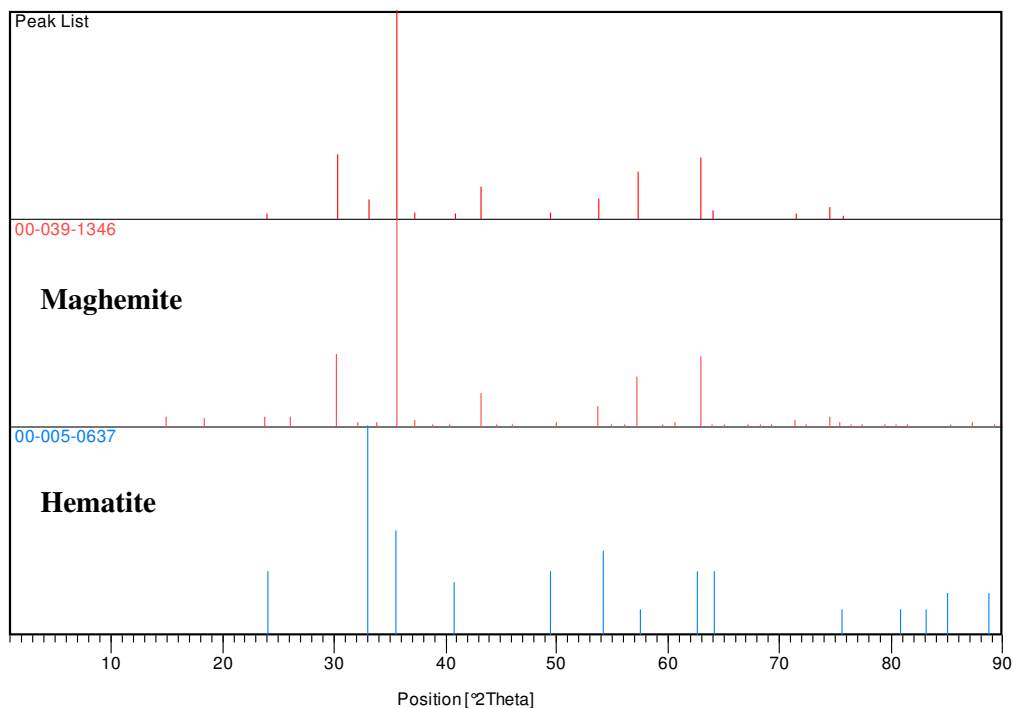


Figure 7.6 Peak matching list of the product formed after heating magnetite at 520°C

The XRD pattern in Figure 7.5 and peak matching list in Figure 7.6 show that the product formed at 520°C was a mixture of maghemite, $\gamma\text{-Fe}_2\text{O}_3$ and hematite, $\alpha\text{-Fe}_2\text{O}_3$. Maghemite formed the major phase of the product. Magnetite, Fe_3O_4 is transformed to hematite, $\alpha\text{-Fe}_2\text{O}_3$ through an oxidation reaction as shown in Equation (7.1).



A number of researchers have shown that the size of the magnetite particle has an effect on the oxidation kinetics of this reaction. The oxidation kinetics no longer remains simple as the magnetite crystal size has a marked impact on the oxidation kinetics and reaction products (Feitknecht, 1964; Gallagher et al., 1968; Gillot et al., 1978; Jolivet & Tronc, 1988). Schwertmann and Cornell, (2003) reported on the influence that temperature and crystal size have on the oxidation product. They found

that at temperatures between 200 and 250°C, magnetite crystals smaller than 300nm were transformed via the mixed phase into maghemite which was transformed into hematite at temperatures above 500°C. In larger crystals (>300nm), the complete transformation of magnetite was retarded due to the long diffusion pathways and for the transformation to occur completely, the temperature had to be raised above 500°C (Schwertmann & Cornell, 2003). The particle sizes used in the study have been shown to be around 200nm (See section 7.3.1). At this particle size a product of maghemite and hematite, with maghemite being the main phase was formed from oxidation at 520°C. Magnetite nanoparticles were then oxidized in air at a higher temperature of 600°C.

7.3.3 Oxidation of magnetite, Fe_3O_4 - Heating Temperature of 600°C.

The X-ray diffractogram and peak matching list (Figure 7.7 and 7.8 respectively) show that pure hematite, α - Fe_2O_3 was produced following oxidation of the magnetite nanoparticles in air at 600°C for 12 hours. Maghemite is an intermediary phase in the oxidation of magnetite to hematite, and was therefore the major oxidation product when the magnetite was heated at 520°C. Pure hematite was however, produced when the oxidation temperature was increased to 600°C. Thus hematite, α - Fe_2O_3 was successfully produced from the oxidation of magnetite nanoparticles. The following section investigates if the oxidation had any effect on the size of the hematite nanoparticles.

