MINERAL PROCESSING USING DEEP EUTECTIC SOLVENTS

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By

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Abstract

Mineral processing using deep eutectic solvents Ahmed Z. Mohamed Hussein Al-Bassam University of Leicester 2018

Processing sulfur containing minerals is one of the biggest sources of acute anthropogenic pollution particularly in the form of acid mine drainage. Sulfur-based minerals are generally roasted to convert them to the oxide, producing SO_2 or leached in acid producing H_2S . This study attempts to show an innovative method for processing sulfide-based minerals using a deep eutectic solvent (DES), Ethaline, which is a mixture of choline chloride and ethylene glycol.

It is shown that pyrite can be solubilised by both electrochemical oxidation and reduction in a DES. A novel method is demonstrated to investigate the redox properties of minerals using a paste made from the mineral powder in a DES. The first bulk electrochemical dissolution of pyrite is shown without the formation of H₂S or SO₂. The solubilised species are investigated using cyclic voltammetry UV-vis spectroscopy and EXAFS. In all cases for the iron minerals studied, it was found that the electrochemistry of the counter ion and not the metal, controlled the ease of dissolution. It is also shown that the soluble species, including elements such as arsenic, can be recovered electrochemically which could potentially decrease acid mine drainage. The electrochemical properties of other iron–sulfur and iron–arsenic minerals are also presented and compared to those of pyrite.

The final part of this study uses different cell designs in an endeavour to optimise the space-time-yield of the electrochemically assisted digestion of jarosite. It was found that the electrochemical digestion of material was up to 20 faster than the chemical dissolution. It was, however found that formation of insoluble precipitates, particularly of lead and zinc sulfates affected the performance of the separator membranes and this could decrease the yield of digested metal. The presence of high concentrations of iron salts led to passivating films on the zinc surface during cementation.

Publications

Parts of this work have already been published in the following papers:

- G. R. Jenkin, A. Z. Al-Bassam, R. C. Harris, A. P. Abbott, D. J. Smith, D. A. Holwell, R. J. Chapman and C. J. Stanley, *Minerals Engineering*, 2016, 87, 18-24. (See Chapter 3).
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A- Conferences

(1) Talk

- 1- Ahmed Al-Bassam, Andrew P. Abbott and Gawen Jenkin, Pyrite Dissolution using Deep Eutectic Solvents, 15-16 December 2015, *Minerals and Metals Production from Mine to Market Conference*, The Institute of Materials, Minerals and Mining, IOM³, Trinity Hall, Cambridge, UK.
- 2- Ahmed Al-Bassam, Andrew P. Abbott and Gawen Jenkin, Dissolution of Pyrite and Other Iron Sulfide Minerals using Deep Eutectic Solvents, 21st meeting of the ELECTROCHEM conference series, University of Leicester, 17th -19th of August 2016, Stamford Court, Manor Rd, Leicester LE2 2LH, UK
- 3- Ahmed Al-Bassam, Andrew P. Abbott and Gawen Jenkin, Dissolution of Pyrite and Other Iron Sulfide Minerals using Deep Eutectic Solvents, 4th July 2017, *Postgraduate Research Day university of Leicester 2017*, Department of Chemistry, University of Leicester, Leicester, UK.

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- 1- 22nd June 2015, *Midlands Electrochemistry Group Meeting (MEG) 2015*, University of Warwick, Coventry, UK.
- 2- 3rd to 8th of July, 2016, 26th EUCHEM on Molten Salts and Ionic Liquids, in Vienna (Austria).
- 3- 26th April 2017, *Midlands Electrochemistry Group Meeting (MEG) 2017*, Department of Chemistry, University Park, Nottingham, NG7 2RD, UK.

Statement

The work explained in this thesis for the degree of Ph.D. entitled "Mineral processing using deep eutectic solvents" was carried out by the author in the Department of Chemistry at the University of Leicester between July 2014 and June 2018.

In this thesis, the work recorded was original except where acknowledged or referenced. None of the work has been submitted for another degree at this or any other university.

Signed Date.....

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Dedication

I would like to dedicate this thesis to:

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My parents in law, for their support, encouragements and patience.

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List of Abbreviations:

DESs	Deep eutectic solvents
ILs	Ionic liquids
RTILs	Room temperature ionic liquids
HBD	Hydrogen bond donor
ChCl	Choline chloride
EXAFS	Extended X-ray absorption fine structure
EG	Ethylene glycol
CV	Cyclic voltammetry
EQCM	Electrochemical quartz crystal microbalance
SEM	Scanning electron microscopy
EDX	Energy dispersive analysis using X-ray
ICP-MS	Inductively coupled plasma- mass spectroscopy
PGE	Platinum group element
OD	Oxygen donor ligand

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Chapter 1 Introduction

1.1 Overview

The Earth's crust is composed of about 25% metals by mass.¹ Aluminium (8%) is considered the most abundant metal on earth crust followed by iron (5%) calcium (4%) and sodium (2.5%). A few metals e.g. silver, gold, palladium and platinum are found in their elemental form in the environment.¹ Usually most metals are found in nature as crystalline inorganic minerals.² An ore is a relatively high concentration of a particular mineral that exists in rocks.¹

The major ore source of aluminium is bauxite which is made up of the minerals gibbsite $(Al(OH)_3)$, diaspore (α -AlO(OH)) and boehmite (γ -AlO(OH)). Chloride minerals are considered the main resource of alkali metals, while other metals like Fe, Ti and Sn come from oxide minerals such as, hematite (Fe₂O₃), rutile (TiO₂) and cassiterite (SnO₂)¹. Oxide ores are poorly soluble in water but can be solubilised in strong acids and bases.³

Sulfide minerals are of considerable interest for an economical class of metals such as copper, lead, zinc and iron, in addition to precious metals such as gold, platinum and silver which are usually associated with these minerals.⁴ The most abundant sulfide minerals are pyrite (FeS₂), pyrrhotite (Fe_{1-x}S), arsenopyrite (FeAsS), chalcopyrite (CuFeS₂), chalcocite (Cu₂S), covellite (CuS), galena (PbS), sphalerite (ZnS) and stibnite (Sb₂S₃). Sulfide minerals are poorly soluble in ordinary solvents because of the strong binding of sulfur with these metals, therefore the processing of these metals requires extreme conditions to extract the metals.⁴ Hydrometallurgy, while commonly used, can be non-specific and therefore inefficient in its extraction of metals.⁵

This thesis will examine and discuss the possibility of using electrochemical dissolution for iron sulfide based minerals by using deep eutectic solvents (DESs) at ambient temperature, with the aim of creating a closed-loop process.

1.2 Sulfide minerals and ores

Most metal sulfides are highly symmetrical in their crystal forms.⁶ The classes of metal sulfides are also included of other associated groups such as arsenides, selenides, tellurides and antimonides.⁷ Sulfide minerals are historically well-known and commonly

form with ferro-metals and other metals, such as Cu, Zn, Pb, Ni, Mo and Co. In addition they also host precious metals, such as Ga, Ge, In, Ag, Au, as well as platinum group metals.^{8, 9} The most popular sulfide minerals are iron sulfides like pyrite (FeS₂) and pyrrhotite (Fe_{1-x}S).¹⁰

Most of these minerals were classified at the end of nineteenth century, and the relevant physicochemical properties such as chemical composition, crystal form, hardness, specific gravity, etc. were characterised. Moreover, the developments of optical microscopy and microprobe has led to more in-depth analysis in terms of measuring grain size, surface area, textures, determining phase change and chemical composition.¹¹ These studies have also shown that natural sulfide ores usually include metal impurities, and this makes them very complicated to examine in standard conditions and in comparison to synthetic sulfide salts.¹²

Metals sulfide are recognized as consisting of different crystal phases e.g. semiconducting or metallic; leading these materials to behave in various forms such as diamagnetic, antiferromagnetic and ferromagnetic.⁸ These lead to differences in electrochemical and electronic behaviour of metals sulfide and this has received considerable attentions for potential use in the electronics industry.^{8, 13-17}

The behaviour of metal sulfides is complicated in water due to the reaction of S^{2-} with H₂O below 200 °C which can lead to many species e.g. HS⁻, H₂S _(aq), and SO₄²⁻. At high temperature S²⁻ may be formed. The mechanism of species transport for metal and sulfur in solution is also via a range of complexes.¹² Metal sulfide ores have a complex chemical structures due to the electronic configuration of the outer shell in sulfur ($3s^23p^4$) which has an ability to diffuse within a structure and delocalize its bonds. For example, Gamble and Shannon (1974), noted that the lengths of inter molecular bonds was inversely proportional to the increased covalency in a molecule.¹⁸

Sulfide ores frequently require large volumes of strong acids or bases to solubilize them.^{12, 19} For example, aqua regia is known as one of the best lixiviants as it is a strong acid and an oxidising agent. Its use, often liberates gases such as NO and NO₂ when it reacts with metals.²⁰ Thus, the hydrometallurgical processing of ores which requires oxidation before extraction can be complex and lead to environmental issues.⁵

1.2.1 Iron sulfide minerals

The production of iron from natural resources rose dramatically from 1.04 billion tonne in 2001 to the 2.93 billion tonne in 2012, due to the rapid growing demand for steel production.²¹ However, the majority of this production comes from iron oxide ores.

Iron sulfide ores are common and an important class of minerals to study.⁸ Pyrite (FeS₂) is the Earth's most common sulfide and the dominant iron sulfide in hydrothermal and sedimentary mineral deposits, whereas pyrrhotite (a group of minerals with compositions between FeS and Fe₇S₈) is the dominant iron sulfide in magmatic mineral deposits.²² The variation in atomic structures of pyrite and pyrrhotite is temperature-dependent; pyrrhotite is stable up to 1192 °C, while pyrite decomposes above 742 °C.⁸

Marcasite (FeS₂) is a metastable polymorph of pyrite that forms in some low-temperature hydrothermal systems. Apart from minor sulfuric acid production, these iron sulphide minerals are not of economic interest, yet are often present in larger proportions than the ore minerals that a deposit is being mined for. This results in large volumes of iron sulfides being discarded to the waste (tailings) during mining operations. These tailings require careful management to avoid oxidation of the iron sulfides and the production of sulfuric acid that results in acid mine drainage if not treated.²²

Arsenopyrite (FeAsS) can form a significant constituent in some hydrothermal ore deposits, in particular those that contain gold, whereas loellingite (FeAs₂) is a relatively rare mineral formed in high temperature hydrothermal or metamorphic ore deposits. Whilst these minerals can be a source of arsenic, more generally they present challenges in ore metallurgy and require additional treatment to contain the arsenic and discard it in an environmentally acceptable form. Whilst none of these common Fe–S–As minerals are of significant economic value they can often host economic quantities of precious metal mineral inclusions – typically gold and silver minerals in pyrite, arsenopyrite and loellingite, whereas pyrrhotite is often a host to PGE minerals. Sometimes gold and PGE may be present as nanoparticles or dissolved within the crystal lattice.²²

1.3 Metallurgical processing

The general principles of metal extraction process from their ore are similar in most cases they involve a combination of physical and chemical methods. The physical treatments are commonly called unit operations and these include; crushing, grinding, reducing particles size, mixing, filtration, distillation, and comminution, whereas the chemical treatments involve operations like, leaching, smelting, roasting, electrolysis, decarburization, dephosphorization, degassing and deoxidation.²³

The raw materials commonly have many impurities and require initial physical treatments to increase the purity of the feed materials. This is often followed by physical separations of minerals in extractive metallurgy which depend on the differences of physicochemical properties of the minerals. Metallurgy is the industrial method that deals with metals production from their raw materials, whether from their primary ore resources or secondary resources through scrap recycling²⁴. There are many different methods to extract metals from their ores. Usually the principles of all metallurgical processes include different kinds of separation to enhance the grade or the concentration of metal values separation process streams.

According to Hayes, metallurgical operation can be achieved by through five main stages to produce pure metals.⁵

- Separation which involves removing undesirable material from the metal intended for separation. This step may be accomplished through mineral processing usually based on either selection of the physicochemical properties of the desired phases of metal or the metallurgy achieved by the leaching and followed by precipitation.
- Metal compound/solution formation represents formation of a compound which has different chemical structure from the feed materials, for instance, solubilized of metals into aqueous solvent.
- Crude metal production includes production of metals with impurities; this step is achieved by one of the metallurgical processes such as pyrometallurgy or hydrometallurgy.
- 4) Metal purification means the disposal of undesired compounds from impure metals resulting from the third step through pyrometallurgical processes like removal of carbon via oxygen furnace or using electrochemical processes, such as electrorefining.

5) Product preparation involves using all the essential processes to ensure that the product is ready for market. It may involve processes such as blending, shaping, packaging, etc.

The reasons for the variety of physical and chemical combination processes in modern mineral processing is due to the differences of these raw materials, in addition to the presence of different type of impurity in these materials. The hierarchy of these extractive metallurgical stapes are illustrated in the below, *Figure 1-1*.



*Figure 1-1: The hierarchy of processes in metal production*⁵

The recycling of metals from secondary sources can be achieved in two stages: initial physical separation and then directly purification. However, the production of metals from their primary resources can only be accomplished by a combination of all five stages. This is the reason that recycling in less expensive and less environmentally damaging than primary recovery.

The chemical separations in extractive metallurgy can by generally categorised into three major different types of operations, pyrometallurgy, hydrometallurgy and electrometallurgy.²⁴ The principles of using these operations to extract metals from their natural resources will be described in the following sections.

1.3.1 Pyrometallurgy

Pyrometallurgy is one of the earliest metallurgical processes which utilizes elevated temperature to produce metals from raw materials.²⁵ This can be carried out by using temperature between 300 - 2000 °C in most cases, under controlled conditions of oxygen to optimise the product obtained. There are three main reasons for applying high temperature when processing of metals. Firstly, the stability of these metals and their compounds are significantly altered with temperature. Secondly, the chemical reactivity and mass transport are increased at higher temperature. Thirdly, the separation of metals from mixtures can be easier when the metal and slag are in a molten state.^{9, 26}

Generally, pyrometallurgical operations involve drying, calcination, roasting, and smelting.⁹ The presence of water in minerals is either in the form of waters of crystallization or as bulk water in the ore. The dehydration process refers to the elimination of water from crystallization, while the dehydroxylation is to eliminate associated water, due to the decomposition of hydroxyl groups in the material and formation of vapour water. Dehydroxylation occurs in the calcination stage whereas drying involves both dehydration and dehydroxylation.

The presence of water in initial ores is always unfavourable during metals extraction and leads to poor quality metals. One example is that removing water suddenly from a mixture that requires charging in an electric furnace at high temperature can cause charge blow off. Therefore, drying the ores by heating up the mixture gradually under controlled conditions is essential to release water as steam.⁹ This is not generally an issue as there is a lot of waste heat generated around pyrometallurgical plants.

The general expression of drying water can be described by the following two equations below:⁹

$$MX_n \cdot m H_2O \rightarrow m (H_2O) + MX_n$$
 (dehydration) (1-1)

$$M(OH)_{n(s)} \rightarrow MO_{0.5 n(s)} + 0.5 n H_2O_{(g)} \quad (dehydroxylation)$$
(1-2)

From the above equations the equilibrium constants, K_1 and K_2 for both dehydration and dehydroxylation respectively can be expressed in the below two equations:

$$K_1 = P_{H20}^m$$
, i.e. $P_{H20} = K_1^{1/m}$ for dehydration (1-3)

$$K_2 = P_{H20}^{n/2}$$
, i.e. $P_{H20} = K_2^{2/n}$ for dehydroxylation (1-4)

Generally, the condition below can be applied at the required temperature for removing water in a drying process.

$$K_1^{1/m} > K_2^{2/n} \tag{1-5}$$

The equilibrium constant of water removal as steam from the hydrate form is greater than that of hydroxide forms. Thus, water removal as vapour in drying of the material takes place when the surrounding water vapour pressure in the system is lower than the equilibrium vapour pressures of water.

Generally, heating up the material to 400 °C is enough to eliminate all the water of crystallization in materials. However, that may cause strong binding between the remaining small trace of water molecules and material. Heating up the material to 600 °C, or more than 1000 °C in some cases, can eliminate this trace of water.⁹ The evaporation of water by drying the material is considered an endothermic process, so the enthalpy of this process increases as the amount of water content in the material increases. This leads to a decrease in the equilibrium pressure of steam in the system. Drying can also be done by reducing the surrounding pressure by evacuation.⁹

Fluidised beds, rotary kilns, the fixed beds, or vacuum retort can be used to dry minerals. For example, using rotary kiln dryer to dry garnierite nickel ore. This technique is usually used to remove water from this nickel ore which normally consists of more than 30% water, as shown in the equation below:⁹

$$(Ni, Mg)_3(OH)_4 \cdot Si_2O_5 \cdot n H_2O \rightarrow (Ni, Mg)_3O_2 \cdot Si_2O_5 + (n+2) H_2O$$
 (1-6)

Calcination deals with the removal of volatile species by thermal decomposition of materials. This can be frequently exploited for hydrates and carbonates ores in pyrometallurgical operation and can be generally expressed by the following equations:⁹

$$MCO_{3 (s)} \rightarrow MO_{(s)} + CO_{2 (g)}$$
(1-7)

In the equations of 1-2 and 1-7, the solid forms of $M(OH)_n$ and MCO_3 have to be hydrates and carbonate ores respectively, while MO is introduced here as a solid oxide. Hydroxides decomposition is illustrated briefly in the previous paragraphs of drying and calcination such as $Al(OH)_3$ converting to Al_2O_3 .²⁴ However, in case of the calcination of carbonate ores and their consumption temperatures, there are some useful examples that are worth mentioning here such as FeCO₃ and MgCO₃ which decompose at 200 °C and 400 °C respectively, while limestone CaCO₃ decomposes at 900 °C.⁹ Calcination can be achieved in pyrometallurgical process by using a shaft furnace, a rotary kiln furnace or a fluidized bed-reactor.

Roasting is regarded as one of the most essential processes in a pyrometallurgical operation system and is mostly applied for sulfidic ores. This process can be achieved by passing highly-pressurized oxygen over sulfide ores which will be heated up. In other words, it means solid-gas phase reactions take place. This process oxidises sulfides to oxides.²⁷ Roasting process is usually carried out using flash reactor or a fluid bed reactor. The general description of roasting can be illustrated in the equations below:

1) Metal sulfides are oxidized to metal oxides:

$$MS_{(s)} + \frac{3}{2}O_{2(g)} \leftrightarrow MO_{(s)} + SO_{2(g)}$$
(1-8)

2) Formation of sulphates, oxysulphates and SO₃:

$$MS_{(s)} + 2O_{2(g)} \leftrightarrow MSO_{4(s)}$$
(1-9)

$$2MS_{(s)} + \frac{7}{2}O_{2(g)} \leftrightarrow MO.MSO_4 + SO_{2(g)}$$
(1-10)

$$\operatorname{SO}_{2(g)} + \frac{1}{2} \operatorname{O}_{2(g)} \leftrightarrow \operatorname{SO}_{3(g)}$$
 (1-11)

$$MO_{(s)} + SO_{3(g)} \leftrightarrow MSO_{4(s)}$$
 (1-12)

Thermodynamics can be applied in metallurgical processes to indicate the stability of different phases under different conditions. The equilibrium constant (K_{eq}) can be related to the standard Gibb's energy ΔG° :

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{1-13}$$

$$\Delta G^{\circ} = -RT \ln K_{eq} \tag{1-14}$$

For example, the decomposition of pure metal oxides to pure metals are determined by the thermal heat and partial pressure of oxygen gas as shown in the equation 1-15:

$$M_x O_{y(s)} \leftrightarrow x M_{(s)} + y/2 O_{2(g)} \quad K_{eq} = P_{O2}^{y/2}$$
 (1-15)

The partial pressures of the gases should be maintained at a low level but a high temperature. It is however difficult to remove these gases even with modern vacuum pump systems, therefore, chemical reagents which have high affinity for these gases are added to the mixture to decrease the partial pressures. For example removing oxygen from Fe₃O₄ by using 1/104 ratio of CO/CO₂ gas to form FeO at temperature between 500-900 °C. FeO can be reduced to Fe at temperatures between 900-1300 °C which is the process behind steel production in a blast furnace. ²⁶

Smelting can be accomplished by pouring immiscible liquids to the molten materials to enable separation of metallic phase from slag (oxidic form) and/or matte (sulfidic form) phase and the separation depends on differences in their solubility and density. It is not essentially to involve metals refining in this process, however the adjustment of the slag composition can be achieved by either oxidizing or reducing it.²⁴

The separation of dissolved metals in this process depends on the partition coefficient of particular metals between these liquid/liquid phases.²⁶ One of the most popular examples is the production of iron by using blast furnace, as shown in *Figure 1-2* below. The main materials used together to feed the blast furnace are roasted iron ores which are usually hematite (Fe₂O₃), limestone (CaCO₃), and coke (C). Coke is a form of carbon which forms by heating coal without air to remove the impurities. The reactor can be ignited by blasting the hot air into the mixture and producing CO, and then increasing the temperature to about 2000 °C in the lower part of the reactor. The continuous formation of CO causes the reduction of Fe₂O₃ to elemental iron. Elemental iron can absorb the heat and melts in the bottom of the furnace. The limestone decomposes at high temperatures to produce lime (CaO) and CO₂ and that reacts with excess coke to produce more CO as a reactant.²⁸



*Figure 1-2: A blast furnace for producing iron metal from iron oxide ores.*³⁰

This section attempts to provide more detailed information regarding the pros and cons of pyrometallurgical processes on the ecosystem and economy. Iron is produced by pyrometallurgical operations from their natural resources such as hematite, magnetite, goethite, siderite and pyrite (Fe₂O₃), (Fe₃O₄), (FeOOH), (FeCO₃) and (FeS₂) respectively. Although iron is found in nature in over 300 ores, the first three oxide forms are the major source of this metal.²⁹

Valuable metals such as Cu, Pb, Zn, Ni, and Co are mostly produced from sulfidic ores using pyrometallurgy.²⁴ Around 90% of the world's copper is produced by pyrometallurgical processes from sulfidic ores such as chalcopyrite, bornite, and chalcocite (CuFeS₂), (Cu₅FeS₄) and (Cu₂S) respectively.³⁰ Chalcocite and copper oxide however, are processed using hydrometallurgical processes.³¹ Metallic zinc and lead are

produced from sphalerite (ZnS) and galena (PbS) respectively. Nickel is primarily produced from pentlandite ((Fe, Ni)₉S₈).^{32, 33}

Despite extensive usage, pyrometallurgy has several weaknesses, most notably from its environmental effect due to the emission of harmful gaseous, dust and solid waste such as CO₂, CO, SO₂, H₂S, CS₂, Cl₂, HCl, H₂, H₂O and NO_x, in addition to the organic volatile compounds and dioxins.²⁶ These gases are well known to have negative impacts on many living organisms. Moreover, solid waste such as dioxin and ash which contains toxic heavy metals such as arsenic, lead, and cadmium are produced.

A large amount of thermal processing of sulfidic ores is carried out by injecting oxygen gas into a molten phase producing SO₂ gas as a side product. The pyrometallurgical treatment of chalcopyrite, for example, produces two tonnes of SO₂ gas for each tonne of metallic copper. The impact of SO₂ emissions has been discussed in various reviews.³⁴⁻³⁷ Pyrometallurgy can also release volatile heavy metals into the environment. The Global Mercury Assessment reported that the emission of mercury as a vapour from smelting plants for Cu and Zn in 1995 was approximately 175 tonnes.³⁸ However, Hylander and Herbert reported that this had grown to 275 tonnes in 2005. They concluded that 228 tonnes of Hg could be recovered from these processes.³⁹ In addition to volatile metals, volatile non-metals are also an issue. The most important of these is arsenic which is produced by smelting copper sulfide.⁴⁰ The toxicity of arsenic to humans is well documented.⁴¹⁻⁴³

The economic impacts of pyrometallurgy are mostly the energy to operate the process and the cost of waste discharge treatment. In terms of energy consumption in pyrometallurgy, the smelting process only requires about 40% of the total consumed energy. So, It is quite easy to estimate the cost of consumed energy which is determined to a large extent by the world's oil prices.⁴⁴

Metal processing industries are under constant regulation and lobbying to reduce environmental emissions.⁴⁵ Many end-of-pipe treatments have been considered in modern pyrometallurgical plants to minimise sulfur-based gas emissions into the atmosphere. The solid waste, primarily in the form of slags, acids and dusts need to be to remove toxic heavy metals, such as lead, arsenic, and mercury. Ash are especially complicated as they require cooling, gas cleaning and flotation to recover the metal from this waste instead of discarding into soil.²⁶

There have been some moves to change pyrometallurgical processes into hydrometallurgical to tackle some of these issues. Alumina and zinc for instance were produced by pyrometallurgical routes but Bayer introduced an aqueous process for alumina production and several companies have moved to acid electrolysis for zinc production.^{25, 46}

1.3.2 Hydrometallurgy

Hydrometallurgy uses lower temperatures to extract metals from their raw materials with aqueous and/or organic solutions.⁵ The liquid used to digest the ore is known as the lixiviant. The historical developments have been reviewed by Habashi.⁴⁶ Hydrometallurgical processes are usually carried out at less than 50 °C. High temperature hydrometallurgical process can be carried out under high pressure but these are less common.²⁶ The presence of impurities may inhibit the leaching of metals and so physical and chemical pre-treatments are necessary. These pre-treatments involve comminution, concertation, chemical change and structural modification. The comminution includes increasing the surface area of ores to maximise contact with the lixiviant e.g. decreasing the particle size from 10 mm to 1 mm causes a 10-fold increase in the surface area. Concentrating the minerals feed before leaching is important to reduce the gangue and increase the concertation of metals in the ores.

The pre-treatment before hydrometallurgical processes can also involve pyrometallurgical treatments to achieve chemical changes in the minerals and improve chemical solubilisation. For examples, the metal salts on the left-hand side of equations 1-16 to 1-19 are insoluble in ordinary solvents but the materials on the right obtained after pyrolysis can be separate using hydrometallurgy.⁴⁷

$$AuTe_{2(s)} \leftrightarrow Au_{(s)} + 2Te_{(g)}$$
(1-16)

$$CuS_{(s)} + 2O_{2(g)} \leftrightarrow CuSO_{4(s)}$$
(1-17)

$$ZnS_{(s)} + 1.5O_{2(g)} \leftrightarrow ZnO_{(s)} + SO_{2(g)}$$

$$(1-18)$$

$$V_2O_{5(s)} + 2NaCl_{(s)} + H_2O_{(g)} \leftrightarrow 2NaVO_{3(s)} + 2HCl_{(l)}$$

$$(1-19)$$

The kinetics of minerals dissolution can be also enhanced by changing the structure, stoichiometry and dislocation density of ores. The production of fresh cracks/ defects in the mineral during chemical and/or physical changes can increase the exposure of the solid to the lixiviant.⁴⁸

Hydrometallurgy is generally considered to have a lower environmental effect compared with pyrometallurgy as most of the lixiviant is recovered and recycled.⁴⁹ Hydrometallurgy is summarized by *Figure 1-3* and was first implemented at the end of the nineteenth century to extract aluminium from bauxite and gold form a variety of ores using cyanide.⁴⁶ The application of these methods tends to be complex due to the variability of materials that need to be processed such as native metals, metals oxides, metals sulfides, carbonates, phosphates, silicates, sludge and alloys.³



*Figure 1-3: Schematic diagram of the steps involved in metal extraction and recovery*¹

Characteristically, hydrometallurgy consists of three processes: first, digestion or leaching which involves dissolution of solid minerals to be separated by hydrometallurgical solvents, often this process can be accelerated by chemical reagents. Attempts have also been made to leach metals biologically.²⁰ Bio leaching of metal can be carried out by several types of bacteria (e.g. *Thiobacillus, thiooxidans, T. ferrooxidans*) or fungi (*Aspergillus niger, Penicillium simplicissimum*) which are able to form organic and inorganic acids. Brandl *et al.* found that there is a growth in these kinds of bacteria and fungi in the presence of electronic waste. Also Brandl *et al.* found that up to 95% of

the Al, Pb, Ni and Zn which are present in electronic waste might be leached into the solution, while 65% of the Sn and Cu were leached into solution.⁵⁰ Although biological leaching is not highlighted in this study, it can be recognized that solubilisation of metals in this method may have a small environmental impact. The methods are generally slow, however and relatively expensive.

Chemical leaching uses solutions such as H_2SO_4 , HNO_3 , HCl, NH_3 , $FeCl_3$, and CN^{-24} For example, leaching of copper from copper oxide ores is achieved by using aqueous sulfuric acid. Metal oxides are directly leached by the leaching solution, while metal sulfides need an oxidizing agent to increase the solubility of the sulfides in the leaching solution. For instance, H_2O_2 is added as oxidizing agents into Cl_2/Cl^- leaching solution to oxidize sulfide metals into metal oxides which are solubilized easily in acid.⁵¹ Another example of leaching is using sodium cyanide (NaCN) with oxygen to leach gold ores.⁵²

The relative stability of metals and metal ores in aqueous media can be conveniently represented by Pourbaix diagram (*E*-pH). The Pourbaix diagram represents the stability of thermodynamic species between different equilibrium phases at given pH and *E* values. This diagram is derived from the Nernst equations, which plots different lines between different equilibrium phases as chemical composition and potential are altered. The pH of a leaching solution can be altered by adding acid or base to the solution. On the other hand, the potential (*E*) of leaching solution can be controlled, whether chemically by adding oxidizing or reducing agents, or electrically by applying external potential to the regime.²⁶

The Pourbaix diagram of Fe-S-H₂O (*Figure 1-4*) is dominated by the presence of Fe₂O₃ which has a high stability and low solubility in water in the pH range 3-14. However, below pH 2 it converts rapidly to Fe³⁺ and becomes soluble. The oxidation of pyrrhotite (FeS) in pH 2 results in decomposition to elemental sulfur, and pyrite (FeS₂) which has a higher stability at pH 2. The importance of Pourbaix diagram of iron sulfide in aqueous system is not only related to the stability of iron compounds, but also for other sulfides minerals which have iron sulfides like chalcopyrite (CuFeS₂).²⁶

Physical separations of the pregnant leach solution must be applied after the leaching process to obtain a clear solution with no suspended particles. The second stage is precipitation which involves the separation of metal species from the leach solution. This

is attained by adding precipitation agents or changing the pH of the leaching solution.³ Commonly, metals are precipitated as sulfides, hydroxides or carbonates, removing iron by precipitating goethite (FeO(OH)) or jarosite normally (KFe₃³⁺(OH)₆(SO₄)₂) from the solution during zinc processing.⁵ Another example is the separation of metal sulfides like nickel and cobalt from leaching solution which can be achieved by using H₂S gas at 1 atm. and pH 1.⁵ Moreover, thermal precipitation can be also be used to separate solids from liquids by changing the solution temperature such as CuSO₄ in the presence of H₂SO₄ and water.⁵³



Figure 1-4: Pourbaix diagram for the Fe-S-H₂O system at 25 °C.³¹

Although Pourbaix diagram is essential to illustrate the thermodynamic stability of species, it is does not explain the kinetics of a reaction. This limitation can be illustrated by considering that ferric ions Fe^{3+} and while they should precipitate as solid $Fe(OH)_3$ by increasing the pH they instead form colloidal iron-hydroxyl polymer in the presence of oxygen; rather than precipitated. Therefore, separation of solid particles from liquid in this matter becomes more complicated due to complex phase behaviour. This problem can be solved by controlling the rate of base addition and the temperature.²⁶

The extraction of metal ions utilizing immiscible solvents can be achieved by mixing both aqueous and organic solvents. This process can be done by using one of the following solvent extractions method such as solvating extractants, chelating extractants, cation exchange extractants, and anionic extractants.²⁶ Aqueous solvents have an ability to convert metal atoms to metal ions by surrounding them with high polar water molecules. However, organic solvents metals can be only dissolved by the formation of neutral complexes.⁵⁴ For instance, iron can be dissolved in aqueous solvent and forms Fe³⁺ ions, while in organic solvents cannot be dissolved. However, in the presence of high acidity and high chloride concentration in solution the neutral complex of H⁺FeCl4⁻ is formed, and it can be dissolved in organic solvent by solvating.⁵

The exact hydrometallurgical process depends on the composition of raw material and the degree of purity needed for the recovered metal. Particularly, the extraction efficiency of metals in hydrometallurgical operations are directly proportional to the rate of the reactions. The low temperatures in hydrometallurgical operations make the reaction rates slower than that in pyrometallurgical processes.⁵⁵

Metal digestion can be achieved by oxidation processes either using oxidizing agents or by electrolysis. The recovery of metals from the lixiviant is mostly carried out by 4 methods; electrowinning, cementation, precipitation and ion exchange;³ as illustrated in *Figure 1-5*.



Figure 1-5: Flow chart showing the steps involved in metallurgical processing.⁷

Electrowinning, or electrorefining, is generally an efficient electrochemical reaction where metal is dissolved at the anode and collected in a purer state at the cathode.⁵⁶ It is commonly applied to silver, zinc, lead and copper.^{3, 5} Usually the sensitivity of the electrodeposition process is affected by the pH of the solution which affects the solution properties such as solubility of metals and electrochemical window.⁵⁷ On the other hand, using complexing agents such as NH₃ and CN⁻ can be useful to overcome the issue of metals solubility so as to control the speciation of metal ions in solution and deposition of the metal to be collected.³ In the case of using aqueous solutions in metal electrodeposition, hydrogen may be liberated at the cathode and oxygen at the anode which leads to a reduction in the quality of the deposit and a decrease in current efficiency.³

Cementation is an electrochemical spontaneous reaction method used to recover metal ions from leaching solutions to their elemental state by using a sacrificial metal which is dissolved, this can be seen, for example, in the cementation of gold from its leaching solution ammonium thiosulfate by utilizing copper as a sacrificial metal.⁵⁸ Another example of cementation is the displacement of dilute solution (1-2 kg/m³) of Cu²⁺ ions with elemental iron or zinc, as shown in equation (1-20) below.⁵⁹ A metallic copper can be deposited onto the surface of metallic iron or zinc as a weak adherent layer which can be removed by washing it with high velocity of liquid stream.

Cementation is usually applied as a primary method to recover valuable or toxic metals such as gold, copper, silver and cadmium, in addition to purify an electrolyte in electrolytic operation. Smelting or electrorefining should be followed cementation to ensure that residual species will be recovered.

$$Cu^{2+}_{(aq)} + Zn^{\circ}_{(s)} \leftrightarrow Cu^{\circ}_{(s)} + Zn^{2+}_{(aq)}$$
(1-20)

Precipitation is used to separate metal out from leaching solutions and this is achieved by either adding precipitating agents to separate metal from solution, or adjusting pH of the leaching solution. An alternative technology of precipitation tends to use chelating agents in biphasic solvents to remove metal ion from aqueous (polar) media into usually non-aqueous (non-polar) media.⁶⁰

Ion exchange involves using acidic polymeric resin to exchange metal ions in solution by hydrogen ions in the resin and bind the metal ions with polymeric matrix.

1.3.3 Electrometallurgy

Electrometallurgy deals with extraction of metal ions from their liquors by utilizing an electrochemical reaction which involves oxidation- reduction reaction (redox) in an electrochemical cell.²⁴ This reaction involves transferring electrons between a solid surface of conductive electrode and molecules in an electrolytic solution. The electrochemical cells which usually contains two conductive electrodes: an anode and a cathode, as shown schematically in *Figure 1-6*. The anode is defined as the positive pole where the electrons are donated and oxidation occurs, while the cathode is considered as the negative pole where these electrons are accepted and reduction takes place. These electrodes can be made from any conductive substances such as metals, semiconductors, graphite and conductive polymers. These two electrodes are immersed in electrolytic solution, such as aqueous, organic and molten salts which contain ions that move freely.



Figure 1-6: Electrochemical reaction occur in simple electrochemical cell.²⁶

There are two types of electrochemical reaction in an electrochemical cell. First, the Galvanic cell in which a reaction spontaneously occurs generating electrical energy like that which occurs in a battery.

e.g.
$$Zn + Cu^{2+} \rightarrow Cu + Zn^{2+}$$

Secondly, electrolytic reactions which occur when external potential is applied across between the electrodes of the cell.²⁶

e.g.
$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

Both kinds of electrochemical reactions, spontaneously and non-spontaneously can be exploited in metallurgical processing. The first in the form of cementation and the second for electrowinning as demonstrated but the examples given for copper recovery. The main advantage of utilizing electrolytic cells is the purity and simplicity of the process.²⁶

Electrowinning and electrorefining are the major electrometallurgical operation methods. Electrowinning deals with reduction of metal ions in electrolytic solution to the metallic form such as, electrowinning of copper, zinc, sodium and magnesium²³, in addition to the production of aluminium by molten salts in the Hall-Héroult process.²⁴ Electrorefining is a common method for purification of impure solid metals. The impure metal is anodically dissolved and pure metal is recovered at the cathode. This is used extensively for zinc, copper and lead.^{23, 24}

An important example of developing hydrometallurgy is gold leaching solution. For many years, gold has been considered as one of the most noble metals which can be dissolved in liquid mercury to form an amalgam, however it is insoluble in all strong individual acids or alkalies. Jabir Ibn Hayyan invented aqua regia in the eighth century, and it has been used ever since to dissolve gold. It consists of a mixture of 3 volumes of HCl and 1 volume of HNO_3 as shown in the equation (1-21).⁴⁶

$$3HCl + HNO_3 \leftrightarrow Cl_2 + NOCl + 2H_2O$$
 (1-21)

In 1783, the Swedish chemist Carl Wilhelm Scheele found that gold can be dissolved by using a dilute solution of sodium cyanide.⁶¹ However, the application of this discovery was later known by the cyanidation processes in 1887 by the British scientist John Stewart MacArthur. Furthermore, G. Bodländer proposed that hydrogen peroxide was formed during cyanidation process of gold as shown in the equations below.^{26, 62} The global gold production by cyanidation process was widely used during the period of 1900-1910.⁴⁶

Despite the developments in mining engineering, the process is still used but is considered as dangerous due to the excessive use of toxic cyanide.

