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Hydrometallurgical extraction of metals from secondary resources using various reagents

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Declaration

It is hereby declare that this thesis submitted for the degree of Philosophiae Doctor (Chemical Engineering) to the University of the Witwatersrand is my own original work. It has not previously been submitted for any other degree or examination in any other university or faculty.



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Abstract

The advancement and widespread applications of metals in the modern world have led to a growing demand which outstrips their supply. This has resulted in a vital need for recovering precious and critical metals from waste materials, known as secondary resources. Recovering precious, critical and heavy metals not only improves the circularity of metals, but also minimises the deleterious effects of waste materials on the environment. To achieve this crucial aim, research in this thesis focuses on improving gold (Au) yield by finding different ways for pretreatment to break down pyrite, the predominant sulfidic mineral that encapsulates gold in mine tailings. In addition, the research focuses on extracting critical metals such as indium (In) and gallium (Ga) from industrial waste, in this case electric arc furnace dust (EAFD). The results achieved in this research are presented in five publications as explained in brief below:

- The dissolution of pyrite – the predominant host mineral encapsulating gold – to improve gold extraction from mine tailings was studied in a nitric acid (HNO_3) solution. The study showed that when the concentration of HNO_3 is above 2 M, it acts as a powerful acid and oxidant to break down the pyrite structure, while simultaneously exposing the enclosed gold through oxidative dissolution. The conducted experiments confirmed that within 2 h, 3 M HNO_3 effectively dissolved 95% of FeS_2 to release the remaining gold in pyrite at 75 °C. The kinetics of pyrite dissolution was also examined in the temperature range of 25 to 85 °C. The results indicated that the mixed controlled model $(1/3\ln(1-X) + [(1-X)^{-1/3} - 1]) = k \cdot t$, where X is the fractional conversion, k the apparent reaction rate constant, and t leaching time) describing the interfacial transfer and diffusion was governing the kinetics of pyrite dissolution in nitric acid. The activation energy required at low temperatures (25-45 °C) was 145.2 kJ/mol and it reduced at higher temperatures (55-85 °C) to 44.3 kJ/mol. Therefore, nitric acid pretreatment is an effective method for mine tailings containing pyrite with enclosed gold. Nitric acid can be recovered in an eco-friendly manner by capturing the emission of NO_x gases from the nitric acid decomposition and can be economically attractive when regenerating the starting acid/oxidant (see publication: “*The Kinetics of Pyrite Dissolution in Nitric Acid Solution*”).
- To gain insight into the dissolution of minerals encapsulating gold, such as pyrite and chalcopyrite, an electrochemical study was conducted in nitric acid media using cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV scans were measured to identify the oxidation-reduction peaks for pyrite and chalcopyrite. Based on the corresponding CV scans and visual observations, anodic and cathodic reactions for oxidised and reduced species were

deduced for each identified peak which occurs at a specific potential. An EIS study was then conducted at the particular oxidative potentials, to gain further indications on the relevant reactions, hence providing supporting evidence of the dissolution mechanism. The EIS study at low potential (i.e. 0.5 V vs Ag/AgCl (3 M KCl) reference electrode) showed that the dissolution reaction was controlled by a diffusion process due to the accumulation of certain species, i.e. $\text{Fe}(\text{OH})_3$ and S^0 , on the pyrite electrode, and $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}$, CuS_2 , and S^0 in the case of chalcopyrite. This was confirmed in the EIS curve through the appearance of the linear Warburg diffusion effect. Increasing the potential beyond 0.7 V leads to reactions at which the previously formed species covering the surface of the electrodes and causing a diffusion barrier, oxidised further converting them to soluble species. This was reinforced by the omission of Warburg-like effects in the EIS data (see publication: *“A comparison of the Electrochemical Oxidative Dissolution of Pyrite and Chalcopyrite in Diluted Nitric Acid Solution”*).

- Due to environmental awareness, neoteric eco-friendly solvents like ionic liquids (ILs) and deep eutectic solvents (DESSs), which can be used as alternatives to conventional leaching reagents for recovering metals, are gaining increasing attention among researchers. Hence, a new hydrometallurgical method using ILs to extract Zn, In, and Ga, along with Fe as a common impurity from EAFD, that was spiked with 5% of both In and Ga, was examined. EAFD is a valuable metal-containing waste generated in significant amounts during the process of steelmaking from iron scrap material in an electric arc furnace. With critical metal recovery as the main goal, two ILs: $[\text{Bmim}^+\text{HSO}_4^-]$ and $[\text{Bmim}^+\text{Cl}^-]$, were studied in conjunction with three oxidants $\text{Fe}_2(\text{SO}_4)_3$, KMnO_4 , and H_2O_2 , to determine which IL and oxidant combination performs best for extracting the target metals. Following the initial tests, the influence of parameters such as the IL concentration, oxidant concentration, solid-to-liquid ratio (S/L), time, and temperature were optimised to achieve the maximum extraction of the target metals. Results from a series of experiments found the optimum condition to be; 50 ml 30% v/v $[\text{Bmim}^+\text{HSO}_4^-]$, 1 g of $\text{Fe}_2(\text{SO}_4)_3$ oxidant (2%), S/L ratio of 1/20, at 85 °C for 240 min leaching time, resulting in extractions of 92.7% Zn, 80.2% Fe, 97.4% In, and 17.03% Ga. The dissolution kinetics of the studied metals over a temperature range of 55–85 °C was diffusion-controlled (see publication: *“A New Hydrometallurgical Process for Metal Extraction from Electric Arc Furnace Dust Using Ionic Liquids”*).
- Environmental and safety concerns about traditional methods for gold extraction, and the potential volume of enclosed gold in mine tailings in sulfidic minerals (i.e. pyrite), were the motivations to find effective, efficient and ecologically benign ways to break down the pyrite structure to expose the locked gold to improve its extraction. Hence, the feasibility of the dissolution of pyrite was studied in a deep eutectic solvent (DES) as a novel solvent. DESs are an

analogue of ILs, which are gaining increasing attention as a potential solvent with eco-friendly features. Therefore, the viability of pyrite dissolution in a DES containing choline chloride – a quaternary ammonium salt $[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]^+\text{Cl}^-$ – and ethylene glycol $[\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}]$, named ethaline, was examined both theoretically through density functional theory (DFT) calculations and experimentally. DFT calculations determined whether Cl^- and/or $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$, the two ligands provided by ethaline, can make the most probable and stable complex with Fe^{2+} and/or Fe^{3+} . To do so, the reaction Gibbs free energies (ΔG) for possible complexes that Cl^- and $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ can form with Fe were calculated. In addition, the energy gaps between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO gap) were considered. Among the proposed complexes, the tetrahedral complex $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$, with Fe^{3+} chelation taking place through the O-donors of the ligand $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$, had the lowest ΔG (–71.4 eV) indicating the simultaneous formation of the complex, as well as the largest HOMO-LUMO gap (1.3 eV) specifying the most stable complex. For experimental evaluation, the effect of the pH of the ethaline solvent mixed with hydrogen peroxide (H_2O_2) oxidant, and the different S/L ratios on Fe extraction (indicating pyrite dissolution) were examined. The results show that a pH of 8 provides the desired condition at which ethylene glycol is deprotonated to $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$, was the favorable ligand for Fe complexation. It was found that the S/L ratio of 1/20 was optimal and achieved 23.7% Fe extraction. The theoretical and experimental work correlated in indicating $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ as the favourable ligand. However, the ethaline solvent as the leaching solution did not achieve adequate Fe extraction, as it did not succeed in properly breaking down pyrite to expose the locked gold (see publication: “*The Feasibility of Pyrite Dissolution in a Deep Eutectic Solvent Ethaline: Experimental and Theoretical Study*”).

- DFT modelling was also applied to theoretically calculate the possibility of the extraction of In and Ga, in the IL medium. To investigate this aim, three imidazolium-based ILs, namely $[\text{Bmim}^+\text{HSO}_4^-]$, $[\text{Bmim}^+\text{Cl}^-]$, and $[\text{Bmim}^+\text{NO}_3^-]$ were selected for DFT calculations. They all have the same cationic part $[\text{Bmim}^+]$, but different anionic parts, i.e. $[\text{SO}_4^{2-}]$, $[\text{Cl}^-]$, and $[\text{NO}_3^-]$, which are similar to the most commonly used mineral acids H_2SO_4 , HCl , and HNO_3 , respectively. The ΔG for different complexes were calculated to determine which of the available ligands, i.e. sulfate (SO_4^{2-}), chloride (Cl^-), and nitrate (NO_3^-), provided by each IL most likely form the most stable complex with In and Ga. The obtained values for ΔG confirm that IL $[\text{Bmim}^+\text{HSO}_4^-]$, owing to the $[\text{SO}_4^{2-}]$ O-donor ligand, resulted in the dimer complexes of $[\text{In}_2(\text{SO}_4)_3]$ and $[\text{Ga}_2(\text{SO}_4)_3]$ having the lowest ΔG and the largest HOMO-LUMO gap, indicating the most probable and stable complexes (see publication: “*Indium and Gallium Extraction Using Ionic liquids: Experimental and Theoretical Study*”).

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List of Abbreviations

Abbreviations	Meaning
CV	Cyclic Voltammetry
DESS	Deep Eutectic Solvents
DFT	Density Functional Theory
EAFD	Electric Arc Furnace Dust
EIS	Electrochemical Impedance Spectroscopy
FTIR	Fourier-Transform Infrared
HBA	Hydrogen Bond Acceptor
HBD	Hydrogen Bond Donor
HOMO	Highest Occupied Molecular Orbital
m.p.	Melting Point
ILs	Ionic Liquids
LUMO	Lowest Unoccupied Molecular Orbital
S/L	Solid-to-Liquid ratio
SEM	Scanning Electron Microscopy
XRD	X-ray Diffraction
ΔG	Reaction Gibbs Free Energy

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“I was taught that the way of progress is neither swift nor easy.”

Marie Curie

“Never regard your study as a duty, but as the enviable opportunity to learn to know the liberating influence of beauty in the realm of spirit for your own personal joy and to the profit of the community to which your later work belongs.”

Albert Einstein

Chapter 1

Introduction

1.1. Background

Metals have been used by humans for thousands of years, and they have played a crucial role in human progress and development. From the discovery of bronze to the development of iron and steel alloys, metals have been used to make tools, weapons, coins for trading, and jewellery for beauty. While the use of metals has changed based on desires and discoveries over the centuries, humans have continued to be fascinated by their strength, malleability and shapability. With widespread applications, metals have been integral to transportation, communication, making powerful and durable structures, and energy production (Wernick & Themelis 1998). In modern times, metals have also been used in large quantities for the production of electronic equipment, conductors, computers and smartphones. Hence, metals are fundamental to various industries (Gramatyka et al., 2007).

Advanced automated industry facilitates the mass production of various equipment and/or products containing different metals, leading to a growing demand which outstrips supply (Oguchi et al., 2011; Krishnan et al., 2021). Gold mining and extraction for more than a century generated large amount of mine waste, referred as tailings, which may still contain some gold locked in sulfidic minerals, such as pyrite. Tailings are leftover materials after the extraction of the target metals, and can be classified as a valuable secondary resource. Hence, any further metal recovery has the potential for financial rewards. Additionally, tailings are an environmental burden, which leads to interest in reprocessing them to clear the occupied land for rehabilitation (Ndlovu et al., 2017; Matinde et al., 2018).

Tailings are only one category of secondary resources or waste. Industrial waste that has been produced over many years of advanced industrialisation through a wide range of metallurgy and/or non-metallurgy processes, generates a substantial amount of metal-containing by-products from which metals can be recovered (Jadhav & Hocheng, 2012). Among the different metal-containing industrial wastes, electric arc furnace dust (EAFD) is one of the valuable industrial wastes. EAFD is a by-product of the steelmaking process that involves melting iron scraps and end-of-life iron-based products in an electric furnace. During the melting process, the temperature in the furnace can be as high as at least 1600 °C, at which some of the elements within the iron scraps vaporise and, after cooling create a significant amount of fine dust. Although EAFD is considered a waste product, it contains

valuable metals like Zn, Fe, and Cu that can be recovered and returned to the industry for production (Kukurugya et al., 2015; Kalpakli et al. 2021).

According to the World Steel Association, about 30% of the world's steel production is now based on reusing iron scrap, and this is expected to increase in the future. It has been estimated that, for every ton of steel produced from iron scraps, an electric arc furnace generates around 20 kg of dust. Besides the valued metals like Zn and Fe, this dust contains various heavy metals and other pollutants such as Cr and Pb which can have negative environmental impacts if not properly managed. Therefore, effective dust collection and management systems are necessary to minimise the environmental impact by recovering the desired metals and heavy metals (Halli et al., 2017).

For some metals, like rare earth elements (REEs), indium (In) and gallium (Ga) there are no naturally occurring large, high-concentration deposits that are extractable. The recovery of these valuable and critical metals from secondary sources is becoming crucial due to both their relative scarcity and growing demand (Shen et al., 2010; Silva et al., 2019). Therefore, not only the growing demand, but also the scarcity of some metals and the substantial waste produced requires developing efficient ways to recover metals from different waste materials as secondary sources, rather than mining them from the Earth's crust (Zhang & Xu, 2016).

1.2. Problem statement

Metals are fundamental and essential materials for almost all industries. The increasing demand for metals world wide has put a strain on the available, but limited, sources in nature, which makes it necessary to explore alternative ways of sourcing metals. One promising approach is to recover metals from different waste materials known as secondary resources, such as industrial waste, used electronic equipment and mine waste (tailings), which contain valuable metals such as Au, Ag, Cu, Zn and Ni (Ndlovu et al., 2017; Krishnan et al., 2021).

Recovering metals from waste materials not only helps to meet the increasing demand which outstrips the supply, but also contributes to the circular economy. Therefore, managing waste materials by recovering metals from them has added economic benefits, reducing the deleterious impact of the waste materials on the environment, shifting the focus from underground mining to the metals recovery from different waste materials and preserving scarce mineral resources for the future.

However, the recovery of metal(s) is often hindered by the complex nature of the waste material, and the costs associated with the recovery process. Moreover, some of the conventional methods for metal recovery from these waste materials are usually environmentally unfriendly and inefficient.

Therefore, it is essential to develop innovative approaches for metal recovery from secondary resources that are sustainable, cost-effective, and eco-friendly.

An efficient metal recovery process should turn the waste materials into valuable resources, while minimising the environmental impact of the activity. Hence, the goal of this work is to examine different reagents, like nitric acid (HNO_3) and deep eutectic solvents (DES), as new alternative solvents to develop a pretreatment method to break down the pyrite structure enclosing the remaining gold in mine tailings. ILs are also studied as alternative solvents to develop an efficient and effective method for metals recovery from EAFD, another valuable industrial waste.

1.3. Research questions

The key questions to be answered by this research are the following:

- Can nitric acid pretreatment dissolve pyrite to expose the remaining gold in mine tailings?
- Which kinetic model would describe the pyrite dissolution in nitric acid solution in the temperature range of 25-85 °C?
- Can a green emerging DES ethaline, with H_2O_2 as a pretreatment method break down pyrite.
- Can theoretical calculations with DFT determine which ligands ($[\text{Cl}^-]$ and/or $[\text{O-CH}_2\text{-CH}_2\text{-O}^-]$) provided by DES ethaline, would produce the most probable and stable complex with Fe to indicate pyrite dissolution?
- Can ILs as a novel method extract metals (Zn, Fe, In and Ga) from EAFD?
- Which kinetic model would describe the extraction of metals (Zn, Fe, In and Ga) from EAFD using a IL $[\text{Bmim}^+\text{HSO}_4^-]$ solution?
- Can DFT calculations determine which of the ILs $[\text{Bmim}^+\text{HSO}_4^-]$, $[\text{Bmim}^+\text{Cl}^-]$, and $[\text{Bmim}^+\text{NO}_3^-]$ providing $[\text{SO}_4^{2-}]$, $[\text{Cl}^-]$, and $[\text{NO}_3^-]$ ligand, respectively, can make the most feasible and stable complex with In and Ga?

1.4. Aims and objectives of the research

To answer the research questions, one can formulate an overall aim and objectives for the investigation. Keeping the recovery of metals from secondary resources in mind, this research aimed to examine pyrite dissolution as a primary host mineral enclosing gold in different media such as nitric acid (HNO_3) solution and a DES named ethaline, to develop a pretreatment method before gold extraction to improve its recovery from mine tailings. In addition, using different ILs to extract critical

metals, i.e. In and Ga along with Zn and Fe, from valuable industrial waste EAFD. It should be noted that Zn and Fe are the predominant metals in EAFD. Furthermore, to make it easier to study the extraction, the EAFD was spiked with 5% In and Ga. To tackle this research effectively the objectives were as follows:

- Examining pyrite dissolution in nitric acid (HNO_3) as a pretreatment method considering a wide range of operating conditions such as 1-4 M nitric acid concentration, 25-85 °C temperature, 53 to 212 μm particle size, and 1000-4000 rpm stirring speed.
- Determining the kinetics of pyrite dissolution in nitric acid solution at a range of 25-85 °C.
- Performing electrochemical studies for further understanding of the dissolution mechanism of sulfidic minerals encapsulating gold, such as pyrite and chalcopyrite, in nitric acid as the electrolyte through cyclic voltammetry (CV) and impedance spectroscopy (EIS).
- Using a neoteric DES comprising choline chloride and ethylene glycol, called ethaline, mixed with hydrogen peroxide (H_2O_2) oxidant as a pretreatment method to break down pyrite and compare it to nitric acid leaching.
- Applying density functional theory (DFT) calculations to determine which ligands provided by DES ethaline, i.e. $[\text{O}-\text{CH}_2-\text{CH}_2-\text{O}^-]$ and/or $[\text{Cl}^-]$, can make the most probable and stable complex with Fe as an indication of pyrite dissolution.
- Examining an alternative novel way to extract In and Ga from EAFD using two ILs $[\text{Bmim}^+\text{HSO}_4^-]$, and $[\text{Bmim}^+\text{Cl}^-]$, mixed with three different oxidants (H_2O_2 , KMnO_4 , FeSO_4), to find the optimum conditions for metal extraction.
- Determining the kinetic model that controls the extraction of the metals (Zn, Fe, In and Ga) from EAFD using IL $[\text{Bmim}^+\text{HSO}_4^-]$ solution at a temperature range of 55-85 °C.
- Applying DFT modelling to theoretically determine which of three ILs $[\text{Bmim}^+\text{HSO}_4^-]$, $[\text{Bmim}^+\text{Cl}^-]$, and $[\text{Bmim}^+\text{NO}_3^-]$ can make the most feasible and stable complex with In and Ga. These three ILs were selected since the anionic parts ($[\text{SO}_4^{2-}]$, $[\text{Cl}^-]$, and $[\text{NO}_3^-]$) are similar to those of the most commonly used mineral acids, H_2SO_4 , HCl , and HNO_3 . Ultimately the theoretical outcomes are to be compared with the experimental results of these investigations to make a comprehensive conclusion about the feasibility of this approach for waste metal recovery.

1.5. Hypotheses

This research contains three main premises:

- It is viable to conduct a pretreatment using a nitric acid solution for dissolving pyrite in mine tailings and thereby exposing the encapsulated gold.
- It is feasible to break down pyrite enclosing gold in mine tailings with the DES named ethaline – comprised of choline chloride and ethylene glycol– as a novel eco-friendly solvent mixed with H₂O₂ oxidant to develop a pretreatment method.
- It is possible to use IL – [Bmim⁺HSO₄⁻] and/or [Bmim⁺Cl⁻]– as an alternative to the conventional sulfuric acid leaching for metals extraction (Zn, Fe, In, and Ga) from EAFD.

1.6. Contribution of the research

This research developed a pretreatment method using nitric acid to dissolve pyrite encapsulating gold in mine tailings to enhance gold recovery yield. Moreover, the studied kinetics of pyrite dissolution in nitric acid in a temperature range of 25 to 85 °C follows the mixed–controlled model $(1/3 \ln(1-X) + [(1-X)^{-1/3} - 1]) = k.t$, where X is the fractional conversion, k is the apparent reaction rate constant, and t (leaching time) describes the interfacial transfer and diffusion-controlled kinetics of pyrite dissolution. The electrochemical study was also conducted for further understanding the oxidative dissolution of pyrite in nitric acid solution. This research has contributed to developing a new hydrometallurgical method for the extraction of Zn, Fe, In and Ga from EAFD using ILs as an alternative to conventional leaching methods.

In addition to the experimental work, theoretical evaluation through DFT calculations was conducted to develop a better understanding of metal-ligand complexation in DES and IL media. Often in a leaching solution, there is more than one ligand that can form complexes with the target metal. To determine which available ligand is likely to form the most stable complex, DFT evaluation through calculating the reaction Gibbs free energy (ΔG) and the HOMO-LUMO gaps can give one an indication of the feasibility of a particular complex forming. Therefore, to determine whether Cl⁻ and/or [C₂H₄O₂]²⁻, the two ligands provided by the DES ethaline, can form the most stable complex with Fe²⁺ and/or Fe³⁺ as an indication of pyrite dissolution, DFT calculations were performed. It was found the tetrahedral complex of [Fe(C₂H₄O₂)₂]⁻ was the most stable.

Moreover, among the three studied ILs –[Bmim⁺HSO₄⁻], [Bmim⁺Cl⁻], and [Bmim⁺NO₃⁻]– for In and Ga extraction, it was found that the IL [Bmim⁺HSO₄⁻], due to the [SO₄²⁻] O-donor ligand, resulted in the dimer complexes of [In₂(SO₄)₃] and [Ga₂(SO₄)₃] with the lowest ΔG , and the largest HOMO-LUMO gap indicating they were the most possible and stable complexes.

Neoteric eco-friendly solvents such as IL and DES were investigated for metal extraction, but their effectiveness was limited toward some of the studied metals, although not all of them. For instance, the IL [Bmim⁺HSO₄⁻] achieved 97.4% In extraction from EAFD, while the maximum Ga extraction was less than 20%. The pyrite dissolution in DES ethaline was also less effective (23.7%). Thus, more research on different metals should be done with these novel solvents (IL and DES) to find methods which have a higher success rate.

1.7. Layout of the thesis

This thesis comprises eight chapters. The introduction chapter outlined the motivation for this research, the problem statement, the aims and objectives, the hypothesis and the contribution of this research. Chapter 2, is a literature review on the importance of the extraction of valuable metals from secondary resources including tailings and metal-contained industrial waste. The remaining gold in mine tailings is predominantly enclosed in pyrite, which is a common host mineral for gold. Thus, the occurrence of gold in pyrite, different pretreatment methods to enhance and facilitate gold extraction from refractory sulfidic gold ores/tailings, mechanism of oxidative dissolution, electrochemical study, and the theoretical study via DFT are all topics discussed in this Chapter. The following Chapters (3-7) each present a peer-reviewed publication. To improve the gold yield from mine tailings, pretreatment can be conducted to break down pyrite to expose the enclosed gold. For this purpose, the oxidative dissolution and kinetics of pyrite dissolution in nitric acid solution were investigated and presented in a published research paper in Chapter 3. In Chapter 4, an electrochemical study on sulfidic minerals encapsulating gold, i.e. pyrite and chalcopyrite, was done to complement the dissolution study and gain further supporting evidence for the kinetics of the dissolution mechanism in nitric acid. In Chapter 5, a new hydrometallurgical method using ILs ([Bmim⁺HSO₄⁻] and [Bmim⁺Cl⁻]) was studied to extract Zn, In, and Ga, along with Fe as a common impurity, from EAFD. The DFT evaluation compared with the experimental work was outlined in Chapters 6 and 7, including two publications. In Chapter 6, the viability of pyrite dissolution in a DES medium named ethaline containing [choline chloride (1):ethylene glycol (2.5)] was studied, and likewise in Chapter 7, the feasibility of In and Ga extraction in three ILs [Bmim⁺HSO₄⁻], [Bmim⁺Cl⁻], and [Bmim⁺NO₃⁻]. This is followed by the conclusions (Chapter 8), which provides a summary of the main findings and makes recommendations for future research.

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Chapter 2

Literature Review

2.1. Background: Refractory ores/tailings and industrial waste

The word “refractory” relating to ores means “difficult to treat”. Refractory ores are defined as a type of gold ore that is not amenable to the cyanide leaching process and typically gives inadequate gold yields (less than 80% or in some cases less than 50%). Improvement in gold recoveries can be attained with the use of significantly larger amounts of reagents (cyanide and oxidant) and/or further treatment processes (Vaughan, 2004). In other words, in refractory ores, gold particles are encapsulated in the sulfidic host minerals and are inaccessible to leaching reagents. Hence, after conventional cyanide leaching, some gold ultimately remains in the processed ore residue known as tailings.

Therefore, tailings which are the discharged materials from industrial operations after the extraction process, contain the encapsulated gold in the sulfidic minerals, which are categorised as secondary resources and still retain their refractory features (Ndlovu et al., 2017). Thus, to extract the enclosed gold, the host mineral matrix should be destroyed, typically by chemical means such as oxidative dissolution methods to expose the gold particles (Goodall & Scales, 2007). Mineralogy, physical and chemical composition, and leachability of a tailings material depend on the previous extraction processes, leaching reagents used for extraction, the amount of extracted gold, the amount of remaining gold, and gold occurrence in a host mineral (Falagán et al., 2017).

The most common feature of refractory ore is the invisible locked gold (both chemically or physically) within the sulfidic minerals i.e. pyrite, pyrrhotite, and chalcopyrite. The grade of refractoriness depends on the severity of its causes in the gold ore (Vaughan, 2004; Adams, 2005; Goodall & Scales, 2007). The grade of refractoriness of a refractory ore can be classified from extremely refractory with less than 50% recovery to non-refractory (free-milling) with 90-100% recovery. This is represented in Table 2.1 (La Brooy et al., 1994).

Table 2.1: Classification of refractory gold ore (La Brooy et al., 1994).

<50% recovery	Extremely refractory
50-80% recovery	Moderately refractory
80-90% recovery	Mildly refractory
90-100 recovery	Non-refractory (free-milling)

Figure 2.1 illustrates various forms in which gold grains can appear in sulfidic minerals. Gold can appear as (1) liberated (free-milling), (2) along grain boundaries, (3) enclosed in the sulfide matrix, (4) at the boundaries between sulfide grains, (5) alongside fractures and/or crystal defects, and (6) as colloidal particles or in solid solution in the sulfide mineral. Gold can be invisible as a solid solution within the pyrite grains (Marsden & House 2016).

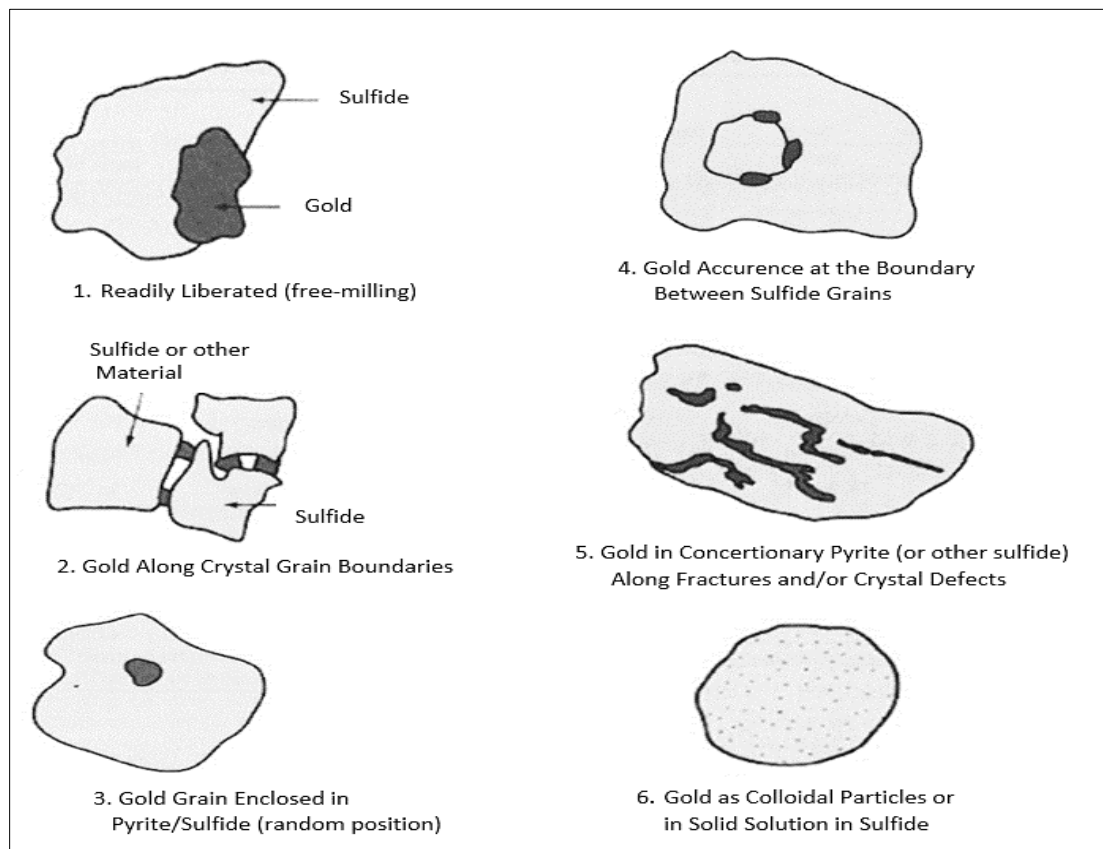


Figure 2.1: The different forms in which gold appears in the sulfide ore structure (Marsden & House, 2016).

The term invisible gold was defined since it was difficult to observe and identify with optical microscopic analysis (Cho et al., 2020). Invisible gold also has been used to define micro-disseminated gold in sulfide minerals, like pyrite and arsenopyrite, which makes it inaccessible or harder to release from the host minerals. The concentration of gold in different sulfide and arsenide minerals is summarised in Table 2.2 (Adams, 2005).

Table 2.2: Gold concentration in different minerals (Adams, 2005).

Mineral	Au concentration (ppm)
<u>Iron sulfides</u>	
Pyrite	< 0.1–8800
Marcasite	< 0.1–31
Pyrrhotite (roaster)	< 0.1–5
<u>Arsenic minerals</u>	
Arsenopyrite/Arsenian	< 0.2–17,000
Tennantite	< 0.2–72
Enargite-Luzonite	< 0.3–62
Gersdorffite	< 0.1–5
Realgar	< 0.1–4
Orpiment	< 0.1–3
<u>Copper sulfides</u>	
Chalcopyrite	< 0.1–7
Bornite	< 0.1–14
Covellite	< 0.1–74
Chalcocite	< 0.1–44
<u>Antimony sulfides</u>	
Tetrahedrite	< 0.2–59
Stibnite	< 0.1

Since gold can be enclosed in pyrite at relatively high concentrations, it is worth considering the lattice structure and the occurrence of gold in pyrite.

2.1.1. The lattice structure of pyrite

Pyrite is one of the dominant iron sulfide minerals, commonly found in igneous, sedimentary, metamorphic, and hydrothermal veins. It has a sparkly goldish metallic (brass-yellow) colour. For this reason, it is often mistaken as gold and hence is known as fool's gold. Pyrite is a diamagnetic semiconductor, with a high hardness of 6-6.5 (Mohs scale). It is a predominant host for gold, in which gold is occluded in its structure, which makes it "refractory ore" (Marsden & House, 2016).

Pyrite consists of iron (Fe^{2+}) and disulfide (S_2^{2-}) ions in its chemical structure. Geologically pyrite has three typical crystal forms: (a) cubic, (b) octahedral and (c) pyritohedral, as shown in Figure 2.2. Although the cubic morphology often occurs in nature, natural minerals are not perfectly cubic and typically form twins, which can also be a combination of these forms (Arrouvel & Eon, 2018).

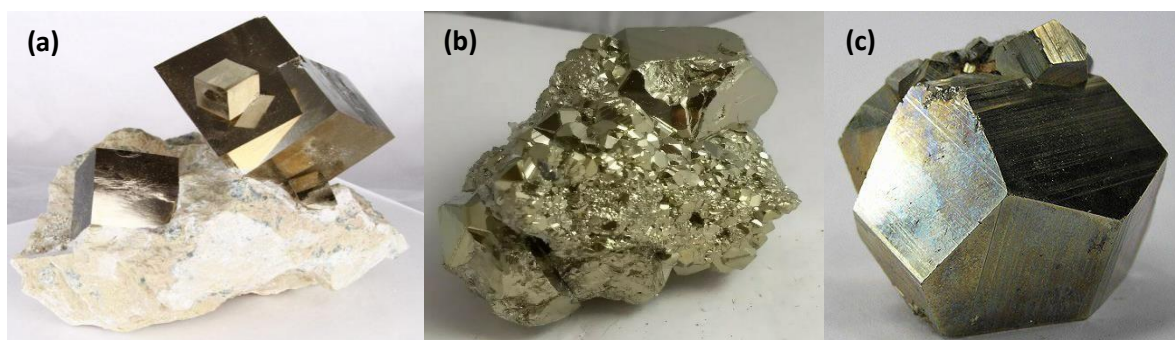


Figure 2.2: Three typical pyrite crystal forms: a) cubic, b) octahedral and c) pyritohedral (Chang et al., 2022).

In a unit cell of the cubic crystal, the iron ions are placed at corners and face central, coordinating with six sulfur atoms in the cubic frame. The dumbbell-shaped disulfide ions (S_2^{2-}) are positioned at the centre and along the edges of the cubic lattice, coordinating with three iron atoms and one sulfur, as illustrated in Figure 2.3 (A), with (B) showing a natural cubic crystal. The arrangement of atoms is thus described by a face-centred cubic (FCC) structure (Arrouvel & Eon, 2018).

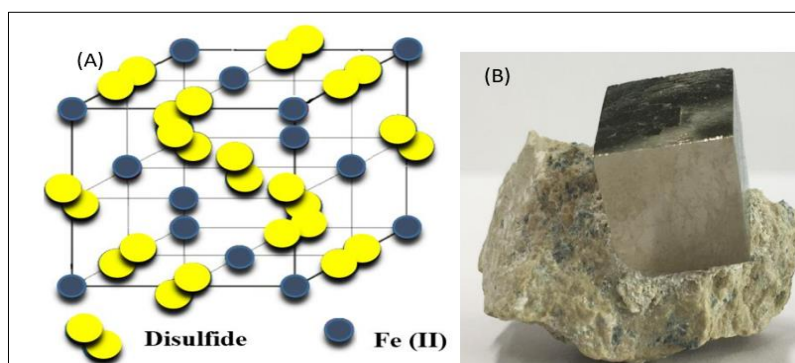


Figure 2.3: (A) Cubic structure of pyrite (Fe II): blue spheres at corners and centre of the faces, S: yellow spheres at the centre of the cubic lattice), (B) natural cubic crystal.

2.1.2. Gold occurrence in pyrite

Gold is either chemically bound in the crystal lattice of sulfide minerals, particularly pyrite and arsenopyrite, as a solid solution (invisible gold) or it occurs as discrete metallic nanoparticles and microparticles (Au^0) (Zhang et al., 2017). One way to explain this phenomenon is by considering the rate of crystal growth. When the crystal growth is fast, it reduces the residence time for Au^+ ions on the crystal surface and subsequently restricts the diffusion of Au^+ ions, which promotes the trapping and encapsulation of gold within the growing pyrite/arsenopyrite crystal lattice (Fougerouse et al., 2021). Thus, the rapid crystal growth results in gold concentration evenly distributed as a solid solution within the pyrite/arsenopyrite crystal lattice (Fougerouse et al., 2016). Inversely, at slow crystal growth, the residence time is higher for Au^+ ions at the sulfide surface, enhancing the diffusion capability of Au^+ ions from one adsorption spot to another on the crystal surface. Consequently, more

dynamically favourable Au-Au bonds can form, causing the in situ growth of Au⁰ nanoparticles (cluster). Figure 2.4 illustrates the rapid and slow crystal growth causing solid solution and nanoparticles, respectively (Fougerouse et al., 2016).

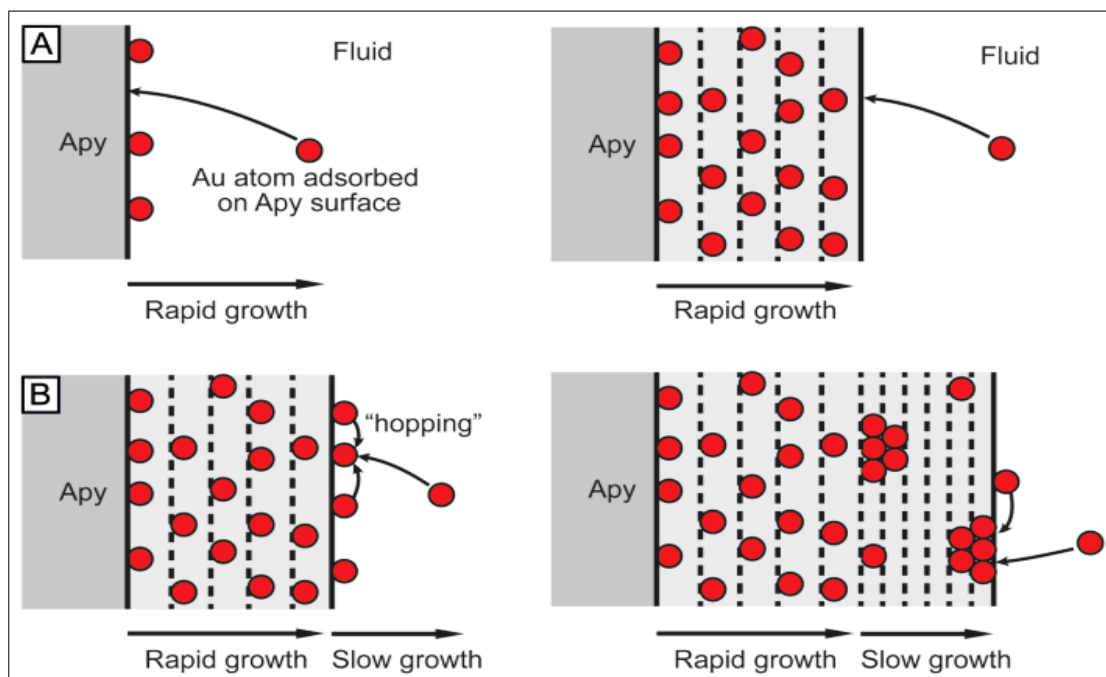


Figure 2.4: Rapid and slow crystal growth causing solid solution and nanoparticles (Fougerouse et al., 2016).

2.1.3. Industrial waste

Industrial waste is manufactured waste through a wide range of metallurgy and non-metallurgy processes generating a substantial amount of by-products, product residue, slime, slag, sludge, kiln dust, and ashes that contain precious critical and heavy metals. Hence, metal-containing industrial wastes are counted as secondary resources from which to recover metal(s), although the amount of metal(s) in the produced waste depends on the process and the raw material used (Jadhav & Hocheng, 2012; Silva et al., 2019; Grzegorz et al., 2023).

Among the different industrial wastes electric arc furnace dust (EAFD) is one of the valuable industrial wastes mostly containing a high quantity of Zn and Fe. EAFD is produced during the process of melting iron scraps and end-of-life iron-based products. During the melting process, the furnace temperature can reach 1600 °C or higher, at which many of the elements within iron scraps, such as Zn, Fe, Cr, Mn, and Pb, are volatilised. When the furnace cools down, this vapour phase produces a large amount of fine powder known as EAFD (Oustadakis et al., 2010). Currently, steel production from secondary resources is >600 million tons per year globally, and it has been estimated that an electric arc furnace generates approximately 20 kg of dust per ton of steel produced from iron scraps (Halli et al., 2018).

Due to different metals content, the produced EAFD is simultaneously an environmental contaminant if deposited on land (owing to Pb and Cr) and a valued industrial waste on account of the substantial amounts of useful metals, including Zn, Fe, Cu, and Ni, which can be recovered and returned to the steel production (Kukurugya et al., 2015).

Today, the global demand for critical and valuable metals is increasing swiftly due to a wide range of applications in numerous devices. The high demand for these metals consequently outstrips their supply and production (Rüşen & Topçu, 2017). Furthermore, the substantial waste produced during different industrial processes raises environmental concerns that have led to an emphasis on waste management, which can occur through recovering the desired metals for production (Quijorna et al., 2014; Al-harashsheh et al., 2019).

The global metal industry is therefore pursuing various routes to recover critical and valuable metals from not only primary sources but also different secondary sources (waste materials). This includes the waste from electroplating anode slime, electrical/electronic equipment (WEEE), printed circuit boards (PCBs), and batteries which mainly contain valuable metals, i.e. Cu, Ag, Au, Pt, Pd, Ni and Li, that can be recovered to fulfil the amplified demand (De Buzin et al., 2017; Grzegorz et al., 2023). As part of this move, there is an emphasis on the use of energy-efficient processes that are eco-friendly and improve metal circularity (Stathopoulos et al., 2013; Theocharis et al., 2021). Table 2.3 summarises different types of waste and the included metals (Jadhav & Hocheng, 2012).

Table 2.3: The different types of waste and the included metals (Jadhav & Hocheng, 2012).

Waste-type	Metals in the waste
Generated waste by industry	Fe, Zn, Cu, Cr, Pb, Ni, Mn, Ba
Metal finishing industrial wastes	Cr, Cd, Zn, Ni, Cu, Au, Ag
Fly ash	Cu, Zn, Ni, Al, Cr, Pb
Petroleum spent catalyst	Ni, Co, Mo
Electronic waste	Ni, Al, Cu, Sn, Au, Ag, Pd, Pt
Batteries waste	Ni, Li, Cd, Ag

2.2. Means of pretreatment

In the case of refractory ores and mine tailings, pretreatment is required to remove as much sulfide and sulfur compounds from the host mineral matrix as possible to expose the confined gold, improve tailings leachability, and ultimately enhance gold extraction (Fleming, 2009). There are different approaches such as thermal, oxidative, chemical, and physical to process refractory ores and mine

tailings, as presented in Table 2.4. A processing route can be a synergistic combination of more than one of these methods to expose the encapsulated gold for leaching reagents (Adams, 2005).

Table 2.4: Processing route for refractory ores and mine tailings (Adams, 2005).

Type	Industrial Processes	Pilot Processes
Thermal	Whole roasting	Pyrolysis
	Concentrate roasting	Flash roasting
	Smelting	Microwave
Oxidative	Acid pressure oxidation	Bio-heap leaching
	Alkaline pressure oxidation	Nitrous species catalyzation
	Biological oxidation	
	Nitric acid oxidation	
Chemical	Hot caustic digestion	Ammonia leaching
	Chlorine	
	Pressure cyanidation	
Physical	Fine grinding	Ultrafine grinding
	Electrical charge/spark	

2.2.1. Roasting and microwave heating

Generally, roasting of sulfidic mine tailings (i.e. pyrite) is accomplished using oxygen/air as the oxidant at a temperature of 600-1000 °C. At these high temperatures, the sulfur in the pyrite oxidises to become sulfur dioxide (SO₂). This forms porous iron oxides, i.e. Fe₂O₃ and Fe₃O₄, and exposes the enclosed gold in the roasted calcine (Marsden & House, 2016). This process has the undesirable side effect of releasing SO₂ which needs to be captured and treated. Furthermore, large amounts of energy is needed to provide the high temperatures. Depending on the partial oxygen pressure used for roasting pyrite, the following oxidative reactions (2.1, 2.2, and 2.3 for partial, whole and magnetizing roasting, respectively) occur to produce calcine and SO₂ (Runkel & Sturm, 2009):



To overcome the drawbacks of the traditional roasting process, recently microwave radiation offers an alternative approach in an attempt to oxidise sulfidic minerals to form a porous structure with microcracks that can expose the enclosed gold (Choi et al., 2017). Microwaves are electromagnetic radiation with wavelengths from 1 mm to 1 m and frequencies between 0.3 GHz and 300 GHz. For

domestic use, the frequency and wavelength are 2.45 GHz and 12.4 cm, respectively, to lessen interference with communication devices such as mobile phones, radar, television, and satellites (Diaz et al., 2015). Microwave radiation offers energy through electromagnetic radiation and can provide a strong electric field to heat a dielectric material. Microwave systems have a magnetic field that changes direction continuously, a phenomenon that induces dielectric materials to change their dipole positions synchronously with the field, as well as contributing to rubbing against each other which creates heat inside the material (Al-Harabsheh & Kingman, 2004; Wen et al., 2017).

In microwave heating, the thermal distribution is uniform throughout the material, while in conventional roasting is from the surface to the interior and can be inadequate to cause a uniform thermal distribution to the inner part of the material. In dielectric heating, when the heating value reaches the threshold, the material starts to crack because of the induced thermal stress and a phase change can occur, such as an oxidation reaction from pyrite (FeS_2) to Fe_2O_3 (hematite) or, in partial oxidation, Fe_{1-x}S (pyrrhotite). Hence, in the case of occluded gold in sulfidic minerals (pyrite), gold can be exposed (Huang & Rowson, 2002; Wen et al., 2017). The mechanism of thermal diffusion in both conventional roasting and microwave heating is illustrated in Figure 2.5 (Wen et al., 2017).

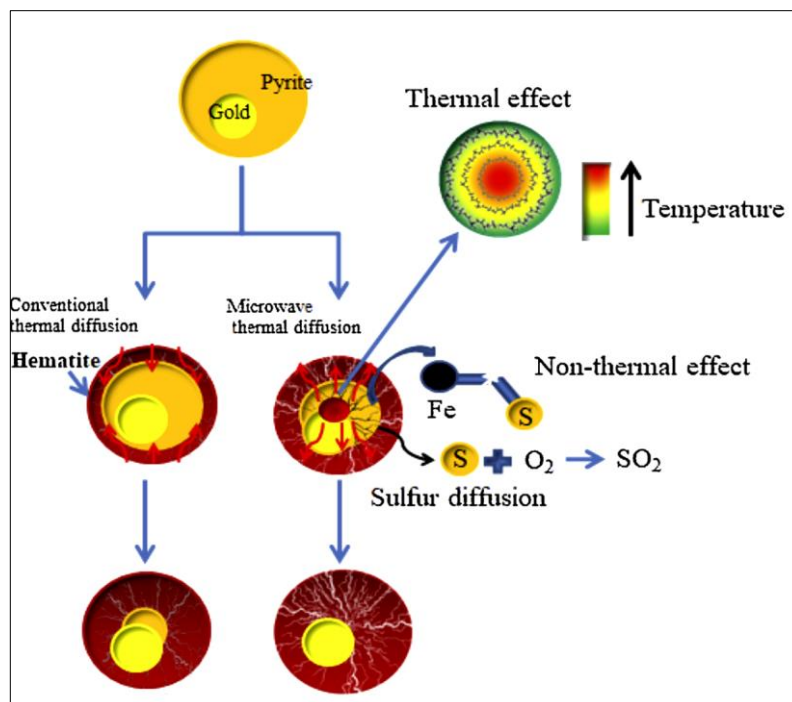
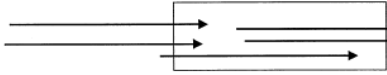
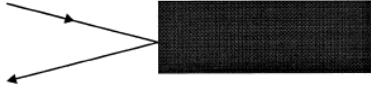
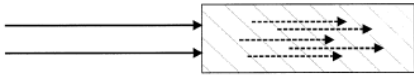


Figure 2.5: Diagram showing a mechanism of conventional and microwave thermal diffusion (Wen et al., 2017).

Depending on how materials interact with microwave radiation, they are divided into three groups (Table 2.5): (1) *transparent* because they transmit the radiation, (2) *conductor* because they reflect

the radiation, and (3) *absorber* because the radiation is partially or fully captured, which leads to the heating up of the material (Haque, 1999).

Table 2.5: The interaction between material and microwave radiation (Haque, 1999).

	Material type	Penetration
	Transparent (no heat)	Total transmission
	Conductor (no heat)	None
	Absorber (material is heated)	Partial to full absorption

Minerals generally fall into either the absorbent or transparent group (Table 2.6). Pyrite, which gold is mainly associated with, is an absorbent material. Therefore, sulfidic ores and tailings containing pyrite can absorb microwave radiation which heats up and induces microcracks. These cracks improve the leachability along with exposing embedded gold (Charikinya et al., 2015).

Table 2.6: Absorbent and transparent minerals (Charikinya et al., 2015).

Phase	Mineral
<i>Absorbent</i>	Sphalerite ((Zn,Fe)S)
	Pyrite (FeS ₂)
	Pyrrhotite (Fe _{1-x} S)
	Galena (PbS)
	Chalcopyrite (CuFeS ₂)
	Arsenopyrite (AsFeS)
	Fe oxides/hydroxides
<i>Transparent</i>	Quartz (SiO ₂)
	Calcite (CaCO ₃)
	Chlorite (Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ (OH) ₂ .(Mg,Fe) ₃ (OH) ₆
	Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄
	Phosphate [PO ₄] ³⁻
	Feldspar (KAlSi ₃ O ₈ –NaAlSi ₃ O ₈ –CaAl ₂ Si ₂ O ₈)
	Garnet (SiO ₄) ₃

considerably after they treated the ore through microwave heating. After 70 min. microwave radiation time, the temperature of the ore reached 850 °C, changing pyrite (FeS_2) to Fe_2O_3 (hematite) or Fe_{1-x}S (pyrrhotite). Microcracks also formed on the surface of the treated pyritic ore. They confirmed that microwave heating can be applied as an effective pretreatment to improve gold extraction in hydrometallurgical processes (Choi et al., 2017).

The decomposition of marcasite and pyrite using microwave heating in a nitric acid solution was investigated by Huang and Rowson (2002). Marcasite and pyrite both have the same chemical composition as FeS_2 , but are polymorphs because they are crystallographically different. Marcasite has orthorhombic crystal structures, while pyrite has cubic structures. The microwave heating showed that in 10 min, 93% of pyrite was decomposed in 4 M nitric acid solution, but marcasite had completely decomposed in 5 min. Compared to pyrite, marcasite has a faster decomposition rate and is readily dissolved under nitric acid-microwave heating conditions. This is due to the different crystal structure of pyrite and marcasite, although both of them are FeS_2 (Huang & Rowson, 2002).

Bio-oxidation is another means of treating refractory sulfidic ores and/or mine tailings. Bio-oxidation is the process of using microorganisms, which consume sulfur, and so remove sulfur from the sulfidic ore and/or mine tailings. The oxidation process is mostly based on the action of aerobic, acidophilic, chemolithotrophic bacteria such as *Thiobacillus ferrooxidans* or *Leptospirillum ferrooxidans* in water at pH 2 and at 30 °C. The bacterium uses air as an oxidant under atmospheric conditions. Despite the environmental advantages of the process, such as low energy consumption and no sulfur dioxide emissions, it has long reaction/residence times (in a range of 15–150 h) because of the slow rate of bacterial oxidation. Furthermore, it requires cooling equipment, as the oxidation reaction is exothermic (Romero et al., 2003).

Bio-oxidation of carbonaceous double refractory gold ore as pretreatment before acidic thiourea leaching was investigated by Xu et al. (2020). For this aim, a combination of *A. ferrooxidans* and *L. ferrooxidans* bacteria was used in a shaking incubator at 30 °C, 160 rpm with an initial pH of 1.8, with 10 g/L pulp density for 8 days. Simultaneous decomposition of sulfidic minerals (like pyrite) and deactivation of the carbonaceous part occurred. Ultimately, acidic thiourea leaching resulted in 78.7% gold extraction (Xu et al., 2020). Ma et al. (2020) examined the kinetics of oxidative dissolution of pyrite with potassium peroxydisulphate ($\text{K}_2\text{S}_2\text{O}_8$, 0.4 M) solution. Kinetics of pyrite leaching was studied at a temperature range of 30–70 °C, with 10 g/L pulp density, 500 rpm stirring for 7 h. The obtained activation energy was 65.3 kJ/mol indicating a diffusion-limited system with about 80% Fe extraction originating from pyrite dissolution (Ma et al., 2020).

2.2.2. Traditional leaching reagents

Apart from roasting, microwave heating and bio-oxidation, another way to treat refractory sulfidic ores and/or mine tailings is a hydrometallurgical approach through a leaching method. Leaching is a method for treating solid materials with chemical reagents (liquid) in an attempt to selectively convert the desired metal(s) from an insoluble state in a solid matrix to a soluble state in a leaching liquid medium, while most of the impurities remain insoluble. This procedure generally contains three basic steps: 1) close contact between the solid matrix containing the target substance and the leaching reagent, 2) separating the leached solid (residue) from the pregnant solution, and 3) recovery of the extracted desired metal from the pregnant solution (Ndlovu et al., 2017).

Hydrometallurgical leaching involves principally the dissolution of solid materials in an acidic and/or basic aqueous medium, followed by extracting the target metals (Syed, 2012). Typically, industrial leaching solutions contain water, acids (such as HNO_3 , H_2SO_4 , HCl), bases (such as NaOH , NH_4OH), as well as complexing agents and oxidising agents (such as H_2O_2 , Fe^{3+} , Cl_2 , HClO and NaClO) to improve the rate of leaching (Niemczewska et al., 2004).

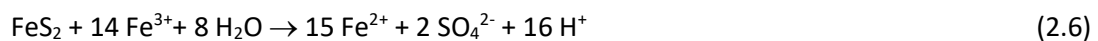
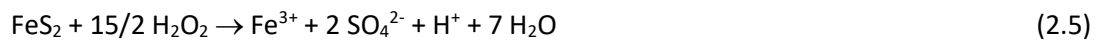
Nitric acid (HNO_3) is an oxidising acid that can selectively dissolve metals such as Fe, Cu, Pb, Ni, and Ag to form soluble metal nitrates, but not metals like Sn and Au. Since the early 1980s, nitric acid has been explored as an oxidant for the treatment of refractory gold ores (Marsden & House, 2016). Nitric acid garnered even more attention in the late 2010s since it can treat refractory pyritic and arsenopyritic gold ores and tailings hydrometallurgically without using high temperature, high pressure, and ultra-fine grinding (Rogozhnikov et al., 2019). It has powerful oxidising abilities at a concentration above 2 M (Teimouri et al., 2022). The powerful oxidative ability of nitric acid ($> 2 \text{ M}$) results in fast oxidation kinetics for pyrite and arsenopyrite, capable of decomposing sulphidic minerals. The main disadvantage of nitric acid is its relatively high cost; although it can be regenerated from the reaction products NO_x gases with water and O_2 to justify its cost (Li, 2009; Gao et al., 2009).

Pressure oxidation comprises oxidising sulfidic ore under acidic or basic conditions in the presence of oxygen as the oxidant at high pressure (4500 kPa) and elevated temperatures ($\geq 250 \text{ }^\circ\text{C}$) (Rusanen et al., 2013). The process is undertaken in an autoclave to maintain high pressure and temperature. The oxygen overpressure promotes the desired mass transfer in the process and, consequently, increases the reaction rate and shortens the residence time. These conditions destroy the sulfide lattice of the host mineral and so liberate gold particles, thereby making them accessible to the leaching reagent (Rusanen et al., 2013).

A kinetic study of pressure oxidation of pyrite in 0.5 M H₂SO₄ was investigated by Long and Dixon (2004). Kinetics of pyrite dissolution was conducted at a temperature range of 170-230 °C with 690 kPa O₂ pressure, 800 rpm stirring speed for 2h. Kinetic study exhibits a 0.5-order dependency on the concentration of dissolved oxygen, indicating an electrochemical leaching mechanism with an activation energy of 41.7 kJ/mol (Long & Dixon, 2004). Rusanen et al. (2013) studied the pressure oxidation of pyrite and arsenopyrite using sulfuric acid. They have found that under a partial oxygen pressure of 1050 kPa and temperature of 225 °C in 1 M H₂SO₄ with a 15% slurry, 40.8% iron and 99.6% sulfur conversion (extraction) was achieved in 1 h (Rusanen et al., 2013). Sung et al. (2022) examined the kinetic of pyrite and arsenopyrite dissolution in a system of 1 M H₂SO₄ and O₂ pressure of 30 atm. The kinetic study was conducted at a temperature range of 180-220 °C exhibited both chemical reaction and oxygen diffusion control. The attained activation energy for pyrite and arsenopyrite dissolution was 34.0 and 47.6 kJ/mol, respectively (Sung et al., 2022).

2.2.3. Mechanism of oxidative leaching

Oxidative pyrite dissolution can be done in an acidic or basic aqueous solution with different oxidants. Some of the commonly used oxidants are oxygen (O₂), hydrogen peroxide (H₂O₂), and ferric ion (Fe³⁺), which lead to pyrite dissolution producing ferrous (Fe²⁺) and/or ferric (Fe³⁺) and sulfate (SO₄²⁻) ions (McKibben & Barnes, 1986). The oxidative reactions for these three commonly used oxidants are written as follows:



Researchers have conducted experiments on oxidative pyrite dissolution under various experimental conditions, like the type of oxidant (Fe³⁺, O₂, H₂O₂), pH, Eh, temperature, stirring speed, and particle size of the ore. Moses and Herman (1991) have done various experiments on pyrite dissolution at circumneutral pH by using Fe³⁺ and O₂ as the oxidants. Likewise, these researchers have recommended that pyrite oxidation and dissolution can be controlled by electrochemical processes (Chandra & Gerson, 2010). Electrochemical process of pyrite dissolution was further investigated and improved through work done by Rimstidt and Vaughan (2003). They combined results from other researchers and their own previous studies to offer a detailed mechanism that presents the fundamental and primary steps of the anodic oxidation of pyrite and the cathodic reduction of oxidants (Fe³⁺ and O₂). They proposed a schematic explanation of the electrochemical mechanism of pyrite oxidation and dissolution with detailed information which is depicted in Figure 2.7 (Rimstidt & Vaughan, 2003).

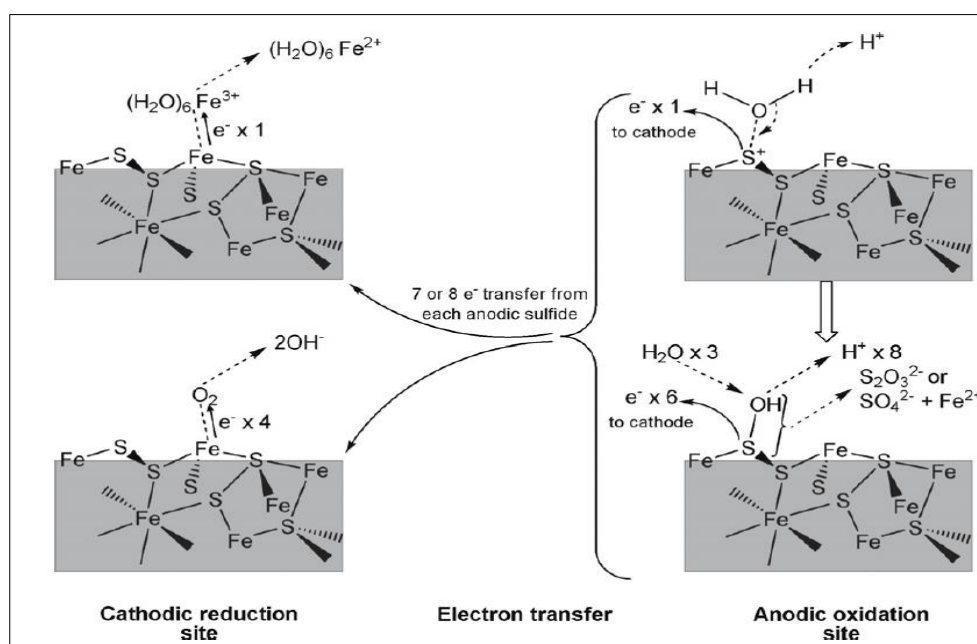


Figure 2.7: Schematic illustration of the electrochemical mechanism of pyrite (Rimstidt & Vaughan, 2003).