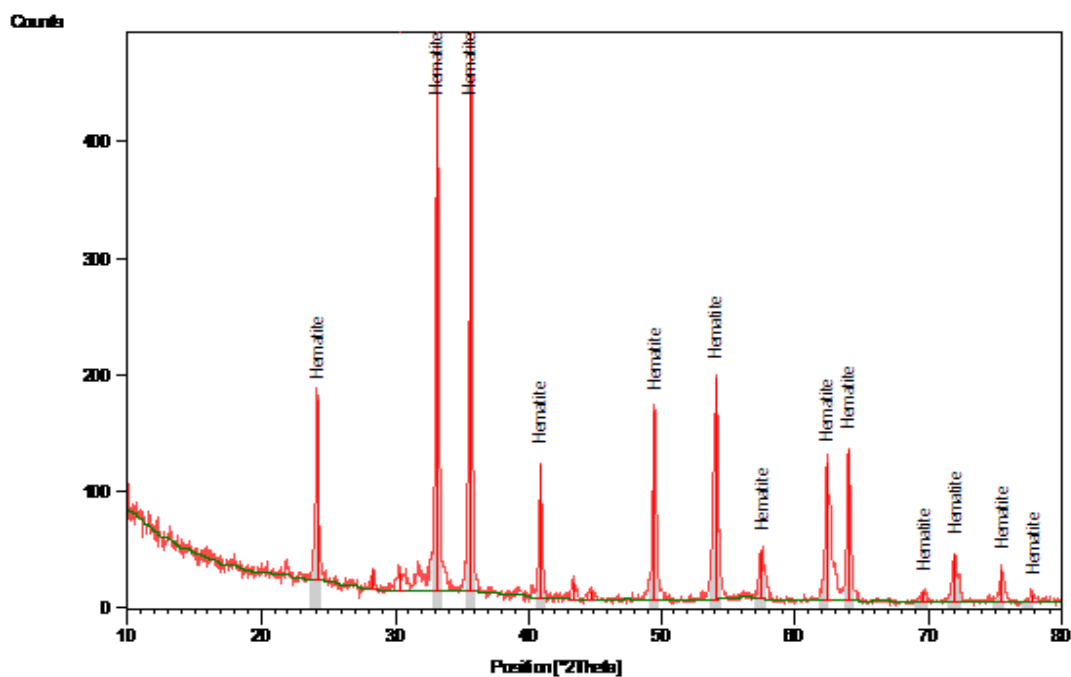


Figure 7.7 X-Ray Diffractogram of the product formed after heating magnetite at 600°C.

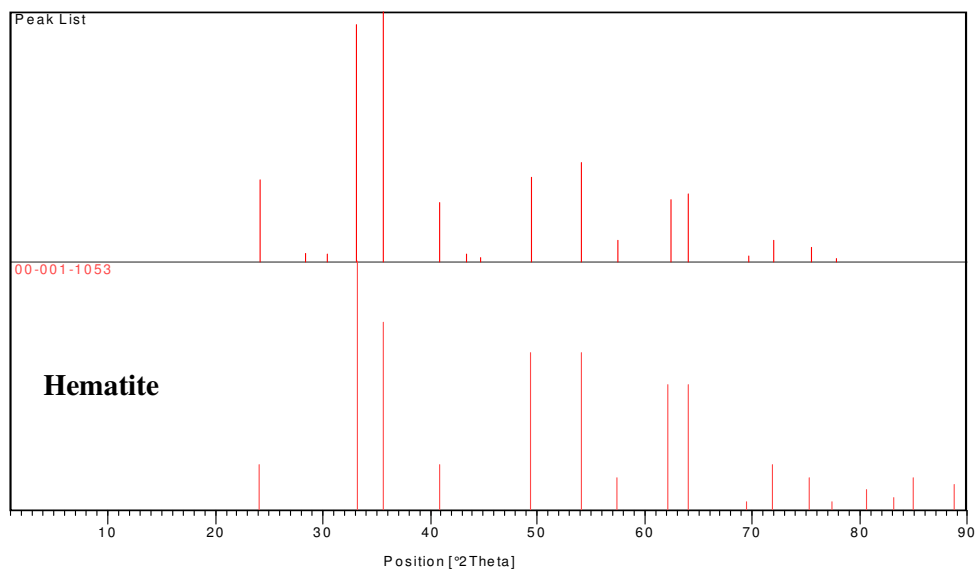


Figure 7.8 Peak matching list of the product formed after heating magnetite at 600°C

7.3.4 Measurement of Hematite Particle Sizes

The hematite particles produced from the successful oxidation of hematite nanoparticles were analysed using SEM. The SEM image of the particles is shown in Figure 7.9.