Anode:
$$\operatorname{Au}_{(s)} \leftrightarrow \operatorname{Au}_{(aq)}^+ e^-$$
 (1-22)

$$Au^{+}_{(aq)} + 2CN^{-}_{(aq)} \leftrightarrow Au(CN)_{2}^{-}_{(aq)}$$
(1-23)

Cathode:
$$O_{2(g)} + 2H^+_{(aq)} + 2e^- \leftrightarrow H_2O_2$$
 (1-24)

$$H_2O_2 + 2H^+_{(aq)} + 2e^- \leftrightarrow 2H_2O$$
(1-25)

Net eq.: Au
$$_{(s)} + 8CN^{-} + O_{2(g)} + 2H_2O \leftrightarrow 4[Au(CN)_2]^{-}_{(aq)} + 4OH^{-}$$
 (1-26)

Safer alternative leaching solutions have been proposed for gold extraction including ferric-thiocyanate, thiourea, thiocyanate-ferric sulfate and ammonical thiosulfate.⁶²⁻⁶⁶ However, these tend to have slow dissolution kinetics, lower recovery and speciation is still not well understood. To overcome these problems, additives like FeCl₃, O₂, and H₂O₂, have been added.⁶²

Gold naturally occurs associated with numerous complex refractory ores such as pyrite, together with various cuprous lead and zinc ores. These ores are problematic as they are resistant to the most leaching solutions even cyanide.⁶⁷ This has been attributed to the existence of significant impurities in solution from the undesirable solubilised metals. Aylmore (2001) claimed that ammonical thiosulfate was less sensitive to contaminants than cyanide.⁶⁸ Moreover, Gong *et al.* (1993) and Deventer (2002) have also claimed that ammonical thiosulfate can solubilize these complex sulfide ores such as chalcopyrite, arsenopyrite, pyrrhotite and lesser level of pyrite.^{69, 70} Yet, numerous researchers argue against this claim by stating that pyrite ores do not leach by ammonical thiosulfate.^{68, 71, 72}

Despite its usefulness and efficiency, hydrometallurgy suffers from consumption of large volumes of aqueous solution. While discharge chemicals to the environment is only a small proportion of what is used, the toxicity of reagents such as, HNO₃, H₂SO₄, CN⁻, aqua regia, and caustic soda can lead to environmental issues when accidentally discharged into water courses. While the majority of chemicals are reused in many hydrometallurgical processes it does lead to large volumes of dilute wash water which

still needs to be treated before being discharged to environment.^{73, 74} This can be an issue in parts of the world where water is a scarce resource particularly Peru and Australia.

For example, Mudd (2007) collected and analysed data for water and energy consumption, cyanide use and the emission of greenhouse gases resulting from gold mining.⁷⁵ These data were collected from the world's largest production in the period 1991 to 2006. Mudd found that the average volume of water consumed in gold mining was around 1.42 kL/t of milled ore or 691 kL/kg of Au produced. Whilst the average consumed energy represented by fossil fuels was found approximately 0.31 GJ/ t of ore or about 143 GJ/kg of produced gold. Moreover, the conversion of consumed energy into emission of greenhouse gases was found to be ~21.7 kg CO_{2-e}/t ore or ~11.5 tCO_{2-e}/kg Au while cyanide consumption was found more than 1000 kg/kg Au.⁷⁵

For these reasons metal extraction processes are being developed utilizing non-aqueous solutions such as RTILs. ILs and their derivatives like DESs permit the speciation of metals to be controlled. ILs demonstrate a good solubility of metals and metal oxides together with high current efficiencies for metal reduction.

1.4 Ionic Liquids

High temperature molten salts are liquid at 500-1000 °C, and have been used for processing metals such as Li, Na and Ti.⁷⁶⁻⁷⁸ However, the negative aspect of using high temperature liquids in electrowinning is the high power consumption and its inapplicability to a wide range of materials and substrates.³ Ionic liquids (ILs) are salts that are liquid below 100 °C and which are generally formed from organic cations with organic or inorganic anions.⁷⁹⁻⁸¹

Room temperature ionic liquids (RTILs) have been studied in many areas such as catalysis, electrochemistry, material chemistry and pre-treatment of biomass.⁸² Their physicochemical properties are distinctly different from molecular solvents and high temperature molten salts. They are viscous with moderate conductivities; they are non-volatile and show unusual solubility for species such as metal oxides.^{80, 82, 83} RTILs have a high capability to control the speciation of metals in solution.⁸⁴ Although these features which make the RTILs play a vital role in many technological aspects, nevertheless these liquids can still have significant toxicities.⁸⁵ Generally, the toxicity of ILs rise when

increasing the length of alkyl chain on the cation of ILs. A lower toxicity ionic liquids have been synthesized by applying a functional group such as imidazoles,⁸⁶ lactams,⁸⁷ amino acids,⁸⁸ in addition to choline⁸⁹ which has been utilized in mineral processing.³

Imidazolium, phosphonium, pyridinium, and tetraalkylammonium salts are widely used as cations, while hexafluorophosphate $[PF_6^-]$, chloride, bis (trifluromethanesulfonyl) amide $[Tf_2N^-]$ and tetrafluroborate $[BF_4^-]$ are common anions.⁸⁴ Some commonly used cations and anions are shown in *Table (1-1)*.



Table (1-1): A selection of cations and anions used to make ionic liquids.³

The melting point of ILs is affected by the asymmetry of cations, and the size of both the cations and anions. ILs that have symmetrical cation and anion.⁹⁰ For example, 1-butyl-3-methlimidazolium has lower melting point than 1-butylpyridinium because the former has one symmetrical carbon group in contrast to the latter which has two symmetrical groups.⁹¹

The first ionic liquids was reported by Walden in 1914, who observed that the formation of methyl ammonium nitrate had resulted from the neutralisation of nitric acid and ethylamine; the compound was noted to have a melting point around 13-14 °C.⁹² In 1934, Graenacher claimed that a solution of different viscosity liquids had been formed by mixing of cellulose with quaternary ammonium salts above 100 °C.⁹³ This claim appeared in a US patent and was used to produce "threads, films and artificial masses".⁹¹

Hurley and Wier in 1951 demonstrated that the electrodeposition of aluminium achieved by mixed of 2 mole equivalents of AlCl₃ with 1 equivalent mole of N-ethylpyridinum bromide.⁹⁴ They noticed that when the composition of AlCl₃ was between 63 to 67 mole % the mixture was liquid below 20 °C. This discovery led to develop the recent ionic liquids. Osteryoung *et al* (1975)⁹⁵ and Gilbert⁹⁶ studied the physicochemical properties of [C₄py]Cl-AlCl₃.

Wilkes and Hussey modified a new system of (ILs) using AlCl₃ with 1-ethyl-3-methylimidazolum which are liquid at room temperature between 33 and 67 mol. % of AlCl₃. They predicted optimum properties of this quaternary ammonium salt based on the molecular orbital energy calculations using MO theory.⁹¹ It seems clear that Wilkes and Hussey's new system [C₂mim]Cl-AlCl₃ (0.33-0.67) mol. % of AlCl₃ had a wider electrochemical potential window and was less viscous than those previously mentioned. This was the "first generation" of ionic liquids³ which was liquid at ambient temperature due to reduce the charge density that leads to decreased lattice energies which leads to a decrease in the freezing point of the ILs.^{97, 98}

In another major study of synthetic ILs, Wilkes and Zaworoko (1992) reported that moisture stable ILs such as 1-ethyl-3-methylimidazolium [C₂mim] salts could be prepared at ambient conditions using discrete anions such as tetrafluroborate.⁹⁹ These are sometimes termed "second generation" ILs or "discrete anion" ILs and are probably the most commonly used liquids at the moment.³ Despite being more stable than the chloroaluminate systems, it should be noted that tetrafluoroborate liquids still exhibit slow hydrolysis to form HF.^{99, 100}

Ionic liquids can have wide electrochemical windows which is why they are commonly used to reduce or oxidize metals. For example, $[BMP(Tf_2NO)]$ has a potential window of about 5.5 V on glassy carbon.^{101, 102} This allows the electrodeposition of metals that have
very negative redox potentials like Al,¹⁰³ Mg,¹⁰⁴ Ge,¹⁰⁵ and Si¹⁰⁶ which are not possible to deposit from other solvents.

The viscosity (η) of ILs is typically in the range of 50 to 5000 cP and is affected by the size of anions and cations.¹⁰⁷ There is a strong inverse correlation between η and molar conductivity (Λ) of ionic liquids,¹⁰⁸. The relatively high viscosity of ionic liquids has often been seen as a drawback for the use of ionic liquids as it decreases the rate of diffusion as given by the Stokes –Einstein equation ¹⁰⁹

$$D = \frac{kT}{6\pi\eta r} \tag{1-27}$$

Where D is the diffusion coefficient of substance, k is the Boltzmann constant, T is temperature, and r is the ionic radius.

As well as affecting the rate of diffusion the high viscosity also affects the conductivity of ILs. The conductivity of the ILs ranges between 10⁻⁵ and 10⁻² Scm⁻¹.^{110,111} Abbott demonstrated that the conductivity and viscosity could be modelled using hole theory.¹¹¹ It was assumed that movement in ILs was limited by the number and size of the voids in the liquid. The liquids have holes of different radii the average of which is controlled by the surface tension of the liquids.¹¹¹ Liquids can be made less viscous by decreasing the surface tension e.g. by fluorinating the anion. It also explains why ILs with larger ions are more viscous as there are less holes of suitable size for the ions to move into the corresponding holes.¹¹²

The last two decades there has seen a growing number of reports of RTILs being used for mineral processing. One of the first was a 1999 patent for the processing of spent nuclear fuel using RTILs which was followed by a study to electro-refine actinides.¹¹³ In hydrometallurgy solvent extraction has been applied to concentrate and separate metals from aqueous solutions using liquids such as kerosene. An analogous process has been carried out by several groups using water immiscible ionic liquids.¹¹⁴⁻¹¹⁷.

Whitehead *et al.* 2004 described the synthesis and application of a hydrogen sulfate salt of n-butyl-methyl-imidazolium cation C₄mim(HSO₄). This was used to extract gold and silver from their sulfidic ores, and it was found that it had a good ability to dissolve the metal ores.¹¹⁸ More recently, Whitehead *et al.* have improved gold and silver leaching

with C₄mim (HSO₄) ferric chloride/thiourea in acidic media. The C₄mim (HSO₄) ferric/thiourea mixture showed improved extraction of gold compared with other bmim salts such as BF⁻, Cl⁻, N(CN)₂⁻, and CH₃SO₃⁻, as well as that leached in aqueous sulfuric acid.¹¹⁸ However, the toxicity and cost of many ionic liquids precludes them from large scale applications such as mineral processing although they have been shown to be useful for biphasic extraction from aqueous solutions.

1.5 Deep Eutectic Solvents (DESs)

Forming eutectics between Lewis acids and halide salts was relatively well known but Abbott *et al.* extended these ideas by using Brǿnsted acids with halide salts.⁹⁷ These so-called Deep Eutectic Solvents (DESs) encompass a variety of inexpensive and relatively benign amides, polyols and carboxylic acid and offer the possibility of developing tuneable fluids for large-scale applications such as metal processing.

The formation of this complex results from an interaction between the hydrogen bond donor (HBD) and the quaternary ammonium halides.¹¹⁹ For instance, mixing a quaternary ammonium salt such as choline chloride (ChCl) (mp = 301 °C) with a HBD such as urea, (mp. = 133 °C), results in eutectic liquid with mp. = $12 °C.^{89}$ The depression in melting points of results from a reduction in both the lattice energy and charge density for those substances during the formation of the DES. This is shown schematically in *Figure 1-7* below which illustrates the phase diagram of most DESs studied.



*Figure 1-7: Schematic representation of a eutectic point on a two-component phase diagram.*⁵⁹

DESs are made up of sustainable chemicals like choline chloride (vitamin B4) which is a simple animal food additive.¹²⁰ According to Global Industry Analysts 2014 ¹²¹, it is generally in the order of $\notin 2/kg$. Urea is a widely-used nitrogen fertilizer; world production mounted to 184 Mt in 2012. Urea is non-flammable and degrades biologically and is about $\notin 0.5/kg$.

The general formula of DESs is {Cat⁺X⁻zY}, where Cat⁺ represents the cation such as ammonium, phosphonium and sulfonium and X⁻ referred to Lewis base, mostly a halide anion whilst z represents the number of molecules that relate with Y which is either Lewis or Brǿnsted acid.¹¹⁹ DESs are generally divided into four main types according to the utilization of the agent of complexation, these are explained in *Table (1-2)*. Abbott *et al*. found that the depression of freezing point of eutectic systems was affected by the mole fraction of hydrogen bond donor in the mixture and larger depressions of freezing point were observed with HBDs of lower molar mass.¹⁰⁷

Туре	General formula	Terms
1	$Cat^{+}X^{-}zMCl_{X}$	M= Zn, Sn, Fe, Al, Ga, In
2	$Cat^{+}X^{-}zMCl_{X}.yH_{2}O$	M= Cr, Co, Cu, Ni, Fe
3	Cat ⁺ X ⁻ zRZ	$Z=CONH_2$, COOH, OH
4	$MCl_X + RZ = MCl_{X-1}^+. RZ + MCl_{X+1}$	M=Al, Zn and Z=CONH ₂ , OH

Table (1-2): General formula for the classification of DESs⁵⁹

The physico-chemical properties of these DESs such as viscosity and conductivity were found to be similar to those in imidazolium ILs.¹⁰⁷ They have also been tested in many applications.⁸²

The capability of DESs to donate or accept electrons or protons makes them good ligands and therefore good solvents to dissolve a wide range of metal salts.³ Type 3 DESs have been recognized in many applied areas such as metals oxide processing,⁹⁸ glycerol removal from biofuels,¹²² and production of cellulose derivative.¹²³ DESs have been used in metal processing for metal electrodeposition, metal electropolishing, and metal extraction.¹¹⁹

Much of the work has been carried out using Ethaline which is a mixture of choline chloride [(CH₃)₃NCH₂CH₂OH]Cl as the salt with ethylene glycol [HOCH₂CH₂OH] as the HBD in a 1:2 molar ratio. ^{119,124} Some of the first signs that DESs would be good for metal oxide processing came when Abbott et al. showed that the solubility of copper oxide (CuO) in Reline (1 ChCl: 2 urea) at 50 °C was 0.12 M.¹⁰⁷ The solubility of other metal oxides such as CuO, ZnO and Fe₂O₃ has been studied in four different DESs. The researchers found that there had been differences in solubility of metals oxide depending upon the HBD; thus the difference in solubility of metal oxides can be applied in metals recovery.⁸² The solubility of the above metals oxide in malonic acid DES has been compared with the same concentration of H⁺ ions in HCl. The results indicate that there are different activities of H⁺ atom in two liquids. Researchers also found that there was no direct relationship between Cl⁻ concentration and the solubility of oxides, but the significant factor is the behaviour of H⁺ atom as a good acceptor for oxygen.⁹⁸ Abbott et al. studied the acidity of ILs and DESs and they found that the pKa of BF_4 – based IL is lower than that of acetate -based IL. It means the acidity depend on the basicity of the anion in ILs and DESs.¹²⁵

The complexation of ZnO in the 1 ChCl: 2 urea eutectic was explored by Abbott *et al.* using mass spectroscopy.¹²⁶ They noticed that the complex formed was [ZnClO.urea]⁻, which supports the theory of H⁺ ions act as acceptors for basic oxygen.

1.6 Ionometalluragy

Ionometallurgy is the term coined to describe the ionic equivalent of hydrometallurgy. With reference to *Figure 1-3*, ionometallurgy has been used to study digestion and recovery (in the form of electrowinning and cementation) but primarily it has been used for liquid-liquid extraction from aqueous acidic solutions. The topic has been reviewed in-depth by Abbott *et al.*¹²⁷

The main advantages for utilizing these ionic liquids rather than aqueous solvents stem from the high concentration of anionic ligand and the high solubility of ionic species in ionic media. Solubilisation of metals in highly ionic media lead to different speciation compared to aqueous solutions which can shift the reactivity of metals with respect to each other. This can result in selective separation either through digestion or separation.¹²⁸ In general ionic liquids enable to separation characteristics of molten salts without the high operating temperatures.

The first study of digestion metal salts by using ILs was probably done by Dai et al. where they found that the dissolution of UO3 in imidazolium chloroaluminate melts enabled a concentration of between 1.5 and 2.5 x 10^{-2} mol. dm⁻³ and the species in solution was found to be $[UO_2Cl_4]^{2-129}$ However, this chloroaluminate melt is very water sensitive. Huang et al. used ILs with discrete anions such as imidazolium PF₆ to study the recovery of nano-scale zinc particles from phosphor ashes.¹³⁰ The modelling of solubility for metal salts in ILs is difficult due to the lack information about the solution species formed. Generally, speciation of metals in solution is changed dependent on the Lewis acidity of the metal and the Lewis basicity of any ligands that are available in the ionic liquid.⁸⁴ Nockemann et al. examined the solubilized speices of europium and yttrium oxides in betaininum bis(trifluoromethylsulfonyl)amide ([Hbet][Tf₂N]), where they found formation of the species [Eu₂(bet)₈(H₂O)₄][Tf₂N]₆, [Eu₂(bet)₈(H₂O)₂][Tf₂N]₆·2H₂O and $[Y_2(bet)_6(H_2O)_4]$ $[Tf_2N]_6$.¹³¹ In another study, the same research group examined the dissolution of uranium oxide in $[C_4 mim][Tf_2N]$, where they suggested that $[UO_2(NO_3)_3]^-$, i.e. for these more highly charged ions, oxide was still bound with uranium.¹³² So, it was concluded that dissolution of metal oxide is either protonated or substituted by anionic species of ILs.

Whitehead *et al.* investigated utilizing of 1-butyl-3-methylimidazolium hydrogen sulphate [C₄mim][HSO₄] with iron (III) sulphate as the oxidant and thiourea as a complexing agent to recover gold and silver from their ores. They found that the process was selective to recover these valuable metals in high yield (over 85% for Au and 60% for Ag) over other metals exist in these ore such as Cu, Pb, Zn and Fe by comparison with sulfuric acid process.^{118, 133}

DESs have been extensively used to solubilize wide range of metals and their salts. Abbott et al. examined the digestion series of 17 metal oxides ranged from Ti to Zn in the three different types of DESs, and they compared their solubility with that in HCl.⁹⁹ The researchers found that some of those metals have higher solubility in DESs than that in HCl. This is because the high concentrations on anionic species (ligands) in DESs, which can form complexes with metal ions in solutions.¹²⁸ The HBDs such as urea, thiourea,

and oxalate are strong complexing agents and are generally used as complexants in aqueous solutions.¹³⁴ The selective choice of these ligands can enable selective solubility for some metal salts.¹³⁵

Metals that are digested from their solid salts in any solution, can be extracted into a different phase to increase their concentration and separate them from undesirable materials. This is generally done using liquid-liquid extraction with immiscible liquids. Generally, these phases are aqueous and a non-polar organic solvent containing a chelating agent that is immiscible with the aqueous phase.¹³⁶ ILs can replace organic solvents to extract metals from aqueous phase, however some of these ILs are slightly miscible with aqueous which decreases the extraction efficiency.¹³⁷ Most extraction of metals from ILs have used imidazolium cations, Rogers *et al.* used ionic liquids with discreet anions for biphasic extractions.¹³⁸ Metals extraction process in ionic liquids can be achieved by using neutral ligands as complexing agents of metal ions, selective extraction of metals through anion interaction and task-specific ionic liquids where a functionality on one of the ions specifically interacts with the metal cation.

Dai et al. used crown ethers and calixarenes to extract metals from aqueous solutions.¹³⁹ It was found that by utilizing ionic liquids as an alternative to the organic solvents a high partition coefficients can be achieved. The extraction mechanism of metals into ILs is different to the mechanism in organic solvent due to differences in metal speciation as they transfer between the immiscible phases. The extraction of strontium, for example, from an aqueous HNO₃ solution using 18-crown ligand, takes two nitrate ions as ligands into an organic solvent to maintain a neutral complex. However, if the IL of [C₅mim][Tf₂N] is used as extraction phase, a cationic strontium complex bound with water is formed. ^{140, 141} Nockemann et al. studied the extraction of Cu, Co and Nd salts in aqueous solution by using hydrophobic ionic liquids of hexafluoroacetylacetonate (hfac) and found the IL phase reacts with the metal salt in the aqueous phase form anhydrous complexes of anionic hfac. The complexes can be precipitated out of solution by the saturation of ionic liquid with metal ions.¹⁴² Separation of metals such as Fe, Co, Cu, Mg and Zn could be efficiently extracted from rare earth elements, such as Nd and Sm in aqueous solution of HCl have been done by using concentrated hydrophobic IL of C_{6,6,6,16} PCl.¹⁴³ Liu et al. found that using a binary mixture of imidazolium and phosphonium ionic liquids high extraction coefficients were obtained.¹⁴⁴

Task-specific ionic liquids (TSILs) are have a functional groups covalently bound to cations of the ILs.^{145, 146} TSILs can be easily prepared by modification cations for example by taking a ligand with amine and functionalised easily to form quaternary amine such as betaine HOOCC₂H₄N(CH₃)₂, where the carboxylate is an effective complexant for a wide range of metals. Nockemann *et al.* examined the dissolution of a series of metal oxides, including Ag₂O, ZnO, CuO, NiO, and PbO, along with various lanthanides, in the protonated betaine bistriflamide -IL [Hbet][Tf₂N].¹⁴⁷ Metal salts can be stripped from the IL using acidic aqueous solutions. Both phases are miscible above 55°C, but it can be separated out below this temperature. Visser *et al.* have modified TSILs by combining the monoaza-crown ethers functional group on imidazolium cations and used for the biphasic extraction of Cs⁺ and Sr²⁺.¹⁴⁸ Other functionalities such as urea or thiourea were covalently attached to imidazolium cations enabling biphasic extraction of Hg²⁺ and Cd²⁺ with higher efficiencies than organic solvents.¹⁴⁹

Generally, the physical properties of ILs are controlled by the cations, whereas the chemistry of ILs are controlled by the anions.¹⁵⁰ Binnemans reviewed the chemistry of *f*block metal extraction using TSILs.¹⁵¹ Jensen et al. studied the extraction of lanthanides from aqueous solutions by using 2-thenoyltrifluoroacetone (Htta) and found Nd(tta)₄⁻ and $Eu(tta)_4$ were formed when $[C_4mim][Tf_2N]$ was used as the solvent.¹⁵² Mehdi *et al.* studied the speciation of Nd^{3+} , Co^{2+} and Cu^{2+} using alkyl imidazolium-based ionic liquids containing hexafluoroacetylacetonate (hfac) anions.¹⁴² They found [C₄mim][Nd(hfac)₄] and [C₄mim][Co(hfac)₃] were formed using X-ray crystallography. Egorov et al. Fe^{3+} , Cu^{2+} , Ni^{2+} and Mn²⁺ from aqueous extracted solutions using trioctylmethylammonium salicylate.¹⁵³ The area of TSILs for extraction of metals has been reviewed by Davis.¹⁵⁴

The recovery of metals ions in ILs and DESs can usually be achieved by one or more of most common method such as electrowinning, cementation and precipitation. Some ILs have large potential windows, for example [BMP][Tf₂N] has a window of 5.5 V on a glassy carbon electrode and [C₄mim][PF₆] is 4.15 V for at a Pt electrode.^{101, 155} The potential window of ILs are decreased by addition of water.¹⁵⁶ Schroeder *et al* and Matsumoto studied the effect of water on the potential limit of imidazolium-based systems and they found that the cathodic limits were reduced by ~2 V.^{155 157}

In principle, metals can be selectively electrowon from solution mixtures if the redox potentials are sufficiently dissimilar.¹⁵⁸ Using appropriate ligands in aqueous electrolytic solutions redox potentials can be selectively shifted. Theoretically, the same behaviour should occur in ILs; yet the relative strengths of any potential metal-anion complexes are still unidentified.

Chloroaluminate liquids were the first to be used for the electrodeposition of metals. The electrodeposition of sodium and lithium was achieved in a Lewis Basic chloroaluminate melt.^{159, 160,84} Chloroaluminate and chlorogallate have been used to electrodeposition of indium and gallium.^{161, 162,163}

Giridhar *et al.* proposed that metals can be extracted from aqueous solution into an IL phase and subsequently electrowon.¹⁶⁴ A tri-*n*-octylmethylammonium-chloride and - nitrate was used to extract palladium from an aqueous HNO₃ solution and it was shown that Pd can be directly electrodeposited onto an electrode in the IL phase.

Selectivity through recovery was demonstrated by Abbott *et al.* who found that metals could be separated from DESs using electrochemistry,¹³⁵ even though the total miscibility of these DESs in water means that the extraction of these metals cannot be done by two immiscible phases. Abbott *et al.* also found that CuO and ZnO are soluble in a ChCl DES mixture: thiourea, while Al₂O₃ was insoluble.¹³⁵ The eutectic mixture ChCl: urea has an ability to recover selectively metal oxides such as Zn and Pb from a waste of metals oxide such as aluminium and iron that result from an electric arc furnace.¹⁶⁵ A less viscous DESs 1ChCl: 1.5 ethylene glycol: 0.5 urea (56 cP at 25 °C) was used in a similar manner. Abbott *et al.* also examined the electrochemical redox behaviour and speciation for a range of metals in Ethaline and aqueous solution.¹²⁷ It was shown that similar speciation was achieved in Ethaline to that in aqueous solutions to which NaCl was added.¹⁶⁶ When the speciation was the same, there was a good correlation between redox potentials in DESs and aqueous brine solutions.

Abbott *et al.* illustrated that iodine can be used as an electro-catalyst because of its ability to dissolve a wide range of metals as it possesses higher positive redox potential of I_2/I^- in Ethaline than common metals. This was demonstrated for the oxidation and recovery of gold.¹²⁷ Hartley (2013) proved that by depending on the redox behaviour and speciation the selective dissolution and extraction of copper/gallium semiconductor alloy have been

accomplished using iodine as electrocatalytic oxidizing agent in Ethaline. These dissolved metals were recovered by electrowinning copper in its metallic form and precipitation of gallium as a hydroxide. Moreover, I₂ dissolved in Ethaline has been used to remove thin layer of gold from paleontological microfossils without causing any damage to the sample.⁸⁴ The same electrocatalytic method was used to separate Cu from Zn and Ga from As. The authors reported that the extraction of Au/Ag from complex sulfidic ore is also possible, although the redox potential of both gold and iodine are approximately similar. However, the high concentration of iodine with I₂Cl⁻ formed in Ethaline has the capability to oxidize even the noble metals which have high oxidation potentials.¹⁶⁷

Cementation is an alternative recovery processing to that electrowinning, which involves immersing reactive metals (sacrificial metals) with high negative redox potentials to an electrolytic solutions including metal ions.¹⁶⁸ This process involves a spontaneous electrochemical reaction between the metal ions in solution and the sacrificial metal (mostly Zn).¹⁶⁹ The same method has been used to cement silver metal on to copper surface for the production of printed circuit boards.^{165, 170}

It has recently been demonstrated by Jenkin *et al.* that there is a numerous types of ores can be dissolved using iodine in Ethaline as an electrocatalyst. The authors examined the micro leaching rate of native gold, electrum and tellurium, as well as galena (PbS), chalcopyrite (CuFeS₂), pyrite (FeS₂) and tellurobismuthite (Bi₂Te₃) using an optical profiler to measure etch rates. The etching of electrum was more rapid than neighbouring grains of galena, chalcopyrite tellurobismuthite and native tellurium, while pyrite was not etched. The etch rate, for electrum was found to be 0.172 μ m/min.¹⁷¹

1.7 Project objective

Abbott *et al.* (2011) coined the term Ionometallurgy for the use of ionic liquids in numerous aspects of metal processing.³ The cost and toxicity of many ionic liquids (ILs) precludes them from large scale applications such as mineral processing although they have been shown to be useful for biphasic extraction from aqueous solutions. Deep eutectic solvents (DESs) are mixtures of simple quaternary ammonium salts and hydrogen bond donors such as ethylene glycol (Ethaline) has been used in this study. They may provide an alternative to conventional metallurgy as they use environmentally

benign components and avoid the production of large volume/low concentration aqueous wastes.

The major aims of this thesis are to study novel redox chemistry through the electrochemical and electrocatalytic dissolution of natural iron sulfide based minerals by utilizing DESs. This method uses pastes to minimise the amount of lixiviant (digesting solution) used to solubilise the mineral. The aims of this thesis can be split into three practical chapters as follows:

- 1- To prove that DESs such as Ethaline can be used to solubilise minerals to extract metals from sulfidic ores. Initially this will be demonstrated using paint casting method with iron pyrite (FeS₂). The method will also be used to determine whether precious metals, such as gold, can be separated from pyrite with which it is commonly found. To achieve these aims a range of electrochemical, microscopic and spectroscopic techniques will be used.
- 2- The electrochemical behaviour of four other common iron sulfide based minerals will be studied; marcasite (FeS₂), pyrrhotite (Fe_{1-x}S), arsenopyrite (FeAsS) and loellingite (FeAs₂). These minerals have been chosen to compare the electrochemical behaviour with pyrite, as they have different crystallography and Fe: S ratios. Moreover, studying the electrochemistry of arsenopyrite and loellingite shows the differences in electrochemistry obtained by replacing sulfur with arsenic atoms in the mineral lattice. This is the first investigation of the electrochemical behaviour of the common Fe–S–As minerals in DESs. The study also shows how the electrochemistry of the Fe–S–As minerals in DESs compares and contrasts with the aqueous system and how elements from ores can be efficiently solubilised and recovered.
- 3- Finally, the information gained in the previous chapters is applied to the remediation of jarosite waste. This material is a by-product of the zinc processing industry and contains a large amount of iron sulphide and iron sulfate. It is an environmental issue due to the high lead and cadmium content. In this study the paste technique will be used in an attempt to solubilise the jarosite waste and recover the lead by cementation and electrodeposition.

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Chapter 2: Experimental

2.1 Materials

2.1.1 Chemicals

All materials and reagents employed in this work with their respective purities and suppliers are shown in *Table (2-1)*.

Chemicals	Purity %	M. Wt	Supplier
Iron (II) chloride tetrahydrate	98%	198.81	Sigma-Aldrich
Iron (III) chloride. anhydrous	97%	162.2	Sigma-Aldrich
Iron (II) disulfide	extra pure	119.967	Fisher Chemicals
Iron (II) chloride. anhydrous	97%	126.75	Acros organics
Sulfur powder	99.98%	30.02	Sigma-Aldrich
Sodium chloride	extra pure	58.44	Fisher Chemicals
Iron sulfide	99.9%	87.91	Sigma-Aldrich
Iron powder	98%	55.85	Alfa Aesar
Iron Disulfide	99.8%	119.98	Sigma-Aldrich
Silver Chloride	99.9%	143.32	Sigma-Aldrich
Iodine	99.999%	253.81	Fisher Chemicals
Nitric Acid. traced metals	67%-69%	63.01	Fisher Chemicals
Hydrochloric Acid	37%	36.46	Fisher Chemicals
Sodium hydroxide	97%	40	Fisher Chemicals
Lead sulfide	99.9%	239.27	Sigma-Aldrich
Zinc sulfide	99.99%	97.46	Sigma-Aldrich
Cobalt (II) chloride hexa-hydrate	99.99%	237.93	Alfa Aesar
Disodium Sulfide nonahydrate	99.99%	240.18	Sigma-Aldrich
Zinc metal Powder	97.5%	65.39	Alfa Aesar
Silver wire	99.99%	107.87	Alfa Aesar
Gold wire	99.9%	196.96	Alfa Aesar

Table (2-1): List of chemicals used in this study

2.1.2 Synthesis of DES

A mixture of choline chloride { HOC_2H_4N (CH₃)₃Cl} (ChCl) and ethylene glycol {EG} were mixed in a 1:2 molar ratio known as Ethaline. The components were mixed in a beaker using a hot plate with magnetic stirrer at 60°C until the mixture became a clear liquid and homogeneous. Both chemicals were supplied by Sigma Aldrich Company at 99% purity. The deep eutectic solvent (DES) prepared above was used as the DES in all the studies.

2.1.3 Minerals

Table (2-2) lists the minerals used in this project

	Sample	Minaral	Conventional	Additional
	identifier	winierai	formula	comments
1	GJ	Pyrite	FeS ₂	
2	E485	Marcasite	FeS ₂	
3	E678	Arsenopyrite	FeAsS	
4	21485	Loellingite	FeAs ₂	Larger fragments are polycrystals
5	Sheff X49	Pyrrhotite	Fe _{1-x} S	
6		Jarosite waste	$KFe_3(OH)_6(SO_4)_2$	

Table (2-2): List of sulfide minerals

Two methods were used to synthesise the mineral based working electrodes used in this study. The first used a single crystal working electrode, where the electrodes were synthesized using small single crystals of natural ores provided by the Department of Geology at the University of Leicester. The ores which were a mixture of sulfides and arsenides are listed in *Table (2-2)*. The electrical connection of each mineral to a copper wire was made using silver conductive paint (RS components). The electrode was made by casting the sulfide particles in epoxy cure2 resin (20-3432-064) with its epoxy hardener (20-3432-032) in a volume ratio of 4:1, respectively, as provided by Buehler, UK. A smooth electrode surface was obtained by using an ATA SAPHIR 520 polisher to remove the rough surfaces of these electrodes with 1200 grade sand paper and then using

0.05 µm liquid alumina. The removal of residual alumina on the sulfide electrodes was achieved via sonication in distilled water for 10 minutes.

The paint casting method involved grinding the mineral into a fine powder (which was sieved to ensure particle sizes of $1-5 \,\mu\text{m}$) and then mixed with a few drops of Ethaline to make a paste that was then painted onto a Pt flag electrode.

2.2 Electrochemical techniques

Electrochemistry is the branch of chemistry that deals with either spontaneous chemical reactions that produce electrons (galvanic cells) e.g. batteries, or non-spontaneous chemical reactions (electrolytic cells) where an external electrical potential is applied across an electrochemical cell to produce electrochemical reactions at the electrodes e.g. electrowinning electrorefining and electroplating. An electrochemical reaction is a heterogeneous reaction which involves the transfer of charge, usually electrons between an electrochemical cell. At the anode, the oxidation occurs where the electrons are transferred from the ions or molecules in solution to the electrode (electrons lost) whilst at the cathode the electrons are transferred from electrode to the ions or molecules (electron gain) and therefore the species there are reduced.¹⁻⁴

2.2.1 Cyclic voltammetry

Cyclic Voltammetry (CV) is an important technique which can identify redox couples of electroactive materials and surface speices.⁵ Qualitative and quantitative analysis can be carried out using the potentials and current intensities of a voltammogram at the working electrode. This technique records the current (I, Amperes) that passes between two swept potentials (E, Volts) at the working electrode. Usually, CVs involve using three types of electrodes immersed in an electrolyte in an electrolytic cell: the first of these is the working electrode (WE) where the redox processes take place; the second is the reference electrode (RE), through which negligible current flows which is used to control the applied voltage at the WE; and the third is the counter or axillary electrode (CE), which allows current to pass [between the WE and CE] by completing the electrical circuit.⁶

A triangular waveform is usually used as a function of time, as shown in *Figure 2-1*, where the potential of the WE is started from some initial potential, E_i to the final

potential, E_f and the plot is formed during the switching potentials, where the swept potential reverses direction towards the E_i again to complete the first cycle of the swept potential.



*Figure 2-1: A plot of applied potential versus time in cyclic voltammetry.*⁷

Figure 2-2 shows the current versus potential plot in cyclic voltammetry (a voltammogram) which can be used to characterise the electrochemical response as one of the three major systems: reversible, quasi-reversible, and irreversible. These systems are dependent on varying parameters such as the rate of electron transfer, the rate of mass transport across the electrode surface/solution interface, and the nature of chemical reaction at the surface of the WE.^{6, 8}

A reversible system is governed by diffusion control, where the rate of electron transfer is faster than the mass transport of the redox species, and the redox system is able to maintain an equilibrium during the potential scan. The current peak increases directly with the increasing concentration of the bulk species, so it is proportional to the square root of the scan rate ($I_p \alpha v^{1/2}$). Also, the ratio of the anodic and cathodic peak current is equivalent and equals unity (-Ipc / Ipa = 1). The amount of peak current for a reverse reaction at 25°C can be determined using the Randles-Sevcik equation, as shown below:

$$i_p = 2.69 \times 10^5 n^{3/2} A C D^{1/2} v^{1/2}$$
(2-1)

where i_p is the value of the anodic or cathodic current in Amperes, *n* is the number of electrons transfer in the system, *A* is the area of electrode in cm², *C* is the concentration of the redox species in solution in mole.cm⁻³, *D* is the diffusion coefficient of the redox species in cm² s⁻¹, and *v* is the scan rate in V s⁻¹.

The formal potential of a reversible system for redox reaction (E') can be calculated using equation (2-2) below, and the concentration of the reactants and the resultants at the electrode surface can be calculated using the Nernst equation (2-3).

$$E' = \frac{Ea + Ec}{2}$$
(2-2)

$$E' = E^{\circ} + \frac{RT}{nF} \ln \frac{[OX]}{[Red]}$$
(2-3)

 E° is standard electrode potential, [Ox] and [Red] are the concentrations of oxidised and reduced species, respectively, *n* is the number of electrons in the redox reaction, and *F* is the Faraday constant.



*Figure 2-2: Cyclic voltammograms of reversible, quasi-reversible and irreversible systems.*⁷

However, in a quasi-reversible system the current is controlled by both electron transfer and mass transport, which tends to be reversible at slow scan rates and irreversible at high scan rates.⁷ In an irreversible system, the Nernst equation (2-3) above cannot be applied due to the rate of electron transfer being slower, in a relative sense, than the mass transport of the species. Furthermore, the potential peaks become broader and are shifted by increasing the scan rate due to the hysteresis.

In this work, the CVs of metal sulfides in Ethaline have been performed by varying the potential limits and holding the potential at different values during the sweep. All the CVs were carried out using an Autolab PGSTAT12 potentiostat controlled by the GPES2 software (version 4.9). A three-electrode system immersed in Ethaline at particular scan rate was used to complete the electric circuit, which consisted of a working electrode – either a 1 mm Pt disc or metal sulfide powder paste on a Pt flag in addition to a native sulfide ore electrode – a silver wire immersed in 0.1 M AgCl dissolved in Ethaline in a glass electrode end with a Vycor glass frit acts as the reference electrode and a Pt flag is used as a counter electrode.

2.2.2 Chronocoulometry

Chronocoulometry an electrochemical technique which measures the charge passed as a function of time when a potential step is applied to an electrode. The charge vs time profile can be used to determine diffusion coefficients and to obtain information about relative rates of electrochemical reactions. The charge-time profiles can be analysed using the integral form of the Cottrell equation as shown in (2-4).⁹

$$Q = \frac{2nFAC_{\circ}D^{1/2}}{\pi^{1/2}}t^{1/2}$$
(2-4)

In this work, chronocoulometric experiments were used to measure the consumption of charge at the mineral electrode, whether this was a paint casted mineral electrode or a single crystal. These chronocoulometric experiments were performed using an Autolab PGSTAT12 potentiostat controlled by the GPES2 software (version 4.9), where the connectivity of the electrodes was exactly identical to cyclic voltammetric experiments.