Based on the proposed mechanism, the oxidative pyrite dissolution in an aqueous medium is an electrochemical process with three steps: (1) the anodic reaction, (2) electron transfer from the anodic to the cathodic anodic sites, and (3) the cathodic reaction, which all occur simultaneously in the actual oxidation process (Rimstidt & Vaughan, 2003). From a molecular point of view, as illustrated graphically in Figure 2.8, the initial step of oxidative leaching is the oxidation of pyrite by removing an electron from its sulfur ions, followed by transferring the electron from the anodic site to the cathodic site, and ultimately the reduction of the oxidant (Fe^{3+} and/or O_2) by accepting the electron. The oxidative electrochemical process requires removing 7 or 8 electrons successively from one disulfide sulfur to produce one sulfate ion, which makes the process complicated. The cathodic and anodic sites can be either on the different surfaces of two pyrite particles or the same particle (Rimstidt & Vaughan, 2003).

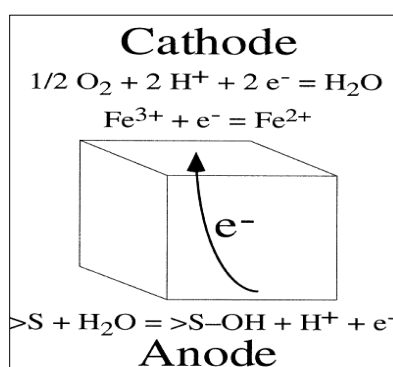


Figure 2.8: Electrochemical process of pyrite oxidation (Rimstidt & Vaughan, 2003).

Another researcher, Crundwell (2013), also studied the oxidative dissolution of sulfidic minerals in detail and proposed the concurrent model of the electrochemical dissolution of a mineral as illustrated in Figure 2.9. During the dissolution reaction, the bonds between the ions (M^{2+} and S_2^{2-}) at the surface of the mineral break, resulting in charged ions moving from the mineral's surface into the bulk solution. This model also agreed that the oxidative dissolution of sulfidic minerals follows an electrochemical mechanism containing oxidation and reduction reactions in which an electron is being transferred between the sulfidic mineral and the oxidant ($Fe^{3+}_{(aq)}$) (Crundwell, 2013).

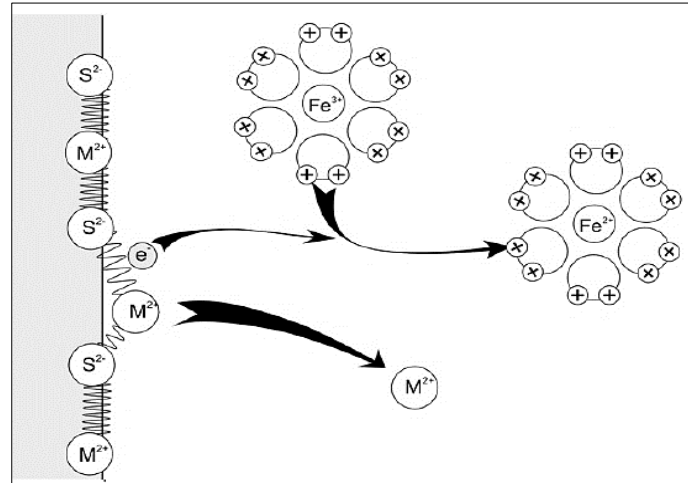


Figure 2.9: The concurrent model of electrochemical dissolution of a mineral (Crundwell, 2013).

Irreversible half-cell oxidation reaction for the dissolution of the mineral can be written as:



In addition, the reversible half-cell reduction reaction for the oxidant can be written as:



The overall electrochemical reaction can be presented as (Crundwell, 2013):



For a comprehensive understanding of the pyrite dissolution, Figure 2.10 illustrates (a) the molecular orbital diagram for pyrite and (b) the energy-band diagram of the pyrite–solution interface at which the anodic dissolution initiates. The molecular orbital diagram of pyrite demonstrates that the conduction band comprises the antibonding e_g^* (doublet of the 3d orbitals of Fe) and the valence band, which consists of the nonbonding t_{2g} and bonding e_g orbitals. The energy gap between the antibonding e_g^* and the nonbonding t_{2g} is referred to as the band gap, which was about 0.9 ± 0.1 eV (Figure 2.10-a) (Holmes & Crundwell, 2000; Bryson & Crundwell, 2014; Crundwell, 2021).

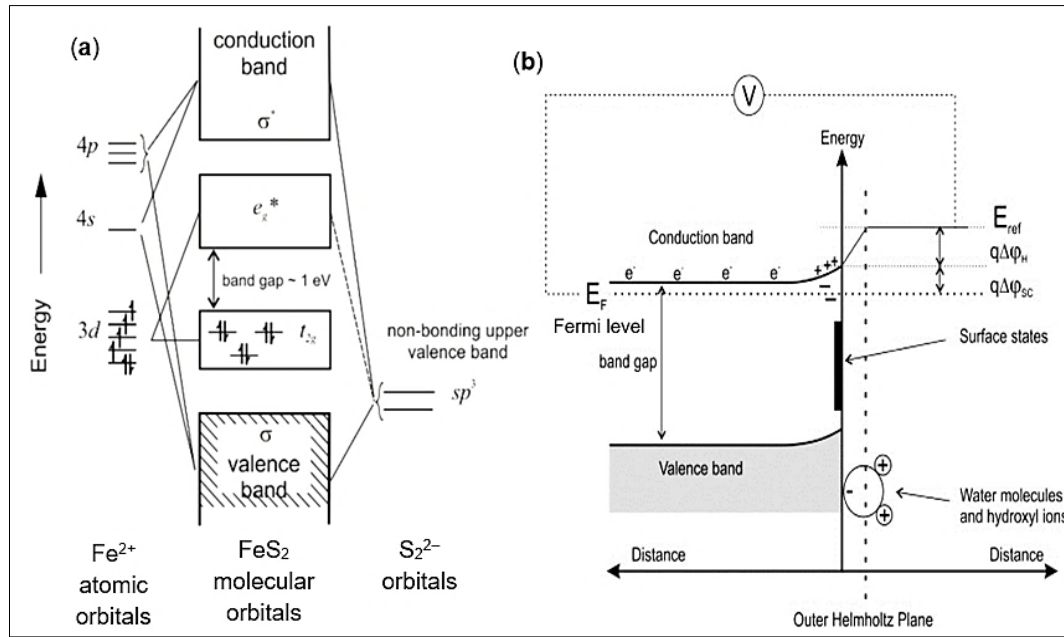


Figure 2.10: (a) The molecular orbital diagram for pyrite (Crundwell, 2021), and (b) the energy-band diagram of a pyrite–solution interface (Bryson & Crundwell, 2014).

Based on the applied potential (or potential of a solution), the Fermi level (E_F) (which is the level of energy that lies between the conduction and the valence band) can have a slightly different level from the surface state (Figure 2.10-b). At a certain potential, the Fermi level can overlap the surface state, and this potential is known as the break down potential. This is the beginning of the anodic dissolution and leads to an anodic current (Bryson & Crundwell, 2014). At even higher potentials, electrons are transferred and removed from the surface bonds, leading to the breaking of the bonds, and ions moving across the Helmholtz layers to the bulk solution. At this point, the rate-limiting step in the dissolution kinetics is the transferring of electrons (charges) across the Helmholtz layers (space-charge layer). By further increasing the potential, the Fermi level does not overlay the surface state anymore. At this point, the speed of the electron transfer reaches its highest value, and the rate-limiting step is the movement of the produced ionic species across the Helmholtz layers to the bulk solution (Holmes & Crundwell, 2000; Bryson & Crundwell, 2014; Crundwell, 2021).

Hence, it is agreed that the dissolution follows an electrochemical mechanism which is potentiostatically controlled between anodic reactions (of sulfate (SO_4^{2-}) and elemental sulfur (S^0) formation) and the cathodic reaction of the oxidant accepting the released electrons. The overall electrochemical reactions can be written as shown in 2.10 and 2.11. This would bring the importance of considering a further electrochemical evaluation for this matter.



2.3. Electrochemical study

The electrochemical study enables a meticulous evaluation, particularly through cyclic voltammetry (CV), which can identify the oxidation-reduction peaks and corresponding species produced during the oxidation-reduction reactions under certain potentials on the surface of the mineral (Holmes & Crundwell, 2000). Thus, coupling an electrochemical study with the dissolution of a mineral enclosing gold, i.e. pyrite, would facilitate further understanding of a mechanism with evidence provided by the electrochemical study (Chandra & Gerson, 2010). Earlier electrochemical studies proposed that the surface products and the intermediates resulting from the oxidative dissolution of pyrite could be elemental sulfur (S^0), metal-deficient sulfide or pyrrhotite ($Fe_{1-x}S_2$), polysulfides (S_n^{2-} , $n>2$), and iron oxides i.e. $Fe(OH)_3$ (Sun et al., 2015; Liang et al., 2011; Zhang et al., 2020).

For a better understanding of pyrite dissolution, researchers conducted various electrochemical studies. The electrochemical oxidation of pyrite under acidic conditions (pH=2) was investigated by Tu et al. (2017). They discovered that at low potential (0.5 V vs. saturated calomel reference electrode-SCE), $Fe(OH)_3$ and elemental sulfur (S^0) formed, covering the surface of the pyrite electrode, which makes further reactions diffusion-limited. Increasing the potential to 0.6 V, the amorphous sulfur-rich layer converts to crystalline S_8 , allowing pyrite oxidation to continue. Higher potential (0.8 V) leads to the formation of $Fe(OH)_3$ and SO_4^{2-} , along with polysulfides (S_n^{2-}), and an iron-rich layer consisting of FeO and Fe_2O_3 which accumulates on the surface of the pyrite (Tu et al., 2017).

In another study, Chiri and Schlegel (2017) examined the oxidation of pyrite in air-equilibrated solutions with different pH values (1-5) and in a temperature range of 25-40 °C through electrochemical impedance spectroscopy (EIS). They found that the oxidative dissolution of pyrite is controlled by electron transfer, which comes from the anodic reactions on the pyrite surface. The electron transfer occurs from the conduction band of pyrite to the adsorbed O_2 (Chiri & Schlegel, 2017). In research by Zhang et al. (2020), the dissolution of several sulfide minerals such as pyrite, pyrrhotite, chalcopyrite, bornite, and chalcocite in acidic sulfate media (bioleaching conditions) was examined with emphasis on cyclic voltammetry, the dissolution mechanism, redox reactions, and the produced decomposition products (Zhang et al., 2020).

2.4. New alternative reagents: Ionic liquids and Deep eutectic solvents

The main reasons for searching substitute reagents for cyanide and conventional leaching reagents arise from the environmental, safety and health concerns posed by their toxicity and difficulty in recycling. Nevertheless, it is challenging to find an alternative reagent to compete with the cyanide process and mineral acids for metal extraction. A prospective reagent for metal extraction should fulfil

some important criteria, such as being efficient, effective, relatively inexpensive, environmentally benign (non-toxic), selective to the desired metal, and compatible with refractory minerals (Hilson & Monhemius, 2006).

2.4.1. Ionic liquids (ILs)

An attractive substitute processing route to conventional leaching reagents is the use of ionic liquids (ILs) as novel solvents. ILs are a relatively new type of solvent, and as their name suggests, they are liquids at temperatures below 100 °C. They comprise large organic cations and inorganic or organic anions of different sizes. They are in a liquid state because of the size difference between the constituting cation and anion results in low lattice energy and a low melting point (Welton, 2004; Park et al., 2014; Ghandi, 2014). Their remarkable properties include not igniting or combusting, non-volatility, negligible vapour pressure, thermal/chemical/electrochemical stability, high conductivity, wide electrochemical window, and recyclability, which all play an important role to yield durable solvents. Owing to these features, their applications are growing in several fields, such as extraction, separation, catalytic reactions, and electrochemistry (Abbott et al., 2017). Table 2.7 summarises the unique properties of ILs (Marsh et al., 2004).

Table 2.7: Properties of ILs (Park et al., 2014).

Properties	Values
Melting point	Preferably below 100 °C
Liquid range	Often > 200 °C
Thermal stability	Usually high
Viscosity	Normally < 100 cP, workable
Dielectric constant	Implied < 30
Polarity	Moderate
Ionic conductivity	Usually < 10 mS/cm
Molar conductivity	< 10 Scm ² /mol
Electrochemical window	Often > 4 V
Vapour pressure	Very low

The first discovered IL was ammonium-based, ethylammonium nitrate [EtNH₃⁺NO₃⁻] with a melting point of 12 °C, reported by Walden in 1914. Ammonium-based ILs have a low melting point, low viscosity, and they are electrochemically stable, which is one of the reasons why they have been used as electrolytes in electrochemical devices (Marsh et al., 2004). The most frequently studied ILs are imidazolium and pyridinium-based ILs with a discrete anion. The most popular discrete anions involve tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), bis(trifluoromethylsulfonyl)imide (Tf₂N⁻), and hydrogen sulfate (HSO₄⁻) (Marsh et al., 2004; Greer et al., 2020).

ILs are “designable” because many cation-anion combinations are possible, and combinations can be modified to give desirable outcomes. The chemical structures of some cations and anions commonly used to produce ILs are illustrated in Figure 2.11 (Greer et al., 2020). This flexibility allows ILs to be deliberately designed for a specific purpose and has led to the notion that they are “designer solvents” (Earle & Seddon, 2000). Their physicochemical properties—melting point, viscosity, density, and hydrophobicity/hydrophilicity—can be adjusted by changing the structure of the ions (cation and/or anion) or by adding other ions (Tian et al., 2010).

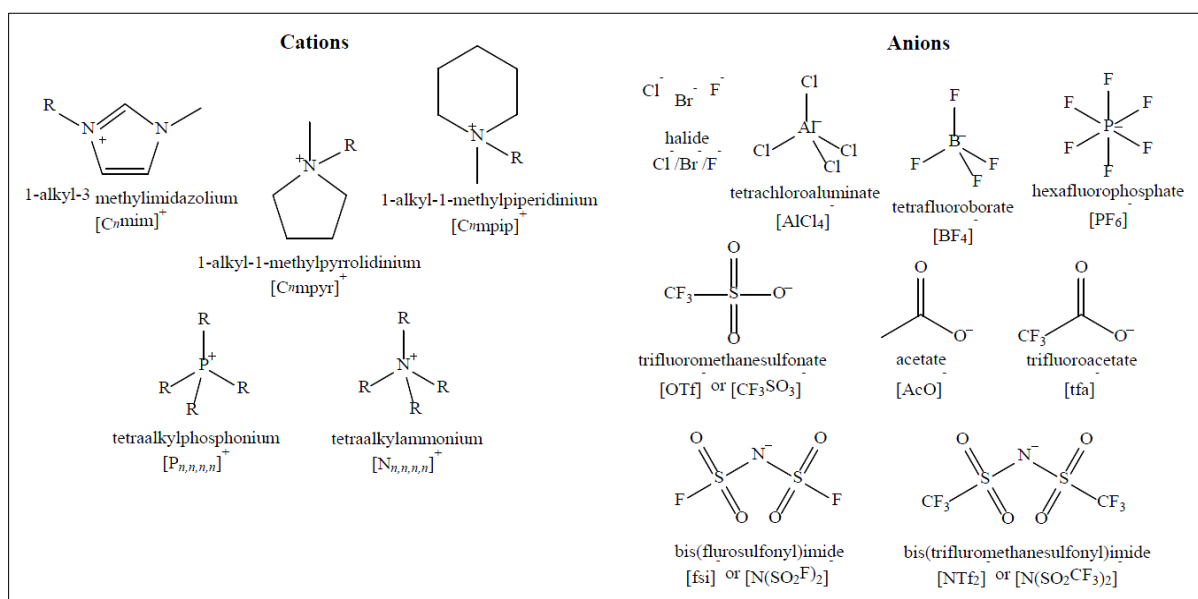


Figure 2.11: Chemical structure of some cations and anions commonly used to produce ILs (Greer et al., 2020).

For instance, in ILs containing 1-alkyl-3-alkylimadazolium as the cation, changing the hexafluorophosphate anion (PF_6^-) with tetrafluoroborate (BF_4^-) increases the water solubility of the resulting IL, while replacing it with bis(trifluoromethylsulfonyl)imide (Tf_2N^-) reduces its water solubility (Marsh et al., 2004). Thus, the water miscibility of an IL can be tailored according to its type of anion, and this can help to design a desirable IL based on its application (Plechkova & Seddon, 2008). Some of the commonly used anions to synthesise ILs are arranged based on the water miscibility as shown in Figure 2.12 (Plechkova & Seddon, 2008). Additionally, increasing the number of carbons in the alkyl chains in the 1-alkyl-3-alkylimadazolium cation can increase the viscosity of the designed IL (Greer et al., 2020).

Water immiscible		Water miscible
$[\text{PF}_6]^-$	$[\text{BF}_4]^-$	$[\text{CH}_3\text{CO}]^-$
$[\text{Tf}_2\text{N}]^-$	$[\text{OTf}]^-$	$[\text{HSO}_4]^-$
$[\text{BR}_1\text{R}_2\text{R}_3\text{R}_4]^-$	$[\text{N}(\text{CN})_2]^-$	$[\text{CF}_3\text{CO}_2]^-$
		$[\text{NO}_3]^-$
		$\text{Br}^-, \text{Cl}^-, \text{I}^-$
		$[\text{Al}_2\text{Cl}_7]^-$, $[\text{Al}_2\text{Cl}_4]^-$

Figure 2.12: Common anions used to synthesise ILs, arranged based on their water miscibility (Plechova & Seddon, 2008).

Besides the use of ILs as alternative extractants, work has also led to progress in designing functional ILs referred to as “task-specific ionic liquids”, which was invented by Davis and Forrester in 1999. Task-specific ionic liquids (TSILs) consist of functional groups attached directly to the cation and/or anion structure (Ratti, 2014). The covalent attachment of some functional groups to cations/anions, or both, of an ordinary IL, imparts to it the capacity to function not only as a green solvent, but also as a catalyst and a reagent in many chemical reactions (Ratti, 2014). Some practical functional groups that have been attached to imidazolium rings are listed in Figure 2.13.

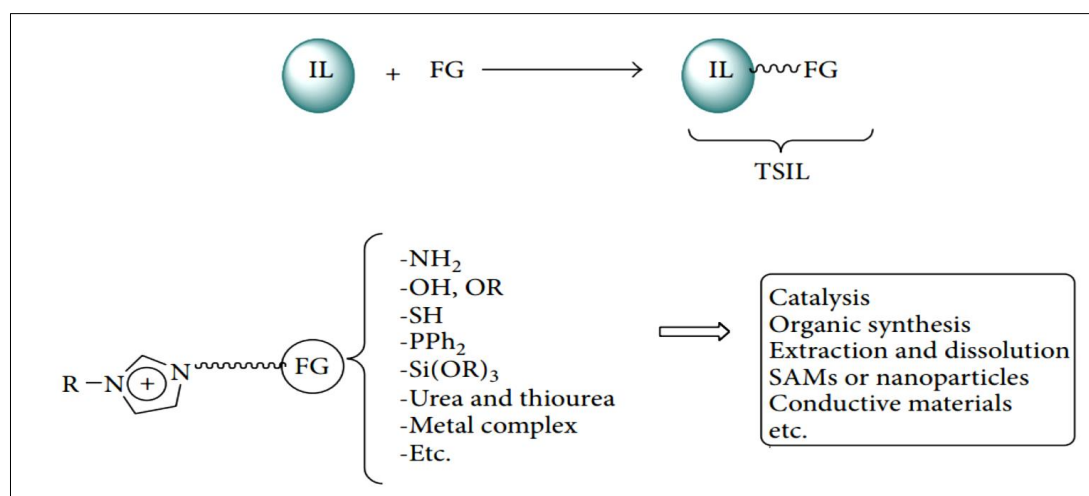


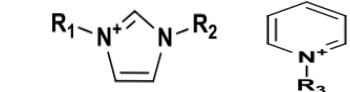
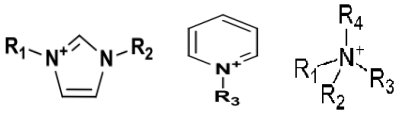
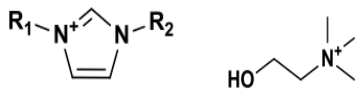
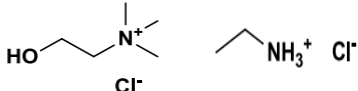
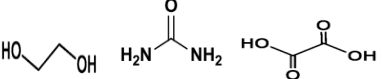
Figure 2.13: Task-specific ionic liquids (TSILs) (Ratti, 2014).

According to the chemical behaviour of ILs, they are classified as protic and aprotic depending on the nature of the constituent cation and anion. Protic ILs consist of small aliphatic amines as the cation and organic acids as the anion (Peric et al., 2014). In other words, protic ILs are made by combining a Brønsted acid and base in which the cation typically has H^+ with a dynamic positive charge. In contrast, aprotic ILs contain a large organic cation, such as imidazolium and pyridinium cations, with an inorganic anion like Br^- , Cl^- , PF_6^- , and Br_4^- . The cation in aprotic ILs has R^+ (an alkyl chain attached to imidazolium and/or pyridinium ring) with a stable positive charge (Peric et al., 2013).

It should be mentioned that recently the ‘green feature’ of some ILs has been contested, mainly due to their poor biodegradability (Li & Row, 2016) and their large-scale application may be restricted because they are expensive solvents (Qinghua et al., 2012). Meanwhile, in 2003, a new class of solvents named “deep eutectic solvents (DESs)” as an analogue of ILs, was discovered by Abbott et al. (2003).

Table 2.8 summarises three generations of ILs with the typical cations and anions used, and also DESs, that normally contain a quaternary ammonium salt as a hydrogen bond acceptor (HBA) and an organic compound capable of donating protons as a hydrogen bond donor (HBD). The similarities between DESs and ILs are noticeable, in that they share several physicochemical properties such as low vapour pressures, low melting points, large liquid ranges, and resistance to combustion (Smith, 2013). DESs overcome some drawbacks of ILs, such as high price, difficult synthesis, and poor biodegradability (Qinghua et al., 2012).

Table 2.8: Summary of three generations of ILs with the typical cations and anions used, and DESs (Qinghua et al., 2012)

Sequential generation	Typical cations	Typical anions
First-generation of ILs (Water and moisture-sensitive)	 Imidazolium Pyridinium R=Alkyl	Chloroaluminate, Metal halide i.e. AlCl_4^-
Second-generation of ILs (Water and air-stable, most studied ILs)	 R=Alkyl	BF_4^- , PF_6^- , Me_2CO_2^- $\text{N}(\text{SO}_2\text{CF}_3)_2^-$
Third-generation of ILs	 R=Oxygenated alkyl	Amino acids (Organic acids), alkylsulfates (RSO_3^-), alkylphosphates (RPO_4^-)
Deep eutectic solvents (DESs)	Typical quaternary ammonium salts (hydrogen bond acceptor) 	Typical hydrogen bond donors 

2.4.2. Deep eutectic solvents (DESs)

At the beginning of this century, a new class of solvent, termed DESs, was introduced by Abbott et al. (2003). The first DES was formed by mixing choline chloride ($[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]^+\text{Cl}^-$) and urea ($\text{CO}(\text{NH}_2)_2$) at a ratio of (1:2), resulting in a substance that was liquid at room temperature with a melting point of 12 °C; while, the melting points of the starting components choline chloride and urea were 302 °C and 133 °C, respectively (Smith et al., 2014).

A deep eutectic solvent (DES) typically contains two or three safe and relatively cheap components that have the capability of hydrogen bond interactions with each other, to make an eutectic mixture with a melting point lower than the constituting components. For instance, in a DES, a quaternary ammonium salt like choline chloride acts as a hydrogen bond acceptor (HBA) and ethylene glycol, urea, thiourea, oxalic acid, and glycerol act as hydrogen bond donors (HBD). HBDs should have the ability to form a complex with a halide anion, i.e. Cl^- , of the quaternary ammonium salt (Qinghua et al., 2012).

The most used component in reported DESs is choline chloride (ChCl). Choline chloride is a quaternary ammonium salt that is non-toxic, biodegradable, and comparatively cheap (compared to imidazolium and pyridinium cations). It is categorised as a provitamin and has been used as a nutrient substance in vitamin B, and animal food (Qinghua et al., 2012). It can be extracted from biomass, as well as be produced through a gas phase reaction between ethylene oxide, hydrochloric acid, and trimethylamine with trivial auxiliary waste production (Smith et al., 2014). Figure 2.14 illustrates the proposed hydrogen bond interaction (between the H of the amino group in urea and Cl^-) for the choline chloride-urea (1:2) DES (Longo & Craveiro, 2018). The structures of some halide salts performing as HBAs and various organic compounds as HBDs used to make DESs are depicted in Figure 2.15 (Longo & Craveiro, 2018).

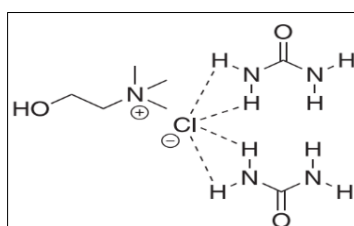


Figure 2.14: Proposed schematic hydrogen bond interaction for choline chloride-urea (1:2) (Longo & Craveiro, 2018).

DESs are a distinct class of solvents capable of hydrogen bonding. A eutectic mixture is formed when components (HBA and HBD) are mixed in a specific ratio to meet the eutectic point. Figure 2.16 illustrates the eutectic point of a binary mixture of HBA and HBD in a DES, in which ΔT_f is the difference between the actual freezing (melting) point ($T_{f(\text{real})}$) of the binary combination of HBA/HBD with the ideal value ($T_{f(\text{ideal})}$) for this mixture. ΔT_f is correlated to the amount of interaction between the two

constituent compounds (HBA/HBD), typically through hydrogen bonding. Accordingly, the more the interaction, the larger ΔT_f would be, or the lower the freezing point of the produced DES (Smith et al., 2014; Makoś et al., 2019). The reason for the considerable reduction in the freezing point (melting point) of a eutectic solvent compared to its pure starting components, is due to charge delocalization that happens through hydrogen bond formation between the halide anion of the HBA and the HBD (Longo & Craveiro, 2018; Kalhor & Ghandi, 2019). DESs, like ILs, can be designable since physicochemical properties like melting point, viscosity, and conductivity of a DES can be altered by combining different halide salts (HBA) with various HBDs in different ratios to make a DES with desired properties (Qinghua et al., 2012; Welton, 2018; Greer et al., 2020).

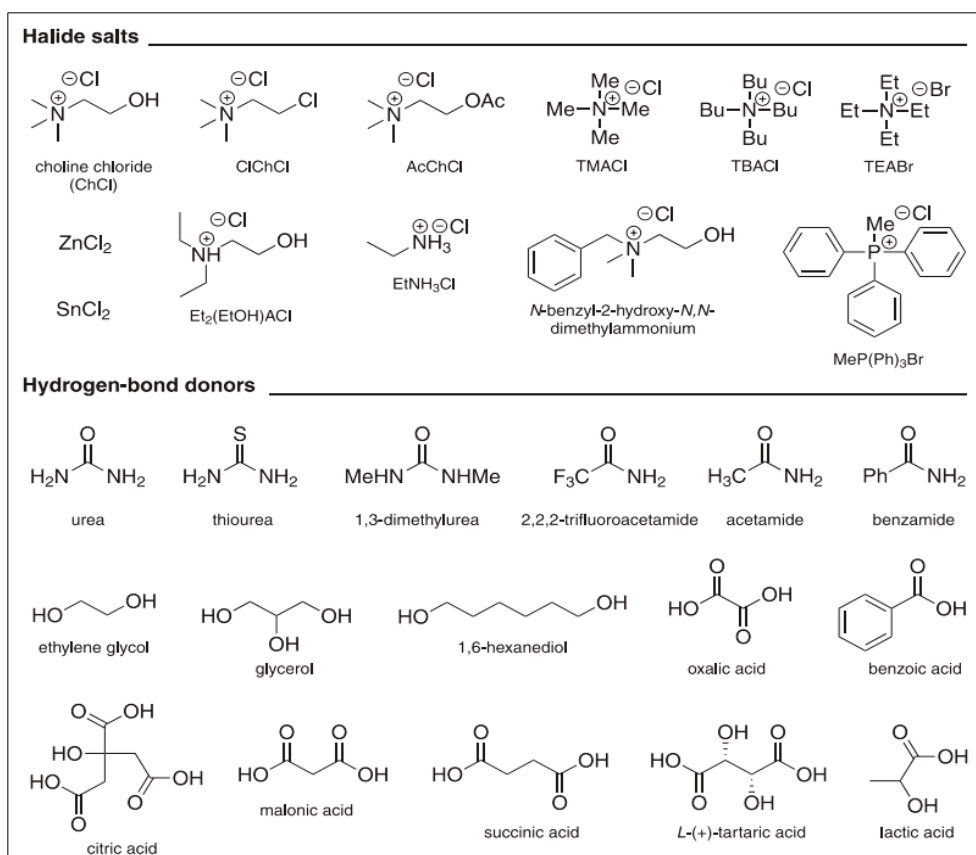


Figure 2.15: The structure of some halide salts and HBDs (Longo & Craveiro, 2018).

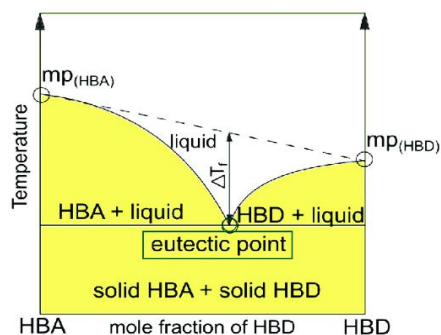
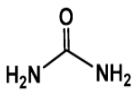
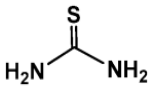
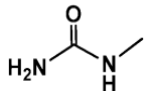
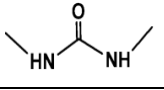
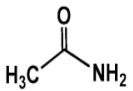
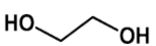
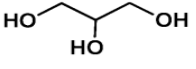
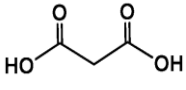
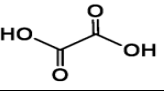
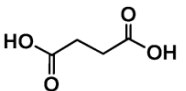


Figure 2.16: Graphic illustration of the eutectic point of a two-constituent (HBA and HBD) phase diagram (Makoś et al., 2019).

To date, all the reported melting points of the studied DESs are below 150 °C. DESs having melting points below 50 °C attracted more attention as an eco-friendly, safe and inexpensive solvent. In the case of choline chloride-based DESs, the stronger the hydrogen bond interactions triggered by the HBD with the halide anion Cl^- , the lower the melting point of the resulting DES. Thus, the type of HBD has a significant effect on the melting point of a DES (Qinghua et al., 2012). Table 2.9 summarised choline chloride-based DESs with different HBDs which all have melting points lower than 100 °C. The melting point (m.p.) of choline chloride is 302 °C, and T_m and T_f are the melting points of the HBD and the resulting DES, respectively (Qinghua et al., 2012).

Table 2.9: Choline chloride-based DESs with different HBD having melting points lower than 100 °C (Qinghua et al., 2012).

HBD		ChCl:HBD (molar ratio)	T_m /°C (m.p. of HBD)	T_f /°C (m.p. of DES)
	Urea	1:2	134	12
	Thiourea	1:2	175	69
	1-Methyl urea	1:2	93	29
	1,3-Dimethyl urea	1:2	102	70
	Acetamide	1:2	80	51
	Ethylene glycol	1:2	− 12.9	− 66
	Glycerol	1:2	17.8	− 40
	Malonic acid	1:1	135	10
	Oxalic acid	1:1	190	34
	Succinic acid	1:1	185	71

Usually, DESs have relatively high viscosities (>100 cP) at ambient conditions, which is attributed mainly to their extensive hydrogen bond network, electrostatic interactions, and Van der Waals forces between the components. Consequently, these interspecies interactions reduce the movement of

free species inside the DES, causing high viscosity. Factors affecting the viscosity of a DES include the chemical nature of DES constituents (type of the halide salt and HBD), the molar ratio of HBA/HBD, and temperature. Highly viscous DESs could adversely affect their potential applications; thus, preparing DESs with low viscosity to increase their applicability is desirable (Kalhor & Ghandi, 2019).

Increasing the temperature of DESs has an important effect on reducing the viscosity by increasing the mobility of species in DESs. For instance, increasing the temperature from 25 to 55 °C reduced the viscosity of ChCl/urea (1:2) from 750 to 95 cP, ChCl/glycerol (1:2) from 259 to 52 cP, and ChCl/malonic acid (1:1) from 1124 to 161 cP, verifying the great influence of increasing temperature on decreasing DESs viscosity (García et al., 2015).

Furthermore, adding water to a DES can decrease its viscosity to a large extent, depending on the amount of water (Kalhor & Ghandi, 2019). For example, the viscosity of ChCl/urea (1:2) decreased from 527.3 cP (pure state) to 200.6 cP at 30 °C, with just the addition of 0.1-mole fraction water (García et al., 2015). Thus, the addition of a small amount of water to the DES can improve fluidity leading to decreased viscosity, while also increasing the conductivity of the DES (Ma et al., 2018).

The reason why adding water to a DES can reduce its viscosity can be explained as follows: before the addition of water, there is a great affinity for HBD to undergo H-bonding with chloride ions (in the case of the choline chloride-based DES). After adding water, the interactions among hydrated species weaken and the HBD preferentially forms hydrogen bonds with water molecules which have a higher polarity than other species (HBD-water > HBD-Cl⁻), i.e. chloride ion in the system (Zhekenov et al., 2017; Hammond et al., 2017; Kumari et al., 2018). As a result, diluting a DES with water weakens the hydrogen interactions between the HBD and HBA, thus reducing its viscosity (Kumari et al., 2018).

Therefore, DESs can be a potential alternative to traditional metal processing leachants/reagents, one that is environmentally benign and has components that are commercially available and inexpensive (Abbott et al., 2017). DESs possess the interesting physicochemical properties of ILs but are cheaper, easier to make, biocompatible, biodegradable, and recyclable (Florindo et al., 2018; Vilková et al., 2020). There is increasing interest due to these remarkable properties of DESs as neoteric solvents (Smith et al., 2014) in various research fields like synthesis (Carriazo et al., 2012; Yu et al., 2022), catalysis (Musale & Shukla, 2016; Zainal-abidin et al., 2017), dissolution and extraction (Tomašević et al., 2016; Peng et al., 2016; Vieira et al., 2018; Nakhle et al., 2021), electrochemistry (Miyazaki et al., 2011; Qinghua et al., 2012), desulfurization (Lee et al., 2020; Khan & Srivastava, 2022), CO₂ capture (Trivedi et al., 2016; Adeyemi et al., 2017; Pina et al., 2017; Liu et al., 2020), and for water treatment/purification (Aruchamy et al., 2020; Taghizadeh et al., 2021; Moradi et al., 2022).

2.5. Density functional theory (DFT)

Computer modelling through DFT is a quantum-mechanical technique widely applied for the last two decades in physics and chemistry to calculate and evaluate the electronic structure of atoms, molecules, compounds and complexes using numerical models. It provides qualitative and quantitative information on the ground state properties of a compound and/or complex. The era of DFT started in the 1960s when Kohn and Sham proposed their equation as given in Equation 2.12 (Mourik et al. 2014; Qi et al., 2016).

$$\left\{ h_1 + j_0 \int \frac{\rho(2)}{r_{12}} d\tau_2 + V_{xc}(1) \right\} \varphi_m(1) = \varepsilon_m \varphi_m(1) \quad \text{Kohn - Sham equation} \quad (2.12)$$

In equation (2.12), the first term on the left represents the kinetic and potential energy contribution for one electron, the second term represents the potential energy of repulsion between electrons 1 and 2, the third term V_{xc} is exchange-correlation potential, which is a function of the electron density and originates from the electron-electron interactions (Qi et al., 2016). In the equation, ε_m is the energy associated with the electron in the orbital and φ_m is the Kohn-Sham wave function for the electron.

Principal idea for DFT is to avoid dealing with the complex many-electron wave function (φ) and instead, focus on the electron density ($\rho(r)$), which is a function of spatial coordinates. The electron density is a simpler and more tractable quantity, as it only depends on three spatial variables (x, y, z). Thus, the energy of the molecules is a function of the density and the density is a function of the position, $\rho(r)$, as written in Equation 2.13:

$$\rho(r) = \sum_m |\varphi_m(r)|^2 \quad (\text{electron probability density}) \quad (2.13)$$

Since then technological advances in computing have led to the use of DFT in chemistry, solid-state physics, biology and material sciences (Mourik et al., 2014). In the case of metal extraction through leaching, DFT calculation of metal-ligand complexes can provide information on objective geometry, electron spectroscopy, non-covalent interactions, and especially thermodynamics, i.e. reaction Gibbs free energy (ΔG) and enthalpy (ΔH) of reactions (Mohammadnejad et al., 2015).

The reaction Gibbs free energy (ΔG) of the possible complexes that can form between the desired metal and the available ligands in the leaching solution can be calculated through DFT. Moreover, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the proposed complexes can be calculated, which provides useful information. Typically, a low Gibbs free energy (ΔG) represents a high possibility of a metal-ligand

complex forming and a large gap between HOMO and LUMO indicates the stability of the formed complex (Zia et al., 2019).

There has been growing interest among researchers to employ DFT modelling and calculations in their studies due to insightful information that facilitates understanding metal-ligand interaction and complexation. Conradie and Ghosh (2007) have done DFT calculations on the spin crossover on Fe-salen complexes as transition metals using different exchange-correlation functions such as B3LYP, OLYP and OPBE (Conradie & Ghosh, 2007). In theoretical research by Gómez-Díaz et al. (2010), gold-cyanide interactions like $[\text{AuCN}]$ and $[\text{Au}(\text{CN})_2^-]$ were evaluated as a fundamental study for cleaning the leached ore from cyanide (Gómez-Díaz et al., 2010). The electrochemical activities of different complexes of tris(β -diketonato) Fe(III) were examined both experimentally with cyclic voltammetry (CV) and theoretically through DFT calculations using the OLYP functional by M.M. Conradie and J. Conradie (2015). They were testing the electron-donating ability of a β -diketone ligand based on the R1 and R2 side groups and ultimately the impact on $\text{Fe}^{3+}/\text{Fe}^{2+}$ reduction (M. M. Conradie & J. Conradie 2015).

Mohammadnejad et al. (2015) studied the role of sulfur species in gold passivation in cyanide and thiosulfate solutions with DFT modelling (Mohammadnejad et al., 2015). In another study reported by Mohammadnejad et al. (2017) DFT modelling was applied to evaluate the interaction of different gold complexes, such as with chloride $[\text{AuCl}_4^-]$, thiourea $[\text{Au}(\text{SC}(\text{NH}_2)_2)_2]$, and thiosulphate $[\text{Au}(\text{S}_2\text{O}_3)_2^{3-}]$, with silicate species in a solution at different pH between 1-13 (Mohammadnejad et al., 2017). Bleda et al. (2015) studied the preferred spin state of different Fe(II) complexes in the octahedral form of $\text{Fe}(\text{SCN})_2(\text{phen})_2$ using OLYP, OLAP3, O3LYP, and BLYP functions in their DFT modelling (Bleda et al., 2015). In research by J. Conradie (2022), the electronic structure, geometry optimised structure and the properties of copper complexes with (1,10-phenanthroline) to be used in a solar cell were calculated with DFT using a B3LYP function (J. Conradie, 2022).

2.6. Summary

Sustaining the world's increasing population and its demand for metals requires finding effective alternative ways to recover metals from waste materials (Kumar et al., 2020). Furthermore, some valuable and critical metals are naturally scarce, making it vital to recover them from waste materials. There is no shortage of waste material either. It is important to find effective recovery methods with limited environmental impact for improved circularity of metal production.

In summary, research in this thesis starts by exploring the optimal nitric acid pretreatment process to expose enclosed gold in pyrite, as it often occurs in mine tailings, intending to enhance gold extraction

efficiency. The use of nitric acid as a pretreatment process for pyrite dissolution (given its oxidative ability) is well documented in the literature. A study of the literature confirmed the effectiveness of nitric acid for pyrite dissolution. However, this research reports on a wider range of leaching conditions including various nitric acid concentrations and temperatures to determine the optimum conditions for efficient pyrite dissolution. The outcome of the research was refined and optimal conditions were set as a pretreatment process with nitric acid for sulfidic refractory ores and mine tailings to dissolve as much pyrite as possible to release the enclosed gold. An electrochemical study on sulfidic minerals enclosing gold, i.e. pyrite and chalcopyrite, was also done to complement the dissolution study and gain further supporting evidence for the kinetics of the dissolution mechanism in nitric acid.

With a deeper understanding of the above traditional leaching method and its mechanisms, the second part of this research focused on alternative and novel leaching solvents, specifically ILs and DESs. These solvents are potentially more environmentally benign than commonly used mineral acids. The literature on ILs and more so DESs for metal extraction is still limited and, as a relatively young field of study, still in its infancy. Ethaline, a DES composed of choline chloride and ethylene glycol, was evaluated for its feasibility for pyrite dissolution. In addition to adding new knowledge to the field, this made for an interesting – albeit not direct – comparison between nitric acid and DESs leaching for pyrite dissolution.

Next, the study extended to metal extraction from another waste material, EAFD, using ILs as alternative solvents to conventional H_2SO_4 leaching. To date, there has not been any published research on metal(s) extraction from EAFD using ILs. This thesis therefore lays the foundation for metals extraction from EAFD using the ILs $[\text{Bmim}^+ \text{HSO}_4^-]$ and $[\text{Bmim}^+ \text{Cl}^-]$.

By combining the experimental work with theoretical DFT calculations, this research aims to provide a comprehensive and innovative approach. Thus, the experimental work on metal(s) extraction with ILs and DESs was complemented with DFT calculations to provide an inclusive understanding of metal-ligand complexation of target metal(s) with the ligand(s) derived from the novel solvents (ILs and DES ethaline). DFT modelling has not been used in studying these solvents before, yet it was important and helpful in identifying the best ligand provided by the novel solvent to form the most stable complex with the target metal and determine the preferred coordination (i.e. tetrahedral, octahedral, or dimer complex). This novel multifaceted approach was found to improve the overall understanding and effectiveness of the proposed metal extraction methods.

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Chapter 3

The Kinetics of Pyrite Dissolution in Nitric Acid Solution

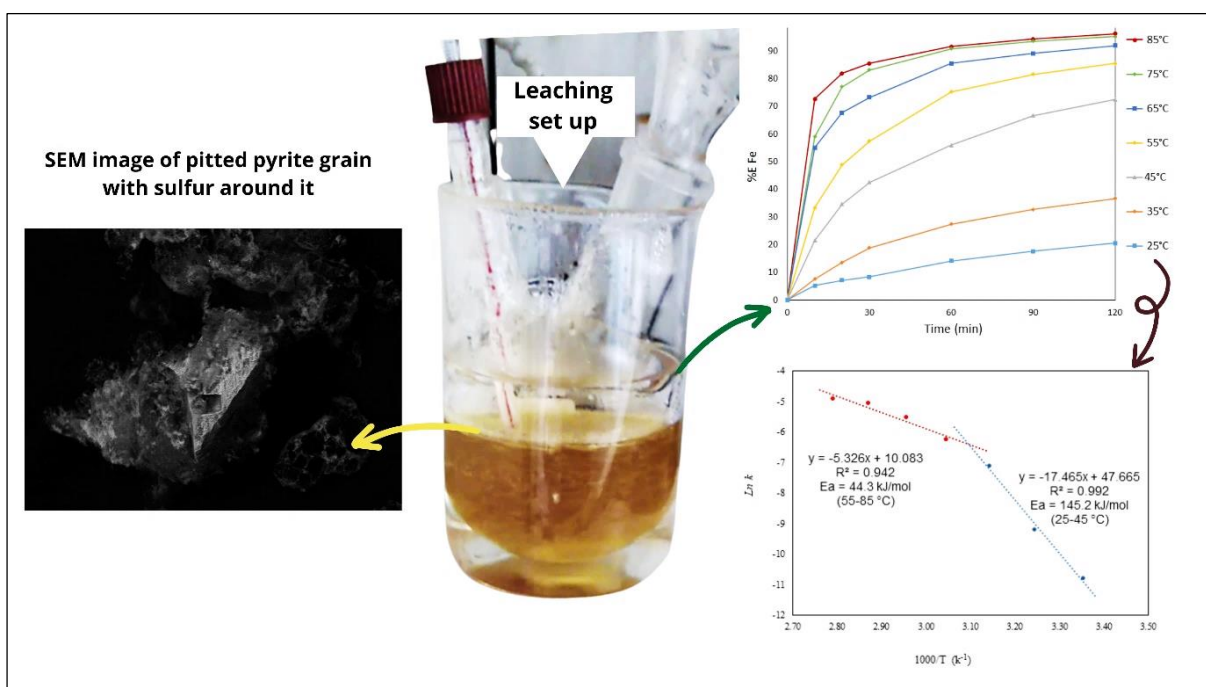
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Highlights

- Pyrite (FeS_2) dissolution in nitric acid (HNO_3) solution as a pretreatment method for mine tailings was examined.
- Within 2 h, a 3 M HNO_3 solution at 75 °C effectively dissolved 95% of FeS_2 making its gold content amenable to leaching.
- A mixed-controlled kinetics model ($\frac{1}{3}\ln(1-X) + [(1-X)^{-1/3} - 1] = k \cdot t$), describing the interfacial transfer and diffusion best described the kinetics of pyrite dissolution at a temperature range of 25–85 °C.

Graphical abstract



Article

The Kinetics of Pyrite Dissolution in Nitric Acid Solution

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Abstract: Refractory sulphidic ore with gold captured in pyrite has motivated researchers to find efficient means to break down pyrite to make gold accessible and, ultimately, improve gold extraction. Thus, the dissolution of pyrite was investigated to understand the mechanism and find the corresponding kinetics in a nitric acid solution. To carry this out, the temperature (25 to 85 °C), nitric acid concentration (1 to 4 M), the particle size of pyrite from 53 to 212 µm, and different stirring speeds were examined to observe their effect on pyrite dissolution. An increase in temperature and nitric acid concentration were influential parameters to obtaining a substantial improvement in pyrite dissolution (95% Fe extraction achieved). The new shrinking core equation $(1/3\ln(1-X) + [(1-X)^{-1/3} - 1]) = kt$ fit the measured rates of dissolution well. Thus, the mixed-controlled kinetics model describing the interfacial transfer and diffusion governed the reaction kinetics of pyrite. The activation energies (E_a) were 145.2 kJ/mol at 25–45 °C and 44.3 kJ/mol at higher temperatures (55–85 °C). A semiempirical expression describing the reaction of pyrite dissolution under the conditions studied was proposed: $1/3\ln(1-X) + [(1-X)^{-1/3} - 1] = 88.3 [\text{HNO}_3]^{2.6} r_0^{-1.3} e^{-44280/RT} t$. The solid residue was analysed using SEM, XRD, and Raman spectrometry, which all identified sulphur formation as the pyrite dissolved. Interestingly, two sulphur species, i.e., S_8 and S_6 , formed during the dissolution process, which were detected using XRD Rietveld refinement.

Keywords: pyrite; nitric acid; oxidative leaching; mechanism; mixed kinetic model; sulphur species



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1. Introduction

High-grade resources with easily extractable gold are becoming increasingly depleted. To fulfil the high demand for gold, owing to its versatile applications, extracting gold from low-grade and more challenging gold ores is desirable. Many of these sources are refractory in nature: they are not amenable to conventional cyanidation [1,2]. In general, three factors can contribute to making a gold ore refractory: (1) Very fine gold particles (<10 µm) enclosed in impermeable gangue minerals, often sulphides; such fine gold cannot be adequately liberated, even with fine grinding, and so remain inaccessible to the leaching solution. (2) Preg-robbing, which happens in carbonaceous ores by the adsorption of gold complexes onto a fine-grained carbonaceous mineral existing in the ore. (3) Copper–gold ores (complex ores) containing minerals, e.g., metallic copper, copper oxides, chalcocite, and bornite, can react with cyanide to form copper–cyanide complexes, which lead to a high cyanide consumption [3].

The degree of refractoriness depends on the severity of its causes in the gold ore, which can be one or a combination of these [4]. The most common reason for refractory ore is the invisible locked gold (chemically or physically) within the host minerals in the form of nanoparticles of native gold, colloidal particles, and solid solution [5]. The term “invisible gold” is used since it is difficult to observe with optical microscopy [6]. Pyrite and arsenopyrite are the predominant hosts for gold occluded in their structures [7].

As the gold is locked inside the sulphidic host mineral, it is necessary to break down the host matrix to expose the encapsulated gold. This justifies the pretreatment of the refractory gold ore before extracting gold to oxidise the impervious sulphidic mineral to obtain a permeable matrix for acceptable gold recovery [8]. Generally, the pretreatment is performed either pyrometallurgically or hydrometallurgically. The most common oxidative pretreatment methods are roasting [9], pressure oxidation [10], and bio-oxidation [11,12], and have also been investigated as options to destroy pyrite. Roasting requires high temperatures, e.g., 600 to 1000 °C, depending on the mineralogy of the ore, and is associated with releasing harmful gases, such as SO₂, which pollute the environment if not captured. Pressure oxidation uses high pressure (4500 kPa) and temperature (≥ 250 °C), which pose safety risks, as well as high capital expenditure for specialised equipment and operating costs. Bio-oxidation typically demands a long processing time for pretreatment, namely, 4 to 8 days, depending on the ore [13–16].

Consequently, developing an oxidative pretreatment process with mild conditions, a low operating cost, and relatively fast kinetics is crucial. A hydrometallurgical process using nitric acid may be a potentially efficient way to oxidise and dissolve the sulphidic matrix of the host minerals, i.e., pyrite to expose the enclosed gold. While nitric acid is an oxidising acid that is capable of oxidising most metals, the emphasis of this study is on the oxidation of pyrite. Several investigations reported the oxidation of various minerals, such as chalcopyrite, galena, and arsenopyrite, using nitric acid [17,18].

In nitric acid (HNO₃), the nitrogen (N) in NO₃[−] is in its highest oxidation state, which is +5; therefore, the NO₃[−] possesses strong oxidant abilities. This feature can be used for the oxidative pretreatment of refractory sulphidic ore, ultimately improving gold yield [19,20].

Nitric acid as an oxidising acid was the focus of some research investigating the kinetics of sulphidic gold ore dissolution. Gao et al. [13] investigated the kinetics of refractory gold concentrate ore (high sulphur and arsenic) with a diluted nitric acid solution. The ore dissolution was increased by increasing the nitric acid concentration and temperature and decreasing the particle size. The experimental results were evaluated using a shrinking particle model, and it was found that the reaction kinetics were controlled by the diffusion of NO₃[−] to the surface of the particles. The obtained activation energy was 12.3 kJ/mol in a 25% nitric acid solution. The kinetics of refractory sulphidic gold ore dissolution using nitric acid was studied by Rogozhnikov et al. [5] at temperatures of 70–85 °C. Increasing the temperature and nitric acid concentration improved the iron dissolution as an indication of sulphidic gold ore dissolution during 1 h of leaching. The new variant of the shrinking core model representing an interfacial transfer and diffusion fitted the results well. The reaction order concerning the nitric acid concentration was 0.84 and the obtained activation energy was 60.3 kJ/mol.

Although other researchers have investigated the dissolution of pyrite in other different mineral acids, such as H₂SO₄, HCl, and HClO₄ [21–25], this investigation focused on HNO₃. Nitric acid was chosen in preference to sulfuric acid and hydrochloric acid because it is the only acid that, during the dissolution process, yields a potentially recyclable product (nitric oxide and nitrous gas), which can be absorbed in a column and regenerated as a reagent (HNO₃). This option clearly changes the economic prospects of any proposed process. Above all, HNO₃ was investigated for the removal of pyrite contained in coal [26,27].

This research explored a wider range of experimental conditions than have been conducted to date. More than other research on this topic, it made use of a variety of solid analyses on the residue (SEM-EDS, XRD, XRD Rietveld refinement, and Raman spectroscopy) to examine changes in the morphology of the remaining pyrite grain and the produced product(s).

Therefore, this work attempted to describe the oxidative dissolution mechanism of pyrite in nitric acid by investigating the corresponding kinetics of the reactions. To attempt this, pyrite dissolution in nitric acid was studied at different leaching conditions by examining pyrite dissolution in the temperature range of 25 to 85 °C, concentrations of

nitric acid from 1 to 4 M, various-sized fractions of pyrite from 53 to 212 μm , and different stirring rates. The selected temperature and acid concentration ranges employed covered a larger set of conditions than previous investigations, and could potentially also resolve the discrepancy in the vastly different activation energies reported in the earlier work referred to above. While the recovery of gold from refractory ores in which it is encapsulated in pyrite was the ultimate aim of this research, we endeavoured to first understand and focus on the dissolution of the pyrite only, rather than investigating any release of the gold. Once one understands how the pyrite can be broken down, it can be applied to refractory gold ores to establish how the gold recovery can be enhanced. Knowledge generated by this study could be used as a foundation to develop a nitric acid pretreatment process for sulphidic refractory gold ores.

2. Materials and Methods

2.1. Materials

The pyrite (FeS_2) sample used in this study was obtained from Mintek, South Africa. Figure 1 displays the X-ray diffractogram (XRD) (Bruker, Karlsruhe, Germany) of the phase composition of the pyrite sample. Table 1 presents the chemical composition of the pyrite sample determined via X-ray fluorescence (XRF). To determine the particle size distribution (PSD), the pyrite sample was measured 3 times via laser diffraction (Mastersizer 2000). The average particle size and the standard deviation were determined and calculated to be $d_{10} = 3.3 \pm 0.6 \mu\text{m}$, $d_{50} = 18 \pm 3.2 \mu\text{m}$, and $d_{90} = 77 \pm 2.2 \mu\text{m}$ (Figure 2). The pyrite sample was dried in an oven and screened with stainless steel sieves to obtain different fraction sizes in the range of 53–212 μm using an electronic sieve shaker (Eriez model ES 200, Malvern, Worcestershire, UK).

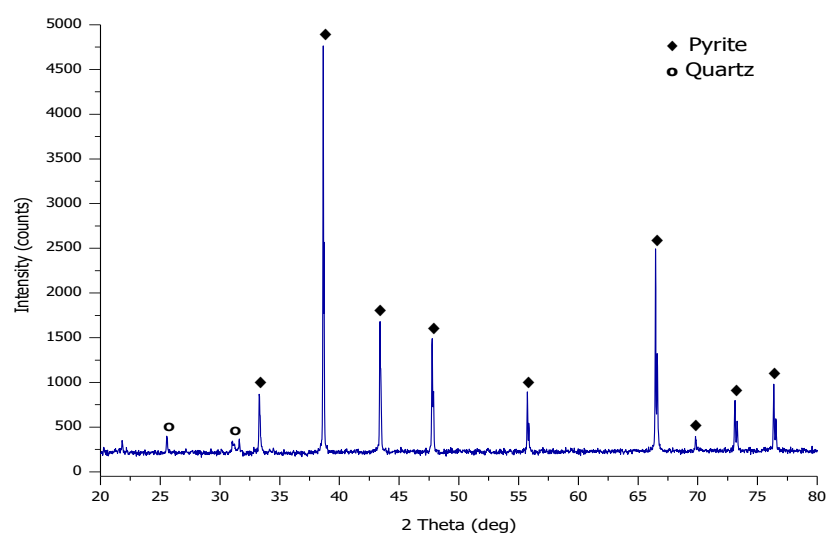


Figure 1. The XRD pattern of the phase composition of a pyrite sample.

Table 1. The chemical composition of the pyrite sample as determined using XRF.

Chemical Composition	Al_2O_3	SiO_2	TiO_2	CaO	S *	FeS_2	LOI
Wt%	2.25	4.19	0.45	1.38	13.41	69.12	9.16

* Measured using a Leco instrument (not bound in the pyrite).

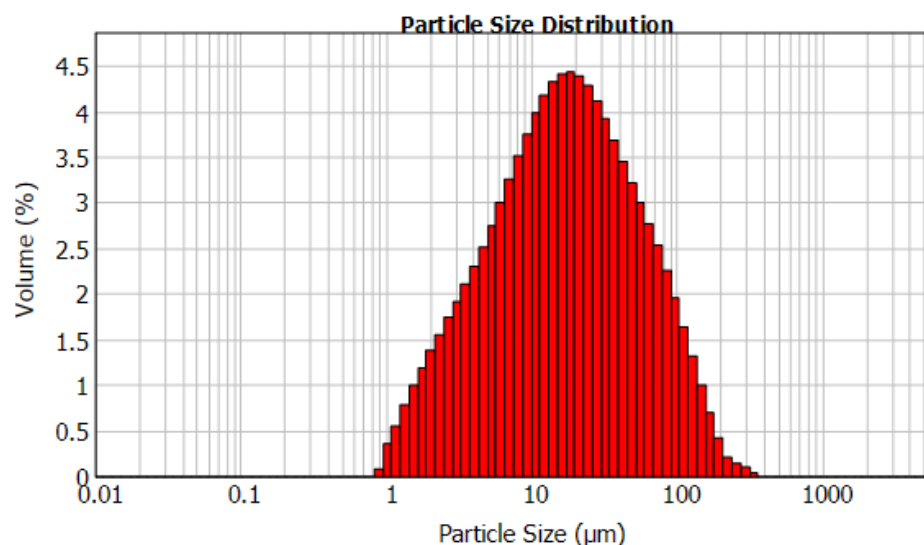


Figure 2. The particle size distribution (PSD) of the pyrite sample.

2.2. Experimental Procedure

The oxidative leaching of pyrite with nitric acid was conducted in a 250 mL two-neck round-bottom flask as a reaction vessel, which was immersed in a water bath on a hot plate magnetic stirrer. A thermometer was positioned inside the reaction vessel to measure the temperature inside the leaching solution, and a water-cooled condenser was fitted to lead the nitrous gases to an absorption column. The experiment was temperature-controlled during stirring to provide a uniform pulp density. To examine the pyrite dissolution in nitric acid, a 10 g pyrite sample (particle size +75–106 μm) was added to the 200 mL of 3 M nitric acid (solid to liquid ratio of 1:20) when the temperature inside the leaching solution reached the desired temperature (25 to 85 °C). During the experimental runs, samples were withdrawn from the reaction vessel at regular time intervals (10, 20, 30, 60, 90, and 120 min) with a pipette and filtered using a 45 μm syringe filter. The iron content of the pregnant leached solution (PLS) was analysed using atomic absorption spectroscopy (AAS) (Agilent, Santa Clara, CA, USA) and used as an indication of pyrite dissolution. This formula was used to calculate the percentage of the extracted iron from the pyrite sample.

$$\%E_{\text{Fe}} = \frac{\text{Amount of Fe in PLS analysed by AAS (mg/L) Volume of solution (L)}}{\text{Total amount of Fe (mg/g) Amount of pyrite used in the experiment (g)}} \times 100$$

After the experiments, the leached pulp was filtered using a Buchner funnel with filter paper. The residue (leached pulp) was washed with distilled water, dried in an oven at a temperature of 80 °C for 30 min, weighed, and analysed further for residue characterisation. The same procedure was followed for the other experiments using different nitric acid concentrations of 1–4 M, various size fractions of pyrite from 53 to 212 μm, and different stirring rates at a temperature of 65 °C to investigate their effect on pyrite dissolution in nitric acid solution.