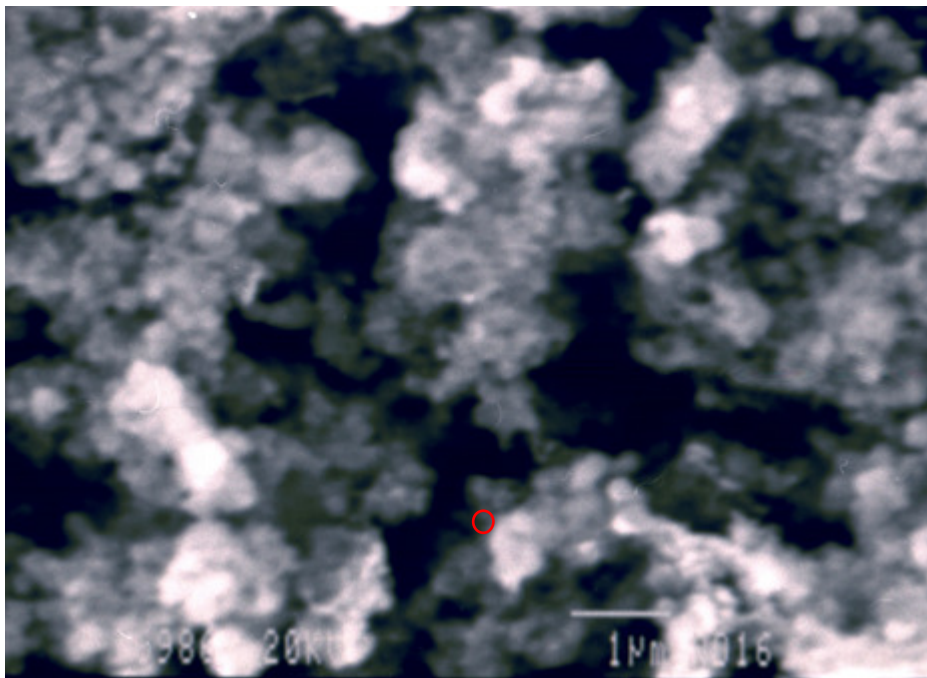


Figure 7.9 SEM image of hematite particles (produced after oxidation of magnetite at 600°C). A discrete hematite particle is shown encircled in red.

A comparison of Figure 7.4, which shows the precursor magnetite nanoparticles and Figure 7.9 which depicts the product hematite particles shows that no appreciable changes in the sizes of the particles occurred. The hematite particles are spherical in shape and occur as globular aggregate clusters. A discrete hematite particle (encircled in red on the SEM image) is about 200nm in size.

7.3.5 BET Characterization of Hematite Product Nanoparticles

The surface characteristics of the hematite nanoparticles were determined using Branauer-Emmett- Teller (BET) analysis to determine if any appreciable changes in the adsorption properties of the particles had occurred during the oxidative transformation. Table 7.1 shows the BET data of both the precursor magnetite nanoparticles and the hematite nanoparticles formed after the oxidation reaction.

Table 7.1 BET data on magnetite precursor nanoparticles and the product hematite nanoparticles.

Iron oxide	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Diameter (nm)
magnetite, Fe ₃ O ₄	20.77	0.0765	14.73
hematite, α -Fe ₂ O ₃	18.69	0.0698	12.92

There are no significant changes in the BET properties of hematite nanoparticles when compared to the precursor magnetite nanoparticles. The surface area and porosity values of the hematite nanoparticles are typical of biogenic iron oxide precipitates (Crosby et al., 1983). The slight reduction in the surface area and porosity values of the hematite particles could be possibly due to slight annealation which occurs during the oxidative transformation.

7.4 Summary & Conclusions

The optimum conditions required for magnetite, Fe₃O₄ precipitation from leach liquors generated from pyrite biooxidation were successfully identified in the preceding chapter. The synthesis of hematite, α -Fe₂O₃ nanoparticles from this precursor magnetite, Fe₃O₄ were then studied in this chapter. The effect of stirring on

the particle size of this magnetite precursor, during the course of aging was examined. Stirring had an overall effect of reducing the magnetite particle size, with the discrete particle size decreasing from a size of around $3.5\mu\text{m}$ in diameter where no stirring occurred during aging to discrete particle sizes of around $0.2\mu\text{m}$ (equivalent to 200nm) when stirring was employed during aging. The phase transformation of these precursor magnetite nanoparticles into the required product hematite particles was investigated. Magnetite nanoparticles were successfully transformed into hematite via an oxidative transformation in air at a temperature of 600°C and a holding time of 12 hours. The oxidative transformation did not have any appreciable effect on the size of the particles and their BET absorption characteristics. Therefore, hematite nanoparticles with an average diameter size of 200nm were formed from an oxidative transformation of magnetite nanoparticles in air at 600°C .

Chapter 8

Conclusions and Recommendations

8.1 Conclusions

Pyrite was bioleached using *Acidianus* spp., a thermophilic microorganism to produce leach liquors which were mainly acidic ferric sulphate solutions. The review of literature suggested that various iron oxides, oxyhydroxides and basic sulphates could be precipitated from the aging of acidic ferric sulphate solutions via a forced hydrolysis reaction. These iron oxides/oxyhydroxides would then be used as the precursor materials for hematite particle formation.