2.2.3 Chronopotentiometry

Chronopotentiometry, was used to measure the open circuit potential (OCP) and can provide information on oxidation-reduction reactions that occur in the absence of an applied potential. It is extensively used to study the corrosion of electroactive materials.¹⁰ OCP can be defined as the potential of a working electrode immersed in an electrolytic solution against a reference electrode where no electric potential is applied and no current is flowing (zero current). The resulting graph of the OCP represents a galvanic potential as a function of time, which records the stripping of a galvanic potential of electroactive materials at equilibrium. In this work, the OCP has been measured by a three electrode system using an Autolab/PGSTAT12 potentiostat controlled by the GPES software. The working electrodes were weather paint-casted iron sulfide minerals or using the polished electrode of a whole grain particle of each iron base sulfide mineral versus an Ag/AgCl reference electrode in Ethaline, with a Pt flag as the counter electrode.

2.2.4 Electrochemical Quartz Crystal Microbalance (EQCM)

When any electrochemical dissolution or deposition of a solid phase process takes place at an electrode surface, the mass will change at the electrode surface. This change in mass can be detected using an electrochemical quartz crystal microbalance (EQCM). The principle of operation of EQCM depends on the piezoelectric characteristics of the QCM cell. In this study AT-cut α -quartz crystal were used to monitor changes in mass at the electrode surface during redox reactions. This cell includes an oscillator quartz crystal cell, where the piezoelectric crystal is created by two inert metal electrodes placed perpendicular to a thin quartz crystal wafer disc.¹¹

Mechanical oscillations can be generated inside a quartz crystal lattice as a result of applying an alternating potential which is capable of generating a distortion of the quartz crystal. The application of an electrical potential across the quartz crystal can also create a mechanical strain and change its piezoelectric properties. Thus, the application of an electric field across the cell can make the crystal resonate.¹²

The cut mode of the quartz and the thickness can be exploited to detect the change in mass of an electrode deposited on the crystal by measuring changes in the vibrational frequency of the crystal cell.¹¹ The mechanical vibrations of the quartz crystal can be attributed to a shift in resonant frequency of the crystal, which can itself be correlated to the change in mass of the crystal. The change in mass (due to deposition on the crystal surface) can be measured from the change in resonant frequency by utilizing the Sauerbary equation, equation (2-5).¹³

$$\Delta f = -\frac{2f_{\circ}^2}{\rho v A} \,\Delta m \tag{2-5}$$

Where Δf is the change in crystal frequency, Δm is the change in mass, ρ is the density of quartz (2.65 g.cm⁻³); υ is the wave velocity of quartz crystal (3.34x10⁵ cm s⁻¹); A is the area of crystal electrode in cm² and f_{\circ} is the fundamental frequency.

In this study, EQCM was used to monitor the micro-weight of FeS₂ powder change versus charge (Q) on a gold quartz crystal. A three-electrode electrochemical system immersed in Ethaline was used by applying a GAMRY eQCM 10M; a gold quartz crystal was employed as the working electrode where ~5 μ m³ pyrite particles are painted on the electrode surface versus Ag/AgCl as the reference electrode and a Pt flag as the counter electrode, using the Gamry 5.65v control software.

2.3 Surface characterisation techniques

2.3.1 Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX)

The surface morphology of the deposited species from the electrochemical dissolution of iron sulfide minerals and polished electrode of ores was characterised by using scanning electron microscopy (SEM) or backscattered electrons (BSE), whilst elemental analysis of the deposit compositions was carried out via energy dispersive X-ray spectroscopy (EDX). The SEM might be considered as a kind of 'electron microscope' that can be used for surface imaging and determining the morphology of a specimen by applying a high energy electron beam generated by an electron gun in a vacuum chamber. SEM images are constructed by removing two different electron signals; secondary electrons and back-scattered electrons from the atoms into the sample due to the interaction of the incident electron beam with those atoms.

However, EDX is considered an analytical technique when used in combination with SEM for qualitative and quantitative elemental analysis in the determination of the chemical composition of a sample. This technique depends on the emission of characteristic X-rays which are emitted from an element when a core shell electron is ejected from an atom and an outer or core shell electron relaxes back into the hole. By collecting all the different X-ray wavelengths emitted, an elemental analysis of the sample can be achieved.¹⁴ A Phillips XL30 ESEM instrument was used to obtain the SEM or BSE images with an accelerating voltage between 15 and 20 keV, providing an average beam current of about 120 μ A, and using the INCA software for EDX analysis. All EDX results will be reported in atomic weight % in the results chapters.

2.3.2 3D Optical Profilometry

3D optical images were captured on a Zeta Instruments Zeta-2000 optical profiler using the inbuilt Zeta3D software version 1.8.5. The technology of the Zeta-2000 enables imaging of surfaces with very low reflectivity and very high roughness. The highest magnification possible with this instrument was 100x, and it can measure the profile of a sample with an accuracy of at least 0.5 μ m.

The optical profilometry captures a light image reflected from the sample surface before and after electrochemical or chemical dissolution, where both optical scans are focused on exactly the same surface area. This optical profiler measures the precise micro-scale of the X, Y and Z dimensions to provide accurate 3D colour images. This optical profiler utilises positioning software to build up a 3D colour image from the surface. Images are created by defining image profiles that are in focus at different heights. These are then analysed to produce a reconstructed 3D topography of the surface. The dissolution rate of sulfide minerals and associated metal was measured by constructing a cross line over a sample area and a flat surface of an insoluble phase as a reference height such as the black resin or a non-conductive grain particle.

2.3.3 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is one of the most useful analytical techniques that can be utilized to provide qualitative and quantitative information about the compounds present in crystalline and powder forms. It is a powerful and non-destructive technique for characterization of crystalline materials due to its ability to obtain an information on the crystal phases, structures, and orientations, in addition to the grain size. X-ray diffraction data was obtained using a Phillips model PW 1730 X-ray generator, with a PW 1716 diffractometer and PW 1050/25 detector. The X-ray tube was a long fine focus Cu anode with Ni K α filtered radiation. Typical operating settings were 40 kV, 30 mA, scanned between 15 and 110° 2 θ with a step size of 0.02° 2 θ . Angle calibration was carried out using a synthetic Si sintered standard. The identification of an unknown X-ray diffraction pattern (or diffractogram) can be achieved by comparing this data with an internationally recognised database containing reference patterns. ^{15, 16}

Bragg introduced a simple description of the beams diffracted from crystals.¹⁷ It was suggested that the X-ray radiation incident on the atoms of a surface which are arranged

in parallel planes in the crystal lattice would be reflected where each plane only allows a tiny amount of the radiation to be emitted. The diffracted beams are formed when the reflections of parallel planes of atoms overlap constructively. The detector takes this small amount of emitted radiation and converts it to a signal, as shown in *Figure 2-3.*¹⁸ Bragg derived an equation, which allows the determination of the interatomic spacing between atoms, *d*, in the specimen and the wavelength, λ , of the X-rays, as shown in equation 2-6 below.

$$n\lambda = 2d\sin\theta \tag{2-6}$$

where θ is the angle of reflection at which constructive interference occurs and *n* is the order of diffraction (n = 1, 2, 3, ...) corresponding to occasions when the path difference between the two reflected rays in the diagram is an integral number, *n*, of the wavelength, allowing constructive interference to occur.¹⁹



Figure 2-3: Geometry used for the simplified derivation of the Bragg equation.¹⁹

2.4 Determination of speciation using UV-Vis spectroscopy

UV-Vis spectroscopy has been used to detect the speciation of dissolved minerals in Ethaline following oxidation and reduction. The fundamental aspect of UV-Vis spectroscopy is the absorption of light by the sample that subsequently induces electronic transitions. Each electronic transition has a particular energy level requirement and will thus only absorb at specific wavelengths. The absorption in electronic transition of metal complexes can be attributed to charge transfer bands (CT bands) and *d-d* transitions for

metal complexes, where CT bands are very strong transitions ($\varepsilon_{max} = 10^3 - 10^5$) and are are completely allowed. By contrast, *d*-*d* transitions would be expected to be much weaker than the CT bands as they tend to be formally forbidden by at least one of the two selection rules ($\varepsilon_{max} = 1 - 10^3$ if partially allowed, or $\varepsilon_{max} = 10^{-3} - 1$ if fully forbidden).¹⁴

The data obtained for the dissolution iron based sulfide and arsenide minerals were compared with standard salts of FeCl₂, FeCl₃ and also FeSO₄.7H₂O dissolved in Ethaline, in addition to the cathodic dissolution of elemental sulfur. UV-Vis spectra can provide information about the speciation of iron in solution. The spectra were obtained using a Shimadzu 1601 UV-Vis spectrometer with a UV probe-controlling program. The optical quartz cells used in this study measured 10 mm on each short edge and had a 2 ml capacity. The baseline was obtained by scanning the empty cells in their chambers. The absorbance (Abs.) of iron chloride complexes was obtained by scanning the wavelength (λ) between 750 nm and 200 nm at ambient temperature. The standard iron (II) and (III) chloride salts were first prepared at a 1 x 10⁻³ M concentration in a 50 ml volumetric flask, and subsequently diluted to 5 x 10⁻⁵ M to ensure the data obeyed the Beer-Lambert law, equation (2-7), to give us clear spectra.²⁰ These standards were then compared with anodic and cathodic dissolution of sulfide minerals in Ethaline.

 $A = \mathcal{E} b C \tag{2-7}$

Where *A* is the absorbance, ε molar absorptivity in (L.mole⁻¹.cm⁻¹), *b* is the path length in cm and *C* concentration in mole/L.

2.5 Mineral processing and metal recovery

Hydrometallurgical processes generally solubilise minerals using strong acids and bases, or highly reactive ligands, such as cyanide. The change the speciation of metals producing ionic species which have a higher solvation enthalpy so they can dissolve.² In this thesis the anodic dissolution of iron base sulfide minerals in Ethaline will be studied. In addition the dissolution of metals from a jarosite waste (obtained from the production of zinc) will be investigated.

Inductively coupled plasma (ICP) utilizes the conversion of atoms of the elements in the sample to excited ions which emit characteristic electromagnetic radiation. ICP-MS was used to quantify the concentration of metal ions in solution. The metal ions are then

separated and detected by the mass spectrometer.²¹ The ICP-MS used was a Thermo Scientific iCAP Qc ICP-MS. Samples were calibrated against standard solutions containing known amounts of iron, lead and zinc chloride.

2.5.1 Electrochemical dissolution of sulfide minerals by DESs

Figure 1-5 in the introduction described the two methods used for solubilising materials, either chemical oxidation or electrochemical dissolution. In this thesis, all the five iron-based ores (pyrite, marcasite, pyrrhotite, arsenopyrite and loellingite) were tested to examine their dissolution via electrochemical dissolution, both anodically and cathodically. In Chapter 5 the anodic dissolution of a jarosite waste was investigated.

Bulk dissolution of jarosite: To investigate whether electrolytic dissolution of minerals could be carried out on a larger scale an electrolytic cell was constructed consisting of two glass beakers as shown in *Figure 2-4*. The base of the inner beaker was a course glass frit. The volume of the outer beaker was 2.5L. In the base of the outer beaker, a 500 g sample of jarosite was placed and 750 ml of Ethaline was added to form a thick paste. A large circle of iridium oxide coated titanium mesh was positioned in the middle of the jarosite sample. The edges were roughened so that it would act as a stirred when the beakers were agitated on an orbital shaker. The anode was placed directly under the glass frit of the inner beaker.

When the inner beaker was inserted into the jarosite paste Ethaline percolated through from the lower beaker and the liquid was initially transparent. The copper cathode was positioned inside the cylinder about 1 cm above the frit. Additionally, a Zn sheet was immersed inside the inner beaker for cementation of more electropositive dissolved metal ions.

A constant voltage of 2.25 V was applied over a period of 13 days with a shaking speed 20 rpm at a constant temperature of 50°C achieved by a fixed heater belt on the outer beaker wall. Samples of the solution from both beakers, and also the cathodic and galvanic deposit, were collected and renewed at 2-day intervals for examination by SEM/EDX. The final solution in the anodic compartment (outer beaker) was dark green in colour whereas the cathodic compartment (inner beaker) was a yellow-brown colour.

ICP-MS analysis of both the anodic and cathodic solutions were undertaken to determine the concentration of iron, zinc and lead. Moreover, the solid residue was examined using ICP-MS prior to, and post electrolysis (after washing with a 1:1 solution of ethanol and deionised water).



Figure 2-4: Images of an electrolytic cell of anodic dissolution for jarosite contaminated by traces of lead and zinc in for 13 days at a constant voltage at 2.25 V and temperature of $50^{\circ}C$.

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Chapter 3: Electrochemical dissolution of pyrite in DESs

3.1 Introduction

Processing sulfur containing minerals is one of the biggest sources of acute anthropogenic pollution particularly in the form of acid mine drainage. This study attempts to show an innovative method for processing sulfide-based minerals. The aim of this chapter is to show that DESs such as Ethaline can be used to solubilise minerals and extract metals from their sulfidic ores. A novel method will be demonstrated to investigate the redox properties of minerals using a paste made from the mineral powder in a DES. Initially this will be demonstrated using paint casting method with iron pyrite (FeS₂). The method will also be used to determine whether precious metals, such as gold, can be extracted from pyrite with which it is commonly found. Additionally, this method provides an understanding of the speciation of pyrite as it dissolves in Ethaline. To achieve these aims, a variety of different electrochemical techniques, microscopic and spectroscopic, will be used.

3.2 Pyrite (FeS_2)

Pyrite (FeS₂) is a gold coloured mineral *Figure 3-1A* which is commonly known as fool's gold as it is often mistaken for gold. It was the first mineral structure investigated by Bragg using x-ray diffraction in 1914. Pyrite is one of the most abundant and widespread sulfide minerals in the earth's crust and is frequently found in marine sediments, igneous rocks, sedimentary rocks and coal beds.¹⁻⁴ A fresh pyrite surface exhibits a brassy, bright metallic lustre.⁵

The chemical structure of pyrite is well known as an Fe(II) and disulfide $(S_2^{2^-})$ which resembles NaCl-type crystal structure, where Fe(II) cations occupy the sodium atom position and the dumbbell-shaped $(S-S)^{2^-}$ disulfide anions occupy the chloride atom position.^{2, 6-8} The crystal symmetry of iron atoms Fe (II) in pyrite are positioned at face cantered and corners of the cubic lattice. Where the dumbbell disulfide ions $(S_2^{2^-})$ are positioned at the centre of the cube and at the middle length of the cube edges. Every iron ion is coordinated with six sulfur atoms in a tilted octahedron, whereas every sulfur ion is coordinated with three iron atoms and one other sulfur ion, as illustrated in *Figure 3-1B*.^{9, 10} Although pyrite has a cubic crystal structure, it has comparatively low symmetry with a space group $Pa3.^9$ Pyrite crystals have a wide range of morphologies due to the environmental factors during the formation of pyrite crystals such as temperature, pressure and the fluid chemistry.¹¹ Pyrite exists in different morphologies such as cubic form, usually {100} crystal faces, pyritohedral form {210} faces with pentagonal shaped and octahedral form {111} with triangular faces, as well as {110} faces are found occasionally.^{11, 12} Therefore, natural pyrite can form either in a single morphology or in a variety of crystal morphologies.¹³ Pyrite is likely to show conchoidal fracture rather than {100} fracture.^{8, 13}



Figure 3-1: Occurrence of natural pyrite as a cubic crystal (A), pyrite crystal structure (B).

The crystallographic calculations of interatomic length distance in the pyrite structure between the dumbbell disulfide atoms (d_{S-S}) has been found equal to 2.20 Å and 2.14 Å, whilst the length distance between ferrous and sulfide atoms (d_{Fe-S}) has been found 2.27 Å and 2.27 Å.^{14, 15} The Fe-S bond in pyrite tends to be predominantly covalent due to the marginal difference in electronegativity of Fe and S, where the 3d valence electrons of the Fe atom are shared with 3p valence electrons of S atom.^{16, 17} Pyrite is considered as a semiconductor material which is used as a potential photovoltaic absorber in solar cells as a result of its high optical absorption coefficient ($\alpha > 6.0 \times 10^5$ cm⁻¹ for hv > 1.3 eV) and high electron mobility (230 cm² V⁻¹ S⁻¹).¹⁸⁻²⁰

Pyrite exists in nature as either an N-type semiconductor or a P-type semiconductor depending on the geological condition during the pyrite formation.^{21, 22} The conductivity levels of semiconductor pyrite are governed by four factors: pressure, temperature, existence of trace elements, and S: Fe stoichiometric ratios.¹⁶ For example, pyrites which are formed at relatively low temperatures tend to be P-type semiconductor, while those formed at high temperatures tend to be N-type semiconductors which might be ascribed to sulfur deficiency.^{16, 17} The mean values of conductivity of N-type and P-type of pyrite are in the region of 57 (Ω .cm)⁻¹ and 0.53 (Ω .cm)⁻¹ respectively.¹⁶

The nature of trace elements which are associated with pyrite can also affect the semiconductor properties of pyrite; for instance, some kinds of these trace elements have electron-donating properties (N-type) and some of them have electron-accepting properties (P-type). For example, pyrite which are associated with high arsenic (As) tend to behave P-type semiconductor properties, in addition pyrite which has high cobalt (Co) and nickel (Ni) tends to be N-type.^{16, 22} The stoichiometric ratios of S: Fe in pyrite also have a significant effect on semiconductor properties, if the ratio is less than 2, pyrite exhibits an N-type, if it is more than 2, it is P-type. Indeed some natural pyrites have been found with alternating N and P type domains.^{23, 24}

Wei and Osseo-Asare investigated the anodic and cathodic dissolution of N-type pyrites as microelectrodes in a solution of 1 M HNO₃ and they found that the anodic dissolution rate of pyrite was much faster than the cathodic rate.²⁴ They also observed that the illumination of pyrite microelectrode increased by anodic dissolution, but had no effect on cathodic dissolution so they concluded that anodic dissolution of N-type pyrites could occur through hole-transfer in the valence band.

Abraitis *et al.* used mixed sulfide minerals and observed that materials with higher rest potential are more cathodic and less reactive. They concluded that the preferential dissolution rates of the anodic sulfides would be dependent on the diversity of pyrite's rest potential which was resulting from impurities or semiconductor type.¹⁶

Pyrite is usually used to produce sulfuric acid, but has little economic value.¹³ It is however commonly associated with other important minerals such as sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS₂), and precious metals such as gold and silver.²⁵ The dissolution or oxidation of pyrite is economically crucial in mineral flotation and leaching

to separate pyrite from other valuable metal and/or minerals. Pyrite can be considered electrochemically inert, in comparison with other sulfide minerals as a result of having a relatively high potential roughly 0.66 V in acidic solution versus standard hydrogen electrode (SHE) and under the standard conditions.²⁶

Pyrite can be decomposed using two main metallurgical processes; pyrometallurgy and hydrometallurgy. Firstly, pyrometallurgical treatment of pyrite can produce elemental iron and sulfur by two thermally decomposed steps of concentrated pyrite at 650 -700 °C under nonoxidizing condition to produce unstable sulfur gas and pyrrhotite. Then pyrrhotite is reduced by carbon at 950 °C in the presence of lime to yield Fe, CaS and CO as shown in equations below.²⁷

$$\operatorname{FeS}_2 \to \operatorname{FeS} + 1/2S_{2\,(g)}$$
 (3-1)

$$FeS + CaO + C \rightarrow Fe' + CaS + CO_{(g)}$$
(3-2)

Where the products of the second reaction should be separated, then produce iron and calcium sulfide. Sulfur, lime and SO_2 can be produced by reacting calcium sulfide with calcium sulfate. The heat of this process is provided by oxidation of carbon monoxide gas through the heat exchange. These processes can be carried out in three consequent fluidized beds reactors and the overall chemical reaction of thermal decomposition of pyrite is:

$$FeS_2 + C + \frac{1}{2}O_2 + 3CaSO_4 \rightarrow Fe^{\circ} + 3CaO + 4SO_{2(g)} + \frac{1}{2}S_{2(g)} + CO_{2(g)}$$
(3-3)

It can be concluded that the thermal decomposition of pyrite can produce pyrrhotite and 42% elemental sulfur, in addition to discharging gases such as SO₂ and CO₂.

3.2.1 Oxidation of pyrite

The mechanism of pyrite oxidation in aqueous systems is much more complex due to the variations of leaching condition such as leach solutions, pH, concentration of oxidants, temperature, leaching time, potential applied and the presence of oxygen.²⁵

Generally, the first step in hydrometallurgy is dissolution in a leaching solution which is usually a strong acids and/or alkaline solutions. In addition, oxidizing agents are often added as described in chapter one. ⁹ Oxidation is considered a major part of pyrite

dissolution.²⁸ Accidental flotation of pyrite leads to an increase in the concentration of S and Fe in the metal of interest.^{3, 29} Additionally, pyrite generally contains arsenic which must be removed pre-smelting.¹⁶ Unintentional aqueous oxidation of pyritic minerals has a significant negative impact on environmental discharges.²³ The oxidation of pyrite in aqueous solutions has been extensively reviewed including chemical, electrochemical and bacterial mechanisms.³⁰ It is worth mentioning here that pyrite's bacterial oxidation involves catalysis of an oxidation reaction by *Thiobacillus bacteria*, like *T. ferrooxidans*.

Pyrite oxidation reactions are not considered as equilibria. The chemical oxidation mechanism of pyrite in aqueous solutions can be illustrated by the reactions below ^{31, 32}:

$$\operatorname{FeS}_{2} + \frac{7}{2} \operatorname{O}_{2 (aq)} + \operatorname{H}_{2} \operatorname{O} \rightarrow \operatorname{Fe}^{2+} + 2 \operatorname{SO}_{4}^{2-} + 2 \operatorname{H}^{+}$$
(3-4)

$$Fe^{2+} + \frac{1}{4}O_{2(aq)} + H^+ \rightarrow Fe^{3+} + \frac{1}{2}H_2O$$
 (3-5)

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$$
 (3-6)

Dissolved O_2 and Fe^{3+} in aqueous solutions have a capability to oxidize pyrite. Moses *et al.* examine the rate of chemical oxidation of pyrite at ambient temperature in a variety of solutions saturated with dissolved oxygen and Fe^{3+} in a pH range from 2 to 9, by monitoring the concentration of sulfate or sulfur over the period of oxidation.³³ It was found that Fe^{3+} at low pH has an oxidation rate twice that of dissolved O_2 . The same was true even at higher pH where the solubility is lower. O_2 and Fe^{3+} solution are both required in the dissolution mechanism as Fe^{3+} aids the solubility of pyrite and O_2 is important in maintaining high Fe^{3+} concentrations.

Additionally, aqueous leaching of pyrite by Fe^{3+} and dissolved O₂ have been investigated under other varying conditions such as oxidant concentrations, pH, Eh, grain size, temperatures, and stirring speeds.^{30, 33-39} Researchers found that sulfate (SO₄²⁻) formed as main product and releases non-oxidized ferrous iron into solution. It could also form other species depending on oxidation conditions such as elemental sulfur (S⁰), H₂S gas, Fe(OH)₃, polysulfide, iron oxide, and iron (III) oxyhydroxide, in addition to the formation of intermediates such as SO₃²⁻, S₂O₃²⁻ and S_nO₆²⁻. They also established that 0.5 M of Fe³⁺ with 120 psi of O₂ and not more than 800 rpm stirring speed at 80-100 °C has a significant positive effect on dissolution of pyrite. Reducing the grain size has a more significant influence on dissolution rates than any other single factor. They achieved 90% dissolution of 20g of pyrite in 1L of 0.5 M Fe³⁺ with 120 psig O_2 at 100 °C in 4 h.

McKibben and Barnes also examined the oxidation rate of pyrite chemically by utilizing hydrogen peroxide (H₂O₂) at low pH at 30 $^{\circ}$ C.⁴⁰

$$\operatorname{FeS}_2 + \frac{15}{2} \operatorname{H}_2O_2 \to \operatorname{Fe}^{3+} + 2\operatorname{SO}_4^{2-} + \operatorname{H}^+ + 7 \operatorname{H}_2O$$
 (3-7)

Researchers found that SO_4^{2-} and Fe^{3+} were the only detectable species with no metastable sulfoxy intermediates detected. Moreover, they indicated that the pH range 2-4 had no influence on oxidation rate of pyrite. They showed using SEM analysis that H_2O_2 attacked only the highly energetic parts of the pyrite surface rather than the whole grain surface which represents the "effective or reactive" sites such as grain edges, corners, fractures and cleavages.⁴⁰

The oxidation rates of pyrite in H₂O₂ with different acidic solutions were in the order H₂SO₄ \geq HCl> HClO₄.⁴¹⁻⁴⁴ They showed using XPS that Cl⁻ adsorbed onto the leached surface of pyrite in Fe³⁺ with Cl⁻ oxidants and they suggested that Cl⁻ ions inhibit deposition of elemental sulfur and sulfide ions onto the pyrite surface and prevent the formation of passive layers such as iron hydroxides and/or oxides.⁴⁵ Furthermore, the adsorption of Cl⁻ ions as a strong Lewis base onto pyrite surfaces is able to replace hydrated Fe hydroxy/oxide to form dissolved Fe-chlorides complexes. Therefore, it can be argued that the presence of Cl⁻ ions with oxidant solutions may also remove of S⁰ and/or S²⁻ in addition to hydrated Fe hydroxy and/or oxide from pyrite molecules by adsorption of Cl⁻ ions on pyrite surfaces.⁴⁶⁻⁴⁸ The solubility of pyrite and other sulfide minerals can be enhanced electrochemically to improve the recovery of metals^{25, 49}

The investigations of electrochemical dissolution behaviour of pyrite in aqueous media, in addition to the effect of pH and temperature have been extensively studied.⁴⁹⁻⁵⁵ For instance, the anodic electrochemical oxidation of pyrite in different aqueous acids such as HCl, H₂SO₄, HClO₄ and HNO₃ were studied and found to have similar behaviour.^{56, 57} Moreover, anodic oxidation of pyrite in aqueous media at temperatures up to 175 °C in the absence of oxygen was found to produce mostly Fe²⁺ ions with little Fe³⁺ ions in solution with sulfate and elemental sulfur.⁵⁸ Wei and Osseo-Asare used X-ray diffraction

to show that the oxidation of pyrite produced elemental sulfur.²⁴ The oxidation of pyrite in alkaline solutions hardly takes place due to the insolubility of iron hydroxide, however the researchers found reversible peaks which are attributed to the $Fe(OH)_2/Fe(OH)_3$ couple.

Although the mechanism of pyrite reduction and oxidation in 1 M HCl has been studied by several groups, there is still significant doubt about the mechanism.^{23, 51, 54} Pyrite oxidation consists of three steps: a cathodic reaction, an electron transfer and an anodic reaction. If oxygen is the oxidant then the cathodic reaction is the reduction of oxygen, which is followed by electron transfer to the iron centre followed by a reaction of the sulfur with water and oxygen to make the sulfate anion as shown in *Figure3-2*, the overall reaction being:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2+}$$
 (3-8)

This is confirmed from the iron–sulfur Pourbaix diagram which shows sulfate as the most stable species at more positive over-potentials.⁵⁹ Thus, the major products of oxidation reaction behaviour of pyrite in aqueous solution are sulfate and ferrous ions, whilst the other products are elemental sulfur, polysulfide, hydrogen sulfide, ferric hydroxide, iron oxide and iron(III).²⁵ However cathodic reduction of pyrite in aqueous solution involves reduction of Fe³⁺ to form Fe²⁺ and dissolved oxygen.³⁷ In another study, the reduction of pyrite in aqueous solution was found to produce FeS and S^{2-.60} So, the oxidation of pyrite in both chemically and electrochemically tend to discharge noxious gases such as H₂S from corrosive solutions such as H₂SO₄.

There is however no such literature in ILs or DESs. In order to understand the electrochemical behaviour of sulfide minerals in DESs, the redox behaviour of these metals with their resulting speciation in that solvent should be understood first, as discussed in the section **3.4**.



Figure 3-2: The electrochemical oxidation mechanism of pyrite in aqueous Fe^{3+} and O_2 oxidants suggested by Rimstidt and Vaughan.²³

3.3 Paint casting for electrochemical studies

Studying the electrochemistry of any conducting materials relies on maintaining electrical conductivity with a charge collector and electrolyte in the electrochemical cell.⁶¹ For minerals which have a variety of impurities and different crystal faces which can exhibit anisotropic behaviour voltammetry can be complex and poorly reproducible. The minerals themselves show relatively poor conductivity so a large crystal can induce a resistive artefact in the voltammogram.⁶²

Studying the electrochemistry of natural insoluble sulfide minerals is usually achieved by selecting a high purity of solid crystal mineral as the working electrode. This can be prepared by connecting the back surface of this crystal with a metal wire by using silver epoxy, and then casting the whole assembly with non-conductive resin. In order to obtain an electrode with smooth surface of one crystal face, grinding and polishing should be applied. Some minerals have poor conductivity and anisotropy which affect the electrochemical signals leading to broad distorted peaks in voltammetry. ⁵¹

An alternative method is using carbon paste electroactive electrodes (CPEEs) which have been widely applied in the electrochemical investigation of insoluble organic compound and sulfide minerals due to its easy preparation and large potential window.⁶³⁻⁶⁸ CPEEs are made by mixing graphite with the ground electroactive minerals and an organic binder such as Nujol or silicone oil to make a paste. A metal wire is inserted in this composite.⁶⁹ This electrode permits to study the electrochemistry of sulfide minerals.⁷⁰ However, this type of electrodes have some inherent issues such as limited life time as a consequence of the continuous oxidizing of the sample in the presence of the binder, as well as the viscosity of the binder which can affect the electrode performance.⁶⁹ Although there are some experimental issues with using CPEEs, they still enable the study of mineral electrochemistry.

The mechanical immobilization of solid materials onto carbon electrodes (VMP-Voltammetry of Microparticles) was developed to solve the problems with CFEEs. The preparation of this electrode depends on mechanical stabilizing of solid minerals onto graphite or metal electrodes without a binder by impregnating it with paraffin and then pasting it onto an electrode surface. Although this electrode permits direct electrochemical examination of solid minerals it has an obvious limitation in preparation. For example, paraffin may cover a part of particles rather than the whole grain and in terms of quantitative analysis it is not possible to measure the exposure of the active area.⁷¹

Carbon paraffin electrodes (CPfEs) are constructed by combining CPEs and VMP electrodes. CPfEs can be formulated by mixing approximately 1g of graphite with a suitable weight of paraffin wax and then heating the mixture to the 70 °C. The molten graphite/ paraffin mixture is poured into the mould where the desired quantity of solid minerals are placed and then a metal wire immersed into this mixture. Finally, the solidified composite is covered with Teflon tape to prevent the lateral part of the electrode coming into contact with the electrolyte.⁷¹ The mechanical stabilization of mineral particles and cooling of graphite/paraffin mixture onto sample particles can support the particles immobilization. Thus, CPfEs can be easily modified and also have a good electrical conductivity and the active area can be determined. However, the voltammetry of the microparticles depends on the morphology, purity and texture of the mineral grains.

Several other types of carbon electrodes have been used to study the electrochemistry of insoluble material such as glassy carbon and carbon fibre electrodes.^{39, 66} In spite of its

usefulness and the high electrical window, most of these electrodes require pre-treatments to prepare, such as heating and physical polishing.

This chapter presents a novel and simple method which has been used to study the electrochemistry of sulfide minerals in a deep eutectic solvents (DES). To circumvent the resistive issues this novel method was devised to determine the electrochemical properties of pyrite. In addition to reducing particles size, in this method the high viscosity and conductivity of DESs play a significant role to bind the microparticles of minerals onto the electrode surface, and also minimizes the resistivity. A sample of pyrite was ground in a pestle and mortar and the fine powder was mixed with Ethaline to make a thick paste. This paste was then painted onto a Pt flag as a working electrode which has been bent flat to a 90° to lay the mineral paste over electrode surface, as illustrated in *Figure 3-3*.

This technique has recently been demonstrated to be effective for the dissolution and electrochemical recovery of galena (PbS) and the signal was shown to be relatively independent of the mineral loading, and has been named paint casting.⁶¹ The use of a paste method to dissolve and recover elements from ores ensures the minimum volume of solvent (lixiviant). The solute is processed from saturated solutions ensuring small distances over which mass transport occurs.



Figure 3- 3: (A) shows the paste of pyrite and 2 drops of Ethaline, while (B) and (C) shows the paste painted onto the surface of Pt flag (middle) working electrode

Cyclic voltammogram of a polished single pyrite crystal is shown in *Figure 3-4A* and this can be compared with that of paint cast pyrite in (B). The cyclic voltammogram of

paint cast pyrite has a two clear oxidation peaks and three reduction peaks, while the single crystal has a broad oxidation peak and a broad reduction peak with several possible overlapping signals. Paint casting also produces a larger Faradic current than the single crystal.

Figure 3-4C shows that paint casting technique can measure the electrochemistry of sulfur paste which has a high electrical resistivity. This will be described in more depth in the **section 3.4.1**. Additionally, the cyclic voltammogram of pyrite obtained using a pyrite CPfE electrode in acetic acid/acetate buffer, at pH = 4.5 and 20 mV.s⁻¹ and 25 °C, shows one oxidation peak and two reduction peaks with a smaller current than that using the paint casting technique.⁵⁰



Figure 3- 4: Cyclic voltammogram of single pyrite crystal casting by non-conductive risen (A), cyclic voltammogram of pyrite paste painted on Pt flag (B), cyclic voltammogram of elemental sulfur paste on Pt flag (C), cyclic voltammogram of 0.05 M FeCl₂ in Ethaline on Pt disc (D), all these above voltammograms are conducted in Ethaline using Ag wire as reference electrode and 50 mV.s⁻¹ scan rate.

In conclusion, the application of paint casting technique in electrochemistry of semiconducting minerals has shown improved resolution of electrochemical signals and less resistivity compared to other methods. It is also easier to prepare than comparable modified electrodes.

3.4 Electrochemical analysis of pyrite (FeS₂) in Ethaline

ILs and DESs have the ability to control the speciation of soluble metal salts due to the feature of the high concentration of coordinating anions, in addition to wide potential window. The stability of potential window of type (III) DESs depends upon the pKa of hydrogen bond donor (HBD).⁷² Although the electrochemical potential window of type (III) DESs are narrower than some imidazolium ILs with discrete anions, the window is quite sufficient to deposit metals with high current efficiencies such as zinc and nickel.⁷² Cyclic voltammetry will be applied to identify the potential window of Ethaline and the redox couples of soluble metals sulfide.

In this study, Ethaline was chosen as it has a lower viscosity and a higher conductivity than most other DESs. Ethaline has also a good stability in air and moisture; in addition, it is transparent which allows any colour change to be observed. So, for these reasons it can be used under ambient laboratory conditions. The electrochemical potential window of ILs and DESs is usually more than 2.0 V and depending on the resistance of cation to reduction and anion to oxidation. However, this potential window might be regulated by the reaction of any presence impurities with ILs. For example, presence of water can decrease the potential windows.⁷³

Figure 3-5 illustrates the potential window of Ethaline, where it found between (+1.3 V and -1.3 V) on both types of working electrode 1 mm Pt disk and 1 cm² Pt flag versus Ag/AgCl reference electrode at room temperature. This means that the potential window of Ethaline is around 2.6 volts. ⁷³ This is in agreement with other studies on the stability of this DES. ⁷⁴



Figure 3- 5: Cyclic voltammogram of pure Ethaline at a 1mm Pt disk working electrode using Ag/AgCl reference electrode and at scan rate 10 mV.s⁻¹in 20 °C.

3.4.1 Cyclic Voltammetry of pyrite

The electrochemical behaviour of pyrite was measured using cyclic voltammetry for an individual pyrite crystal. *Figure 3-4A* shows the voltammogram for a single grain of pyrite as a working electrode in Ethaline as the electrolyte at a sweep rate of 50 mV s⁻¹. It can be seen that a broad oxidation wave occurs with two maxima at ca. +0.20 V and +0.31 V. A broad reduction peak is also obtained with a maximum at ca. -0.53 V. The signals will clearly be made up of contributions from the Fe^{II/III} couple and the complex redox chemistry of the S₂²⁻ anion.⁷⁵⁻⁷⁷

Figure 3-4B shows the cyclic voltammogram of the FeS₂ coated Pt flag electrode in Ethaline. It can clearly be seen that the cyclic sweep voltammetry of ground pyrite has five separate peaks. The cyclic sweep was started from 0 V and swept in an anodic direction to 1.0 V. The potential was then swept to -1.0 V then back to 0 V at a scan rate of 50 mV s-1. Two peaks can be observed on the anodic scan. These are inferred to be due to the S₂^{2-/S₈⁰ at ca. 0.45 V and the Fe^{II}/Fe^{III} at ca. 0.7 V. On the cathodic scan three peaks can be observed. The first reduction peak at ca. 0.51 V is most probably the reduction of Fe^{III} to Fe^{II} whilst the second and third reduction peaks may be related to the reduction of sulfur species.}

To prove the origin of each of the peaks observed with pyrite the electrochemistry of sulfur paste, painted onto a Pt electrode, was studied in Ethaline and the results are shown in *Figure 3-4C*. The cyclic voltammogram has one anodic peak O₁ (ca. 0.0 V) and two cathodic peaks marked R₁ and R₂ (at about -0.39 V and -0.52 V) respectively. It should, however, be noted that there is a pronounced shoulder in the anodic sweep between -0.5 and -0.3 V which is probably the reverse process for R₂. The cyclic voltammogram of sulfur has also been reported by Manan *et al.* who used a Pt electrode to study sulfur electrochemistry but using an ionic liquid, 1-butyl-3- methyl-imidazolium dicyanamide as the electrolyte.⁷⁸ They assigned the two cathodic processes to

$$R_1: 3S_8 + 8e^- \to 4S_6^{2-} \tag{3-9}$$

$$R_2: 2S_6^{2-} + 2e^- \to 3S_4^{2-} \tag{3-10}$$

According to the above literature, elemental sulfur (S₈) can be reduced in two 2-electron steps. The first reduction peak of sulfur is attributed to the formation of S_6^{2-} from reduction of elemental S₈, while the second reduction peak has been attributed to the reduction of S_6^{2-} to form $S_4^{2-.78}$ A direct comparison of the redox potentials is difficult due to the differences in the liquid junction potential and the reference electrode.⁷⁹ However the shapes and relative differences between O₁, R₁ and R₂ are very similar to those reported by Manan confirming the validity of the assumption.

Figure 3-4D shows the cyclic voltammogram for FeCl₂ dissolved in Ethaline. The classical one electron oxidation and reduction is what would be expected for a reversible redox couple. The speciation of FeCl₂ and FeCl₃ in Ethaline has been studied previously by using EXAFS, where it was found to form $[FeCl_4]^2$ and $[FeCl_4]^-$ respectively.⁸⁰ Comparing *Figure 3-4D* with *Figure 3-4B* it is logical to infer the peak assignments for iron based species shown in *Figure 3-4B*. The redox processes for sulfur shown in *Figure 3-4C* are not as well defined as those shown in *Figure 3-4B* but this is to be expected given the poor conductivity of elemental sulfur and the difference can clearly be ascribed to a resistive artefact.