2.3. Analysis

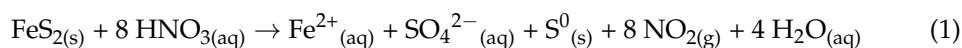
The pregnant solution taken at regular time intervals was analysed using atomic absorption spectroscopy (AAS) to obtain the amount of iron extracted. The compositions of solid residues were examined using scanning electron microscopy (SEM) (ZEISS Sigma, Manchester, UK), XRD, and Raman spectroscopy. SEM was performed using a ZEISS Sigma 300 VP equipped with a field emission gun and connected to “Smart SEM” software to examine the morphology of the leached residue. The sample preparation for SEM analysis was achieved by mounting a sample (pyrite/residue) on carbon tape fixed to an aluminium stub. The samples were coated with C and PdAu to facilitate imaging.

The aluminium stubs were then inserted into the stage of the SEM and examined. The phase analysis was inspected with a Bruker D2 Phaser XRD spectrometer with a Co anode (wavelength = 1.79 Å) using a 2θ range of 20–90° with 0.0274° increment steps. Raman spectra were acquired using the 514.5 nm line of a Lexel Mode 95-SHG argon-ion laser and a Horiba LabRAM HR Raman spectrometer (Horiba, Lille, France) equipped with an Olympus BX40 microscope attachment. The incident beam was focused onto the sample using a 100 × LWD objective (N.A. = 0.80) and the backscattered light was dispersed via a 600 lines/mm grating onto a liquid nitrogen-cooled CCD detector. The data were acquired and analysed using LabSpec v5 software (version 5.64, Horiba, Lille, France). The power of the laser at the sample was 0.4 mW to ensure that there was no localised heating of the samples.

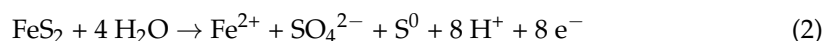
3. Results and Discussion

3.1. Mechanism of the Pyrite–Nitric Acid Dissolution

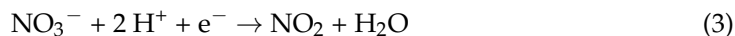
Pyrite dissolution in nitric acid is an electrochemical reaction that consists of anodic and cathodic reactions [20]. The anodic dissolution of pyrite and the cathodic reduction of the oxidant happen simultaneously on the pyrite particle's surface. The driving force for these reactions to occur is the potential difference across the pyrite–solution interface [21,22]. The general reaction of pyrite with nitric acid (HNO₃) can be expressed as



The anodic reaction (oxidation of pyrite) is given by



The cathodic reaction (reduction in oxidant NO₃[−]) is given by [18]



In pyrite, when the bond between Fe²⁺ and S₂^{2−} breaks, there is no change in the oxidation number of iron (Fe²⁺). This can be explained since iron is the electropositive element in FeS₂, causing it to transfer to the solution as it is (without releasing an electron). Thus, the oxidation number of iron in the pyrite lattice was +2, and the released iron species (Fe²⁺_(aq)) into the solution are still +2. It can, however, further oxidise to (Fe³⁺_(aq)) in an oxidative medium. However, sulphur, which is the electronegative element, loses an electron(s) and undergoes recombining reactions [28,29]. Sulphur has an oxidation number of −1 in the lattice; hence, when the bond breaks, the shared electron from sulphur is released to form sulphur (S⁰_(s)) and even sulphate (SO₄^{2−}_(aq)) when seven to eight electrons are released by sulphur (Equation (2)). The released electrons are captured by the oxidant (NO₃[−]), which is reduced to NO_{x(g)} (NO, NO₂) after accepting the electrons (Equation (3)).

The proposed pyrite dissolution mechanism in nitric acid solution is illustrated in Figure 3, presenting the ions at the surface of the pyrite mineral; the species Fe²⁺_(aq), S⁰_(s), and SO₄^{2−}_(aq) being released into the bulk solution; and the oxidant (NO₃[−]) taking the released electrons by S to form NO_{x(g)}, i.e., NO_{2(g)} [21,28]. To keep the figure simple, the water molecules and the solvated ions were not included, just the main reducing and oxidising species were presented.

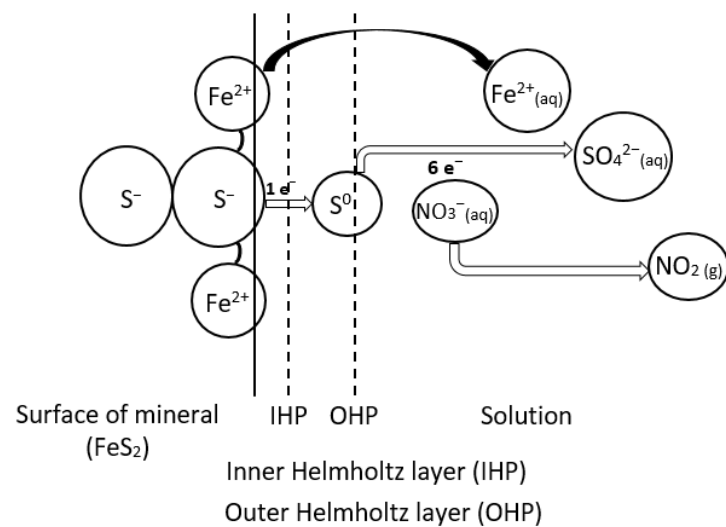


Figure 3. The proposed pyrite dissolution mechanism in nitric acid solution.

Figure 4 represents the energy band diagram of the pyrite–solution interface. Based on the applied potential (or potential of a solution), the Fermi level (E_F) (which is the level of energy that lies between the conduction and the valance band) can have a slightly different level from the surface state. At a certain potential, the Fermi level can overlap the surface state, and this potential is known as the breakdown potential. This is the beginning of the anodic dissolution and leads to an anodic current [21,22]. After reaching the breakdown potential and even higher, electrons are transferred and removed from the surface bonds, leading to the breaking of the bonds, and ions moving across the Helmholtz layers to the bulk solution. At this point, the rate-limiting step in the dissolution kinetics is the transferring of electrons (charges) across the Helmholtz layers (space-charge layer). By further increasing the potential, the Fermi level does not overlay the surface state anymore. At this point, the speed of the electron transfers reaches its highest value, and the rate-limiting step is the movement of the produced ionic species across the Helmholtz layers to the bulk solution. Hence, this model is described as an interfacial kinetics model [21,22].

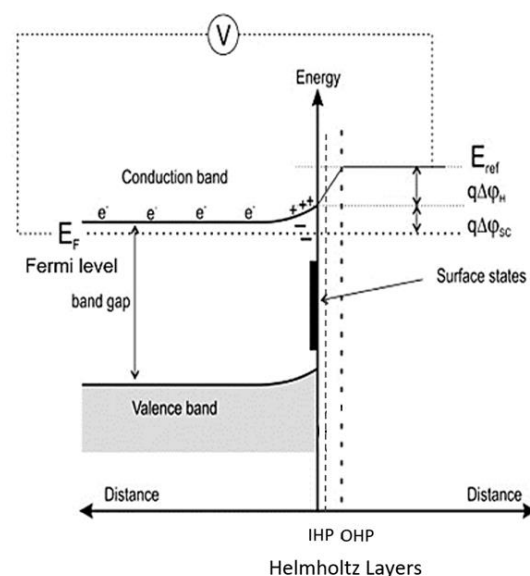


Figure 4. The energy band diagram of a pyrite–solution interface adopted from [21].

3.2. Effect of Temperature

The evaluation of the effect of temperature was conducted on pyrite dissolution in 3 M nitric acid, where the temperature varied from 25 to 85 °C. Temperature vastly influences the process because it affects the rate of the leaching process, i.e., both the diffusion and the reaction rate [13]. The results of this experiment are presented in Figure 5. There was less than 20% and 40% iron extraction at temperatures of 25 and 35 °C. However, a marked increase to over 70% of iron extraction occurred at 45 °C. This was followed by a moderate increase in iron extraction to 85% at 55 °C, and the most iron extraction of more than 95% at 75 °C and 85 °C.

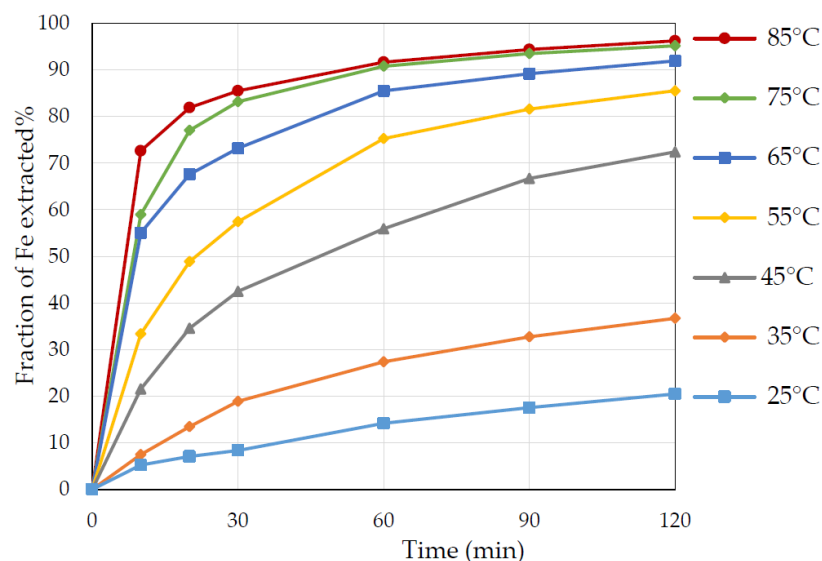


Figure 5. The extraction of iron from pyrite at different temperatures from 25 to 85 °C. Conditions: 3 M nitric acid, S/L ratio 1 to 20, particle size +75–106 µm.

3.3. Effect of Nitric Acid Concentration

The strong oxidative ability of nitric acid came from a concentration higher than 2 M in the solution. By definition, when the concentration of nitric acid increases, the $[\text{NO}_3^-]$ concentration (oxidant) and the acidity $[\text{H}^+]$ of the solution increase, and therefore, ultimately, the oxidative power in the solution escalates [13]. This is explained from the standard electrode potential (E^0) provided by NO_3^- from nitric acid in Equation (4), and the corresponding Nernst Equation (5), as follows:



$$E = E^0 + \frac{0.059}{n} \log \frac{[\text{H}^+]^2 [\text{NO}_3^-]}{P_{\text{NO}_2}} \quad (5)$$

A 1 M nitric acid solution, for example, contains $[\text{NO}_3^-] = 1 \text{ M}$ and $[\text{H}^+] = 1 \text{ M}$. By substituting $E^0 = 0.80 \text{ V}$, $n = 1$ (number of electrons), $[\text{NO}_3^-]$ and $[\text{H}^+]$ 1 M, and the partial pressure of $\text{NO}_{2(g)}$ 1 atm in the Nernst Equation (5), it would produce a half-reaction potential of 0.80 V, calculated as follows:

$$E = E^0 + 0.059 \log [1]^2 [1] = 0.80 + 2 \times 0.059 \times \log [1] = 0.80 \text{ V}$$

One has to keep in mind that this calculation is an approximation because of activities (taking the activity coefficient together with the concentration into consideration) rather than only concentrations should be used in the equation. While the effect in a 1 M nitric acid solution will be small, it will increase as the solution becomes more concentrated to 4 M and deviates from an ideal solution. In a concentrated ionic solution, the activities can

differ from concentrations by as much as 50% and are usually lower than the concentration values. Nevertheless, it is clear that increased values for the nitrate ion and hydrogen ion concentrations in the equation will still result in an increase in the calculated E value. It is unlikely that the vapour pressure in the denominator will change. Therefore, even taking into account a 50% lower value for the nitric and hydrogen ion concentrations in a 4 M concentration solution, it will still cause an increase in the calculated value of E to 0.853 V (higher potential). This explains the stronger oxidative power for pyrite dissolution in the more concentrated nitric acid solution, and thus the increase in the pyrite dissolution.

As illustrated in Figure 6, increasing the concentration of nitric acid escalated the iron extraction, with a marked increase occurring between 1 and 2 M from 45% to approximately 74% iron extraction. This was followed by another notable increase between 2.5 and 3 M from 75% to 85% iron extraction, but the increase was less notable between 3 and 4 M. The highest iron extraction of close to 95% occurred with 4 M nitric acid. Thus, it was found that a substantial pyrite dissolution occurred at concentrations above 2.5–3 M, where HNO_3 had an adequately strong oxidising ability.

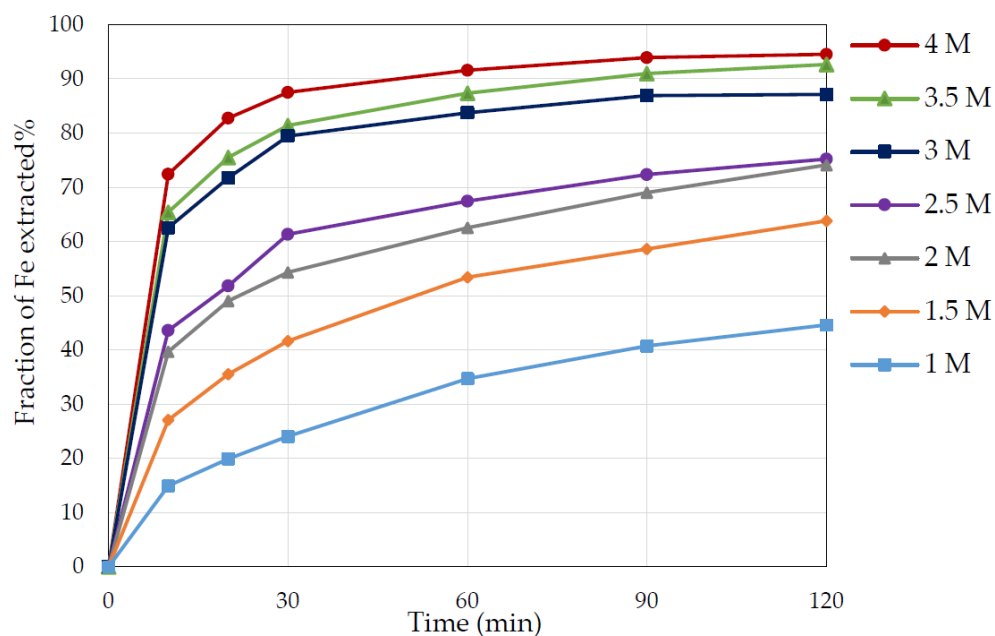


Figure 6. Time dependence of iron extraction from pyrite with different nitric acid concentrations (1–4 M). Conditions: temperature 65 °C, S/L ratio 1 to 20, particle size +75–106 μm .

3.4. Effect of Particle Size

To determine the effect of the particle size of pyrite, leaching experiments were carried out with different particle size fractions from 53 to 212 μm in a 3 M nitric acid solution. As illustrated in Figure 7, iron extraction was enhanced by decreasing the particle size. The reason for the improvement when decreasing the particle size was that the chemical reaction happens on the surface of the pyrite particles. Therefore, the smaller the particle size, the bigger the available surface area for the reactions to take place [13]. The different particle sizes of pyrite contributed to a high Fe extraction of more than 75% to approximately 92%.

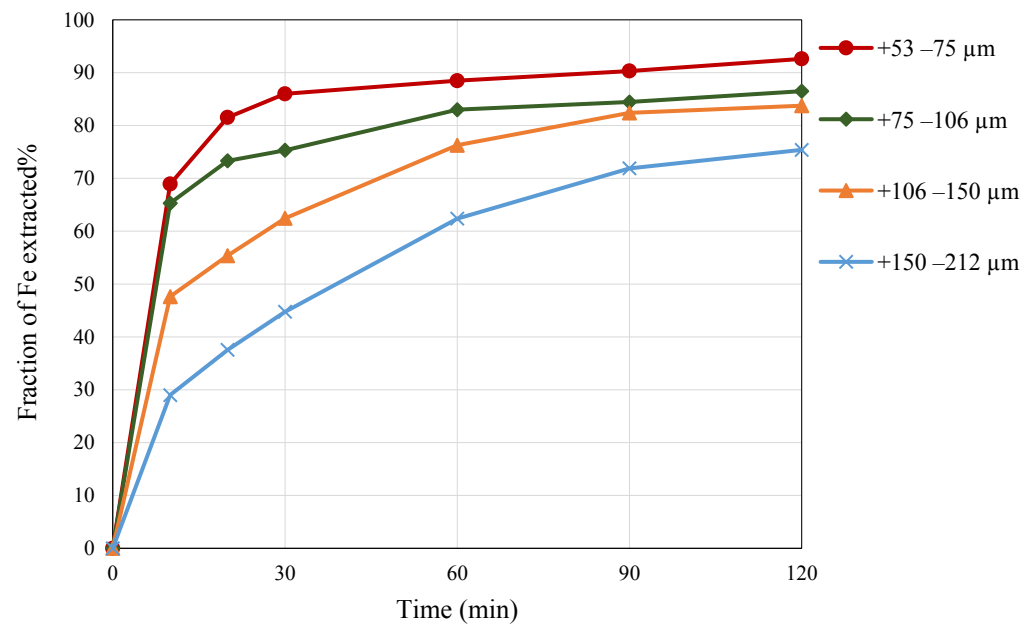


Figure 7. The effect of particle size on Fe extraction as a function of time. Conditions: 3 M nitric acid, temperature 65 °C, S/L ratio 1 to 20.

3.5. Effect of Stirring Speed

In heterogeneous solid–liquid reactions, particularly those controlled by diffusion, determining the influence of the stirring speed is important. Therefore, experiments were conducted with different stirring speeds to determine its effect on the pyrite dissolution. As illustrated in Figure 8, increasing the stirring speed increased the Fe extraction, and thus, pyrite dissolution. The stirring speeds (1000 to 4000 rpm) resulted in a satisfactory Fe extraction above 80% to close to 98%. Mass transfer resistance is present in a heterogeneous system, and hence, by increasing the stirring speed, the turbulence intensity surges, the thickness of the diffusion layer reduces, the mass transfer increases, and subsequently, the reaction kinetics improves [13].

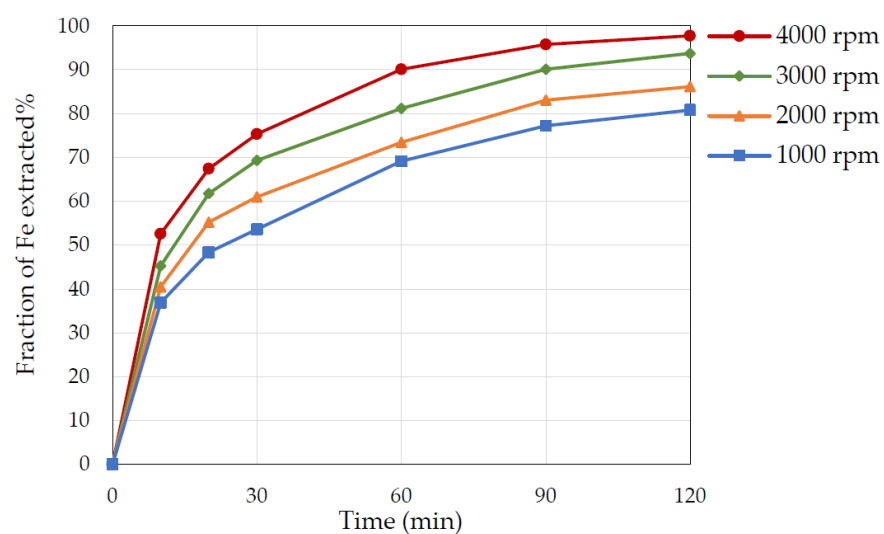
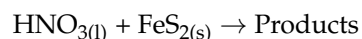


Figure 8. The effect of stirring speed on Fe extraction as a function of time. Conditions: 3 M nitric acid, temperature 65 °C, S/L ratio 1 to 20, particle size +53–75 µm.

3.6. Kinetic Model

Leaching is a heterogeneous reaction between solid particles and a liquid [30]. In the case of pyrite leaching in nitric acid solution, the reaction(s) took place at the interface of pyrite (solid phase) and nitric acid (liquid), and the leaching reaction could be expressed as follows:



Generally, during leaching, the following sequence of events occurs: the diffusion of the leaching agent (nitric acid) through a thin liquid film surrounding the pyrite particles; anodic and cathodic reactions occur on the surface of the pyrite particles (including charge transfer); then, the diffusion of the produced products, i.e., Fe^{2+} , S^0 , SO_4^{2-} , and NO_x , into the bulk solution takes place. The slowest process(es) acts as a limiting step(s) and controls the kinetic model [30].

To determine the kinetics of pyrite dissolution in nitric acid, experimental results of the studied parameters were evaluated using the new equation proposed by Dickinson and Heal [31] in the shrinking core model. Further references indicated below provide additional confirmation of our choice. The Dickinson and Heal model defines the interfacial transfer and diffusion (mixed model) through the product as $1/3\ln(1-X) + [(1-X)^{-1/3} - 1] = k.t$. Here, X is the fractional conversion, t is time (min), and k is the rate constant (min^{-1}). Thus, the mechanism of pyrite dissolution in nitric acid occurs, which consists of anodic and cathodic reactions occurring at the pyrite–solution surface (interfacial layer); then, the movement of the produced ionic species diffuses into the bulk solution and can be kinetically described by this equation.

Hence, the function of the equation $1/3\ln(1-X) + [(1-X)^{-1/3} - 1] = k.t$ versus time was plotted to obtain the correlation coefficient (R^2) for each temperature to establish its fitness. The resulting consistent straight line with R^2 close to one for all studied temperatures (Figure 9) indicated that the interfacial transfer and diffusion through the product (mixed model) controlled the reaction kinetics of pyrite dissolution in the nitric acid medium.

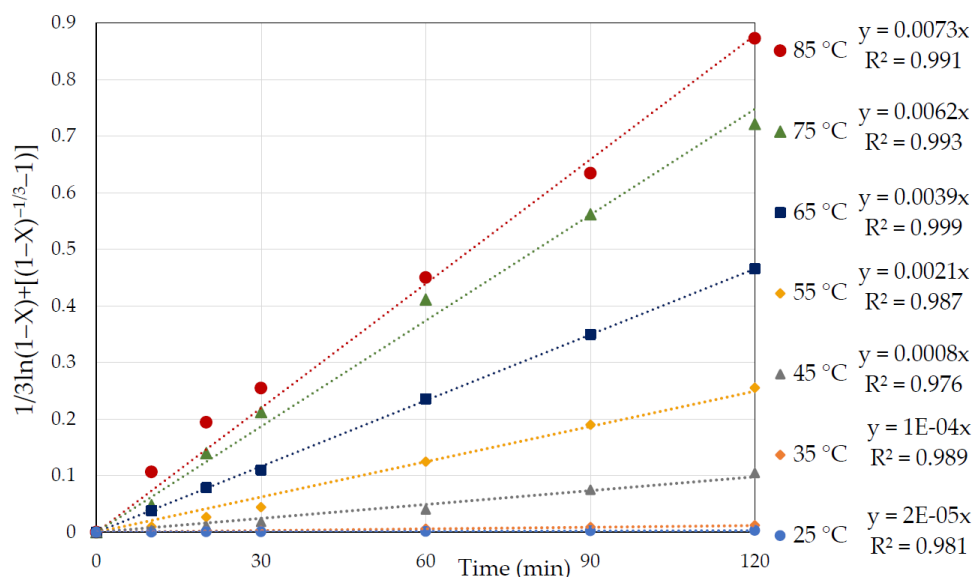


Figure 9. Graphs of $1/3\ln(1-X) + [(1-X)^{-1/3} - 1] = k.t$ vs. time (min) at various temperatures of 25 to 85 °C for the dissolution of pyrite in 3 M nitric acid.

The suitability of the other shrinking core model equations as a limiting step to control the kinetics of pyrite dissolution was also evaluated. They included diffusion through the product layer ($1 - 3(1-X)^{2/3} + 2(1-X) = k.t$), diffusion through the liquid film ($X = k.t$), and the surface chemical reaction ($1 - (1-X)^{1/3} = k.t$). However, their R^2 values were not close to one, making them unfit descriptions of the reaction. This could be attributed to the

different stages in pyrite dissolution, which makes the interfacial transfer and diffusion mixed model a better fit.

This kinetic model agreed with the work by Rogozhnikov et al. [5], who investigated the kinetics of the dissolution of refractory sulphidic gold-containing concentrated ore in nitric acid solution in the temperature range of 70–85 °C. It was also in agreement with the more recent work by this group on the effect of pyrite and ferric ions on the kinetics of arsenopyrite leaching in nitric acid solution [1]. Moreover, the research by Li et al. [32] on the kinetics of cerium leaching from a mixed rare earth concentrate with nitric acid was also described by the new version of the shrinking core model based on the interfacial transfer and diffusion through the product.

The rate constant (k) was obtained from the slope of each straight line in Figure 9. Figure 10 represents the graph of $\ln k$ as a function of $1000/T$, where the slope of this graph is equal to $-E_a/R$. As shown in Figure 10, the slope changed over the studied temperature range, with a higher activation energy of 145.2 kJ/mol at the lower temperature (25–45 °C), and a lower activation energy of 44.3 kJ/mol at higher temperatures (55–85 °C).

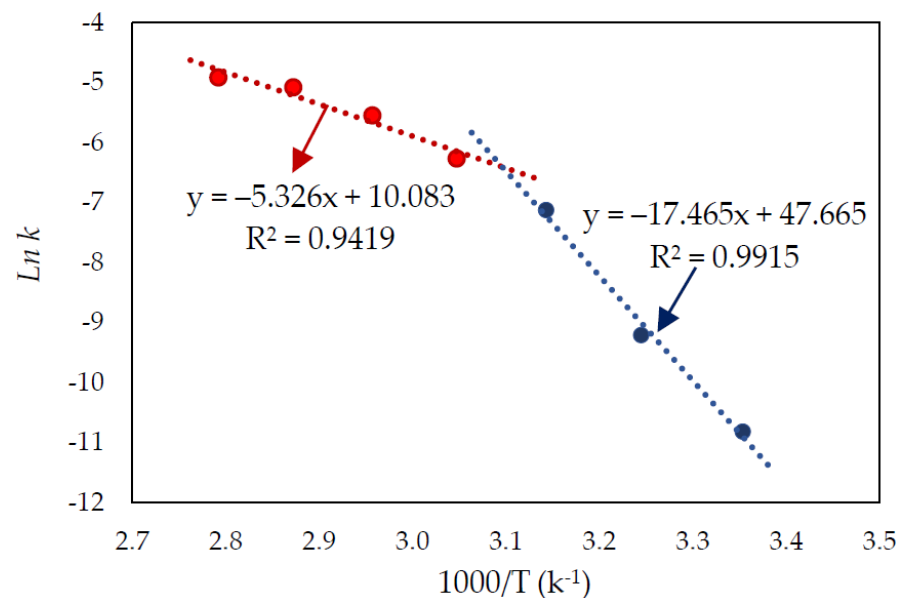


Figure 10. Arrhenius plot of $\ln k$ vs. $1000/T$ (K^{-1}).

The function of the equation $1/3\ln(1 - X) + [(1 - X)^{-1/3} - 1] = k \cdot t$ versus time was also evaluated with the experimental results on pyrite dissolution in varied concentrations of nitric acid solution from 1 to 4 M. As was the case for varying temperatures, the new variant of the shrinking core model produced a straight line, which fit with R^2 values close to one for the different nitric acid concentrations (Figure 11).

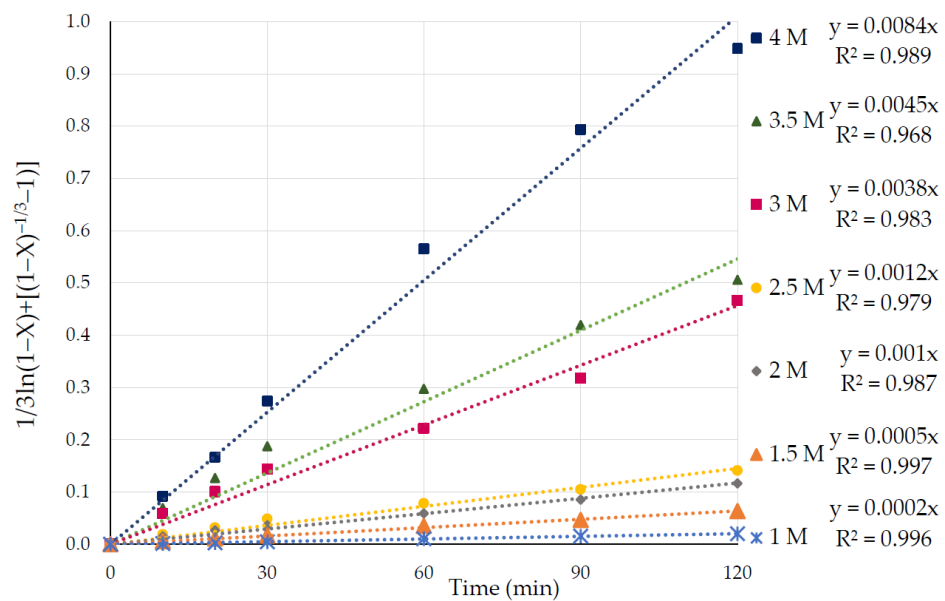


Figure 11. Graph with curves of $1/3\ln(1-X) + [(1-X)^{-1/3} - 1]$ vs. time (min) at different concentrations of HNO_3 at a temperature of 65 °C.

The slope of each straight line from Figure 11, at various HNO_3 concentrations at a temperature of 65 °C, was plotted as $\ln k$ versus $\ln(\text{HNO}_3)$ to determine the reaction order with regard to HNO_3 (Figure 12). Based on the slope of the graph, the resulting empirical order with regard to HNO_3 was 2.55.

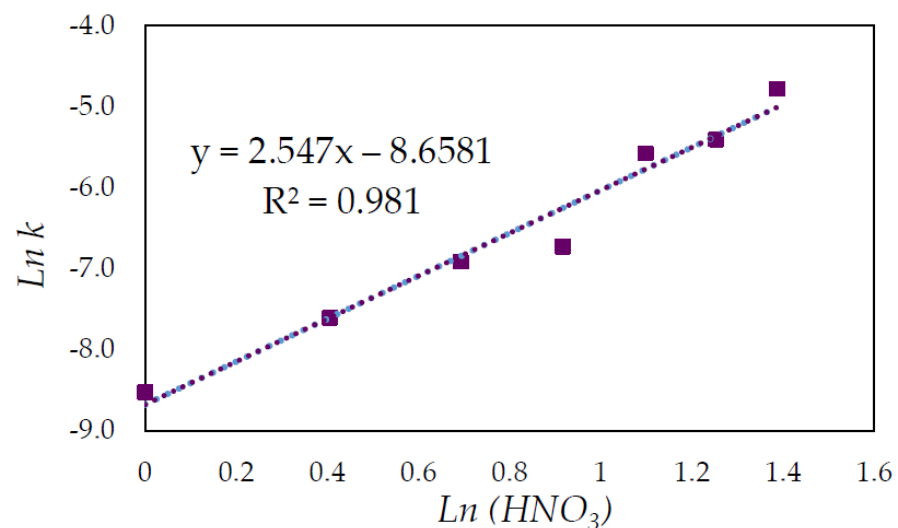


Figure 12. Plot of $\ln k$ as a function of $\ln(\text{HNO}_3)$.

The same process was performed with the obtained results on the pyrite dissolution with different particle size fractions from 53 to 212 μm . The plot of the equation vs. time produced straight lines. The slope of each straight line was plotted as $\ln k$ versus $\ln(r_0)$ to determine an empirical order concerning r_0 , which was calculated to be -1.3 , based on the slope (Figure 13).

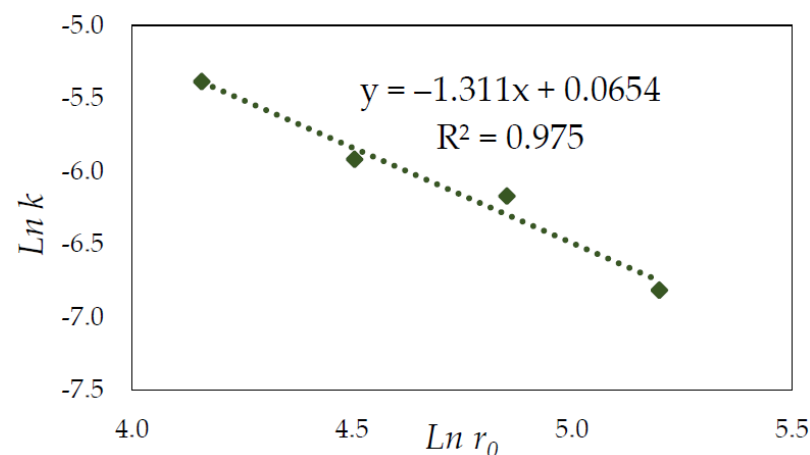


Figure 13. Plot of $\ln k$ as a function of $\ln(r_0)$.

By substituting the Arrhenius equation $k = k_0 e^{-E_a/RT}$ in the new shrinking core mixed-model equation of $1/3\ln(1-X) + [(1-X)^{-1/3} - 1]] = k.t$, we obtained its expression as $1/3\ln(1-X) + [(1-X)^{-1/3} - 1]] = k_0 e^{-E_a/RT}.t$. Based on the obtained values, the following semi-empirical expression for pyrite dissolution in HNO_3 was derived for the high-temperature range (55–85 °C):

$$1/3\ln(1-X) + [(1-X)^{-1/3} - 1]] = k_0 [\text{HNO}_3]^{2.6} r_0^{-1.3} e^{-44280/RT}.t$$

As presented in Figure 14, all of the experimental results were used to evaluate the proposed semiempirical expression and also to determine the k_0 from the slope (88.3) of the plotted graph. Therefore, the semiempirical expression for pyrite dissolution in HNO_3 under the studied conditions could be expressed as

$$1/3\ln(1-X) + [(1-X)^{-1/3} - 1]] = 88.3 [\text{HNO}_3]^{2.6} r_0^{-1.3} e^{-44280/RT}.t$$

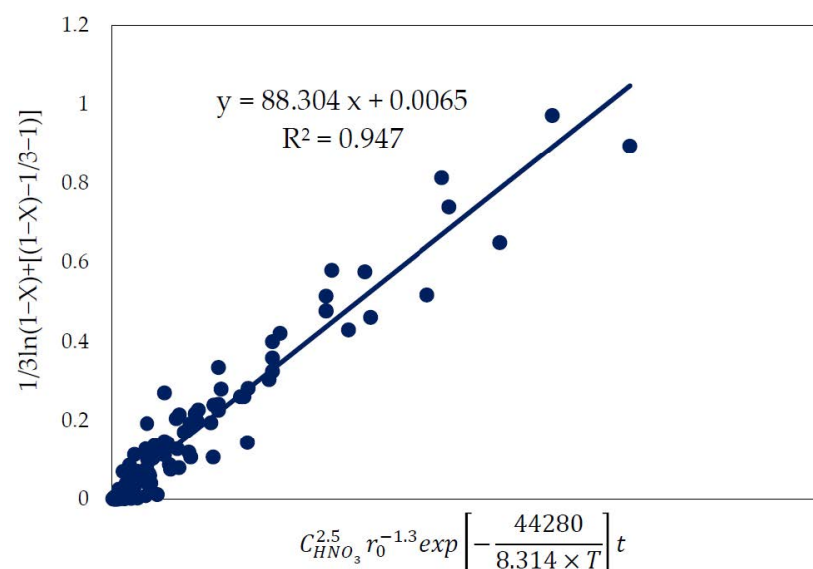


Figure 14. Relation of the applied kinetic equation and the acquired semiempirical expression.

3.7. Characteristics of Solid Residue

The pyrite sample before leaching and after leaching (residue) with nitric acid was examined with SEM-EDS. The SEM-EDS of pyrite before leaching detected 33.5% and 29.2% (weight%) of S and Fe, respectively. However, on the residue, the amount of sulphur increased to 49.5% and the Fe decreased to 4.5% owing to the formation of sulphur as the

result of the oxidative dissolution of pyrite (Figure 15). Figure 16 shows the SEM images of the residue at 25, 45, 65, and 85 °C after leaching in 3 M nitric acid for 120 min. As the temperature increased, more pyrite particles dissolved, leaving fewer pyrite particles at the higher temperatures of 65 and 85 °C. This confirmed the positive effect of increasing the temperature on the dissolution of pyrite. Moreover, due to the oxidative dissolution of pyrite in nitric acid, sulphur formed as an amorphous product around the pitted pyrite grain. Therefore, in the nitric acid medium, the surface of the pyrite grain became rough and pitted with cavities (Figure 17) and the oxidative dissolution led to the formation of sulphur, as seen in the images.

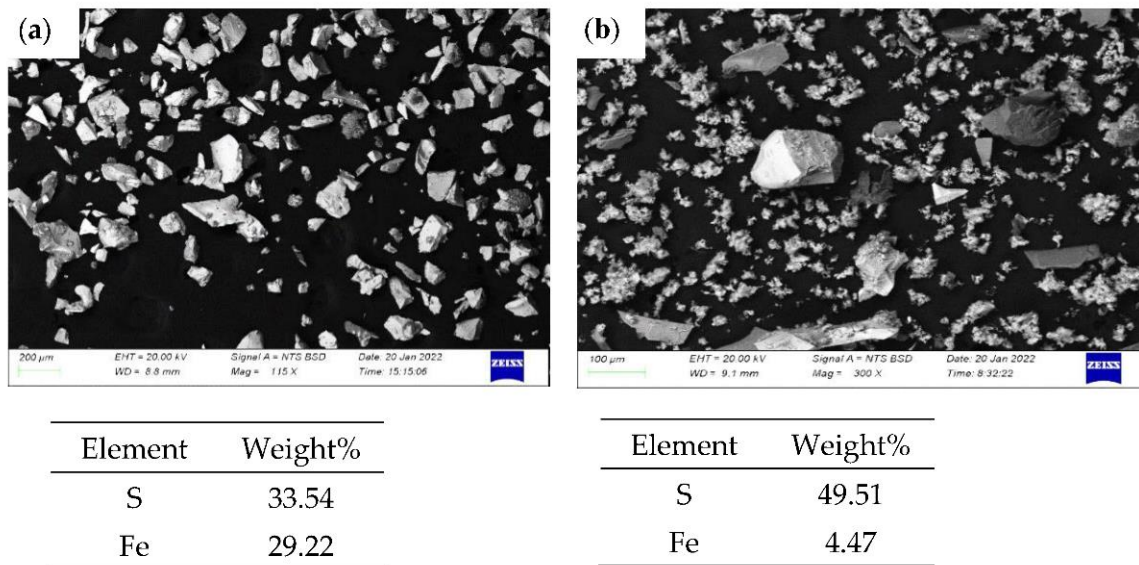


Figure 15. The backscattered SEM-EDS images of (a) pyrite before leaching and (b) after leaching in nitric acid.

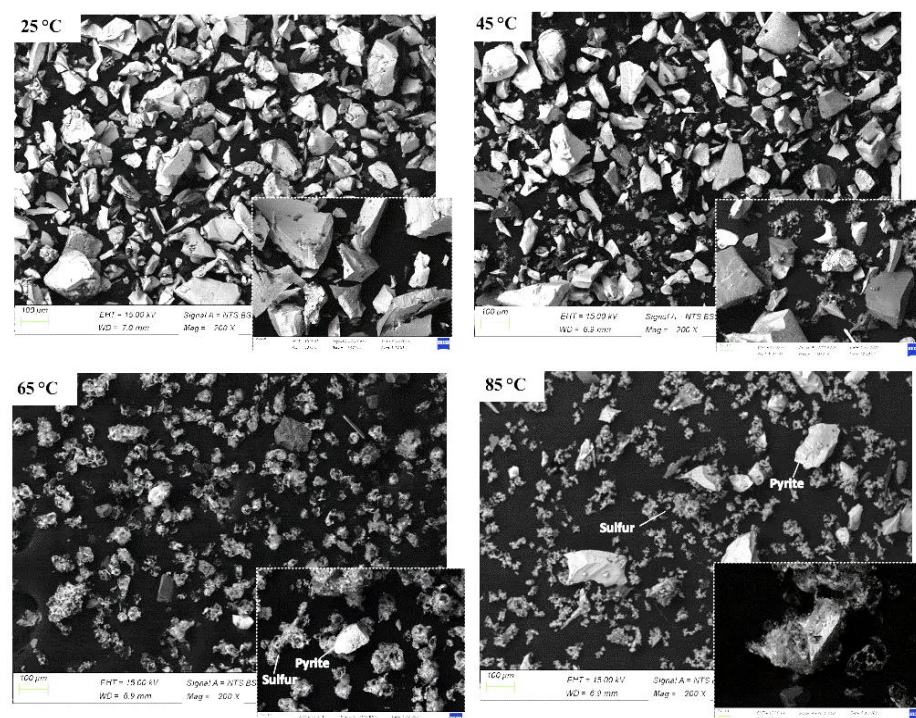


Figure 16. SEM images of pyrite residue at different temperatures of 25, 45, 65, and 85 °C.

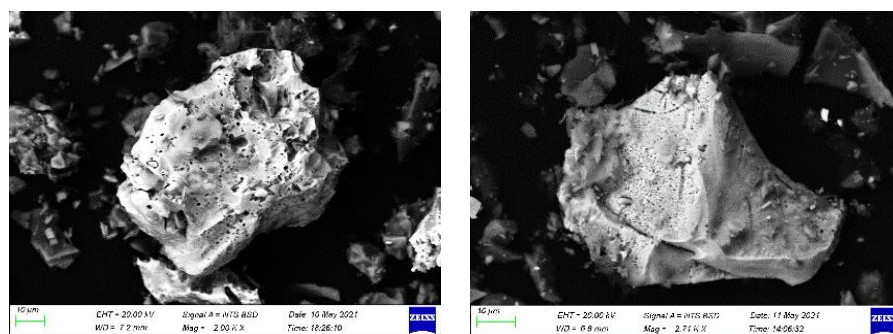


Figure 17. SEM images of leached pitted pyrite particles in 3 M nitric acid at a temperature of 65 °C.

The pyrite samples were examined with XRD before and after leaching in 3 M nitric acid at different temperatures of 25, 45, 65, and 85 °C. As illustrated in Figure 18, by increasing the temperature, the intensity of the pyrite peaks decreased owing to the pyrite dissolution. Interestingly, a new sulphur phase appeared, confirming the sulphur formation seen in the SEM images.

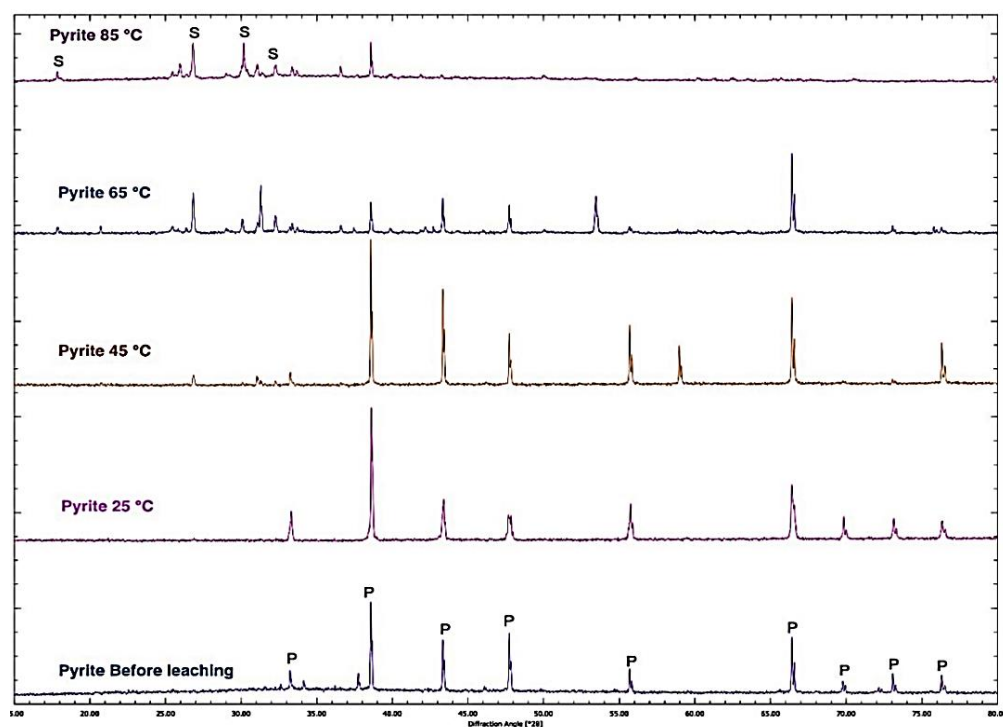


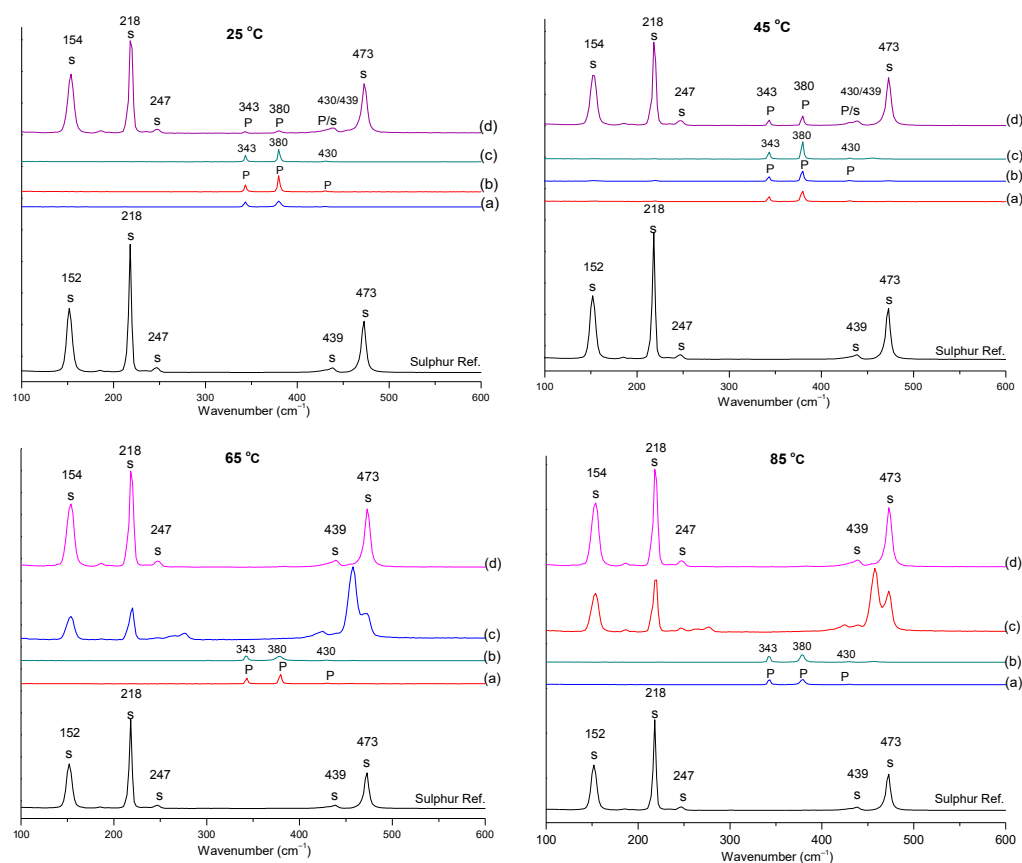
Figure 18. The XRD pattern of pyrite samples before leaching and the residue of leached pyrite in 3 M nitric acid at different temperatures of 25, 45, 65, and 85 °C.

Moreover, the XRD Rietveld refinement inspected the solid residue qualitatively and quantitatively by detecting each phase and its amount at different temperatures. Table 2 summarizes the results for the XRD Rietveld refinement for different temperatures. Hence, after leaching in 3 M nitric acid at 65 °C, 11.3% (mass percent) and 0.09 (mole fraction) of pyrite remained while producing mostly sulphur (S_8) and sulphur epsilon (S_6) with 74% and 10.7%, respectively. However, at 85 °C, the pyrite was mostly dissolved (only 5% (mass percent) and 0.04 (mole fraction) remained) and 84% sulphur (S_8) and 11% sulphur epsilon (S_6) were produced as products of the oxidative dissolution. The mole fractions of pyrite indicated in brackets in Table 2 further confirmed how incongruent the dissolution was.

Table 2. The XRD Rietveld refinement for different temperatures.

Temp./Phases	Pyrite (FeS ₂) (Mole Fraction)	Quartz (SiO ₂)	Sulphur (S ₈)	Sulphur Epsilon (S ₆)
Leaching at 25 °C	96.5% (0.8)	0.5%	3.1%	–
Leaching at 45 °C	85.1% (0.7)	3.8%	11.1	–
Leaching at 65 °C	11.3% (0.09)	3.3%	74.7%	10.7%
Leaching at 85 °C	5% (0.04)	–	84.0%	11.0%

Figure 19 illustrates the spectra for the Raman analysis of the solid residue of pyrite after leaching in 3 M nitric acid at various temperatures. The Raman laser contacted each residue at four spots (a, b, c, and d) and detected both pyrite and sulphur at all studied temperatures. To see the pyrite and sulphur shifts clearly, their Raman shifts were depicted separately as the last two graphs presented in Figure 19. As depicted in the spectra, pyrite had three shifts at frequencies of approximately 343, 380, and 430 cm^{−1}, and sulphur had three strong and two weak shifts situated at 154, 218, 247, 439, and 473 cm^{−1}, respectively. The positions of the pyrite and sulphur shifts in the Raman analyses agreed with research by Xia et al. [33] and Toniazzi et al. [34]. Xia et al.'s [33] work focused on the surface analysis of sulphur species on oxidised pyrite, while Toniazzi et al.'s [34] work focused on sulphur speciation and quantification at the surface of pyrite. The Raman analysis also confirmed the formation of the sulphur product as the result of oxidative leaching of pyrite in nitric acid.

**Figure 19.** Cont.

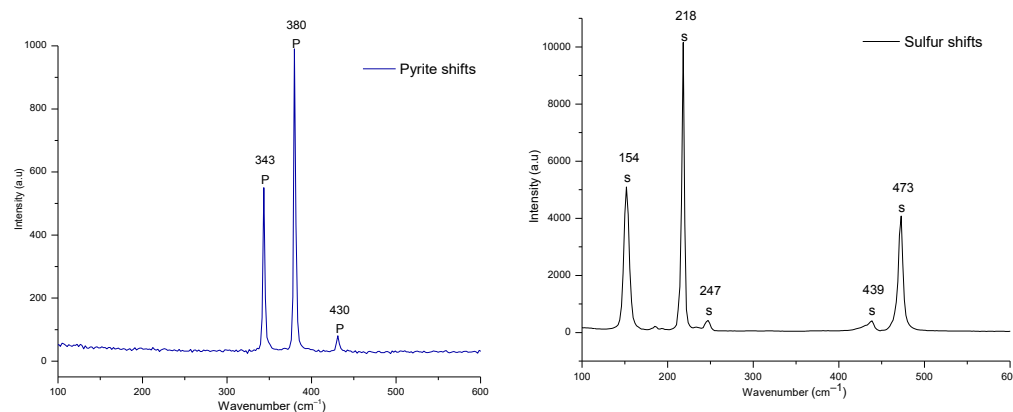


Figure 19. The Raman spectra of pyrite residue leached in 3 M nitric acid at various temperatures of 25, 45, 65, and 85 °C, showing the Raman spectra of pyrite and sulphur separately.

4. Conclusions

The oxidative dissolution of pyrite in nitric acid solution was investigated by altering influential leaching parameters. This study found the following:

- Pyrite dissolution at temperatures higher than 45 °C and up to 85 °C was between 72% and 95% after 120 min leaching in 3 M HNO₃.
- At nitric acid concentrations between 2.5 M and 4 M, HNO₃ had a powerful oxidising ability, resulting in an ample pyrite dissolution of between 74% and 95%.
- Reducing the fraction size of pyrite from +150–212 µm to +53–75 µm led to an increase in iron extraction from 75% to approximately 92%.
- Increasing the stirring speed from 1000 rpm to 4000 rpm resulted in Fe extraction of 80% to 98%.

The proposed new version of the shrinking core model, i.e., $(1/3\ln(1-X) + [(1-X)^{-1/3} - 1]) = k.t$, fit the kinetic results well. Thus, the mixed–controlled kinetic model describing the interfacial transfer and diffusion governed the reaction kinetics of pyrite dissolution in a nitric acid solution.

The activation energies (E_a) of pyrite dissolution at lower temperatures (25–45 °C) and higher temperatures (55–85 °C) were calculated as 145.2 kJ/mol and 44.3 kJ/mol, respectively.

The semiempirical expression for pyrite dissolution in HNO₃ under the studied conditions could be formulated as

$$1/3\ln(1-X) + [(1-X)^{-1/3} - 1] = 88.3 [\text{HNO}_3]^{2.6} r_0^{-1.3} e^{-44280/RT} .t$$

- The SEM images of the residue at different temperatures showed the surface of the pyrite grain became rough and pitted with cavities, and the oxidative dissolution in the nitric acid led to the formation of sulphur as the product.
- The XRD pattern of pyrite before leaching and the residue of leached pyrite in 3 M nitric acid at varied temperatures revealed that the intensity of the pyrite peaks decreased with an increasing temperature due to the pyrite dissolution and a new sulphur phase appeared.
- The XRD Rietveld refinement identified two sulphur species, i.e., S₈ and S₆, which formed during the dissolution process.
- The Raman analysis also confirmed the formation of sulphur at all the studied temperatures.

Author Contributions: Conceptualisation, S.T. and J.H.P.; methodology, S.T. and J.H.P.; software, S.T.; validation, S.T., J.H.P. and L.v.D.; formal analysis, S.T.; investigation, S.T.; resources, J.H.P.; data curation, S.T.; writing—original draft preparation, S.T.; writing—review and editing, S.T., J.H.P., C.B. and L.v.D.; visualisation, S.T.; supervision, J.H.P., C.B. and L.v.D.; project administration, J.H.P. and L.v.D.; funding acquisition, J.H.P. All authors have read and agreed to the published version of the manuscript.

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Chapter 4

A Comparison of the Electrochemical Oxidative Dissolution of Pyrite and Chalcopyrite in Diluted Nitric Acid Solution

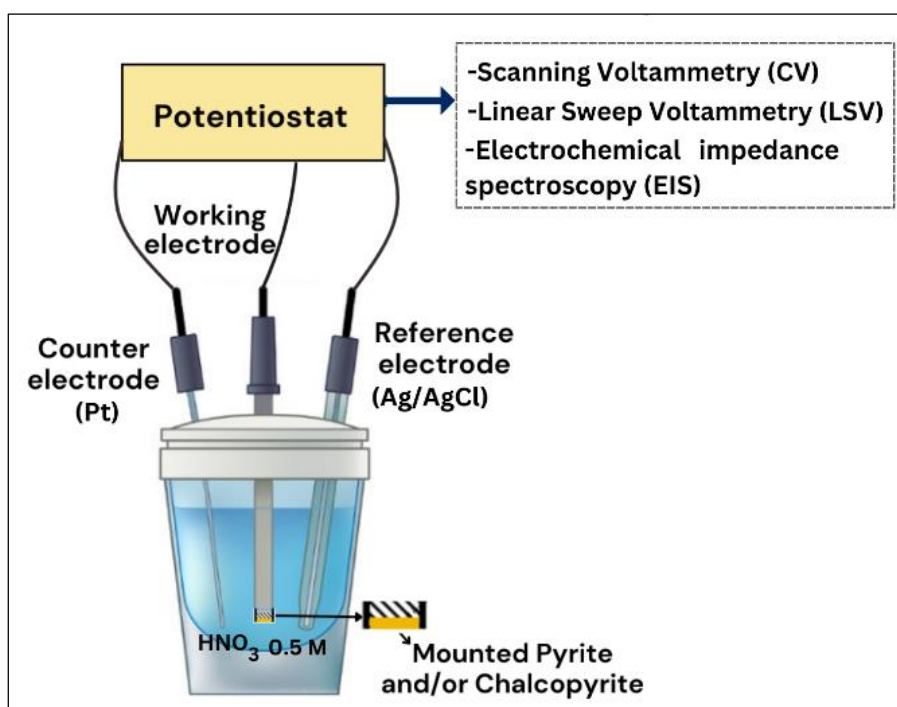
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Highlights

- The electrochemical oxidation of pyrite and chalcopyrite in 0.5 M HNO_3 solution was studied using electrochemical techniques.
- Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using both pyrite and chalcopyrite electrodes to detect all possible redox reactions and to gain information about the possible formed products and the dissolution mechanism.
- The dissolution kinetics for both pyrite and chalcopyrite is diffusion-controlled.

Graphical abstract



A Comparison of the Electrochemical Oxidative Dissolution of Pyrite and Chalcopyrite in Dilute Nitric Acid Solution

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Abstract: Understanding the oxidation of sulfidic minerals, especially those of pyrite and chalcopyrite, under acidic conditions has important outcomes, such as exposing any encapsulated gold not recovered by traditional cyanidation processes and providing insight into acid mine drainage. This investigation studied the electrochemical oxidation of pyrite and chalcopyrite in a nitric acid solution (0.5 M) using electrochemical techniques. Cyclic voltammetry (CV) was performed using electrodes of each mineral to detect the possible redox reactions and hence suggest products formed from each mineral. Electrochemical impedance spectroscopy (EIS) was also run on each mineral at specific potentials corresponding to regions for anodic reactions detected to gain further information about the reaction mechanism and possible products. The partial oxidation of pyrite at low anodic potentials (0.4 to 0.6 V vs Ag/AgCl) produces $\text{Fe}_{1-x}\text{S}_2$ and $\text{Fe}(\text{OH})_3$, with a sulfur-rich layer forming S^0 which accumulates on the electrode's surface, leading to a diffusion controlled dissolution process. As the potential increases above 0.7 V, there is sufficient driving force to fully oxidise pyrite and the species already formed on the electrode's surface to soluble species by producing SO_4^{2-} . This eradicates the diffusion barrier and causes extensive oxidation of pyrite at high potentials (0.9 V). A similar process occurred for chalcopyrite with preferential oxidation of iron at low potentials (0.3 to 0.5 V), forming mainly iron and copper deficient sulfides (like $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}$, Cu_2S , CuS) and S^0 which partially covers the chalcopyrite electrode's surface, causing a diffusion barrier. Increasing the potential to beyond 0.7 V leads to these previously formed layers converting to soluble species. EIS provides evidence supporting the reactions and the formed products at the investigated potentials.