To investigate the feasibility of this proposition, the objectives of this study were defined as follows:

- Investigation of the feasibility of bacteria accelerated pyrite to hematite transformation.
- Establishment of the conditions (pH and concentration of ferric ions) under which the forced hydrolysis/aging of ferric sulphate yields iron hydroxides or oxides which can be used as precursor materials for hematite nanoparticle preparation.
- Optimization of these parameters (pH and ferric ions).
- Determination of the conditions necessary for the phase transformation of the generated iron oxyhydroxides or oxides into hematite nanoparticles.

The experimental methodology used included both chemical and biogenic tests. Initially aging was done on acidic ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$ systems prepared from reagent grade chemicals under various pH conditions. The acidic ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$ systems used in the chemical aging tests simulated the actual systems

which were expected to exist in the biogenic systems. The findings were useful in identifying important parameters which could affect the forced hydrolysis reaction which occurred during aging. The preliminary biogenic studies were used to study pyrite oxidation by *Acidianus* microorganisms. The biogenic leach liquors were aged under acidic conditions and a more basic pH range of 6-9 to determine the effect of the pH on the nature of the precipitate formed. The more influential parameters affecting the hydrolysis reaction during aging, namely pH and iron concentration in the bioleach liquors, were then optimized. The optimum pH and iron concentration to be employed in the production of a precursor iron oxide were identified. This precursor iron oxide material required for hematite nanoparticle formation was then transformed *via* a phase transformation reaction to the required hematite α -Fe₂O₃ product. Size control of the precipitate particles was also done to reduce the particles to the required nano range.

8.1.1 Chemical Aging Tests

In the chemical aging tests, Fe₂(SO₄)₃-H₂SO₄ systems prepared from reagent grade chemicals were aged to yield various iron oxides and basic sulphates through a forced hydrolysis reaction. These tests were useful as they provided a benchmark against which the biological tests could be based. The effect of the pH and concentration of ferric ions used in the systems was studied. Aging was done on 0.045M and 0.154M Fe₂(SO₄)₃ in 0.1M H₂SO₄ systems. Basic iron sulphates of the general formula Fe₄(OH)₁₀SO₄ were precipitated when both the 0.045M and 0.154M systems were aged under acidic conditions. The formation of the FeSO₄⁺ complex in acidic ferric sulphate solutions suppressed the formation of iron oxides and oxyhydroxides. When aging of these systems was done under more basic pH conditions (pH 6-9), XRD analyses showed that iron oxyhydroxides and oxides such as wustite FeO, goethite α -FeOOH and magnetite Fe₃O₄ were precipitated. The findings show that the pH conditions employed during aging could alter the nature of the precipitate formed.

8.1.2 Biogenic Studies

During the preliminary biogenic studies, pyrite oxidation using thermophilic *Acidianus* bacteria was studied. The effect of the composition of the culture medium on the rate of bioleaching, where the form of the sulphur substrate used in the culture medium, either as elemental sulphur S_8 or potassium tetrathionate $K_2S_4O_6$ was studied. Higher bioleaching rates were experienced in the potassium tetrathionate $K_2S_4O_6$ medium where 74% of the iron in the pyrite was solubilized compared to the lower bioleaching rate of 22% experienced in the elemental sulphur S_8 based medium. The leach liquors generated after 14 days of leaching in the $K_2S_4O_6$ based media were subsequently aged under different pH conditions. Under acidic conditions potassium jarosite, $KFe_3(SO_4)_2(OH)_6$ was the main phase identified in the precipitates using X-ray diffractometry. A mixed product of magnetite and hematite was precipitated when aging was done within a pH range of 6-9.

8.1.3 Optimization of Crucial Factors –pH and iron concentration during aging

In these tests the broad pH range of 6-9, where mixed products of iron oxides and oxyhydroxides were precipitated was narrowed into smaller pH intervals and aging was done at these smaller pH intervals of 1 unit each. Bioleach leach liquors of varying initial iron concentrations were also aged, in order to optimize the effect of this parameter on the nature of the biogenic precipitate. The optimum conditions to be used during aging to produce a precursor iron oxide which could be used in hematite production were identified as a pH of 7-8, initial iron concentration of 0.23M (attained after 14 days of bioleaching) for an aging period of 8 days at a temperature of 85°C to 90°C. Under these conditions magnetite, Fe_3O_4 was precipitated as the precursor material for hematite, α - Fe_2O_3 nanoparticle synthesis.

8.1.4 Hematite Nanoparticle Production

The work entailed the synthesis of hematite nanoparticles from the magnetite precursor material. Since the generation of particles in the nanosize was crucial in the study, the effect of stirring during the course of aging was investigated to determine its impact on the particle size. In tests where no stirring occurred during aging, the average magnetite particle diameter size was 3500nm. However, in instances where stirring was employed during aging, a reduction in the discrete magnetite particle diameter size occurred with particles averaging 200nm in diameter. These precursor magnetite nanoparticles were then transformed into hematite particles *via* an oxidative transformation. The optimum conditions for this transformation were a temperature of 600°C and a holding time of 12 hours. No appreciable changes in the size of the particles occurred and the oxidative transformation of magnetite in air produced hematite nanoparticles with a mean diameter size of 200nm.