The issue with using a silver wire pseudo reference electrode was that if Fe^{3+} is produced by anodic dissolution then this could oxidise the silver wire and Ag^+ ions could complicate the redox response.⁸¹ The silver wire reference electrode was replaced by the more stable [Ag| AgCl (Ethaline)] reference electrode, where the silver wire was immersed in 0.1 M AgCl dissolved in Ethaline. This was isolated from the analytic solution by a Vycor glass frit. In all further voltammetric experiments in this thesis the [Ag| AgCl (Ethaline)] reference electrode has been used.

Figure 3-6 shows the redox properties for pyrite and FeCl₂ vs the [Ag| AgCl (Ethaline)] reference electrode. Comparing these data with those presented *Figure 3-4* it can be seen that the potential is shifted by about 200 mV by changing the reference electrode. This is in keeping with the results by Hartley who found that the redox potential for the $Ag^{+/0}$ couple behaved in a Nernstian manner i.e. the redox potential shifted approximately 59 mV for each order of magnitude change in the concentration. The difference in redox potential corresponds to a roughly 4 orders of magnitude difference in the Ag^+ concentration which is approximately what would be expected.



Figure 3- 6: Cyclic voltammogram of pyrite paste onto Pt flag in Ethaline (A), Cyclic voltammogram of 0.1M FeCl₂ on Pt electrode in Ethaline (B), the above cyclic voltammograms have done at 20 °C and 10 mV s⁻¹ versus Ag/AgCl reference electrode.

To determine whether the electrochemical signal was proportional to the amount of pyrite in the paste voltammetry was run as a function of pyrite loading on to Pt flag in Ethaline and the results are shown in *Figure 3-7A*. It can be seen that the current is roughly proportional to the mass of pyrite.^{82, 83} This shows that paint casting could be used in electrochemical analysis of minerals to provide a quantitative assay for mineral content.



Figure 3-7: (A) Loading different weight of pyrite paste onto Pt flag at 10 mV.s⁻¹ vs Ag/AgCl and Pt flag counter electrode, (B) loading mass of pyrite paste versus positive charge.

3.4.2 Electrochemical Quartz Crystal Microbalance (EQCM) of pyrite

The above assignments for the redox processes seem logical and it appears that iron goes into solution as an Fe^{II} complex. This would mean that the redox properties of S_2^{2-} could control the dissolution of pyrite. To confirm this assignment EQCM can be used to determine the molecular mass of dissolved pyrite species in Ethaline during the electrochemical redox reaction. EQCM can be used to measure small changes in mass with the charge that flows through the cell. This is monitored using changes in the oscillating frequency of the quartz crystal, as described in equations (3-11) and (3-12) below.⁸⁴

Sauerbrey equation:
$$\Delta f = -\frac{2f_o^2}{A \cdot P_o V_o} \Delta m$$
 (3-11)

Where Δf is the frequency change in Hz, f is the resonant frequency in Hz, Δm is the mass change in ng or μ g, A is the piezoelectrically active surface area in cm², P_o is the density of quartz in g.cm⁻³, V_o is the shear wave viscosity in the quartz crystal.⁸⁴ The negative sign refers to the inversely proportional between the changes in mass versus frequency. The constant factors between Δf and Δm in Sauerbary equation can be simplified to the value of 1.02, in case of using 10 MHz AT-cut quartz crystal. According to Sauerbary equation the change in crystal frequency versus mass results a linear correlation and Faraday's law can be applied.

$$mass(m) = \frac{Molcualar weight(M)}{number of electrons(z). Farady constant(F)} x Q$$
(3-12)

Where Q is the charge transferred in Coulombs C.

Pyrite crystals were painted onto the gold electrode on the quartz crystal resonator and the electrode was cycled from -0.8 V to +0.8 V vs Ag/AgCl at 10 mV.s⁻¹ scan rate for two scans in Ethaline, as shown in *Figure 3-8A*.



Figure 3- 8: Cyclic voltammogram of ~5µm³ size of pyrite particles in Ethaline pasted onto Au-QCM cell as WE versus Ag/AgCl RE and Pt flag CE in 10mV.s⁻¹(A), mass versus time of two scan for pyrite (B), mass versus potential of pyrite particles in Ethaline (C), and mass versus charge of pyrite cyclic voltammogram in Ethaline (D).

Figure 3-8B, shows the corresponding change in mass of pyrite as a function of time. Two cycles are shown to demonstrate the reproducibility of the process. On the first onset of pyrite oxidation marked (A black) a decrease in mass is observed due to pyrite dissolution. As the potential increases, the mass decreases up to the peak current marked (B) where upon the mass increases either because the solution close to the electrode surface has reached supersaturation and some material is deposited on the electrode surface or a side process occurs e.g. sulfide is oxidised to sulfur. Exactly the same response is observed on the second cycle.

A plot of charge passed *vs*. mass change can be seen in *Figure 3-8D*. It can be seen that on the anodic scan there is a mass loss associated with the peak marked Fe^{II/III}. By measuring the change in mass with charge the species dissolving can be estimated. If the process is 100% current efficient then the slope should equal the molar mass divided by the number of electrons times the Faraday constant (Faraday's Law).

If the soluble species is Fe^{III} originating from a 1 electron oxidation, then the slope should be 5.8×10^{-4} g C⁻¹. The data from *Figure 3-9* show the slope of is 6.3×10^{-4} g C⁻¹, which is close to the theoretical value. It should however be noted that there are other alternative loss processes such as the loss of FeS²⁺ which would correspond to a slope of 4.6×10^{-4} g C⁻¹ or FeS₂²⁺ which would be 6.3×10^{-4} g C⁻¹; exactly the same as that observed. It is important therefore to get an idea of speciation from UV-Vis spectroscopy.



Figure 3- 9: Mass vs charge of $\sim 5\mu m^3$ pyrite particles in Ethaline (A), the slope of mass versus charge of pyrite particles in Ethaline for first scan (B).

3.5 Bulk electrolysis of pyrite

As was shown in *Figure 1-5*, material can be solubilized by electrochemical dissolution (anodic or cathodic) or chemical dissolution. In this section, the anodic and cathodic dissolution of pyrite have been carried out from a paste electrode. The pyrite paste in Ethaline was painted onto an iridium coated titanium electrode as the anode which has been found to be anodically stable in DESs. The cathode was also the same material.⁸⁵ These electrodes were immersed in a 50 ml beaker of Ethaline at 50 °C.

Bulk electrolysis was carried out on the pyrite paste electrode to investigate the solubility of the oxidised and reduced products in Ethaline. *Figure3-4B* shows that pyrite has both oxidative and reductive signals. Bulk electrolysis was carried out in a two-electrode set up, applying 2 V between the electrodes for 24 hours; the first experiment held the mineral paste at a cathodic potential and the second held it at an anodic potential. At the end of this period the Ethaline solution had turned yellow/brown where the electrode had been held at a positive potential *Figure 3-10*. This suggests that the iron dissolved as Fe³⁺ and this ties in with the EQCM result, which shows the same.⁸⁶ When the solution was left to stand exposed to air, a brown precipitate formed after about 3 days which is likely to be an oxide or hydrated oxide of iron formed from the reaction with absorbed atmospheric moisture.



Figure 3- 10: Photograph showing a sample of Ethaline before electrolysis (centre) after both reduction of pyrite (left) and oxidation of pyrite (right) at a constant potential of 2 V. Both samples had been allowed to stand for a total of 3 days after electrolysis.

The solution obtained when the sample was held at a negative potential turned a grey/blue colour as shown in *Figure 3-10*. It was thought that FeS could be formed upon reduction and while FeS is soluble in Ethaline, giving a solution of the same colour, the speciation in solution is unknown. The speciation of the dissolved pyrite following bulk electrolysis in Ethaline was studied using UV-Vis spectroscopy.

3.6 UV-Vis spectra of dissolved pyrite

UV-Vis spectroscopy is a common technique for determining speciation both quantitatively and qualitatively. It can also detected the amounts of different complexes present in solution. Usually, the speciation of metals salt in ILs and DESs is governed by either the counter ion of the dissolved metal salt and/or the anion component of the ionic liquid.^{87, 88} The UV-Vis spectra of the solutions obtained from bulk anodic and cathodic dissolution were compared with solutions of potential solution species namely FeCl₂, FeCl₃ and FeS.

In this study, UV-Vis spectroscopy was used to investigate the speciation of the soluble species formed upon oxidative and reductive dissolutions in Ethaline. The spectrum obtained from the oxidative dissolution of pyrite in Ethaline was compared with the spectra of FeCl₂ and FeCl₃ standard solutions in Ethaline, and can be seen in *Figure 3-11A*. It has previously been shown by using EXAFS that most transition metal halide salts dissolved in Ethaline exist as a tetrachlorometallate anion.⁸⁹ It was found that FeCl₂ dissolves to form FeCl₄²⁻ however the EXAFS spectrum of FeCl₃ in Ethaline shows evidence of some oxygen ligands probably originating from ethylene glycol.

Figure 3-11A however suggests that the solution obtained from the oxidation of pyrite does not correlate well with that for the dissolution of FeCl₃ suggesting that the soluble species is not a simple tetrachloroferrate. There is better correlation with the absorbance spectrum of FeCl₂ which would tie in somewhat with the EQCM data above, but the lack of a good fit suggests that a different ligand is also attached to the iron, most probably sulfur or oxygen. This also supports the hypothesis that the dissolution of iron is accompanied by sulfur. To confirm the solution speciation EXAFS was carried out (see chapter 4).

The same process was carried out for the reductive dissolution of pyrite and the results are shown in *Figure 3-11B*. While FeS_2 is insoluble in Ethaline, FeS shows limited solubility. The peak maximum of FeS occurs at about 270 nm. Solutions obtained from both the anodic and cathodic dissolution of pyrite have absorbance maxima at about this wavelength.



Figure 3-11: Comparison of UV-Vis spectra of the FeCl3 and the FeCl2 in Ethaline and with solution obtained from (A) the anodic dissolution and (B) the cathodic dissolution of pyrite ore in Ethaline at 20 °C.

The key question to answer is whether the sulfur and iron remain bound together in solution on dissolution. To understand this better the speciation arising from the electrochemical dissolution of the individual components (Fe and S) was carried out and the solution species compared with those from pyrite dissolution.

Firstly the cathodic electrolysis of 4 g elemental sulfur pasted onto iridium coated titanium as cathode was carried out in 50 ml Ethaline at 2 V. It is thought that a variety of sulfur containing ions of the form S_x^{2-} (where x = 1, 2, 4, 6, 8) was obtained from this experiment.⁵⁹ It has observed that the Ethaline turned golden/ brown in colour but on standing for 24 h a brown colloidal dispersion formed which was probably from elemental sulfur formed by reoxidation of the polyanion as shown in *Figure 3-12*.



Figure 3-12: Cathodic dissolution of sulfur in Ethaline at 2 V for 24 hours

The comparison of normalized absorption spectra of cathodic dissolution of elemental sulfur in Ethaline with anodic and cathodic dissolution of pyrite shows that both anodic and cathodic electrolysis of pyrite have a peak at 270 nm which is the same as that produced from the cathodic dissolution of sulfur as shown *Figure 3-13*. This is however the wavelength at which iron species also absorb making the definitive assignment of solution species difficult.



Figure 3-13: Normalized UV-Vis absorption spectra of anodic and cathodic dissolution of pyrite in Ethaline at the maximum absorbance of cathodic electrolysis of elemental sulfur in Ethaline.

Anodic dissolution of a pure iron metal electrode was carried out in 10 ml Ethaline at 3 V for 6 hours. *Figure 3-14A* shows the UV-Vis spectra of anodic dissolution of pure Fe metal electrode at 3V and the absorption band appeared at 224 nm; which is similar to the

band obtained from the anodic dissolution of pyrite. It has been shown previously by using EXAFS that Fe^{3+} ions are oxophilic metal ion and can be linked with oxygen atom.^{85, 89} It could be suggested that Fe^{3+} combined with oxygen by adsorbed moisture (H₂O) in Ethaline or glycolate molecules.

Figure 3-14B shows the UV-Vis spectrum of anhydrous $FeCl_3$ dissolved in ethylene glycol and it can be seen that there are two bands at 224 nm and 346 nm. Where these bands could be attributed to the Fe^{3+} oxygen from glycolate or water in ethylene glycol and/or Fe^{2+} iron chloride.



Figure 3- 14: (A) UV-Vis spectra of anodic dissolution of Fe pure metal electrode and chemically dissolved iron dust, and (B) dissolution of FeCl₃ in ethylene glycol

From all the above UV-Vis spectra, oxidised pyrite has two bands at 224 nm and 270 nm which can be correlated to the Fe^{III} that is more likely linked with an oxygen atom for the first band and/or a sulfur species or Fe^{II} linked with sulfur. However, reduced pyrite has two clear bands at 270 nm and 365 nm and two associated shoulders. Where the first band can be attributed to the other reduced sulfur species or iron-sulfur species, while the second can be possibly related to a charge transfer to $[FeCl_4]^{2-.90}$

3.7 Electrochemical deposition of pyrite species

Bulk electrolysis was carried out in the cell as reported previously.⁶² The anodic material was iridium coated titanium which has been found to be anodically stable in the DES and the cathodic material was a copper sheet. After electrolysis of the mineral paste on the anodically polarised electrode for 16 h it was found that pyrite has a black deposit was

obtained on the copper cathode and the morphology (SEM) and composition (EDX) of the deposit is shown in *Figure 3-15*.

The deposit contained iron with amounts of sulfur, oxygen and carbon. The samples are non-magnetic showing that it was not elemental iron which was deposited. The electropolishing of stainless steel has previously been studied in the same DES and it was found that when the iron was oxidised through anodic polarisation a brown solid was formed in solution, similar to that shown in *Figure 3-10*. This was found to be an iron glycolate species and it is proposed that the deposit shown in *Figure 3-15* is likely to contain glycolate as a ligand.⁹¹

If the carbon and oxygen only came from the glycolate ligand, it would be expected that the C: O ratio would be 1. In this case the C: O ratio is <1 meaning that some iron oxide must also be present. The deposit obtained from loellingite (FeAs₂) (in chapter 4) contains a high As: Fe ratio, whereas the S: Fe ratio for the deposit obtained from pyrite is much lower. This shows that when the mineral dissolves under anodic polarisation the metal enters the solution with the sulfur or arsenic still attached but some exchange clearly occurs in solution. This confirms the idea that the EQCM result shown in *Figure 3-9* corresponds to the pyrite possibly forming $[FeS_2]^{2+}$ when it dissolves in the DES.





Figure 3-15: SEM images and elemental compositions (EDX) of the cathode deposit obtained after the electrolysis of pyrite in Ethaline at a current density of 5mA.cm⁻²

3.8 In-situ chronocoulometry and 3D microscopy of pyrite

Jenkin *et.al* recently investigated the leaching rate of pyrite, galena, chalcopyrite, and electrum (gold and silver) as well as tellurobismuthite (Bi₂Te₃) at 45–50 °C in an oxidative catalytic reagent of I₂ dissolved in a DES (Ethaline) by a novel technique employing an optical profiler.⁹² It was found that pyrite was not oxidised by I₂ in Ethaline whereas all other sulfide minerals could be dissolved albeit at different dissolution rates. Electrum was found to be etched the fastest and chalcopyrite was the slowest. Therefore, it can be suggested that pyrite and any other sulfide minerals could be liberated by electrolysis first and then dissolved by subsequent oxidation.

Chronocoulometry is an electrochemical technique used to measure charge as a function of time. The current or charge are usually fitted to one of the forms of the Cottrell equation listed below:⁹³

Cottrell equation:
$$i = \frac{nFAC_{\circ}D^{1/2}}{\pi^{1/2}}t^{-1/2}$$
 (3-13)

Integrated Cottrell equation:
$$Q = \frac{2nFAC_oD^{1/2}}{\pi^{1/2}}t^{1/2}$$
 (3-14)

For the both equations above, where *i* is the current in Amps and *Q* is the total charge consumed in C, *n* is the number of electrons transferred, *F* is Faraday constant (96485 C/mole), *A* is the area of electrode surface in cm^2 , *D* is the diffusion coefficients of the species in cm^2/s , *t* is the time in s and *C*_o is the concentration of the species in mol cm⁻³. This can only strictly be applied to processes where the reagent and product diffuse to and from the electrode surface. It is therefore not strictly applicable to dissolution or deposition processes.

The 3D optical profilometry captures a reflected light image of the sample surface before and after electrochemical dissolution both are focused on the same surface area. This optical profiler measures the precise micron-scale of XY and Z dimensions and that can be provide an accurate 3D colour images of a surface. Images are created by defining image profiles that are in focus at different heights. These are then analysed to produce a reconstructed 3D topography of the surface. The average etch depth of pyrite was measured by constructing a cross line over a sample area and a flat surface of an insoluble phase as a reference height such as the black resin or non-conductive grain particle.

An in-situ method has been utilized to monitor the electrochemical dissolution of pyrite. A sample was made with several randomly oriented crystals of pyrite connected to a copper sheet electrode and the whole material was encased in a non-conducting resin before being polished back to expose the randomly oriented pyrite crystals. The electrically connected pyrite crystals were held at a constant potential of +1.2 V vs. Ag/Ag⁺ for 4 hours and the sample was then analysed using optical profilometry to measure the different effects and etch rates on different crystal orientations of pyrite during anodic dissolution in Ethaline.

Figure 3-16 shows an image of a sample of these crystals before and after they were electrochemically polarised. The dark area between the crystals is an electrically insulating resin. It can be seen that there is a certain degree of anisotropy with regard to the dissolution rates. Crystal B is largely undissolved whereas A, C and D are dissolved to different extents. Crystal A has dissolved to a depth of approximately 50 μ m, whereas C and D have dissolved by approximately 10–20 μ m, as shown in *Figure 3-17A*. One explanation for this could be that the orientation of the exposed crystal faces caused dissolution at different rates. For example, there is a degree of anisotropy to the dissolution rate.

Figure 3-17B shows cross sectional profile of the sample shown in *Figure 3-16* together with the charge versus time plots (the total charge was 0.82 C). This charge is mostly due to the loss of pyrite.

The total charge (Q) in the equation (3-14) above is directly proportional to the square root of time for reversible system. However, in this study the charge obtained can be associated with liberated mass followed by Faraday first law of electrolysis. This can be achieved by measuring the etch depth or volume of pyrite removed against a material which does not chemically dissolve. This was attempted using two polished crystals of pyrite which were mounted in the same resin; one of which could be electrochemically polarised while the other was electrically isolated, shown in *Figure 3-18*.



Figure 3- 16: 3D colour optical microscopy images of pyrite grains before and after anodic polarization at +1.2 V in Ethaline for 4 hours at room temperature.



Figure 3- 17: (A) Cross-sectional profile across the line. (B) Chronocoulometry of pyrite sample in Ethaline at +1.2 V for 4 hours at room temperature.

Figure 3-18 shows a series of 3D coloured images of electrochemical dissolution of a pyrite. It can be seen that as the time and voltage are increased the pitting of the electrochemically polarised sample increases compared to that of the isolated sample. What is unusual, however, is that isolated sample also pits slowly with time. This must results from the evolution of Fe^{III} during the etching of the polarised sample which can then chemically oxidise the isolated pyrite sample.

The conductive pyrite surface has an exposed area of 0.011 cm^2 to the electrolysis in Ethaline at different anodic potential +2 V and +5 V, one hour for each scan. The etch

depth of dissolution images (2-5) in *Figure 3-18* have been normalised by comparing them to the height of the unpolarised sample. The etch depth is plotted in *Figure 3-19*. The total charge of 16.16 C equates to a mass loss of 0.01 g of pyrite assuming that the process is 100% current efficient and it is a 2-electron transfer process. Given that pyrite has a density of 5 g cm⁻³ and the molecular weight of 119.98 g. mol⁻¹ this equates to a volume loss of approximately 0.002 cm³ over an area of 0.011 cm² or an etch depth of 0.18 cm. Given that the maximum etch depth was about 45 µm it can be concluded that the etching process shows a very poor current efficiency.





Figure 3- 18: 3D optical microscopy images of 2 pyrite grains (left polarised, right isolated) (1) before (2) after 1 h, 2V (3) 2 h 2 V (4) 3 h 5 V and (5) 4 h 5 V.



Figure 3- 19: Normalized Cross-sectional profile across the line for (A) changing voltage at applied (2 and 5) V each one for 2 hours, and (B) maximum etch depth versus time of the 3D colour images in Figure 3-18.

The maximum dissolution rates of pyrite are derived from *Figure 3-19B*, by measuring the slope of the best straight line for each applied voltage +2 V and +5 V. The values of these dissolution rates were 0.041 μ m/min and 0.173 μ m/min respectively, while the average dissolution rate was found to be equal 0.107 μ m/min.



Figure 3- 20: Charge versus time of conductive pyrite grain dissolved at different applied voltage +2 V and +5 V for two hours for each dissolution, and (B) etch depth versus charge of conductive pyrite grain.

No.	Step/	step difference/ $\mu m =$	Correction	Total
Image.	μm	{(reference step) - (dissolved step)}	etch depth/µm	Consumed
				Charge/C
1 ^{ref.}	13.35	0	0	0
2	11.48	1.87	1.87	1.52
3	10.25	3.10	4.97	3.84
4	2.77	10.58	15.55	8.54
5	8.14	5.22	20.77	7.62
summation		20.77		16.16

Table (3-1): Calibration of the 3D profiler step data for dissolution of conductive pyrite grain of applied constant voltage at +2 V and +5 V for four hours.

3.9 Anisotropy of pyrite crystal

To test whether anisotropic etching occurs with pyrite an array of randomly oriented pyrite crystals (>20) were attached to a copper plate using a conducting adhesive and then set in an insulating resin (Buehler epoxy cure 2 resin with its epoxy hardener in a 4 : 1 volume ratio). The sample was then polished using a diamond abrasive to ensure a flat surface, as seen in *Figure 3-21* below. This was then analysed using XRD and the results are shown in *Figure 3-22A*.



Figure 3-21: Pyrite crystals were attached in a randomly orientation on a copper plate

As would be expected from a randomly oriented natural mineral a variety of crystal faces are observed. The sample was put into Ethaline and held at +1.2 V vs. Ag/Ag+ for 4 hours. Following that period the sample was removed, washed with water and dried. The sample was re-analysed using XRD and the results are also shown in *Figure 3-22A*. The

data were normalised to the [200] signal and it can be seen that following dissolution the relative ratios of the peaks have changed. The signals for the diagonal crystal planes for example, [311], [321], [111] and [222] are significantly decreased. This would be expected since these faces would have the largest proportion of energetically unfavourable atoms. It is proposed that these diagonal crystal faces are preferentially etched below the analysis surface as shown in *Figure 3-16* before and after etching such that the XRD signal is much lower for them, leaving predominantly the [200] face. It can clearly be seen from *Figure 3-22A* that anisotropic electrochemical etching of pyrite does occur in Ethaline. This observation helps to explain the differences between the electrochemical response for pyrite shown in *Figure 3-4A and B* as the former has only one crystal plane exposed to the electrolyte whereas the latter has a variety. *Figure 3-22B* shows the effect of cathodic polarisation of pyrite at -1.2 V for 4 h in Ethaline for the same sample of pyrite crystals were used in Figure 3-22A (after repolishing). The XRD data of the cathodic dissolution of pyrite showed that the [111], [210], [211], [220] and [311] crystal planes are slightly reduced but not like that under anodic dissolution. It is clear that the rate of cathodic dissolution is far slower than anodic dissolution. The crystal planes identified in both figures were carried out according to the literature.⁹⁴⁻⁹⁶



Figure 3- 22: Normalized XRD spectra of pyrite crystal before and after anodic etching in Ethaline at +1.2V for 4 hours (A), normalized XRD spectra of pyrite crystal before and after cathodic etching in Ethaline at -1.2V for 4 hours (B).

During the experiment involving the cathodic polarization of pyrite at -1.2V for 4 hours a yellow precipitate deposited on the anode in the cell as shown in *Figure 3-23*. Cyclic voltammetry of the yellow precipitate in Ethaline showed a response similar to that for

elemental sulfur. This suggests that the reduction of pyrite releases a sulfide into the solution which oxidises to form sulfur.



Figure 3- 23: Yellow precipitate deposited on to anode in the reduction polarizable of pyrite at -1.2V for 4 hours (on the left), cyclic voltammograms for the yellow precipitation in Ethaline (on the right).

3.10 Conclusion

In the present study, it has been shown that pyrite (FeS₂) can be electrochemically dissolved in a DES, Ethaline at ambient temperature. It was shown that mineral electrochemistry can be studied by painting a paste of the mineral in a DES onto an electrode and this is a generic method by which the electrochemistry of powdered materials can be studied. The cyclic voltammogram of natural pyrite in Ethaline was observed to have two anodic peaks and three cathodic peaks. The two anodic peaks could be probably attributed to the formation of elemental sulfur and Fe (III), whereas the three cathodic peaks are related to the reduction of Fe(III) to Fe(II) with the remaining peaks attributed to the reduction of sulfur to form a polymeric anion. A method for achieving bulk mineral dissolution and elemental recovery using electrolysis has been demonstrated. Anodic polarisation of pyrite led to bulk dissolution although this was highly anisotropic, with some sections showing dissolution rates of $6.42 \,\mu m \,h^{-1}$. The use of pastes for mineral processing decreases the lixiviant volume and ensures minimal volume of DES usage.

The UV-Vis spectra of pyrite bulk dissolution in Ethaline observed that the species have a central iron atom coordinated of with oxygen and maybe sulfur as well. The electrochemical dissolution of pyrite at higher over-potentials produces some Fe(III) species which appears to chemically dissolve pyrite by a different mechanism. Although pyrite can be solubilised both anodically and cathodically the rate of anodic dissolution is far faster than that of cathodic dissolution.

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Chapter 4: Redox behaviour of other iron based ores

4.1 Introduction

In **Chapter three**, the method of paint casting was developed was utilized to study the solubilisation of pyrite using electrochemical techniques in Ethaline to extract metal from natural sulfidic ores. The cyclic voltammogram of pyrite in Ethaline showed good electrochemical resolution due to the pyrite crystal being ground into very fine particles and distributed onto a large surface area working electrode. In this method, the resistivity of large particles is reduced and a large number of pyrite crystals can be exposed to the electrolyte in different crystal faces. The objective of this chapter is to study the electrochemical behaviour of four related iron-based minerals, marcasite (FeS₂), pyrrhotite (Fe_{1-x}S), arsenopyrite (FeAsS) and loellingite (FeAs₂). These minerals have been chosen to compare and contrast their electrochemical behaviour with pyrite, as they have different crystallography, Fe:S ratios and arsenopyrite (FeAsS) and loellingite (FeAs₂) have As in place of sulfur. The aim is to show how these changes affects the electrochemistry and recovery of metals from these ores.

As mentioned in chapter one, the main sources of copper, lead, zinc, and nickel are in extraction from sulfide minerals, which are converted to the respective metals by pyrometallurgical processes which produce gases such as SO₂, CO₂ and CO. Emissions of sulfur dioxide need to be carefully controlled from these sulfide smelters. Hydrometallurgical routes involve the oxidation of sulfides to sulfur or sulfate, either by using oxidants such as strong acids, oxygen, ferric ions, and cupric ions, or by direct anodic oxidation in an electrolyte.¹ However, the hydrometallurgy of leaching sulfide minerals can cause environmental problems such as the discharge of toxic leaching solvents into water resources. Therefore, the chemical and electrochemical dissolution of sulfide minerals such as pyrite, marcasite, pyrrhotite and arsenopyrite have been widely studied in aqueous systems due to the influence of oxidation on these sulfide minerals upon ground water and surface water overflow. Where these minerals cause serious acid mine drainage problems rapid remedial measures are always required. The oxidation of sulfides by an oxidant is regarded as an electrochemical reaction at an anode as anodic oxidation of the sulfide – with the cathodic reduction of the oxidant – can subsequently be studied by electrochemical techniques.²

In the case of pyrite in Chapter 3, the chemical and electrochemical oxidation of pyrite in an aqueous medium has been discussed. From this, it can be concluded that the behaviour of pyrite is changed by applying different environmental conditions such as leaching solution, oxidizing agents, pH, temperature, etc. The chemical dissolution of pyrite in Ethaline shows no solubility even when using I₂ as an oxidizing catalyst in DESs. However, the electrochemical oxidation of pyrite in DES shows some clear electrochemical signals such as Fe^{III/}Fe^{II} and S⁰/S6²⁻/S4²⁻. However, the detection of species of Fe and sulfur ions in DES is relatively unobserved, even though there are many indications that glycolate molecules can form complexes with dissolved iron. Although the minerals have similar compositions the physicochemical properties, such as the resistivity of these minerals, types of impurities present, lengths of atomic bonds, atomic structures, energy band gaps, the stability of the minerals, are all very different.

Marcasite (FeS₂) is a metastable isomeric form of pyrite; where pyrite has a cubic crystal structure, marcasite is orthorhombic, as shown in *Figure 4-1*. This means marcasite has an identical molecular weight to pyrite and a similar atomic ratio of iron to sulfur.³ The length of the unit cell in the crystal lattice of cubic pyrite are similar, but marcasite has lower symmetry and stability. The Fe–S bond lengths in marcasite (2.23–2.24 Å) are very similar to those of pyrite, however the S-S dimer distance is slightly longer at around 2.21 Å, compared to pyrite where they are about 2.08 Å. The Fe–Fe distances in the crystal lattice are shorter than those of pyrite, which can have a significant effect on the band gap. The band gap of pyrite is around 0.95 eV whereas marcasite is about 0.34 eV.⁴ Therefore, marcasite accordingly exhibits a higher conductivity. ⁵



Figure 4-1: Crystal structures of a) pyrite and b) marcasite⁶

Pyrrhotite (Fe_{1-x}S) is a stable form of monosulfide which is usually formed alongside pyrite in a hydrothermal mechanism. Pyrrhotite has 62.33% Fe and 37.67% S with a wide range of sulfur ratio x ranged (0.00-0.17).³ Pyrrhotite has a superstructure as a consequence of a wide range of compositional formulae, however the most well-known structure of pyrrhotite is monoclinic with an energy band gap of about 0.80 eV.^{7, 8} Pyrrhotite has a relatively low resistivity range of about 2 to 160 x $10^{-6} \Omega m$, while the resistivity of pyrite is higher at about 1.2 to 600 x $10^{-3} \Omega m$.²

Arsenopyrite (FeAsS) has 34.30% Fe:, 46.01% As: and 19.69%.S: ³ It has octahedral coordination where iron atoms are coordinated octahedrally through both corners and edges by six atoms, three of which are arsenic and the other three are sulfur. Each arsenic and sulfur atom is coordinated tetrahedrally by three iron atoms and one sulfur or arsenic atom to form $\{As-S\}^{-2}$ dimers. The bond lengths in arsenopyrite are about 2.35, 2.25 and 2.33 Å for Fe–As, Fe–S and $\{As-S\}^{2-}$, respectively. As a consequence of different bond lengths for Fe–S and Fe–As, the Fe–Fe metal distances also change along the *c* axis. The crystal structure of arsenopyrite is monoclinic, where iron is octahedral and shares only

corners which are more distorted and less symmetric than cubic pyrite, Arsenopyrite has an energy band gap of about 1.19 eV.^{5,9}

Loellingite (FeAs₂) is a very rare mineral with a molecular weight of 205.69 g.mol⁻¹ and the ratios of iron and arsenic are 27% and 72.85.³ Loellingite has the same structure as marcasite (orthorhombic), whose $\{S-S\}^{2-}$ dimers are replaced by $\{As-As\}^{2-}$ dimers in loellingite. The reported bond distance of Fe–As, and the bond distance of As–As are about 2.36 Å and 2.49 Å, respectively.^{10, 11} The length of $\{As-As\}^{2-}$ dimers in loellingite are longer than the bond length of $\{S-S\}^{2-}$ in marcasite and are slightly less electronegative than the corresponding $\{S-S\}^{2-}$ dimers. Presumably, the greater electronegativity of sulfur compared to arsenic can create a distortion in the iron octahedron and reduce the interatomic Fe–Fe bond length.

4.2 Electrochemical behaviour of iron-based minerals

4.2.1 Sample Analysis

Figure 4-2 shows 2D-images of freshly polished samples of marcasite, pyrrhotite, arsenopyrite and loellingite under 3D profilometre (at the top), and a comparison with their backscattered electron (BSE) images and EDX data for the different colour spots (at the bottom), which are marked by red rectangles (at the top). BSE were used to find the areas with different chemical compositions. The heavier elements can backscatter electrons more strongly than lighter elements and thus seem brighter in the BSE image.¹²

Marcasite shows high purity and homogeneity with only traces of silica and alumina. Pyrrhotite appears to have different crystal faces and is contaminated with trace amounts of zinc or zinc sulfide. Zinc is denser than the iron and sulfur in pyrrhotite, and therefore appears as a brighter crystallite in the BSE image and blue in the 2D coloured image. Arsenopyrite has traces of As₂O₃ in EDX. This could be attributed that to the oxidation of arsenic by bacteria. Loellingite is contaminated with approximately 10% atom% Co, which may be CoAs₂ or {(Co,Fe)As}, and with relatively small amounts of S or {AsS}²⁻, as shown in *Figure 4-2D*. In addition As₂O₃ may also be observed in loellingite. The presence of these contaminations could affect the voltammograms of ores however the contaminants are either non electroactive e.g. silica and alumina, or they are present in less than 5 At%.



Figure 4- 2: (At the top) 2D stitching coloured images captured by 3D profilometre with a 20x lens and whole grain of each (A) marcasite, (B) pyrrhotite, (C) arsenopyrite, and (D) loellingite compared with their backscattered electron images, as captured by SEM and EDX analysis.

4.2.2 Cyclic voltammetry of other iron-based minerals

Electrochemical methods, especially voltammetric methods, have previously been used to determine the reactivity and assay of minerals in aqueous electrolyte.¹³⁻¹⁵ Although it is not possible to attribute each observed peak using only voltammetric methods, cyclic voltammetry has been used to evaluate the effect of ligands on the oxidation and reduction potentials of the central ion in the complex and the cluster lattice.¹⁶ This voltammetric information plays a significant part in many approaches such as the metal complex in an intermediate oxidation state, selection of oxidizing agents and solar cell.^{17, 18} However, the electrochemistry of chalcogenides in non-aqueous media are generally unknown.¹⁹ Thus, voltammetric techniques will be exploited to study the electrochemistry of these minerals in DESs.

The electrochemistry of marcasite has long been associated with pyrite in terms of qualitative analysis. Marcasite has a higher oxidation rate and produces more oxidized species than pyrite.²⁰ The main oxidized species of marcasite in aqueous medium are elemental sulfur, thiosulfate, sulfate and Fe^{II/III} hydroxide, whilst the reduced species are Fe^{III/II} hydroxide and reduced sulfide as S_2^{2-} and H_2S or polymeric sulfur such as $S_2O_4^{2-}$.^{20, 21}

The electrochemical investigation of natural or synthetic pyrrhotite has been widely studied in the literatures using cyclic voltammetry in aqueous system at different pH values of 4.6, 9.2 and 13.0.²²⁻²⁴ All of these studies pointed out that the anodic reactions of pyrrhotite produced sulfur as a major product; furthermore, ferric oxide may be deposited on the surface of the pyrrhotite. Thiosulfate and sulfate are also found as rare by-products depends on alkaline conditions, as shown in the equation below.²⁵ Hamilton and Woods proposed that the oxidation process of pyrrhotite is significantly inhibited in alkaline solution due to the formation of iron oxide/ hydroxide on pyrrhotite surfaces.²²

$$Fe_{(1-x)}S \rightarrow (1-x) Fe^{2+} + S + 2(1-x) e^{-}$$
 (4-1)

In addition to the electrochemical behaviour of marcasite and pyrrhotite, arsenopyrite is considered an inconvenient contaminant due to its arsenic content which causes environmental problems. Arsenopyrite, like other sulfide minerals, is difficult to leach in aqueous media, even at low pH. The dissolution rate can be improved by the application

of a potential in a pH range of 0.0-2.5.^{20, 26, 27} Sisenov et al. proposed that at low pH arsenopyrite was covered by a passivation layer of sulfur at applied potentials of more than 0.5 V, and in this way is difficult to leach.²⁸ The electrochemical dissolution of arsenopyrite was studied by Fernandez and co-workers by detecting the solution species in 0.01 M KCl, where they found that Fe^{2+} , Fe^{3+} , As^{3+} , As^{5+} , S, SO₄⁻² and other polysulfide species are present in electrolyte.^{29, 30} Zheng and Lin concluded that the oxidation of arsenopyrite involves two steps: the first is the oxidation of S⁻ to S and the additional oxidation led to the formation of SO₄²⁻; the second step is the oxidation of arsenite ions (H₂AsO₃⁻) to arsenate ions (H₂AsO₄⁻).²⁷

On the other hand, the electrochemical behaviour of loellingite (FeAs₂) is not well studied in the literature because it is relatively rare, and is generally an impurity. Beattie and Poling recorded the cyclic voltammetry of loellingite in media of different pH and found that in basic solutions (pH 10.6) loellingite behaves in a similar manner to arsenopyrite.²⁰

Figure 4-3 shows the cyclic voltammograms of polished crystal of marcasite, pyrrhotite, arsenopyrite and loellingite (packed in resin) in Ethaline versus an Ag/AgCl reference electrode. As shown previously for pyrite, the CVs are less well resolved than the paint cast samples seen in the previous chapter due to the anisotropy of the minerals.