1 Introduction

Pyrite and chalcopyrite, which often occur together, are widespread sulfide minerals present in the earth's crust. Pyrite (FeS_2), the most common iron sulfide mineral, is used in the production of sulfur and sulfuric acid [1]. Chalcopyrite (CuFeS_2), the most abundant copper mineral, forms the basis of copper production. Researchers recently developed novel applications of pyrite and chalcopyrite, based on their non-toxic, semi-conductive properties, their abundance and low material cost. These minerals have various electrochemical applications, such as in solar energy collectors in solar panels, as solid-state sensor materials [2], as a depolarizer anode in hydrogen

production [3], and as a cathode or an anode material for lithium-based batteries [4].

Pyrite is often processed to extract its associated precious metals, particularly gold. Pyrite oxidation is important to improve gold extraction from sulfidic refractory ores and mine tailings since pyrite oxidation exposes encapsulated gold [5-8]. On the other hand, there are some environmental problems caused by sulfide minerals. In mining operations and tailings, exposure of sulfide minerals to air and water generates acid mine drainage (AMD) due to oxidative dissolution. This can lead to groundwater contamination [9-11]. The co-existence of pyrite in coal also leads to the emission of sulfur dioxide at power stations in which coal is burned for power generation [12,13].

Global development towards industrialization, automation, consumerism and depletion of high-grade ores lead to a growing demand for valuable and critical metals outstripping supply [14]. Nowadays, to meet the high demand, the focus is on extracting valuable metals from sulfidic refractory low-grade ores, mine tailings, and industrial waste. Thus valuable metal extraction from pyrite and chalcopyrite oxidation, made the electrochemistry of these minerals the subject of many investigations. An electrochemical study, particularly when using cyclic voltammetry (CV), can detect redox processes occurring at certain applied potentials on the surface of the mineral. Furthermore, the E_{H} -pH diagrams of pyrite and chalcopyrite can predict the relevant products formed based on redox reactions under the same conditions [15,16].

Despite extensive electrochemical research on the oxidative dissolution of these two minerals, the associated redox reactions, the composition of the products, a passive surface layer, and the intermediates remain in dispute. Earlier studies postulated that the passive layer and the intermediates resulting from the oxidative dissolution of pyrite and chalcopyrite could be metal-deficient sulfides such as pyrrhotite ($\text{Fe}_{1-x}\text{S}_2$), copper-rich species ($\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}$, Cu_2S , CuS), and sulfur segments (elemental sulfur (S^0) and polysulfides S_n^{2-} , $n > 2$), as well as iron-rich layers composed of Fe_2O_3 , FeO , $\text{Fe}(\text{OH})_3$, and $\text{Fe}(\text{OH})_2$ [16-19].

The electrochemical oxidation of pyrite under acidic conditions (pH = 2 adjusted with 10% H₂SO₄) was investigated by Tu et al. [19]. They found that at a low potential (0.5 V vs saturated calomel reference electrode – SCE) Fe(OH)₃ and elemental sulfur (S⁰) formed, covering the surface of the pyrite electrode, which resulted in reactions being diffusion-limited. Increasing the potential to 0.6 V (vs SCE), the amorphous sulfur-rich layer converted to crystalline S₈, and allowed pyrite oxidation to continue. Higher potential values of 0.8 V (vs SCE) led to the formation of Fe(OH)₃ and SO₄²⁻, along with polysulfides (S_n²⁻), and an iron-rich layer consisting of FeO and Fe₂O₃ which accumulated on the surface of the pyrite [19]. In research by Zhang et al. [20] the dissolution of several sulfide minerals such as pyrite, pyrrhotite, chalcopyrite, bornite, and chalcocite in acidic sulfate media was examined by CV with the emphasis on the dissolution mechanism, redox reactions, and the decomposition products. Similarities were noted across the various sulfidic minerals. Typically, an inhibitory layer is developed during the initial oxidation stages of these minerals. This layer, comprising elemental sulfur, polysulfides, and metal-deficient sulfides, impedes subsequent dissolution processes. By further oxidation of these sulfur-rich substances (for example by applying higher potentials), complete dissolution of sulfide mineral can occur in acidic conditions. This process not only removes the sulfur-rich layer from the surface, but also contributes to additional acid generation [20].

Lazaro & Nicol [21] studied the anodic dissolution of chalcopyrite in 0.5 M sulfuric acid solution. They found evidence of the formation of Cu²⁺, Fe²⁺, and soluble sulfur species (H₂S) at the early stage of oxidative dissolution of chalcopyrite at 60 °C. The electrochemical evaluation of the surface oxidation of chalcopyrite in 0.5 M sulfuric acid solution was also investigated by Ghahremaninezhad et al. [17]. They applied potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and Mott-Schottky methods to find evidence and confirmation of the oxidative layer formed on the surface of the chalcopyrite electrode. A thin layer of Cu_{1-x}Fe_{1-y}S₂ (y > x) formed on the electrode's surface while polishing the chalcopyrite electrode during the preparation and initial immersion in the electrolyte for stabilization. The thickness of this layer slowly increased by moving from the open circuit potential (OCP ~ -0.235 V vs MSE – saturated mercury/mercury(I) sulfate electrode) to 0.10 V vs MSE (~0.53 V vs Ag/AgCl). By increasing the potential up to 0.30 V vs MSE (~0.73 V Ag/AgCl) the formed layer partly dissolves to produce a layer of Cu_{1-x-z}S₂. At higher potentials of >0.30 – 0.42 V, both these layers dissolved, and extensive dissolution of the chalcopyrite electrode begins. Further increasing the potential to 0.75 V vs MSE (~1.18 V Ag/AgCl) led to the formation of CuS and Fe₂(SO₄)₃ concomitantly [17].

Old mine dumps in South Africa still contain residual gold, which is nowadays recovered by the company DRDGold in their ERGO plant in Johannesburg. However, a substantial portion of this residual gold is refractory and encapsulated in mostly pyrite

particles and to a lesser extent chalcopyrite. A previous paper by Teimouri et al. [22] considered the dissolution kinetics of the mine tailings (which contain mostly pyrite) in nitric acid as a potential route to improve the recovery of gold from them. To date, most studies of this nature were conducted in sulfuric acid solutions and there is no guarantee that the dissolution mechanism would be the same in nitric acid.

Part of the motivation for this research was to provide independent confirmation of the electrochemical behaviour of pyrite and chalcopyrite in nitric acid solution (0.5 M). To do so, cyclic voltammetry (CV) scans of pyrite and chalcopyrite were evaluated at different scan rates and in different potential ranges, and then the possible redox reactions at specific potentials were postulated. Linear sweep voltammetry (LSV) focused on the oxidative dissolution potential regions, and this assisted in the selection of the potentials at which to explore measurements using electrochemical impedance spectroscopy (EIS). It is foreseen that this approach would yield new information on unlocking gold residues from mine tailings which can be employed to improve the recovery thereof. In addition, it will clarify if the mechanism of dissolution remains unchanged in nitric acid as compared to that in sulphuric acid commonly used. It also aims to clarify whether there are substantial differences between the dissolution behaviour and mechanisms of pyrite and chalcopyrite. In the final instance, it will be attempted to show how this all relates to the kinetics of dissolution of these minerals.

2 Experimental

2.1 Preparation and characterization of pyrite and chalcopyrite electrodes

To create the working electrode from the minerals (pyrite and chalcopyrite), a small piece of each mineral was encapsulated in an epoxy resin matrix. One end of the mineral was connected to a copper wire using silver glue, while the surface on the other end was left exposed. After the epoxy resin dried overnight, the exposed surface area of the pyrite/chalcopyrite was polished with a rotating disc covered with consecutively finer-grained silicon carbide papers. To smooth the surface and remove any surface defects, the exposed surface was polished using a rotating disc covered with a soft cloth impregnated with alumina (0.5 µm) mixed with deionized water. After polishing, the electrodes were thoroughly rinsed with deionized water to remove any alumina particles. The exposed surface area of both pyrite and chalcopyrite electrodes was measured under a microscope connected to Nikon EIS-Elements software. The surface area for pyrite and chalcopyrite were 53.4 mm² and 56.7 mm², respectively. The preliminary phase analysis for pyrite and chalcopyrite used to make the electrodes was analysed with X-ray diffraction (XRD) (Bruker D2 Phaser). In addition, scanning

electron microscopy and energy dispersive spectrometry (SEM-EDS) (ZEISS Sigma) to determine their chemical composition was also performed.

2.2 Electrochemical measurements

The electrochemical techniques applied in this work include cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS). To ensure the initial stability of the pyrite and chalcopyrite electrodes, they were immersed in 0.5 M HNO_3 solution as the electrolyte, and the open circuit potential (OCP) was measured. This was done for 120 min (until a stable value was maintained) before the EIS measurements were initiated at each DC bias potential for each of the electrodes. The cyclic voltammograms (CV) of pyrite and chalcopyrite in 0.5 M HNO_3 solution were obtained using a Metrohm Autolab PGStat10 potentiostat controlled by General Purpose Electrochemical (GPE) software connected to a typical three-electrode electrochemical cell. The prepared pyrite or chalcopyrite working electrode (WE) was used along with a Pt counter electrode and Ag/AgCl (3 M KCl) reference electrode (both supplied by Metrohm). The WE was polished before each set of experiments. All potential values quoted in this work are with respect to this reference electrode and a potential step of 4 mV was used for all voltammetric measurements. The LSV was measured in the potential range from -0.1 to 0.9 V (vs Ag/AgCl). The EIS measurements were conducted using a BioLogic VMP300 potentiostat-frequency response analyser (FRA) under DC bias at different potentials in the frequency range of 10^{-2} – 10^6 Hz with 10 mV amplitude. The EC-Lab Z-fit software was used to fit the obtained Nyquist plots. All experiments were conducted at room temperature in a static solution.

3 Results and Discussion

3.1 Characterization of pyrite and chalcopyrite electrode

The pyrite and chalcopyrite minerals that were used to make the electrodes, were analysed by XRD, as well as SEM-EDS to identify the main phases, the chemical composition and purity of the minerals. Figure 1 (a- pyrite and b- chalcopyrite) represents the XRD patterns showing mainly the presence of pyrite and chalcopyrite, with some impurities such as quartz (SiO_2) in both minerals and sphalerite (zinc sulfide mineral with (Zn, Fe)S chemical composition) in the chalcopyrite. Figure 2(a,b) shows the SEM-EDS of pyrite (FeS_2) (formula weight = 119.98 g) with the detection of 53.9% sulfur (S) and 46.1% iron (Fe) (as wt.%), which is close to the theoretical percentage of the main elements for pyrite, with sulfur 53.5% and iron 46.6%. Figure 2(c,d) shows the SEM-EDS analysis of chalcopyrite (CuFeS_2) (formula weight = 183.5 g), and identified 35.6% sulfur (S), 30.6% iron (Fe), and 33.8% copper (Cu) (as wt.%), which is again close to the

theoretical percentages of these main elements with sulfur, iron, and copper as 34.9%, 30.4%, and 34.6% (wt.%), respectively.

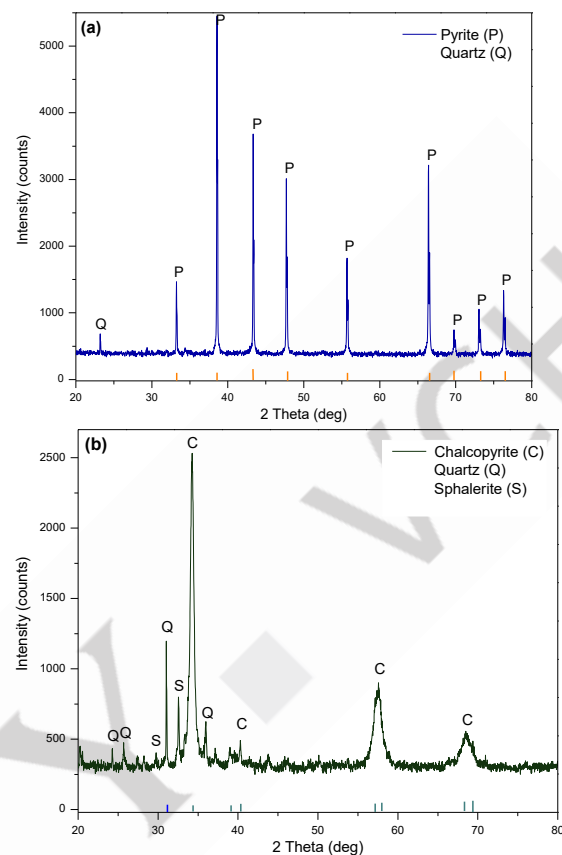


Figure 1: XRD patterns of (a) pyrite and (b) chalcopyrite.

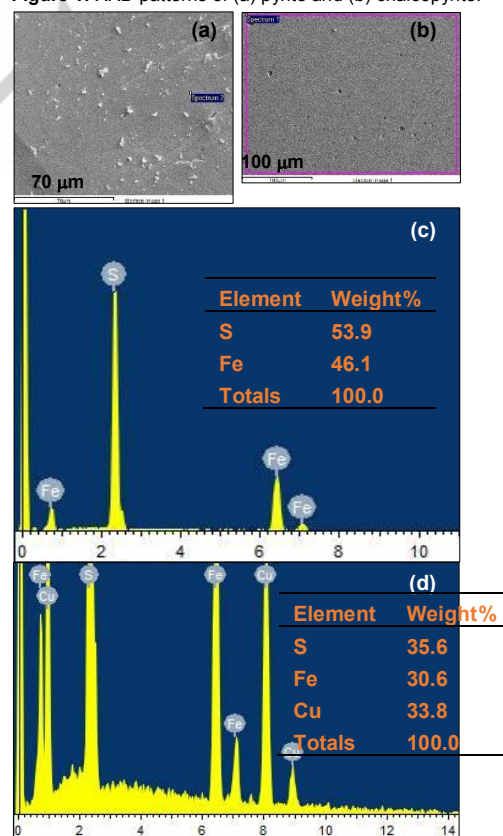


Figure 2: SEM-EDS of (a,c) pyrite and (b,d) chalcopyrite electrode.

3.2 Cyclic voltammetry (CV) for pyrite

A typical three-cycle CV scan of a freshly polished pyrite electrode as the WE in 0.5 M HNO₃ is presented in Figure 3, which indicates that after the initial scan, the pyrite electrode is stable and yields reproducible scans. The CV scan was started at E_{OCP} (~0.4 V) towards an anodic direction at a scan rate of 1.5 V/s and data were collected within the potential range of +0.9 to –0.5 V. In the anodic (oxidation) section, three anodic peaks were detected, labelled A₁, A₂, and A₃, and correspondingly, in the cathodic (reduction) part, three cathodic peaks C₁, C₂ and C₃ appeared.

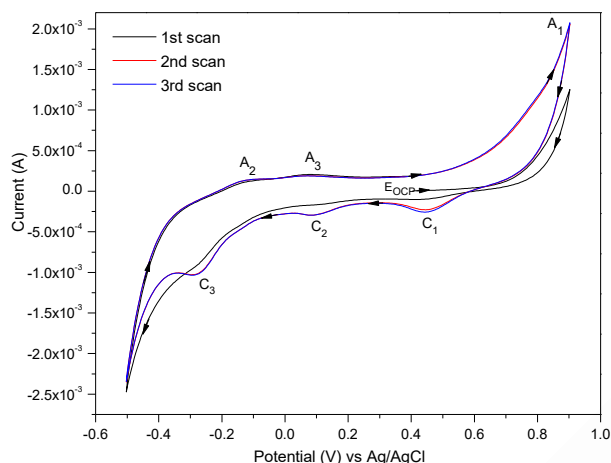


Figure 3: A three-cycle CV scan of pyrite mineral as the WE with 1.5 V/s scan rate in 0.5 M HNO₃. The arrows on the scan show the direction of the applied potential.

Figure 4 represents the voltammograms (for the third cycle) of pyrite each at a different scan rate of 0.5, 1, 1.5 and 2 V/s. As illustrated, increasing the scan rate from 0.5 to 2 V/s, increased the current response of the redox peaks. The peaks were not clearly distinguishable at lower scan rates (such as 0.05 V/s); even at a scan rate of 0.5 V/s (Figure 4) the oxidation peaks A₂ and A₃ are subtle. Fast scan rates allow for the detection of transient species at higher concentrations before they undergo chemical reaction or diffusion which decreases their concentrations at the electrode surface. Hence the scan rate of 2 V/s which led to pronounced redox peaks was applied in the subsequent CV scans.

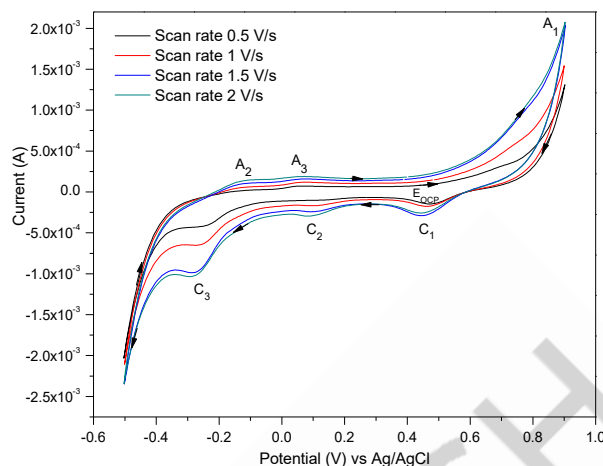


Figure 4: The CV scans for pyrite as the WE at different scan rates in 0.5 M HNO₃.

3.2.1 Effect of changing the potential range on pyrite

The effect of changing the potential range on the positive side from 0.9, 0.8, 0.7, 0.6, 0.5 and 0.4 V while keeping the cathodic potential fixed at –0.5 V on the CV scans of the pyrite electrode, is illustrated in Figure 5. Altering the positive potential to a smaller range (+0.8 V) first affects the anodic peak A₁ and the cathodic peak C₁. By further shortening the positive potential range to +0.6 V the cathodic peak C₂ becomes very small, and then the peak C₃ by reducing the range to +0.5 V. Therefore, when the potential range becomes shorter the associated redox reactions cannot be driven fully, hence the related redox peaks appear smaller. This illustrates a clear association between the redox process at A₁ and C₁, as well as at C₂, and C₃ with A₂, and A₃.

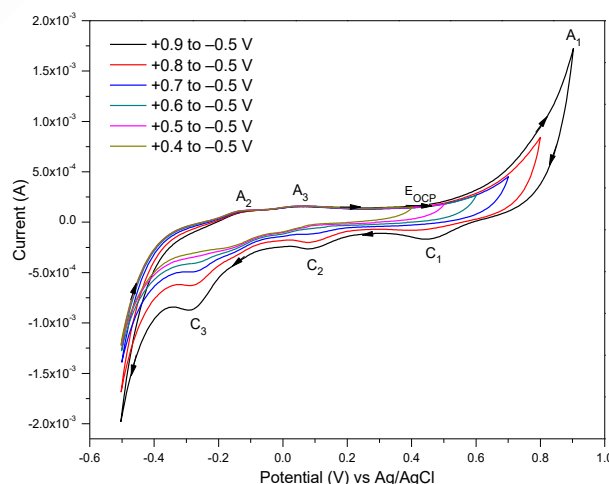


Figure 5: Changing the potential range on the positive side of the pyrite CV scan (the 3rd cycle) measured at 2 V/s scan rate in 0.5 M HNO₃.

To determine the effect of sweeping to different negative potentials, the direction of the scan was reversed by starting at E_{OCP} and moving to –0.5, –0.4, 0.0, +0.2 and +0.3 V, and then

sweeping to a fixed positive potential of +0.9 V, as shown in Figure 6. Making the negative potential smaller (to −0.4 V) the cathodic peak C₃ and the related anodic peaks A₂ and A₃ become smaller. By further reducing the range to 0.0 V, the cathodic peaks C₂ and C₁ become smaller, and the anodic peak A₁ is also affected. With the cathodic vertex reduced to +0.2 V, no reduction peaks appeared and the A₁ peak became even smaller. Thus, at a shorter negative potential range, the cathodic reactions do not occur completely, consequently the related cathodic peaks (C₃, C₂ and C₁) and the correlated anodic peaks are smaller.

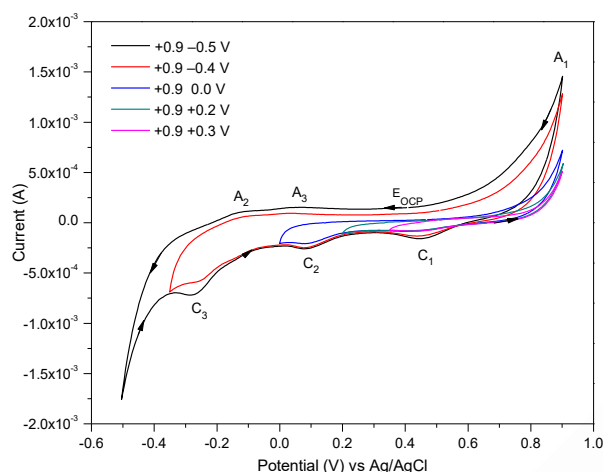
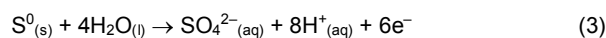
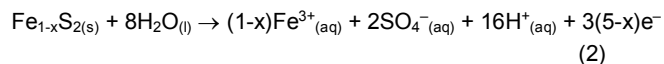
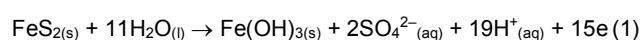


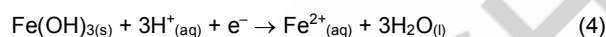
Figure 6: Changing the potential range on the negative side of the pyrite CV scan (the 3rd cycle) measured at 2 V/s scan rate in 0.5 M HNO₃.

3.2.2 Interpretation of the redox peaks in pyrite CV scan

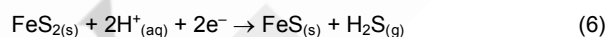
The current increased exponentially during the anodic sweep from $E_{OCP} = \sim +0.4$ V to +0.9 V (see Figure 3). At the highest potential (+0.9 V) at peak A₁, a complete oxidation of FeS₂ to Fe(OH)₃/Fe³⁺ and SO₄²⁻ with several electrons released is expressed in reaction 1. This can be observed by the sharp escalation of current for a small increment of the potential in the voltammogram [19,20]. No oxygen evolution was observed at +0.9 V which would cause bubble formation on the electrode surface (this was the case even when the electrode was maintained at this potential for longer periods while doing EIS measurements). For successive scans, at this high potential (+0.9 V), the previously formed iron deficient sulfide (Fe_{1-x}S₂) and S⁰ (formed during partial oxidation of pyrite at 0.05 V at A₃) can further oxidise based on reactions 2 and 3 [23,24]. Visual scrutiny after the CV scan showed some dark purple/black substance(s) covering the surface of the pyrite electrode. This is likely evidence of formed ferric hydroxide Fe(OH)₃ as confirmed in research by Tu et al. (2017) [19].



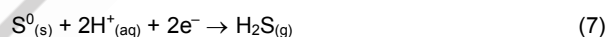
Reversal of the potential in the cathodic direction results in three reduction peaks. The first reduction peak C₁ at +0.45 V is assigned to the reduction of Fe(OH)₃/Fe³⁺ to Fe²⁺, i.e. a one-electron reduction based on reactions 4 and 5 [19,20][25,26].



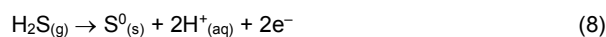
The second reduction peak C₂ detected at $\sim +0.1$ V represents the reduction of FeS₂ to FeS and H₂S based on reaction 6 [19,20]:



The third cathodic peak C₃ detected at ~ -0.25 V represents the reduction of S⁰ (formed during partial oxidation of pyrite at A₃) to H₂S as given by reaction 7 [19,20,27]. The current produced at the negative vertex potential (−0.5 V) is associated with hydrogen evolution.

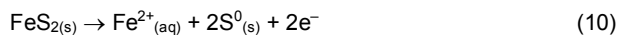
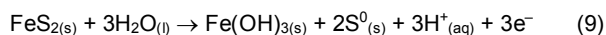


When the scan was reversed to the positive potential direction again, an oxidation peak A₂ was detected at −0.15 V. This is associated with the oxidation of the produced H₂S (at C₃) back to elemental sulfur (S⁰), as expressed in reaction 8 (reverse of reaction 7). The intensity of peak A₂ is anticipated to be low because the H₂S_(g) generated is dispersed fairly quickly, resulting in its concentration being low near the electrode [19,20,27].



The oxidation peak A₃ at +0.05 V, represents initial, partial oxidation of FeS₂ to Fe(OH)₃/Fe³⁺, Fe²⁺ and S⁰, based on reactions 9 and 10. Partial oxidation may also result in sulfur-rich intermediate products, i.e. iron deficient sulfide (Fe_{1-x}S₂) and polysulfides (S_n²⁻). The accumulation of these substances on the electrode's surface leads to a diffusion layer, which only at higher potentials (at A₁) can further oxidise to other species including SO₄²⁻ and thus eliminate the diffusion barrier [19,20,24,27].

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3.3 Cyclic voltammetry (CV) for chalcopyrite

A similar set of experiments was run on the freshly polished chalcopyrite electrode in 0.5 M HNO_3 and the three-cycle CV scan is presented in Figure 7. The scan was initiated from the $E_{\text{OCP}} = \sim +0.15$ V (as marked in the graph) in the anodic direction to +1 V, then reversed in the cathodic direction to -0.7 V. In the initial anodic sweep from E_{OCP} only peak A_3 was detected, but on the subsequent anodic scans peaks A_4 and A_5 as well as A_1 and A_2 were observed (five anodic peaks in total). On the subsequent scans peak A_3 is also shifted in a more positive direction. Furthermore, in the cathodic part, four reduction peaks appeared.

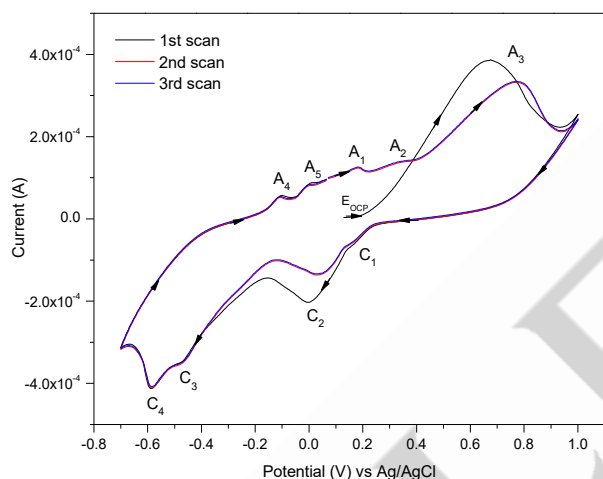


Figure 7: A three-cycle CV scan of chalcopyrite mineral as the WE, measured at 0.02 V/s scan rate in 0.5 M HNO_3 .

The voltammograms (for the third scan) of chalcopyrite at different scan rates of 0.02, 0.05, and 0.08 V/s are displayed in Figure 8. Where a faster scan rate resulted in more pronounced peaks for the pyrite electrode, the opposite was true for chalcopyrite with the slower scan rate of 0.02 V/s generally producing more pronounced redox peaks, thereby indicating which redox processes occur at slower rates. A scan rate of 0.02 V/s was applied in the subsequent CV scans.

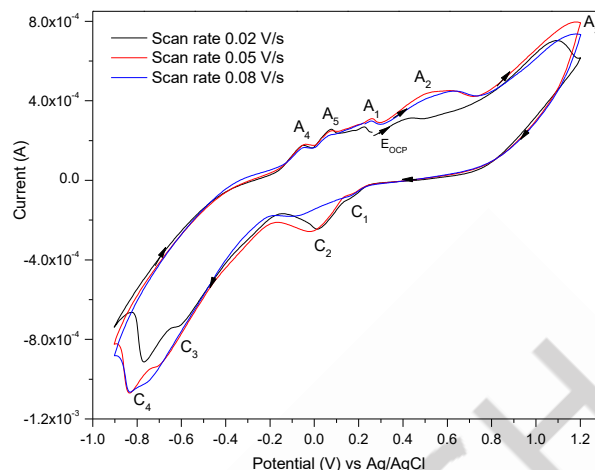


Figure 8: The CV scans for chalcopyrite as the WE at different scan rates in 0.5 M HNO_3 .

3.3.1 Effect of changing potential range on chalcopyrite

The effect of reducing the vertex potential in the positive range to +1, 0.9, 0.8, 0.7, 0.6, 0.3, 0.2, and 0.125 and measuring to -0.7 V on the CV scans of chalcopyrite are illustrated in Figure 9. By reducing the positive potential range, the anodic reactions at A_3 and A_2 do not fully occur, hence this affects the cathodic reactions occurring at C_1 and C_2 , as the current of these cathodic peaks reduced noticeably. Thus, by observing these CV scans with a gradual reduction in the positive potential range, one can deduce that the anodic reactions at A_3 and A_2 are related to the cathodic reactions at C_1 and C_2 .

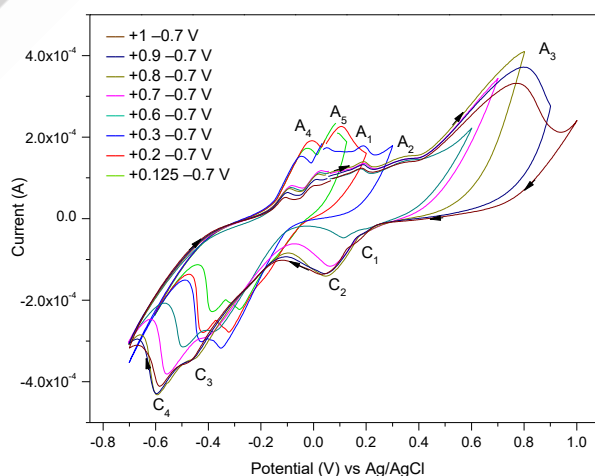


Figure 9: Effect of sweeping to different potentials in the positive range of the CV scans (the 3rd cycles) of the chalcopyrite as the WE, at 0.02 V/s scan rate in 0.5 M HNO_3 .

The effect of sweeping to different negative vertex potentials, commencing at E_{OCP} and sweeping to -0.7 , -0.5 , -0.4 , -0.3 , -0.2 , -0.1 , 0.0 , and $+0.1$ V before reversing to a fixed positive potential at +1 V in the CV scans of the chalcopyrite electrode, are depicted

in Figure 10. Reducing the negative potential range, the cathodic reactions at C_4 and C_3 do not occur fully, hence the anodic reactions at A_4 and A_5 are not driven to completion, thus the associated peaks (A_4 and A_5) appeared smaller. Further reducing the negative vertex potential affects the subsequent redox reactions occurring at A_1 , A_2 and A_3 , as well as C_2 and C_1 , as the detected redox peaks become smaller. Therefore, reducing the negative potential range gradually, indicated that the cathodic reactions at C_4 and C_3 are associated with anodic reactions at A_4 and A_5 , and the cathodic reactions at C_2 and C_1 , are related to reactions happening at A_1 , A_2 and A_3 .

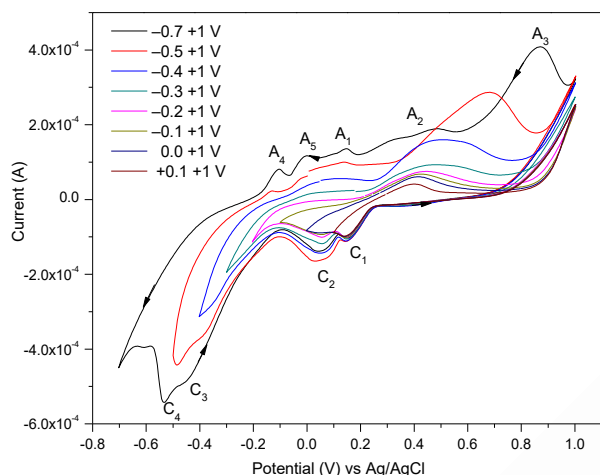
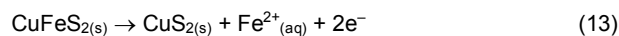
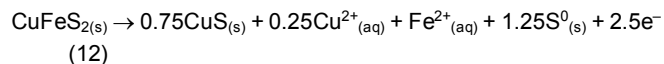
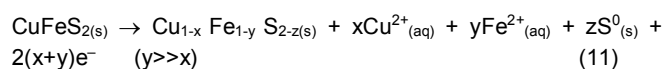


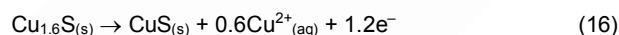
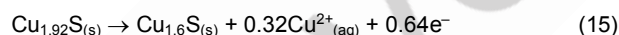
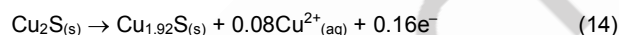
Figure 10: Effect of sweeping to different potentials on the negative range on the CV scans (the 3rd cycles) of the chalcopyrite as the WE measures at 0.02 V/s scan rate in 0.5 M HNO₃.

3.3.2 Interpretation of the redox peaks in chalcopyrite CV scan

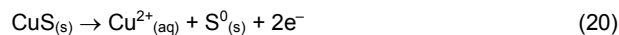
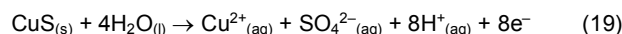
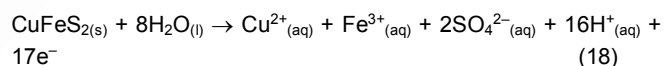
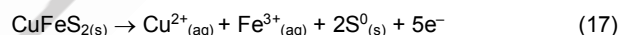
The current increased fairly rapidly during the anodic sweep soon after starting from $E_{OCP} = \sim +0.15$ V, to give the peak A_3 (see Figure 7). On subsequent scans an anodic peak A_1 was detected at +0.2 V. This can be attributed to the partial oxidation of chalcopyrite (CuFeS_2), where the preferential dissolution of Fe over Cu and S takes place to form copper-sulfur-rich species such as the nonstoichiometric segment $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}$ (reaction 11), covellite (CuS) (reaction 12), and CuS_2 (reaction 13). Although reaction 13 shows CuS_2 as the product, the stoichiometry may not be exactly 1:2 as given here, but a more sulfur-rich product, since some Cu can be oxidised as shown in reaction 11. The produced S^0 (in reactions 11 and 12) can be related to a sulfur-rich layer containing sulfur intermediate products, i.e. polysulfides (S_n^{2-}). Accumulation of these products leads to a thin passive layer partially covering the electrode's surface, which slows the dissolution rate down [16-18][20][28,29].



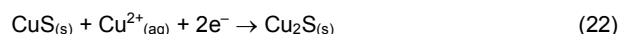
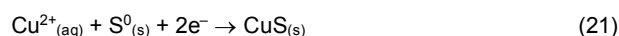
Peak A_2 appeared like a broad shoulder at around +0.35 V. This is associated with the stepwise oxidation of Cu-rich chalcocite (Cu_2S) (produced in the reduction process C_1) to a series of Cu-deficient and non-stoichiometric sulfides such as djurite ($\text{Cu}_{1.92}\text{S}$), digenite ($\text{Cu}_{1.6}\text{S}$), and covellite (CuS) based on reactions 14, 15, and 16 [16,20,30].

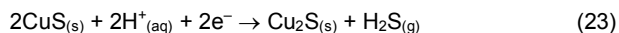


From ~ 0.6 V, a sharp escalation in anodic current was observed and the oxidation peak A_3 appeared at 0.9 V (more positive than the initial peak for A_3 seen on the very first scan), indicating oxidation of chalcopyrite (CuFeS_2) to Cu^{2+} , Fe^{3+} and $\text{S}^0/\text{SO}_4^{2-}$, based on reactions 17 and 18, as well as further oxidation of CuS to Cu^{2+} and $\text{S}^0/\text{SO}_4^{2-}$, according to reactions 19 and 20 [16,20,29,31].

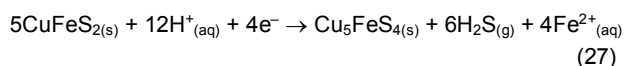
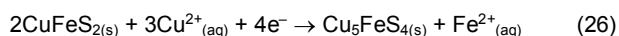
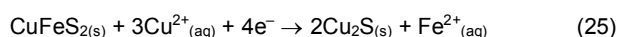


Reversal of the potential to the cathodic direction results in four discrete reduction peaks. The first reduction peak C_1 identified at ~ 0.2 V, indicates the reduction of S^0 , thereby reincorporation of Cu^{2+} to form covellite (CuS) and further chalcocite (Cu_2S) as written in reactions 21, 22 and 23, as well the reduction of Cu^{2+} to Cu^0 (reaction 24) [20,28,31].

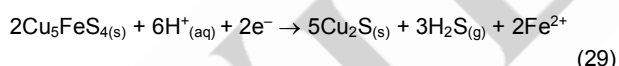
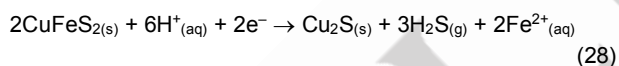




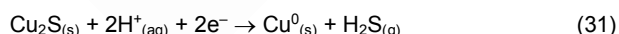
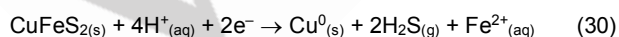
The second reduction peak C_2 detected at ~ 0.05 V represents the reduction of remaining chalcopyrite at the surface according to three different possible reactions: (1) reduction to chalcocite (Cu_2S), (2) reduction to bornite (Cu_5FeS_4), and (3) reduction to Cu_5FeS_4 and hydrogen sulfide (H_2S), according to reactions 25, 26 and 27, respectively [16-17,20]. The reduction at C_1 involves two electrons while that at C_2 involves four electrons, hence the height of C_2 is bigger than C_1 , as expected [16,32,33].



As the potential moved further in a negative direction, the cathodic current increased significantly after -0.1 V. The reduction peaks C_3 and C_4 appeared close to each other at around -0.45 V and -0.55 V, respectively. At peak C_3 (-0.45 V) CuFeS_2 and Cu_5FeS_4 can undergo further reduction to Cu_2S , H_2S , and Fe^{2+} as expressed in reactions 28 and 29 [16,20,31-33].

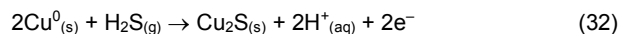


At peak C_4 (at -0.55 V) CuFeS_2 and Cu_2S can undergo further reduction to form elemental copper (Cu^0) and hydrogen sulfide (H_2S), as articulated in reactions 30 and 31 [16,20,31].



When the scan switched to the positive potential direction again, two oxidation peaks A_4 and A_5 were detected nearby at -0.15 V and -0.05 V, respectively. This is related to the oxidation of some of the reduction products formed during chalcopyrite reduction. Peak A_4 is associated with the oxidation of Cu^0 and H_2S to

chalcocite (Cu_2S) according to reaction 32 (reverse of reaction 31). Peak A_5 is related to the oxidation of H_2S to elemental sulfur (S^0) based on reaction 33 [20,32,33].



It should be mentioned that the slight differences in the position and height of the redox peaks in this study on pyrite and chalcopyrite electrodes compared to previous research could be due to small variations in the studied mineral chemical composition, possible impurities, and surface roughness, as well as the electrolyte used [19].

3.4 Linear sweep voltammetry study (LSV)

The linear sweep voltammetry (LSV) of a freshly polished pyrite electrode at 2 V/s scan rate in 0.5 M nitric acid solution is presented in Figure 11. The voltammogram for pyrite displayed three distinctive parts, similar to the research reported by Liu et al. [24] and Tu et al. [19]. In the first region (-0.1 to 0.05 V), the current increases almost linearly with increasing potential. The voltammogram begins with a small negative current which could be associated with the reduction of pyrite (FeS_2) to H_2S (reaction 6). Then the oxidation of H_2S to S^0 (reaction 8 at A_2) occurs initiating the anodic current. In the second region (about 0.1 V to 0.55 V), the current is somewhat independent of the increasing potential and increases only slowly. This could be related to the partial oxidation of pyrite (reaction 9 at A_3) due to formation of $\text{Fe}(\text{OH})_3$, and a sulfur-rich-layer containing sulfur (S^0), polysulfides (S_n^{2-}), and iron deficient sulfide ($\text{Fe}_{1-x}\text{S}_2$), which, due to their accumulation on the electrode surface, form a thin passive layer that slows down oxidation, acting as rate-limiting layer. In the third section (from 0.6 V to above 0.8 V), the current increased sharply with increasing potential, due to the improved reaction-driven force. Thus, a potential higher than $+0.6$ V is sufficient to convert the insoluble species forming the inhibiting layer to soluble ions, thus eliminating the rate-limiting surface layer. The high potential at this region can also lead to extensive pyrite oxidation which corresponds to the CV curve of pyrite at A_1 [19,20][23,24].

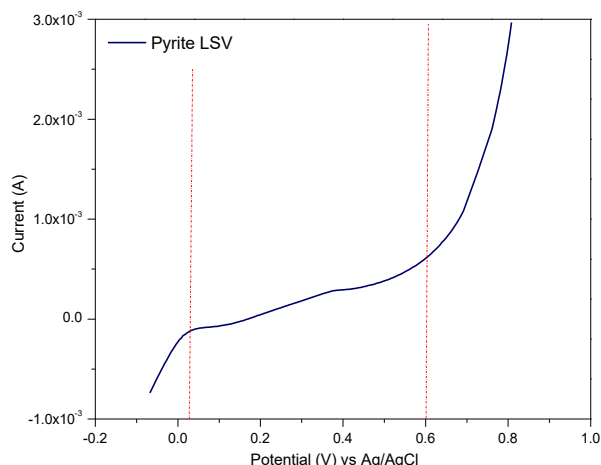


Figure 11: The linear sweep voltammetry (LSV) curve of pyrite electrode at 2 V/s scan rate in 0.5 M HNO_3 .

Figure 12 illustrates the LSV of the chalcopyrite electrode at a 0.02 V/s scan rate in 0.5 M nitric acid solution. Generally, three main sections were presented in the chalcopyrite LSV curve corresponding to the CV scan with the main anodic peaks. The first part which is at the lower anodic potential (-0.1 V to $+0.2$ V) displays a relatively passive section, where the current does not increase significantly with increasing potential. In this part, the voltammogram begins with a small negative current indicating the reduction of CuFeS_2 to H_2S and Cu^0 (reaction 30). This section could be associated with the anodic reaction at A_5 , at which the oxidation of H_2S to S^0 (reaction 33) occurs and partially covers the surface of the electrode [16-18,29]. In the second region ($+0.2$ V to $+0.8$ V), the current rises gently and is accompanied by two oxidation reactions, (1) the partial oxidation of chalcopyrite at A_1 , forming a non-stoichiometric thin passive layer ($\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_2$) and, (2) a series of oxidation reactions of Cu_2S to CuS and Cu^{2+} (at A_2), which causes the moderate upsurge in the oxidative current. From the potential values of $+0.6$ V to $+0.8$ V, the current was constant, which can be due to the accumulation of these copper-rich-sulfur species, forming another passive surface layer which reduces the

oxidation rate [16,17,32,33]. A subsequent sharp increase in the oxidative current happened after $+0.8$ V, proving the extensive oxidation of chalcopyrite (at A_3) by releasing several electrons which results in a noticeable increase in the current in a short increment of increased potential [16,31].

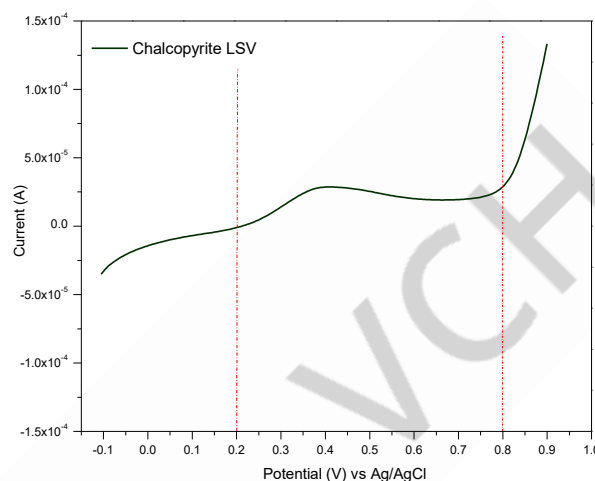


Figure 12: The linear sweep voltammetry (LSV) curve of chalcopyrite electrode at 0.02 V/s scan rate in 0.5 M HNO_3 .

3.5 Open circuit potential (OCP)

Before EIS measurements were conducted, the open circuit potential (OCP) was monitored to ensure the system had effectively reached thermodynamic equilibrium which took about 120 min. Figure 13 represents the OCP of freshly polished (a) pyrite and (b) chalcopyrite electrodes as a function of time. For pyrite, the OCP started from around 0.44 V and gradually reduced and stabilised at ~ 0.41 V, with an overall change of ~ 0.03 V (30 mV) in 120 min. The OCP for chalcopyrite began at ~ 0.36 V and increased before stabilising at ~ 0.40 V, with a total variation of ~ 0.04 V (40 mV).

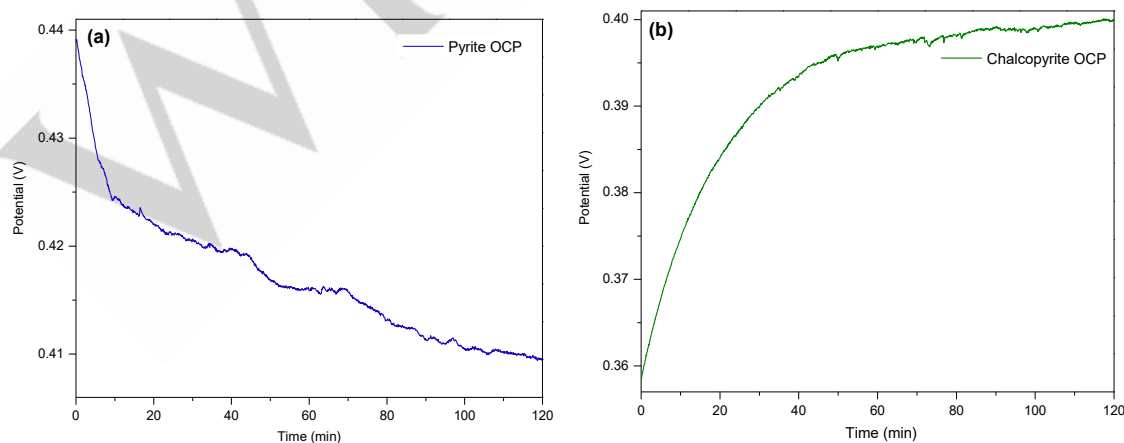


Figure 13: The open circuit potential (OCP) of (a) pyrite and (b) chalcopyrite as the working electrode in 0.5 M HNO_3 for 120 min.

3.6 Electrochemical impedance spectroscopy (EIS) study for pyrite and chalcopyrite

Electrochemical impedance spectroscopy (EIS) is a powerful technique to provide supporting evidence for the product(s) formed as a result of an electrochemical reaction(s) at a specific potential on the surface of the working electrode [17]. In the case of pyrite and chalcopyrite as the working electrodes, several oxidation peaks were detected in the anodic part of their CV scans. Therefore, to examine these processes more closely, EIS measurements were conducted using specific DC bias potentials with a 10 mV AC amplitude.

Figure 14 (a to f) presents the Nyquist plots and fitted data using the indicated equivalent circuits for pyrite at 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 V. The Nyquist plots for the pyrite electrode at low anodic potentials (0.4 and 0.5 V) displayed a slight shift along the x-axis, followed by a very small incomplete semicircle in the high-frequency region, and a largely straight line indicating a typical Warburg impedance (W) feature in the middle and low-frequency region. The shift along the x-axis represents the resistance of the electrolyte solution (R_{el}), and the small incomplete semicircle in the high-frequency region represents the charge transfer resistance (R_{ct}) and interfacial double layer capacitance (Q_{dl}) represented by a constant phase element due to inhomogeneities across the surface. The Warburg impedance (W) corresponds to the presence of a diffusion process (semi-infinite diffusion) [19,23,24]. This can be due to the produced $Fe(OH)_3$ and S^0 (or other sulfur-rich-layers) during partial oxidation of pyrite (as at A_3) covering the surface of the pyrite electrode, making the process diffusion controlled at these low frequencies [19]. The equivalent circuits used to fit the data are given in Figure 14 (a and b) were $[R_{el}+Q_{dl}/(R_{ct}+Q_p/(R_p+W))]$, with R_p the passive layer

resistance and Q_p the capacitance associated with that passive layer (also represented by a constant phase element). This is due to the products formed during the partial oxidation of pyrite partially covering the electrode's surface [19,23,24].

The Nyquist plot at 0.6 V (Figure 14-c) shows a trivial shift along the x-axis presenting the resistance of the electrolyte solution (R_{el}). This is followed by a small incomplete semicircle in the high-frequency region associated with Q_{dl} and R_{ct} . The middle to the low-frequency region of the depressed curve indicates the Warburg element (W), which represents more bounded diffusion signifying a thinner passive layer as it is oxidised when moving into the transpassive region [19,24].

The Nyquist plots at 0.7, 0.8, and 0.9 V (Figure 14 d-f) were similar to each other, except for the magnitude of the impedance which decreased with increasing bias potential. At high frequencies, the Nyquist plots again show a small shift along the x-axis indicative of R_{el} , and a small incomplete arc indicative of Q_{dl} and R_{ct} . In the low-frequency region, the curve extended to the fourth quadrant, indicating a clear inductive feature (L). Tu et al. [19] and Lui et al. [24] associated this with the adsorption and desorption of some sulfide species produced during the rapid and extensive anodic dissolution of pyrite at high potentials (A_1). However, since induction involves the ability to store magnetic energy, another possibility could be the existence of species whose transient magnetisation energy is being observed at high frequencies. No specific diffusion process was evident, again indicating that the oxidative driving force above 0.6 V is adequate to remove the accumulated species from the electrode's surface. At higher potentials, the circuit including the inductive reactant (L) and R, which is the resistance associated with the inductance process as $[R_{el}+Q_{dl}/R_{ct}(R+L)]$, was used for the equivalent circuit.

Table 1: Values of the equivalent circuit elements at the studied bias potentials for pyrite.

Applied potential (V)	R_{el} (Ω)	Q_{dl} (10^{-6} F s ⁿ)	n	R_{ct} (Ω)	Q_p (10^{-6} F s ⁿ)	n	R_p (Ω)	W (10^{-6} S s ^{0.5})	L (H)	$\chi^2/ Z $
0.4	8.9	1.2	0.81	1865	25.7	0.79	563526	31132	–	0.22
0.5	8.7	1.7	0.72	1302	21.6	0.68	492227	16354	–	0.43
0.6	8.5	5.3	0.76	1037	11.2	0.72	70453	1562	–	0.37
0.7	8.4	0.56	0.71	908.7	–	–	3757*	–	28.6	0.42
0.8	8.3	0.43	0.66	92.3	–	–	174.9*	–	17.4	0.36
0.9	8.2	0.41	0.62	17.1	–	–	44.2*	–	6.7	0.32

R_{el} is the electrolyte resistance, Q_{dl} is the capacitance for the double layer, R_{ct} is the charge transfer resistance, Q_p is the capacitance for the passive layer, n is the degree of deviation from ideal capacitance (C, n=1), R_p is the resistance of the passive surface layer, W is Warburg impedance, L is an inductive element, and * is R_L the resistance related to the inductive process.

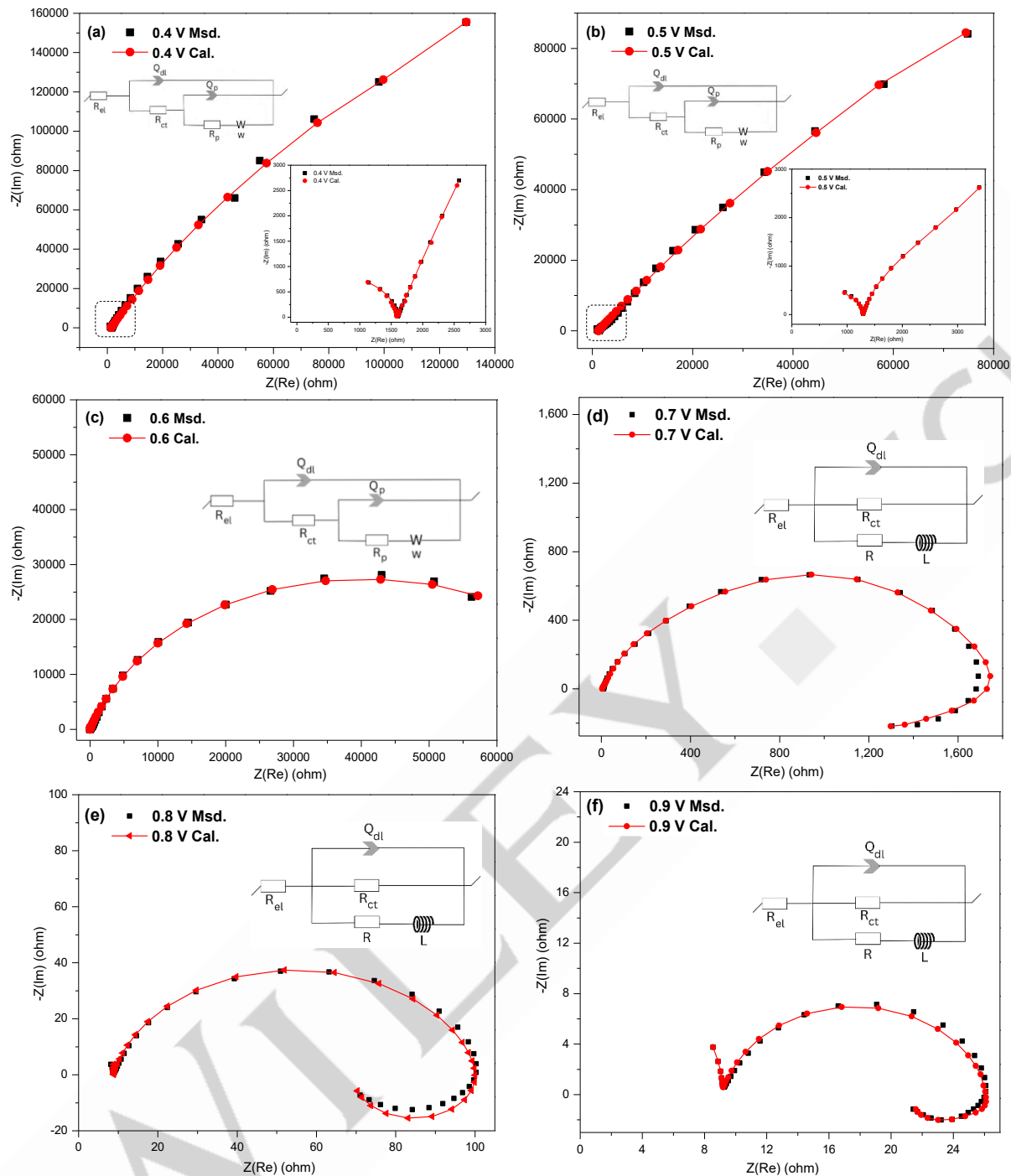


Figure 14: The measured and calculated Nyquist plots with the corresponding circuit models for pyrite in 0.5 M HNO₃ at different bias potentials (a: 0.4 V (OCP), b: 0.5 V, c: 0.6 V, d: 0.7 V, e: 0.8 V, f: 0.9 V).

Table 1 summarises the results for the parameters in the equivalent circuits at the studied potentials for pyrite. As expected the values for R_{el} (the resistance of the 0.5 M HNO₃ solution) were all similar at $\sim 8 \Omega$. The charge transfer resistance (R_{ct}), associated with the rate of electron transfer for the different anodic reactions, showed a decreasing trend when increasing the bias potentials, implying a faster rate of pyrite oxidation. Similarly, the values for the resistance related to the surface passive layer (R_p) decreased

by increasing the potentials. The high R_p values at lower potentials (especially 0.4 and 0.5 V) signify the high resistance due to the passive layer partially covering the surface, while increasing the potential led to anodic reactions which eliminated the passive layer. Furthermore, the values for n define the degree of deviation for the double-layer capacitance (Q_{dl} , presented by a constant phase element) from the ideal capacitance (C , at $n=1$). By increasing the applied potential, the values for n gradually

declined. This indicates that at higher potentials, the surface of the electrode becomes rougher due to the rapid dissolution reactions, and also more inhomogeneous and thus more distributed reaction rates occur. Hence, the higher the potential, the smaller the value of n . Moreover, the small values for $\chi^2/|Z|$ indicate a decent fit between the experimental and fitted values using the stated equivalent circuits [19,24,27].

Figure 15 (a to f) presents the Nyquist plots and fitted data using the indicated equivalent circuits for chalcopyrite at 0.3 to 1 V. All the plots start with a slight shift along the x-axis indicative of R_{el} and a small incomplete semi-circle in the high-frequency region related to the double layer capacitance (C_{dl} or Q_{dl}) and the resistance for the main charge transfer (R_{ct}). At low bias potentials (0.3 and 0.5 V), there is a semicircle in the mid-frequency range correlated with the capacitance (which shows a distributed behaviour due to an inhomogeneous surface) and resistance of the surface passive layer (denoted Q_p and R_p , respectively), which is followed by a straight line indicating Warburg diffusion (W) in the low-frequency region. The species covering the surface of the chalcopyrite electrode at these potentials, which account for the diffusion process, likely are predominantly iron-deficient sulfide leaving a copper-rich-sulfur passive layer (i.e. $Cu_{1-x}Fe_{1-y}S_{2-z}$, $Cu_{1-z}S_2$, CuS_2 and CuS) and S^0 [16-18,28]. As the bias potential was increased from 0.3 V to 0.5 V, the resistance of the passive layer (R_p) decreased, thus indicating less resistive oxidative reactions at 0.5 V. Also the angle of the straight line in the high-frequency region (Warburg diffusion) is deviating from 45 degrees, which could be related to the diffusion process at 0.5 V at which the semi-infinite condition is slightly changing. The equivalent circuits used to fit the data given in Figure 15 (a and b) were $[R_{el}+Q_{dl}/(R_{ct}+Q_{dl}/(R_p+W))]$.

At high anodic potentials (0.7 to 1 V), the Nyquist plots start with an incomplete semi-circle in the high-frequency region as before, followed by a semicircle in the middle to low-frequency regions with no evidence of the semi-infinite Warburg diffusion. The

resistance associated with the middle to low-frequency semicircle decreased as the bias potential was increased, indicating the oxidative dissolution of the copper-rich-sulfur layer and S^0 to form soluble species [16-18].

Table 2 gives the values of all of the elements from the equivalent circuits at the studied potentials for chalcopyrite. As was anticipated, the values for the electrolyte solution resistance (R_{el}) were close to one another because the same solution was used for the different potentials. Increasing the anodic potentials from 0.2 to 1 V, showed a decreasing trend for the resistance related to the surface passive layer (R_p). This suggests that the total impedance decreased and subsequently the oxidation rate increased. Raising the applied potentials can cause the charge transfer resistance (R_{ct}) to fluctuate, which could be due to the different complicated electrochemical reactions occurring on the surface of chalcopyrite electrode at each specific potential [16-18].