8.2 Potential Application in Industry

Various iron oxides have been traditionally prepared from the forced hydrolysis of dilute ferric salt solutions prepared from reagent-grade chemicals. The production of the iron oxyhydroxides and oxides at industrial scale has been negated because of the high costs and low productivity emanating from the use of these dilute solutions (10^{-2} to 10^{-3} M Fe). This study has revealed that it is possible to produce various iron oxides from the forced hydrolysis of biogenic leach liquors of relatively higher concentration (10^{-1} M Fe), showing the tremendous potential for the adoption of this work at industrial scale. In addition, the findings can also be used in forecasting the boundary conditions for iron precipitation in biogeochemical systems. Jarosites, iron hydroxides and oxides have been shown to precipitate under various pH conditions in this work. The precipitation of these compounds can therefore be used to control the solubility of the ferric ion in bioleaching and biogeochemical systems.

Acid mine drainage (AMD) is currently the single most significant threat to South Africa's environment. It is well known that whilst a number of chemical processes contribute to AMD, pyrite oxidation is by far the greatest contributor. This work has shown that useful materials such as hematite nanoparticles can be formed from the treatment of the predominantly acidic ferric sulphate solutions formed from AMD. This study therefore, can provide new insights in tackling the problems associated with acid mine drainage (AMD). The findings in this research can thus be used in AMD treatment and in other industrial systems where iron removal is problematic.

8.3 Recommendations

Based on the findings from this work, the following recommendations for further work are made:

Effect of seeding & stirring speed on particle size during aging

It is recommended that the effect of seeding on the size of particles precipitated, during aging be studied. Seeding the bioleach liquor at the onset of aging with magnetite nanoparticles will allow secondary nucleation to occur. This may be a parameter which can be used in the size control of the precipitates. The effects of secondary nucleation and the progression of the precipitation reaction on the precipitate product will then be determined. The effect of the use of stirring speeds greater than those used in this work, on the size of the particles could be studied further.

Aging the leach liquor under more basic conditions

Further work can be done on the hydrolysis reaction under more basic pH values than those used in this study. The effect of a more alkaline pH during the hydrolysis reaction on the nature of the precipitate particles will be investigated. It might be

possible to form mixed or pure products of hematite particles. If this is feasible it will be necessary however to determine if the higher costs incurred from the consumption of greater quantities of NaOH would offset the costs borne during the thermal oxidation of magnetite to hematite (since magnetite was identified as the suitable precursor material for hematite synthesis in the pH range used in this study). The shape and size of the particles should be analyzed to determine if more basic conditions had any significant effect on the particle morphology.

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APPENDIX A

9K Culture Medium (Silverman and Lundgren, 1959)

$(\text{NH}_4)_2\text{SO}_4$	3g
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.5g
K_2HPO_4	0.5g
KCl	0.1g
$\text{Ca}(\text{NO}_3)_2$	0.01g

300ml of 14.74% (w/v) solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was used as the energy source.

Make up to 1L with distilled water and adjust pH to 2.0 using concentrated H_2SO_4 .

APPENDIX B

Culture medium for Extreme Thermophiles (Brock et al., 1972)

$(\text{NH}_4)_2\text{SO}_4$	1.3g
KH_2PO_4	0.28g
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	0.25g
$\text{CaCl}_2 \cdot \text{H}_2\text{O}$	0.07g
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	0.02g
Yeast extract	2g

Trace elements were also added in the following concentrations (mg/L) $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, 1.80; $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$, 4.50; $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.22; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.05; $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, 0.03; $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$, 0.03 and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 0.01.

Make up to 1L with distilled water and adjust pH to 2.0 using concentrated H_2SO_4

APPENDIX C

Chemical Aging Tests

Sample Calculations

Table C1 Elemental Composition of Pyrite Ore from ICP Analysis

Element	(%)
Fe	57.4
S	42.4
Other Elements	0.2

Case 1: Assuming 100% dissolution of Fe in FeS₂ into solution (17.22g Fe)

In the testworks an equivalent of 3% w/v of pyrite (Section 3.3). Thus 1L of culture medium contains 30g of pyrite. This corresponds to an iron content of (0.574*30) and represents the maximum iron which can be leached into solution (Table C1).