The voltammogram of marcasite is identical to that of the voltammogram found in the literature by Giannetti and Almeida.^{21, 31} *Figure 4-3A* shows two oxidation current peaks at (ca. +0.07 V and +0.15 V), where the first is attributed to the oxidation of the sulfide, potentially to elemental sulfur or a polysulfide at +0.07 V, and the second at +0.15 V may be attributed to the further oxidation of elemental sulfur on the mineral surface. This could produce sulfur chloride compounds such as SCl₂ or S₂Cl₂ as chloride ions dominate in Ethaline, however this is readily hydrolysed and is unlikely to be a long-lived species. In aqueous media thiosulfate (S₂O₃²⁻) is formed which could also be a possibility in DESs given the traces of water present. The formation of thiosulfate in aqueous medium has been shown to be thermodynamically possible, as suggested by Paul for anodic dissolution of galena (PbS) and illustrated in the equations below.^{32, 33} Two reduction peaks are observed at ca. +0.38 V and -0.24 V which correlate to the reduction of iron and sulfur species as illustrated in the previous chapter.

$$2S + 3H_2O \to S_2O_3^{2-} + 6H^+ + 4e^-$$
(4-2)

$$S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8e^-$$
 (4-3)



Figure 4- 3: Cyclic voltammograms of single grain particles of marcasite, pyrrhotite, arsenopyrite and loellingite in Ethaline at 20°C and at a scan rate of 10 mV.s⁻¹

Figure 4-3B shows the cyclic voltammogram of polished pyrrhotite ore, where there are three oxidations and two reduction peaks. The first two oxidation peaks are identical to those in marcasite, and which are attributed, respectively, to the formation of elemental sulfur and a polymeric sulfide form or thiosulfate, as mentioned above. However, the cyclic voltammogram is found to be very similar to that obtained by Hamilton and Wood at pH 4.6 in a buffered solution of acetic acid/sodium acetate, with the exception of the O_{II} peak.²² The O_I peak is attributed to the formation of elemental sulfur and the third oxidation peak, O_{III}, to the stripping of ferrous ions into the solution, as illustrated in equation (4-1) above. Therefore, the accumulation of elemental sulfur layers on the electrode surface might be expected to take place. This accumulation of sulfur on the pyrrhotite surface could explain the difficulty of getting Fe²⁺ to diffuse into the electrolyte

and increase the concentration of the remaining ferrous ions corresponding to the sulfur at the mineral surface. At more positive potential close to ca. +0.45 V, Fe^{II}, is oxidized to Fe^{III}. The O_{II} of pyrrhotite could also be due to the formation of sulfur chloride or thiosulfate (S₂O₃²⁻).¹⁵

$$2FeS + 3H_2O \rightarrow S_2O_3^{2-} + 2Fe^{2+} + 6H^+ + 8e^-$$
(4-4)

The reduction peaks of pyrrhotite can be attributed to the reduction of $\text{Fe}^{\text{II/II}}$ to $\text{Fe}^{\text{II/II}}$ at R₁ ca. +0.3 V and R_{II} could be assigned to the reduction of sulfur/intermediates (S₈/S₆²⁻/S₄²⁻) at the electrode surface, as illustrated in **section 3.4.1** of Chapter 3.

Figure 4-3C shows the cyclic voltammogram of a polished crystal particle of arsenopyrite as a working electrode in Ethaline, where it can be observed that there are two obvious oxidation peaks (O_I and O_{II}) and two reduction peaks (R_{II} and R_{III}). The oxidation peaks can be assigned to either formation of elemental sulfur or an amorphous layer of As_2S_3 , while the reduction peaks could be attributed to ($S_8/S_6^{2-}/S_4^{2-}$) or As_2S_2 , as illustrated in equation (4-5) below in aqueous media.¹⁵ However, it can be seen that there are very small oxidation and reduction peaks, which can be attributed to $Fe^{II/III}$ and $Fe^{III/II}$ signifying O_{III} and R_I , respectively. This is possibly because of the accumulation of a solid insoluble precipitate of As_2S_3 (orpiment) on the arsenopyrite particle electrode, which prevents liberation of more iron ions into Ethaline. Arsenic ions such as As^{III} and As^V can be rapidly deposited onto the amorphous As_2S_3 in the presence of sulfide ions.³⁴⁻³⁶

$$As_2S_3 + 2H^+ + 2e^- \rightarrow As_2S_2 + H_2S$$

$$(4-5)$$

Figure 4-3D illustrates the cyclic voltammogram of loellingite in Ethaline, in which three clear oxidation peaks and three reduction peaks can be observed. As discussed above, the electrochemistry of loellingite behaves in a similar manner to that of arsenopyrite; however, O_{III} at ca. + 0.63 V was observed to have a higher oxidation potential and current. This could be because of formation of an iron-arsenic complex.

The voltammetric responses of polished single mineral crystals are difficult to interpret unambiguously due to overlapping peaks, resistive artefacts and anisotropic effects of different crystal faces. The paint casting methods decreases these three artefacts producing more reproducible CVs with better defined redox peaks and less iR artefacts. In the next section paint casting is applied to powdered samples of the same minerals in Ethaline.

Figure 4-4 shows the application of the paint casting method for the comparison of the voltammetric responses of five iron-sulfur and iron-arsenic minerals. In all cases, the Fe^{II/III} redox couple is clearly discernible at about +0.5 V as a reversible, diffusioncontrolled process especially at the fairly slow voltage scan rate of 10 mV.s⁻¹. The redox potentials are relatively unaffected by the nature of the mineral. Relatively little is known about the electrochemical properties of the minerals studied here. Almeida and Giannetti, as mentioned above in section 4.2.1, studied arsenopyrite by mixing it with carbon powder and making it into an electrode and electrochemically oxidising it in an aqueous acetate buffer solution.³⁷ A relatively poorly resolved voltammogram was obtained which contained most of the redox processes shown in Figure 4-4D. The electrochemical response for the sulfur or arsenic component is clearly different for each mineral. Comparing pyrite and marcasite, which are chemically the same (both FeS_2), it can be seen that the relative peak heights for the iron-based redox couple compared to the sulfur peaks are significantly different. For pyrite, the sulfur signal is significantly smaller than that for iron, whereas the reverse is true for marcasite. Pyrite has a cubic crystal structure rather than the orthorhombic crystal structure found in marcasite.³⁸ In contrast, pyrrhotite has a relatively weak redox signal for sulfur. This could be due to it being predominantly S^{2-} rather than S_2^{2-} which could be why the cathodic signal at ca.-0.2 V is so weak. In arsenopyrite, the anionic component is nominally $(SAs)^{2-}$ with the iron being principally in the Fe^{II} form.³⁹ In addition, these materials have significantly different band gaps in the pure state; pyrite is 0.95 eV whereas marcasite is 0.34 eV and arsenopyrite is 1.19 eV. It would therefore be expected that marcasite would be easier to oxidise than either of the other two minerals.



Figure 4- 4: Cyclic voltammograms of 20 mg of (A) pyrite, (B) marcasite, (C) pyrrhotite, (D) arsenopyrite and (E) loellingite pasted onto a Pt flag in Ethaline at $20^{\circ}C$ and at a scan rate of 10 mV.s⁻¹

It is immediately apparent from *Figure 4-4* that the relative signals for the sulfide/arsenide oxidation compared to that for iron are different despite the ratios of the elements being similar in most cases. Comparing pyrite and marcasite; although the redox peaks are at similar potentials, the relative intensity of the peaks are different. The absolute oxidation peak for the Fe^{II/III} signals are similar but the sulfide oxidation peak is considerably bigger for marcasite than pyrite. This suggests that the two processes are

separate from each other i.e. the S or As is oxidised releasing Fe^{II} which is subsequently oxidised to Fe^{III}.

4.2.3 Determination of relative dissolution rates

As was previously shown in *Figure 3-7A* the voltammetric signal was proportional to the amount of pyrite in the paste. *Figures 4-5 and 4-6* show the same analysis of anodic charge vs mass loading for the other 4 minerals. It is clear that the current is also proportional to the loading mass of the minerals. From the plots of mass vs charge, it can be seen that the relative dissolution rates are in the order marcasite > loellingite > arsenopyrite > pyrrhotite.



Figure 4- 5: Cyclic voltammograms produced when loading different weights of (A) marcasite, (B) pyrrhotite, (C) arsenopyrite and (D) loellingite were pasted onto a Pt flag in Ethaline versus an Ag/AgCl reference electrode at 20°C and a scan rate of 10 mV.s⁻¹



Figure 4-6: shows the plots of mass loading vs charge of Figure 4-5

An alternative method of determining the relative rate is using a chronocoulometry analysis. In all the experiments 40 mg of ground mineral was painted onto the Pt electrode surface and a potential of ± 1.2 V was applied to the electrode. The results of these experiments are shown in *Figure 4-7*. The results show that marcasite has the highest total charge, followed by pyrrhotite, pyrite, arsenopyrite, and loellingite. This is slightly different to that observed above using cyclic voltammetry. It should, however be noted that the two experiments probe different processes. Cyclic voltammetry shows a more mechanistic aspect of the dissolution process whereas chronocoulometry shows the kinetic aspects of dissolution. The experiment in also runs for 1800 s whereas the voltammogram is only in the dissolution regime for *c.a.* 80 s. Chronocoulometry therefore gives a more accurate picture of the relative dissolution rates. This will be proven later using bulk electrolysis and ICP-MS.



Figure 4-7: Chronocoulometry of 40 mg of each pyrite, marcasite, pyrrhotite, arsenopyrite, and loellingite pasted onto a Pt flag in Ethaline over 30 minutes at +1.2V and 20 °C.

The band gap (Eg) of a semiconductor is the energy gap between the valence band and conduction band of substance. In a conductor materials such as metals, this energy gap is very small, where the valence bands and conduction bands overlap. The energy gap in insulators materials is very large resulting in negligible excitation of electrons to the conduction band.⁴⁰ Conductance in semiconductor materials takes place as a result of electron movement from valence band to conduction band due to a relatively small energy gap between them.⁴¹ The excited electron from valence band to a vacant hole in conduction band is delocalised and becomes free to move around the lattice. The excited electron leaves a positively charged hole in valance band, which permits remaining electrons in the valence band to move freely by passing from hole to hole.⁴²

Chemically, the valence band represents the Highest Occupied Molecular Orbital (HOMO), while the conduction band represents the Lowest Unoccupied Molecular Orbital (LUMO). The flow of current in semiconductors is due to the electrons transfer from the valence band (HOMO) to the conduction band (LUMO) over a relatively short energy gap. By applying a potential the free electrons in the conduction band move towards the positive pole (the anode) and a current will be generated, however the

electrons in the valance band also move between vacant positive holes which will be generating a hole current towards the negative pole (the cathode). Thus, the total current represent the summation of the electron current in conduction band and the hole current in the valence band.⁴³ Therefore, it is reasonable to predict that the semiconductor with a small band gap can be oxidized faster and therefore producing faster dissolution rate than that one which has large band gap. So, it is logical to compare energy band gap with the electrochemical dissolution rates of iron-based sulfide minerals. *Table (4-1)* shows the correlation between dissolution rates of iron-based sulfide minerals in *Figure 4-7* and their band gap were collected from literatures, in addition to that OCPs data in *Figure 4-9*.

Sulfide minerals	Band gap / eV	Electrochemical	OCP / V
		dissolution rate / C	
Pyrite	0.95	4.39	-0.069
Marcasite	0.34	8.17	-0.187
Pyrrhotite	0.80	6.48	-0.084
Arsenopyrite	1.19	3.80	-0.183
Loellingite		3.29	-0.192

Table (4-1): The band gap and dissolution rate of iron based sulfide minerals in
Ethaline.

The band gap data of iron based minerals versus their data of electrochemical dissolution in *Table (4-1)* has been plotted in the *Figure 4-8* below. This shows that there is a good correlation between the energy band gap and electrochemical dissolution rate of different iron-based sulfide minerals in Ethaline at ambient temperature. The data in *Figure 4-8* suggest that minerals with a band gap greater than about 1.75 eV will have a negligible dissolution rate at the conditions carried out in *Figure 4-7* i.e. to gain faster electrochemical dissolution the electrode potential will have to be increased.



Figure 4- 8: Band gap data of pyrite, marcasite, pyrrhotite and arsenopyrite versus their electrochemical dissolution of painted 40 mg for each minerals onto Pt flag as working electrode in Ethaline for 30 minutes.

The reactivity of the various minerals can be predicted from the open circuit potential at zero current (OCP) which is defined as the voltage of the working electrode as measured against a reference electrode when using a high impedance voltmeter, and no current flows between the terminals of the immersed electrodes in the electrolytic solution.⁴⁴ Measuring OCP as a function of time is essential for estimating corrosion reactions and reactivity of materials.⁴⁵ Moreover, the influence of the presence of impurities in these minerals has the ability to inhibit the reactivity of minerals by increasing the OCP as a result of anodic protection by these active impurities which have a lower OCP.¹³ So, minerals with lower open circuit potentials should, in principle, chemically dissolve faster into the electrolyte than those with higher open circuit potentials.



Figure 4- 9: Open-Circuit Potential (OCP) of iron-based ores painted onto a Pt flag electrode as paint casting for pyrite, marcasite, arsenopyrite, loellingite and pyrrhotite.

Figure 4-9 shows the OCP for 5 iron-based minerals pasted onto a Pt electrode and immersed in Ethaline and the voltage was measured against an Ag/AgCl reference electrode for 10 minutes. In most cases the OCP decreases with time showing that there is a slow chemical dissolution of the minerals. Pyrite and pyrrhotite have a slightly higher OCP than the other 3 minerals meaning that they should be slightly slower to chemically dissolve than the other minerals.

4.3 Bulk electrolysis of iron-based minerals in DESs

The anodic bulk electrolysis of 2 g of each of the iron-based minerals was carried out using the equipment shown in *Figure 4-10*. The mineral powder was made into a thick paste and put into a holder which was made from acrylonitrile butadiene styrene (ABS) plastic using a 3D printer. The paste was separated from the cell using a sheet of filter paper to stop the mineral grains escaping from the anodic compartment. Iridium oxide coated titanium mesh was used as the electrode material in both compartments. A 10 mA constant current was applied between the two electrodes of iridium-coated titanium (2 cm² electrode surface area) covered with 2 g of the paste of each mineral except for loellingite where 5 mA was applied for 24 hours.

The speciation of the resulting solutions from the anodic dissolution of iron-based sulfide minerals in Ethaline was studied using cyclic voltammetry and UV-vis spectroscopy, as shown in *Figures 4-11* and *4-12*, respectively.



Figure 4- 10: Schematic diagram of a 3D printed separated cell (on the left), consisting of a 3D printed separated cell placed into a beaker with the mineral separated from the two electrodes by a piece of filter paper in the Ethaline (on the right).

Although the anodic dissolution, as demonstrated in *Figure 4-11* for all of the minerals, should result in the formation of Fe^{III} it is evident that the solutions all have a different colour, which would not be the case if the iron had formed [FeCl₄]⁻. In the extreme, loellingite forms a green solution on dissolution, which is characteristic of Fe–As complexes such as those formed in the so-called green rust.¹⁹ It seems logical, therefore, that upon dissolution the iron and chalcogenide remain bonded to each other in the soluble complex. The colour could also arise from other metal impurities such as Co. There is some evidence for cobalt being incorporated in the deposit obtained on the cathode (< 3 wt%) but this may be too small to colour the solution. Thus, cobalt ions (Co) were characterised in Ethaline solutions, and their characteristic peak was observed in the UV-Vis analysis of the loellingite solution, as it will be seen in *Figure 4-14D*. Bulk electrolysis was carried out in the cell as reported previously.^{46, 47}

Bulk anodic electrolysis of marcasite in Ethaline, produced a yellow colour similar to that of anodic dissolution of pyrite in Ethaline, as shown previously in *Figure 3-10*. Since marcasite and pyrite are crystallographic isomers of each other it would seem logical that the dissolution products are similar and it is not surprising that they have different dissolution kinetics.



Figure 4- 11: Bulk electrolysis of 2 g of anodically dissolved marcasite, pyrrhotite, arsenopyrite and loellingite in Ethaline at a constant current density of 10 mA.cm⁻² (except for loellingite, which was 5 mA. cm⁻²) for 24 hours at 50°C.

4.3.1 Cyclic voltammetry of electrolysed minerals

Figure 4-12 shows the cyclic voltammograms of Ethaline solutions obtained in *Figure 4-11*, using a platinum disc as a working electrode against an Ag/AgCl reference electrode. Obviously, all the oxidative voltammograms in this figure indicate the presence of Fe^{III/}Fe^{II} peaks. Moreover, the reduction of sulfur species are also observed in marcasite pyrrhotite and arsenopyrite. However, the peak current of reductive sulfur species in the solution obtained from the oxidative dissolution of loellingite did not appear as there is no sulfur in the compound. A new oxidative and reductive couple was however found at -0.2 V and -0.7 V, which could be attributed to the reduction of elemental arsenic (As) and As^{III}, respectively.

The interpretation of the voltammograms of dissolved arsenopyrite and loellingite species in Ethaline is based on the thermodynamic phase diagrams of arsenic in aqueous media. The Pourbaix diagrams for the As-O-H and As-S-O-H systems are shown in *Figure 4*-

 $13.^{48-50}$ This is because As⁰ and As^{III} in aqueous medium have stable phases at the reduction region and also at low pH.



Figure 4-12: Cyclic voltammograms of anodic dissolution of (A) marcasite, (B) pyrrhotite, (C) arsenopyrite and (D) loellingite in Ethaline with a Pt disc working electrode versus an Ag/AgCl reference electrode and Pt flag as the counter electrode at a 10 mV.s⁻¹ scan rate

The Pourbaix diagrams in *Figure 4-13* show that As is only stable over quite a small potential window.



Figure 4-13: E-pH diagrams for the As-O-H (left) and As-S-O-H (right) systems⁴⁸

4.3.2 UV-Vis spectra of iron-based minerals dissolved in Ethaline

As previously mentioned in **section 3.6.1**, the speciation of metal salts in ILs and DESs is controlled by either the counter ion of the dissolved species or the anion of DESs or ILs. UV-Vis spectra of the solutions obtained from bulk anodic dissolution were compared with chemically dissolved species of, specifically, FeCl₂, FeCl₃, FeS, and FeSO₄.7H₂O in Ethaline.

Figure 4-14 shows the UV-Vis spectra of the solutions obtained in *Figure 4-11* of the anodic dissolution of marcasite, pyrrhotite, arsenopyrite and loellingite in Ethaline. *Figure 4-14A* shows the anodic dissolution of marcasite in Ethaline, which is significantly different to that of pyrite. Marcasite shows two spectroscopic peaks at ca. 224 nm and ca. 300 nm. The first peak at 224 nm can be attributed to the dissolution of Fe in Ethaline to form an Fe^{II}-glycolate complex, as shown previously in *Figures 3-14A*. This is because ethylene glycol is considered a reducing agent and can be reduced by combining with a metal.^{51, 52} That is why both FeCl₂ and FeCl₃ dissolved in ethylene glycol were observed in the same UV-Vis spectrum, as seen previously in *Figures 3-14B*. The second peak at 300 nm was found to be very similar to that of FeSO₄.7H₂O dissolved in Ethaline, which could be correlated to the Fe^{III} linked with the sulfate complex, i.e.

FeSO₄⁺ in aqueous.⁵³ While no evidence of sulfur being oxidised to sulfate has been found there are plenty of oxygen donating ligands which could produce similar species. The EXAFS results below add more detail to possible speciation.

Figure 4-14B shows the UV-Vis spectra observed for anodic dissolution of pyrrhotite, which showed they have a similar absorption shoulder at ca. 290 nm. This absorption band for pyrrhotite was found to be extremely similar to the UV-Vis spectra recorded for the leachate sample after the oxidative electrolysis of pyrrhotite in an aqueous solution containing glycine.^{54, 55} This spectrum could be correlated to the binding of a Fe atom with oxygen with the organic ligand. This interpretation was further supported by the EXAFS findings, namely that FeCl₄⁻ was linked with the oxygen atom in glycolate.⁵⁶

Figure 4-14C shows the UV-Vis spectra of oxidative bulk electrolysis of arsenopyrite in Ethaline. The oxidative arsenopyrite produced clear absorption bands at approximately 210 nm, 224 nm, and 276 nm and 330 nm. The absorption peak at 210 nm can be attributed to the Fe^{II} chloride complex where the same band is observed for all iron salts dissolved in Ethaline.⁵⁵ Whilst the 224 nm absorption band could correspond to some Fe^{II}-oxygen complex in Ethaline and the absorption shoulder at 276 nm could correspond to sulfide speciation in Ethaline, as illustrated in Figure 3-13 in Chapter Three. However, the new absorption band at 330 nm could be attributed to the oxidation of the As atom in arsenopyrite to As^{III} chloride in Ethaline or a thio-organoarsenic compound species formed by the coordination of an arsenic atom with ethylene glycol. Similar organoarsenic species have previously been reported in the literature.^{57, 58} Arsenic has a wide range of complexes in aqueous solution such as H₃AsO₄, H₂AsO₄⁻, HAsO₄²⁻, AsO₄³⁻ , $H_3AsO_3^{-1}$, $HAsO_3^{2-1}$ and AsO_3^{3-1} ; moreover, metal arsenate complexes such as FeH₂AsO₄²⁺, FeHAsO₄⁺ and FeAsO₄ are also known to exist. Metal arsenite (As^{III}) species usually exist as neutral and a stable complexes, such as H₃AsO₃, which make it difficult to remove them.⁵⁹ An understanding of the arsenic and metal compounds formed

as arsenite (As^{III}) and arsenate (As^V) complexes is essential to any study of the electrochemical behaviour of semiconductors and the solubility of metals.⁵⁹ However, as a consequence of the high toxicity of arsenic compounds on the ecosystem, the interpretation of arsenic data will for the most part be based on the As and As-S Pourbaix diagram shown above.



Figure 4- 14: UV-Vis spectra of anodic electrolysis of 2g (A) marcasite (FeS₂), (B) pyrrhotite (Fe_{1-x}S), (C) arsenopyrite (FeAsS) and (D) loellingite (FeAs₂) following electrolysis at a current density of 5 mA cm⁻², whilst the electrolysis of (A) marcasite (FeS₂) was obtained at a current density of 2.5 mA cm⁻² in Ethaline at 50°C for 24 h

Figure 4-14D shows the UV-Vis spectra recorded for the anodic dissolution of loellingite in Ethaline. The absorption peaks appeared at 233 nm and 330 nm, in addition to three additional, albeit much less intense, absorption peaks that appeared between 600 and 720 nm. The peaks at much higher wavelength are uncharacteristic of iron complexes and could arise from the impurities of cobalt that were found in the mineral. While it was only present at 3 wt% in loellingite the high extinction coefficient could dominate the colour of the solution. ICP-MS analysis of the solution obtained by anodic dissolution of loellingite in Ethaline found to be 150 mg/L of Co. A solution containing 150 mg/L of CoCl₂.6H₂O was made up in Ethaline, and the resulting solution was similar in colour and identical peaks were observed in the UV-Vis spectra between 600 and 720 nm. This can be seen in *Figure 4-15*. Thus, the absorption bands at 233 nm and 600-720 nm have been attributed to the tetrahedral cobalt tetrachloride complex, [CoCl₄]^{2–}, which has previously been characterized in Ethaline via EXAFS.⁴⁷



Figure 4- 15: Comparison of coloured solutions resulting from anodic dissolution of loellingite and 150 mg/L of Co prepared by dissolution of 1.9 mg of CoCl₂.6H₂O in 50 ml Ethaline (left-hand image), and the UV-Vis spectrum of 150 mg/L of Co salt dissolved in Ethaline (right-hand image).

Therefore, it is clear that altered bands observed for loellingite were confined between 250-420 nm for the anodic electrolysis could be attributed to As complexes such as As-chlorides, As-glycolate and Fe-As- complexes. Hence, the shoulder observed for the anodic bulk dissolution of loellingite in this confined range can be seen at 330 nm, which is similar to that of arsenopyrite.⁶⁰ This does show an important principle since the dissolution of pyrite and other iron-based minerals is mainly important for its ability to release other metals into solution upon anodic oxidation.

In an endeavour to understand speciation of iron in Ethaline, colleagues at the University of Freiberg carried out EXAFS analysis on solutions prepared above as well as those prepared for iron chloride in Ethaline. It was only solutions of pyrite and pyrrhotite which were concentrated enough to yield spectra which could be analysed. All of the spectra were collected and analysed by Dr Jennifer Hartley.

Table (4-2) contains the fit parameters for the EXAFS spectra for solutions of iron chlorides and iron-based minerals dissolved by electrolysis in Ethaline. Both iron (II) and iron (III) chlorides saw similar speciation to the other metal halides previously studied forming tetrachloride based complexes (probably tetrahedral in geometry) of the form [FeCl₄]²⁻ and [FeCl₄]⁻. The speciation does not appear to be significantly affected when

six waters of hydration are added. The addition of a 20 fold molar excess of water to iron does appear to change the speciation somewhat with a mixture of Cl- and O-donor (OD) ligands, potentially forming species such as [FeCl₂(OD)₂₋₃]⁺, where OD could be water or ethylene glycol. The addition of water has previously been used to precipitate iron complexes from DESs.^{61, 62} This is the same as was previously observed for copper complexes in the same DES.⁶³

(Å ²)
(7) 1.58 %
(8) 2.06 %
(9) 1.35 %
3) 1.01 %
4)
(8) 2.88 %
1) 2.46 %
3) 6.66 %
11)
2) 3.38 %
13)
2) 4.46 %

Table (4-2): EXAFS fit parameters for solutions of iron chloride and iron-based minerals dissolved by electrolysis in Ethaline (top) and water (bottom).

When iron (II) chloride was dissolved in an aqueous 1M NaCl solution, the fit suggested a coordination of six OD, most probably corresponding to the hexa-aqua complex. The bond length and Debye-Waller factor from this $[Fe(H_2O)_6]^{2+}$ complex matches the OD parameters from the mixed species fit for iron(III) chloride in Ethaline with 20 mol.% added water.

Analysing the bond lengths produced by the fits does not give conclusive proof of whether it is a single species or a mixed ligand species. The bond length will naturally depend on the oxidation state of the metal and the type of ligand. M-O complexes usually have bond lengths in the region 2.0 to 2.1 Å, whilst M-Cl are generally 2.1 to 2.3 Å. The data in *Table (4-2)* are all in this region. The coordination number is always a good indicator of the presence (or lack thereof) of another ligand type. The fluorescence data gives almost 5 x Cl, whilst transmission gives 4.4 x Cl. These are unusual and suggest mixed coordination, but not conclusively. Fortunately, both spectra have the same coordination with the mixed coordination model.

After electrodissolution of pyrite and pyrrhotite in Ethaline, yellow/brown solutions were formed, potentially indicating the presence of different complexes to those obtained from the dissolution of either ferrous or ferric chloride, as illustrated in *Figure 4-16* below.



Figure 4- 16: Solutions obtained by anodic electrolysis of pyrite (A) and pyrrhotite (B) in Ethaline, dissolution of anhydrous salt for FeCl₃ (C) and FeCl₂ (D) in Ethaline and FeCl₃ (E) and FeCl₂ (F) in deionized water.

4.4 Determination of mineral dissolution kinetics using ICP-MS

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is an analytical technique utilized for the determination of trace element concentrations. The inductively coupled plasma (ICP) is usually combined with an ICP torch used to convert argon gas to a stream of plasma (charged ions), where these carrier ions can be separated by applying a magnetic field and then detected by mass spectrometry. The sample is injected either as a liquid or a dissolved solid sample into a nebulizer, where the elements are first converted

first into gaseous atoms and then ionized to a plasma via an ICP torch for detection by mass spectrometry.

Figure 4-17 shows the concentration of iron ions obtained from anodic bulk dissolution of 2g of marcasite, pyrrhotite, arsenopyrite and loellingite in 50 ml Ethaline at a constant current of 10 mA analysed using ICP-MS. A 50 μ L sample every four hours for 24 hours and then diluted to 50 ml in a volumetric flask using 2% HNO₃. Marcasite and pyrrhotite showed fastest iron dissolution kinetics which corresponds to the data obtained using chronocoulometry above.

Loellingite and arsenopyrite behave in a similar manner and show that the dissolution of these minerals is slower than the iron-sulfur minerals. This could be because the dissolution of both of these minerals could produce an oxidation product of arsenic which could slow subsequent dissolution of the underlying mineral.⁶⁴ Analysis of the arsenic content of these two solutions should indicate whether there is any anomalous behaviour in the dissolution kinetics. *Figure 4-18A* shows the ICP-MS analysis of the As concentration from the anodic dissolution of 2 g of arsenopyrite and loellingite in 50 ml Ethaline at a constant current of 10 mA and at 50°C for 24 hours. It can be seen that initially the concentrations of arsenic in the two solutions is the same which is clearly unusual since loellingite should release twice as much arsenic as arsenopyrite. *Figure 4-17 shows* that the release of iron from the two minerals occurs at similar rates.



Figure 4- 17: ICP-MS analysis data of the concentration of dissolved iron due to anodic dissolution of 2 g marcasite, pyrrhotite, arsenopyrite and loellingite in 50 ml Ethaline at a constant current of 10 mA and at 50°C for 24 hours.

Figure 4-18A shows the removal of arsenic from arsenopyrite and loellingite in Ethaline for the same experiment shown in *Figure 4-17*. The dissolution of loellingite should result in twice as much arsenic in solution as the dissolution of arsenopyrite. Initially the concentrations of arsenic in solution are similar from both solutions but it levels off for arsenopyrite with time. The difference in the dissolution between the two minerals can be gauged by correlating the release of arsenic with the release of iron and this is also shown in *Figure 4-18B*. The dissolution of loellingite releases two arsenic atoms for every iron and a good linear correlation is observed. For arsenopyrite, the slope is significantly lower than the expected value of 1. This suggests that less arsenic is released to solution that would be expected. It can be concluded that arsenic dissolution is more difficult than sulfur which explains why loellingite and arsenopyrite have slower dissolution kinetics than marcasite and pyrrhotite. The Pourbaix diagram in *Figure 4-13* shows the presence of AsS and As₂S₃ as stable forms and these could be produced during the oxidation. This could increase the resistance of the surface and decrease the rate of mineral dissolution.



Figure 4- 18: A) ICP-MS data of the concentration of dissolved arsenic for the anodic dissolution of 2 g of arsenopyrite and loellingite in 50 ml Ethaline at a constant current of 10 mA and at 50°C for 24 hours B) correlation of iron and arsenic solution concentrations.

4.5 Analysis of deposits from solubilized minerals

4.5.1 SEM/EDX technique

The solutions of solubilised minerals were all electrolysed using a copper sheet cathode and an iridium-coated titanium anode for 16 hours. It was found that for all solubilised minerals gave a black deposit on the copper cathode. The morphology (SEM) and composition (EDX) of the deposits are shown in *Figure 4-19*. All of the deposits contained iron but with different amounts of sulfur, arsenic, oxygen and carbon. None of the samples are magnetic, showing that it is not elemental iron which is deposited. This suggests that at least some of the material is an insoluble Fe^{II} complex.

The electropolishing of stainless steel has previously been studied in the same DES, and it was found that when the iron was oxidised through anodic polarisation a brown solid was formed in solution. This was found to be an iron glycolate species and it is proposed that the deposits shown in *Figure 4-19* are likely to contain some glycolates as ligands.⁶⁵ If the carbon and oxygen only came from the glycolate ligand, it would be expected that the C: O ratio would be 1. In all cases, the C: O ratio is < 1, meaning that some iron oxide must also be present. The deposit obtained from loellingite contains a high As: Fe ratio, whereas the S: Fe ratio for the deposit obtained from pyrite is much lower. The loellingite deposit shows a trace (0.33 At %) of Co. This shows that when the mineral dissolves

under anodic polarisation, the metal enters the solution with the sulfur or arsenic still attached but some subsequent exchange clearly occurs in solution.

This confirms the idea that the EQCM result shown in *Figure 3-9* corresponds to the pyrite, possibly forming $[FeS_2]^{2+}$ when it dissolves in the DES. The electrolysis of arsenopyrite results in only As and no S in the deposit, indicating that arsenic is a stronger ligand than sulfur and becomes incorporated into the deposit more easily. For this methodology to be used on a practical scale, the DES would have to be recovered and recycled. This can be done by adding an equal volume of water to the DES. This reduces the viscosity and allows the resultant paste to be filtered. The addition of water precipitates any remaining iron in solution, leaving a colourless aqueous solution of DES. The water can subsequently be removed by evaporation. This has been demonstrated for numerous electrochemical processes on a pilot plant scale (> 500 kg) and is described more fully in the literature.⁶⁶ The EDX data in *Figure 4-19* also shows that the atomic percentage of iron with sulfur deposited is less than that of iron with arsenic, the reason being that iron-sulfide complexes are weaker than those of iron arsenide. XRD analyses were carried out on the deposits obtained in *Figure 4-19* however, the deposits were less than 10 µm in thickness and the only signals were for the copper substrate.



Figure 4- 19: SEM images and elemental compositions (EDX) of cathode deposits obtained after the electrolysis of (A) marcasite (FeS₂), (B) pyrrhotite (Fe_{1-x}S), (C) arsenopyrite (FeAsS) and (D) loellingite (FeAs₂) following electrolysis at a current density of 5 mA cm⁻². The deposition of (A) marcasite (FeS₂) was obtained at a current density of 2.5 mA cm⁻² in Ethaline at 50°C for 16 hours.

4.5.2 Galvanic deposition on Zn as a method of recovering metals

Cementation is a method by which metals can be recovered galvanically from solution i.e. when a more electronegative metal is immersed in a solution containing more electropositive metal ions the electronegative metal is oxidised and the electropositive metal is reduced. This is a method which is commonly applied to the recovery of metals from solution. One issue with it is that frequently when a layer of metal has formed on the substrate surface it prevents sustained deposition so coatings are often thin and not adherent. Cementation has been extensively studied in DESs and it was found that sustained deposition occurs. This has been demonstrated for Ag on Cu and Pb and Cu on Zn.⁶⁷⁻⁶⁹

Figure 4-20 shows the cementation of metals onto zinc sheet from the solutions produced form the anodic bulk dissolution of iron-based minerals in Ethaline at 50°C. It may be
expected that elemental iron would not cement on to zinc but instead any Fe^{3+} would be reduced to Fe^{2+} . The deposits were obtained on zinc in *Figure 4-20* shown below are also shows that all four samples are not magnetic although the deposit obtained from pyrrhotite is magnetic. This is the first time that cementation has been demonstrated for a non-metallic deposit.



Figure 4- 20: Cementation of solution obtained from anodic bulk dissolution of species of marcasite, pyrrhotite, arsenopyrite and loellingite in Ethaline at 50°C.

Figure 4-21 shows the SEM and EDX analyses of galvanic depositions onto the zinc substrate in *Figure 4-20*. The analysis data shows the atomic ratio of each element with respect to that of Fe. It should first be noted that the deposit composition is significantly different from that obtained by electrolytic deposition. Interestingly, no sulfur was observed in any of the deposits and arsenic was only observed for the deposit obtained from loellingite. This is more evidence that the sulfur is not attached to the iron when it dissolves.



Figure 4- 21: SEM and EDX of deposits obtained by cementation onto a Zn sheet of the solutions formed from the anodic dissolution of (A) marcasite, (B) pyrrhotite, (C) arsenopyrite and (D) loellingite in Ethaline over 24 hours at 50°C.

4.6 Conclusion

In this chapter a variety of iron-based minerals (marcasite, pyrrhotite, arsenopyrite and loellingite) were shown to electrochemically dissolve by anodic polarisation into Ethaline. The electrochemical behaviour of the four minerals was found to be controlled by the electrochemistry associated with the arsenic or sulfur moiety and despite marcasite being an isomer of pyrite, the redox properties were found to be significantly different.

The rate of mineral dissolution was measured using chronocoulometry and this was confirmed by measuring the iron and arsenic concentrations in solution as a function of time using ICP-MS. It was found that marcasite was the fastest dissolving mineral followed by pyrrhotite and loellingite and arsenopyrite were considerably slower. The electrochemical signal was proportional to the mineral loading showing that electrochemistry could in principle be used as an assay method. The rates of mineral dissolution did not correlate with the open circuit potentials (OCP) obtained by the paint casting method. Pyrite had the least negative OCP -0.069 V, followed by pyrrhotite at -0.084 V, arsenopyrite at -0.183 V, marcasite at -0.187 V and finally loellingite at -0.192

V. This shows that the dissolution kinetics is not simply governed by the thermodynamics of oxidation.

Although none of the methods used indicated a definite simple dissolution mechanism it is useful to consider a generic mechanism to highlight why the kinetics of dissolution are so complex. Considering first a simple iron sulfur compound undergoing an oxidation.



Scheme 4-1: Potential products produced by the oxidation of iron-sulfur compounds.

The initial oxidation process involves removal of electrons from the S_2^{2-} anion. This releases Fe^{II} into solution. EQCM shows that at higher over-potentials this becomes Fe^{III}. EXAFS and UV-Vis spectroscopy show that the dissolution of pyrrhotite and marcasite do not produce iron tetrachloride anions upon dissolution but rather there is most probably a mixed ligand complex with an oxygen donor involved. Some of the FeCl_x(OD)_y complexes are known to have low solubility and may cause precipitates. Likewise, previous studies in the group have shown that the electrolytic dissolution of iron produces for elemental sulfur forming on the electrode surface under some circumstances but voltammetry also shows that sulfur can be electrochemically oxidised, presumably with some oxygen donor. No oxidised products of sulfur have been detected to date.

UV-Vis spectra of solutions obtained from bulk anodic dissolution of iron- sulfur and iron-arsenic minerals showed that the anodic dissolution of marcasite and pyrrhotite have two absorbance bands at 224 nm and 300 nm, which could be attributed to Fe^{II}- glycolate complexes. By contrast, the UV-Vis spectra of the dissolution product of arsenopyrite

shows that Fe^{II} has a different coordination with bands at 210, 224, 276 and 330 nm the last of which may be associated with and As^{III} –Cl complex. The UV-vis spectrum of loellingite also shows an absorbance bands attributable to $[\text{CoCl}_4]^{2-}$ at 600 and 720 nm.

A comparison of the ICP-MS data for the bulk dissolution of loellingite and arsenopyrite showed that the ratio of As: Fe for loellingite (FeAs₂) was 1.9 which is close to that expected from the stoichiometry. The As: Fe for arsenopyrite (FeAsS) was 0.74 which is considerably below that expected. This could suggest that insoluble arsenic-sulfur compounds are formed on the mineral surface which could account for the slower dissolution rate of the arsenic based minerals.

Galvanic deposition of the solutions obtained from anodic dissolution of iron-based sulfide minerals onto a Zn sheet for 24 hours at 50°C showed that all the deposited species are black and non-magnetic, except for pyrrhotite which showed a magnetic deposit. The analysis of the SEM and EDX data obtained for the galvanically deposited species showed that sulfur does not deposit; however, arsenic is deposited from loellingite. The loellingite sample unfortunately was contaminated with a cobalt containing mineral. While this complicate the analysis as the blue colouration was seen in the dissolved sample, it did also demonstrate the principle that traces of critical metals can be released from ore bodies using electrochemical oxidation.

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Chapter 5: Metal recovery from jarosite

5.1 Introduction

In the previous chapters the electrochemical dissolution of relatively pure iron based minerals has been demonstrated. In this chapter a mixed metal waste material containing iron, zinc, and lead, primarily in the form of sulfides and sulfates is studied to highlight the issues that may arise when designing plant to recover metals from complex matrices. Two cell designs are demonstrated to show how mass transport and space time yield can be optimised.

Metal processing produces large volumes of aqueous waste through the digestion process and the less valuable metals are often separated out using precipitation. This solid residue ends up in tailings heaps and landfill where issues are associated with leaching of heavy metals into the water supply. These types of waste are considered the largest waste streams in Europe. Some of these wastes can be re-used, for example, wastes from copper, zinc and lead processing usually have an acceptable iron content which can be used as secondary source of iron. For instance, 200,000 tonnes per annum of lead slag are used to produce lead from recycling of secondary lead sludge, in addition to neutralization of 280,000 tonnes of those sludge with sulfuric acid.¹ So, large amounts of lead and other metals wastes are discharged to the tailing pots.