In summary, the results determined from the EIS data for pyrite and chalcopyrite at different potentials correspond to the reactions taking place during anodic dissolution as detected in their CV scans at the specific potentials. Both with pyrite and chalcopyrite electrodes the anodic dissolution at low potentials – (0.4 to 0.6 V for pyrite) and (0.3 to 0.5 V for chalcopyrite) – preferentially starts with dissolving iron (Fe), hence forming a sulfur-rich $Fe_{1-x}S_2$, $Fe(OH)_3$, S^0 [19] and copper-rich -sulfur species i.e. $Cu_{1-x}Fe_{1-y}S_{2-z}$, $Cu_{1-z}S_2$, CuS_2 , CuS , respectively [16-17][22][30,31]. These nonstoichiometric species accumulate and partially cover the electrode's surface acting as a passive layer, resulting in a diffusion barrier, and slowing down the oxidation process. Increasing the potential to above 0.7 V the species in the passive layer further oxidise, thereafter eradicating the diffusion layer, and leading to faster and massive oxidation of the remaining pyrite and chalcopyrite.

Table 1: Values of the elements from the equivalent circuits for the studied potentials for chalcopyrite.

Applied potential (V) ^a	R_{el} (Ω)	Q_{dl}/C_{dl} (10^{-7} F s ⁿ)	n	R_{ct} (Ω)	Q_p (10^{-6} F s ⁿ)	n	R_p (Ω)	W (S s ^{0.5})	$\chi^2/ Z $
0.3	7.4	2.5	0.81	727	14.5	0.78	16206	1992	0.21
0.5	7.3	2.4	0.86	635	18.4	0.76	15734	1512	0.32
0.7	7.7	0.34	1	1250	7.7	0.84	14114	–	0.36
0.8	7.6	0.83	1	2994	3.7	0.86	10399	–	0.39
0.9	7.4	1.6	1	2518	2.4	0.83	4246	–	0.23
1	7.1	1.4	1	2873	1.1	0.81	1640	–	0.28

^a R_{el} is the electrolyte resistance, Q_{dl}/C_{dl} is the capacitance for the double layer, R_{ct} is the charge transfer resistance, Q_p is the capacitance for the passive layer, n is the degree of deviation from ideal capacitance (C , $n=1$), R_p is the resistance of the passive surface layer, and W is Warburg impedance.

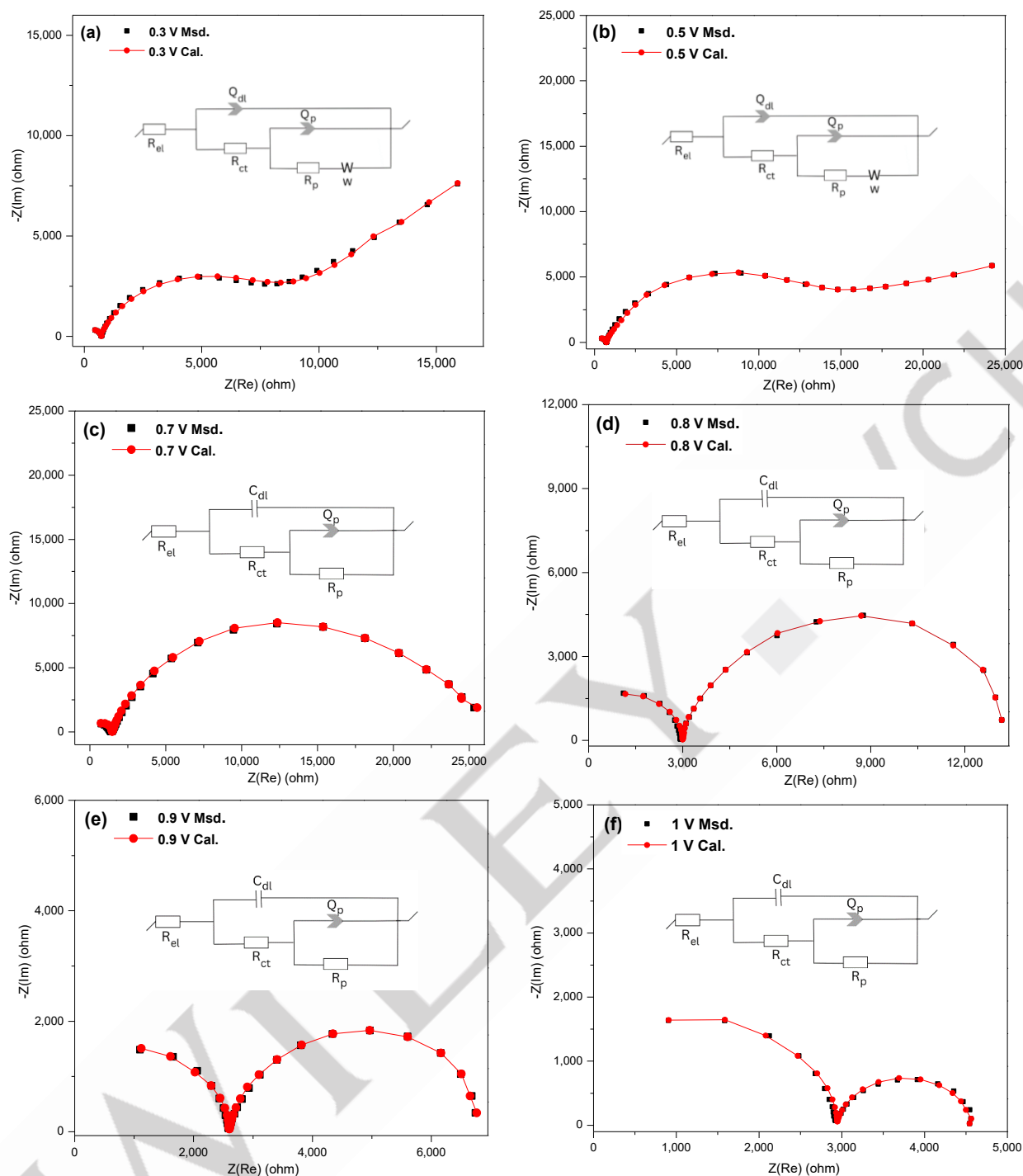


Figure 15: The experimental measured and calculated Nyquist plots with the corresponding circuit models for chalcopyrite in 0.5 M HNO_3 at different potentials (a: 0.3 V, b: 0.5 V, c: 0.7 V, d: 0.8 V, e: 0.9 V, f: 1 V).

In the Nyquist plots presenting the EIS results with the corresponding equivalent circuits the passive layer was confirmed with the existence of a Warburg diffusion (W) element in the indicated circuit at low-potentials for pyrite and chalcopyrite. The same equivalent circuit with Warburg diffusion (W) element fit the EIS data for both pyrite and chalcopyrite at low potentials. At higher potentials, some differences appeared between the

Nyquist plots for pyrite and chalcopyrite. For pyrite, the semicircle in the low-frequency region extends to the fourth quadrant and presents an inductive feature (L), which could be associated with the adsorption and desorption of some sulfide species produced during the rapid and extensive anodic dissolution of pyrite at high potentials (0.7 V to 0.9 V) [19]. However, the Nyquist plots for chalcopyrite at higher potentials contain an incomplete semi-circle followed by a semi-circle, and their magnitude becomes smaller

as the potential is raised to 1 V, signifying a decrease in the impedance with less resistance, and faster and massive dissolution. Hence, different equivalent circuits fitted the EIS results for pyrite and chalcopyrite at high potentials.

These results were compared to similar studies performed in H_2SO_4 solutions, a commonly used acid for the dissolution of pyrite and chalcopyrite. The following observations are noted: (i) Both HNO_3 and H_2SO_4 are acids capable of dissolving these minerals, with HNO_3 being a stronger oxidant due to N being more electronegative than S. Thus the oxidative dissolution of these minerals in both these acids can break down the host mineral to expose any encapsulated gold and improve its recovery. (ii) Pyrite dissolves faster in HNO_3 than H_2SO_4 , however, the latter is more suitable for chalcopyrite dissolution. This is due to the passive layer formed on chalcopyrite dissolving more readily in H_2SO_4 than HNO_3 , although higher potentials are required in H_2SO_4 (as compared to that in HNO_3) [22,34] (iii) The dissolution kinetics for both pyrite and chalcopyrite is diffusion-controlled in HNO_3 and H_2SO_4 . (iv) Pyrite oxidation occurs faster (with a higher anodic and cathodic current density being noted) compared to chalcopyrite in HNO_3 . The slower chalcopyrite dissolution is likely caused by the formation of copper-rich-sulfur species (such as $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}$, CuS_2 and $\text{Cu}_{1-z}\text{S}_2$), which also slows the diffusion of Fe ions through these formed passive layers [28,34].

4 Conclusion

Understanding the oxidation of pyrite and chalcopyrite is an important issue because of exposing any encapsulated gold to enhance its extraction yield from refractory ores and mine tailings. CV scans along with EIS measurements were employed to study the electrochemical behaviour of pyrite and chalcopyrite in 0.5 M nitric acid as the electrolyte. Anodic oxidation of pyrite (FeS_2) at low potentials (0.4 to 0.6 V) begins with the oxidation of iron which results in the formation of $\text{Fe}_{1-x}\text{S}_2$, $\text{Fe}(\text{OH})_3$ and elemental sulfur (S^0) that partially cover the surface of the pyrite electrode and cause a diffusion barrier, thus diminishing further anodic reactions. Increasing the potentials to above 0.7 V leads to reactions in which the products accumulated on the electrode's surface convert to soluble species, i.e. S^0 to H_2S or SO_4^{2-} , hence eradicating the diffusion barrier and leading to extensive oxidation of pyrite at high potentials.

The electrochemical oxidation of chalcopyrite was somewhat similar to that of pyrite since at low potentials (below 0.5 V), iron is preferentially dissolved (Fe), hence some copper rich-sulfur species like $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}$, CuS_2 , CuS and S^0 formed and accumulated on the chalcopyrite electrode's surface to cause a passive layer. Increasing the potential to above 0.7 V leads to reactions at which the species in the formed passive layer are oxidised to soluble species, thereby eliminating the diffusion barrier. The Nyquist plots from the EIS measurements provide evidence supporting the reactions and the suggested products

at the studied potentials. As a result, the existence of a semi-infinite diffusion described by the Warburg element in fitting the EIS data at low potentials for both pyrite and chalcopyrite indicates a diffusion-controlled dissolution process. Moreover, at high potentials (above 0.6 V) faster and more active dissolution of the mineral occurs, confirming the elimination of the passive layer covering the electrodes' surface.

Some other related findings are:

- Nitric acid is a powerful oxidative acid to dissolve sulfidic minerals such as pyrite and chalcopyrite, and it is also regenerable [5,8,14], which can reduce the operating cost of a process.
- Breaking down the pyrite matrix with a nitric acid pre-treatment to expose any enclosed gold can lead to improved extraction yield from refractory sources.
- The electrochemical studies in this research suggest that a potential over 0.7 V is required to dissolve both pyrite and chalcopyrite significantly in nitric acid solution.
- The previous study by Teimouri et al. (2022) [22] showed that when nitric acid concentration is above 2 M, it has a powerful oxidative ability to dissolve pyrite.

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Conflict of interest: The Authors declare that there is no conflict of interest in this work.

Keywords: Pyrite, chalcopyrite, oxidative dissolution, nitric acid, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS).

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Chapter 5

A New Hydrometallurgical Process for Metal Extraction from Electric Arc Furnace Dust Using Ionic Liquids

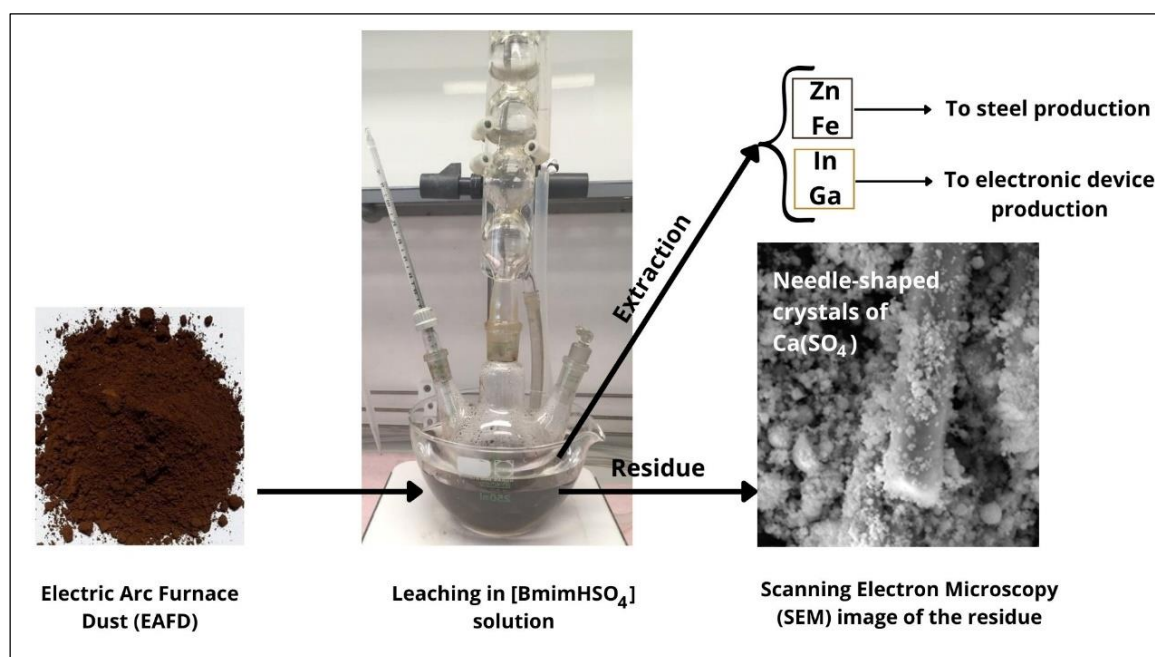
Samaneh Teimouri, Johannes Herman Potgieter, Mari Lundström, Caren Billing,
and Benjamin P. Wilson

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Highlights

- Used ionic liquids [Bmim⁺HSO₄⁻] and [Bmim⁺Cl⁻], as alternative solvents to extract Zn, In, Ga and Fe as main impurities from electric arc furnace dust (EAFD).
- Conducted experiments to demonstrate the optimum condition occurred with 30% v/v [Bmim⁺HSO₄⁻], 1 g Fe₂(SO₄)₃ oxidant, S/L ratio = 1/20, and 85 °C for 240 min leaching time.
- Observed 92.7% Zn, 80.2% Fe, 97.4% In, and 17.03% Ga extraction under the optimum conditions.
- The dissolution kinetics of studied metals over a temperature range of 55–85 °C was diffusion-controlled.

Graphical abstract



Article

A New Hydrometallurgical Process for Metal Extraction from Electric Arc Furnace Dust Using Ionic Liquids

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Abstract: This research proposes a new hydrometallurgical method for Zn, In, and Ga extraction, along with Fe as a common impurity, from electric arc furnace dust (EAFD), using ionic liquids. EAFD is a metal-containing waste fraction generated in significant amounts during the process of steelmaking from scrap material in an electric arc furnace. With valuable metal recovery as the main goal, two ionic liquids, [Bmim⁺HSO₄[−]] and [Bmim⁺Cl[−]], were studied in conjunction with three oxidants: Fe₂(SO₄)₃, KMnO₄, and H₂O₂. The results indicated that the best combination was [Bmim⁺HSO₄[−]] with [Fe₂(SO₄)₃]. An experimental series subsequently demonstrated that the combination of 30% v/v [Bmim⁺HSO₄[−]], 1 g of [Fe₂(SO₄)₃], S/L ratio = 1/20, a 240 min leaching time, and a temperature of 85 °C was optimal, resulting in maximum extractions of 92.7% Zn, 97.4% In, and 17.03% Ga. In addition, 80.2% of the impurity metal Fe was dissolved. The dissolution kinetics of these four elements over a temperature range of 55–85 °C was found to be diffusion controlled. The remaining phases present in the leached residue were low amounts of ZnO, Fe₃O₄, ZnFe₂O₄, and traces of Ca(OH)₂ and MnO₂, and additional sharp peaks indicative of PbSO₄ and CaSO₄ appeared within the XRD pattern. The intensity of the peaks related to ZnO and Fe₃O₄ were observed to have decreased considerably during leaching, whereas some of the refractory ZnFe₂O₄ phase remained. SEM-EDS analysis revealed that the initial EAFD morphology was composed of spherical-shaped fine-grained particle agglomerates, whereas the leached residue was dominated by calcium sulphate (Ca(SO₄))-rich needle-shaped crystals. The results clearly demonstrate that [Bmim⁺HSO₄[−]] is able to extract the target metals due to its acidic properties.

Keywords: ionic liquid [Bmim⁺HSO₄[−]]; electric arc furnace dust (EAFD); kinetics; metal extraction; XRD; SEM-EDS



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1. Introduction

The global demand for critical and valuable metals is growing rapidly due to their wide-ranging applications in various modern electronic devices and is consequently beginning to outstrip their current supply and production [1]. The global metal industry is therefore pursuing novel, efficient routes to recover critical and valuable metals from not only different primary sources but also secondary and waste resources, including electric arc furnace dust (EAFD), zinc electroplating anode slime, and electrical/electronic equipment (WEEE) to fulfil the heightened demand. As part of this shift, there is greater emphasis on the use of energy-efficient processes that are environmentally benign and improve material circularity [2].

The predominant process used for recycling end-of-life iron-based products (secondary resource) into steel is the electric arc furnace (EAF) [3,4]. During this process, the furnace temperature can reach 1600 °C or higher, at which many of the elements within iron scraps, such as Zn, Fe, Cr, Mn, and Pb, can be volatilised. When the furnace cools down, this vapour phase produces a large amount of unwanted powder known as electric arc furnace dust (EAFD) [5]. Currently, steel production from secondary resources is >600 M tons per year globally, and it has been estimated that an EAF generates approximately 20 kg of dust per ton of steel produced from iron scraps [4]. Owing to the elemental content, the EAFD produced during the steelmaking process is simultaneously an environmental pollutant if deposited on land—due to containing Pb and Cr—and a valuable industrial waste because of the substantial amounts of useful metals, such as Cu, Ni, Zn, and Fe, which can be recovered and returned to the steel production process [6].

Pyrometallurgical and hydrometallurgical processes have been investigated to recover valuable metals from EAFD. The pyrometallurgical Waelz process is a dominant technique used industrially to recover over 80% of steel dust [7]. Rütten (2008) investigated the Waelz process and recovered about 90% Zn. He used coke (silica and/or lime) as the reducing agent, through which the carbothermal reduction of Zn and Fe oxides occurred in a rotary kiln at a temperature of 1200 °C [8]. Hydrometallurgical-type processes are also considered to be appropriate for the extraction of valuable metals—even at low concentrations—from waste and secondary resources, such as EAFD. Interestingly, although Paul Walden [9] synthesised the first ionic liquid (ethyl ammonium nitrate [EtNH₃NO₃]) as early as 1914, it was only towards the end of the twentieth century that ionic liquids started to gain prominence among researchers from different disciplines, including hydrometallurgy, as potential novel solvents for the extraction and recovery of valuable and critical metals [9,10].

Traditionally, in the scientific literature, acidic solutions of HCl, H₂SO₄, and HNO₃ have been used for the hydrometallurgical extraction of target metals such as Zn from EAFD [5,6,11–15]. For example, Kukurugya et al. (2015) investigated the extraction and behaviour of Zn, Fe, and Ca from EAFD using a H₂SO₄ solution to determine the influence of the sulphuric acid concentration, liquid-to-solid (L:S) ratio, temperature, and leaching time. Their research found that under optimal conditions of 80 °C with 1 M H₂SO₄ and an L:S ratio of 50, a maximum Zn extraction of 87% was achieved. Due to the fast dissolution of Zn, the maximum feasible extraction of Zn into the leaching solution could be accomplished within the first few minutes of leaching, eliminating extended leaching times [6]. The extraction of Zn and Fe from EAFD with H₂SO₄ has also been investigated by Oustadakis et al. (2010). In this work, the influence of parameters such as the H₂SO₄ concentration, temperature, and solid-to-liquid (S/L) ratio on the efficiency of metal extraction were examined by the statistical analysis of experiments (factorial design). It was found that the highest Zn extraction of 80% with simultaneous 45% Fe dissolution was achieved with 3 M H₂SO₄ at 60 °C and a 10% S/L ratio [5]. In contrast, Halli et al. (2018) employed the alkaline roasting of EAFD with NaOH at 450 °C, followed by organic acid leaching with 0.8 M citric acid at 40 °C for 2 h with oxygen purging. Under these conditions, the selective leaching of Zn over Fe was obtained (100% Zn vs. <10% Fe), and additionally, over 80% Pb was extracted [4].

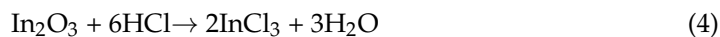
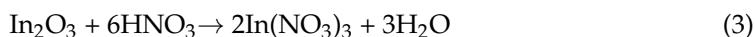
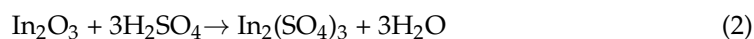
Ionic liquids essentially belong to the molten salt family and comprise ions, typically a large organic cation and organic or inorganic anions of different sizes. The size difference between the cation and anion lowers the lattice energy, which makes them liquid at temperatures below 100 °C [11]. By careful consideration of their properties, different cations and anions can be combined to synthesise thousands of distinct ionic liquids with variable physicochemical properties based on the application of interest or intended purposes [10]. Ionic liquids may have remarkable properties, such as low melting points, negligible vapour pressure, and excellent thermal/chemical/electrochemical stability, and can potentially be recycled and reused, which has the added benefit of reducing the levels of chemical consumption as, for example, part of an industrial leaching process [16]. Recently, the use of ionic liquids as lixiviants has been studied for the extraction of valuable metals from

different raw materials. For instance, Rüßen and Topçu (2017) examined the recovery of gold from copper anode slime with an acidic ionic liquid, 1-ethyl-3-methyl-imidazolium hydrogen sulphate (EmimHSO₄). A maximum Au extraction of almost 90% was achieved when using an 80% ionic liquid concentration and an S/L ratio of 1/25 g/mL at 75 °C for 4 h [1]. The same authors (Topçu and Rusen, 2020) investigated Cu extraction from anode slime using 1-butyl-3-methylimidazolium-based ionic liquids with different anionic parts, i.e., HSO₄[−], Cl[−], and BF₄[−]. Their findings demonstrated that the most effective ionic liquid was 1-butyl-3-methylimidazolium hydrogen sulphate (BmimHSO₄) under conditions of a 50% ionic liquid concentration, an S/L ratio of 1/20 g/mL at 50 °C, and an 8 h leaching time, which yielded almost 30% Cu extraction [9].

The recovery of In and Ga is becoming essential due to both their relative scarcity and growing demand, especially for their use in light-emitting diodes (LEDs) and other electronic devices [17]. Theocharis et al. (2021) investigated the extraction and recovery of In, Ga, Cu, Zn, and Mo from end-of-life thin-film solar panels containing CIGS (copper indium gallium selenide, CuGa_{1−x}In_xSe₂). The CIGS photovoltaic panels were dismantled and thermally processed at 550 °C for 15 min to delaminate the ethylene vinyl acetate (EVA) and the thin layer of coated glass. Once prepared, the thermally treated samples were leached with 6 M HNO₃ to extract the In, Ga, Cu, Zn, and Mo. The leachate solution was then subjected to solvent extraction using D₂EHPA to separate and recover the extracted metals [2]. Zhan et al. (2015) examined an alternative method for the recovery of In and Ga from discarded light-emitting diodes (LEDs) by applying pyrolysis, physical disintegration (crushing, screening, and grinding), and vacuum metallurgy separation. The latter is a heating separation/purification process under vacuum, in which the boiling point of metals can be significantly reduced, thereby requiring less energy. These methodologies achieved In and Ga extractions of ~96% and ~94%, respectively, under optimal conditions of 1100 °C heating, 0.01–0.1 Pa vacuum pressure, and a holding time of 1 h [16].

To separate and recover Zn from a leached liquor, solvent extraction and electrowinning techniques have been applied [17–20]. For Fe recovery, the precipitation technique [21] is mostly used, and the solvent extraction process is used for In and Ga [22,23]. The EAFD residue after the required treatment to remove hazardous heavy metals, i.e., Cr and Pb, was disposed of in a landfill [24]. Recently, there has been research on the use of EAFD residue in the production of ceramics, red clay bricks [25–28], building blocks, and cement [24].

In acidic solutions (H₂SO₄, HNO₃, and HCl), In can be readily extracted according to Reactions (1)–(4) [29]. The stable oxidation state of both In and Ga is +3. Since they both belong to the Boron family of elements (i.e., group 13) of the periodic table, one can extrapolate that the same/similar reactions also occur for Ga treated with these acidic solutions.



Based on these acidic reactions, three imidazolium-based ionic liquids with similar anions to these mineral acids—[Bmim⁺HSO₄[−]], [Bmim⁺NO₃[−]], and [Bmim⁺Cl[−]—were selected for this study. Figure 1 illustrates the chemical structures of the cationic part (1-butyl-3-methylimidazolium–Bmim⁺) and the different anions (Cl[−], HSO₄[−], and NO₃[−]) that compose the three distinct ionic liquids. However, as [Bmim⁺NO₃[−]] has limited availability due to global production issues, it was excluded from this investigation.

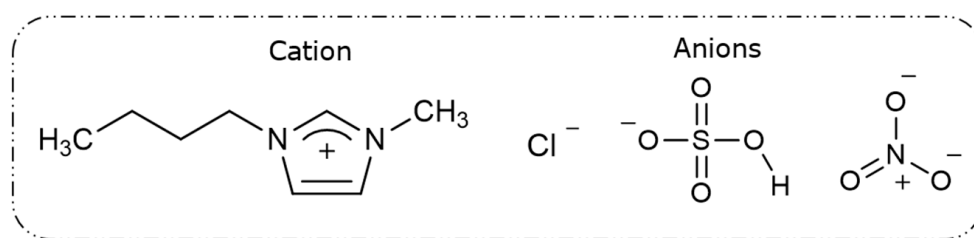


Figure 1. Structures of the cation (1-butyl-3-methylimidazolium–Bmim⁺) and different anions (Cl[−], HSO₄[−], and NO₃[−]) composing the ionic liquids.

This work aims to determine the feasibility of using imidazolium-based ionic liquids for Zn, In, and Ga extraction from EAFD, along with Fe as a common impurity. The effects of ionic liquid with the same imidazolium cation (1-butyl-3-methylimidazolium) and different anionic components (HSO₄[−] and Cl[−]) were examined experimentally. This involved the investigation of two ionic liquids—[Bmim⁺HSO₄[−]] and [Bmim⁺Cl[−]—with three oxidants (Fe₂(SO₄)₃, KMnO₄, and H₂O₂) to determine which ionic liquid and oxidant combination performs the best in extracting the target metals. Following the initial tests, the influence of parameters such as the concentration of the ionic liquid, oxidant concentration, solid-to-liquid (S/L) ratio, time, and temperature were optimised to achieve the maximum extraction of Zn, In, Ga, and Fe (as the impurity) from electric arc furnace dust (EAFD). A kinetic study of the dissolution of these elements from EAFD in a 30% *v/v* [Bmim⁺HSO₄[−]] solution was conducted over a temperature range of 55–85 °C, and the results were evaluated using shrinking-core models. The leached residue of EAFD was also analysed by X-ray diffraction (XRD), scanning electron microscopy in conjunction with energy-dispersive X-ray spectroscopy (SEM-EDS), and particle size distribution (PSD) analysis to identify changes in the main phases and particles following leaching in the ionic liquid medium. To the authors’ knowledge, this approach has not been researched previously for EAFD and can contribute to a novel process for metal recovery from this source and increase the knowledge about the use of ionic liquids for various metal extractions from secondary resources.

2. Experimental Procedures

2.1. Materials

The electric arc furnace dust (EAFD) employed in this research was obtained from the Ovako Imatra Oy steel production plant in Finland and was used “as received”. Table 1 lists the results for the total acid leaching of a well-mixed representative EAFD sample indicating the chemical composition of the EAFD used, as determined by atomic absorption spectroscopy (AAS), inductively coupled plasma–optical emission spectrometry (ICP-OES), and sulphur/carbon analysis, adapted from Halli et al. (2017) [14]. From the analyses, it was determined that the main components within the EAFD were Zn, Fe, Ca, Mn, and Pb. Additionally, the mineralogy of the material was studied by X-ray diffraction (XRD), and the resultant pattern is presented in Figure 2. The XRD phase analysis identified the main phases in EAFD as zincite (ZnO), zinc ferrite (ZnFe₂O₄), and magnetite (Fe₃O₄), with some minor phases of Ca(OH)₂, PbO, MnO₂, and MgO. The mineral phase evaluation from XRD correlated well with the chemical composition determined after total acid digestion. The particle size distribution (PSD) of the EAFD sample was measured by laser diffraction, as shown in Figure 3. As shown, the frequency and cumulative distribution of EAFD particles primarily comprise two distinct size fractions: very fine grains of 0.01–0.15 μm and a portion of coarser particles of about 10–100 μm. From the PSD, it was found that 50% of the particles were below 14.2 μm, while the majority of the particles (90%) were <100 μm.

Table 1. Chemical analysis of the main elements in the EAFD sample (total acid digestion, measured by * AAS, ** ICP-OES, and *** S/C analyser) [14].

Element	Content [wt%]
Zn	33.2 *
Fe	17.9 *
Ca	3.6 **
Mn	2.5 *
K	2.4 **
Na	1.8 **
Pb	1.64 *
C	1.17 ***
S	1.05 **
Si	0.83 **
Mg	0.64 **
Al	0.36 **
Cr	0.23 **
Cu	0.20 **
Ni	0.03 **
V	0.02 **
P	0.02 **

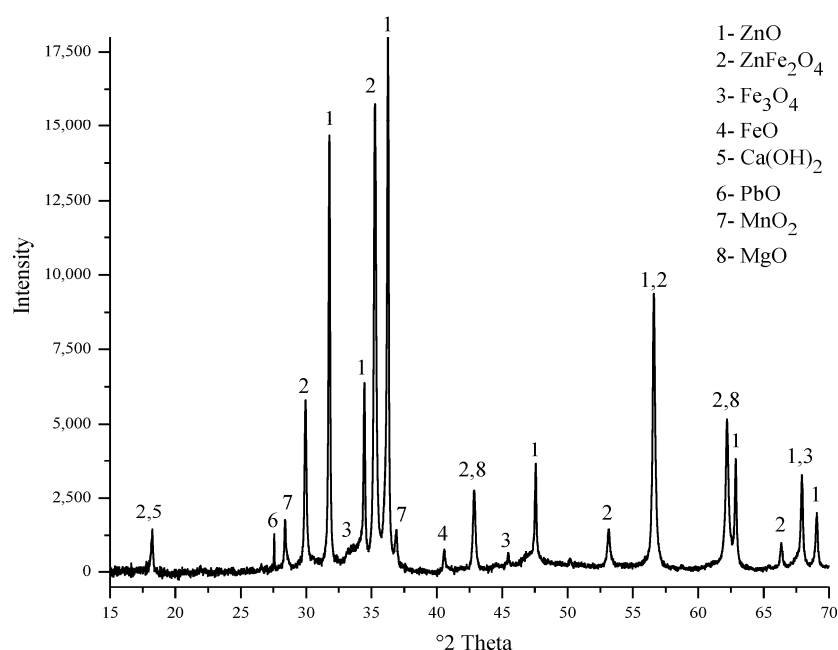


Figure 2. XRD pattern (mineral phase) of the EAFD.

2.2. Apparatuses

The instrumentations used in this research were as follows: the leached solution was analysed by AAS (atomic absorption spectroscopy, Varian AA240, Palo Alto, California, USA) for the contents of In, Ga, and Fe and by ICP-OES (inductively coupled plasma–optical emission spectrometry, Perkin Elmer Optima 7100 DV, Beaconsfield, Bucks, PA, USA) for Zn, as well as a sulphur/carbon analyser (Eltra CS-580 analyser, Haan, Germany) to determine the chemical composition of the EAFD. Phase analysis was carried out by XRD (X-ray diffraction, PANalytical-X’Pert PRO Powder, Almelo, Netherlands), applying a 40 mA current and 45 kV acceleration voltage, with a CuK α radiation source. The particle size distribution of the EAFD was measured by a Mastersizer 3000 (Malvern Instruments Ltd., Malvern, UK). The pH and redox potential in the leaching solutions were measured with a digital pH electrode (HI 11,310, Hanna Instruments, Woonsocket, Smithfield, RI, USA).

and InLab Ag/AgCl 3M KCl (Mettler Toledo, Columbus, OH, USA) reference electrode, respectively. The morphological examination of the EAFD particles was conducted with an SEM-EDS (scanning electron microscopy, A LEO 1450, Carl Zeiss Microscopy GmbH, Jena, Germany) in conjunction with EDS (energy-dispersive X-ray spectroscopy, Link Inca X-sight 7366, Oxfordshire, UK).

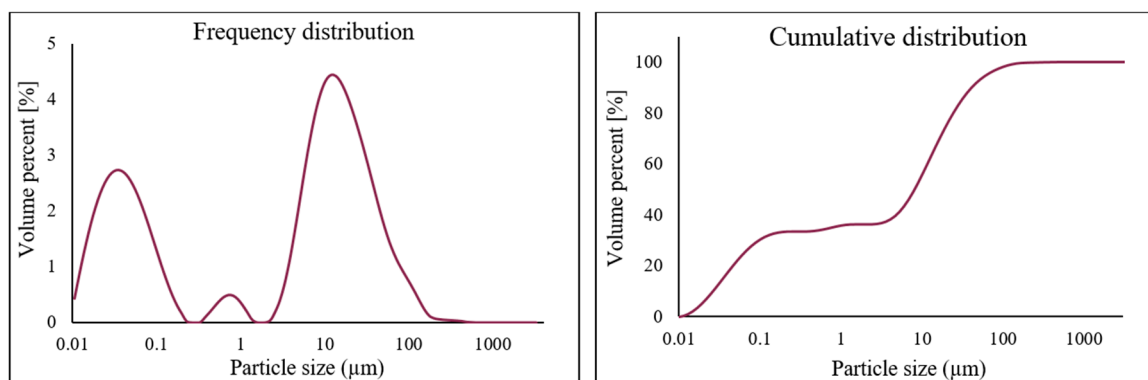


Figure 3. Particle size distribution (PSD) of the EAFD.

The chemicals employed in this research were two ionic liquids, 1-butyl-3 methylimidazolium hydrogen sulphate [$\text{Bmim}^+\text{HSO}_4^-$] and 1-butyl-3 methylimidazolium chloride [Bmim^+Cl^-], and three oxidants, ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$), potassium permanganate (KMnO_4), and hydrogen peroxide (H_2O_2). Indium and Ga oxide (In_2O_3 and Ga_2O_3) were also added to the EAFD sample in order to ascertain the possibility of In and Ga recovery from this type of matrix. All of the chemicals were purchased from Merck/Sigma-Aldrich, Finland, and related solutions were made using ultrapure water ($>18 \text{ M}\Omega\text{-cm}$, Millipore Milli-Q, Merck, Espoo, Finland).

2.3. Procedures

The leaching of EAFD with ionic liquid as the primary lixiviant was conducted under atmospheric pressure in a 250 mL three-neck round-bottom reactor immersed in a water bath placed on top of a hot-plate magnetic stirrer. One neck of the reactor was attached to a condenser, one was used to accommodate a thermometer that was immersed in the leaching solution, and the third opening was used for sampling. Agitation was provided by a stirring bar within the reactor in order to suspend the particles in the ionic liquid solution and produce a uniform pulp. A typical leaching experiment was carried out: a pre-determined amount of ionic liquid solution with a known concentration was heated to the desired temperature, and then the selected oxidant and a known amount of EAFD enriched with 5% each of In_2O_3 and Ga_2O_3 were added to the preheated ionic liquid solution.

Initial experiments were performed using two ionic liquids ($[\text{Bmim}^+\text{HSO}_4^-]$ and $[\text{Bmim}^+\text{Cl}^-]$) and three oxidants to determine which combination of ionic liquid and one of the three proposed oxidants would be the most effective and lead to the highest extraction of the target metals from EAFD. The specific experimental conditions were as follows: 50 mL of ionic liquid ($[\text{Bmim}^+\text{HSO}_4^-]$ or $[\text{Bmim}^+\text{Cl}^-]$) with a concentration of 50% (v/v), oxidant concentration (one of either KMnO_4 (0.5 g), $\text{Fe}_2(\text{SO}_4)_3$ (0.5 g), or H_2O_2 50% (1 mL)), a temperature of 65°C , S/L = 1/20, a stirring speed of 500 rpm, and a leaching time of 8 h.

After determining the most effective ionic liquid and oxidant combination, the operating parameters, namely, 50 mL of ionic liquid with different concentrations (30, 40, 50, and 60% v/v), oxidant masses (0.25, 0.5, 0.75, 1 g for KMnO_4 or $\text{Fe}_2(\text{SO}_4)_3$) or oxidant volumes (1, 1.5, 2, and 2.5 mL for 50% H_2O_2), S/L ratios (1/10, 1/15, 1/20, and 1/25 g/mL), and temperatures (55°C , 65°C , 75°C , and 85°C), were examined to determine the optimal conditions for maximum Zn, In, and Ga extraction from EAFD. To monitor the progress of the dissolution experiment, 2 mL aliquots of the leach solution were taken from the reactor using a pipette

at regular time intervals between 0.5 and 8 h and analysed to determine the contents of the target metals. For the kinetic studies (carried out at 55, 65, 75, and 85 °C), 100 mL of a 30% (*v/v*) ionic liquid solution was prepared, and 2 mL aliquots were withdrawn from the reactor at the following intervals: 10, 20, 30, 45, 60, 90, 120, 180, and 240 min. In all cases, 2 mL of fresh ionic liquid was added to the reactor after each withdrawal to maintain the appropriate S/L ratio.

3. Results and Discussion

3.1. The Combination of Ionic Liquid and Oxidant

To determine the most effective ionic liquid and oxidant combination for the extraction of Zn, In, and Ga from EAFD, two imidazolium-based ionic liquids, [Bmim⁺HSO₄[−]] and [Bmim⁺Cl[−]] (50 mL, 50% *v/v*), were mixed with one of three selected oxidants, KMnO₄ (0.5 g), Fe₂(SO₄)₃ (0.5 g), or 50% H₂O₂ (1 mL) (Figure 4). After conducting the experiments, it was found that [Bmim⁺HSO₄[−]] performed considerably better than [Bmim⁺Cl[−]] due to the ability of [Bmim⁺HSO₄[−]] to act as a Brønsted acid, which allows the anionic species [HSO₄[−]] to release the associated proton [H⁺] into the solution [16–18]. Furthermore, the sulphate [SO₄^{2−}] is able to act as a better ligand (compared to Cl[−]) to form a stable complex with the target metals. Equation (5) shows this dissociation of [Bmim⁺HSO₄[−]] in an aqueous solution to release [H⁺].

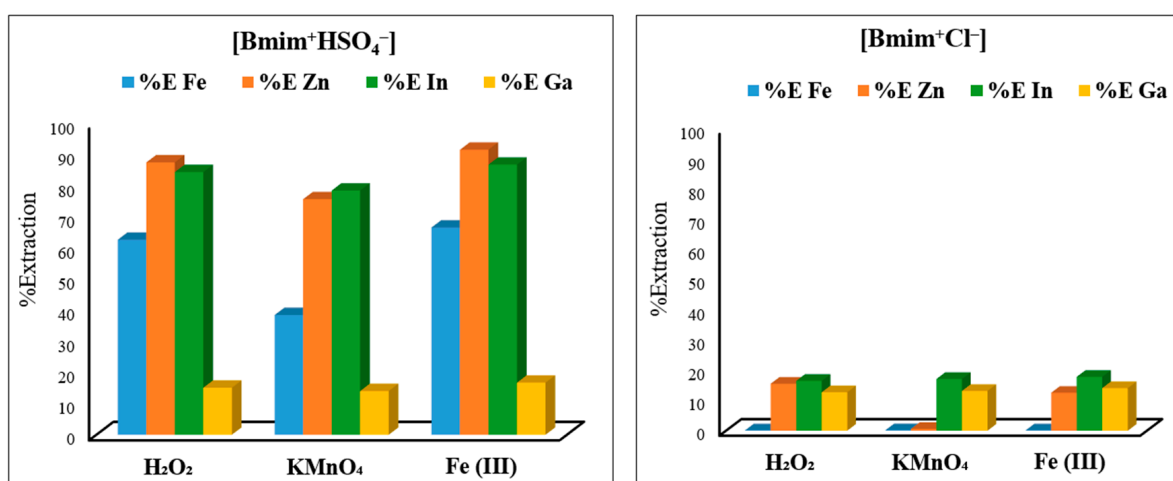
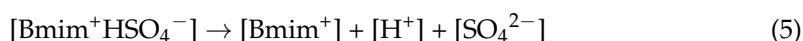


Figure 4. Metal extraction percentages achieved by the combination of ionic liquids [Bmim⁺HSO₄[−]] and [Bmim⁺Cl[−]] with the three oxidants H₂O₂ 50% (1 mL), KMnO₄ (0.5 g), and Fe₂(SO₄)₃ (0.5 g). Experimental conditions: 50 mL of 50% (*v/v*) ionic liquid solution, S/L ratio of 1/20, stirring speed of 500 rpm, temperature of 65 °C, and total leaching time of 8 h.

Therefore, one of the main characteristics of [Bmim⁺HSO₄[−]] is its ability to substantially lower the leaching solution's pH, making the solution acidic [16,17]. For instance, it was found that for 50% *v/v* [Bmim⁺HSO₄[−]], the pH was ~0.88, whereas for the equivalent 50% *v/v* [Bmim⁺Cl[−]], the leaching solution's pH was ~4.7. As the results in Figure 4 show, [Bmim⁺HSO₄[−]] with the addition of any one of the three selected oxidants led to a satisfactory extraction, with Fe₂(SO₄)₃ being the best oxidant. Among the three studied oxidants, Fe₂(SO₄)₃ was selected due to being cheaper and safer to handle, in addition to achieving slightly more metal extraction. For [Bmim⁺HSO₄[−]], the extraction of Zn and In was the highest, followed by the typical EAFD impurity Fe. In contrast, irrespective of the ionic liquid and oxidant combination used, the Ga extraction remained low. [Bmim⁺Cl[−]] combined with the studied oxidants resulted in the low extraction of the target metals.

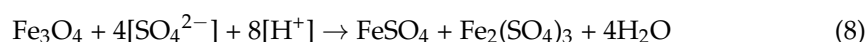
Consequently, the combination of $[\text{Bmim}^+\text{HSO}_4^-]$ with $\text{Fe}_2(\text{SO}_4)_3$ was selected as the most suitable for the optimisation in the rest of the experiments.

3.2. The Effect of Ionic Liquid Concentration

When it comes to leaching, the concentration of the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ plays a significant role due to its high viscosity. In its pure state, $[\text{Bmim}^+\text{HSO}_4^-]$ is very viscous (900 mPa) [30]. However, when mixed with water, there is a noticeable reduction in viscosity due to its acidic properties, as it can release protons into the aqueous phase [16,17,31]. To find the optimal concentration of $[\text{Bmim}^+\text{HSO}_4^-]$ required for metal extraction from EAFD, specific amounts of $[\text{Bmim}^+\text{HSO}_4^-]$ were mixed with deionised water to prepare different ionic liquid concentrations of 30, 40, 50, and 60% *v/v*. Experiments were carried out under the following conditions: 0.5 g of oxidant $\text{Fe}_2(\text{SO}_4)_3$, an S/L ratio of 1/20, a stirring speed of 500 rpm, and a temperature of 65 °C, and 2 mL leachate aliquots were withdrawn at regular time intervals over an 8 h period. Each leachate sample was then filtered and analysed with AAS and ICP to determine the amounts of extracted Fe, In, Ga, and Zn.

As can be seen in Figure 5, at concentrations of 50% and 60% $[\text{Bmim}^+\text{HSO}_4^-]$, the levels of extracted metals were lower than when the ionic liquid concentration was 30% and 40%. These results suggest that at higher concentrations (50% and 60% *v/v*) of $[\text{Bmim}^+\text{HSO}_4^-]$, the viscosity of the leaching solution is high enough to act as a barrier to the free movement and collision of ions, leading to less extraction. At the lower $[\text{Bmim}^+\text{HSO}_4^-]$ concentrations of 30% and 40% *v/v*, the extraction of target metals is possibly increased as a function of the balance between the reduced viscosity and the applicable concentration of the ionic liquid, in addition to the proper acidity that it provides, which gives rise to more comparable results. Of the elements of interest, Zn has the highest extraction, reaching 90% with a 40% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$ solution. This is due to the high solubility of ZnO in acidic solutions [6]. After Zn, In has the next highest extraction of 84%, followed by Fe with 70% under the same conditions. Conversely, Ga was found to have a low extraction level (<20%), irrespective of the $[\text{Bmim}^+\text{HSO}_4^-]$ concentration used. The extraction efficiency of the metals with 30% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$ was not significantly different to that with the 40% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$ solution. Consequently, in order to make any future extraction methodologies more economically viable, 30% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$ was selected as the optimal concentration and was used in further investigations.

An aqueous solution of $[\text{Bmim}^+\text{HSO}_4^-]$ containing $[\text{H}^+]$ and $[\text{SO}_4^{2-}]$ displays similar properties to a sulphuric acid solution (H_2SO_4) [16,18]. Similar to a leaching process using sulphuric acid, the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ solution can also be recycled and reused in the leaching process, which can justify its initial higher cost. Bearing this in mind, Reactions (6)–(8) are proposed to occur during the extraction of zinc and iron from their main sources, ZnO, ZnFe_2O_4 , and Fe_3O_4 , from EAFD in an acidic solution [6]:



3.3. The Effect of Oxidant Concentration

To examine the effect of the oxidant concentration on the extraction of Zn, In, Ga, and Fe (impurity) from EAFD, different amounts of $\text{Fe}_2(\text{SO}_4)_3$ (0.25, 0.5, 0.75, and 1 g) were added to 30% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$ as the leaching solution. As the results in Figure 6 indicate, increasing the amount of the oxidant improved the extraction of the metals of interest. This can be expected since the availability of higher concentrations of the oxidant would provide a stronger oxidative power to the leaching solution for metal extraction. The extraction of Fe improved from around 48% to 74% when the amount of the oxidant was increased from 0.25 g to 1 g. Although Zn was previously found to have a high level of extraction (Figure 6), further minor increases in extraction to over 90% were measured with

a 1 g addition of the oxidant. The extraction of In was also enhanced to 87%, whereas Ga extraction reached 18.7% with an increase to 1 g of $\text{Fe}_2(\text{SO}_4)_3$.

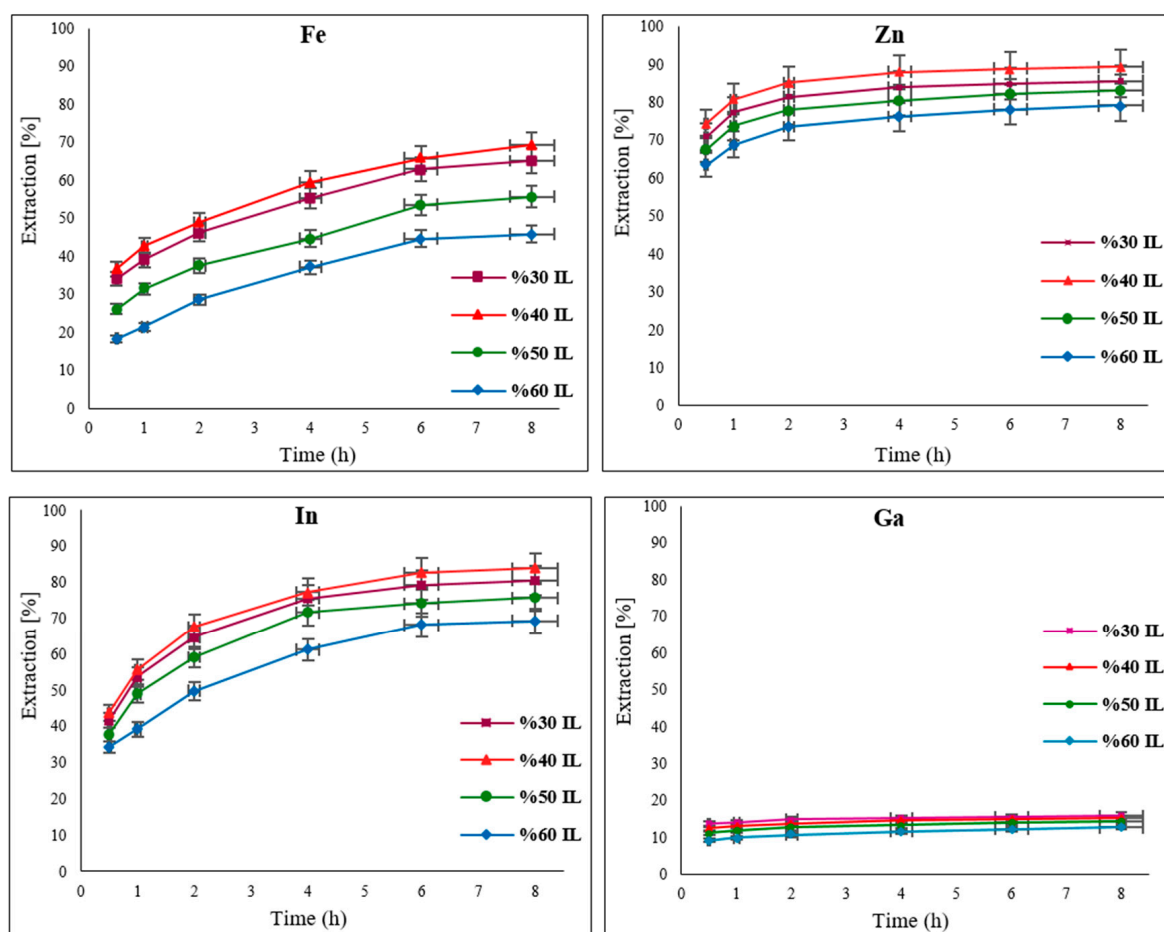


Figure 5. Effect of different concentrations of $[\text{Bmim}^+\text{HSO}_4^-]$ of 30, 40, 50, and 60% *v/v* on the extraction of Fe, Zn, In, and Ga from EAFD. Experimental conditions: 50 mL of ionic liquid solution with specified concentrations, oxidant $\text{Fe}_2(\text{SO}_4)_3$ (0.5 g), S/L ratio of 1/20, stirring speed of 500 rpm, temperature of 65 °C, and total leaching time of 8 h.

3.4. Effect of Solid-to-Liquid (S/L) Ratio

In a leaching process, which typically involves a heterogeneous solid–liquid reaction, the correct ratio of solid to liquid (S/L) is important. To determine the optimal ratio, different amounts of EAFD were added to 50 mL of 30% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$ to make the following S/L ratios: 1/25, 1/20, 1/15, and 1/10. It was observed that the different S/L ratios had slightly different effects on the extraction of the studied elements (Figure 7). For Fe, a ratio of 1/15 resulted in over 73% extraction. In the case of Zn, higher extraction occurred when there was more solid (EAFD) available in the leaching solution [6]; therefore, a ratio of 1/10 provided the best results for Zn, with 91% extraction. In the case of In and Ga, a ratio of 1/25 was ideal, with about 80% In and 17% Ga extracted. Depending on the mineralogy of materials, a high amount of solid in the leaching solution can sometimes contribute to ineffective mixing within the solution. This is due to the higher-density mixture causing ineffective dispersion and mass transfer within the mixture [32–35]. With a high amount of solid in the mixture, the amount of the ionic liquid solution can also be a limiting reagent in the dissolution reaction. From Figure 7, to compromise between the different trends in leaching with varying S/L ratios, an S/L ratio of 1/20 was selected as the optimal compromise for the remainder of the experiments since it produced higher In and Ga extraction, as well as reasonable Zn and Fe extraction. It was also observed that no

significant further extraction of the elements of interest takes place beyond 4 h of leaching. Therefore, the following experiments at different temperatures were conducted for up to 4 h (240 min) of total leaching time.

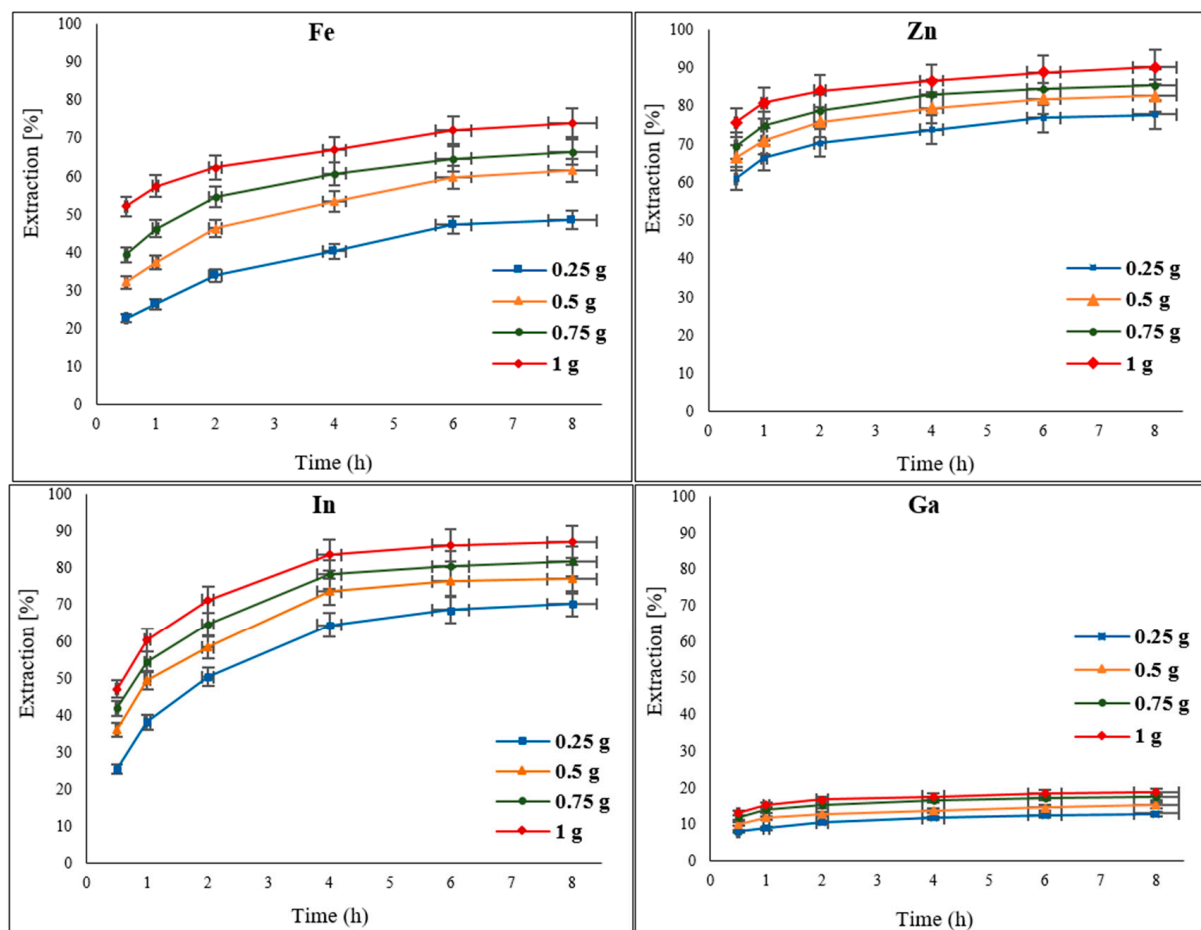


Figure 6. Effect of different concentrations of the oxidant $\text{Fe}_2(\text{SO}_4)_3$ (0.25, 0.5, 0.75, and 1 g) on the extraction of Fe, Zn, In, and Ga from EAFD. Experimental conditions: 50 mL of 30% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$, S/L ratio of 1/20, stirring speed of 500 rpm, temperature of 65 °C, and total leaching time of 8 h.

3.5. Effect of Temperature

The influence of temperature on the leaching of the target metals from EAFD in 30% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$ was examined by varying the temperature from 55 to 85 °C. Generally, when increasing the temperature, the extraction of the metals improved due to enhanced diffusion and the increased rate of the reaction [17,20,21,32]. Results displaying the extraction of Fe, Zn, In, and Ga at regular time intervals of 10, 20, 30, 45, 60, 90, 120, 180, and 240 min are presented in Figure 8. The influence of increasing temperature is more significant for Fe than for Zn; hence, there is a noticeable improvement in Fe extraction from 55.5% at 55 °C to 80.2% at 85 °C. Although Zn extraction was initially high (77.6% at 55 °C), there was still a noticeable increase to 92.7% when the temperature was raised to 85 °C. Indium extraction improved significantly from 67.5% to 80.9% with a change in temperature from 55 to 65 °C. With a further temperature increase to 85 °C, In extraction reached over 97%. There was also a discernible improvement in Ga extraction to almost 18% at the maximum studied temperature of 85 °C. These results show that the extraction of the target metals increases significantly in the first hour, after which it becomes more moderate with extended leaching time.

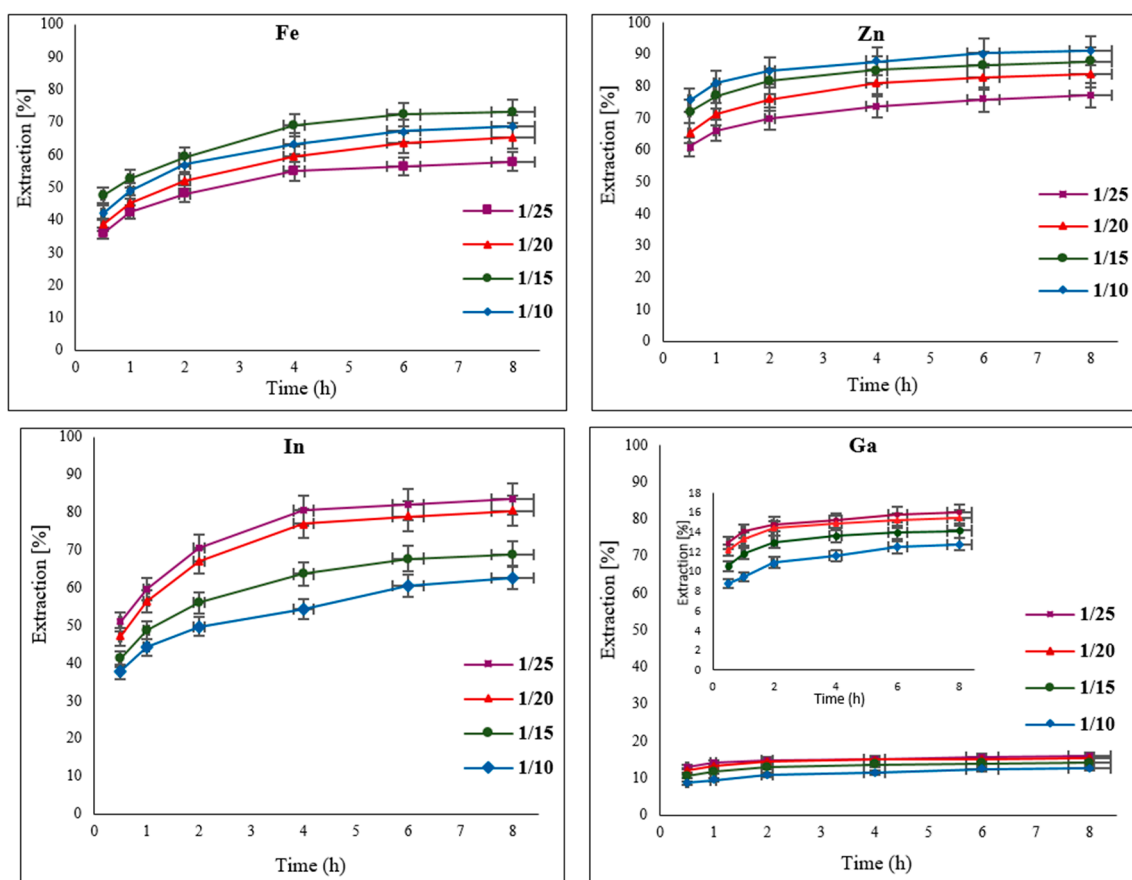


Figure 7. Effect of different solid-to-liquid (S/L) ratios (1/25, 1/20, 1/15, and 1/10) on the extraction of Fe, Zn, In, and Ga from EAFD. Experimental conditions: 50 mL of 30% *v/v* [Bmim⁺HSO₄[−]], 1 g of oxidant Fe₂(SO₄)₃, stirring speed of 500 rpm, temperature of 65 °C, total leaching time of 8 h.