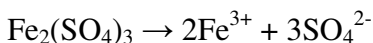
Fe₂(SO₄)₃ Concentration Calculations

Solution equivalent of $0.574 \times 30 = 17.22\text{g/L}$ of Fe

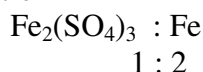
Thus Mass of Fe₂(SO₄)₃ required

Basis : 1Litre of solution

M_r molar mass of Fe₂(SO₄)₃ = 400g/mol



Mol ratio



$$\begin{aligned} \text{Moles of Fe in } 17.22\text{g} &= \frac{17.22}{56} \\ &= 0.3075 \end{aligned}$$

Thus mass of Fe₂(SO₄)₃

$$\begin{aligned} &= \frac{1}{2} \times \frac{17.22}{56} \times 400 \\ &= 61.5\text{g} \end{aligned}$$

$$\begin{aligned} \text{Mol Fe}_2(\text{SO}_4)_3 &= 0.15375\text{M} \\ &\approx 0.154\text{M} \end{aligned}$$

Case 2: Assuming an arbitrary value of 5g Fe in solution

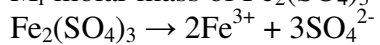
Fe₂(SO₄)₃ Concentration Calculations

Assuming a solution equivalent of 5g/L of Fe

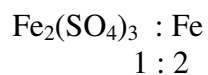
Thus mass of $\text{Fe}_2(\text{SO}_4)_3$ required

Basis : 1 Litre of solution

M_r molar mass of $\text{Fe}_2(\text{SO}_4)_3 = 400 \text{ g/mol}$



Mol ratio



$$\text{Moles of Fe in 5g} = \frac{5}{56}$$

$$= 0.0893$$

Thus mass of $\text{Fe}_2(\text{SO}_4)_3$

$$= \frac{1}{2} \times \frac{5}{56} \times 400$$

$$= 17.857 \text{ g}$$

$$\text{Mol } \text{Fe}_2(\text{SO}_4)_3 = 0.0446 \text{ M}$$

$$\approx 0.045 \text{ M}$$

H_2SO_4

Concentration of $\text{H}_2\text{SO}_4 = 0.1 \text{ M}$

APPENDIX D

Biogenic Studies - Sample Results

***The Fe values are the average of three readings determined using AAS. E_h refers to the standard hydrogen electrode and is calculated by adding 197mV to the Redox potential (Ag/AgCl) in 3M KCl value.**

Bioleaching –Potassium Tetrathionate Based Medium

Day	pH	Redox Potential E (mV)	E_h (mV)	Fe Conc (g/L)
0	2	214	411	0
1	2.15	213	410	1.36
2	2.06	220	417	1.64
4	2.09	229	426	2.43
5	2.18	242	439	3.08
6	2.33	274	471	3.64
7	2.44	305	502	4.01
8	2.70	321	518	4.58
9	3.23	322	519	5.92
10	3.76	330	527	6.6
11	4.28	336	533	7.95
12	4.16	337	534	8.27
13	4.02	341	538	12.8
14	4.01	343	540	12.8

Bioleaching : Sulphur- Based Medium

Day	pH	Redox Potential E (mV)	E_h (mV)	Fe Conc (g/L)
0	2.05	242	439	0
1	2.53	244	441	1.06
2	2.69	240	437	1.21
4	2.78	235	432	1.33
5	3	233	430	1.6
6	3.09	238	435	1.64
7	3.15	257	454	1.8
8	3.54	278	475	2.01
9	3.83	279	476	2.51
10	3.92	284	481	2.52
11	3.92	299	496	3.01
12	3.82	303	500	3.31
13	3.79	308	505	3.82
14	3.81	310	507	3.81

APPENDIX E

Sample Results

pH Optimization Tests

Aging /Forced Hydrolysis of Biogenic Leach liquors obtained after 14 days of bioleaching (0.23M Fe concentration) under different pH conditions. The aging period was 8 days. E_h refers to the standard hydrogen electrode and is calculated by adding 197mV to the Redox potential (Ag/AgCl) in 3M KCl value.

E1 Aging Under Acidic pH (no pH control)

Day	pH	Redox Potential E (mV)	E_h (mV)
0	3.50	315	512
1	3.35	304	501
2	3.14	286	483
3	2.95	273	470
4	2.47	258	455
5	2.32	249	446
6	2.29	242	439
7	2.15	223	420
8	2.08	220	417

E2 Aging within a pH range of 6-7

Day	pH	Redox Potential E (mV)	E_h (mV)
0	6.38	16.2	213.2
1	6.56	14.9	211.9
2	6.67	8.3	205.3
3	6.74	4.3	201.3
4	6.88	-3.5	193.5
5	6.91	-4.2	192.8
6	6.89	-5.6	191.4
7	6.96	-8.1	188.9
8	7.00	-11.6	185.4

E3 Aging within a pH range of 7-8

Day	pH	Redox Potential E (mV)	E _h (mV)
0	7.01	-11.4	185.6
1	7.26	-14.8	182.2
2	7.56	-32.3	164.7
3	7.72	-42.0	155.0
4	7.79	-45.9	151.1
5	7.79	-46.2	150.8
6	7.90	-52.8	144.2
7	7.89	-51.4	145.6
8	7.93	-54.1	142.9

E4 Aging within a pH range of 8-9

Day	pH	Redox Potential E (mV)	E _h (mV)
0	8.01	-59.1	137.9
1	8.40	-81.7	115.3
2	8.76	-102.9	94.1
3	8.90	-110.8	86.2
4	8.72	-100.2	96.8
5	8.77	-103.0	94.0
6	8.83	-106.5	90.5
7	8.96	-114.4	82.6
8	9.01	-116.8	80.2

APPENDIX F

Elemental Composition Calculations of Precipitates

Sample Calculations

Potassium jarosite, $KFe_3(SO_4)_2(OH)_6$

The theoretical composition of potassium jarosite was calculated from stoichiometric considerations.