The production of zinc is one of the largest metal processing industries. World production of zinc reached was approximately 13.7 million tonnes in 2017.² This is because the importance of zinc in applications such as galvanizing, where 60% of worldwide production of zinc is used to extend the life of steel and increase resistance to corrosion for 10-20 years. As more galvanised products are made, the more natural supplies of zinc ores are consumed, producing increasing amounts of tailings. The concern with these tailings dams is in the heavy metals discharged in to the environment. Therefore, the recovery and recycling of these heavy metal wastes is taking on an increasing importance in reducing pollutants and saving energy. This can also provide an alternative source of metals and reduce the costs of convenient disposal.

Zinc production involves roasting, leaching, conversion, concentrate leaching, purification, electrolysis and melting, as illustrated in *Figure 1-5*. The associated tailings

contain many hazardous metals such as As, Se, Cd, Ti, Hg, Pb and sulfides leading to acid mine drainage and leaching of heavy metals into the ground surface and natural water resources.³ So, the key step towards avoiding these environmental issues and reducing costs of disposal is re-mining these hazardous metals from anthropogenic extractive waste and landfills to achieve a closed-loop approach for maximum recovery of metals.

In this chapter, DESs are used to determine whether they can digest metals from jarosite which is a by-product of the zinc industry. The process by which jarosite is produced is shown schematically in *Figure 5-1*.



Figure 5-1: Flow chart of production Zn involves precipitation of jarosite and other wastes^{4, 5}

Zinc production can use many different sources of zinc ore concentrates but the most important ores are sphalerite (ZnS), and wurtzite ((Zn,Fe)S). Sphalerite provides around 90% of total zinc production and contains 52% Zn, 1-13% Fe, up 3% Pb, and around 31% S, in addition to other trace metals such as Hg, Cd, Cu, Se and Co.⁴ The first main step in the production of zinc metal is roasting the mixture of zinc ore concentrates in two parallel fluidized bed furnaces. This stage involves the conversion of metal sulfides to metal

oxides by heating zinc sulphide ores to an elevated temperature in the presence of air. The metal oxides formed are very soluble in H_2SO_4 .

In this process, Hg and Se are removed from the exhaust gases by a scrubbing process. The sulfur is oxidized to sulfur dioxide and transferred to the associated sulfuric acid plant. However, the iron content leads to conversion to zinc ferrite ($ZnO.Fe_2O_3$), as shown in equations (5-1) to (5-3).

$$ZnS + 1.5 O_2 \rightarrow ZnO + SO_2 \tag{5-1}$$

$$2 \operatorname{FeS} + 3.5 \operatorname{O}_2 \to \operatorname{Fe}_2 \operatorname{O}_3 + 2 \operatorname{SO}_2 \tag{5-2}$$

$$Fe_2O_3 + ZnO \rightarrow ZnO. Fe_2O_3$$
 (5-3)

The second stage is a neutral leaching by the ground calcine obtained from the roasting furnaces. In this stage, the mixture is initially highly acidic with the pH ultimately increasing to about 4-5 in order to convert the solution of ZnO to its soluble ZnSO₄ form which stays in solution. Separation of zinc sulfate (ZnSO₄) from iron can be achieved at about 80°C, as illustrated in equations (5-4) and (5-5) below. In this stage, lead compounds form lead sulfate precipitates which transfer to the filtration process of solid/liquid separation.⁶ However, the remaining, undissolved, zinc ferrite will be treated during the ferrite leaching stage.

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$$
(5-4)

$$Fe_2(SO_4)_3 + 3 ZnO + 3 H_2O \rightarrow 2 Fe(OH)_3 + 3 ZnSO_4$$
 (5-5)

In the ferrite leaching stage zinc ferrite (ZnO. Fe_2O_3) is leached and iron is precipitated as jarosite, as shown in equation (5-6) below.

ZnO.
$$Fe_2O_3 + 4 H_2SO_4 \rightarrow Fe_2(SO_4)_3 + ZnSO_4 + 4 H_2O$$
 (5-6)

The jarosite and leaching residue are filtered, washed, neutralized and discharged into the tailings pond. The solution containing zinc is returned to the neutral leaching stage. The ferrite leaching step uses sulfuric acid (30 to 60 g/L) and is conducted at 100°C.

Natural jarosite is produced in an acid soil environment at pH < 3. It is produced by bacterial and/or air oxidation of pyrite.⁷ The precipitation of iron as synthetic jarosite is a

widely used conversion process in the zinc industry.^{4, 8, 9} This process involves precipitation of high concentrations of ferric ions with the chemical formula of $M_n(Fe^{3+})_6(SO_4)_4(OH)_{12}$ by addition of ammonia in the presence of monovalent alkali cations such as K⁺, Na⁺, NH4⁺, H₃O⁺, Ag⁺ or divalent cations such as Pb²⁺. M represents the monovalent or divalent cation, and *n* is equal to 2 for monovalent cations or 1 for divalent cations.⁷ Jarosite formation occurs by hydrolysis of ferric ions according to equation (5-7) below:

$$Fe_2(SO_4)_3 + (NH_4)_2SO_4 + 12 H_2O \rightarrow 2 NH_4[Fe_3(SO_4)_2(OH)_6] + 6 H_2SO_4$$
 (5-7)

The fourth stage in this process is solution purification, which involves removing of all the valuable metal ions other than zinc such as Cu, Co, Ni and Cd, by three cementation steps with metallic zinc dust and arsenic trioxide, as shown in the following equations.¹⁰⁻¹³

$$Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$$
(5-8)

$$2 \operatorname{Co}^{2+} + 2 \operatorname{As}^{3+} + 5 \operatorname{Zn} \to 2 \operatorname{CoAs} + 5 \operatorname{Zn}^{2+}$$
(5-9)

$$6 \operatorname{Cu}^{2+} + 2 \operatorname{As}^{3+} + 9 \operatorname{Zn} \to 2 \operatorname{Cu}_3 \operatorname{As} + 9 \operatorname{Zn}^{2+}$$
(5-10)

$$2 \operatorname{Ni}^{2+} + 2 \operatorname{As}^{3+} + 5 \operatorname{Zn} \to 2 \operatorname{NiAs} + 5 \operatorname{Zn}^{2+}$$
(5-11)

$$Cd^{2+} + Zn \rightarrow Cd + Zn^{2+}$$
(5-12)

The first cementation step includes precipitation of Cu, while the second removes Co and the remaining Cu and Ni, whereas the last cementation step consists of Cd precipitates. Electrowinning is the fifth stage, which involves reduction of zinc ions in the purified solution to metallic zinc on aluminium cathodes and the recirculation of sulfuric acid to the leaching stage, as shown in the equations below. Finally, the metallic zinc is mechanically stripped from the aluminium cathodes.

At the cathode:	$Zn^{2+} + 2e^- \rightarrow Zn^0$	(5-13)
At the anode:	$\mathrm{H_2O} \rightarrow \mathrm{I_2'O_2} + 2\mathrm{H^+} + 2\mathrm{e^-}$	(5-14)
Total reaction:	$Zn^{2+} + H_2O \longrightarrow Zn^0 + \frac{1}{2}O_2 + 2H^+$	(5-15)

The melting plant is the final stage of this process which consists of melting the zinc sheet to pure molten zinc which is either cast as metallic zinc or moved to galvanizing step for other elements according to the costumers' needs.

The advantages of direct leaching are those of converting sulfide and sulfur species to elemental sulfur rather than sulfuric acid, which has already saturated the markets.⁴ The general chemical reactions of metal sulfides in the process of leaching zinc ores in sulfuric acid under oxidizing conditions in atmospheric reactors are illustrated in the equations below.

$$MS + H_2SO_4 + \frac{1}{2}O_2 \to MSO_4 + H_2O + S^0$$
(5-16)

 $Fe_2(SO_4)_3 + MS \rightarrow 2 FeSO_4 + MSO_4 + S$ (5-17)

 $2 \text{ FeSO}_4 + \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2$ (5-18)

Where M represents a metal such as Zn, Fe Cu, Cd, Pb, Co etc. The above three reactions take place in the presence of iron ions, where the Fe^{3+} in equation (5-17) oxidize sulfide ions to elemental sulfur and themselves reduce to Fe^{2+} . This is then oxidized by oxygen to Fe^{3+} again, as illustrated in equation (5-18). Therefore, one can predict the likelihood that the majority of jarosite includes metal sulfate and metal sulfides compounds, in addition to metal oxides in some extent.

5.2 **Results and Discussion**

5.2.1 Chemical composition analysis of jarosite

This study involved one sample of jarosite and the weight percent of each element determined using the ICP-OES are shown in *Table (5-1)*. The source of the jarosite could not be revealed for confidentiality reasons.

Element	w/w%	Element	w/w %	Element	w/w %
Ag	0.017	Ge	0.002	S	28.5
Al	0.45	Hg	0.01	Sb	0.074
As	0.48	In	0.007	Se	0.0029
Ca	3	Mg	0.22	Si	2.9
Cd	0.05	Mn	0.15	Ti	0.001
Cu	0.078	Na	1.8	F	0.011
Fe	17.4	Pb	4.1	Zn	3.1

Table (5-1): Chemical composition analysis of jarosite obtained by ICP-OES.

The results in *Table (5-1)* show that the total percentage weight of all elements is 62.353%, with the remaining 37.647% being H₂O. The percentage weight of 28.5% of sulfur corresponds to the approximate 9.19% SO₄, in addition to 19.31% of S⁰ and S²⁻. The results in *Table (5-1)* were those supplied with the sample and they contained no information about the variability of the sample. One of the main issues with the sample as provided was the inhomogeneity. To ensure greater homogeneity the sample was processed. The damp 5 kg clay jarosite was divided into three different sections. From Each section approximately 1 kg was taken and these were blended together and dried in an oven at 60°C for one week. This dried jarosite was ground by electric mixer until a fine powder (< 0.5 µm) was produced.

The percentage of chemical composition of jarosite powder used in this work was analysed using ICP-MS. This was completed after fully digesting of 0.1 ± 0.0002 g jarosite in a mixture of concentrated acids, namely 3 ml 29 M HF/5 ml 16 M trace metal HNO₃/ 3 ml 6 M HCl, under stirring and heating at 120°C for 7 days, in addition to sonicating in an ultrasonic bath. Finally, one part of the digested jarosite was diluted 1000-fold using ultrapure deionised water and then injected into the ICP-MS device. *Table (5-2)* shows the weight percentage of Fe, Pb and Zn metals ion in solid dried jarosite sample. This experiment has been performed six times, from which the relative standard deviation (RSD) was obtained. The variability in the iron content is acceptable however the standard deviation of lead and zinc are very high. For this reason experiments were only carried out on single samples in the following analysis and only the trends in metal concentration with digestion time can be used with any certainty. This is a relatively common trait of industrial samples such as this one.

Element	w/w %	RSD %	ppm (mg/kg)
Fe	18.2	0.88	182000
Pb	3.0	1.66	30000
Zn	2.9	2.40	29000

 Table (5-2): Percentage ratio of major elements in solid jarosite and their relative standard deviation

The main issue with the jarosite is the lead content and the separation of this from the other main metals in the sample, namely Fe and Zn. In the next section digestion of the sample was attempted using the paint casting method and the digestion rates of the different components were determined.

5.2.2 Cyclic voltammetry of jarosite and other related components in Ethaline.

In order to understand the qualitative electrochemical behaviour of jarosite, it is critical that the electrochemistry of the pure components of the mixture are analysed by cyclic voltammetry. *Figure 5-2* shows the cyclic voltammogram of the powdered jarosite produced by coating a Pt flag electrode as the working electrode. Samples were prepared in the same manner as that in Chapters 3 and 4 and the CVs were performed in Ethaline at a sweep rate of 10 mV s⁻¹ versus an Ag/AgCl reference electrode and Pt flag as auxiliary electrode. The potential sweep was started at 0 V and swept in an anodic direction to 0.8 V. The potential was then swept to -0.85 V and then back to 0 V. It can clearly be seen that the cyclic voltammetry of jarosite powder has three separate oxidation peaks, which can be assigned as a_I at ca. -0.30 V, a_2 at ca. 0.17 V and a_3 at ca. 0.42 V. In addition, three signals are also observed on the cathodic sweep that can be assigned as c_I for ca. 0.35 V, c_2 for ca. -0.40 V and c_3 for -0.66 V.



Figure 5-2: (A) Cyclic voltammogram of paint casted jarosite (B) cyclic voltammograms of loading different weights of jarosite. Both cyclic voltammograms have performed in Ethaline versus Ag/AgCl reference electrode and using a Pt flag as a counter electrode.

The redox signals at a_3/c_1 in *Figure 5-2A* could be attributed the Fe^{II/III} redox couple as previously illustrated in **chapters 3** and **4**. Assignment of the other signals is difficult without knowing the redox behaviour of the other components. *Figure 5-2B* shows the cyclic voltammograms of loading different weights of jarosite on a Pt flag in Ethaline only 10 mg of jarosite were used a different CV was obtained than at higher loadings. When 20 to 100 mg of jarosite were loaded on the electrode a constant shape of voltammogram was observed. This is another indication of the inhomogeneity of the sample.



Figure 5- 3: Cyclic voltammogram of solid powder of pure (A) Li₂SO₄, (B) PbSO₄,
(C) FeSO₄.7H₂O and (D) ZnSO₄ painted on to a Pt flag as the working electrode versus an Ag/AgCl reference electrode and Pt counter electrode in Ethaline

Figure 5-3 shows the cyclic voltammograms paint cast samples of (A) Li_2SO_4 , (B) PbSO₄, (C) FeSO₄.7H₂O and (D) ZnSO₄ painted on to a Pt flag electrode in Ethaline. In the previous chapters the dissolution of the sulfides and arsenides has been correlated to dissolution of the anion, however, the oxidation of sulfate does not occur under the conditions of the experiment. *Figure 5-3A* shows that there is a small reduction peak for sulfate from Li_2SO_4 and some associated reoxidation of SO_4^{2-} . Since Li_2SO_4 will have little or no conductivity, the signal probably comes from the chemical dissolution of some of the salt from the paste. The same is therefore true for the other sulfates. FeSO₄.7H₂O has a significant solubility and the signal for the Fe^{II}/Fe^{II} redox couple can be clearly seen. Although ZnSO₄ is also readily soluble, the peak at -0.4 V was assigned as being due to under-potential deposition. Bulk deposition is not generally observed for Zn when the solution concentration is less than 0.05 M. Cihangir recently showed that this was due to the formation of a passivating film of zinc glycolate forming on the electrode surface.¹⁴

It is interesting that lead sulfate has some solubility in Ethaline and the characteristic peaks for lead deposition and stripping are observed in *Figure 5-3B* at -0.66 and -0.5 V respectively. The peaks at -0.21 and -0.12 result from the deposition and stripping of a Pt-Pb alloy and have been observed recently for the paint casting of galena (PbS).¹⁵ *Figure 5-3D* shows the lowest redox signals (1/2 to $1/10^{\text{th}}$ the current of the other samples) which is not surprising given the low solubility of zinc sulfate.

The highest anodic peak current in *Figure 5-2A* is for a_2 and cannot be associated with any of the sulfate-based species but must instead be associated with a sulfide-based species. As analogous signal was recently reported for the oxidation of galena (PbS) in Ethaline.¹⁵ Therefore, it can be attributed to the oxidation of a metal sulfide present in jarosite such as PbS, ZnS and FeS.¹⁶⁻¹⁸ The cathodic peaks at c_2 and c_3 at ca. -0.40 V and ca. -0.66 V, respectively, were found to be very similar to peaks in the cyclic voltammogram of PbS powder painted onto a Pt electrode in Ethaline, where c_2 at -0.4 V is indicative of the reduction of sulfide species and c_3 at -0.66 V is ascribed to the deposition of lead.¹⁵ There is no doubt that the highest oxidation peak at a_2 in the voltammogram of jarosite can be attributed to the oxidation of sulfur or a sulfide species which is not surprising given the large percentage of S in the jarosite sample (28.5%).

5.3 Electrochemical dissolution of jarosite in Ethaline

The chemical dissolution of jarosite produced as a by-product of mining zinc ores has been studied extensively in the literature as an important source of metals.^{8, 19, 20} However, most of this research has focussed on leaching jarosite using strong acidic media such as HCl, H₂SO₄, HF, HNO₃ and acetic acid. In spite of the use of strong acids to increase metal solubility in jarosite, it is difficult to leach these metals due to presence of high concentrations of soluble impurities resulting in poor selectivity, in addition to the high acid consumption. Palden *et al.* proposed that by replacing aqueous acids with ionic liquids, such as quaternary ammonium chloride salts ([A336][Cl]) or quaternary phosphonium chloride salts ([C101][Cl]) equilibrated with aqueous HCl, the chemical leaching of jarosite to produce Zn and Pb ions can be significantly improved.²¹ The high reactivity and selectivity that can be achieved for leaching these metal ions using ILs can be attributed to the high affinity of non-hydrated anions (organic anions) to binding with metal ions.²¹

DESs could also be used as lixiviants for jarosite in both chemical and electrochemical dissolution routes. Ethaline has previously been used to digest zinc and lead oxides from electric arc furnace (EAF) dust. It was shown that the oxides dissolves quite quickly in Ethaline to which oxalic acid has been added. It should, however be noted that zinc and lead oxides are relatively Brønsted basic compared to the sulfates and sulfides.²²

The aim of this study is to test 3 cell designs to highlight the aspects which control the dissolution of the jarosite samples. The basic aspects of these cells are listed in *Table (5-3)*.

Cell	Cell 1		3	
Design				
Separator	None	Filter paper	Glass frit	
Ethaline mass / g	56.5	84.75	847.5	
Jarosite mass / g	4	2	500	
Time/ hour	24	36	312	
Current/mAm	20*	20*	29 (initial)	
Voltage/V	2.5 (initial)	2.6 (initial)	2.25*	

Table (5-3): Three cell designs and their different parameters (Red terminal is the anode and black is the cathode. refers to constant parameter*

5.3.1 Cell 1

Solid jarosite samples were tested for their chemical and electrochemical dissolution in Ethaline. Chemical dissolution was carried out by putting 4 g of jarosite in 50 ml Ethaline at 50°C for 24 h with constant stirring in a sealed beaker. Electrochemical dissolution of jarosite was carried out with 4 g of jarosite in 50 ml Ethaline but an iridium-coated titanium mesh was inserted into the jarosite and 20 mAm constant current was applied for 24 h. At the end of this time the solid residues were filtered washed with water and

analysed. ICP-MS was used to measure the Fe, Pb and Zn metal ratios in Ethaline before and after digestion and the results are shown in *Table (5-4)*.

Table (5-4): Content of Fe, Pb and Zn in 4 g of jarosite in the solid sample before after chemical and electrochemical dissolution of jarosite in 50 ml of Ethaline at 50 °C for 24 hours

Process	Metal content/ ppm			
1100055	Fe	Pb	Zn	
Metal content in Jarosite (mg/kg)	182000	30000	29000	
(g of metal in 4 g of sample)	(0.72)	(0.12)	(0.116)	
Chemical dissolution in Ethaline (mg/L)	425	168	367	
(% of solid removed)	(3%)	(7%)	(16%)	
Electrochemical dissolution in Ethaline (mg/L)	9066	384	2288	
(% of solid removed)	(63%)	(16%)	(98%)	

The results show that the dissolution of iron is 21 times faster than through straight chemical dissolution. Lead is twice as fast and zinc is six times as fast. Given that the original sample contained 0.72 g of Fe it can be seen that chemical dissolution was only able to extract 3 % of the original iron whereas electrochemical dissolution could extract 63% of the iron. The extraction of lead was less impressive with only 16% of the original metal removed, whereas 98 % of the zinc was removed through electrochemical dissolution compared to 16% removed chemically. What is unusual about these results is the significant effect that electrochemical dissolution has upon the dissolution of zinc. Given that both zinc sulfide and zinc sulfate are not very electrochemically active, it is unusual to see such a significant effect of an electrochemical potential applied across the sample. One explanation for this could be that the zinc is present as a double salt i.e. Fe(ZnSO₄)₂ which is only released when the iron is oxidised and hence solubilised.

In aqueous solutions, the speciation of sulfur is strongly governed by the pH of the solution and the cell potential. At low pH, the product is mainly the S⁻ and/or S²⁻ whereas at pH 7, SO_4^{2-} dominates, as illustrated in the Pourbaix diagram of sulfur in the literature.^{23, 24} Recently, Abbott *et al.* showed that galena powder (PbS) paint casted of onto a Pt flag in Ethaline (chloride ions dominate) leads to the formation of soluble lead and sulfur species in Ethaline.¹⁵ The sulfur species was proposed to be a polyanion.

5.3.2 Cell 2: Kinetics of electrochemical dissolution of jarosite in Ethaline

A major issue in dealing with the selectivity of electrochemical dissolution of complex mixtures such as jarosite is whether all of the components dissolve at the same rate or whether one or more metals dissolve preferentially whilst precipitation take place for others. Ideally, selective dissolution can be used where the potential difference for oxidation between the components of the mixture is wide enough to separate, as occurs in alloys.^{25, 26} To examine this issue further, the electrochemical leaching kinetics of jarosite in Ethaline were studied.

The kinetics of the anodic dissolution of jarosite was examined in Ethaline using the 3D printed plastic acrylonitrile butadiene styrene (ABS) cell used in Chapter 4 (*Figure 4-10*). Jarosite powder (2 g) was pasted on the iridium-coated titanium mesh anode, which was set up inside the chamber of the plastic cell with filter paper membrane. A constant current of 20 mA was applied between the two electrodes which had an immersed surface area of 2 cm² in Ethaline for 36 hours. The metal ion concentrations were determined using ICP-MS, where 50 μ L samples of solution were collected using a micropipette every four hours. The samples were dilute 1000 fold using 2% traced HNO₃.



Figure 5-4: : Electrochemical leaching kinetics for Fe, Pb and Zn from 2 g of jarosite in 75 ml Ethaline at 20 mAmps constant current at 50°C for 36 hours.

Table (5-5): Content of Fe, Pb and Zn in 2 g of jarosite in the solid sample before after chemical and electrochemical dissolution of jarosite in 75 ml of Ethaline at 50 °C for 36 hours

Process	Metal content/ ppm			
	Fe	Pb	Zn	
Metal content in Jarosite (mg/kg)	180000	30000	29000	
(g of metal in 2 g of sample)	(0.36)	(0.06)	(0.058)	
Electrochemical dissolution in Ethaline (mg/L)	784	32	610	
(% of solid removed)	(16%)	(4%)	(79%)	

Figure 5-4 shows that the metal concentration had reached a steady state in solution after 36 h. These concentrations are significantly below the saturation concentrations of metals in solution so it cannot be because the solutions are saturated. *Table (5-5)* converts the limiting metal concentrations to the percentage of metal that was in the original jarosite sample so the limitation cannot be due to the digestion of the whole sample. It is also evident that the amount of metal extracted from the sample was significantly less than that expected in the previous bulk electrolysis experiment. Given that this experiment had a larger solvent: mineral ratio it must be a factor of the experimental set up which limits the metal dissolution.

Comparing the conditions for Cell 1 with those of Cell 2 it can be seen that apart from the DES: jarosite ratio, the main difference between the cells was that a filter paper separator was used in Cell 2 to separate the anode from the cathode. While this should not significantly affect the digestion of the mineral it will add a resistance to the cell and it was noted that during the electrolysis the current dropped over the course of the experiment. Looking at the filter paper membrane after the experiment it was noted that it was heavily coloured with iron-based precipitates (*Figure 5-5A*) which will decrease ion transport through the membrane increasing the resistance and decreasing the cell current. It is probably that this was the cause of limiting concentration of metal in solution. Once the metal dissolves in the anodic compartment it will diffuse from the area of high metal concentration to one of lower metal complex precipitate the driver for diffusion is decreased. It could also account for the lower than expected mass of iron in solution due to the physical precipitation of metal complex in the membrane blocking the pores. It was

found that the mass of the filter paper had increased by about 0.3g during the experiment confirming this idea.

Figure 5-5B shows samples of Ethaline containing the same mass of metal sulphates. It can be seen that the zinc sulfate is fully dissolved, iron sulfate is partially dissolved and lead sulfate is practically insoluble.



Figure 5- 5: (A) shows the filter paper used in the electrolytic cell 2, (B) shows solutions prepared by dissolving ZnSO₄, FeSO₄ and PbSO₄ in Ethaline.

Previous studies by Hartley using a filter paper membrane in an experiment to separate copper from a copper-indium-gallium alloy found that copper was reduced on the surface of the filter paper to form dendritic crystals.²⁷ This was thought to occur because paper contains sugars which can act as reducing agents.

5.3.3 Recovery of metals using electrowinning and cementation.

As shown above the dissolution rate of jarosite in Ethaline was significantly improved using electrolysis compared to chemical dissolution. Once the metals have dissolved in solution they need to recover. As it was shown in *Figure 1-3* in **chapter 1** the recovery of digested metal ions can be achieved by: electrowinning cementation, precipitation and ion exchange. In this section, the electrowinning of metal ions produced by anodic dissolution of jarosite in Ethaline followed by deposition onto a copper substrate as a cathode will be explored. Additionally, the cementation of anodically dissolved metal ions onto a zinc sheet as a sacrificial metal will also be examined. In a previous study by Abbott *et al.* electric arc furnace dust was chemically dissolved in Ethaline containing oxalic acid.²² The matrix contained Pb, Cd, Fe, Zn, Al and Cu and was different to the jarosite sample in that it contained high concentrations of sulfides and sulfates rather than oxides, as was the case with the EAF dust.

In the EAF dust experiments the oxide dissolved almost all of the zinc oxide due to the low pH. The majority of the lead and cadmium were also dissolved. Dissolution of the iron was much slower and aluminium and calcium oxides were almost totally insoluble. The study recovered the lead and cadmium from solution using zinc powder and achieved almost quantitative removal of the metals in 24 h. The group then used electrowinning to recover the zinc from solution but they found that this was a slow and inefficient method. Alternatively they added a dilute ammonia solution to the DES and found that they could precipitate the zinc much more rapidly and efficiently although this did necessitate the regeneration of the liquid.

Electrowinning is the application of a fixed voltage or current to a cell with the aim of recovering metal on the negatively polarised electrode. This is considered a non-spontaneous reaction process due to the driving force being by applied by a voltage between the electrodes.²⁸ By contrast, cementation is a galvanic deposition (spontaneous process) which involves immersing a sacrificial metals with high negative redox potentials in solutions containing the metal ions.²⁹ Metal ions in solution can be reduced and deposited as a solid on to a scarified metal which is subsequently oxidized.²² In principle, this method can be applied to recover dissolved metals ions in ILs and DESs. Abbott *et al.* described how a galvanic coating of silver metal can be obtained by using a copper surface as a scarified metal in DESs, in addition to deposition of copper metal on aluminium and in the recovery of lead onto zinc.^{22, 30} Generally, this galvanic deposition, in the example of lead ions in DESs, is driven by the difference between the redox potential of Pb^{2+/0} ions and Zn^{0/2+} in DESs, as illustrated in equation (5-19) below.

$$Pb^{2+}(sol) + Zn(s) \leftrightarrow Pb(s) + Zn^{2+}(sol)$$
(5-19)

Figure 5-6 shows electrochemical deposition of digested jarosite species on to a copper substrate as a cathode in Ethaline, and also the galvanic deposition of a similar sample onto an immersed zinc sheet. In the first experiment 3.1 mg of a black deposit was recovered onto a copper substrate, which was found to have a weak attraction to a magnet. However, the mass of the galvanic deposit was less than the starting mass due to inefficient mass recover as zinc will slowly react with Ethaline (see below).

The colour of the solution changes after electrowinning the dissolved jarosite solution, but the solution in which cementation occurred did not notably change colour, as shown in *Figure 5-7*. This clearly shows that electrowinning is more efficient at extracting metal ions than cementation. It also appears as if cementation reaches a limiting thickness of material recovery. This was not the case with the EAF dust experiments where balls of lead which were several mm in diameter were recovered from solution using fine zinc dust. It must be concluded that either the high iron concentration or the presence of sulfide or sulfates is poisoning the cementation process.



Figure 5- 6: Electrochemical deposition of jarosite species onto Cu substrate at 3.33 mA.cm-2 (on the left) and galvanic deposition of these species onto Zn sheet substrate (on the right). Both depositions were run for 24 hours at a constant temperature of 50°C in Ethaline.



Figure 5-7: The colour of the solution obtained after electrochemical deposition of jarosite species in Ethaline onto a copper sheet (on the left), and comparison of colour solutions obtained after galvanic deposition of jarosite species onto a zinc sheet in Ethaline

Figure 5-8 shows the SEM analysis of the jarosite species deposited onto copper (electrochemically) and onto zinc sheet (galvanically), as shown in *Figure 5-6*. The results observed that the atomic ratio of the metal ions deposited onto the copper substrate were 18.7 Fe: 1.2 Zn: 1 Pb: 0.5 S. This is similar to the elemental ratio of the metals in the jarosite sample 4.3 Fe: 1 Zn: 1 Pb although it does show that it is less efficient at winning Pb back from solution than Fe.

Galvanic deposition on to a zinc sheet resulted in an elemental ratio of 3.9 Fe, 1 Pb: 1 S: 0.5 Cu, and 0.4 Cd which is similar to that obtained for the original jarosite sample. This shows that cementation is not selective for Pb over Fe. The previous work by Abbott *et al.* extracting Pb from EAF dust found that Pb was efficiently extracted from a mixture of Ethaline with oxalic acid. The reason behind this is probably because the chemical dissolution of lead oxide resulted in negligible iron in solution. The EAF dust also contained negligible sulfate in solution which meant that there was almost no precipitation of lead from solution as PbSO₄ which is almost certainly the case for jarosite.

Figure 5-6 also shows that the deposit obtained through cementation was much thinner than that obtained using electrolysis. Cementation of metals on a range of substrates has shown that sustained deposition can be obtained with thick metallic deposits being obtained. The thin deposits obtained here could be due to the high sulfur content

producing a poorly conducting deposit which is not self-sustaining as it effectively produces an insulator on the zinc surface.

Figure 5-8 shows the dark brown colour of the solution following dissolution resulting from a high iron content in the liquid. When this solution was electrolysed to remove the metal ions, solution changed colour to an orange-brown. Cementation, however, did not change the solution colour significantly as a much smaller iron concentration was removed from solution.



Figure 5-8: SEM analysis of jarosite species in Ethaline deposited electrochemically onto a copper substrate (left), and the galvanic deposit on a zinc sheet (right)

5.4 Cell 3: Scaled up jarosite processing trials

The previous sections have shown that small scale anodic dissolution of jarosite in a static cell in Ethaline enables the dissolution of Fe, Pb and Zn at a significantly faster rate than would be achieved using chemical dissolution. The fact that the liquids are viscous and the volume of liquid is relatively large means that the dissolution rate will be compromised by mass transport. Scaling up this technology would require a large volume of DES which would make the process expensive. In the first version of the experiment 4 g of Jarosite were used with 50 ml of Ethaline: a mass ratio of solvent: mineral of almost 14:1. This is typical for the ratios that would be used for hydrometallurgical processes. In this section a scaled up cell will be tested where 500 g of jarosite will be extracted using 750 ml of Ethaline; a solvent: mineral ratio of 1.7:1. As will be discussed later in this chapter rations of less than 1:1 should be possible with different cell designs. The aim behind the larger scale cell was to demonstrate that larger throughputs of samples could be achieved through innovative cell design. Stirring a cell with a large volume of lixiviant in would cause the mineral to be distributed throughout the liquid and hence lose contact

with the anode. Using a thick paste would enable the mineral to be kept in contact with the electrode at all times. In a novel twist it was decided that rather than trying to stir the solution with a mechanical stirrer the electrode would be used as the stirrer. In the first incarnation of this idea it was practically simpler to put the digestion cell on an orbital shaker and maintain both electrodes in a fixed position, as shown in schematic diagram in *Figure 5-9*.



Figure 5- 9: Schematic diagram showing the dynamic electrochemical dissolution of 500 g jarosite in 750 ml of Ethaline at 2.25 V constant voltage for 13 days

In cell 2, the use of a filter paper membrane was seen as an issue due to the formation of precipitates. In cell 3 a porous glass frit (2 μ m pore size) was used to decrease the formation of precipitates. The experiment was run for 13 days to see how much metal could be digested. The copper cathode was changed every 2 days and the mass and elemental composition was quantified using EDX. *Figure 5-9* shows a schematic of this new cell design, where this cell design is constructed of two glass beakers, one inside the other to form the electrolytic cell. The outer beaker contains 500 g of jarosite at the base with 750 ml of Ethaline In practice, less DES could have been used and it was only the necessity to submerge the cathode that required so much DES. The anode was a large

surface area iridium oxide coated titanium mesh with roughened edges to help stir the jarosite slurry during electrolysis. The anode was fixed to the wall of inner beaker by using Kapton tape. The inner beaker was clamped in place to remain static during the experiment. The electrochemical deposition was carried out on a copper cathode in the smaller cell and cementation was performed on a zinc sheet. The aim was to cement the lead and electrowon the zinc and iron. A heater belt was fixed on the wall of outer beaker and set to 50°C. Further details of this cell design can be seen in *Figure 2-4* of chapter 2.

Table (5-6): Content of Fe, Pb and Zn in 500 g of jarosite in the solid sample before after electrochemical dissolution of jarosite in 750 ml of Ethaline at 50 °C for 13 d

Process	Metal content/ ppm		
	Fe	Pb	Zn
Metal content in Jarosite before electrolysis (mg/kg)	180000	30000	29000
(g of metal in 500 g of sample)	(90)	(15)	(14.5)
Metal content in Jarosite after electrolysis (mg/kg)	114000	15000	10000
(g of metal in 291 g of residue)	(33)	(4.4)	(3)
% metal removed	63%	71%	80%

Table (5-6) shows the Fe, Pb and Zn content in 500 g of jarosite in the solid sample before after electrochemical dissolution (determined using ICP-MS) of jarosite in 750 ml of Ethaline at 50 °C for 13 d. It can be seen that the dissolution of zinc is similar to that obtained using cell 2, the dissolution of lead is however, much higher.

An accurate and total mass balance is not possible in this experiment due to the complexity of the experiment. This is shown schematically in *Figure 5-10A*.



Figure 5-10: (A) Schematic diagram showing the mass balance of metals in the different phases following dissolution (B) photograph of the cell at the end of the experiment.

The metal which was in the jarosite dissolves in the anodic compartment producing a green solution (M_2) . Some of the metal permeates the frit into the cathodic compartment (M_3) . There is obviously a supersaturation still occurring near the frit as there is a fine suspension which could not be recovered by filtration (M_4) . Some of the metal is recovered on the cathode (M_5) and some is recovered on the sacrificial zinc electrode (M_6) . The dissolution of the zinc is not 100 % efficient and so more zinc is added to the solution than was present in the jarosite sample.

Figure 5-10B shows that the anodic and cathodic cells are different colours which almost certainly comes from the different oxidation states of iron. It is likely that although the iron dissolves as an Fe^{II} species, it is further oxidised to Fe^{III} which is shown in *Figure 5-11* using the UV-vis spectra of the solutions in the two compartments and comparing them with ferric chloride in Ethaline.



Figure 5-11: A comparison of UV-Vis spectra for anodic dissolution of jarosite in Ethaline for 13 days with dissolved metal chloride salts of FeCl₃, PbCl₂ and ZnCl₂ in Ethaline.

The electrolyte solution in the cathodic compartment is yellow arising from the reduction of Fe^{III} to Fe^{II}. This assignment can also be seen from *Figure 5-10B*. The cathodic and anodic compartments were sampled every two days during the experiment and *Figure 5-12* shows that the cathodic compartment remained a pale orange/ brown colour throughout the experiment whereas the anodic compartment started out orange/ brown and turned increasingly green as the experiment continued. This shows that the efficiency of the experiment decreased as it progressed. Initially the iron dissolved as Fe^{II} but with time it was oxidised to Fe^{III}. This would require additional energy to then reduce back to Fe^{III} and the Fe⁰ in the cathodic compartment. However, Fe^{III} was observed to be a chemical catalyst for the dissolution of pyrite in Chapter 3 and this could enhance the rate of metal dissolution.



Figure 5- 12: A comparison of collected electrolytic solutions from the oxidative zone (before passing the glass membrane) and those collected from reductive zone (after passing the glass membrane)

ICP-MS was used to determine Fe, Pb and Zn concentrations in these solutions and the results are shown in *Figure 5-13*. Zinc ion concentrations are always greater than those of other ions during the experiment due to the higher solubility coupled with galvanic deposition of other metals onto outer layer of the zinc sheet which led to it dissolution, as well as anodic dissolution of the zinc in the jarosite.

The metal concentrations in the cathodic region are considerably lower than those in the anodic region as the cathodic region is constantly being depleted of metal through electrolysis and cementation.



Figure 5-13: concentration of Fe, Pb and Zn ions produced from anodic dissolution of 500 g of jarosite in 750 ml of Ethaline in both the anodic region (bottom) and cathodic region (top) for the scaled-up cell during 13 days of electrolysis.

The concentrations of metals in both compartments remained roughly constant throughout the 13 days of the experiment except for Zn which increased half way through the experiment in the cathodic compartment. This could be due to a change in the efficiency of the cementation process with more Zn being released into solution. An increase in the Fe^{III} concentration coming from the anodic compartment will cause an increase in the rate of zinc dissolution.

Figure 5-14 shows the cyclic voltammograms of the collected solutions from the anodic (lower) compartment and cathodic (upper) compartment of cell 3 after 13 days of electrolysis. The cyclic voltammogram shows a significant difference between the samples from the two compartments. In the anodic compartment where there is a significantly higher metal ion concentration clear redox waves for the Fe^{III/II} couple and

that Pb^{II/0} are observed. However, the cathodic compartment has a much lower metal ion concentration and redox signals are much smaller and no signals can be distinguished.



Figure 5- 14: Cyclic voltammogram for electrolytic solutions collected from oxidation zone (black) and that reduction zone (dash red) of electrolytic cell of jarosite in Ethaline after 13 days using Pt disc as working electrode against Ag/AgCl as a reference electrode and Pt flag as a counter electrode

The concentration of Zn in the anodic compartment after 13 days corresponds to 3.75 g whereas that in the cathodic compartment is 0.76 g (assuming that approximately half the Ethaline was in each compartment). It was not possible to do a full mass balance as it would be difficult to dismantle the cell and retain the different metal concentrations in their respective compartments so *Figure 5-13* can only be used to show trends. The increase in the mass of the copper cathode was only 3.76 g over the entire 13 days of the experiment and the average mass ratio was Fe 1.4: Zn 2.7: Pb 1 (53 wt % Zn) which would account for less than 2 g of Zn.