3.6. Kinetic Study

To study the kinetics of Fe, Zn, In, and Ga dissolution in the 30% *v/v* [Bmim⁺HSO₄[−]] solution with the oxidant Fe₂(SO₄)₃ (1 g), the experimental results from varying the temperature from 55 to 85 °C were evaluated with the shrinking-core model. The functions from this model considered the surface chemical reaction $[(1 - (1 - X)^{1/3}) = k.t]$, diffusion through the product $[1 - 3(1 - X)^{2/3} + 2(1 - X) = k.t]$, and diffusion through the liquid film $[X = k.t]$, where k is the apparent rate constant, and X is the concentration of the leachate from the leached solution. Each function was plotted over time (min), and the graph that produced straight lines with correlation coefficients (R^2) close to 1 was considered suitable for the fitting of the experimental results and estimating the kinetic model controlling the dissolution reaction [36]. Accordingly, it was found that the kinetics of the dissolution of Fe, Zn, In, and Ga were best described by diffusion through the product. This suggested kinetic model agrees well with a previous study that also followed a diffusion-controlled model [6].

Figure 9 illustrates the fitness of the diffusion equation over time for Fe, displaying straight lines for each studied temperature. The graph clearly shows that the dissolution reaction was faster with a steeper slope in the first hour of leaching before becoming more moderate. The reason for this could be that more EAFD and oxidizing reagent, which helps leaching, were accessible to extract Fe from the easily extractable magnetite (Fe₃O₄) before they gradually decreased such that Fe needed to be subsequently extracted from a refractory phase such as zinc ferrite (ZnFe₂O₄), which is a slower and/or more difficult process and which reduces the rate of extraction.

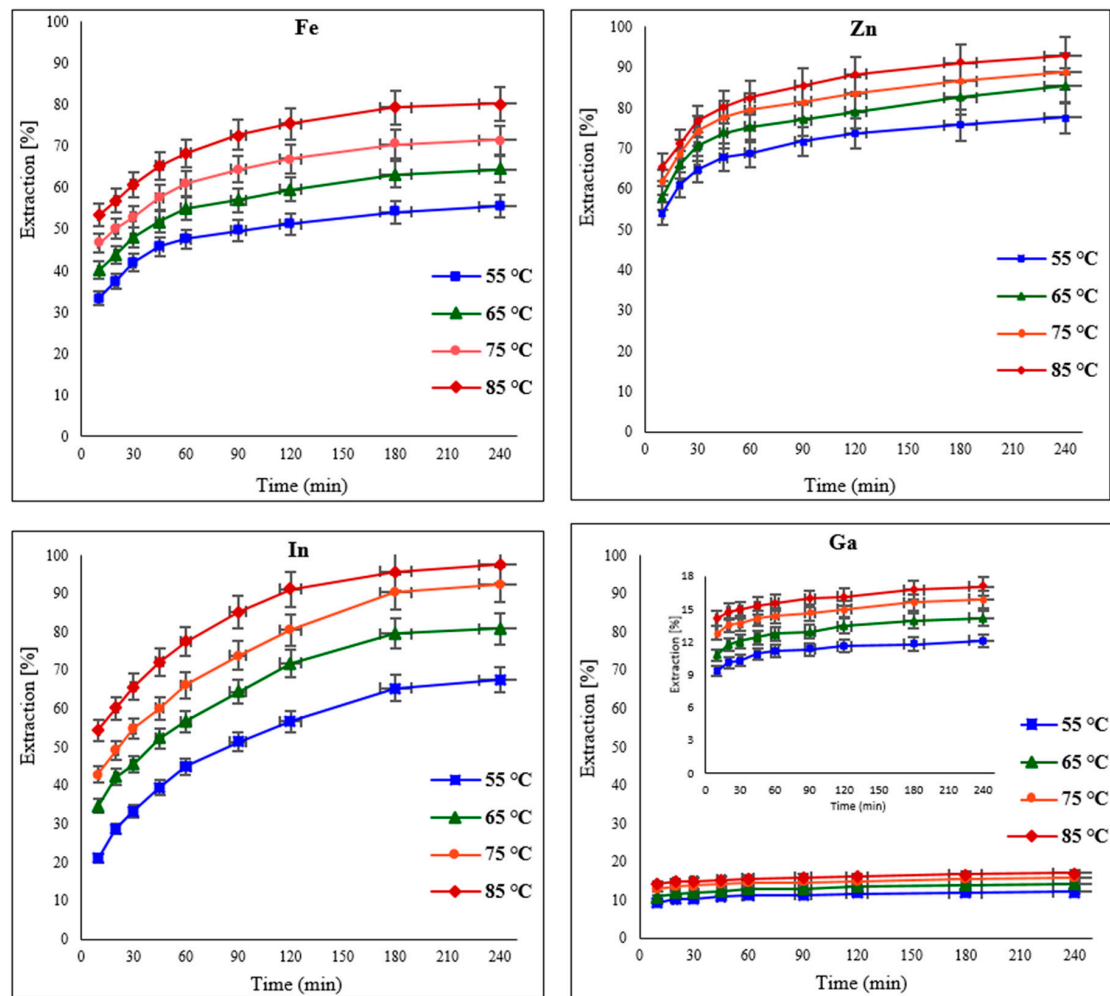


Figure 8. Effect of varying temperatures (55, 65, 75, and 85 °C) on the extraction of Fe, Zn, In, and Ga from EAED. Experimental conditions: 100 mL of 30% *v/v* [Bmim⁺HSO₄[−]], 1 g of oxidant Fe₂(SO₄)₃, S/L ratio of 1/20, stirring speed of 500 rpm, and total leaching time of 4 h (240 min).

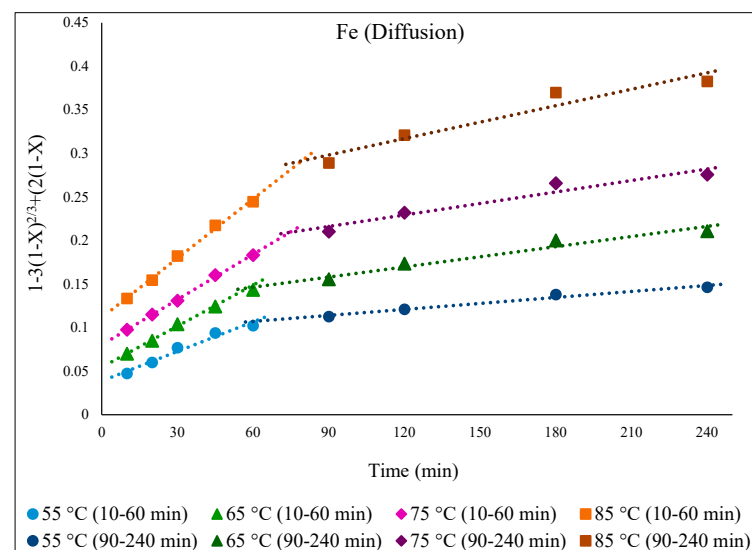


Figure 9. Graph of $[1 - 3(1 - X)^{2/3} + 2(1 - X) = k \cdot t]$ over time at different temperatures of 55–85 °C for the dissolution of Fe from EAED in 30% *v/v* [Bmim⁺HSO₄[−]] solution with 1 g of oxidant Fe₂(SO₄)₃.

By applying the Arrhenius equation, $k = Ae^{-E_a/RT}$, from the plot of $\ln k$ vs. the inverse of the studied temperatures ($1000/T$), the activation energy (E_a) for each part of the reaction can be obtained from the slope in Figure 10 (slope = $-E_a/R$). As expected, E_a for the initial part of the curve—which comprises Fe extraction from a more easily extractable phase (Fe_3O_4)—was lower than the second portion, which is related to Fe extraction from a phase that is more chemically resistant (ZnFe_2O_4), with calculated values of 20.8 and 34.6 kJ/mol respectively.

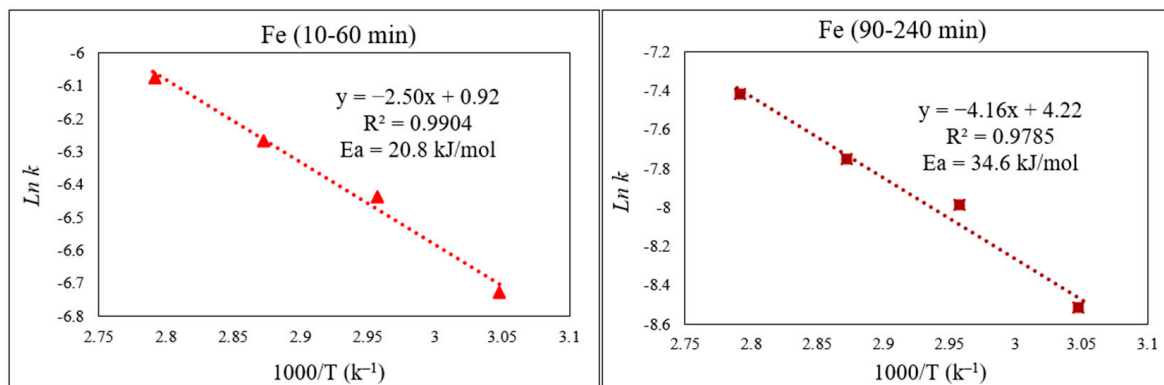


Figure 10. Arrhenius graph of $\ln k$ vs. $1000/T$ for the first part (10–60 min) and the second part (90–240 min) of Fe extraction.

As for Fe, the kinetic process of Zn extraction was also governed by diffusion. Figure 11 demonstrates the functionality of the diffusion equation over time (min), displaying linear relationships for Zn extraction at different temperatures (55 to 85 °C). In general, the extractable Zn comes primarily from the ZnO phase, with a minor contribution from the slower-dissolving refractory ZnFe_2O_4 phase. Towards the latter part of the reaction, i.e., after 1 h, the extracted Zn originates mostly from the ZnFe_2O_4 phase, as the ZnO phase has already largely dissolved [6,11].

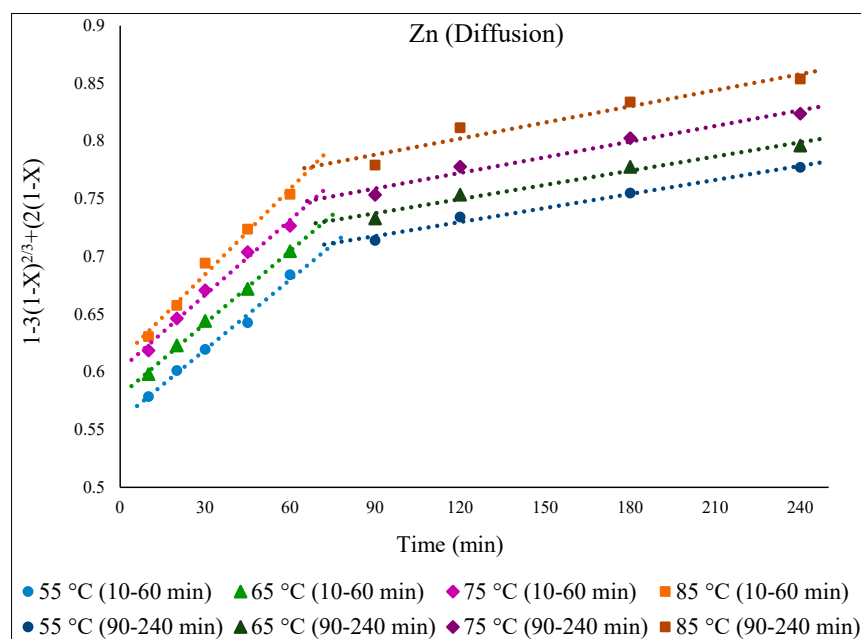


Figure 11. Plot of $[1 - 3(1 - X)^{2/3} + 2(1 - X) = k.t]$ over time (min) showing progress at different temperatures of 55–85 °C for the dissolution of Zn from EAFD in 30% v/v $[\text{Bmim}^+\text{HSO}_4^-]$ solution with 1 g of oxidant $\text{Fe}_2(\text{SO}_4)_3$.

From the Arrhenius plots (Figure 12), the obtained E_a for the initial part of the Zn extraction was 7.4 kJ/mol, whereas for the second part, E_a = 8.2 kJ/mol. These noticeably low activation energies for Zn extraction, irrespective of the Zn-containing phase, clearly explain the faster dissolution of Zn and its higher extraction yield compared to those of Fe.

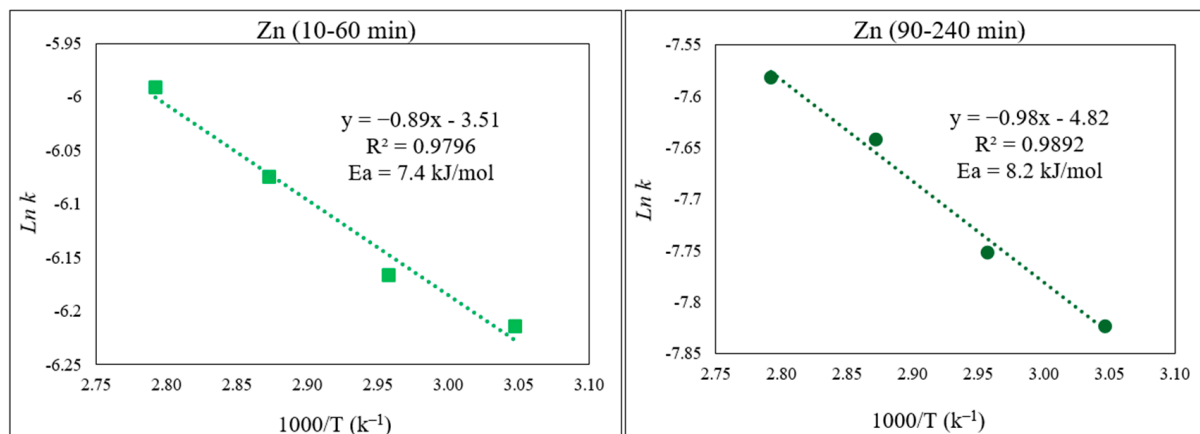


Figure 12. Arrhenius plot of $\ln k$ vs. $1000/T$ for Zn for the first part of the extraction (10–60 min) and the second part (90–240 min) of the extraction.

Figure 13 presents the kinetic dissolution process of In in the 30% *v/v* [Bmim⁺HSO₄[−]] solution controlled by the diffusion model. The process for In extraction takes place in a single step for each studied temperature, with R^2 values close to one indicating a good fit. The activation energy determined from the plot of $\ln k$ vs. $1000/T$ was 33.6 kJ/mol (Figure 14), which is in good agreement with a diffusion-controlled process [31,36].

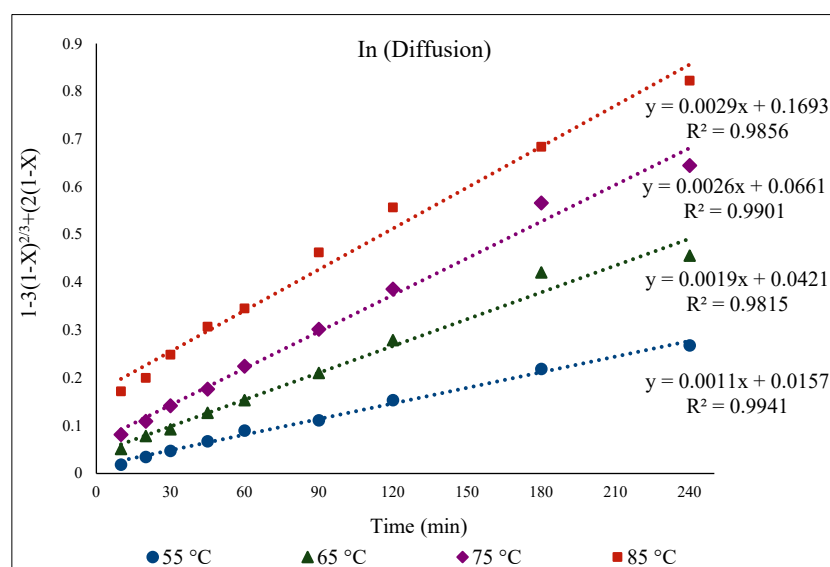


Figure 13. $[1 - 3(1 - X)^{2/3} + 2(1 - X)] = k \cdot t$ over time (min) for temperatures from 55 to 85 °C for In extraction in 30% *v/v* [Bmim⁺HSO₄[−]] solution with 1 g of oxidant Fe₂(SO₄)₃.

There was a low extraction yield of Ga throughout this work, most likely due to Ga being inherently less active or soluble in the ionic liquid medium. Nevertheless, the kinetics of Ga dissolution in the 30% *v/v* [Bmim⁺HSO₄[−]] solution (Figure 15) correlated well with the diffusion-controlled model, again showing two distinct kinetic regions. The activation energy for Ga in the first part of the extraction (10–45 min) was 12.2 kJ/mol, and it was 30.3 kJ/mol in the second part, correlating with the slower Ga extraction depicted in Figure 16.

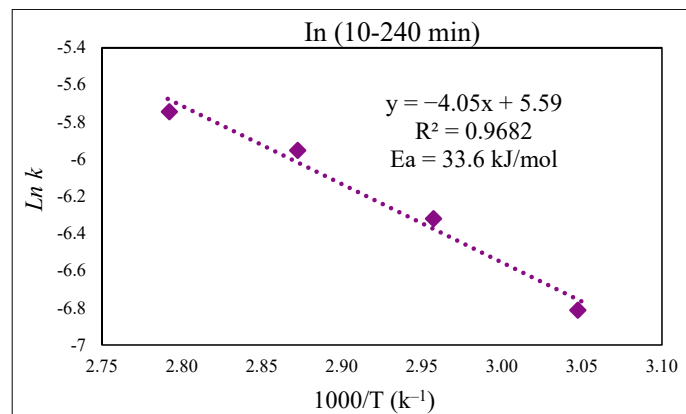


Figure 14. Arrhenius graph of $\ln k$ vs. $1000/T$ for In.

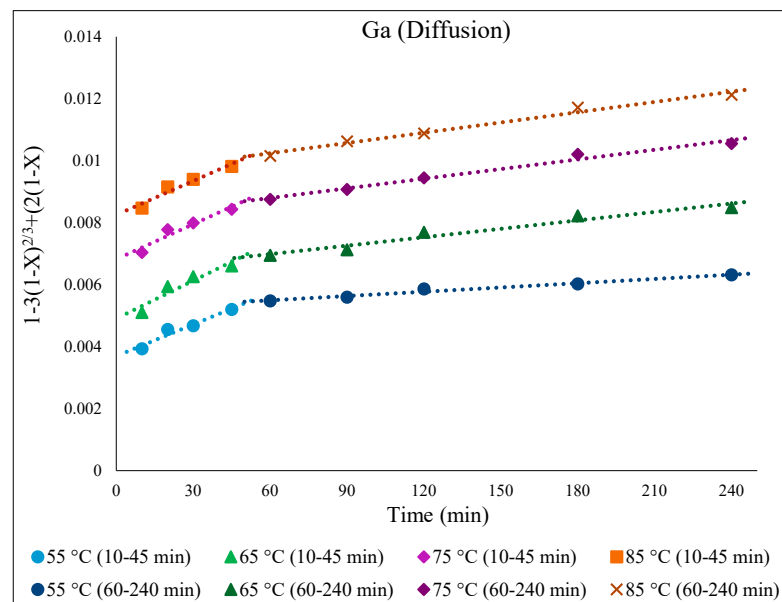


Figure 15. $[1 - 3(1 - X)^{2/3} + 2(1 - X) = k.t]$ over time (min) for temperatures from 55 to 85 °C for Ga extraction in 30% v/v $[\text{Bmim}^+\text{HSO}_4^-]$ solution with 1 g of oxidant $\text{Fe}_2(\text{SO}_4)_3$.

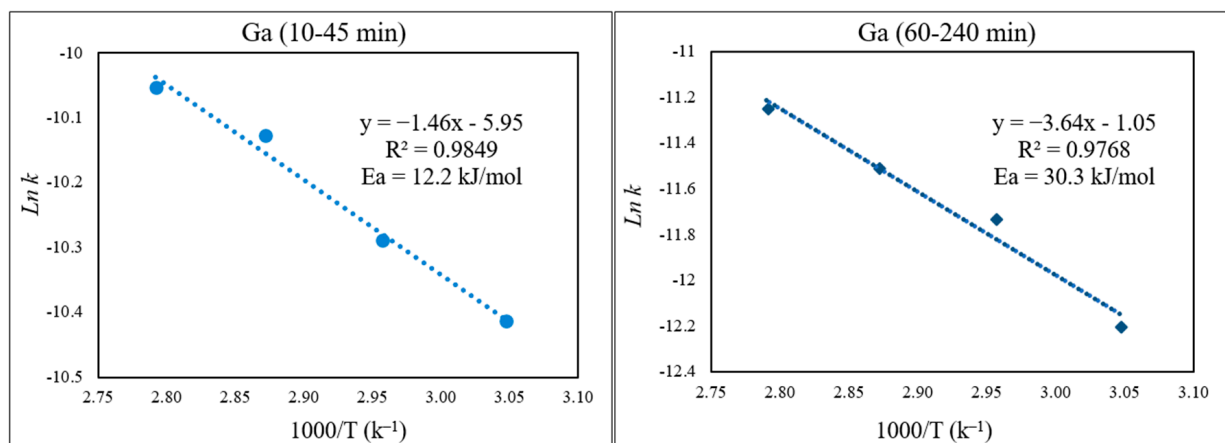


Figure 16. Arrhenius plot of $\ln k$ vs. $1000/T$ for Ga for the first part (10–45 min) and the second part (60–240 min) of the extraction.

The kinetic model controlling the dissolution of target metals in a leaching system can be predicted from the magnitude of the activation energy that a process requires. Typically, activation energies below 40 kJ/mol indicate a diffusion-controlled process, while values greater than 40 kJ/mol indicate chemical reaction control [31,36,37]. Therefore, in this research, the activation energies for Fe, Zn, In, and Ga were all below 40 kJ/mol and in the range of diffusion-controlled processes. Table 2 also lists the extraction efficiency and activation energies for Zn and Fe extraction from EAFD using a 1 M H₂SO₄ solution at temperatures from 20 to 95 °C, adapted from work conducted by Kukurugya et al. (2015) [6], to compare to the results obtained in this work using a 30% v/v [Bmim⁺HSO₄[−]] solution.

Table 2. The values for activation energy and extraction efficiency (%E) for Zn and Fe.

Reagent Used	E _a for Zn (kJ/mol)		%E Zn	E _a for Fe (kJ/mol)		%E Fe	Reference
	1st Part	2nd Part		1st Part	2nd Part		
1 M H ₂ SO ₄	1.7	42.3	87%		35.6	79%	[6]
30% v/v [Bmim ⁺ HSO ₄ [−]]	7.4	8.2	92.7%	20.8	34.6	80.2%	This research

While the recoveries of Fe and Zn in both media are very similar, the activation energies in the ionic liquid medium are generally lower, indicating that it is potentially a more favourable medium to use for leaching. Because it is recyclable, it supports the decision to use ionic liquid [Bmim⁺HSO₄[−]] as a leachant.

3.7. Analysis of the Solid Residue

3.7.1. XRD Analysis

The EAFD sample (before leaching) and the residue (after leaching in 30% v/v [Bmim⁺HSO₄[−]] solution at temperatures from 55 to 85 °C) were examined by XRD and compared to another experiment with 2 M H₂SO₄ at 85 °C. As can be seen in Figure 17, the EAFD before leaching mostly contains ZnO, ZnFe₂O₄, and Fe₃O₄, as well as small amounts of Ca(OH)₂, PbO, MnO₂, and MgO. After leaching in 30% v/v acidic ionic liquid [Bmim⁺HSO₄[−]], the intensity of the peaks belonging to ZnO and Fe₃O₄ decreased considerably, indicating their dissolution, while some of the ZnFe₂O₄ phase, which has a refractory nature, remained. In addition, some crystalline phases, such as PbSO₄ and CaSO₄, appeared in the XRD pattern after leaching. It was noticed that by increasing the temperature of the extraction process, the intensity of the peaks indicating different phases, including ZnFe₂O₄, decreased, indicating that the further dissolution of these phases occurred. The XRD pattern for the residue in the 30% v/v [Bmim⁺HSO₄[−]] solution was similar to that in 2 M H₂SO₄, showing that the acidic ionic liquid [Bmim⁺HSO₄[−]] can act similarly to H₂SO₄ as a leaching solution [5,6].

3.7.2. PSD Analysis

The particle size of the leached residue of EAFD was inspected using laser diffraction to determine whether the size of particles changed after leaching in the 30% v/v [Bmim⁺HSO₄[−]] solution. Figure 18 displays the frequency and cumulative distributions of the studied EAFD before and after leaching at temperatures of 65 and 85 °C. The graph shows that the size of the particles decreased after leaching compared to the unleached sample, as well as the occurrence of smaller particles at the higher temperature (85 °C). This is indicative of the particle dissolution that takes place as the metals are extracted.

3.7.3. SEM-EDS Analysis

Backscattered electron (BSE) scanning electron microscopy in conjunction with energy-dispersive spectroscopy (SEM-EDS) was utilised to acquire additional information about the morphology and mineralogical species involved in the studied EAFD. Figure 19 displays the SEM-EDS analysis of the EAFD before leaching, which provides the chemical composition

(Table 3) and the coloured map of the main elements in the examined area. The main elements detected by SEM-EDS were Zn (38.5%), O (27.5%), Fe (20.4%), Ca (3.5%), and Mn (2.6%), which correspond to the main phases identified by XRD as ZnO, ZnFe₂O₄, Fe₃O₄, and traces of Ca(OH)₂ and MnO₂. From a morphological point of view, the EAFD has spherical-shaped fine-grained particles in an agglomerated form with some small rectangular particles. Based on the observation of the morphology and chemical content, the spherical particles have considerable amounts of Fe and Zn, whereas the rectangular particles have a high Ca content. This observation agrees with other research on leaching EAFD in sulphuric acid [5,6,10].

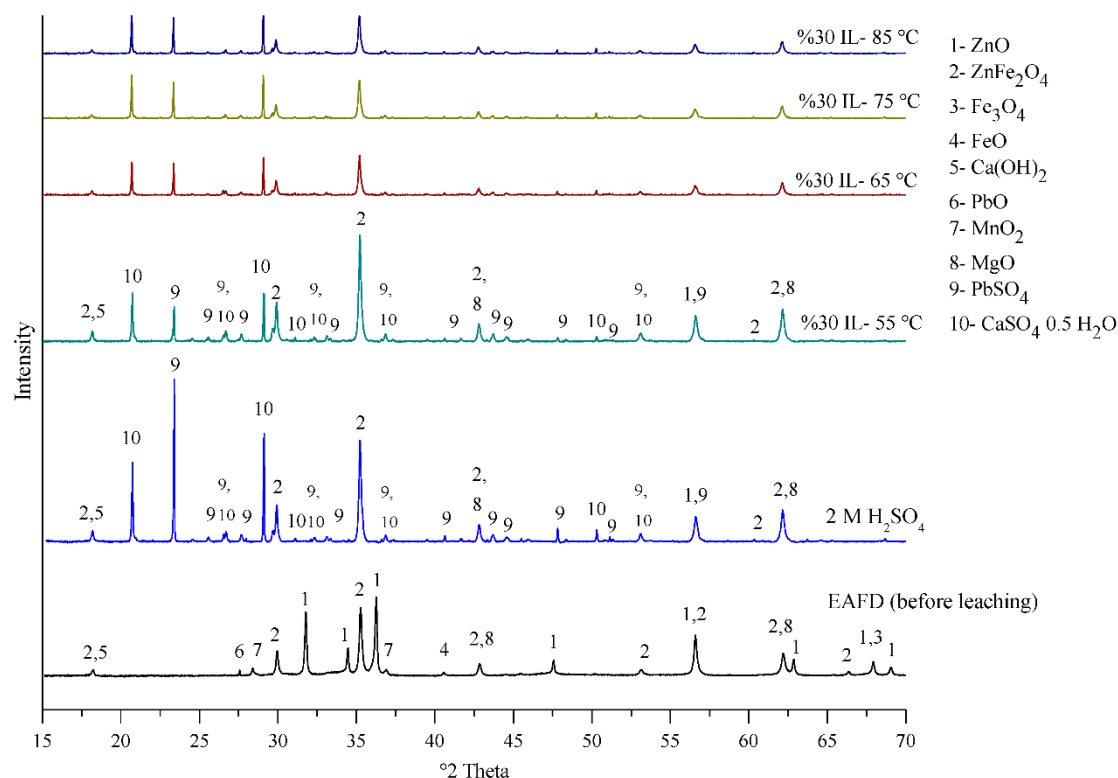


Figure 17. XRD pattern of EAFD before and after leaching in 30% *v/v* [Bmim⁺HSO₄[−]] solution at different temperatures (55 to 85 °C) and in 2 M H₂SO₄ (85 °C) for comparison.

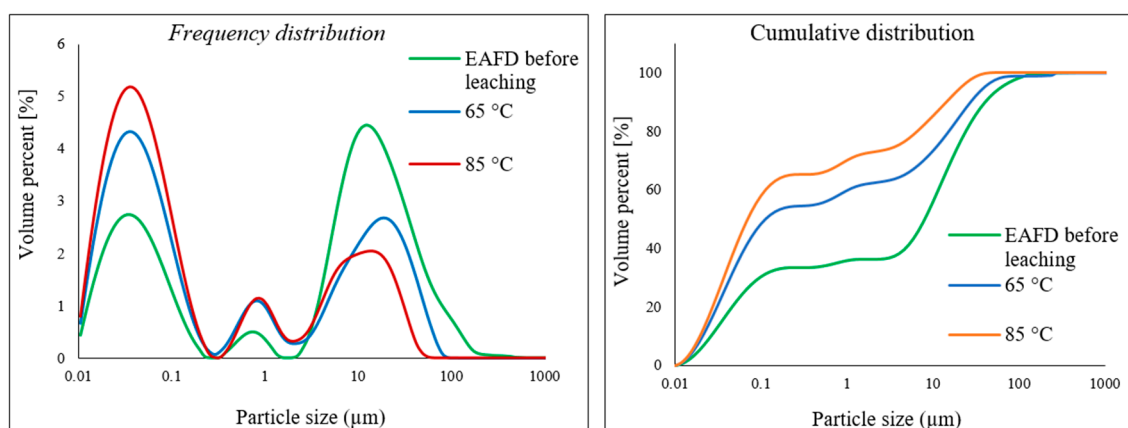


Figure 18. Comparing the PSD of the EAFD before leaching and the particles leached in 30% *v/v* [Bmim⁺HSO₄[−]] solution at 65 and 85 °C.

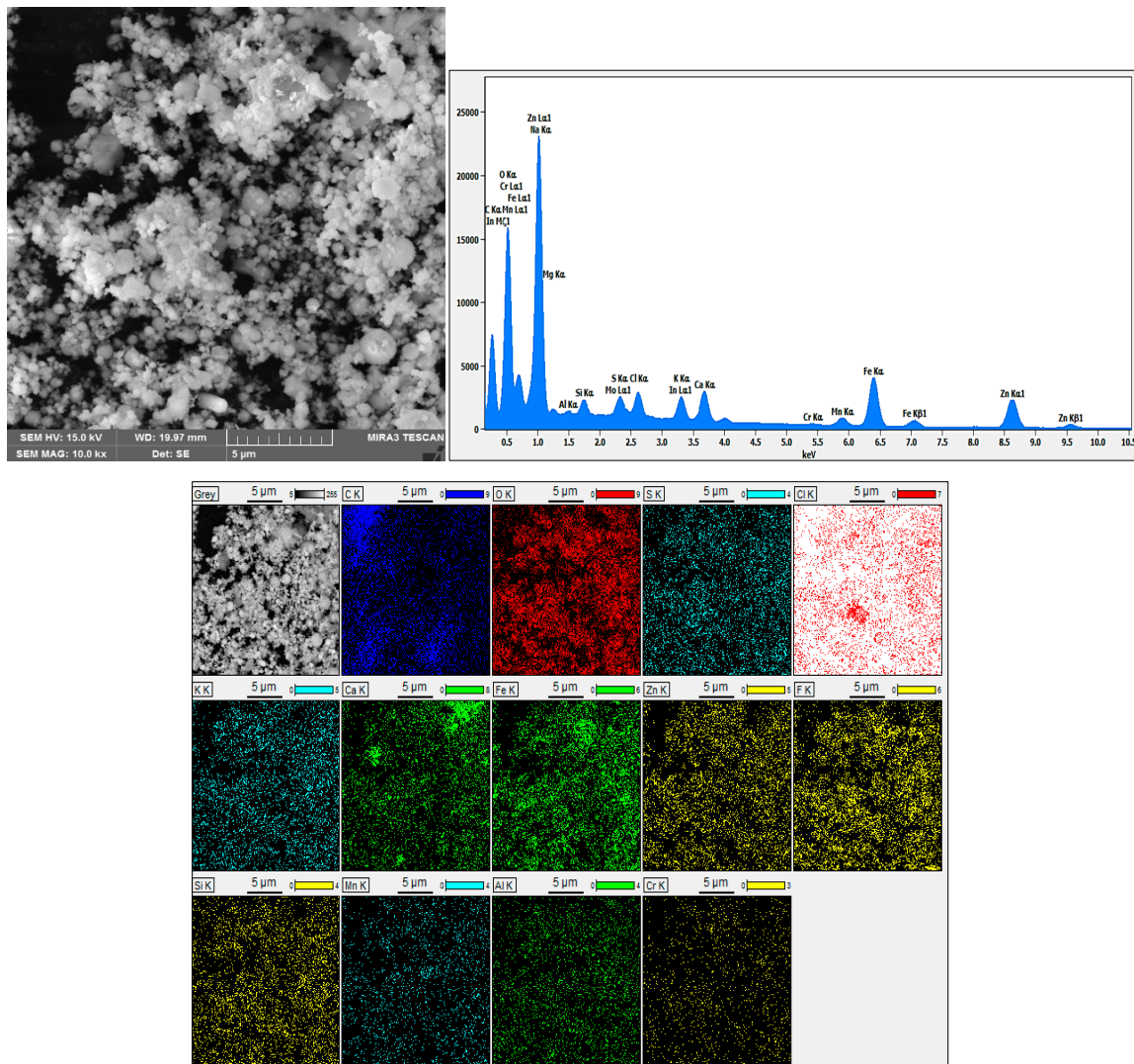


Figure 19. SEM-EDS image of EAFD before leaching, with the chemical composition and the coloured map of the elements in the examined area.

Table 3. The chemical composition of the elements in the examined area.

Element	Content [wt.%]
Zn	38.5
O	27.5
Fe	20.4
Ca	3.5
Mn	2.6
K	1.97
Mo	1.96
Cl	1.19
Si	1.14
S	0.41
Mg	0.39
Al	0.28
Cr	0.24
Total	100

The EAFD residue after leaching in the 30% v/v [Bmim⁺HSO₄[−]] solution at different temperatures (55 to 85 °C) was also examined with SEM-EDS (Figure 20). After leaching,

some needle-shaped crystals appeared, which were found to be calcium sulphate $\text{Ca}(\text{SO}_4)$ crystals. No obvious differences appeared in the leached residue attributable to the different leaching temperatures used.

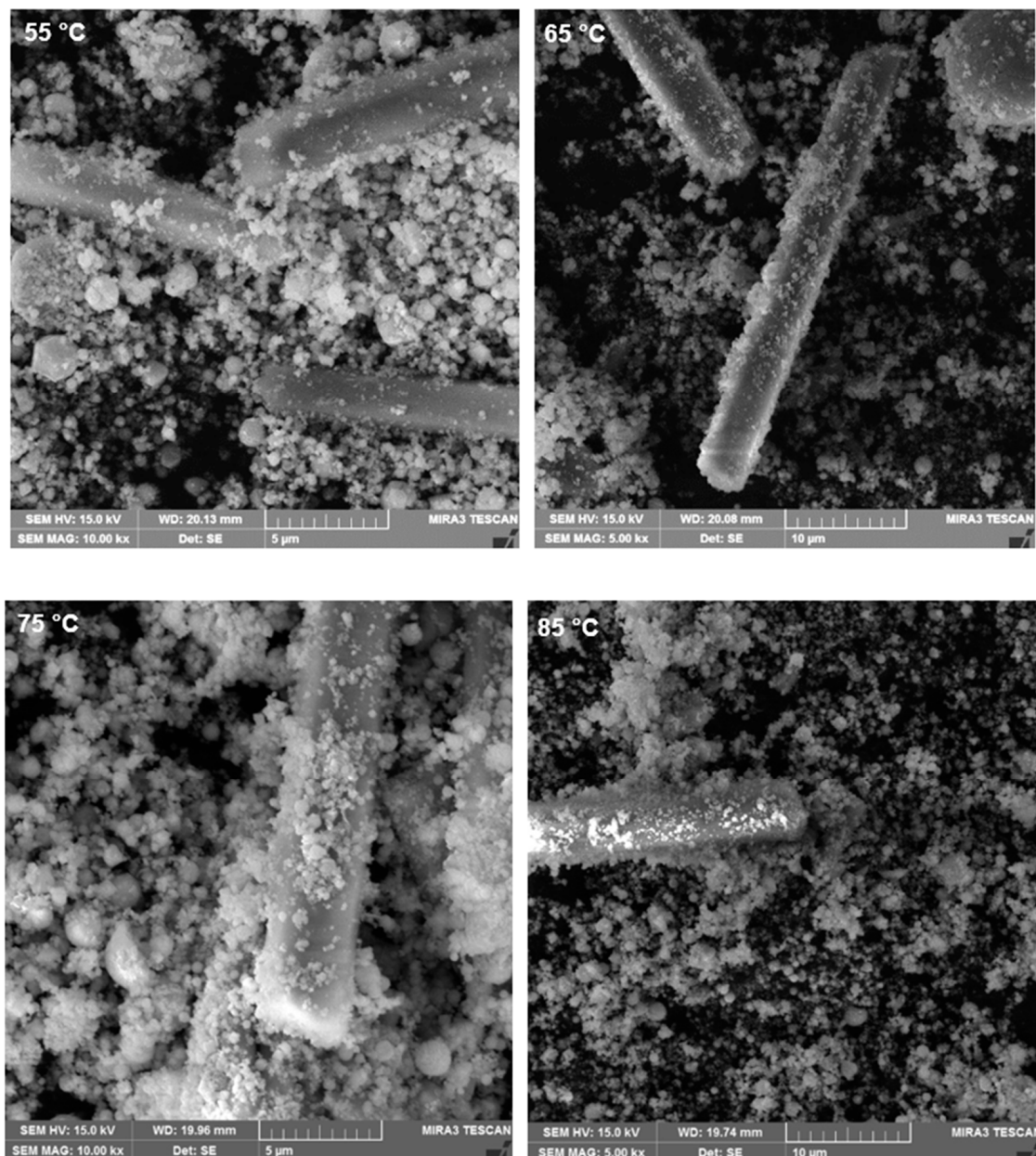


Figure 20. SEM images of the EAFD residue after leaching in 30% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$ solution at different temperatures (55 to 85 °C).

Figure 21 demonstrates a more detailed SEM-EDS analysis of the EAFD residue after leaching in the 30% *v/v* $[\text{Bmim}^+\text{HSO}_4^-]$ solution at 85 °C. Points 1 and 4 are directed at a bright semi-round-shaped particle mostly consisting of Pb, O, and S, which were most likely PbSO_4 particles. Points 2 and 5 focus on the needle-shaped crystal, confirming it comprised CaSO_4 , since it had high Ca, S, and O contents. Point 3 focuses on a round-shaped particle mostly containing Fe, Zn, and O, indicating that this was most likely ZnFe_2O_4 . Table 4 summarises the chemical composition determined at each point under examination.

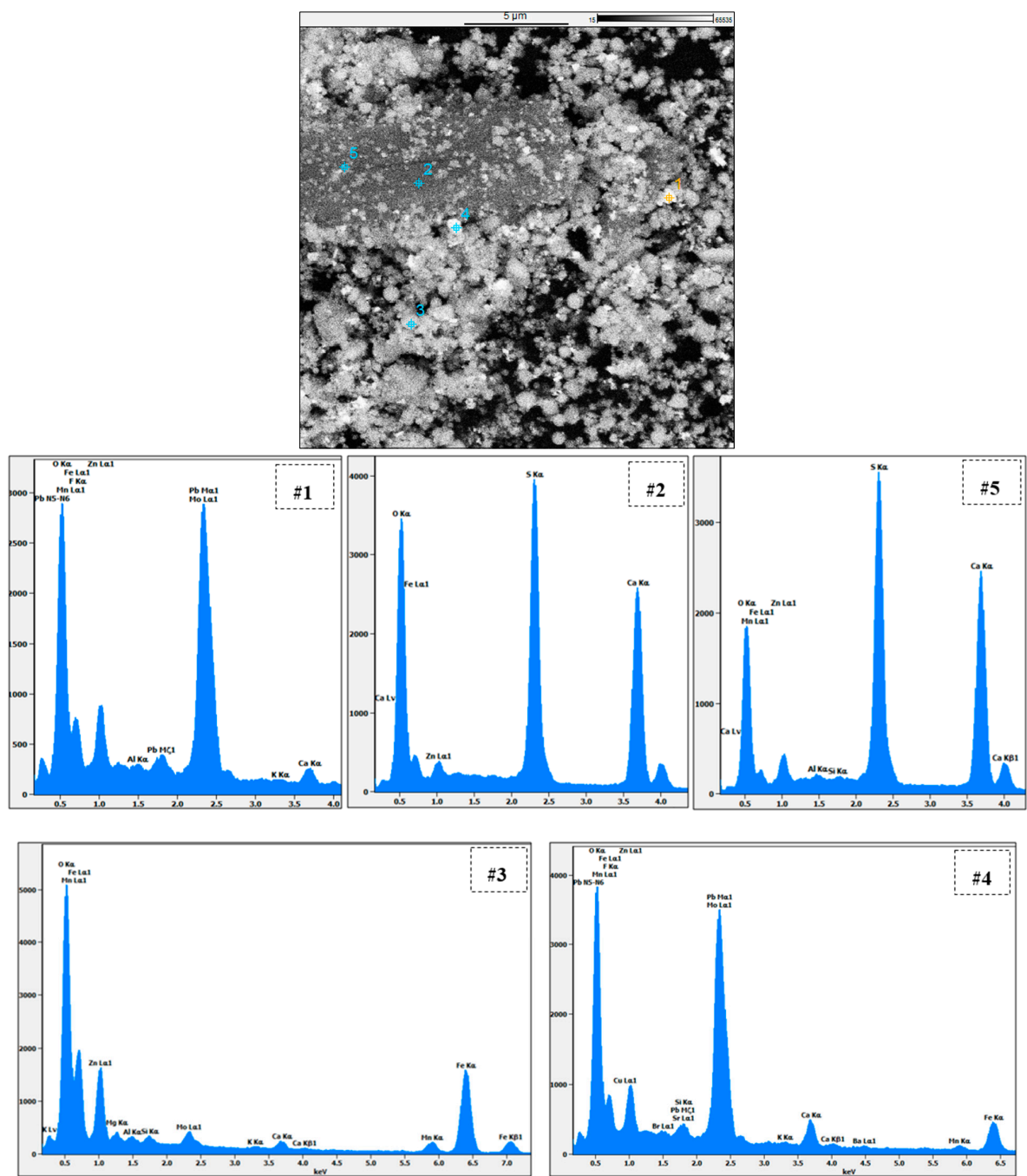


Figure 21. Point analysis with SEM-EDS of the EAFD leach residue in 30% *v/v* [Bmim⁺HSO₄[−]] at 85 °C.

Table 4. Chemical composition of the selected points (1 to 5) on the EAFD residue leached in 30% *v/v* [Bmim⁺HSO₄[−]] at 85 °C.

Area	Content [wt.%]													
	Zn	O	Fe	Pb	Mo	Mn	Mg	Ca	Cu	K	S	Si	F	Al
#1	5.6	31	15.7	27.7	11.0	1.8	—	1.5	—	0.22	3.2	—	1.9	0.33
#2	1.6	52.1	6.7	—	—	0.51	—	21.7	—	—	17.4	—	—	—
#3	11.2	36.4	42.9	—	2.8	3.2	1.01	0.1	—	0.13	—	0.7	—	0.5
#4	4.5	38.6	10.7	13.8	21.4	1.4	—	2.8	1.35	0.18	2.2	0.33	1.9	—
#5	5.1	40.3	8.5	—	—	1.1	—	25.1	—	—	19.7	0.11	—	0.19

Figure 22 presents a scheme for the proposed treatment process(es) of EAFD leaching showing the residue and the leached solution with the different metallic elements, as well as the recovery methods.

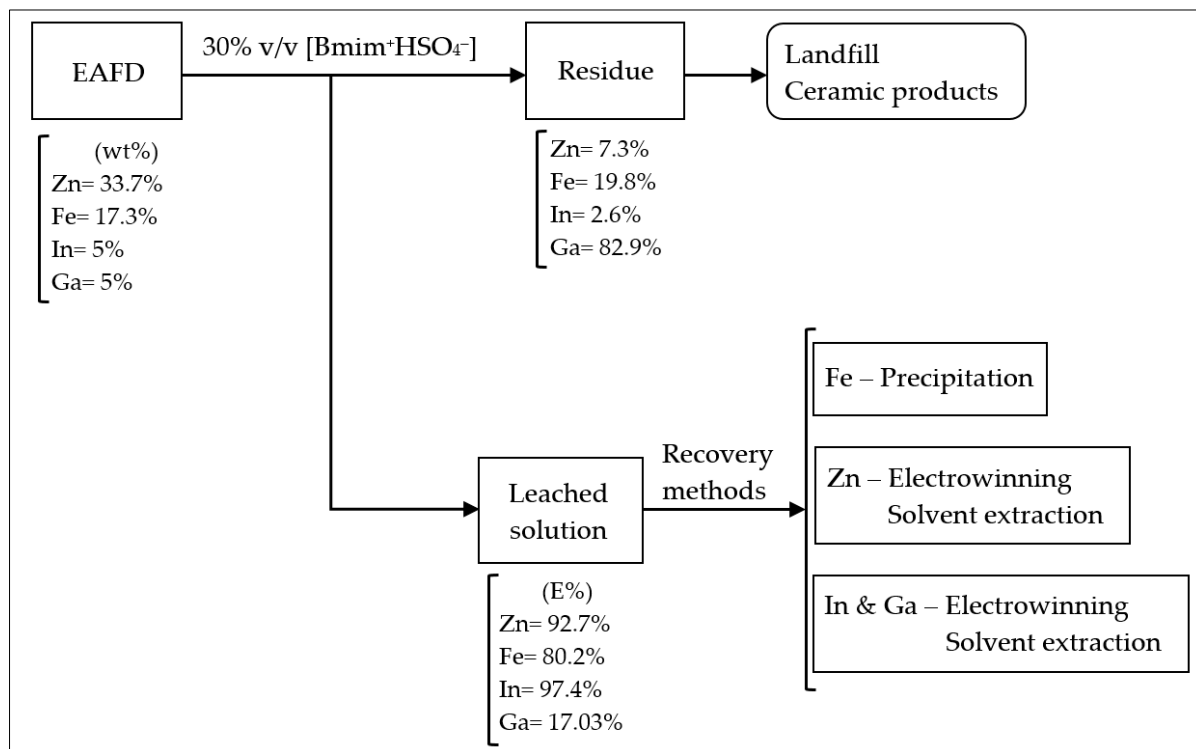


Figure 22. A scheme for the proposed treatment process(es) of EAFD leaching showing the residue and the leached solution.

4. Conclusions

This research focused on a new hydrometallurgical technique using ionic liquids for the extraction of Zn, In, and Ga, as well as Fe as a common impurity, from EAFD, combined with oxides of In and Ga simulating industrial waste. Two ionic liquids, $[\text{Bmim}^+\text{HSO}_4^-]$ and $[\text{Bmim}^+\text{Cl}^-]$, were tested with three oxidants, $\text{Fe}_2(\text{SO}_4)_3$, KMnO_4 , and H_2O_2 , to determine the best combination of ionic liquid and oxidant to extract the target metals.

The results showed that the optimal combination was $[\text{Bmim}^+\text{HSO}_4^-]$ and $\text{Fe}_2(\text{SO}_4)_3$. Influential experimental parameters such as the concentration of the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$, oxidant concentration, solid-to-liquid ratio, time, and temperature were optimised to find the optimal conditions for the maximum extraction of all of the target metals. The experimental observations were as follows:

- The obtained optimal extraction conditions were 30% v/v $[\text{Bmim}^+\text{HSO}_4^-]$, 1 g of $[\text{Fe}_2(\text{SO}_4)_3]$ oxidant, an S/L ratio of 1/20, and a 4 h leaching time at a temperature of 85 °C.
- Under these optimal conditions, the maximum extraction obtained was 92.7% Zn, with a simultaneous Fe dissolution of 80.2%
- If In and Ga were present in the studied raw material, up to 97.4% In and 17.03% Ga extraction could be achieved from oxide phases with 30% v/v $[\text{Bmim}^+\text{HSO}_4^-]$ as the leaching solution; hence, the process is not very successful for Ga extraction.
- The dissolution kinetics of the target metals in the 30% v/v $[\text{Bmim}^+\text{HSO}_4^-]$ solution from EAFD in the temperature range of 55–85 °C was diffusion-controlled.
- The dissolution of the desired metals was faster in the first hour of leaching, before becoming more moderate.

- The calculated activation energy for the dissolution reactions of all four elements investigated indicated diffusion-controlled reaction kinetic processes, as the activation energy remained below 40 kJ/mol.

The main phases of EAFD identified by XRD were ZnO, ZnFe₂O₄, and Fe₃O₄, with traces of Ca(OH)₂ and MnO₂. After leaching in the 30% *v/v* [Bmim⁺HSO₄[−]] solution, the intensity of the ZnO and Fe₃O₄ peaks decreased substantially, indicating their dissolution. The peaks of the ZnFe₂O₄ phase, which is naturally refractory, remained, and the intensity decreased with increasing temperature, indicating further dissolution. In addition, PbSO₄ and CaSO₄ phases appeared in the XRD patterns.

- The SEM-EDS analysis revealed that the morphology of the studied EAFD was agglomerated spherical-shaped fine-grained particles. After leaching, needle-shaped calcium sulphate (CaSO₄) crystals appeared.
- PSD analysis showed that the size of the particles decreased after leaching in the 30% *v/v* [Bmim⁺HSO₄[−]] solution when compared to the unleached sample. Moreover, the higher the temperature, the smaller the particles became.

The advantage of using acidic ionic-liquid-like [Bmim⁺HSO₄[−]] as the leaching solution for metal extraction is that the ionic liquid is potentially recyclable and can be used again in the leaching process, which can reduce operational costs in the long run. As this study has shown, when compared to sulphuric acid, the ionic liquid [Bmim⁺HSO₄[−]] achieved a similar or slightly higher extraction of the studied metals, with faster dissolution kinetics and lower activation energies.

Author Contributions: Conceptualization, J.H.P., M.L. and B.P.W.; Methodology, S.T.; Validation, S.T., J.H.P., M.L. and B.P.W.; Formal analysis, S.T.; Investigation, S.T.; Data curation, S.T. and B.P.W.; Writing—original draft, S.T.; Writing—review & editing, S.T., J.H.P., M.L., C.B. and B.P.W.; Visualization, C.B. and B.P.W.; Supervision, J.H.P. and M.L.; Project administration, J.H.P., M.L. and B.P.W.; Funding acquisition, M.L. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors have no conflict of interest to report.

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Chapter 6

The Feasibility of Pyrite Dissolution in a Deep Eutectic Solvent Ethaline: Experimental and Theoretical Study

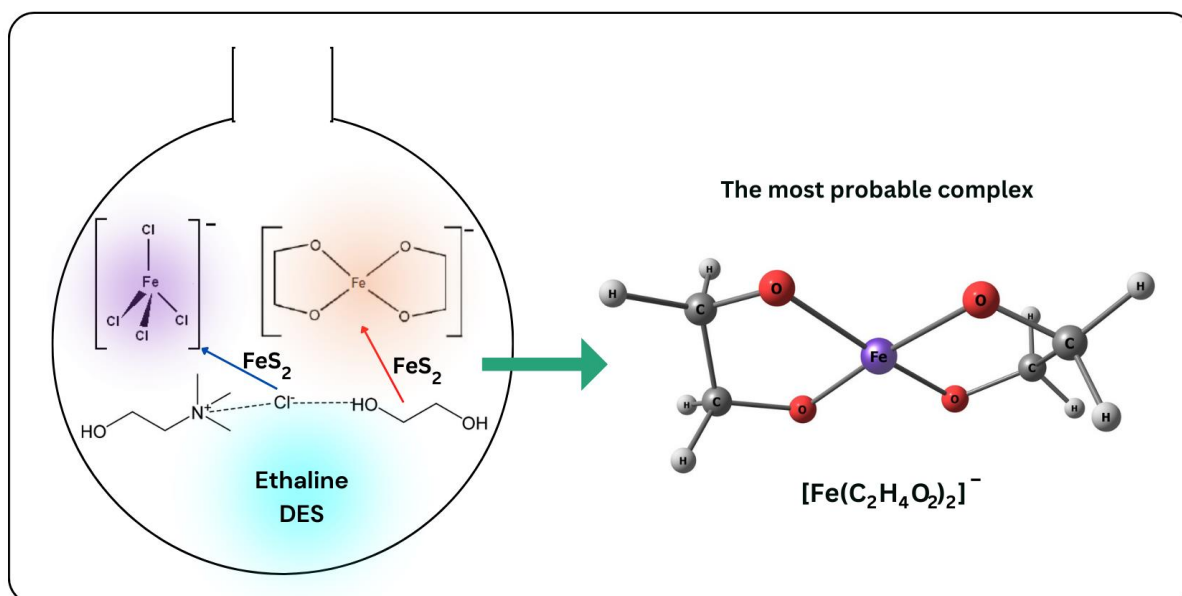
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Highlights

- Pyrite dissolution in DES, namely ethaline comprising choline chloride and ethylene glycol, was examined both experimentally and theoretically.
- Experiments were conducted to study the effect of pH of the Ethaline solvent and S/L ratio on the efficiency of Fe extraction as indicators of pyrite dissolution.
- Density functional theory (DFT) revealed that between the two ligands $[\text{Cl}^-]$ and $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ provided by EDS ethaline, the latter ligand most likely makes the most stable complex in the form of tetrahedral $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$ indicating pyrite dissolution.

Graphical abstract





The feasibility of pyrite dissolution in the deep eutectic solvent ethaline: Experimental and theoretical study

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ABSTRACT

Environmental concerns about the traditional gold extraction process, and the potential volume of encapsulated gold in sulfidic minerals i.e. pyrite, have motivated researchers to find effective, efficient and ecologically benign ways to expose the enclosed gold for improved extraction. Neoteric deep eutectic solvents (DESSs) are an analogue of ionic liquids (ILs) which are gaining more attention as eco-friendly solvents. This study examined the viability of pyrite dissolution in a DES comprised of choline chloride (ChCl) and ethylene glycol (EG), called Ethaline. The pH of the ethaline solvent mixed with hydrogen peroxide oxidant, and different solid-to-liquid ratios were examined. Ethaline solution with pH 8 provided the desired condition at which EG is deprotonated to $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$, a favourable ligand for Fe complexation and thus pyrite dissolution. A solid-to-liquid ratio of 1/20 was optimal and achieved 23.6% Fe extraction as an indication of pyrite dissolution. Density functional theory (DFT) was applied to determine which of the two ligands provided by ethaline (Cl^- and/or $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$) can form the most stable complex with Fe^{2+} and/or Fe^{3+} . As a result, the tetrahedral complex $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$ with the ligand $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ through O-donor chelating with Fe^{3+} was found to be the most probable and stable complex. However, the ethaline solvent did not deliver adequate Fe extraction compared to commonly used reagents/solvents like mineral acids, to fully break down pyrite and expose any encapsulated gold.

1. Introduction

Finely disseminated gold enclosed in sulfidic minerals (known as refractory ore) is typified by relatively low to moderate gold yield with the cyanidation process [46]. Among the sulfidic minerals, pyrite is a predominant host for gold, in which gold is occluded in its structure. Since the gold is locked inside the sulfidic host mineral, i.e. pyrite, it is necessary to break down the sulfidic matrix to expose the encapsulated gold [12]. This justifies the extra effort on the refractory gold ore and mine tailings to oxidise the impervious sulfidic mineral to obtain a permeable matrix to achieve satisfactory gold recovery through different methods and reagents [42].

The hydrometallurgical process involves principally the dissolution of minerals in an acidic and/or basic aqueous medium, followed by extracting the target metals [46]. Typically, industrial leaching solutions

contain water, acids (H_2SO_4 , HNO_3 , HCl), bases (NaOH , NH_4OH), complexing agents and oxidising agents such as H_2O_2 , Fe^{3+} , Cl_2 , HClO , to improve the rate of leaching [35]. Cyanide also has been used extensively for gold extraction for more than a century. However, besides being toxic and hazardous, in the case of refractory ores, cyanide is unable to extract the enclosed gold from pyrite [41,60].

The main reasons for searching for an eco-friendly and efficient substitute for cyanide and some other acidic and/or basic lixiviants arise from the environmental, safety, and health concerns posed by their toxicity [19,60]. However, it is challenging to find an alternative reagent to compete with these powerful reagents to improve gold extraction from sulfidic refractory ores/mine tailings. A prospective reagent to break down the sulfidic structure of the host mineral to expose the enclosed gold and ultimately extract it, should fulfil some important criteria, such as being effective, relatively inexpensive,

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environmentally benign (non-toxic), and compatible with sulfidic refractory gold ores/mine tailings [16,14].