Potassium jarosite has the chemical formula, $KFe_3(SO_4)_2(OH)_6$

$$\begin{aligned} \text{The Molar masses, } M_r \text{ of Potassium jarosite} \\ &= 39 + 3(56) + 2[32 + 4(16)] + 6(17) \\ &= 501 \text{ g/mol} \end{aligned}$$

Thus theoretically $KFe_3(SO_4)_2(OH)_6$ contains the following amounts of Fe, K and S.

$$\begin{aligned} \text{Fe} &= \frac{168}{501} & \text{K} &= \frac{39}{501} & \text{S} &= \frac{64}{501} \\ &= 33.5\% & &= 7.8\% & &= 12.7\% \end{aligned}$$

These calculated compositions were then compared with the actual values determined from the ICP data in Table 6.2. Table 6.2 shows that precipitate I contained 28.2% Fe, 14% S and 8.1% K.

The percentage difference between these two values was then calculated for each element.

$$= (\text{theoretical value}) - (\text{measured ICP value}) / (\text{theoretical value})$$

$$\begin{aligned} \text{Deficiency of Fe in precipitate} &= \frac{(33.5 - 28.2)}{33.5} \times 100\% \\ &= 15.8\% \end{aligned}$$

$$\begin{aligned} \text{Thus the amount of Fe present in precipitate} &= (100 - 15.8)\% \\ &= 84.2\% \end{aligned}$$

Thus Fe in the precipitate is 84% of the theoretical value, or is deficient by 16%.

Similarly for K,

$$\begin{aligned} \text{Deficiency of K in precipitate} &= \frac{(7.8 - 8.1)}{7.8} \times 100\% \\ &= -3.8\% \end{aligned}$$

Thus K is in excess by 3.8%; or present in the precipitate at 103.8% of the theoretical amount.

Similarly for S,

$$\text{Deficiency of S in precipitate} = \frac{(12.7 - 14)}{12.7} \times 100\%$$

$$= -10.2\%$$

Thus S is in excess by 10.2%; or present in the precipitate at 110.2% of the theoretical amount.

Magnetite, Fe₃O₄

Since magnetite has the chemical formula Fe₃O₄

The Molar masses, M_r of magnetite

$$= 3(56) + 4(16)$$

$$= 232\text{g/mol}$$

Thus magnetite theoretically contains the following amount of Fe

$$Fe = \frac{168}{232}$$

$$= 72.4\%$$

This value was then compared with the actual values of the Fe content as determined by ICP analysis found in Table 6.2. The deficiency or excess of Fe was then calculated accordingly.

The purity of the precipitate (in terms of Fe)

$$= (\text{theoretical value}) - (\text{measured ICP value})/(\text{theoretical value})$$

Thus for the precipitate formed at a pH of 7-8

$$Purity = \frac{71.2}{72.4}$$

$$= 98.3\%$$

For the precipitate formed at a pH of 8-9

Similarly for the precipitate formed at a pH of 8-9. Again as mentioned in Chapter 6, these calculations were only done for the major phases present in the precipitates as identified by XRD (Table 6.1)

$$Purity = \frac{67.8}{72.4}$$

$$= 93.6\%$$

Maghemite, $\gamma\text{-Fe}_2\text{O}_3$

Since maghemite has the chemical formula Fe_2O_3

The Molar masses, M_r of maghemite

$$= 2(56) + 3(16)$$

$$= 160\text{g/mol}$$

Thus maghemite theoretically contains the following amount of Fe

$$Fe = \frac{112}{160}$$

$$= 70\%$$

Thus for the precipitate formed at a pH of 6-7

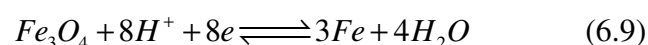
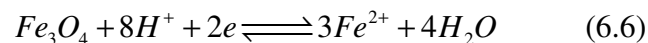
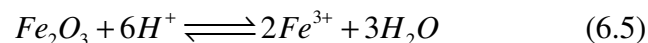
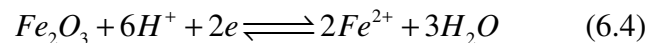
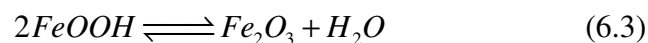
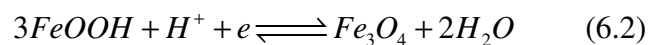
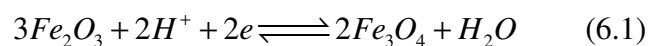
$$Purity = \frac{65.5}{70}$$

$$= 93.6\%$$

APPENDIX G

Calculations for E-pH relationships used in the construction of the Pourbaix Diagram at the optimum aging conditions.