According to *Table (5-6)* the initial jarosite sample started with 14.5 g of Zn. Analysis of the residue after 13 days showed that 11.6 g were removed of which 3.75 g was in the anodic compartment and 0.76 g was in the cathodic compartment. If only 2 g can be accounted for in the electrodeposition experiments then 5.09 g remain unaccounted for.

Some will be in the residue on top of the frit which could not be collected and some was still precipitated in the glass frit. While an accurate mass balance could not be achieved, the experiment has shown a number of issues about cell design which was the main aim of this chapter.

5.4.1 Electrowinning vs cementation

The previous study using EAF dust showed that cementation was an effective method to separate iron oxide and zinc oxide from lead and cadmium oxide. Attempting this using jarosite showed different results.

Figure 5-15 shows the copper cathodes of the material electrowon from solution following the anodic dissolution of jarosite. The deposits are black and dense in all cases and similar to those shown in *Figure 5-6*. *Table (5-7)* shows that the masses obtained on each surface were relatively similar with time at roughly 0.6 ± 0.2 g for each 2 day electrolysis.

Figure 5-15 also shows the zinc sheets used to galvanically cement metal from the same Ethaline solutions. It can be clearly seen that these deposits have different morphologies and colours. *Table (5-7)* shows that the masses obtained on each zinc sample. In most cases the mass of the sample at the end of the experiment was less than that at the start. If the process was 100 % efficient and iron was being exchanged for zinc then a slight decrease might be expected but since a significant proportion of the exchange was with lead a small increase in mass might be expected.


Figure 5-15: Shows jarosite electrowon dissolved species in Ethaline on to copper sheets cathodically at ~1.55 mA.cm⁻² and zinc sheets galvanically for 13 days.

cementation.							
	Time /day	Deposition weight	Deposition weight				

Table (5-7): net weight of deposits onto 6 copper cathodes and 5 zinc sheets used for

Time /uay	Deposition weight	Deposition weight	
	onto Cu plates/g	onto Zn sheets/g	
2	0.43	-0.039	
4	0.56	-0.016	
6	0.87	-0.005	
8	0.54	0.0005	
10	0.72	0.0006	
13	0.50		

For the case of EAF dust recovery, the exchange of lead for zinc was sustained but jarosite appears to reach a limiting thickness which was relatively thin $> 1 \,\mu$ m. The reason behind this could be due to the formation of a passivation layer from metals oxides or metal which are non-conductive. This could also be the reason that the electrodeposited layers reach a limiting thickness.

SEM and EDX analysis was carried out on the copper and zinc sheets shown in *Figure 5-15* and the results are shown in *Figures 5-16 and 5-17*. The metals present are expresses in the molar ratios of the elements. For the electrolysis experiments, zinc was recovered most in the electrodeposits which may be expected since it is the highest concentration in solution, however, its reduction potential is the most negative. Given that the elements are present in the solid in the ratio 6 Fe: 1 Zn: 1 Pb it is interesting to note that the recovered elemental ratio is 1.4 Fe: 2.7 Zn: 1 Pb. This shows that there is a significant concentration of Zn and Pb over iron by this method.



Figure 5- 16: SEM images and EDX analysis for ratio of jarosite species in Ethaline deposited on to copper sheets as a function of time (in days).

Elemental analysis shows that there is significant oxygen in the deposit which correlates well with the iron content which may provide evidence of an iron oxide passivating the metal surface.



Figure 5- 17: SEM images and EDX analysis of metal species cemented on to zinc sheets as a function of time in days

Elemental analysis of the Pb: Fe ratio of the cemented product shows that in most cases the lead content is larger than the iron content which again shows that cementation demonstrates a selectivity for elemental recovery. The greater success observed with EAF dust could be due to speciation or concentration of metals in solution. EAF dust dissolution resulted in a lower concentration of iron in solution and the only anion present was chloride. The high sulfate concentration in jarosite could lead to other solution processes such as the precipitation of lead sulfate.

5.4.2 Precipitation Processes

It is well known that these lead compounds are sparingly soluble or insoluble in aqueous electrolytes. However, these same compounds have an acceptable solubility in ChCl/urea of DES, as previously demonstrated by Abbott *et al.* and Liao *et al.* in separate studies.^{16, 22, 31} The presence of sulfate in solution could cause the re-precipitation of some metals once they had been dissolved. To investigate the extent of this process the jarosite sample was analysed before and after digestion using SEM, EDX and XRD.

Figure 5-18 shows the SEM and EDX analyses of jarosite residue stuck onto carbon conductive adhesive tape before and after electrolysis in Ethaline for 13 days. The results show that the average atomic weight percentages for Fe, Pb and Zn over multiple probe regions on the jarosite specimen before electrolysis in Ethaline were about 19.7%, 3.1% and 2.74%, respectively which ties in with the ICP-MS results above. After digestion in Ethaline for 13 days, these were found to be 17.8%, 2.1% and 0.87%, respectively. The sample prior to digestion is relatively uniform and not particularly crystalline however, after digestion numerous long crystals had formed. Elemental analysis of a small spot showed that these contained lead, sulfur and oxygen in roughly the correct ratios to be PbSO₄.



Figure 5-18: A comparison of SEM images and EDX charts of jarosite residues before electrolysis (left) and after electrolysis (right) in Ethaline for 13 days.

XRD analysis of the sample before and after digestion showed a complex spectrum, however distinct signals for iron and lead sulfate could be detected, as shown in *Figure 5-19*. It was also evident that the signals for lead sulfate had increased for the sample post electrolysis. This seems to suggest that the dissolution of jarosite solubilises sulfate into the DES which interacts with lead ions also discharged into the solution and the high

lattice energy of lead sulfate results in it being deposited in the cell at the end of the experiment. This could ultimately explain why lead is less successfully cemented from solution than was seen in an all chloride based medium.



Figure 5- 19: Normalized XRD spectra of jarosite residue before and after anodic leaching in Ethaline at +2.25V for 13 days. The assignment of XRD peaks for FeSO₄ and PbSO₄ are taken from the literature.^{8, 32, 33}

The change in speciation of the solid jarosite can be investigated using cyclic voltammetry of jarosite residue paint-casted on a Pt flag pre- and post-electrolysis in Ethaline. *Figure 5-20* shows the voltammograms of the sample pre- and post-electrolysis and it can clearly be seen that the sample before digestion contains a significant signal for the sulfide oxidation which was demonstrated for the various metal sulfides in Chapters 3 and 4. The residue obtained post electrolysis showed negligible oxidation of the sulfide and the redox signal was dominated by the Fe^{II}/ Fe^{III} redox couple which is probably undissolved iron sulfate as shown in the XRD in *Figure 5-19*.

In cell 2 the filter paper was seen to be an issue because iron (and presumably also lead) salts precipitate in the pores making further electrolysis inefficient. It had been thought that a glass frit with 2 μ m pores would be sufficiently large so that the glass would not block. *Figure 5-21* shows photographs of the two compartments after 2 days and it is

evident that the frit is strongly coloured and a precipitate formed above the frit on the cathodic side of the frit. This means that the same issue with creating a diffusional barrier would exist when a glass separator was used in the cell.



Figure 5- 20: Cyclic voltammograms of 20 mg jarosite residue painted onto a Pt flag as the working electrode before (black) and after (red) anodic dissolution for 13 days in Ethaline against an Ag/AgCl reference electrode and Pt flag counter electrode in pure Ethaline



Figure 5-21: Images showing the precipitate that settled on to the upper surface of glass frit membrane during electrolysis

5.4.3 Space-time-yield

The results in *Tables (5-4), (5-5) and (5-6)* show that the different cell designs to not significantly change the extraction efficiencies of the different elements but it is useful to calculate the amount of material dissolved per unit time per unit volume (the so called space-time yield). Taking the three cells shown in *Table (5-3)* the space time yields for the different elements can be compared (*Table (5-8)*).

Space time yield is another important factor which can be effected on to reaction rate. This can be defined as a mass of metal dissolved per unit volume per unit time at specific temperature and pressure.³⁴ Thus, the comparison space time yield of the dissolved ions in electrolytic solution are tabulated in *Table (5- 8)* below.

Table (5-8): Shows the comparison data of space time yield of the three different cells.

Metal	Cell 1	Cell 2	Cell 3
	$g.ml^{-1}.h^{-1}$	$g.ml^{-1}.h^{-1}$	$g.ml^{-1}.h^{-1}$
Fe	3.8 x 10 ⁻⁴	2.2 x 10 ⁻⁵	2.4 x 10 ⁻⁴
Pb	1.6 x 10 ⁻⁵	8.9 x 10 ⁻⁷	6.8 x 10 ⁻⁵
Zn	9.5 x 10 ⁻⁵	1.7 x 10 ⁻⁵	5.0 x 10 ⁻⁵

The data above show that the space time yields are not significantly different between cells 1 and 3 although both cells are significantly larger than those for cell 2. This shows that the biggest issue in the cell design is the separator which can create diffusional barriers. Stirring does not appear to cause a significant increase to the space-time yield although cell 3 does show that it is possible to work with a significantly lower ratio of lixiviant to sample than would normally be the case in classical hydrometallurgy, which is clearly important when working with a solvent which is more expensive than aqueous solutions. It is clear that this approach would never be economically viable for base metals such as lead, iron and zinc but to some extent the aim was only to highlight some of the issues associated with cell design for scaled up paint casting.

Using simple Ethaline as the lixiviant produces a high concentration of iron to be leached into the DES and this appears to limit the efficiency of the cementation step and the electrolytic winning of metals. An improvement may be to use citric acid as an additive which is good at chelating iron and may results in a lower iron yield and improve the cementation of lead as was observed with EAF dust.

5.4.4 Improvements in cell design.

The issue with the separators has been the formation of precipitates which block the pores and hinder diffusion. The need for a separator is just to keep the paste away from the cathodic compartment so that particles to not get trapped in the electrodeposited or cemented layers. It seems logical therefore that an improved cell design would need to have a vertical separator which was more porous. The amount of DES used could be decreased by decreasing the volume of the cathodic compartment as shown in *Figure 5-*22. This design could result in a system where the mass of DES could be less than the mass of jarosite. The advantage of this design would be that any deposit formed would settle to the base of the cell and not create a saturated layer next to the frit. If the volume of the anodic compartment was 500 ml then the cathodic compartment could be as small as 50 ml.



Figure 5-22: Schematic diagram for a cell which requires a smaller volume of DES.

The results from Cell 3 seem to suggest that an important part of the extraction and recovery process appears to be the cathode area and the ability of the separator to block.

An alternative approach would be to have a continuous flow cell where the solid was slowing introduced at the top of a tall thin tube cell which would increase the separator area (*Figure 5-23*). The electrode/ stirrer could be mounted and moved vertically, possibly using a cam mechanism. A screw could be used at the base of the cell, to remove material which had become exhausted of metal. The design of the separator is crucial to ensure that the porosity of sufficiently small to prevent particle transfer but sufficiently course to prevent blocking. Previous work with EAF dust used a double bag filter to achieve this. This may not be sufficiently robust and so a nylon or metal grid may be required to support a mesh filter. The cell design in *Figure 5-23* ensures that there is a large membrane and cathode area. It also allows for any precipitate that forms to settle to the base of the cathodic cell. It enable a continuous flow process to be established and should circumvent the issues observed with Cell 3.



Figure 5-23: Improved cell design to enable continuous flow and minimise separator blocking.

5.5 Conclusion

This chapter has shown that jarosite can be electrochemically digested to release the three main metals found in it; iron, zinc and lead. It is shown that the electrochemically assisted dissolution can improve the rate of metal dissolution by 20 times for iron compared with chemical dissolution in Ethaline. Three cell designs were tested to determine what factors could affect the rate of jarosite digestion.

In an unstirred and unseparated cell 4 g of jarosite was digested in 50 ml of Ethaline at 50 °C for 24 hours. At the end of this time 63% of the iron had been digested and almost all the zinc. When a paper separator was used in the cell to separate the cathodic and anodic compartments the extraction efficiency decreased to only 16 % of iron and 79 % of zinc. Analysis of the cell after digestion showed that the filter paper had become clogged with a precipitate which was limiting its performance and had blocked diffusion of material from the anodic compartment to the cathodic compartment.

A third cell design scaled up the process significantly using 500 g of jarosite and 750 ml of Ethaline. This cell used a coarse glass frit membrane and carried out the electrolysis for 13 days. It was found that the extraction efficiency increased compared to Cell 2 with 63% Fe, 71% Pb and 80% Zn being extracted. The same issues were observed with the glass membrane i.e. precipitate formation and pore blocking. It was also found that the cementation of lead was not as efficient as had been observed with EAF dust and this was thought to be due to the formation of passivating films which are iron rich on the zinc surface. This could be due to the high iron content in the liquid. Future investigations should investigate the use of additives to precipitate the iron from solution and make the cementing of lead more efficient. It was found that the high sulfate content of jarosite caused lead sulfate to precipitate in the anodic compartment which decreased the efficiency of the cementation process.

Two further cell designs were proposed at the end of this chapter to decrease the effect of separator blocking and increase the area of the cathode thus decreasing the passivation of the electrodes. A vertically oriented cell should allow any precipitates to settle to the bottom of the cell and decrease the blocking of the separator.

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Chapter 6: Conclusions and further work

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Chapter 6: Conclusions and further work

6.1 Conclusions

The dissolution of natural sulfide minerals has not previously been studied in Deep Eutectic Solvents (DESs). The normal processing methods for these minerals is using a combination of hydrometallurgy with pyrometallurgy. These techniques, whilst widespread, have issues associated with consumption of large volumes of acids, toxic reagents, highly corrosive drainage products, and high energy demand. Sulfidic mineral processes produce significant concerns associated with the environment.

DESs are a class of ionic liquids composed from organic cations and organic or inorganic anions, which are liquid at ambient temperatures. These solvents can be designed to be environmentally compatible with low vapour pressure, low toxicity, low-flammability, and biodegradability through judicious choice of the components. DESs have been used for leaching and extraction of various metals from oxides, and can also be used as an electrolytic solution for the electrowinning of dissolved metal ions due to a reasonable ionic conductivity and relatively wide potential windows.

Previous studies have shown that metal oxides can be digested in acidic DESs. The anodic dissolution of 9 metals and 3 alloys has also been studied. Furthermore the first case of electrocatalysis for metal digestion using the I_2/I^- couple in a DES was reported. These have all been used for recovering metals from waste streams including EAF dust, a variety of alloys and semiconductors and in all cases efficient separation of elements was achieved. To date, however, no attempts at recovering elements from primary sources i.e. ores and minerals have been reported

In the present study, the influence of mixing molar ratio of 1:2 choline chloride: ethylene glycol DES which known by Ethaline as an electrolytic solution on the electrochemical behaviour and anodic dissolution of sulfide minerals such as pyrite, marcasite, pyrrhotite, arsenopyrite, loellingite, and also jarosite waste were examined at ambient temperature.

The electrochemistry of natural solid minerals are usually difficult to study due to the presence of undesirable materials (gangue), different allotropic faces, and the need to maintain electrical conductivity with the charge collector electrode in the electrolytic cell.

The first part of this study developed a new, generic technique to create a paste of mineral in a DES and this was then painted on to the electrode surface. This so-called paint casting enable clear cyclic voltammograms to be recorded for a range of minerals. It was shown that pyrite (FeS₂) could be electrochemically dissolved by applied oxidative and reductive potential to an electrode coated in an Ethaline/mineral paste at ambient temperature. The cyclic voltammogram of paint cast pyrite was found to have two anodic peaks and three cathodic peaks. The two anodic peaks were attributed to the formation of elemental sulfur and Fe (III), whereas the three cathodic peaks are related to the reduction of Fe(III) to Fe(II) and to the reduction of sulfur to form polymeric anions. The loading mass of minerals onto electrode appears proportional with electrochemical signal, which could in principle be used as an assay method.

The in-situ 3D profilometry of single crystal pyrite samples under anodic polarisation showed that bulk dissolution was highly anisotropic. The UV-Vis spectra of the DES after bulk dissolution of pyrite showed that the dissolved iron atom was coordinated to oxygen and/or maybe sulfur. At higher over-potentials, Fe(III) species are formed which appears to chemically dissolve pyrite by a different mechanism. Although pyrite can be solubilised both anodically and cathodically the rate of anodic dissolution is far faster than that of cathodic dissolution.

Secondly, the electrochemical behaviour for other iron-based minerals (marcasite, pyrrhotite, arsenopyrite and loellingite) were determined and compared to that of pyrite. It was found that the electrochemistry of all the minerals was controlled by the redox behaviour of the anion rather than the metal. The electrochemistry of marcasite was found to be notably different from pyrite despite being structural isomers of each other. The dissolution rate of these four minerals in Ethaline was measured using both chronocoulometry and bulk electrolysis with ICP-MS analysis of the solution. This result showed that the dissolution rate was in the order marcasite > pyrrhotite > loellingite > arsenopyrite. The dissolution rate was found to be related to the band gap of the bulk mineral.

In principle the speciation of metal chalcogenides in solutions depends on pH, temperature, solution type, ligand concentration and applied potential, etc. This, coupled with the difficulty of analysing speciation of S- and As- containing compounds makes identification of speciation difficult. Thus, the proposed generic mechanism can be

illustrated this combined by taking iron-sulfides as an example. A variety of techniques were applied to gain more information and the general mechanism for sulfide oxidation involves removal of electrons from the S_2^{2-} anion. This releases Fe^{II} into solution. EQCM shows that at higher over-potentials this becomes Fe^{III} . EXAFS and UV-Vis spectroscopy show that the dissolution of pyrrhotite and marcasite have produced a complexes of iron chloride anions with an oxygen donor like, $FeCl_x(OD)_y$. These complexes are known to have low solubility and can precipitated as a passivation layer on electrode surface. In spite of voltammetry showed that sulfur was oxidized in Ethaline, no oxidised forms of sulfur were detected. In-situ microscopy shows some evidence for elemental sulfur forming on the electrode surface under some circumstances. The UV-Vis spectra of solutions obtained from bulk anodic dissolution of marcasite and pyrrhotite have two absorbance bands attributed to Fe^{II} - glycolate complexes. However, the UV-Vis spectra of anodic dissolution of arsenopyrite in Ethaline shows that Fe^{II} has a different coordination bands which may be associated with and As^{III} –Cl complex. UV-Vis spectrum of loellingite shows an absorbance bands attributable to $[CoCl_4]^{2-}$.

The comparison results of ICP-MS for bulk dissolution of loellingite and arsenopyrite showed that the ratio of As: Fe for loellingite (FeAs₂) was 1.9 close to that expected from the stoichiometry. However, the ratio of As: Fe for arsenopyrite (FeAsS) was 0.74 which is noticeably below than that expected. This could be because of insoluble arsenic-sulfur compounds which form on the mineral surface and reduce the electrochemical dissolution rate.

The metals digested from the minerals by electrochemical oxidation were recovered from solution using both galvanic deposition onto zinc and electrochemical reduction. Both techniques were successful in obtaining deposits but it was clear that the deposits contained a significant amount of oxygen and carbon suggesting that they are not largely metallic. SEM and EDX analysis of the galvanic deposits showed that sulfur does not deposit; however, arsenic is deposited from loellingite. The galvanic deposits were thin and patchy whereas the electrolytic deposits were much thicker. It was clear, however that the conductivity of the deposits resulted in them having a limiting thickness through passivity.

In the final part of the study the practicalities of mineral digestion were investigated using three cell designs using different electrode arrangements with and without separators for the two electrolytic compartments. A waste product from the zinc mining process, jarosite was used as a test sample. The aim was to use base metals Zn, Fe and Pb as these were known to give issues with precipitation and passivation. It was found that electrochemical dissolution was up to 20 faster than chemical dissolution for some of the elements present. The presence of large quantities of sulfate was shown to be an issue with precipitate formation. It was shown that solubilisation of zinc was relatively fast and easy but lead was much slower. Iron and lead were found to form precipitates with sulfates. These were especially an issue where membranes were present as they precipitated blocking the separator and decreasing the overall recovery. Cell 3 used a 50% excess of liquid: solid but two further cell designs were proposed (but not tested) where there could potentially be a 50% excess of solid: liquid with the right cell dimensions.

The study has been the first to demonstrate that sulfidic and arsenic ores can be processes without the emission of noxious gases. Iron-sulfide ores are particularly difficult to process but the paint casting method has shown that they can be efficiently processed in DESs using electrochemical digestion.

6.2 Suggestions for further work

This is just the start of a large field of research with is currently continuing within this group. The results are by no means conclusive and there are many areas that need to be investigated to improve this method for metal separation.

Probably the most important first step is to carry out more work to identify the speciation of metals sulfides when they dissolve in DESs. This could be done using suitable numerous techniques. The initial EXAFS study could be extended by getting a higher concentration of mineral in solution. It would be useful to study EXAFS as a function of time to see how reactions in solution lead to precipitation over time. Mass spectroscopy, and Raman spectroscopy could also be used to identify species in solution. It would also be useful to identify the morphology and chemical composition of the deposits obtained on the electrode surfaces using SEM/EDX, XRD and X-ray photoelectron spectroscopy (XPS).

The current study was carried out with just Ethaline, however previous studies have shown that speciation and solubility in solution vary significantly with the identity of the HBD of the DES. Acidic HBDs have been added to Ethaline and been used to precipitate metals such as iron. The study could optimise the solubility behaviour of selected metals by varying the HBD. It would be useful to try to correlate solubility with pH and speciation. Following on from this it would be useful to construct a Pourbaix diagram (Eh-pH) of these chalcogenides in DESs, especially for the redox thermodynamic stable species produced in these solvents, after identification of these species in DESs. These could then be compared with that Eh-pH data in aqueous solutions.

The electrochemistry of oxophillic metals such as Fe, Cr and Ni are not well understood and the formation of metal oxide layers on electrode surfaces is rate limiting in many cases. The effect of concentration on the rate of metal deposition vs the rate of metal passivation needs to be quantified.

The work in Chapter 5 should be repeated for other ores in an attempt to recover of metals such as copper, nickel or the precious metals which are associated with these chalcogenides minerals. Other work in the group has shown that chalcopyrite, CuFeS₂, the main copper ore, can be electrochemically dissolved and relatively pure copper can

be obtained in a 1-step process. It would be useful to test the cells discussed in Chapter 5 using a continuous flow process for this type of mineral. A more in depth study of process kinetics using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) would be useful. It appears that the most important factor in cell design is that of separator structure which needs to be porous enough to stop precipitate formation but course enough to stop particles passing through.

The limiting factor of the initial study appears to be mass transport and so it would be useful to see whether an electrocatalytic approach could be used to dissolve minerals. To do this efficiently novel catalysts would need to be developed. Previously the I_2/I^- couple has been used but new catalytic couples such as O_3 or Br_2/Br^- or FeCl₃ may be able to extend the range of minerals which can be dissolved.

Chapter (7) Appendices:

Mineral	At% Fe	At% S	At% As	Trace elements	Fe	S	As
Pyrite (FeS ₂)	32	68			0.94	2	
Marcasite (FeS ₂)	32	68			0.94	2	
Pyrrhotite (Fe _{1-x} S)	46	54		Mg, Mn, Ca, Si	0.86	0.14	
Arsenopyrite (FeAsS)	34	34	32	Ca, Al, Ag	1	1	0.96
Loellingite (FeAs ₂)	24	2.2	64	9.96% Co, 2.25% S	0.73		1.93

Table 7-1: EDX analysis data of iron-based sulfide minerals used in this research.



Figure 7-1: Chrono-Coulometry of gold-pyrite sample in Ethaline at +1.2 V for 2.5 hours at room temperature (on the left), etching volume of gold versus experimental time (on the right).



Figure 7-2: Series of images of 3D colour optical microscopy of electrochemical connected gold-pyrite sample (1) before and (2-6) after anodic dissolution at +1.2 V for 2.5 hours in Ethaline at room temperature



Figure 7- 3: Cyclic voltammograms of paint casted on to Pt flag of mixing different mass ratio of (A) marcasite and pyrrhotite together, and (B) arsenopyrite and loellingite together versus Ag/AgCl reference electrode and Pt flag counter electrode.



Figure 7- 4: Cyclic voltammograms at multiple scan rates of (A) marcasite, (B) pyrrhotite, (C) arsenopyrite and (D) loellingite pasted onto a Pt flag versus Ag/AgCl reference electrode and Pt flag Counter electrode in Ethaline at 20 °C.



Figure 7- 5: Open-Circuit Potential (OCP) of whole grain sulfide ore electrodes for pyrite, marcasite, arsenopyrite, loellingite and pyrrhotite versus Ag/AgCl reference electrode and Pt flag counter electrode.



Figure 7- 6: Illustrates the change in colour of Ethaline after chronopotentiometric experiments of paint-casted iron-based sulfide minerals versus an Ag/AgCl reference electrode and Pt flag counter electrode over 10 minutes.



Figure 7-7: Solutions produced from cathodic electrolysis of 2 g for each marcasite, pyrrhotite, arsenopyrite and loellingite in Ethaline at a constant current density of 5 mAmps.cm⁻² (except for marcasite, which was 2.5 mAmps. cm⁻²) for 24 hours at 50°C



Figure 7-8: Shows the comparison images of 3D profilometry of marcasite sample immersed in a catalytic solution of iodine dissolved in Ethaline for 12 min. at 50 $^{\circ}$ C.



Figure 7-9: Charge versus square root of time for the chronocoulometry of 40 mg of each pyrite, marcasite, pyrrhotite, arsenopyrite, and loellingite pasted onto a Pt flag in Ethaline over 30 minutes at +1.2 and 20 °C. Related to Figure 4-7 in the body of thesis.



Figure 7-10: Schematic diagram of 3D printed sample holder for 3D profilometry used to stabilize the iron-based sulfide mineral samples for measuring the etch depth.



Figure 7-11: Comparison of colour between anodic dissolution of 2 g loellingite which contains about 10% atomic ratio of Co (on the left) with that does not contains Co (on the right) in Ethaline at constant current 5 mAmps and at 50 °C for 24 hours.



Figure 7-12: UV-Vis spectra for solutions obtained from anodic dissolution of loellingite that contains Co and another which does not contains Co in Ethaline in Figure 7-11 above.



Figure 7-13: Range of coloured solution obtained from iron-based sulfide minerals used in this thesis using Ethaline and Reline in both anodic and cathodic dissolution, in addition to the anodic dissolution of these minerals in aqueous solution of 6M NaCl and chemical dissolution in about 12M HCl.

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The application of deep eutectic solvent ionic liquids for environmentally-friendly dissolution and recovery of precious metals



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ABSTRACT

The processing of ore by hydrometallurgy or pyrometallurgy typically has a high energy demand, and associated release of carbon dioxide. Thus there is a need to develop more energy-efficient and environmentally-compatible processes. This article demonstrates that deep eutectic solvent (DES) ionic liquids provide one such method since they can be used to selectively dissolve and recover native gold and tellurium, sulphides and tellurides.

lonic liquids are anhydrous salts that are liquid at low temperature. They are powerful solvents and electrolytes with potential for high selectivity in both dissolution and recovery. Deep eutectic solvents are a form of ionic liquid that are mixtures of salts such as choline chloride with hydrogen-bond donors such as urea. DESs are environmentally benign, yet chemically stable and, furthermore, the components are already produced in large quantities at comparable costs to conventional reagents.

Electrum, galena and chalcopyrite, as well as tellurobismuthite (Bi₂Te₃), were soluble in DES through an oxidative leach at 45–50 °C. Leaching rates determined by a novel technique employing an optical profiler were very favourable in comparison to the current industrial process of cyanidation. Pyrite was notably insoluble by an oxidative leach. However, pyrite, and indeed any other sulphide, could be selectively dissolved by electrolysis in a DES, thus suggesting a protocol whereby target inclusions could be liberated by electrolysis and then dissolved by subsequent oxidation.

Ionometallurgy could thus offer a new set of environmentally-benign process for metallurgy.

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1. Introduction

The extraction of metals from ores is often an energy-intensive process, requiring either smelting or leaching at elevated temperature, or the use of large quantities of strong acids or bases that require energy to produce. These processes often produce wastes, in gaseous, liquid or solid form, which require treatment before they can be safely disposed, and this waste treatment requires further energy. The energy input equates to a significant cost and an associated CO_2 footprint, both of which it would be desirable to reduce. Furthermore, some treatments, most notably cyanidation hydrometallurgy, has poor public perception and can negatively impact on the "social licence to operate" that all mining operations

* Corresponding author. E-mail address: grtj1@le.ac.uk (G.R.T. Jenkin). must secure. The increasing intolerance to cyanidation has resulted in it being banned from use in a number of countries and states.

The question is whether the minerals processing community can develop new, low-energy, low-cost and more environmentally compatible metallurgical processes for the mining industry on a planet of over 9 billion people? The advent of heap-leaching and biohydrometallurgy have made significant advances in this direction, but there still remain many ores for which the most economic, or only, option is energy-intensive hydrometallurgical or pyrometallurgical treatments.

We propose that ionic liquids could provide new environmentally-friendly approaches to processing a variety of ores, in particular those that are difficult and energy-intensive to treat. There is now a significant literature and extensive application of these liquids in the recovery of metals from scrap and metal oxides (Abbott et al., 2011a,b), the processing of reactive metals (Vaughan and Dreisinger, 2008), as well as applications across a range of chemical processing (Wasserscheid and Welton, 2008). However, there has been only limited attention paid to the possibility of using ionic liquids in processing base and precious metal ores (Whitehead et al., 2004, 2007, 2009; Luczak et al., 2008; Dong et al., 2009). There is a vast array of different types of ionic liquids and many are unsuitable to large-scale applications such as mineral processing due to high cost, lack of availability or toxicity. In the following sections we explain what ionic liquids are, and then show that a group of ionic liquids known as deep eutectic solvents fulfil the requirements for industrial application. We then demonstrate that these ionic liquids can be used to rapidly dissolve a variety of ore minerals, including gold, at low temperatures, and show how the metal can then be recovered by electrolysis.

2. A new type of chemistry - ionic liquids

Ionic liquids are salts that are liquid at low temperature, typically <100 °C. These anhydrous liquids are composed of ions and, like high temperature molten salts, are electrolytes and powerful solvents. In contrast to aqueous liquids, where the solubility of metals is limited by the tendency for water to combine with metal ions and precipitate oxides and hydroxides, in water-free ionic liguids much higher metal concentrations can be achieved. High ligand concentrations are possible allowing much greater control on metal speciation in solution, whilst recovery from solution can be by electrowinning, cementation, ion exchange or precipitation (Abbott et al., 2011b). These features provide potential for high selectivity in both dissolution and recovery. Furthermore, ionic liquids have a wider electrochemical window than aqueous solutions and so can operate beyond the potential range of aqueous solutions making electrowinning of more reactive metals possible, whilst avoiding the evolution of gas at the electrodes (Smith et al., 2014). The higher metal concentrations that can be achieved, together with the fact that ionic liquids can be reused in a closed circuit, means that high volume/low concentration aqueous wastes are not produced.

In order to be suitable for large-scale metallurgical processing a reagent must be of low cost, readily available in large quantities. chemically stable to allow prolonged reuse, be environmentally benign, and have no restrictions (i.e. be a common, simple chemical with well-known characteristics). Unfortunately all the ionic liquids that have previously been tested for dissolution of precious or base metal ores (Whitehead et al., 2004, 2007, 2009; Luczak et al., 2008; Dong et al., 2009) fail to meet one or more of these criteria. Ensuring that all these industry-necessary criteria are met from the outset led to the development at the University of Leicester of the deep eutectic solvents (DESs). These are mixtures of salts, such as choline chloride, with hydrogen-bond donors such as urea or citric acid (Abbott et al., 2004). The eutectic mixtures have melting points that are significantly lower than their individual components, giving a room-temperature ionic liquid. It should be noted that DESs are not an ionic liquid sensu stricto, since they are a mixture rather than a single salt, nevertheless they are anhydrous liquids made of ions and share many properties with ionic liquids sensu stricto, although also exhibit some significant differences (Smith et al., 2014). The solvent properties of DESs can be adjusted by changing the hydrogen-bond donor, giving 10⁵ possible different liquids and allowing the possibility of tailoring the properties of the liquid to a specific process (Abbott et al., 2004). DESs are environmentally benign, yet chemically stable. Their components are common, cheap chemicals, e.g. choline chloride (vitamin B4) is mainly used as an animal-feed additive, being already produced in large quantities (forecast to exceed 500 kt choline chloride p.a. in 2017; Global Industry Analysts, 2014) at low cost ($\sim \in 2/kg$). Urea is a common nitrogen fertilizer (2012 worldwide production capacity was ~184 Mt; Ceresana, 2012) that is non-flammable and completely biodegradable, retailing at $\sim \in 0.5/kg$. The behaviour of d-block metals and group IIIA–VA metals and semi-metals in DESs is well-understood (Abbott et al., 2011b). It has previously been shown that metal oxide extraction by DESs is economically viable even for low value metals (Abbott et al., 2009).

3. Demonstration 1 – dissolution rates of gold and other minerals in a deep eutectic solvent

Here we demonstrate how a variety of minerals can dissolved from ore samples using iodine (I_2) as an oxidising agent within a DES. We show how the dissolution rates can be rapidly estimated using a micro-leach technique with an optical profiler, and compare these observed rates to those of existing techniques. We investigate a quartz vein-hosted orogenic-type gold ore with relatively small gold particles (90% <100 µm, most <40 µm; Dominy and Platten, 2008) because high efficiency of extraction of gold from such an ore would typically demand pyrometallurgy (roasting), a hydrometallurgical step (involving cyanidation), or both. In addition we investigate native tellurium and a telluride mineral, because telluride-bearing gold ores are typically refractory to cyanidation and are lost to tails (Spry et al., 2004; Zhang et al., 2010). Alternatively such ores may need to be roasted to make them amenable to cyanidation (Zhang et al., 2010). In either case tellurium (a rare element increasingly sought after for solar photovoltaic panel construction; Woodhouse et al., 2013) is lost and becomes a potential environmental contaminant. Thus approaches that might liberate and recover gold and valuable associated elements from ores could both increase the value gained from an ore and reduce environmental legacies.

3.1. Experimental

All samples were mounted in resin, cut and polished to produce a standard polished block with a flat surface as used for reflected light microscopy. The electrum, chalcopyrite, galena and pyrite investigated were all in two polished blocks of gold ore sample CGJ CON 002 from the Cononish gold deposit, Scotland, (Curtis et al., 1993; Spence-Jones, 2013; Hill, 2014) courtesy of Scotgold Resources Ltd. This gold-rich sample consists largely of pyrite, with lesser galena and chalcopyrite, in a quartz matrix. The electrum grain that was leached was silver-rich, measured as approximately 50 wt.% Au/(Au + Ag) by SEM-EDX.

Samples of native tellurium (BM 31691, Zlatna, Transylvania, Romania) and tellurobismuthite (Bi₂Te₃; BM 32070, Reed's Mine, Georgia, USA) were obtained as separate polished blocks from collections at the Natural History Museum, London.

The ionic liquid used was Ethaline, a DES mixture of 1 mol. eq. choline chloride and 2 mol. eq. ethylene glycol. Ethaline containing 0.1 mol dm⁻³ iodine was prepared following the procedure of Abbott et al. (2015). Polished blocks were etched by suspending them in a well-stirred solution at either 45 °C (tellurium, tellurobismuthite) or 50 °C (electrum, galena, chalcopyrite, pyrite). One mount of CJG CON 002 was leached for 10 min after which the electrum and pyrite were measured. The other mount of CJG CON 002 was leached for three 5-min leach steps and after each step the galena and chalcopyrite were measured and then returned to the solution without repolishing. The last step for galena etched into some inclusions and so has not been included. The tellurium and tellurobismuthite mounts were measured after leaching for 5 min, and then after a further 10 min. The tellurium was measured in two different locations on the mount. Ethaline was removed from samples by rinsing with water and then air drying prior to measuring etch depth.

2D and 3D optical images of the samples pre- and postdissolution were captured on a Zeta Instruments Zeta 2000 optical profiler using the inbuilt Zeta3D software version 1.8.5. This instrument captures a reflected light image of the sample surface identical to that given by a conventional reflected light microscope used for ore microscopy (Fig. 1A and B). However, in addition, the precise XYZ co-ordinates are captured, so that the same image can be viewed in 3D (Fig. 1C). The Zeta 2000 uses a motorised XY stage and accompanying control and positioning software to construct a 3D colour image of a surface. Images are constructed by determining the features of an image that are in focus at different heights. These are then analysed to produce a reconstructed 3D topography of the surface. Line profiles were measured across grains where the dissolution rate was being measured using a flat surface of an insoluble phase (resin, quartz) to provide a reference height. Only







Fig. 1. Reflected light image of gold ore (A) before, and (B, C) after reaction with a deep eutectic solvent for 10 min at 50 °C. The electrum (el) grain in A has been completely removed in B and C whereas pyrite remains unreacted. C. Shows the same image as B in 3D illustrating the etch pit where the electrum originally was located.

the relatively flat base of an etch pit was measured, away from grain boundaries or inclusions that retard dissolution by partly shielding the grain from the solution. Using distinctive features on the sample surface, care was taken to position the line profiles in precisely the same position pre- and post-dissolution so that an accurate estimate of the difference between the profiles could be measured. Linear etch rates are converted to molar etch rates using appropriate density and molecular masses with appropriate unit conversions.

3.2. Results

Reflected light images of CJG CON 002 pre- and post-dissolution show that the \sim 30 \times 15 µm electrum grain was completely dissolved after the 10 min leach (Fig. 1B). Galena and chalcopyrite were also etched, although chalcopyrite developed an iridescent blue tarnish. Pyrite appeared unreacted and only mildly tarnished in some places. Both native tellurium and tellurobismuthite also dissolved, with the tellurium showing an increase in surface roughness during dissolution.

The etch depths measured versus time are shown in Fig. 2 and given along with calculated dissolution rates in Table 1. Where etch depths were measured at more than one time the dissolution rate was linear within error since the scatter around the linear best fit line through the origin, measured by the standard error of estimate, is less than the measurement error for the instrument of \sim 0.1–0.2 µm as illustrated by the duplicate measurements of tellurium. The dissolution rates are therefore derived from the slope of the best-fit line. The electrum dissolved fastest at $0.172 \,\mu\text{m}/$ min, but note that in 10 min the complete electrum grain had dissolved and thus this represents a minimum dissolution rate. Tellurium dissolved a little slower than this followed by galena, then tellurobismuthite. Tellurobismuthite is strongly anisotropic with a perfect {0001} basal cleavage. Observing the etching rates in two adjacent grains with different orientations suggests that the dissolution rate was \sim 50% faster parallel to the *c*-axis (perpendicular to the cleavage) compared to parallel to the cleavage. Chalcopyrite dissolved slowly compared to the other minerals. There was no measurable dissolution of the pyrite, with fine polishing scratches preserved on the surface.