The rising of novel solvents started back in 1914 when Paul Walden discovered the first ionic liquid (IL), ethylammonium nitrate ($[\text{C}_2\text{H}_5\text{NH}_3]^+[\text{NO}_3]^-$) with a melting point of 12 °C. However, it was only since 2000, that ionic liquids (ILs) started to gain prominence as emerging solvents among researchers in different domains, especially in the extraction and recovery of valuable and critical metals [28,52]. ILs belong to the melton salt family comprising a large organic cation and inorganic or organic anions of different sizes. They are in a liquid state at temperatures lower than 100 °C or even room temperature, because the size difference between the cation and anion results in low lattice energy and a low melting point [45,36].

Recently, the green features of some ILs have been contested, mainly due to their poor biodegradability [24]. Their large-scale application may also be restricted due to being expensive solvents [40]. Meanwhile, Abbott et al. [3] discovered a new class of solvents entitled “deep eutectic solvents (DESs)” as an analogue of ILs. The first DES was formed by mixing choline chloride (ChCl) and urea at a molar ratio of (1:2), resulting in a substance that was liquid at room temperature with a melting point of 12 °C. In contrast, the melting points of the starting components ChCl and urea were 302 °C and 133 °C, respectively [44]. A DES typically contains two or three safe and relatively cheap components that have the capability of hydrogen bond interactions with each other, to make a eutectic mixture with a melting point lower than the constituting components. They are also known as low transition temperature mixtures (LTTMs) [2,40,18]. The reason for the considerable reduction in the melting point of a eutectic solvent compared to its pure starting components is due to charge delocalization that happens through hydrogen bond formation between the halide anion of the hydrogen bond acceptor (HBA) and the hydrogen bond donor (HBD) [26,20].

The most used component in reported DESs is ChCl ($[(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{OH}]^+\text{Cl}^-$), which is a quaternary ammonium salt that is non-toxic, biodegradable, and comparatively cheap (compared to imidazolium and pyridinium cations in ILs). It is categorized as a provitamin and has been used as a nutrient substance in vitamin B, and animal food [40,44]. DESs, like ILs, can be designed for an intended purpose, since the physicochemical properties like melting point, viscosity, and conductivity of a DES can be altered by combining different halide salts (HBA) with various HBD in a different ratio to make a solvent with desired properties [40].

Usually, DESs have relatively high viscosities (>100 cP) at ambient conditions, which is attributed mainly to their extensive hydrogen bond network, electrostatic interactions, and Van der Waals forces between the components [20]. One way to decrease the viscosity of DESs is increasing temperature since it has a significant effect on reducing viscosity by increasing the mobility of species in DESs. Furthermore, adding water to a DES can decrease its viscosity to a large extent, depending on the amount of water used [27,20]. The reason why adding water to a DES can reduce its viscosity is due to the shifting of a great affinity for HBD to form H-bonding with chloride ions (in the case of the choline chloride-based DES) to the water molecules (HBD-water > HBD- Cl^-), since water molecules have a higher polarity than other species, i.e. Cl^- , in the system [61,15,22]. For instance, the viscosity of the ChCl/urea (1:2) mixture decreased from 527.3 (pure state) to 200.6 cP at 30 °C, with the addition of just 0.1 mol fraction of water to the ChCl/urea DES [13].

Therefore, DESs can be a potential alternative to traditional metal processing leachants/reagents, one that is environmentally benign with components that are commercially available and inexpensive [1]. DESs possess similar interesting physicochemical properties to ILs, but are cheaper, easier to make, biocompatible, and biodegradable [55,11]. There is increasing interest due to these remarkable properties of DESs as neoteric solvents [44] in various research fields like synthesis [8,57], catalysis [33,59], dissolution and extraction [51,37,54,34],

electrochemistry [29,40], desulfurization [23,21], CO_2 capture [53,5,38,25], and for water treatment/purification [6,47,32].

Abbott et al. [4] investigated the selective recovery of gold from gold concentrate ore through an electro-catalysis technique using DES called ethaline (mixture of ChCl and EG with a mole ratio of 1:2), with iodine (I_2) as an electro-catalyst oxidant. The gold concentrate ore mostly contains galena (PbS), pyrite (FeS_2), and chalcocite (Cu_2S), with quartz (SiO_2) and a small amount of gold in the form of electrum (a natural alloy of gold and silver). They observed that electrum, galena, and chalcocite were soluble under oxidising conditions by iodine in a DES ethaline, whereas, pyrite was less soluble [4]. In other research, Abbott et al. [1] examined the electrochemical performance of pyrite in a DES ethaline. In a novel approach a pyrite-ethaline paste painted on a Pt flag as the working electrode was used to study the reduction-oxidation reactions. It was observed that the electrochemical dissolution of pyrite occurred in three consecutive steps, namely oxidative reactions, transferring electrons, followed by cathodic reactions. The CV scan detected two anodic peaks associated with the formation of Fe^{3+} and elemental sulfur (S^0), along with three distinct cathodic peaks, one attributed to $\text{Fe}^{3+}/\text{Fe}^{2+}$ reduction, and the other two peaks related to sulfur reduction. Thus, refractory minerals such as pyrite can be dissolved to some extent in ethaline media via electrolysis [1].

Zhu et al. [62] studied a DES made of ChCl-urea-EG for zinc extraction from zinc oxide dust. They found that with a slurry concentration of 50 g/L, and a stirring speed of 600 rpm at 80 °C, the efficiency of zinc extraction was 85.2%. The kinetics of the dissolution process in the DES medium in a temperature range of 60–90 °C was diffusion-controlled with an activation energy of 32.1 kJ/mol. Vieira et al. [54] investigated phenolic compounds extraction from the leaves of a walnut tree (scientific name, *Juglans regia*) with ChCl-based DES as the HBA mixed with 15 different carboxylic acids as the HBD in the molar ratio of 1:2. The evaluation of the different carboxylic acids was assessed based on the number of carboxylic groups, the length of the alkyl chain, and additional hydroxyl and/or phenyl groups on the formed DES for high extraction efficiency. After extraction and analysis, it was determined that the two most effective DESs were the ones containing phenyl propionic acid and butyric acid, separately acting as the HBD. Then three independent variables (time, temperature and water content) in the two effective DESs were optimized by response surface methodology (RSM) using the design of experiments. The optimum condition was 180 min, 30 °C, and 49.3% water content resulting in 34.3 ± 0.2 mg/g dw (dry weight) and 33.7 ± 0.4 mg/g dw phenolic compounds extraction with phenyl propionic acid and butyric acid, respectively [54].

In research by Xu et al. [56], the application of metal-based DES was examined for extractive oxidation using peroxymonosulfate (HSO_5^-) as the oxidant for the desulfurization of fuels. The metal-based DES was prepared by mixing cobalt chloride (CoCl_2), ChCl (HBA) and the HBD such as polyethylene glycol (PEG), glycerol (GL), ethylene glycol (EG), and propionic acid (PR). Among the four different HBDs, the combination of (CoCl_2 -ChCl/2PEG) achieved almost 100% sulfur compound removal as the most effective with a fast reaction. The obtained optimum condition was 2 g of CoCl_2 -ChCl/2PEG, 0.9 g of the oxidant, and 6 g of the studied oil with 500 ppm initial sulfur content, at 20 °C, for 60 min. Comparatively, the efficiency of the different HBDs used in the DES for desulfurization followed this order: PEG > PR > EG > GL. Interestingly, the studied DESs exhibited remarkable recycling and reutilizing performance, being used 6 times without a substantial decline in the desulfurization ability [56].

The desulfurization of fuels was also studied by Lee et al. [23] by evaluating the combination of tetraethyl ammonium bromide salts (C2–C8) as HBA and alkyl diols (C2–C5) as HBDs to prepare 18 different DESs. They have examined these DES for their efficiency in multiple aspects including sulfur removing, solubility with the studied oil, and cost-effectiveness. According to the results the DES prepared with tetraethyl ammonium bromide (TEAB) and 1,4-butanediol (1,4-BD) with a

1:4 M ratio were the most efficient, under experimental conditions of 1:1 DES/oil volume ratio, for 30 min at 25 °C, as well as being efficient for three consecutive uses. Generally, the longer the HBA alkyl chain, the more efficient the DES was for sulfur compound removal due to improvement in the hydrophobicity feature [56].

In this work, the feasibility of pyrite dissolution in a DES comprised of ChCl and EG, named “Ethaline” as a novel eco-friendly solvent was examined both experimentally and theoretically. The dissolution of pyrite was studied in ethaline with hydrogen peroxide oxidant by altering the pH of the ethaline solvent as one of the vital experimental factors, as well as the solid-to-liquid ratio. Ethaline containing ChCl and EG provides two ligands, i.e. Cl^- and $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ that can make complexes with $\text{Fe}^{2+/3+}$, hence destroying the pyrite structure. Therefore, to determine which of these two ligands can form the most probable complex with $\text{Fe}^{2+/3+}$, the reaction Gibbs free energy (ΔG) of the possible complexes was calculated through density functional theory (DFT). Moreover, the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the proposed complexes was calculated. Typically, a low ΔG represents a high probability of a complex to form and a large gap between HOMO and LUMO indicates the stability of the formed complex. All calculations in DFT were performed using Gaussian 16, the B3LYP functional method in the gas phase and the PBEPBE Def2TZVP basis set. Ultimately the experimental results and the theoretical calculations were compared to draw a comprehensive conclusion. The results of this work make a further contribution to the field of pretreating refractory matrices (by breaking down pyrite) to improve gold recovery by using alternative solvents other than cyanide.

2. Experimental

2.1. Apparatuses and chemicals

The pyrite sample used in this work was analysed with XRD (Bruker, Karlsruhe, Germany) for its chemical composition. The leached solution was analysed by AAS (atomic absorption spectroscopy, Varian AA240, USA), to measure the content of extracted Fe. The samples in liquid form, ethylene glycol, and ethaline (before and after pyrite leaching), and also choline chloride (solid) were characterized with Fourier-transform infrared (FTIR) spectroscopy (Spectrum Two, Perkin Elmer, Ynysmaerdy, Pontyclun, UK), at room temperature over a range of 4000 to 400 cm^{-1} . The chemicals used in this research were choline chloride, and ethylene glycol, for synthesizing the deep eutectic solvent ethaline, hydrogen peroxide as the oxidant, hydrochloric acid, and sodium hydroxide for adjusting the pH. All of the chemicals were purchased from Merck.

2.2. Procedure

The ethaline solvent was synthesized through the heating-stirring method proposed by Abbott et al. [2] by mixing ChCl as the HBA with EG as the HBD in a molar ratio of (1:2.5). The molar ratio of (1:2.5) was selected over the more studied ratio of (1:2) since it will result in less viscous DES, favorable for extracting purposes. To synthesize ethaline, the calculated amount of both ChCl and EG were measured accurately, then mixed in a clean beaker and heated to 80 °C on a hot plate and stirred for 1 h to form a colorless uniform solvent. Fig. 1 illustrates the structure of ChCl and EG after being mixed and developing the hydrogen bond to make the ethaline solvent.

To determine the viability of Fe extraction as an indication of pyrite dissolution using ethaline and hydrogen peroxide, different pH values and solid-to-liquid (S/L) ratios were examined experimentally. Ethaline is stable in air and water (moisture) and can be used in experiments under atmospheric conditions [4]. The pyrite leaching experiment in the ethaline medium with hydrogen peroxide oxidant was carried out under atmospheric conditions in a 100 ml three-neck round bottom flask

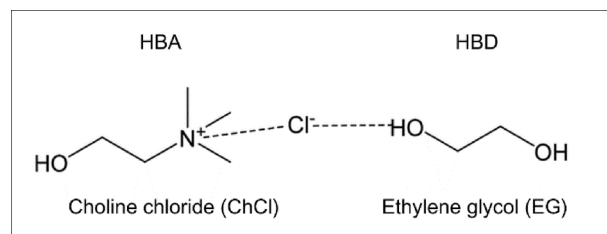


Fig. 1. Structure of ChCl and EG and the hydrogen bonding between them.

immersed in a water bath on top of a hot plate magnetic stirrer. The round bottom flask (leaching reactor) was connected to a water cooling condenser, the other neck holding the thermometer inside the leaching solution and the other one for taking sample at intervals. The mixing was done by a stirring bar inside the flask to provide a uniform pulp at 700 rpm, at a temperature of 65 °C. To follow the progress of the pyrite dissolution, 1 ml leached sample was taken from the reactor at time intervals of 0.5, 1, 1.5, 2, 3, 4, 5, and 6 h, and the same amount of ethaline with adjusted pH was added to the reactor to keep the ratio constant. Then the leached samples taken at intervals were diluted and analysed with AAS for Fe content. The experiments have been repeated and the average value was used to plot the graphs.

3. Results and discussion

3.1. Materials

The pyrite (FeS_2) sample used in this research was obtained from Mintek, South Africa. The X-ray diffraction (XRD) analysis was applied to check the main phase of the pyrite sample. Fig. 2 demonstrates the XRD pattern indicating the phase composition in which the pyrite phase with quartz as a small impurity was detected, proving the purity of the pyrite sample.

3.2. Experimental assessment

3.2.1. Effect of the Ethaline's pH

To evaluate the effect of the pH of the ethaline solvent on Fe extraction from the pyrite (FeS_2) sample, the pH of a 20 ml freshly synthesized ethaline (initial pH 6.2) was adjusted to pH of 4, 6, 8, 10, 11, and 12, and then added to the reactor. Once the temperature reached 65 °C, 1 g of well-mixed representative pyrite sample was added to the heated ethaline to make the S/L ratio of 1/20. A total volume of 2 ml hydrogen peroxide oxidant was also added in small amounts in intervals

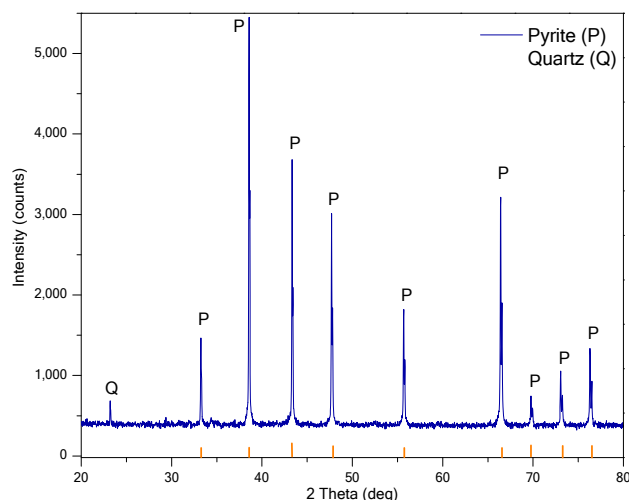
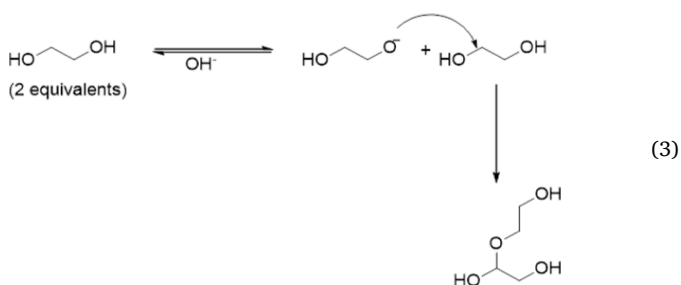
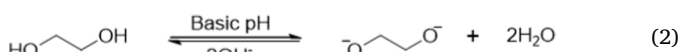
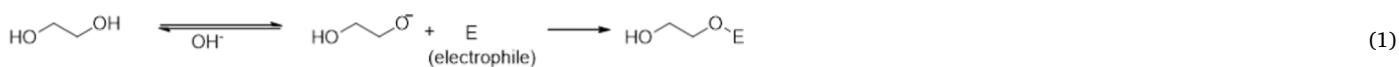


Fig. 2. The XRD pattern of the pyrite sample.

to have oxidant throughout the process. Typically, the chemical potential of H^+ and OH^- in the solution determining the pH, as well as their effect and interactions with other components/molecules in the mixture have a vital role in the extraction process [39].

In ethaline, the EG (CH_2OH-CH_2OH) component with two hydroxyl groups at each end of its structure can deprotonate to $^-(OCH_2-CH_2O^-)$ or $[C_2H_4O_2]^{2-}$ at basic pH as illustrated in reaction (1) [7,58]. Changing the pH in the basic range from 8 to 12 showed that pH 8 was the best for extracting Fe in the ethaline medium. The reason could be that at higher basic pH values the EG with the carbonyl functional group (electrophile), can shift to other structures based on reactions (2) and (3) [7,58]. Thus, increasing the pH to 12 had a reverse effect on Fe extraction and reduced it from 23.6% at pH 8 to 13.8% at pH 12 (Fig. 3).



Acidic pH 4 and 6 (the natural pH of synthesized ethaline) were also evaluated for Fe extraction as the indication of pyrite dissolution. The results show that Fe extraction takes place at acidic pH (6 and 4), but in smaller amounts than at pH 8, with 20.6% Fe extraction at pH 6 and 18.2% at pH 4 (Fig. 3). The more acidic the ethaline solution, the more H^+ ions are presented in the mixture, hence reducing the chance for deprotonation of EG [CH_2OH-CH_2OH] to $[C_2H_4O_2]^{2-}$, which is a

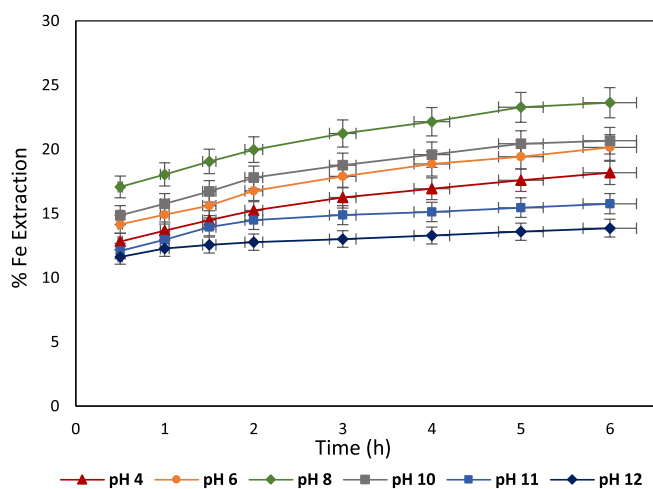


Fig. 3. Effect of the ethaline pH on Fe extraction. Operational conditions: 20 ml ethaline with 2 ml hydrogen peroxide, solid-to-liquid ratio 1/20, stirring speed 700 rpm, at 65 °C, for 6 h leaching time.

favourable ligand to form complexes with Fe. That could be the reason, the Fe extraction decreased at acidic pH.

3.2.2. Effect of solid-to-liquid ratio

The effect of solid-to-liquid (S/L) ratio on pyrite dissolution using ethaline as solvent was examined under the following experimental conditions: 20 ml ethaline (pH = 8), 2 ml hydrogen peroxide oxidant, and stirring speed of 700 rpm at 65 °C for 6 h. The predetermined amount of pyrite was added to the preheated ethaline to prepare the different solid-to-liquid ratios. As the results displayed in Fig. 4, by increasing the amount of solids in the solution to amend the S/L ratio of 1/10, the Fe extraction decreased slightly to 22.5%. This could be due to more solids creating more resistance in mass transfer, hence less

mobility, and alternatively, not enough leaching solution available per unit mass of solid (pyrite) [48,30]. Likewise, decreasing the amount of solid to the ratio of 1/25, also reduced the efficiency of Fe extraction (18%), since less solid (pyrite containing Fe) is present in the ethaline solution for extraction [49]. Therefore, in this system, the S/L ratio of 1/20 was the optimum with the right amount of solid, resulting in 23.6% Fe extraction.

3.2.3. Comparing nitric acid and ethaline

In a previous study by Teimouri et al. [50], pyrite dissolution in a nitric acid (HNO_3) solution was investigated. HNO_3 is an oxidising acid capable of breaking down sulfidic minerals, particularly pyrite. Comparing the results (Fig. 5) indicate that even a low concentration of HNO_3 solution of 1 M, with a shorter leaching time (2 h), leads to more Fe extraction of 44.6% (at 65 °C, S/L ratio 1/20, for 2 h), compared to ethaline leaching (pH = 8, at 65 °C, S/L ratio 1/20, for 6 h leaching) which only attained 23.6% Fe extraction. Although the ethaline DES is inexpensive, eco-friendly, and biodegradable, it was not sufficiently efficient to fully break down pyrite to expose enclosed gold to improve its yield.

3.2.4. Fourier-transform infrared (FTIR) spectroscopy

To evaluate the interaction between $CHCl_3$ and EG making the ethaline solvent, FTIR was employed in the range of 4000–400 cm^{-1} by

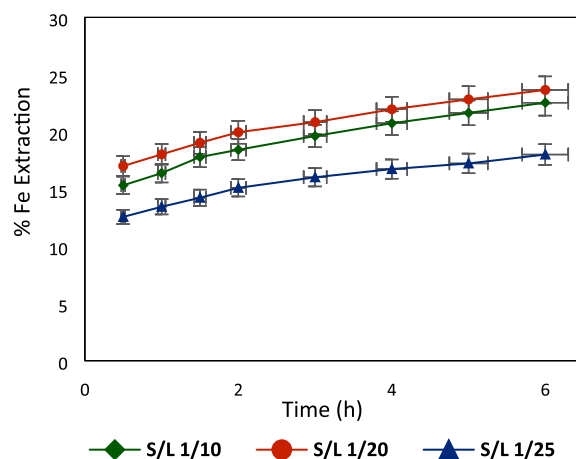


Fig. 4. Effect of the solid-to-liquid ratio on Fe extraction. Operational conditions: 20 ml ethaline, pH 8, stirring speed 700 rpm, at 65 °C, for 6 h leaching.

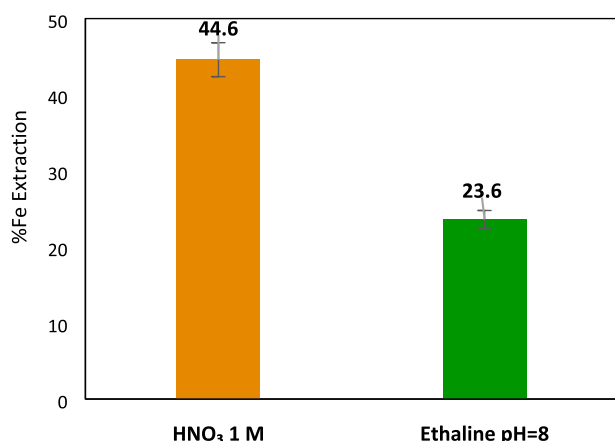


Fig. 5. Comparison of pyrite dissolution in 1 M HNO₃ (at 65 °C, S/L ratio 1/20, for 2 h leaching) and ethaline (pH = 8, at 65 °C, S/L ratio 1/20, for 6 h leaching).

measuring the spectra for (a) ChCl, (b) EG, (c) the synthesized ethaline (ChCl:EG), and (d) the ethaline after extracting Fe from pyrite (Fig. 6). From the synthesized ethaline spectrum, one can observe that it is a combination of the two spectra of ChCl and EG with slight changes, typically in a wavenumber shift indicating the interaction of the functional groups to develop hydrogen bonding to make the ethaline. The spectrum for ethaline shows vibrational bands at 3308 cm⁻¹ and 573 cm⁻¹ associated with stretching and bending of hydroxyl groups (O—H), respectively. The vibrational band at 3029 cm⁻¹ was attributed to C—H stretching, followed by a double peak (hybridized bending) at 2938 cm⁻¹ and 2875 cm⁻¹, which is ascribed to C—H₂ (sp³) stretching. The vibrational (peak) at 1481 cm⁻¹ is related to C—H₂ stretching of an alkyl

group. The vibrational peaks situated at 1206 cm⁻¹, 1137 cm⁻¹, 1085 cm⁻¹, 1037 cm⁻¹, and 882 cm⁻¹ till 573 cm⁻¹ are associated with C—C—O asymmetric stretching and C—O stretching [9,43,17].

The EG and ethaline spectra display similar vibrational patterns, except that the ethaline spectrum shows a weak and strong peak at 3029 cm⁻¹ and 954 cm⁻¹, respectively. The former (3029 cm⁻¹) is derived from the C—H stretching from ChCl, and the latter (954 cm⁻¹) is a characteristic ammonium (C—N) peak in the ethaline [43,17]. Comparing the ethaline solvent before and after leaching also shows that the vibrational stretching has a slight red shift (i.e. the O—H stretching shift from 3308 cm⁻¹ to 3303 cm⁻¹), indicating the engagement of the solvent with pyrite leaching. Interestingly, on the spectra of ethaline after being used for Fe extraction, a double peak at 1715 cm⁻¹ and 1643 cm⁻¹ appeared which can be related to Fe—O—C bound. This observation can indicate that the EG in the form of C₂H₄O₂²⁻ as a ligand in the solution forms complexes with Fe originating from pyrite.

3.2.5. Solid analysis: Scanning electron microscopy (SEM)

Fig. 7 shows scanning electron microscopy (SEM) images of the pyrite sample before and after leaching with ethaline solution (pH = 8, at 65 °C, S/L ratio 1/20, for 6 h leaching). As can be seen from the SEM image, before leaching the surface of the pyrite particles (FeS₂) looks smooth with few defects. However, after leaching in ethaline media, the morphology has changed to some extent as the surface of the pyrite particles looks rough and shows some defects. In addition, the surface of the pyrite grain was partially covered with agglomerated amorphous species, which could be sulfur. Fig. 8, demonstrates the scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDS) of pyrite before leaching detecting 51.2% and 47.7% (wt.%) of S and Fe, respectively approving the grain is certainly pyrite. Furthermore, on the residue, the formed agglomerated amorphous species on the surface of the pyrite grains were inspected with EDS and identified as sulphur

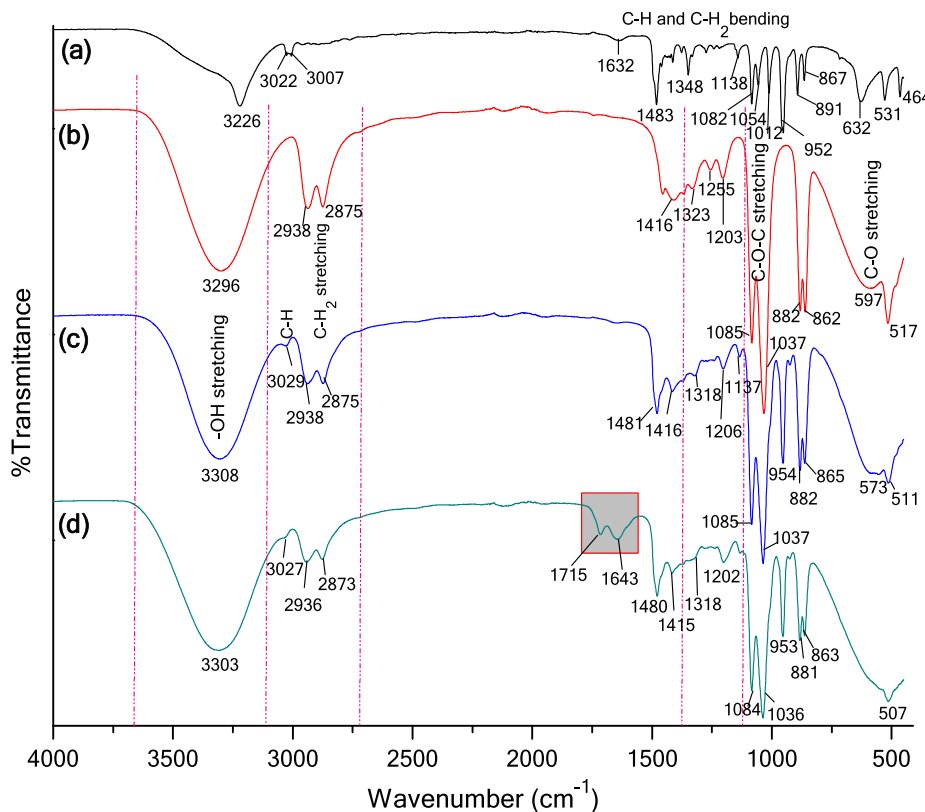


Fig. 6. FTIR spectra for (a) ChCl, (b) EG, (c) the synthesized ethaline (ChCl:EG), and (d) the ethaline after leaching pyrite.

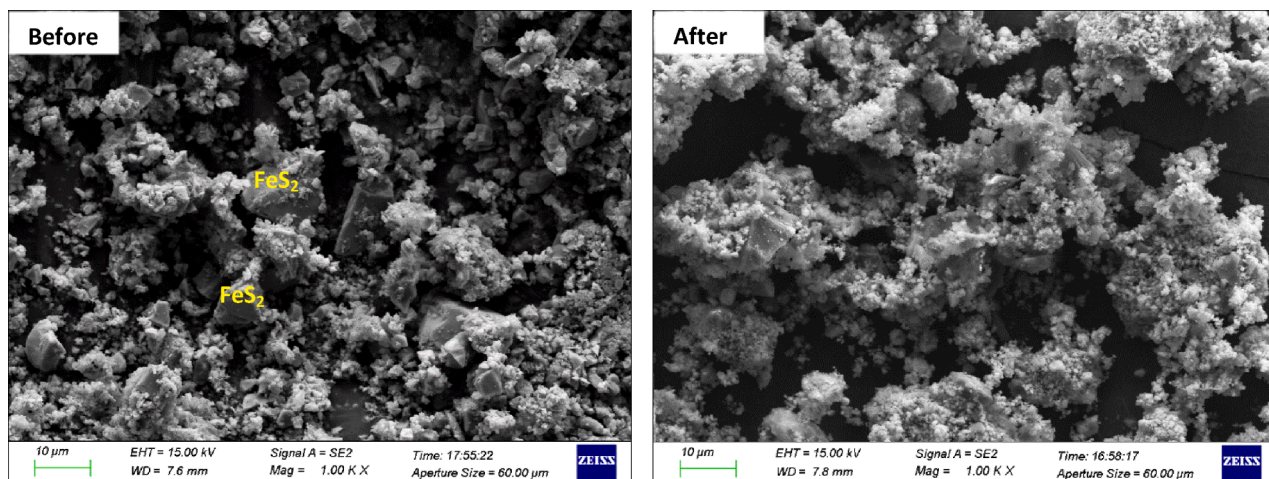


Fig. 7. SEM image of pyrite before and after leaching with DES ethaline (pH = 8, at 65 °C, S/L ratio 1/20, for 6 h leaching).

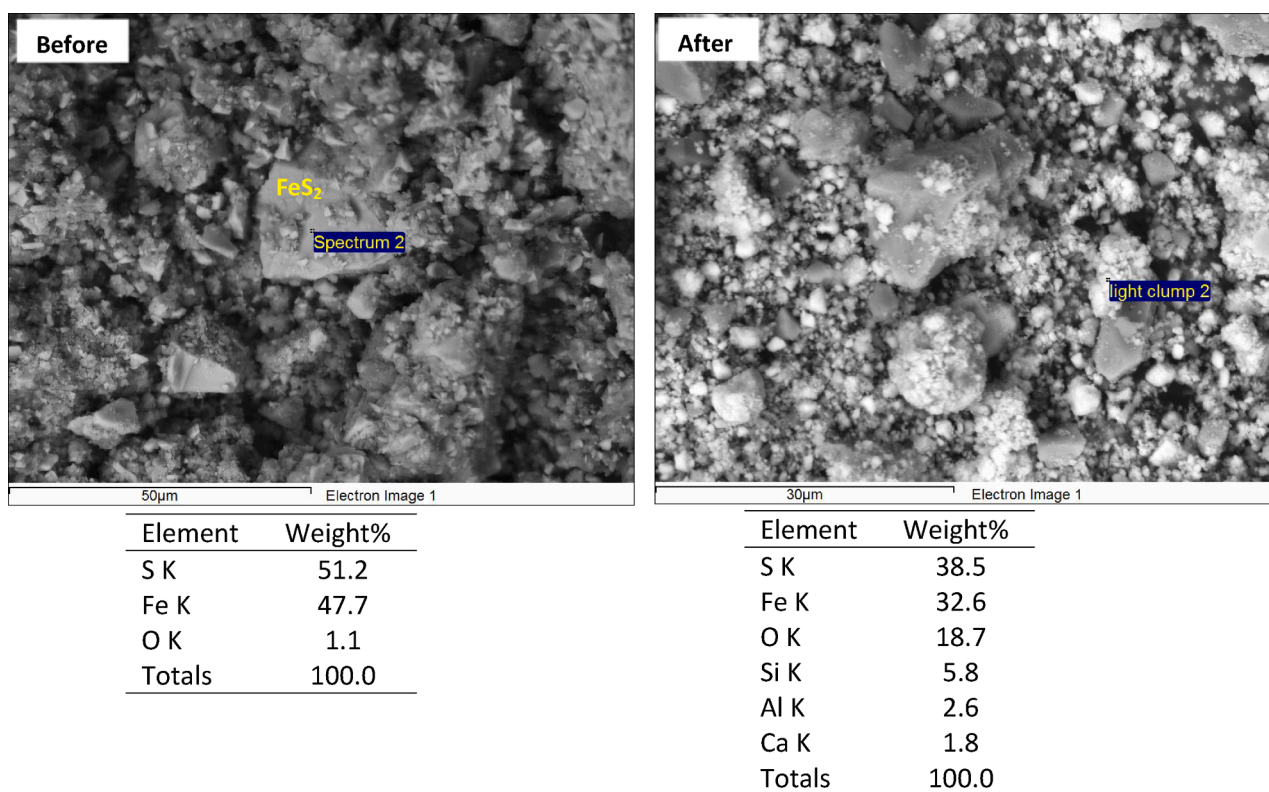


Fig. 8. SEM image and EDS results of the pyrite sample before and after leaching with DES ethaline.

species with 38.5% (wt.%) S. Moreover, the amount of Fe on the residue decreased to 32.6% (wt.%) after leaching with DES ethaline (pH = 8, at 65 °C) for 6 h, which could be due to pyrite dissolution.

3.3. Theoretical part: Density functional theory (DFT)

Density functional theory (DFT), based on the Kohn-Sham equation, was employed in this research to get a better perspective of the ligand–metal complexation, the shape of complexes and their stability [31]. The ethaline solvent has two ligands in its structure, EG in the form of $(C_2H_4O_2)^{2-}$ and Cl^- . To theoretically determine which of these two ligands most likely makes the most stable complex with Fe, DFT evaluation was applied. The possible reactions (4–11) resulting in a different complex format (i.e. tetrahedral, and octahedral), which can occur for

Fe^{2+} and Fe^{3+} with $[C_2H_4O_2]^{2-}$, and Cl^- are given as follows.

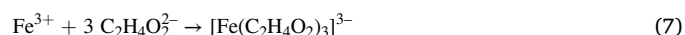
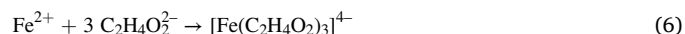
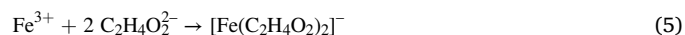
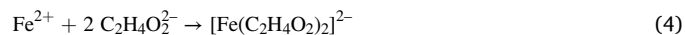


Table 1

The examined and the best multiplicity for each complex, including the ions.

Complex/Ion	Examined Multiplicities	Lowest Energy Multiplicity
$[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^{2-} (\text{Fe}^{2+})$	1, 3, 5	3
$[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^- (\text{Fe}^{3+})$	2, 4, 6	4
$[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_3]^{4-} (\text{Fe}^{2+})$	1, 3, 5	5
$[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_3]^{3-} (\text{Fe}^{3+})$	2, 4, 6	6
$[\text{FeCl}_4]^{2-} (\text{Fe}^{2+})$	1, 3, 5	5
$[\text{FeCl}_4]^- (\text{Fe}^{3+})$	2, 4, 6	4
$[\text{FeCl}_6]^{4-} (\text{Fe}^{2+})$	1, 3, 5	5
$[\text{FeCl}_6]^{3-} (\text{Fe}^{3+})$	2, 4, 6	6
$[\text{Fe}^{2+}]$	1, 3, 5	5
$[\text{Fe}^{3+}]$	2, 4, 6	6
$[\text{C}_2\text{H}_4\text{O}_2]^{2-}$	1, 3, 5	1
$[\text{Cl}]^-$	1, 3, 5	1

It should be mentioned that the different multiplicities, specifying a low spin and high spin, for both Fe^{2+} and the Fe^{2+} -complexes (1, 3, and 5) as well as Fe^{3+} and the Fe^{3+} -complexes (2, 4, and 6), were examined.

The multiplicity that leads to the lowest calculated energy for the formed complexes are listed in Table 1.

The reactions (4–11) were used to calculate the ΔG of each reaction which indicates the possibility of the formation of proposed complexes [10]. The calculation of ΔG for reaction (9), forming $[\text{FeCl}_4]^-$ (product), with Fe^{3+} and Cl^- (reactants), is written as an example:

$$\Delta G (\text{reaction 9}) = \Sigma \Delta G (\text{products}) - \Sigma \Delta G (\text{reactants}) = G ([\text{FeCl}_4]^-) - [G (\text{Fe}^{3+}) + G (4\text{Cl}^-)]$$

$$\Delta G (\text{reaction 9}) = -84463.42 - (-34324.26 + (4 \times -12520.06)) = -58.9 \text{ eV}.$$

The gap between HOMO and LUMO which indicates the stability of each complex was also calculated. The HOMO and LUMO structure of the complexes of Fe^{2+} and Fe^{3+} with each ligand $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ and $[\text{Cl}^-]$ provided by the ethaline solvent are depicted in Fig. 9.

Table 2 summarized the obtained results for ΔG , and the HOMO–LUMO gap for the different complexes for Fe^{2+} and Fe^{3+} with each ligand $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ and $[\text{Cl}^-]$. Typically, the most probable and stable complex is the one with the lowest ΔG and a large HOMO–LUMO gap

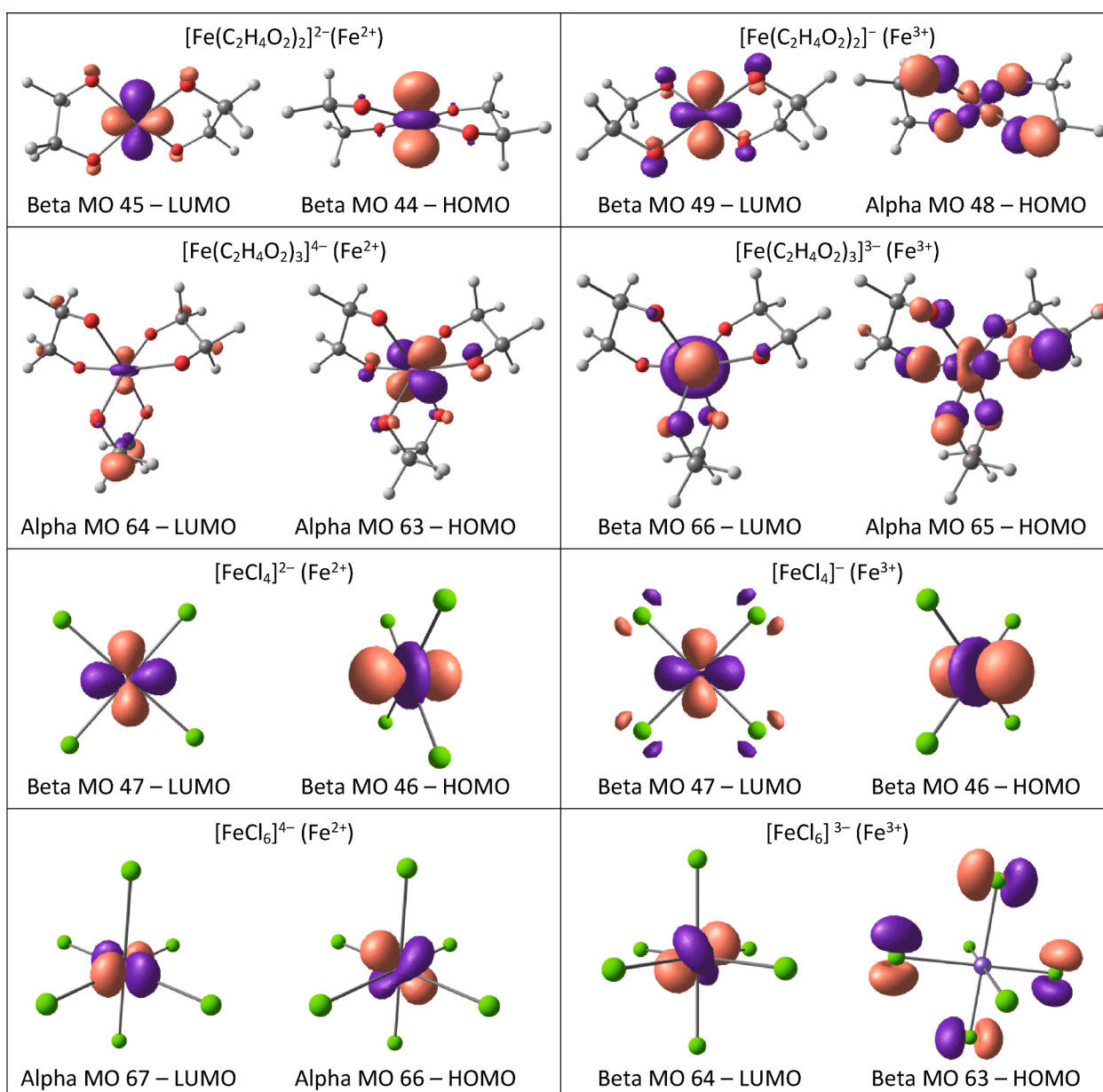
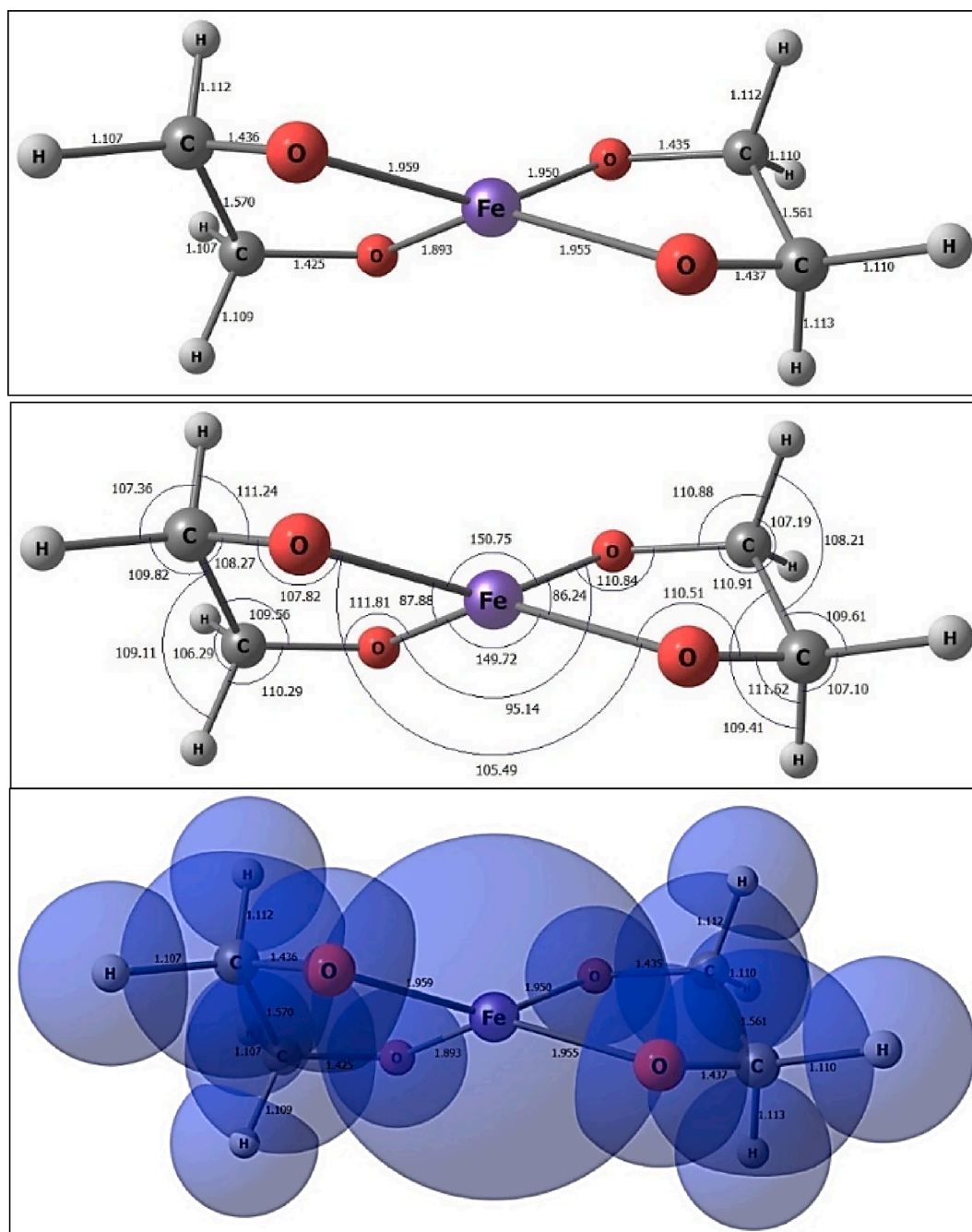


Fig. 9. The LUMO and HOMO of the complexes of Fe^{2+} and Fe^{3+} with ligands $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ and $[\text{Cl}^-]$.

Table 2The complexes of $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$, and Cl^- with Fe^{2+} and Fe^{3+} , ΔG of the formation reaction, and HOMO–LUMO gap.

Fe complex	Fe oxidation state	Complex shape	ΔG (eV)	LUMO–HOMO gap (eV)
$[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^{2-}$	Fe^{2+}	Tetrahedral	– 34.3	0.89
$[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$	Fe^{3+}	<i>Tetrahedral</i>	– 71.5	1.3
$[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_3]^{4-}$	Fe^{2+}	Octahedral	– 23.7	0.31
$[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_3]^{3-}$	Fe^{3+}	Octahedral	– 34.3	1.2
$[\text{FeCl}_4]^{2-}$	Fe^{2+}	Tetrahedral	– 25.02	0.84
$[\text{FeCl}_4]^-$	Fe^{3+}	Tetrahedral	– 58.9	0.53
$[\text{FeCl}_6]^{4-}$	Fe^{2+}	Octahedral	– 7.9	0.55
$[\text{FeCl}_6]^{3-}$	Fe^{3+}	Octahedral	– 48.1	1.1

**Fig. 10.** The most probable and stable complex $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$ in geometry-optimized form, with labelled angles, the length of each bond, and the Van-Deer-Waal sphere.

[31,10]. The calculated ΔG of the reactions forming the proposed complexes were all negative, indicating spontaneous formation. Among them the tetrahedral complex of $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ O-donor chelating ligand with Fe^{3+} in the form of $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$ had the lowest ΔG , and the largest HOMO–LUMO gap, signifying the most likely complex to form. This was also in agreement with FTIR identifying the Fe–O–C bonding as part of this complex, $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$.

The geometry-optimized form of $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$ complex with the labelled length of each bond, angles, and the Van-Der-Waal sphere is presented in Fig. 10.

Although there was research by the Abbott group on pyrite in DES ethaline, the emphasis of their research was on the viability of dissolution through the electrolysis method with iodine as the oxidant [4]. The other research focused on pyrite-ethaline paste on the Pt electrode as a novel electrochemical method to determine the dissolution mechanism [1]. Hence, a direct comparison is not possible, since this work investigates a conventional leaching method for pyrite dissolution in ethaline media with hydrogen peroxide oxidant.

4. Conclusions

The viability of pyrite dissolution in ethaline media with hydrogen peroxide oxidant was examined both experimentally and theoretically. The evaluation at various pH values (4, 6, 8, 10, 11, 12) and solid-to-liquid ratios (1/10, 1/20, 1/25), were conducted with the aim of Fe extraction as an indication of any pyrite dissolution. DFT calculations were employed to theoretically determine the most likely complex to form. The following can be concluded after this study:

- At pH 8 and the S/L ratio of 1/20, the Fe extraction yield was 23.6%, which is lower than what was achieved with a 1 M nitric acid solution yielding 46.3% Fe extraction.
- DFT calculations reveal that the tetrahedral complex of $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ via an O-donor chelating ligand with Fe^{3+} in the form of $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$ had the lowest ΔG , and the largest HOMO–LUMO gap which indicates the most probably and stable complex to form.
- The FTIR spectrometry indicates a double peak at 1715 cm^{-1} and 1643 cm^{-1} , which can be related to Fe–O–C bonding, which only appeared in the spectrum of the ethaline after leaching pyrite, thus proving the formation of the complex between $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ and Fe.

Ethaline DES is however not sufficiently efficient in breaking down pyrite to fully dissolve it to expose any encapsulated gold to improve the yield. Hence, more research is required to be done with DESs on metal extraction to find an effective eco-friendly method that can compete with traditional reagents.

CRedit authorship contribution statement

Samaneh Teimouri: Investigation, Methodology, Formal analysis, Software, Project administration, Data curation, Visualization, Writing – original draft. **Johannes Herman Potgieter:** Supervision, Funding acquisition, Writing – review & editing. **Caren Billing:** Supervision, Resources, Conceptualization, Data curation, Validation. **Jeanet Conradie:** Resources, Software, Conceptualization, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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The NICIS CSIR Centre for High Performance Computing (CHPC, grant CHEM0947) of RSA is acknowledged for processing time. Sincere appreciation is expressed to Dr Alhadjj Malloum for his guidance in DFT modelling.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2023.123468>.

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Chapter 7

Indium and Gallium Extraction Using Ionic Liquids: Experimental and Theoretical Study

Samaneh Teimouri, Johannes Herman Potgieter, Caren Billing, Jeanet Conradie,
Mari Lundström and Benjamin P. Wilson

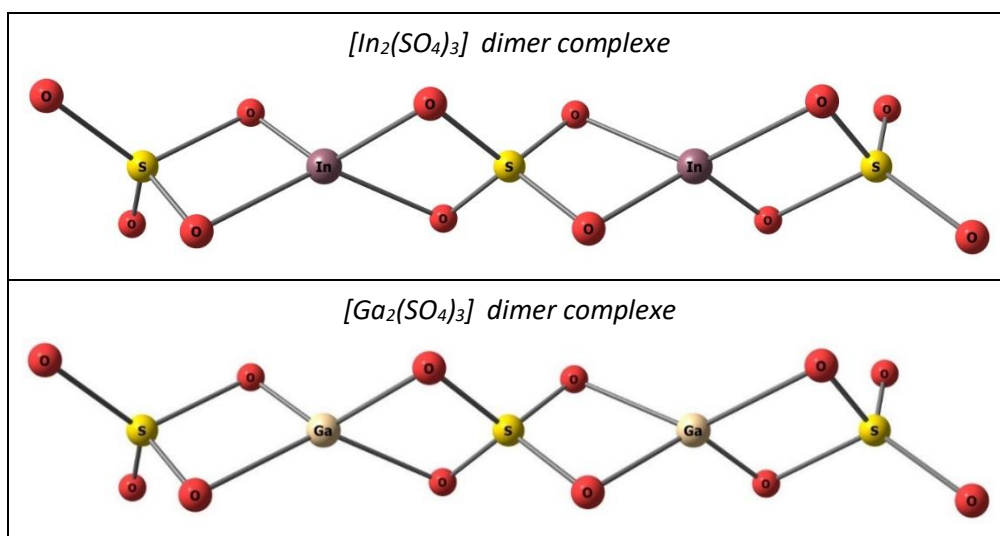
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Highlights

- The feasibility of Indium (In) and Gallium (Ga) extraction was examined both experimentally and theoretically (by DFT calculations) using three ionic liquids namely $[\text{Bmim}^+\text{HSO}_4^-]$, $[\text{Bmim}^+\text{Cl}^-]$, $[\text{Bmim}^+\text{NO}_3^-]$.
- These three ionic liquids were selected due to having similar anionic parts with the most commonly used mineral acids H_2SO_4 , HCl , and HNO_3 .
- The evaluation reveals that the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ owing $[\text{SO}_4^{2-}]$ O-donor ligand most likely makes the most stable dimer complex in the form of $[\text{In}_2(\text{SO}_4)_3]$ and $[\text{Ga}_2(\text{SO}_4)_3]$.
- The theoretical outcome was in agreement with the experimental results as the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ achieved higher extraction on the target metals.

Graphical abstract



Indium and Gallium Extraction using Ionic Liquids: Experimental and Theoretical Study

Samaneh Teimouri, Johannes Herman Potgieter, Caren Billing, Jeanet Conradie, Mari Lundström, Benjamin P. Wilson

Due to their remarkable properties, indium (In) and gallium (Ga) have been used extensively over the last two decades in the production of new electronic devices and semiconductors. Yet natural resources of these critical metals are scarce, and even more so due to the ever increasing need driven by the requirement for green technologies. It is therefore essential to recover elements like In and Ga from waste materials to meet the growth in demand. Consequently, this research studies the extraction of In and Ga using an ionic liquid solution as solvent. The investigation utilized both experimental and theoretical approaches, with In and Ga spiked EAF dust used to simulate a realistic waste matrix. Ionic liquids are emerging solvents, and EAF dust is an industrial waste containing several metals such as zinc (Zn) and iron (Fe). For the experimental part, two ionic liquids namely 1-butyl-3-methylimidazolium hydrogen sulfate $[\text{Bmim}^+\text{HSO}_4^-]$ and 1-butyl-3-methylimidazolium chloride $[\text{Bmim}^+\text{Cl}^-]$ were mixed with three oxidants

iron(III) sulfate $(\text{Fe}_2(\text{SO}_4)_3)$, potassium permanganate (KMnO_4) , and hydrogen peroxide (H_2O_2) to determine the best ionic liquid and oxidant combination. For the theoretical study, density functional theory (DFT) was applied to calculate the Gibbs free energy (ΔG) and the stability of each possible complex that can form with each of the studied ionic liquid media. To this end, three imidazolium-based ionic liquids ($[\text{Bmim}^+\text{HSO}_4^-]$, $[\text{Bmim}^+\text{Cl}^-]$, $[\text{Bmim}^+\text{NO}_3^-]$) which have similar anionic parts as sulfate $[\text{SO}_4^{2-}]$, chloride $[\text{Cl}^-]$, and nitrate $[\text{NO}_3^-]$ with the most commonly used acids as sulfuric acid (H_2SO_4) , hydrochloric acid (HCl) , and nitric acid (HNO_3) were selected for DFT calculations.

Keywords:

Indium and gallium – Imidazolium-based ionic liquids – $[\text{Bmim}^+\text{HSO}_4^-]$ – $[\text{Bmim}^+\text{Cl}^-]$ – $[\text{Bmim}^+\text{NO}_3^-]$ – Electric arc furnace (EAF) dust – Density functional theory (DFT)

Extraktion von Indium und Gallium mit ionischen Flüssigkeiten: Experimentelle und theoretische Studie

Aufgrund ihrer bemerkenswerten Eigenschaften wurden Indium (In) und Gallium (Ga) in den letzten zwei Jahrzehnten in großem Umfang für die Herstellung neuer elektronischer Geräte und Halbleiter verwendet. Die natürlichen Ressourcen dieser kritischen Metalle sind jedoch knapp, und dies umso mehr, als der Bedarf an umweltfreundlichen Technologien ständig steigt. Daher müssen Elemente wie In und Ga aus Abfallmaterialien zurückgewonnen werden, um den wachsenden Bedarf zu decken. In dieser Forschungsarbeit wird daher die Extraktion von In und Ga unter Verwendung einer ionischen Flüssigkeit als Lösungsmittel untersucht. Bei der Untersuchung kamen sowohl experimentelle als auch theoretische Ansätze zum Einsatz, wobei mit In und Ga versetzter EAF-Staub verwendet wurde, um eine realistische Abfallmatrix zu simulieren. Ionische Flüssigkeiten sind aufstrebende Lösungsmittel, und EAF-Staub ist ein Industrieabfall, der mehrere Metalle wie Zink (Zn) und Eisen (Fe) enthält. Für den experimentellen Teil wurden zwei ionische Flüssigkeiten, nämlich 1-Butyl-3-methylimidazoliumhydrogensulfat $[\text{Bmim}^+\text{HSO}_4^-]$ und 1-Butyl-3-methylimidazoliumchlorid $[\text{Bmim}^+\text{Cl}^-]$, mit

den drei Oxidationsmitteln Eisen(III)sulfat $(\text{Fe}_2(\text{SO}_4)_3)$, Kaliumpermanganat (KMnO_4) und Wasserstoffperoxid (H_2O_2) gemischt, um die beste Kombination aus ionischer Flüssigkeit und Oxidationsmittel zu ermitteln. Für die theoretische Studie wurde die Dichtefunktionaltheorie (DFT) angewandt, um die freie Gibbs-Energie (ΔG) und die Stabilität jedes möglichen Komplexes zu berechnen, der sich mit jedem der untersuchten ionischen Flüssigkeitsmedien bilden kann. Zu diesem Zweck wurden für die DFT-Berechnungen drei ionische Flüssigkeiten auf Imidazoliumbasis ($[\text{Bmim}^+\text{HSO}_4^-]$, $[\text{Bmim}^+\text{Cl}^-]$, $[\text{Bmim}^+\text{NO}_3^-]$) ausgewählt, die ähnliche anionische Anteile wie Sulfat $[\text{SO}_4^{2-}]$, Chlorid $[\text{Cl}^-]$ und Nitrat $[\text{NO}_3^-]$ mit den am häufigsten verwendeten Säuren Schwefelsäure (H_2SO_4) , Salzsäure (HCl) und Salpetersäure (HNO_3) aufweisen.

Schlüsselwörter:

Indium und Gallium – Ionische Flüssigkeiten auf Imidazolium-Basis – $[\text{Bmim}^+\text{HSO}_4^-]$ – $[\text{Bmim}^+\text{Cl}^-]$ – $[\text{Bmim}^+\text{NO}_3^-]$ – Elektrolichtbogenofen (EAF)-Staub – Dichtefunktionaltheorie (DFT)

Extraction de l'indium et du gallium à l'aide de liquides ioniques : Étude expérimentale et théorique

Extracción de Indio y Galio mediante Líquidos Iónicos: Estudio experimental y teórico

Paper presented on the occasion of the European Metallurgical Conference EMC 2023, June 11 to 14, 2023, in Düsseldorf, Germany.

1 Introduction

In the electronic world In and Ga are attracting increasing attention due to their varied and essential applications in different electronic devices, light-emitted diodes (LEDs), liquid crystal display (LCD), photovoltaic panels (PV), and semiconductors. In and Ga have remarkable properties such as being soft, malleable, ductile, having high electric conductivity, transparency and the ability to make a strong bond with glass. This latter property makes them irreplaceable and inseparable parts of new electronic devices with touch screens [1]. Nevertheless, there are no naturally occurring single large, high-concentration mineral deposits from which to extract them. In sulfide minerals like sphalerite (ZnS) and galena (PbS) mostly containing zinc (Zn) and lead (Pb), only small amounts of In also exist. Low concentrations of Ga on the other hand occur mainly alongside minerals containing Zn, aluminium (Al), and germanium (Ge) [2,3]. The scarcity and high demand for In and Ga have led researchers to find more efficient ways to recover these elements from waste materials like electrical and electronic equipment waste broadly known as WEEE or e-waste [4].