The possible reactions of interest which occurred during aging within the system between the solids and/or ionic species were identified. These reactions are given in Equations (6.1) to (6.9)



The Gibbs free energy of formation of these species are tabulated in Table G1. The data in Table G1 was used in the calculations to establish the E-pH relationship of the systems described in (6.1) to (6.8).

Table G1 Gibbs free energy of formation. Adapted from Burkin (2001)

Species	Fe ²⁺	Fe ³⁺	Fe ₂ O ₃	Fe ₃ O ₄	FeOOH	H ₂ O(l)
ΔG ⁰ kJ	-78.90	-4.7	-742.2	-1015.4	-490.6	-237.129

The Gibbs energy for each reaction was calculated using the Gibbs free energy of formation data given in Table G1. Standard electrode potentials were then calculated from the reaction Gibbs Energy. The Nernst equation was then applied to formulate the E-pH relationship for the solids and ionic species under consideration. The E-pH relations amongst all the species were then plotted to give a Pourbaix diagram for the aging conditions.

The Pourbaix diagram was constructed at the reaction conditions; temperature of 90°C (363.15K) and iron concentration of 0.23M (12.8g/L) (See Section 3.4 and 6.5 respectively). The corresponding E-pH relationships for the systems described in equations (6.1) to (6.9) are as stated in (6.10) to (6.18) respectively and were used to construct the Pourbaix diagram.

$$E = 0.214 - 0.072pH \quad (6.10)$$

$$E = 0.185 - 0.072pH \quad (6.11)$$

$$E = 0 \quad (6.12)$$

$$E = 0.754 - 0.216pH \quad (6.13)$$

$$pH = 0.792 \quad (6.14)$$

$$E = 1.024 - 0.288pH \quad (6.15)$$

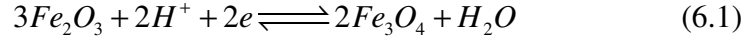
$$E = 0.796 \quad (6.16)$$

$$E = -0.43 \quad (6.17)$$

$$E = -0.0867 - 0.072pH \quad (6.18)$$

A sample calculation for the E-pH relationship for the Fe₂O₃/Fe₃O₄ system is also given as part of this appendix.

Sample calculation for hematite Fe_2O_3 /magnetite Fe_3O_4 system



From the Gibbs Free Energy data given in Table G1

$$\begin{aligned} \Delta G_{\text{reaction 6.1}} &= 2\Delta G_{\text{Fe}_3\text{O}_4} + \Delta G_{\text{H}_2\text{O}} - 3\Delta G_{\text{Fe}_2\text{O}_3} \\ &= 2(-1015.4) - 237.129 - 3(-742.2) \\ &= -41.329 \text{ kJmol}^{-1} \end{aligned}$$

$$\text{but } \Delta G^\theta = -2.303RT \log Q$$

and from Nernst's Equation

$$E = E^\theta - \frac{RT}{nF} \log Q$$

$$\text{However, } Q = \frac{1}{[\text{H}^+]^2} \text{ thus } \log Q = -\log[\text{H}^+]^2$$

$$\log Q = -2 \log[\text{H}^+]$$

$$\log Q = 2 \log[-\text{H}^+]$$

$$\log Q = 2 \text{ pH}$$

Standard potential since $\Delta G^\theta = -nFE^\theta$

$$\begin{aligned} \text{since } E^\theta &= \frac{\Delta G^\theta}{nF} \\ &= \frac{41329}{2 \times 96500} \\ E^\theta &= 0.214 \end{aligned}$$

Applying Nernst

$$E = E^\theta - \frac{RT}{nF} \ln Q$$

at a temperature $T_1 = 90^\circ C = 363.18K$

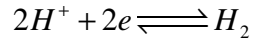
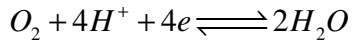
$$E = 0.214 - \frac{(8.314 \times 363.18)}{(2 \times 96500)} \times 2.303 \log Q$$

$$E = 0.214 - \frac{(8.314 \times 363.18)}{(2 \times 96500)} \times 2.303 \times 2 pH$$

$$E = 0.214 - 0.072 pH$$

Therefore the E-pH relation for the reduction of hematite to magnetite given in Equation (6.1) is $E = 0.214 - 0.072pH$ as stated in Equation (6.9)

The stability limits for water were calculated using the reactions for oxygen and hydrogen evolution at $90^\circ C$



Thus, the E-pH relation for the water stability limits were found to be $E = 1.299 - 0.0339pH$ and $E = -0.0339pH$.