3.3. Discussion

3.3.1. Dissolution rates and industrial feasibility

The observation of linear dissolution rates suggest that there is no major biasing of our data over these time and length scales by, for example, enhanced early dissolution due to surface damage by



Fig. 2. Etch depth for different minerals *versus* dissolution time. The electrum dissolution rate is a minimum. $\perp c$ indicates the leach direction is perpendicular to the *c*-axis), \\c indicates leaching parallel to the *c*-axis.

Mineral	Electrum	Galena	Chalcopyrite	$Bi_2Te_3 \perp c$	$Bi_2Te_3 \setminus c$	Tellurium		
Temperature (°C)	50	50	50	45	45	45		
Time (mins)	Cumulative etch depth (μ m)							
5	-	0.42	0.20	0.22	-	0.61, 0.80		
10	1.72*	1.02	0.19	-	-	-		
15	-	-	0.26	0.88	1.29	2.38, 2.13		
	Average dissolution rate							
μm/min	0.172	0.099	0.019	0.057	0.086	0.150		
$mol m^{-2} s^{-1}$	$2.8\times10^{-4^{\ast}}$	5.1×10^{-5}	7.4×10^{-6}	$\textbf{9.3}\times10^{-6}$	$1.4 imes 10^{-5}$	1.2×10^{-4}		

Measured etch depth vs. time and calculated dissolution rates for a selection of minerals in Ethaline containing 0.1 mol cm⁻³ iodine

* NB – minimum values. $\perp c$ = perpendicular to *c*-axis (cleavage parallel), $\langle c \rangle$ = parallel to *c*-axis.

 Table 2

 Compositional data for placer gold concentrates.

Table 1

Sample #	Locality	Total	wt.% Au/(Au + Ag)			
		weight (g)	Bulk XRF	EMP range	EMP average	EDX recovered
1	Crom Allt top	0.17	76.5	44-98	67.3	70.3
2	Crom Allt mid	0.33	64.6	45-99	64.0	82.1
3	Coire Ghamhnain	0.51	75.2	50–98	68.8	82.7

EMP = Electron MicroProbe, EDX recovered = Energy Dispersive X-ray analysis of material electrolytically recovered from solution at the cathode.

polishing, increasing dissolution rate due to the development of surface roughness and hence increased surface area, or later retardation of the reaction due to depletion of the liquid boundary layer. It is assumed that the electrum is also leaching at a linear rate.

Our measured rates can be used to make a simple calculation of the lifetime of a grain dissolving under these conditions. Applying the electrum dissolution rate of $0.172 \,\mu\text{m/min}$ (Table 2) to a 100 µm diameter grain dissolving in a well-mixed DES suggests that dissolution should be complete in ~4.8 h. Given that our electrum dissolution rate is a minimum, it is possible that this time could be shorter. This dissolution rate compares very favourably to cyanidation, for example, our (minimum) electrum dissolution rate translates to 2.8×10^{-4} mol m⁻² s⁻² (Table 1), which is ~40 times greater than the maximum gold dissolution rate in cyanide determined by Wadsworth et al. (2000) of 0.69 \times 10^{-5} mol m^{-2} s^{-2} . Our dissolution rate is at 50 °C vs. 25 °C used by Wadsworth et al., but room temperature dissolution at realistic rates looks perfectly feasible. Leaching rates are expected to increase approximately linearly with iodine concentration, so this could also be used to increase dissolution rate.

These results show strong selectivity in the dissolution process with electrum rapidly going into solution, base metal sulphides dissolving more slowly, and pyrite remaining undissolved. Since pyrite is typically the major gangue in sulphide floatation concentrates this technique could potentially separate the gold without the pyrite. This is assuming the gold is exposed at the pyrite surface and not "locked" as inclusions within it. However, we show below (Section 5) that there are other approaches using DES that could be used to selectively dissolve pyrite to liberate gold inclusions. Since this technique will also dissolve other minerals, such as chalcopyrite, galena and a bismuth telluride from the gold ore, there is the potential to also recover other elements from the ore, simultaneously adding value to the ore and removing potential environmental contaminants from the tailings. Selective recovery of the dissolved species has already been demonstrated for lead from a mixed metal oxide matrix (Abbott et al., 2009) and is demonstrated here for gold in Section 4.

3.3.2. Advantages of the micro-leach optical profiling technique

Use of an optical profiler to monitor dissolution progress as we have done here with ionic liquid could also be applied to monitor the effectiveness of any hydrometallurgical technique. This technique has a number of advantages compared to conventional bulk leaching techniques:

- (1) It obviates the need to analyse solutions to monitor reaction. This can be time consuming, requires the analytical equipment, places limits on the sensitivity of the technique, and produces data that require deconvolution and may be nonunique if a number of phases are dissolving.
- (2) It can monitor the dissolution rate of a number of minerals simultaneously.
- (3) It can determine dissolution rates along different crystallographic axes of anisotropic minerals.
- (4) The sample used can be a portion of a polished section of ore or concentrate that has previously been characterised by microbeam techniques, so that dissolution can be related to mineralogical factors, e.g. composition, zonation, inclusions etc., thus providing direct information of practical use for designing a processing circuit.

Thus this technique potentially has wide application in metallurgical studies of ores.

4. Demonstration 2 – gold and silver recovery from solution

To complete the process, the solubilised gold needs to be recovered from the DES as well as any other dissolved metals of interest. To demonstrate this we used three placer gold samples from the Scotgold exploration licence area collected by R. Chapman, since it was difficult to obtain significant quantities of gold from the Cononish deposit pre-production.



Fig. 3. Composition of electrum used in gold recovery experiment measured by electron microprobe (EMP) on individual grains and bulk XRF, compared with EDX analysis of material recovered by electrolysis.

4.1. Experimental

The gold in the placer samples was electrum thought to be derived from erosion of nearby primary hydrothermal veins similar to those in the Cononish gold mine (Hill et al., 2013; Hill, 2014). The grains are thus similar in composition to the primary mineralisation, although much larger (0.1–3 mm diameter) than the bulk of electrum grains in the ore. By their nature placer gold samples are inhomogeneous and bulk compositions were estimated by both electron microprobe analyses of a subset of grains in each sample and by bulk XRF of the entire loose sample (Table 2 and Fig. 3). Chapman et al. (2006) demonstrate that averages of electron microprobe data of a selection of placer grains provide a good estimate of the bulk composition.

The average of the electron microprobe data shows that the samples have broadly similar bulk compositions, with sample 2 possibly a little richer in Ag. Bulk XRF data shows a similar pattern although rather more Au-rich compositions – this may be due to lack of X-ray penetration into the coarser grains so that compositions sampled were dominated by grain rims, which naturally tend to be slightly Ag-depleted (Groen et al., 1990). There was a large range in individual grain composition and thus the ~90 mg sub-samples used for the dissolution and recovery experiments could differ somewhat from the bulk values depending on the random selection of different composition grains. The XRF data suggests that in addition to the electrum there was 6-24% of aluminosilicate minerals plus pyrite in the samples.

In each experiment, approximately 90 mg of sample was added to 3 mL of Ethaline with 0.1 mol dm⁻³ iodine and stirred at 50 °C for 48 h to completely dissolve all the electrum. The solution was then subjected to electrolysis in a cell with a Ni sheet cathode and iridium oxide coated titanium mesh anode. Electroplating onto the cathode was carried out under constant current of 4 mA cm⁻² for between 2 and 20 h. Full experimental details are provided by Abbott et al. (2015).

4.2. Results

Electrodeposition resulted in a powdery brown/black deposit, the thickness of which increased with deposition time. EDX analysis of these deposits revealed that they consist only of Au and Ag, demonstrating that these elements can be successfully recovered by this process. In addition, the EDX data show that the recovered deposits contained a greater proportion of Au (by 3–18%, Table 1 and Fig. 3) compared to likely compositions of the starting material (best estimated by the mean electron microprobe data). This suggests that Au is preferentially being electroplated.

4.3. Discussion

The iodine used in our demonstration experiments was simply being used as an oxidising agent to allow dissolution of the mineral, with iodide (I^-) being formed as a waste product, e.g. for gold dissolution:

$$2Au + I_2 = 2Au^+ + 2I$$

However, in an industrial process the iodine has the potential to be employed as an *electrocatalyst*, whereby it is continuously recovered *in situ* from the reduced iodide by electrochemical oxidation at the anode of a cell (Fig. 4). Dissolved metals can be selectively deposited at the cathode by adjusting the electrode potential (Abbott et al., 2011a). Quantitative separation of Au and Ag should be possible, given their difference in redox potentials (Abbott et al., 2011a).



Fig. 4. Schematic diagram showing how two elements could be separated from a mixture or compound using iodine as an electrocatalytic oxidation agent in the ionic liquid Ethaline (Abbott et al., 2015). One of the elements is being recovered at the cathode, whilst the other remains in solution. Different cations in the solution could be recovered separately by applying a specific redox potential.

5. Future potential – dissolution of refractory phases by electrolysis

We have shown in Section 3 that a range of ore minerals dissolved by oxidation with iodine into a DES ionic liquid, but pyrite did not react under these conditions. We also attempted to dissolve calaverite (AuTe₂), another notably refractory phase, by this method but instead of dissolution there was a growth in surface relief and tarnish development. Sperrylite (PtAs₂) and moncheite (PtTe₂), which are typically the more abundant platinum minerals in many orthomagmatic deposits (e.g. Schouwstra et al., 2000), were unaffected under the same conditions. A common feature amongst these minerals is that they are a disulphide (pyrite), diarsenide (sperrylite) or ditellurides (calaverite and moncheite) suggesting the mineral structure may be particularly resistant to iodine oxidation. The ability to liberate gold inclusions and even submicroscopic "dissolved" gold from pyrite would be advantageous, as would the ability to dissolve calaverite in order to recover both gold and tellurium. Similarly new routes to treating the common platinum minerals, and which for moncheite could also recover tellurium, would be desirable.

Fig. 5A shows the surface of a calaverite crystal that was made into an electrode that was used in a cyclic voltammetry experiment with an Ethaline electrolyte. After cycling the voltage at room temperature (-1.2 to +1.2 V, scan rate 20 mV s⁻¹) the surface was etched which indicated dissolution (Fig. 5B). The mechanism by which dissolution is taking place is currently being investigated, but preliminary observations suggest that this process will dissolve a range of sulphide minerals, including pyrite. Thus it seems there is the opportunity to develop protocols in which DES ionic liquids can be used for electrolytic dissolution of refractory minerals in order to liberate gold for subsequent oxidative dissolution and electrolytic recovery.

6. Conclusions

Deep eutectic solvent ionic liquids meet all the criteria for a reagent that can be used in large-scale metallurgical processing, being cheap, readily available, chemically stable, environmentally benign and free of restrictions. A micro-leach technique we



Fig. 5. (A) 3D image of the polished surface of a calaverite (AuTe₂) crystal captured with a Zeta 2000 optical profiler. (B) The calaverite surface after cyclic voltammetry experiment in Ethaline, showing clear etching.

developed using an optical profiler allows us to rapidly measure dissolution rates in a sample and compare different minerals. Results demonstrate that electrum, native Te, tellurobismuthite, galena and chalcopyrite were all soluble by oxidation with iodine at low temperatures in a DES solvent, whereas pyrite was not. Dissolution rates varied between minerals with electrum showing the fastest dissolution rate and chalcopyrite the slowest. The dissolution rate of electrum was very favourable compared to the current industrial process of cyanidation. We demonstrate that gold and silver could be recovered from the solution by electrodeposition and that the opportunity exists for separation of the gold and silver by deposition through applying different potentials.

Preliminary work suggests that refractory phases, such as calaverite and pyrite, can be dissolved in DESs by electrolysis, hence suggesting a protocol whereby target inclusion minerals such as gold could be liberated from pyrite by electrolysis and then dissolved by oxidation and electrolytically recovered.

Given that ionic liquids contain no water, it is not appropriate to refer to their application to ore and metal processing as hydrometallurgy. Instead, *iono*metallurgy (Abbott et al., 2011a) with deep eutectic solvents would seem to offer a new set of environmentally-benign tools for metallurgists that could both augment existing processes and ultimately replace some.

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Introduction

Pyrite (FeS₂) is the Earth's most common sulfide¹ and the dominant iron sulfide in hydrothermal and sedimentary mineral deposits, whereas pyrrhotite (a group of minerals with compositions between FeS and Fe₇S₈) is the dominant iron sulfide in magmatic mineral deposits. Marcasite is a meta-stable polymorph of pyrite that forms in some low-temperature hydrothermal systems. Apart from minor sulfuric acid production, these iron sulphide minerals are not of economic interest, yet are often present in larger proportions than the ore minerals that a deposit is being mined for. This results in large volumes of iron sulfides being discarded to the waste (tailings) during mining operations. These tailings require careful management to avoid oxidation of the iron sulfides and the production of sulfuric acid that results in acid mine drainage if not treated.²

Arsenopyrite (FeAsS) can form a significant constituent in some hydrothermal ore deposits, in particular those that contain gold, whereas loellingite (FeAs₂) is a relatively rare mineral formed in high temperature hydrothermal or metamorphic ore deposits. Whilst these minerals can be a source of arsenic, more generally they present challenges in ore metallurgy and require additional treatment to contain the arsenic and discard it in an environmentally acceptable form.



Processing sulfur containing minerals is one of the biggest sources of acute anthropogenic pollution particularly in the form of acid mine drainage. This study attempts to show an innovative method for processing sulfide-based minerals. It is shown that pyrite can be solubilised by both electrochemical oxidation and reduction in a deep eutectic solvent (DES) Ethaline, a mixture of choline chloride and ethylene glycol. A novel method is demonstrated to investigate the redox properties of minerals using a paste made from the mineral powder in a DES. The first bulk electrochemical dissolution of pyrite is shown without the formation of H₂S or SO₂. It is also shown that the soluble species, including elements such as arsenic, can be recovered electrochemically which could potentially decrease acid mine drainage. The electrochemical properties of other iron–sulfur and iron–arsenic minerals are also presented and compared to those of pyrite.

Dissolution of pyrite and other Fe–S–As minerals

Whilst none of these common Fe-S-As minerals are of significant economic value they can often host economic quantities of precious metal mineral inclusions - typically gold and silver minerals in pyrite, arsenopyrite and loellingite, whereas pyrrhotite is often a host to PGE minerals.3,4 Sometimes gold and PGE may be present as nanoparticles or dissolved within the crystal lattice.4-7 Recovery of the precious metals from these sulfide concentrates will typically involve pyrometallurgy and/or hydrometallurgy. Roasting these ores releases SO₂ and/ or arsenic which require capture and treatment, whereas hydrometallurgy involves utilizing large volumes of aqueous solutions with reactive chemical reagents to solubilize the minerals followed by extraction and recovery. Hydrometallurgy results in large volumes of low concentration aqueous wastes that require expensive treatment and if not properly managed risks impacts on the environment through discharge of metals and toxic reagents into water courses. Therefore alternative techniques for the solubilisation of Fe-S-As minerals to liberate precious metals are desirable, in particular if they avoid the environmental drawbacks of current processes.

It has been proposed that ionic liquids could be used in several aspects of metal processing. This so-called ionometallurgical approach has recently been reviewed.⁸ The cost and toxicity of many ionic liquids precludes them from large scale applications such as mineral processing although they have been shown to be useful for biphasic extraction from aqueous solutions.⁸ Aqueous solutions of ionic liquids have also been demonstrated for the extraction of copper from chalcopyrite.⁹ Deep eutectic solvents (DESs) are mixtures of simple quaternary ammonium salts and hydrogen bond donors such as urea

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or glycerol.¹⁰ They may provide an alternative to conventional metallurgy as they use environmentally benign components and avoid the production of large volume/low concentration aqueous wastes. DESs have been shown to demonstrate relatively high solubility for transition metal oxides.^{11,12} It has also been shown that they can be used for direct electroreduction of copper oxide to copper¹³ and for the electrocatalytic dissolution and recovery of metals from alloys.¹⁴ Recently we have shown that iodine in DESs can be used to selectively solubilise minerals from ore samples.¹⁵ It has been shown that DESs can be used on a large scale to recover Zn and Pb from arc furnace dust waste.¹⁶

Here we provide the first investigation of the electrochemical behaviour of the common Fe–S–As minerals in DES. There have been numerous studies which have described the electrochemical behaviour of metal sulfides in aqueous media, in addition to the effect of pH and temperature.^{17–22} These studies demonstrate that the major products of oxidation of pyrite in aqueous solution are sulfate and ferrous ions, whilst other products are elemental sulfur, polysulfide, hydrogen sulfide, ferric hydroxide, iron oxide and iron(m).^{23,24} In another study, the reduction of pyrite in aqueous solution produces FeS, S^{2–} and hydrogen.²⁵

In this study it is shown that DESs can be used to solubilise iron sulfide based minerals through novel redox chemistry. These can be processed using pastes to minimise the amount of lixiviant (digesting solvent) used. We demonstrate here how the electrochemistry of the Fe–S–As minerals in DES compares and contrasts with the aqueous system and how elements from ores can be efficiently solubilised and recovered.

Experimental

The DES used in this study was a 1:2 molar ratio of choline chloride $(HOC_2H_4N(CH_3)_3Cl)$ and ethylene glycol $(HOCH_2CH_2OH)$ (both from Aldrich, 99%) which were stirred at 70 °C until a homogeneous solution was observed. It is referred to in the text by the trade name Ethaline. The water content was less than 1 wt% (thermogravimetry) but the addition of up to 5 wt% water had a negligible effect on the voltammetric response.

All minerals used were natural samples. SEM EDX analyses showed pyrite, marcasite and arsenopyrite to be stoichiometric. The calculated error in the stoichiometry on deposits was found to be ± 0.05 for Fe, ± 0.01 for S, ± 0.01 for As, ± 0.14 for C and ± 0.10 for O. The pyrrhotite appears to have a composition at the maximum vacancy possible (Fe_{0.86}S). The loellingite sample contains ~30 mol% substitution by safflorite (CoAs₂) with minor S (~3 mol% S/(S + As)). The loellingite sample also contains some inclusions of a mineral with the chemistry of moderite [(Co,Fe)As] but no nickel was found in this particular sample. The arsenopyrite, loellingite and pyrhotite samples contain minor amounts of silicates that are inert in Ethaline. The α -sulfur sample was from Sigma Aldrich (99.9%). The mineral electrodes were made by two different methods. In the first method a single crystal of the mineral was connected to a copper wire using silver conductive paint (RS). This was made into an electrode by casting the sulfide particle in a non-conductive resin. A smooth electrode surface was obtained by using an ATA SAPHIR 520 polisher with multiple grades of sand paper and then polished with various abrasives down to 0.05 μ m alumina slurry. Residual alumina was removed by sonication in distilled water for 10 minutes. The second method involved grinding the mineral into a fine powder (which was sieved to ensure particle sizes of 1–5 μ m) and then mixing it with a few drops of Ethaline to make a paste that was then painted onto a Pt flag electrode.¹⁹

All electrochemical experiments were carried out using an Autolab-potentiostat which is controlled by the GPES programme. A three-electrode system was used for all experiments. The working electrode was either a mineral cast in epoxy resin (approximate 1 mm^2 area) or mineral paste on a 1 cm^2 Pt flag electrode. The reference electrode was a silver wire immersed in 0.1 M AgCl in Ethaline contained in a glass tube which was separated from the electrochemical cell by a Vycor glass frit. A 1 cm^2 Pt flag electrode was used as the counter electrode. Electrochemical quartz crystal microbalance studies (EQCM) were carried out using a GAMRY EQCM using Gamry 5.65v controlled software with a 10 MHz gold coated quartz crystal resonator.

UV-Vis spectroscopy was carried out using a Shimadzu 1601 UV-Vis spectrometer. The optical quartz cells used in this study were 10 mm wide with 2 ml capacity. A Zeta-20 3D Optical Profiler was used to measure the etch depth of a pyrite surface during the chronocoulometry experiments.

Results and discussion

Cyclic voltammetry

The electrochemical behaviour of pyrite was measured using cyclic voltammetry for an individual pyrite crystal. Fig. 1a shows the voltammogram for a single grain of pyrite as a working electrode in Ethaline as the electrolyte at a sweep rate of 50 mV s⁻¹. Ethaline was chosen as it has a lower viscosity and a higher conductivity than most other DESs. It can be seen that a broad oxidation wave occurs with two maxima at *ca.* +0.20 V and +0.31 V. A broad reduction peak is also obtained with a maximum at *ca.* -0.53 V. The signals will clearly be made up of contributions from the Fe^{II/III} couple and the complex redox chemistry of the S₂²⁻ anion.^{1,9,16}

Mineral samples can have a variety of impurities and different crystal faces can exhibit anisotropic behaviour which can complicate the appearance of the cyclic voltammogram. The minerals themselves show relatively poor conductivity so a large crystal can induce a resistive artefact in the voltammogram.¹⁹

To circumvent the resistive issues a novel method was devised to determine the electrochemical properties of pyrite.





Fig. 1 Cyclic voltammogram of (a) single pyrite crystal, (b) pyrite paste on Pt, (c) sulfur paste on Pt and (d) $FeCl_2$ (0.1 M) on a Pt electrode, all in Ethaline at 20 °C at a scan rate of 50 mV s⁻¹ all using a Ag/AgCl reference electrode.

A sample of pyrite was ground in a pestle and mortar and the fine powder was mixed with Ethaline to make a thick paste. This paste was then painted onto a Pt flag electrode. This technique has recently been demonstrated to be effective for the dissolution and electrochemical recovery of galena (PbS) and the signal was shown to be relatively independent of the mineral loading.²⁶ The use of a paste to dissolve and recover elements from ores ensures the minimum volume of solvent (lixiviant). The solute is processed from saturated solutions ensuring small distances over which mass transport occurs.

Fig. 1b shows the cyclic voltammogram of the FeS₂ coated Pt flag electrode in Ethaline. It can clearly be seen that the cyclic sweep voltammetry of ground pyrite has five separate peaks. The cyclic sweep was started from 0 V and swept in an anodic direction to 1.0 V. The potential was then swept to -1.0 V then back to 0 V at a scan rate of 50 mV s⁻¹. Two peaks can be observed on the anodic scan. These are inferred to be due to the S₂^{2–}/S₈⁰ at *ca.* 0.45 V and the Fe^{II}/Fe^{III} at *ca.* 0.7 V (*vide infra*). On the cathodic scan three peaks can be observed. The first reduction peak at *ca.* 0.51 V is most probably the reduction of Fe^{III} to Fe^{II} whilst the second and third reduction peaks may be related to the reduction of sulfur species.

To prove the origin of each of the peaks observed with pyrite the electrochemistry of sulfur paste, painted onto a Pt electrode, was studied in Ethaline and the results are shown in Fig. 1c. The cyclic voltammogram has one anodic peak O_1 (*ca.* 0.0 V) and two cathodic peaks marked R_1 and R_2 (at about -0.39 V and -0.52 V) respectively. It should, however, be noted that there is a pronounced shoulder in the anodic sweep

between -0.5 and -0.3 V which is probably the reverse process for R₂. The cyclic voltammogram of sulfur has also been reported by Manan *et al.*²⁷ who used a Pt electrode to study sulfur electrochemistry but using an ionic liquid, 1-butyl-3methyl-imidazolium dicyanamide as the electrolyte. They assigned the two cathodic processes to

$$R_1: 3S_8 + 8e^- \rightarrow 4S_6^{2-},$$
 (1)

$$R_2: 2S_6^{2-} + 2e^- \rightarrow 3S_4^{2-}.$$
 (2)

A direct comparison of the redox potentials is difficult due to the differences in the liquid junction potential and the reference electrode, however the shapes and relative differences between O_1 , R_1 and R_2 are very similar to those reported by Manan confirming the validity of the assumption.

Fig. 1d shows the cyclic voltammogram for FeCl_2 dissolved in Ethaline. The classical one electron oxidation and reduction is what would be expected for a reversible redox couple. Comparing Fig. 1d with 1b it is logical to infer the peak assignments for iron based species shown in Fig. 1b. The redox processes for sulfur shown in Fig. 1c are not as well defined as those shown in Fig. 1b but this is to be expected given the poor conductivity of elemental sulfur and the difference can clearly be ascribed to a resistive artefact.

The mechanism of pyrite reduction and oxidation in 1 M HCl has been studied by several groups.^{14,28,29} Pyrite oxidation consists of three steps: a cathodic reaction, an electron transfer and an anodic reaction. If oxygen is the oxidant then the cathodic reaction is the reduction of oxygen, which is followed by electron transfer to the iron centre followed by a reaction of

the sulfur with water and oxygen to make the sulfate anion, the overall reaction being:

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{2-}.$$
 (3)

This is confirmed from the iron–sulfur Pourbaix diagram which shows sulfate as the most stable species at more positive over-potentials.³⁰

Electrochemical quartz crystal microbalance (EQCM)

Although the above assignments seem logical it does not provide any information about the phases of oxidation and reduction products. EQCM can be used to measure small changes in mass with the charge that flows through the cell. This is monitored using changes in the oscillating frequency of the quartz crystal. Pyrite paste was painted onto the gold electrode on the quartz crystal resonator and the electrode was cycled from -0.8 V to +0.8 V. A plot of charge passed vs. mass change can be seen in Fig. 2. It can be seen that on the anodic scan there is a mass loss associated with the peak marked Fe^{II/III} in Fig. 1b. By measuring the change in mass with charge the species dissolving can be estimated. If the process is 100% current efficient then the slope should equal the molar mass divided by the number of electrons times the Faraday constant (Faraday's Law). If the soluble species is ${\rm Fe}^{\rm III}$ originating from a 1 electron oxidation then the slope should be 5.8×10^{-4} g C⁻¹. The data from Fig. 2 show the slope is 6.3×10^{-4} g C⁻¹, which is close to the theoretical value. It should however be noted that there are other alternative loss processes such as the loss of FeS^{2+} which would correspond to a slope of $4.6 \times 10^{-4} \text{ g C}^{-1}$ or FeS_2^{2+} which would be $6.3 \times 10^{-4} \text{ g C}^{-1}$; exactly the same as that observed. It is important therefore to get an idea of speciation from UV-Vis spectroscopy.

Bulk electrolysis

Bulk electrolysis was carried out on the pyrite paste electrode to investigate the solubility of the oxidised and reduced products in Ethaline. Fig. 1b shows that pyrite has both oxidative and reductive signals. Bulk electrolysis was carried out in a two-electrode set up, applying 2 V between the electrodes for 24 hours; the first experiment held the mineral paste at a cathodic potential and the second held it at an anodic potential. At the end of



Fig. 2 Mass *versus* charge plot of pyrite powder pasted on a Au coated quartz crystal as the working electrode in Ethaline at 20 °C.



Fig. 3 Photograph showing a sample of Ethaline before electrolysis (centre) after both reduction of pyrite (left) and oxidation of pyrite (right) at a constant potential of 2 V. Both samples had been allowed to stand for a total of 3 days after electrolysis.

this period the Ethaline solution had turned yellow/brown where the electrode had been held at a positive potential. This suggests that the iron dissolved as Fe^{3+} and this ties in with the EQCM result, which shows the same. When the solution was left to stand exposed to air a brown precipitate formed after about 3 days which is likely to be an oxide or hydrated oxide of iron formed from the reaction with absorbed atmospheric moisture (Fig. 3). The solution obtained when the sample was held at a negative potential turned a grey/blue colour as shown in Fig. 3. It was thought that FeS could be formed upon reduction and while FeS is soluble in Ethaline, giving a solution of the same colour, the speciation in solution is unknown.

UV-Vis spectroscopy

UV-Vis spectroscopy was used to investigate the speciation of the soluble species formed upon oxidative and reductive dissolutions in Ethaline. The spectrum obtained from the oxidative dissolution of pyrite in Ethaline was compared with the spectra of FeCl₂ and FeCl₃ standard solutions in Ethaline, and can be seen in Fig. 4a. It has previously been shown by using EXAFS that most transition metal halide salts dissolved in Ethaline exist as a tetrachlorometallate anion.³¹ It was found that FeCl₂ dissolves to form FeCl₄²⁻ however the EXAFS spectrum of FeCl₃ in Ethaline shows evidence of some oxygen ligands probably originating from ethylene glycol. Fig. 4a however suggests that the solution obtained from the oxidation of pyrite does not correlate well with that for the dissolution of either FeCl₃ or FeCl₂ suggesting that the soluble species is not a simple tetrachloroferrate. It is likely therefore that a different ligand is attached to the iron, most probably sulfur or oxygen. The identity of the soluble species will be studied in the near future using EXAFS.

The same process was carried out for the reductive dissolution of pyrite and the results are shown in Fig. 4b. While FeS_2 is insoluble in Ethaline, FeS shows limited solubility. The peak maximum of FeS occurs at about 275 nm. Solutions obtained from both the anodic and cathodic dissolution of pyrite have absorbance maxima at about this wavelength. Again EXAFS will be used to investigate the species formed from cathodic dissolution.



Fig. 4 Comparison of UV-Vis spectra of the FeCl₃ in Ethaline and with the solution obtained from (a) the anodic dissolution and (b) the cathodic dissolution of pyrite ore in Ethaline at 20 °C.

In situ chronocoulometry and 3D microscopy

An *in situ* method has been utilized to monitor the electrochemical dissolution of pyrite. A sample was made with several randomly oriented crystals of pyrite connected to a copper sheet electrode and the whole material was encased in a non-conducting resin before being polished back to expose the randomly oriented pyrite crystals. The electrically connected pyrite crystals were held at a constant potential of ± 1.2 V *vs*. Ag/Ag⁺ for 4 hours and the sample was then analysed using optical profilometry to measure the different effects and etch rates on different crystal orientations of pyrite during anodic dissolution in Ethaline. Fig. 5 shows an image of a sample of these crystals before and after they were electrochemically polarised. The dark area between the crystals is an



Fig. 5 3D colour optical microscopy images of pyrite grains (a) before and (b) after anodic polarisation at +1.2 V for 4 hours, (c) cross-sectional profile across the line.

electrically insulating resin. It can be seen that there is a certain degree of anisotropy with regard to the dissolution rates. Crystal B is largely undissolved whereas A, C and D are dissolved to different extents. Crystal A has dissolved to a depth of approximately 50 μ m, whereas C and D have dissolved by approximately 10–20 μ m. One explanation for this could be that the orientation of the exposed crystal faces caused dissolution at different rates *i.e.* there is a degree of anisotropy to the dissolution rate.

To test whether anisotropic etching occurs with pyrite an array of randomly oriented pyrite crystals (>20) were attached to a nickel plate using a conducting adhesive and then set in an insulating resin (Buehler epoxy cure 2 resin with its epoxy hardener in a 4:1 volume ratio). The sample was then polished using a diamond abrasive to ensure a flat surface. This was then analysed using XRD and the results are shown in Fig. 6. As would be expected from a randomly oriented natural mineral a variety of crystal faces are observed. The sample was put into Ethaline and held at +1.2 V vs. Ag/Ag⁺ for 4 hours. Following that period the sample was re-analysed using XRD and the results are also shown in Fig. 6. The data



Fig. 6 Normalised XRD spectra of a pyrite sample before and after etching in Ethaline at ± 1.0 V for 4 hours.

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were normalised to the [200] signal and it can be seen that following dissolution the relative ratios of the peaks have changed. The signals for the diagonal crystal planes *e.g.* [311], [321], [111] and [222] are significantly decreased. This would be expected since these faces would have the largest proportion of energetically unfavourable atoms. It is proposed that these diagonal crystal faces are preferentially etched below the analysis surface as shown in Fig. 5a such that the XRD signal is much lower for them, leaving predominantly the [200] face. It can clearly be seen from Fig. 6 that anisotropic electrochemical etching of pyrite does occur in Ethaline. This observation helps to explain the differences between the electrochemical response for pyrite shown in Fig. 1a and b as the former has only one crystal plane exposed to the electrolyte whereas the latter has a variety.

Other iron-sulfur and iron-arsenic minerals

Fig. 7 shows a comparison of the voltammetric responses of five iron–sulfur and iron–arsenic minerals. In all cases the $Fe^{II/III}$ redox couple is clearly discernible at about +0.5 V as a

reversible, diffusion controlled process. The redox potentials are relatively unaffected by the nature of the mineral. Relatively little is known about the electrochemical properties of the minerals studied here. Almeida and Giannetti studied arsenopyrite by mixing it with carbon powder and making it into an electrode and electrochemically oxidising it in an aqueous acetate buffer solution.³² A relatively poorly resolved voltammogram was obtained which contained most of the redox processes shown in Fig. 7d.

The electrochemical response for the sulfur or arsenic component is clearly different for each mineral. Comparing pyrite and marcasite which are chemically the same (both FeS₂) it can be seen that the relative peak heights for the iron based redox couple compared to the sulfur peaks are significantly different. For pyrite the sulfur signal is significantly smaller than that for iron whereas the reverse is the case for marcasite. Pyrite has a cubic crystal structure rather than an orthorhombic crystal structure found in marcasite.³³ In contrast, pyrrhotite has a relatively weak redox signal for sulfur. This could be due to it being predominantly S^{2–} rather than S₂^{2–}



Fig. 7 Cyclic voltammogram of (a) pyrite FeS_2 , (b) marcasite FeS_2 , (c) pyrrhotite ($Fe_{1-x}S$), (d) arsenopyrite (FeAsS) and (e) loellingite ($FeAs_2$) paste on Pt both in Ethaline at 20 °C at a scan rate of 10 mV s⁻¹.

which could be why the cathodic signal at -0.1 V is so weak. In arsenopyrite the anionic component is nominally $(SAs)^{2-}$ with the iron being principally in the Fe^{II} form.³⁴ In addition these materials have significantly different band gaps in the pure state; pyrite is 0.95 eV whereas marcasite is 0.34 eV and arsenopyrite is 1.19 eV. It would therefore be expected that marcasite would be easier to oxidise than either of the other two minerals.

Bulk anodic electrolysis of all of the minerals shown in Fig. 7 resulted in coloured solutions as shown in Fig. 8.



Fig. 8 Solutions obtained from the bulk anodic electrolysis of five minerals in Ethaline following electrolysis at a constant current density of 5 mA cm⁻² (except for marcasite which was 2.5 mA cm⁻²) for 16 h.



Fig. 9 SEM images and elemental compositions (EDX) of cathode deposits obtained after the electrolysis of (a) pyrite (FeS₂), (c) pyrrhotite (Fe_{1-x}S), (d) arsenopyrite (FeAsS) and (e) loellingite (FeAs₂) following electrolysis at a current density of 5 mA cm⁻². Whilst the deposition of (b) marcasite (FeS₂) was obtained at a current density of 2.5 mA cm⁻² in Ethaline at 50 °C for 20 h.

Although the dissolution for all of the minerals should result in the formation of Fe^{III} it is evident that the solutions all have a different colour which would not be the case if iron was formed [FeCl₄]⁻. In the extreme, loellingite forms a green solution on dissolution, which is characteristic of Fe–As complexes such as those formed in the so-called green rust.³⁵ It seems logical therefore that upon dissolution the iron and chalcogenide remain bonded to each other in the soluble complex. The colour could also arise from other metal impurities *e.g.* Co. There is some evidence of cobalt being incorporated in the deposit obtained on the cathode (<3 wt%) but this is too small to colour the solution. We characterised Co in Ethaline solutions but the characteristic peak was absent from the UV-Vis analysis of the loellingite solution.

Bulk electrolysis was carried out in the cell as reported previously.¹⁹ The anodic material was iridium coated titanium which has been found to be anodically stable in the DES and the cathodic material was a nickel sheet. After electrolysis of the mineral paste on the anodically polarised electrode for 16 h it was found that for all minerals a black deposit was obtained on the nickel cathode and the morphology (SEM) and composition (EDX) of the deposits are shown in Fig. 9.

All of the deposits contained iron but with different amounts of sulfur, arsenic, oxygen and carbon. None of the samples are magnetic showing that it is not elemental iron which is deposited. The electropolishing of stainless steel has previously been studied in the same DES and it was found that when the iron was oxidised through anodic polarisation a brown solid was formed in solution. This was found to be an iron glycolate species and it is proposed that the deposits shown in Fig. 9 are likely to contain glycolates as ligands.³⁶ If the carbon and oxygen only came from the glycolate ligand, it would be expected that the C: O ratio would be 1. In all cases the C: O ratio is <1 meaning that some iron oxide must also be present.

The deposit obtained from loellingite contains a high As: Fe ratio whereas the S: Fe ratio for the deposit obtained from pyrite is much lower. This shows that when the mineral dissolves under anodic polarisation the metal enters the solution with the sulfur or arsenic still attached but some exchange clearly occurs in solution. This confirms the idea that the EQCM result shown in Fig. 2 corresponds to the pyrite possibly forming $[FeS_2]^{2+}$ when it dissolves in the DES. The electrolysis of arsenopyrite results in only As and no S in the deposit showing that arsenic is a stronger ligand than sulfur and becomes incorporated into the deposit more easily.

For this methodology to be used on a practical scale the DES would have to be recovered and recycled. This can be done by adding an equal volume of water to DES. This reduces the viscosity and allows the paste to be filtered. The addition of water precipitates any remaining iron in solution leaving a colourless aqueous solution of DES. The water can be removed by evaporation. This has been demonstrated for numerous electrochemical processes on a pilot plant scale (>500 kg) and is described more fully in the literature.³⁷

Conclusions

In the present study, the influence of Ethaline on the electrochemical behaviour of pyrite (FeS₂) was examined at ambient temperature with the aim of developing a non-acidic dissolution protocol. It is shown that mineral electrochemistry can be studied by painting a paste of the mineral in a DES onto an electrode. The cyclic voltammogram of natural pyrite in Ethaline was observed to have two anodic peaks and three cathodic peaks. The two anodic peaks could be probably attributed to the formation of elemental sulfur and Fe(III), whereas the three cathodic peaks are related to the reduction of Fe(III) to Fe(n) with the remaining peaks attributed to the reduction of sulfur. A method for achieving bulk mineral dissolution and elemental recovery using electrolysis has been demonstrated. Anodic polarisation of pyrite led to bulk dissolution although this was highly anisotropic, with some sections showing dissolution rates of 12 μ m h⁻¹.

The electrochemical properties of 5 iron–sulfur and iron– arsenic minerals were studied and shown to exhibit similar responses for the iron component but the sulfur and arsenic components differed with mineral stoichiometry. Anodic bulk dissolution of all of these minerals led to their solubilisation. Most understandably yielded brown solutions but loellingite produced a green solution showing that the arsenic remained as a ligand on the iron after dissolution. Bulk electrolysis also showed that iron based deposits could be obtained on the cathode surface. The use of pastes for mineral processing decreases the lixiviant volume and ensures minimal volume of DES usage.

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