Most of the research related to In and Ga has focused on their recovery from a leachate solution using different techniques, especially solvent extraction with different extractants. ZHANG et al. (2003) studied the extraction and individual separation of In, Ga, and titanium (Ti) with different carboxylic acids from HCl solution. This research considered the effect of influential parameters on solvent extraction like the initial pH of the solution, extractant concentration, stripping agents, and the existence of foreign ions in the solution [5]. GUPTA et al. (2007) investigated the recovery and separation of In and Ga from HCl solution using the solvent extraction method with bis (2,4,4-trimethylpentyl) phosphinic acid (known as Cyanex 272). They found that solvent extraction of 1 M HCl with Cyanex 272 as the extractant was useful to recover both In and Ga from the HCl solution containing associated metals like Zn, Pb, Al, and Fe [2]. Ma et al. (2011) H2A2 studied the recovery of Zn^{2+} , In^{3+} , and Ga^{3+} using a system containing sec-octylphenoxy acetic acid (CA12, H2A2) and amine N1923 from an HCl solution [3].

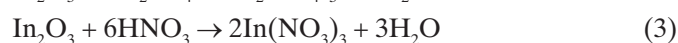
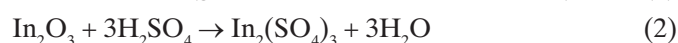
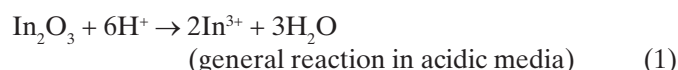
In another study, LEE et al. (2002) examined solvent extraction for separating In and Ga from a H_2SO_4 solution using di-2-ethyl-hexylphosphoric acid (D_2EHPA) as the extractant [6]. NUSEN et al. (2016) which are both commercially available, was selected to recover both Ga(III) investigated a solvent extraction system applying LIX 63 and Versatic 10 extractants that are commercially available, to recover and separate In and Ga from synthetic leach solutions of zinc refinery residues in a H_2SO_4 medium. In the system containing 0.2 M Versatic 10 and LIX 63 as the organic phase with the ratio of A/O = 1 at 40 °C, 97 % In and 99 % Ga were successfully recovered. Stripping of the desired metals was done via a single contact in 0.05 M H_2SO_4 , and almost all of the In (100 %) and 91 % Ga were stripped [7].

More recent research has concentrated on the recovery of scarce and valued metals from waste and secondary resources. For instance, the extraction and recovery of Zn, In, and Ga

from spent indium gallium zinc oxides (IGZO) and gallium zinc oxides (GZO) were investigated by CHEN et al. (2017). The spent IGZO, and GZO were leached in 3 M HNO_3 solution, with a liquid-solid ratio of 50 ml/g, at 80 °C for 2 h. Then solvent extraction was carried out for 5 min to recover In with 0.02 M D_2EHPA as extractant at pH 1, and an A/O ratio of 2. By then adjusting the pH to 3, Ga was recovered within 3 min using 0.015 M D_2EHPA and A/O ratio of 3. Ultimately, the target metals were stripped out with 1 M HCl solution with O/A ratio of 1 for 5 min. This process successfully recovered about 99.9 % of Zn, In, and Ga with 99.5 % purity [8]. THEOCHARIS et al. (2021) examined the extraction and recovery of In, Ga, Zn, copper (Cu), and Molybdenum (Mo) from end-of-life CIGS ($\text{CuGa}_{1-x}\text{In}_x\text{Se}_2$) photovoltaic panels. The CIGS photovoltaic panels were dismantled and thermally processed at 550 °C for 15 minutes for delamination of ethyl vinyl acetate (EVA), the thin layer of coated glass. Then the prepared sample was leached with 6 M HNO_3 , leading to the extraction of In, Ga, Zn, Cu, and Mo. Subsequently, the separation and recovery of the extracted metals from the leachate were attained through solvent extraction using D_2EHPA [9]. Similarly, LIU et al. (2022) studied the recovery and separation of Cu, In, Ga, and selenium (Se) from CIGS-based solar panels. Initially, the crushed solar panels were treated thermally and then leached in 5 M HNO_3 solution with a liquid-solid ratio of 50 ml/g, stirring at 300 rpm at 80 °C for 3 h to extract the target metals. Then the recovery of the extracted metals was attained with D_2EHPA , by which 90 % recovery was achieved for Cu, In, and Ga [10].

There is also some research on the extraction of valuable metals using ionic liquid as an emerging solvent. Ionic liquids are new solvents entirely made of ions, typically a large cation with an anion of different sizes. They are liquid at a temperature below 100 °C and have remarkable physicochemical properties [11,12]. TOPÇU & RUSEN (2020) investigated Cu extraction from copper anode slime using 1-butyl-3-methylimidazolium-based ionic liquids with different anions (HSO_4^- , Cl^- , and BF_4^-). The most effective ionic liquid was $[\text{Bmim}^+\text{HSO}_4^-]$ under the conditions of 50 % v/v ionic liquid/water concentration, 1/20 g/ml solid to liquid ratio at 50 °C, and 8 hours leaching time, yielding 27.7 % Cu extraction [13].

Generally, In can be extracted in acidic solutions of H_2SO_4 , HNO_3 and, HCl in the form of $\text{In}_2(\text{SO}_4)_3$, $\text{In}(\text{NO}_3)_3$, InCl_3 or In_2Cl_6 (dimer complex), based on reactions 1 to 4 [14]. The most stable oxidation state of both In and Ga is +3, and since they both are in the same group (13) in the periodic table one can extrapolate these same/similar reactions for Ga in the acidic solutions.



Therefore, three imidazolium-based ionic liquids $[\text{Bmim}^+\text{HSO}_4^-]$, $[\text{Bmim}^+\text{Cl}^-]$, and $[\text{Bmim}^+\text{NO}_3^-]$ which have a similar anionic part to the commonly used acids (H_2SO_4 ,

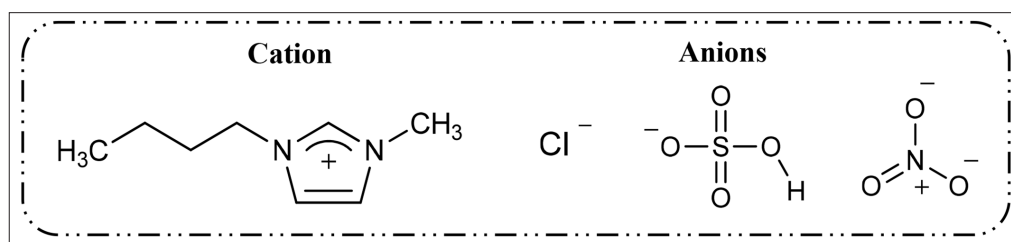


Fig. 1: Chemical structure of the three ionic liquids comprising the same cation and different anions (Cl^- , HSO_4^- , and NO_3^-)

HCl , and HNO_3), were selected for this research. Figure 1 demonstrates the chemical structure of the cationic part (1-butyl-3-methylimidazolium – known as Bmim^+) and the different anions (HSO_4^- , Cl^- , NO_3^-) that create the three chosen ionic liquids. However, the commercial production of $[\text{Bmim}^+\text{NO}_3^-]$ has been discontinued, making experiments with this ionic liquid non-viable. The theoretical calculations with DFT of $[\text{Bmim}^+\text{NO}_3^-]$ therefore only serve to gain a better understanding of the possibility and stability of a complex formed with the $[\text{NO}_3^-]$ ligand.

In this research, the feasibility of extracting In and Ga mixed with EAF dust as a realistic industrial waste containing other metals (like Zn and Fe), which can be dissolved by ionic liquids was examined experimentally and theoretically using imidazolium-based ionic liquids. The effect of the type of ionic liquid which comprises the same cation (Bmim^+), but different anionic parts (HSO_4^- and Cl^-), and the presence of an oxidant mixed with the ionic liquid solution were evaluated. To achieve this aim, two ionic liquids $[\text{Bmim}^+\text{HSO}_4^-]$ and, $[\text{Bmim}^+\text{Cl}^-]$ were separately mixed with three oxidants $\text{Fe}_2(\text{SO}_4)_3$, KMnO_4 , and H_2O_2 , respectively, to determine which combination of the ionic liquid and oxidant are the best to extract the target metals. Subsequently, the influential experimental parameters such as concentration of the ionic liquid, oxidant concentration, solid-to-liquid ratio, time, and temperature were optimized to achieve the maximum In and Ga extraction.

A theoretical study with DFT was also conducted to calculate the Gibbs free energy (ΔG) of the possible complexes which can form with the available ligands i.e. $[\text{SO}_4^{2-}]$, $[\text{Cl}^-]$, and $[\text{NO}_3^-]$ in the ionic liquid media with In and Ga. Furthermore, the gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the possible complexes were calculated. A low Gibbs free energy (ΔG) represents a high possibility of a complex forming and a large gap between HOMO and LUMO indicates the stability of the formed complex. All calculations in DFT were performed using Gaussian 16, the B3LYP functional method in the gas phase and the PBE/PBE Def2TZVP basis set. Ultimately the experimental results and the theoretical calculations were compared to draw a comprehensive conclusion.

The purpose of the study was to first investigate the effect of the co-extraction of metal like Zn, which often occur in natural ores in conjunction with In and Ga, on their leaching efficiency. Secondly to determine how well and to what

extent In and Ga can be extracted by ionic liquids, and lastly to assess the feasibility of employing ionic liquids as more environmentally benign solvents than mineral acids to use in the extraction processes.

2 Experimental

2.1 Materials

The raw material used in this study along with synthetic indium and gallium oxide (In_2O_3 & Ga_2O_3 , 99.9 % purity from Merck (MSD Oy, Espoo, Finland)) was electric arc furnace (EAF) dust – as industrial waste matrix – obtained from Ovako Imatra Oy steel plant in Finland. Chemical composition of the EAF dust was determined by X-ray fluorescence (XRF) and as can be seen from Table 1 the main components of the EAF dust were Zn, Fe, with lower amounts of Ca, Mn, and Pb. The mineralogy of the material was also analysed with X-ray diffraction (XRD) and the pattern displayed in Figure 2. XRD phase analysis evaluation identified the main phases in EAF dust as zincite (ZnO), zinc ferrite (ZnFe_2O_4), and magnetite (Fe_3O_4), with some minor phases of calcium hydroxide ($\text{Ca}(\text{OH})_2$), lead oxide (PbO), manganese dioxide (MnO_2), magnesium oxide (MgO), which corresponded with the results from the XRF analysis

2.2 Apparatuses and chemicals

Chemical leach solution was analysed by AAS (atomic absorption spectroscopy, Varian AA240, USA). The EAF

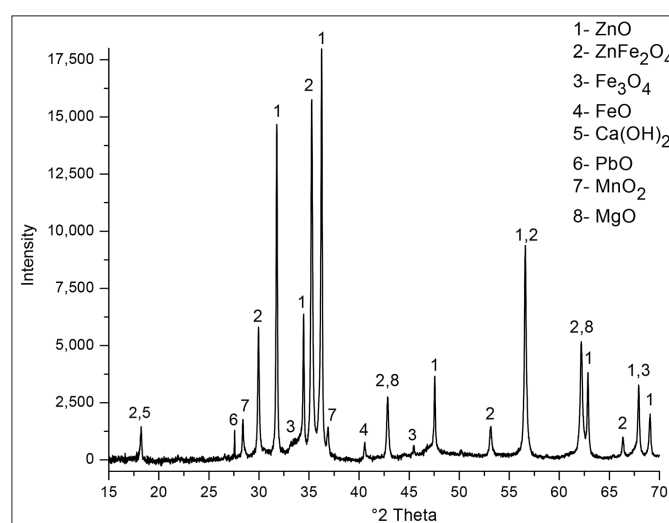


Fig. 2: XRD pattern of the EAF dust as the industrial waste

Table 1: Chemical composition of the EAF dust as valuable industrial waste examined by XRF

Element	ZnO	Fe_2O_3	CaO	MnO	K_2O	PbO	S	SiO_2	MgO	Al_2O_3	Cr_2O_3	CuO	NiO	P_2O_5	Co_3O_4
Content [Wt.-%]	34.7	18.1	3.8	2.7	2.6	1.7	1.2	1.02	0.82	0.53	0.36	0.32	0.17	0.14	0.10

dust chemical composition was examined with XRF (X-ray fluorescence-PANalytical Axios max) and XRD (X-ray diffraction, Malvern PANalytical-X'Pert PRO Powder, Almelo, Netherlands) with CuK α radiation source, with a 40 mA current, and 45 kV acceleration voltage. pH and redox potential in the ionic liquid leaching solutions were measured by a Digital pH electrode (HI 11310, Hanna Instruments, Leighton Buzzard, UK) and InLab Ag/AgCl 3M KCl (Mettler Toledo, Ohio, USA), respectively. Chemicals used in the experimental study were Indium and Gallium oxide (In₂O₃ and Ga₂O₃), two ionic liquids, 1-Butyl-3-methylimidazolium hydrogen sulfate [Bmim⁺HSO₄⁻], and 1-Butyl-3-methylimidazolium chloride [Bmim⁺Cl⁻] along with three oxidants ferric sulfate (Fe₂(SO₄)₃), hydrogen peroxide (H₂O₂), and potassium permanganate (KMnO₄). All chemicals used in this research were all acquired from Merck (MSD Oy, Espoo, Finland).

2.3 Experimental procedure

The leaching experiment in ionic liquid medium as leaching solution was carried out in a 250 ml three-neck round bottom vessel (the reactor) immersed in a water bath on a hot plate magnetic stirrer under atmospheric pressure. The leaching reactor incorporated three access ports one of which was connected to a condenser, and through another a thermometer was inserted into the leaching solution and the final port was utilized for taking sample at predetermined intervals. Mixing was provided by a stirring bar inside the reactor to produce a uniform pulp. The leaching experiment was conducted as follows: the ionic liquid solution with a specific concentration was preheated to the desired temperature, and then a certain amount of EAF dust with 5 % In₂O₃ and Ga₂O₃ with the known amount of the oxidant was added to the heated leaching solution. Experimental conditions for the first part of the research to determine the best combination of ionic liquid and the oxidant were as follows: 50 % (v/v) ionic liquid concentration ([Bmim⁺HSO₄⁻], and [Bmim⁺Cl⁻]), with Fe₂(SO₄)₃ (0.5 g), or, KMnO₄ (0.5 g), or, H₂O₂ (50 %) 1 ml oxidant, at 65 °C, 1/20 solid to liquid ratio, and 8 h leaching time. After finding the best combination of the ionic liquid and oxidant, the influential factors such as concentration of the ionic liquid (30- 40- 50- 60 % v/v), the concentration of the oxidant [Fe₂(SO₄)₃ or KMnO₄ (0.25-0.5-0.75-1 g)] and H₂O₂ (50 %) [(1-1.5-2-2.5 ml)], S/L ratio (1/10-1/15-1/20-1/25 g/ml) and temperature (55, 65, 75, and 85 °C) were studied to discov-

er the optimum condition to attain the highest extraction of In and Ga from the ionic liquid solution mixed with spiked EAF dust. The leachate was filtered and then analysed with AAS to measure the amount of extracted In and Ga along with Zn [15].

3 Results and discussion

The previous research by TEIMOURI et al. (2022) [15] examined the optimum conditions for the extraction of the different metals of interest from the EAF dust spiked with In and Ga using the studied ionic liquids ([Bmim⁺HSO₄⁻] and [Bmim⁺Cl⁻]). Table 2 lists the optimum conditions [15].

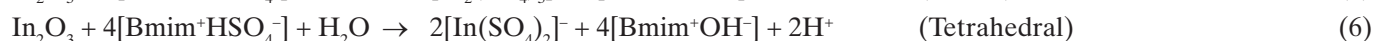
Table 2: The optimum conditions for the extraction of In and Ga and the EAF dust metals of interest from mixed raw material [15]

Factors	Optimum point		
Ionic liquids/Oxidants	[Bmim ⁺ HSO ₄ ⁻]/Fe ₂ (SO ₄) ₃		
Ionic liquid concentration [v/v %]	30 %		
Oxidant concentration [g]	1 g Fe ₂ (SO ₄) ₃		
Solid/Liquid [g/l]	1/20		
Temperature [°C]	85		
Time [min]	240		
Yield [%E]	%E In	%E Ga	%E Zn
	97.4	17.3	92.7
Kinetic model	Diffusion-controlled		
Activation energy [kJ/mol]	In: 33.6	Ga: 30.3	Zn: 8.2

3.1 Theoretical part: Density Functional Theory (DFT)

In this research, DFT calculations based on the Kohn-Sham equation were applied to get a better understanding of the ligand-metal complexation, the shape of the formed complexes and their stability [16]. The studied ionic liquids [Bmim⁺HSO₄⁻], [Bmim⁺Cl⁻], and [Bmim⁺NO₃⁻] have the same cationic part (Bmim⁺) but different anionic parts as [SO₄²⁻], [Cl⁻], and [NO₃⁻], respectively, which act as a ligand to make complex with In and Ga. All DFT calculations were performed using Gaussian 16, the B3LYP functional method in the gas phase and the PBE/PBE Def2TZVP basis set.

The possible reactions (5-13) resulting in a different complex format (*i.e.* dimer, tetrahedral, octahedral), which can occur for In in the form of (In₂O₃) in each ionic liquid are written as follows. Similar reactions can be extrapolated for Ga in the form of (Ga₂O₃), as well:



To theoretically determine which of these ligands $[\text{SO}_4^{2-}]$, $[\text{NO}_3^-]$ or $[\text{Cl}^-]$ provided by each ionic liquid produce the

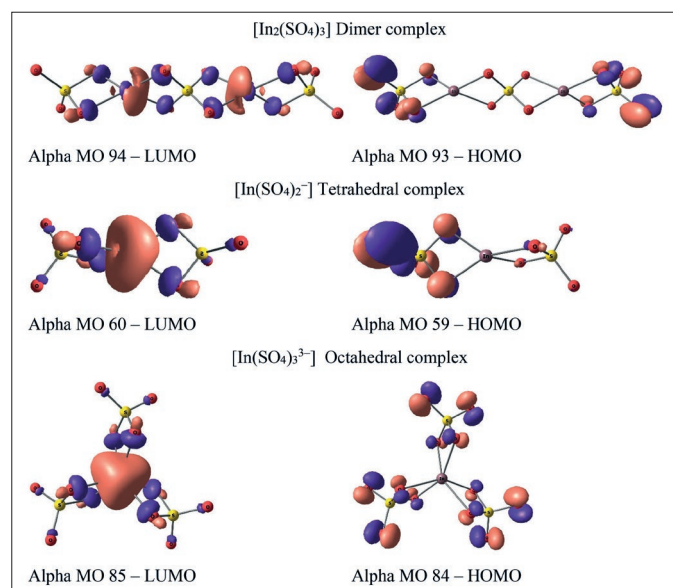


Fig. 3: The LUMO & HOMO of the possible complexes of In with $[\text{SO}_4^{2-}]$ ligand provided by $[\text{Bmim}^+\text{HSO}_4^-]$

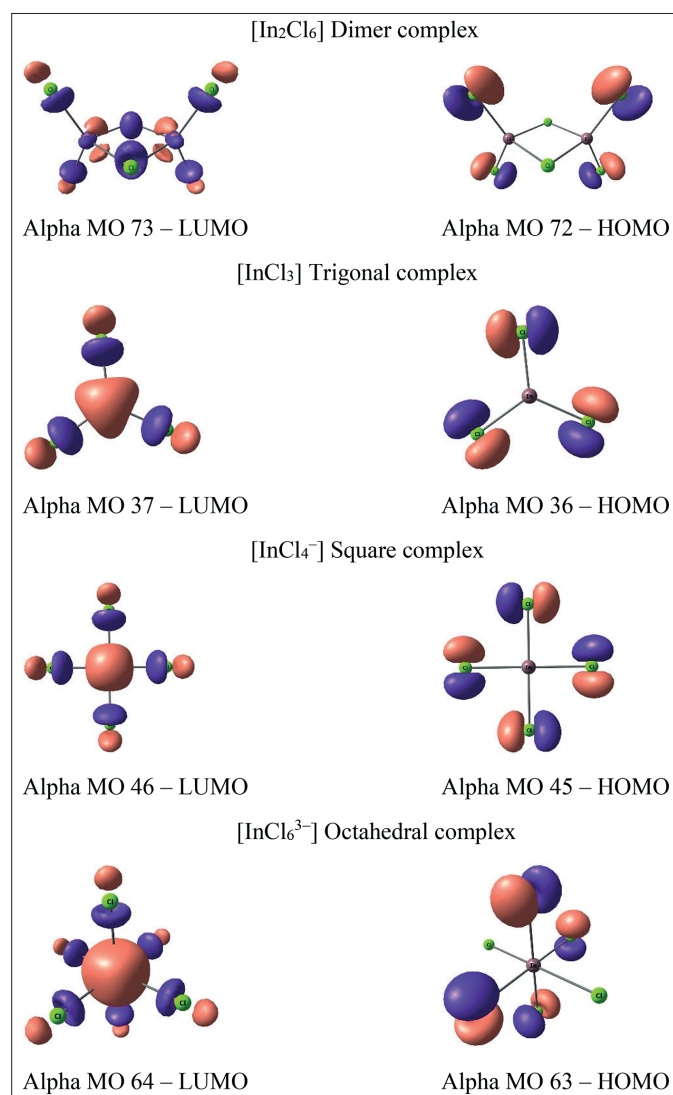


Fig. 4: The LUMO & HOMO of the possible complexes of In with $[\text{Cl}^-]$ ligand provided by $[\text{Bmim}^+\text{Cl}^-]$

most possible and stable complex with In and Ga as the critical metals in the leaching solution, DFT calculations were conducted using High-Performance Computing (HPC). For this aim, the reaction Gibbs free energy (ΔG) which indicates the possibility of the formation of each complex was calculated using the mentioned reactions, and also the gap between HOMO and LUMO which states the stability of a complex [17], among the proposed complexes. Figures 3 to 5 depict the HOMO and LUMO structure of In complexes with each studied ionic liquid. The HOMO and LUMO structure for Ga complexes with the studied ionic liquids were excluded due to limited space since they have similar structure.

There were 18 possible complexes for both In and Ga for the theoretical evaluation. After DFT calculation the obtained results for ΔG , and the HOMO-LUMO gap for all of the different possible complexes of the three ligands with In and Ga are summarised in Tables 3 and 4. Typically, the low ΔG represents a high possibility of a complex to form and a large gap between HOMO and LUMO indicates high stability of the formed complex [17]. Thus, amongst all of these possible complexes, the dimer complex of $[\text{In}_2(\text{SO}_4)_3]$ and $[\text{Ga}_2(\text{SO}_4)_3]$ had the lowest ΔG , and the largest HOMO-LUMO gap indicating the most possible and stable complex to form. Therefore, the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ which provides $[\text{SO}_4^{2-}]$ an O-donor chelating ligand in the leaching solution performs best. It should be mentioned that the dimer complex of the $[\text{Cl}^-]$ ligand provided by $[\text{Bmim}^+\text{Cl}^-]$ with In and Ga producing $[\text{In}_2\text{Cl}_6]$ and $[\text{Ga}_2\text{Cl}_6]$ also be viable due to a small ΔG , and large HOMO-LUMO gap, however, in lower amounts compared to complexes with the $[\text{SO}_4^{2-}]$ ligand. The experiments with $[\text{Bmim}^+\text{Cl}^-]$ as the leaching solution resulted in low extraction (about 21 % In) compared to $[\text{Bmim}^+\text{HSO}_4^-]$ (with 97 % In), which was consistent with theoretical evaluation and indicates that practical experimental conditions also play a part in the extraction efficiency.

However, it should be considered that the DFT calculation for ΔG was conducted in a gas phase hence the ΔG values for even the most possible complex i.e. $[\text{In}_2(\text{SO}_4)_3]$ was

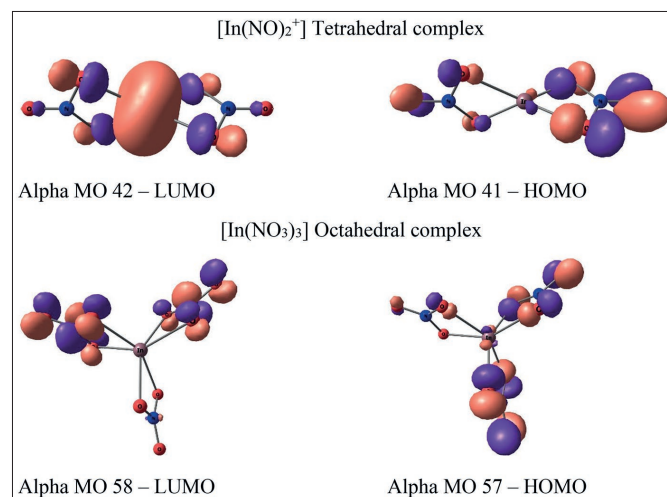


Fig. 5: The LUMO & HOMO of the possible complexes of In with $[\text{NO}_3^-]$ ligand provided by $[\text{Bmim}^+\text{NO}_3^-]$

a small positive number (7.47 eV), not a negative value which indicates a reaction occurs spontaneously. The calculations presented here are to get an idea of the relative

possibility of a reaction to occur. The experiments were conducted in a liquid phase (the ionic liquid/water media with other ions/molecules from the EAF dust also present),

Table 3:

The In complex shape, charge, Gibbs free energy of the formation reaction (ΔG), and HOMO-LUMO gap

Complex	Complex shape	Complex charge	ΔG [eV]	HOMO-LUMO gap [eV]
$[\text{In}_2(\text{SO}_4)_3]$	Dimer	0	7.47	4.14
$[\text{In}(\text{SO}_4)_2]^-$	Tetrahedral	-1	33.74	3.05
$[\text{In}(\text{SO}_4)_3]^{3-}$	Octahedral	-3	109.24	3.81
$[\text{In}(\text{NO}_3)_2]^+$	Tetrahedral	+1	28.30	3.47
$[\text{In}(\text{NO}_3)_3]$	Octahedral	0	13.45	3.89
$[\text{In}_2\text{Cl}_6]$	Dimer	0	10.73	4.06
$[\text{InCl}_3]$	Trigonal	0	11.23	3.99
$[\text{InCl}_4]^-$	Square	-1	43.09	3.14
$[\text{InCl}_6]^{3-}$	Octahedral	-3	127.44	3.42

Table 4:

The Ga complex shape, charge, Gibbs free energy of the formation reaction (ΔG), and HOMO-LUMO gap

Complex	Complex shape	Complex charge	ΔG [eV]	HOMO-LUMO gap [eV]
$[\text{Ga}_2(\text{SO}_4)_3]$	Dimer	0	7.79	5.07
$[\text{Ga}(\text{SO}_4)_2]^-$	Tetrahedral	-1	33.52	4.59
$[\text{Ga}(\text{SO}_4)_3]^{3-}$	Octahedral	-3	110.04	2.95
$[\text{Ga}(\text{NO}_3)_2]^+$	Tetrahedral	+1	28.60	4.49
$[\text{Ga}(\text{NO}_3)_3]$	Octahedral	0	13.38	4.04
$[\text{Ga}_2\text{Cl}_6]$	Dimer	0	11.33	4.95
$[\text{GaCl}_3]$	Trigonal	0	11.64	4.93
$[\text{GaCl}_4]^-$	Square	-1	44.57	3.38
$[\text{GaCl}_6]^{3-}$	Octahedral	-3	130.73	3.50

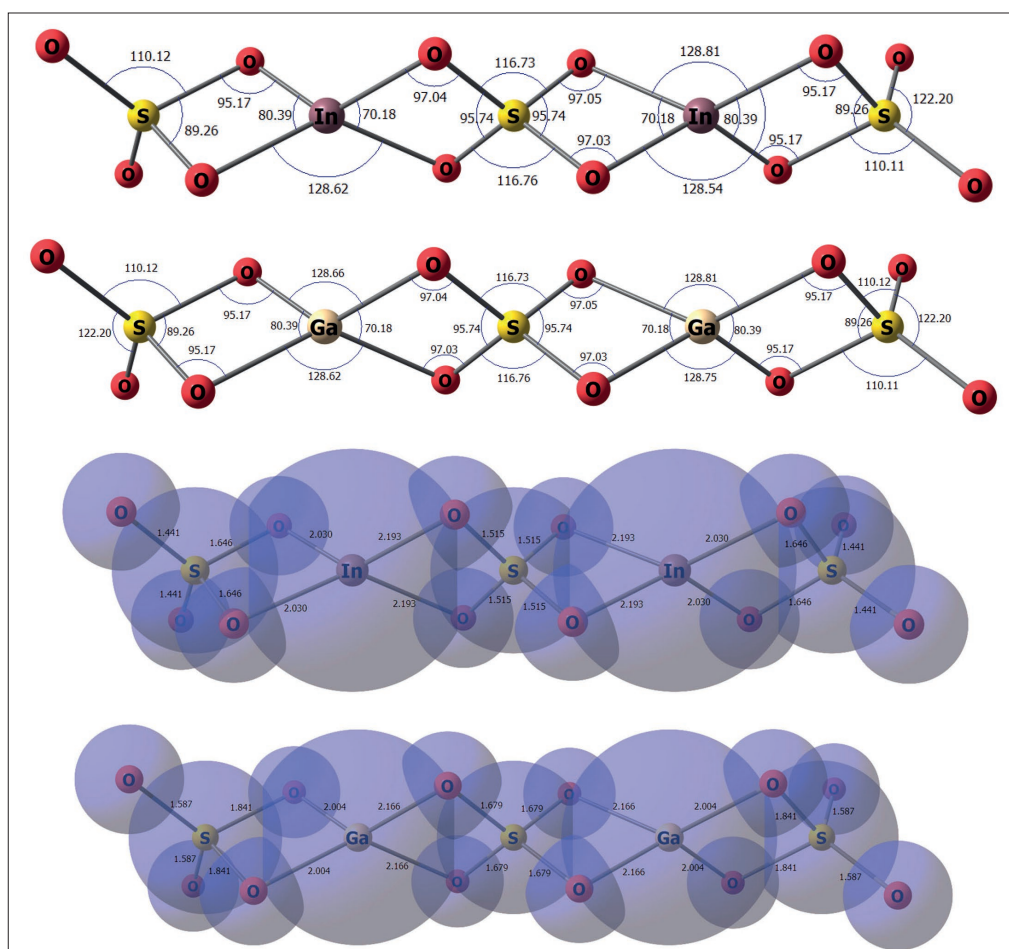


Fig. 6:

The most stable dimer complex of $[\text{In}_2(\text{SO}_4)_3]$ and $[\text{Ga}_2(\text{SO}_4)_3]$ in geometry-optimised form, with labelled angles, the length of each bond, and the van-der-Waals sphere

in which the solvent etc. have a driving force to assist the reaction to happen. For example, when calculating reaction 5 and 10 (producing the dimer complex of $[\text{In}_2(\text{SO}_4)_3]$ and $[\text{In}_2\text{Cl}_6]$ individually) in water as implicit solvent, the free energies reduced to 4.67 and 6.78 eV, respectively. However, in water as implicit solvent, a lower energy product for $[\text{Bmim}^+\text{OH}^-]$, where a H was transferred to the OH^- ion was identified, lowering the calculated ΔG further to 1.53 and 0.50 eV, respectively. Further calculations taking the real solvent environment into account, that is outside the scope of the present work, should lead to spontaneous (negative) reaction energies.

It was also interesting to observe that the higher the charge was for a particular complex, the less the chance for it to form. For instance, the octahedral complexes of $[\text{In}(\text{SO}_4)_3]^{3-}$ and $[\text{Ga}(\text{SO}_4)_3]^{3-}$ with the -3 charge which formed with the $[\text{SO}_4]^{2-}$ ligand, have large ΔG values of 109.24 and 110.04, respectively, indicating a low probability to form. The dimer complex of the sulfate ligand leading to $[\text{In}_2(\text{SO}_4)_3]$ with no charge was the most stable.

Figure 6 illustrates the dimer complex of $[\text{In}_2(\text{SO}_4)_3]$ and $[\text{Ga}_2(\text{SO}_4)_3]$ in the geometry-optimised form, with labelled angles, the length of each bond, and the van-der-Waals sphere interactions around.

Ultimately, the HPC-calculated DFT values were compared with the experimental results on extracting In and Ga using the studied ionic liquids. In the experimental part two ionic liquids $[\text{Bmim}^+\text{HSO}_4^-]$ and $[\text{Bmim}^+\text{Cl}^-]$ were tested to extract In and Ga. The experimental results indicate that $[\text{Bmim}^+\text{HSO}_4^-]$ leads to higher extraction of the desired metals. According to the DFT calculations, the dimer complex of $[\text{In}_2(\text{SO}_4)_3]$ and $[\text{Ga}_2(\text{SO}_4)_3]$ was the most probable and stable complex which could be formed by sulfate $[\text{SO}_4]^{2-}$ ligand. Therefore, the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ not only was experimentally the most effective ionic liquid for metal extraction, but also theoretically confirmed as the best for forming the most possible and stable complexes with In and Ga. Hence, the experimental work and the theoretical calculation with DFT correlate to confirm that the $[\text{Bmim}^+\text{HSO}_4^-]$ is the most effective ionic liquid.

4 Conclusion

The feasibility of a new hydrometallurgical approach using imidazolium-based ionic liquids for In and Ga extraction was examined experimentally and theoretically with DFT calculations. In this case, two ionic liquids $[\text{Bmim}^+\text{HSO}_4^-]$ and $[\text{Bmim}^+\text{Cl}^-]$ were separately mixed with three oxidants to find the best combination for In and Ga extraction. The experimental results indicate the mixture of $[\text{Bmim}^+\text{HSO}_4^-]$ and $\text{Fe}_2(\text{SO}_4)_3$ oxidant was the optimum combination. Then the influential factors were examined to determine the optimum condition for the extraction of In and Ga.

The experimental achievements were as follows:

- The attained optimal conditions were as 30 % v/v $[\text{Bmim}^+\text{HSO}_4^-]$ mixed with 1 gr $[\text{Fe}_2(\text{SO}_4)_3]$, S/L ratio of 1/20, and 240 min extraction time at 85 °C.

- Extraction efficiency for In, Ga, and Zn (originating from EAF dust) under the optimal conditions was 97.4 % and 17.03 %, 92.7 %, respectively.
- Dissolution kinetics of the target metals in 30 % v/v $[\text{Bmim}^+\text{HSO}_4^-]$ solution from raw material evaluated at temperature 55 to 85 °C was administrated by the diffusion model, and it was faster in the first hour of leaching before becoming moderate.
- The obtained activation energy for In, Ga, and Zn was 33.6, 30.3, and 8.2 kJ/mol respectively, which all were in the range of the diffusion-controlled model.

The theoretical study by applying DFT calculations on the possible complexes of In and Ga with three studied ionic liquids ($[\text{Bmim}^+\text{HSO}_4^-]$, $[\text{Bmim}^+\text{NO}_3^-]$, and $[\text{Bmim}^+\text{Cl}^-]$) also confirms that the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ owing $[\text{SO}_4]^{2-}$ O-donor ligand resulted in the lowest ΔG , and the largest HOMO-LUMO gap indicating the most possible and stable complex. Thus, the dimer complex of $[\text{In}_2(\text{SO}_4)_3]$ and $[\text{Ga}_2(\text{SO}_4)_3]$ with the lowest ΔG of the formation reaction calculated in the gas phase, and the largest HOMO-LUMO gap were the most possible and stable complex to form among other possible complexes. Although, the values for ΔG for the dimer complex of In and Ga were small and close together representing the high possibility of their formation theoretically, the experimental results for Ga extraction were low.

Therefore, the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ was not only demonstrated experimentally as the best ionic liquid for In and Ga extraction, but also theoretically confirmed as the best ligand to form the most possible and stable complex. The benefits of using the ionic liquid, like $[\text{Bmim}^+\text{HSO}_4^-]$ for metal extraction instead of the common mineral acids could be, that the ionic liquid is recyclable and can be reused in the extraction process, which justifies the higher operating cost in the long term. To recycle the ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ the extracted metals should be effectively removed from the pregnant ionic liquid solution. For instance, in this work, electrowinning and/or solvent extraction techniques can be applied to remove In, Ga, and Zn [18, 19] from the pregnant IL $[\text{Bmim}^+\text{HSO}_4^-]$ solution and precipitation technique to recover Fe [20], then one can reuse the remaining ionic liquid $[\text{Bmim}^+\text{HSO}_4^-]$ [21, 22]. In addition, these type of ionic liquids are also biodegradable and more environmentally friendly.

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Chapter 8

Conclusions

Centuries of mining and industrial production world wide have produced a substantial amount of waste material that contains metals. These waste materials can be used as secondary resources for metals recovery and come in various forms, including industrial waste, electronic equipment, and mine tailings that still contain unextracted gold enclosed in sulfidic minerals, particularly pyrite (Ndlovu et al., 2017; Matinde et al., 2018). Sustaining the world's increasing population and its demand for metals requires finding new and effective ways to recover metals from waste materials (Kumar et al., 2020). Furthermore, some valuable and critical metals are naturally scarce, making it vital to recover them from waste materials. It is important to find recovery methods with limited environmental impact for improved circularity of metal production (Jadhav & Hocheng, 2012; Ndlovu et al., 2017).

Research in this thesis focused on pyrite dissolution to develop a pretreatment method to expose the enclosed gold to improve the recovery yield from mine tailings/refractory ores, as well as metal recovery from EAFD as a valuable industrial waste, by applying different media (nitric acid solution, DES ethaline as a new eco-friendly solvent, and ILs as an alternative to commonly used acids). Theoretical modelling with DFT and lab experiments were used to study different leaching conditions, with the following key findings:

- Nitric acid ($> 2\text{ M}$) with its powerful oxidative ability can efficiently dissolve pyrite: a pretreatment method using a 3 M HNO_3 solution at $75\text{ }^\circ\text{C}$, can entirely dissolve pyrite particles to expose the inaccessible gold effectively within 2 h.
- DES (ethaline solvent) which is more environmentally benign and novel was less effective compared to nitric acid leaching for breaking down pyrite.
- IL $[\text{Bmim}^+\text{HSO}_4^-]$ offers high extraction of Zn, In and Fe from EAFD, confirming its potential as a prospective alternative solvent for metal extraction compared to commonly used acid leaching methods such as H_2SO_4 .
- DFT calculations determined the best ligand provided by the novel solvents (ILs and DES ethaline), i.e. which form the most probable and stable complex with the target metal(s). The results from these theoretical calculations correlated with experimental findings. This has shown that DFT

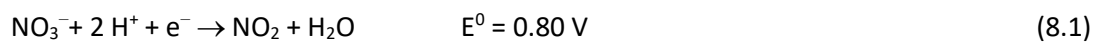
modelling can be used for screening optimal ligands for particular applications as well as supporting experimental work.

In this work, it was hypothesised that novel solvents could offer a viable, if not cost-effective means of metal extraction, since these solvents can be recycled and reused in a closed-loop system. While DES ethaline was less effective for pyrite dissolution, the results for other metal extraction from EAFD using IL proved satisfactory and even promising.

Herewith a summary of the findings from the research, with key points emphasised in bold:

HNO₃ is a powerful, regeneratable acid and oxidant that can be used in a pretreatment method to expose the remaining enclosed gold in mine tailings in pyrite prior to the extraction, as hypothesised. The study confirmed that within 2 h, a 3 M HNO₃ solution at 75 °C effectively dissolved 95% FeS₂ enclosing gold. There was a shift in the kinetics for pyrite dissolution from interfacial transfer to diffusion control (mixed-model) in the 25 to 85 °C range. This research also proposes a semi-empirical expression for pyrite dissolution under these conditions.

HNO₃ was found to be especially effective in concentrations above 2 M, due to the nitrogen (N) in NO₃⁻ being in its highest oxidation state (+5), giving NO₃⁻ strong oxidative abilities (Celep et al., 2017). When the concentration of HNO₃ increases, so does the [NO₃⁻] concentration (oxidant) and the acidity [H⁺] of the solution, which increases the oxidative power in the solution. This is explained by the standard reduction potential (E⁰) for NO₃⁻ in Equation (8.1), and the corresponding Nernst Equation (8.2), as given by (Li, 2009):



$$E = E^0 + \frac{0.059}{n} \log \frac{[\text{H}^+]^2 [\text{NO}_3^-]}{P_{\text{NO}_2}} \quad (8.2)$$

Consider a 2 M HNO₃ solution: by substituting [NO₃⁻] = [H⁺] = 2 M, E⁰ = 0.80 V, n = 1 (number of electrons), and the partial pressure of NO_{2(g)} = 1 atm into the Nernst Equation (8.2), it produces a half-reaction potential of 0.91 V, which is indicative of an oxidative dissolution:

$$E = E^0 + 0.059 \log [2]^2 [2] = 0.80 + 2 \times 0.059 \times \log [8] = 0.91 \text{ V}$$

The results from the experiments looking at the kinetics of pyrite dissolution in nitric acid solution in the temperature range of 25-85 °C fit well with the mixed-controlled kinetics process $(1/3 \ln(1-X) + [(1-X)^{-1/3} - 1]) = k.t$, indicating the interfacial transfer and diffusion control model. Bryson and Crundwell (2014) also noticed that the slope of the graph presenting the steady-state current-potential relationship (as measured at a rotating electrode (840 rpm) in 1 M HCl at 25 °C) changed at 0.9 V vs

Ag/AgCl (Figure 8.1). This was true for the measurement they made between 25-69 °C and it was shown that the current measurements were not affected by ohmic resistance. They attributed this observation to a shifting behaviour in the pyrite dissolution described by interfacial kinetics. This can be explained as the potential increases to 0.9 V the rate of charge (electron) transfer is fast reaching its maximum, while the rate of ions crossing the Helmholtz layer is slower (diffusion) and hence becomes the rate-limiting step (Bryson & Crundwell, 2014).

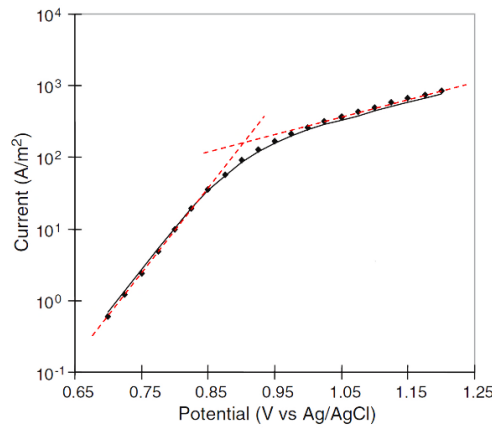


Figure 8.1: The steady-state current-potential curve measured at a rotating electrode. A clear change in slope is seen as the measurements proceeded to higher potentials (Bryson & Crundwell, 2014).

Figure 8.2 demonstrates the Arrhenius plot of $\ln k$ vs $1000/T$ (temperature, K^{-1}) for results obtained in this work, showing that the slope of the graph in the lower temperature range (25-45 °C) is different to that in the higher temperature range (55-85 °C). The data points were divided into two sets (25-45 °C and 55-85 °C) to reflect the slope change from which the activation energy was calculated and found to be 145.2 kJ/mol at low temperatures (25-45 °C), which reduces to 44.3 kJ/mol at higher temperatures (55-85 °C). A semi-empirical expression for pyrite dissolution under these conditions is proposed as follows:

$$1/3 \ln(1 - X) + [(1 - X)^{-1/3} - 1] = 88.3 [\text{HNO}_3]^{2.6} r_0^{-1.3} e^{-44280/RT}$$

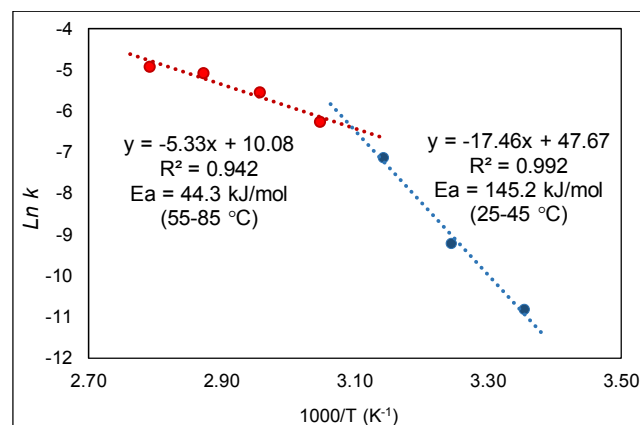


Figure 8.2: Arrhenius plot of $\ln k$ vs $1000/T$ (K^{-1}).

HNO₃ has the additional benefit of being recyclable, which offers economic benefits for its industrial use (Li, 2009; Rogozhnikov et al., 2019). To regenerate HNO₃ for reuse, the released NO_x (X=1 or 2) gas from the reaction between HNO₃ and pyrite (FeS₂) can be captured in an absorption column and mixed with H₂O and O₂. Therefore, HNO₃ is an effective pretreatment method for mine tailings mostly containing pyrite enclosing gold which can be applied in a reusable manner by capturing the emission gases, making it economically attractive and potentially environmentally benign.

Figure 8.3 illustrates a closed-loop process design for nitric acid pretreatment of 60,000 tons of mine tailing per day, assuming 1/3 of the tailing is pyrite (i.e. 20,000 tons) encapsulating gold. Depending on the amount of enclosed gold in pyrite there is potential for improving the yield and ultimately profit growth.

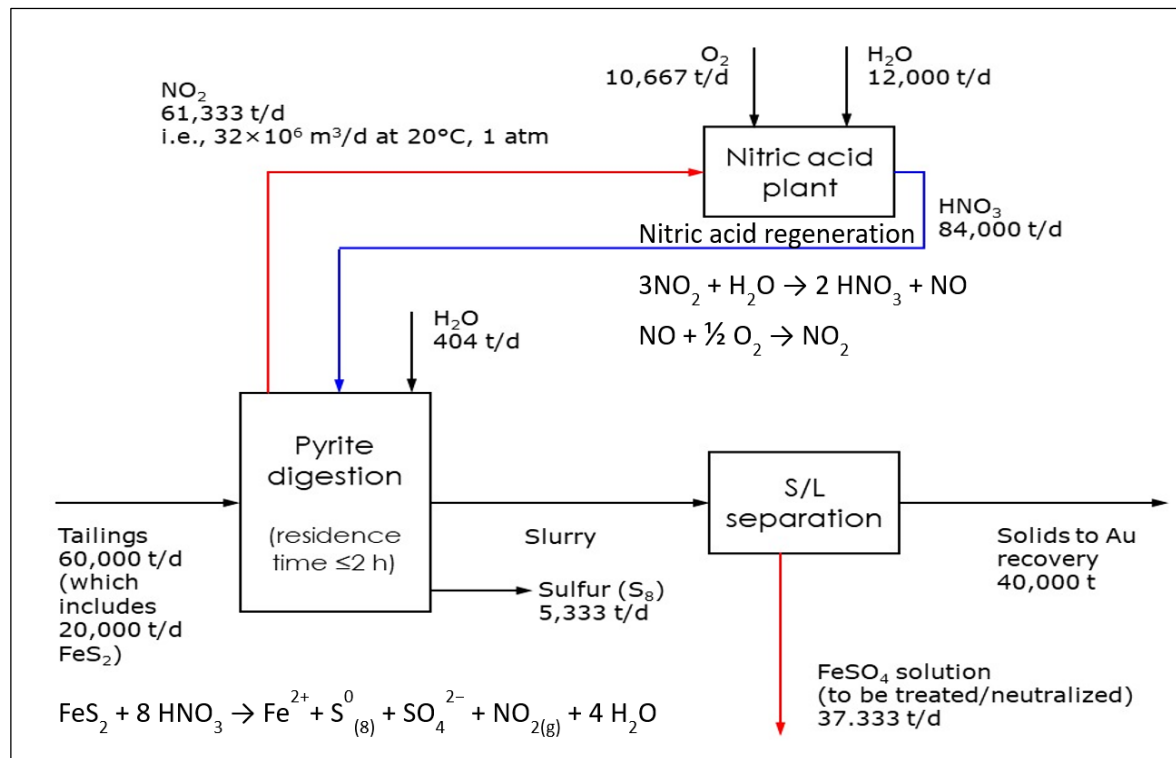


Figure 8.3: Illustration of a closed-loop process design for nitric acid pretreatment of mine tailing containing pyrite.

Electrochemical analyses (CV and EIS) helped to further study the dissolution mechanism of sulfidic minerals (since gold can be enclosed in both pyrite and chalcopyrite), with the results submitted for publication in the research paper *"An electrochemical study of pyrite and chalcopyrite oxidative dissolution in diluted nitric acid solution"*. The analyses confirmed the diffusion-controlled dissolution process found in the kinetics study.

Using CV, the potential of a working electrode (pyrite and chalcopyrite) was cycled with the resulting oxidation and reduction peaks indicating the redox reactions that occur. The EIS of pyrite and chalcopyrite at specific potentials corresponding to anodic peaks in the CV scans helped obtain further information about the reaction mechanism and products formed.

At low anodic potentials (below 0.6 V vs Ag/AgCl), iron oxides (i.e. $\text{Fe}(\text{OH})_3$) and a sulfur-rich layer containing S^0 partially covering the pyrite electrode's surface, and $\text{Cu}_{1-x}\text{Fe}_{1-y}\text{S}_{2-z}$, CuS_2 , and S^0 accumulated on the chalcopyrite electrode, leading to a diffusion process. As the potential increased above 0.7 V, it provided a sufficient anodic driving force to further oxidised the species that covered the electrode surface to soluble species, i.e. S^0 to H_2S or SO_4^{2-} which eradicated the diffusion barrier. High applied potentials at 0.9 V caused extensive oxidation of both pyrite and chalcopyrite, as seen in a sharp anodic current escalation in a short increment of the potential.

The EIS study supported the findings by CV in terms of the reactions and formed products. For instance, the existence of a Warburg diffusion effect in the EIS study at the low potentials for both pyrite and chalcopyrite confirmed the diffusion-controlled dissolution process, which was also found in the kinetic study. Moreover, the disappearance of the Warburg diffusion element at high potentials showed the removal of species covering the electrode surface and causing the diffusion hurdle. Consequently, extensive dissolution occurs, exhibiting less resistance in the process.

To assess and compare the suitability of ILs as an alternative to mineral acids metal extraction from EAFD as a metal-containing waste, a series of experiments were set up to extract Zn, In, Ga and Fe from EAFD spiked with 5% In and Ga.

Two ILs ($[\text{Bmim}^+\text{HSO}_4^-]$ and $[\text{Bmim}^+\text{Cl}^-]$) and three oxidants ($\text{Fe}_2(\text{SO}_4)_3$, H_2O_2 , and KMnO_4 , individually mixed with each of the ILs) were examined. The IL $[\text{Bmim}^+\text{HSO}_4^-]$ with $\text{Fe}_2(\text{SO}_4)_3$ as oxidant proved the best combination to extract 92.7% Zn, 80.2% Fe, 97.4% In, and 17.03% Ga, with the optimum condition being 30% v/v $[\text{Bmim}^+\text{HSO}_4^-]$, 1 g of $\text{Fe}_2(\text{SO}_4)_3$ oxidant (2%), S/L ratio = 1/20, at 85 °C for 240 min leaching time. The dissolution kinetics of the studied metals (Zn, Fe, In and Ga) over a temperature range from 55 to 85 °C was diffusion-controlled, as confirmed by the activation energies obtained for dissolution of each of the metals being lower than 40 kJ/mol.

The extraction efficiency of Zn and Fe with the IL $[\text{Bmim}^+\text{HSO}_4^-]$ and the related activation energies were compared to H_2SO_4 leaching by Kukurugya et al. (2015) in Table 8.1. The comparison revealed that the IL $[\text{Bmim}^+\text{HSO}_4^-]$ as leaching solvent for EAFD was as efficient or marginally better than the H_2SO_4 leaching, with higher extraction efficiency and lower activation energies required in the dissolution kinetics using the IL.

Table 8.1: The activation energy and extraction efficiency values for Zn and Fe from EAFD.

Reagent used	E _a for Zn (kJ/mol)		%E Zn	E _a for Fe (kJ/mol)		%E Fe	Reference
	*1 st part	2 nd part		*1 st part	2 nd part		
1 M H ₂ SO ₄	1.7	42.3	87%	35.6	—	79%	Kukurugya et al., (2015)
30% (v/v) [Bmim ⁺ HSO ₄ ⁻]	7.4	8.2	92.7%	20.8	34.6	80.2%	This research

Note: *1st and 2nd parts refer to the two stages of the kinetics dissolution of Zn and Fe from their two main mineral phases. In this case, Zn extraction starts from a more easily extractable phase ZnO, then the refractory ZnFe₂O₄ phase. The extractable Fe comes primarily from dissolving Fe₃O₄, then the ZnFe₂O₄ phase that is more chemically resistant.

Figure 8.4 demonstrates a scheme for the proposed leaching process using the IL [Bmim⁺HSO₄⁻] for metal extraction from EAFD (spiked with 5% In and Ga), presenting the residue and the leached solution with the different metallic elements, and ultimately the recovery methods for each metal.

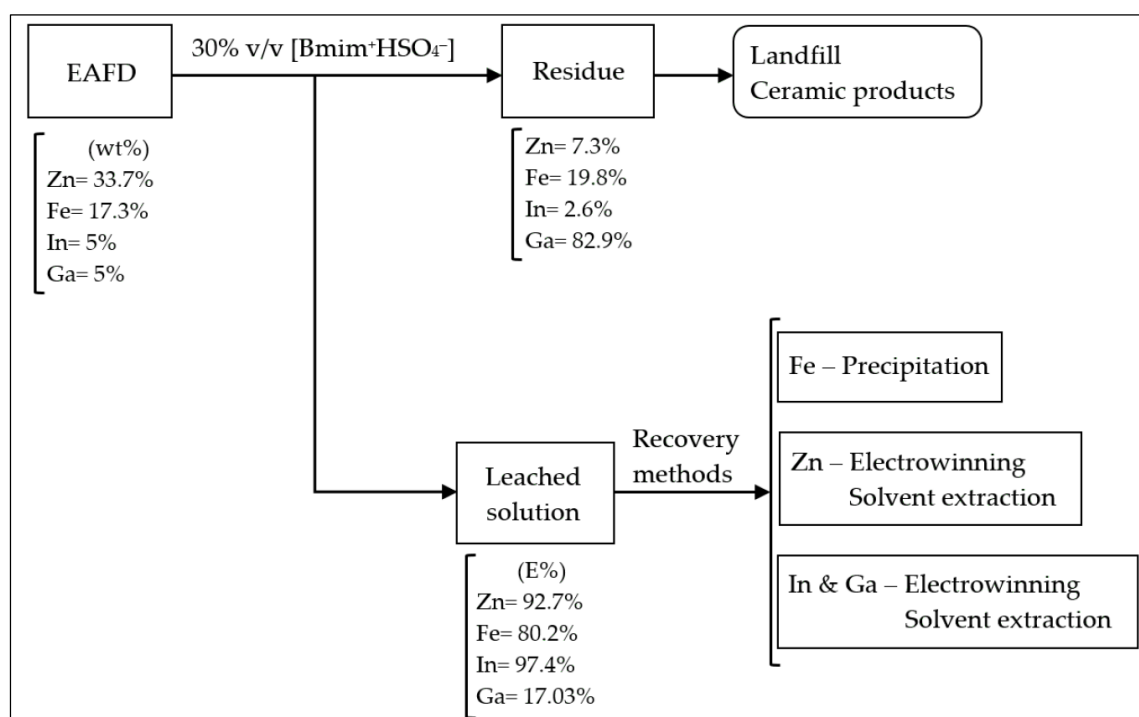


Figure 8.4: A schematic design for the leaching process using IL [Bmim⁺HSO₄⁻] for metal extraction from EAFD, and the ultimate recovery methods for each metal.

DFT modelling for metal extraction with the available ligands in the DES ethaline and three ILs proved useful for identifying optimal ligand-metal complexations and the results correlated with that from the lab experiments.

Theoretical modelling and thermodynamic calculation of ΔG for reactions indicating ligand-metal complexation helped comprehend a leaching system by comparing the results for different ligands to determine which ligand can form the most stable complex with the target metal.

The viability of pyrite dissolution in a DES composed of choline chloride and ethylene glycol, called ethaline, was examined both theoretically and experimentally. DFT was used to determine whether Cl^- and/or $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$, the two ligands provided by choline chloride and ethylene glycol, respectively, form the most likely and stable complex with Fe^{2+} and/or Fe^{3+} as an indication of pyrite dissolution. The ΔG for different possible complexes were calculated and the HOMO-LUMO gaps were also considered. Among the proposed complexes, the tetrahedral complex $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$ with the ligand $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ through O-donor chelating with Fe^{3+} , had the lowest ΔG (-71.4 eV) and the largest HOMO-LUMO gap (1.3 eV) (Figure 8.5). A negative value for ΔG indicates that the reaction occurs spontaneously and a large HOMO-LUMO gap indicates a stable ligand-metal complex.

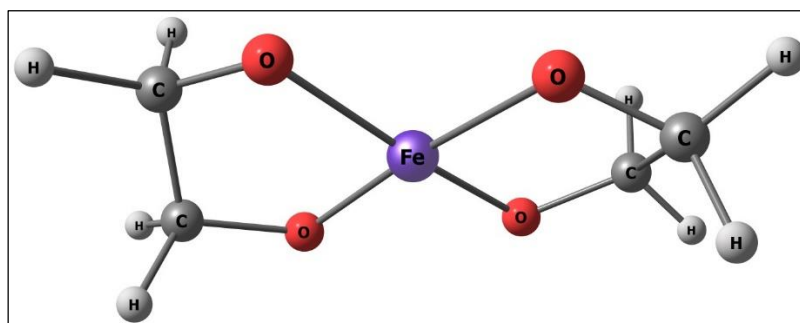


Figure 8.5: The most stable and probable complex formed between Fe^{3+} with ligand $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$, as the tetrahedral $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$.

Fourier-transform infrared (FTIR) spectroscopy was used to characterise the synthesised ethaline solvent and the ethaline solution after pyrite dissolution (i.e. Fe extraction). In the ethaline solution's spectrum, the appearance of a double peak at 1715 cm^{-1} and 1643 cm^{-1} can be attributed to the Fe-O-C bond, derived from the complex between $[\text{C}_2\text{H}_4\text{O}_2]^{2-}$ and Fe^{3+} . This observation agrees with the DFT calculation showing $[\text{Fe}(\text{C}_2\text{H}_4\text{O}_2)_2]^-$ to be the most likely and stable complex to form. As only a 23.7% Fe extraction was achieved, the ethaline solvent did not deliver adequate extraction compared to traditional reagents.

DFT modelling was also applied for In and Ga extraction in the ILs medium. In and Ga are traditionally extracted using mineral acids H_2SO_4 , HCl , and HNO_3 . For this reason, three imidazolium-based ILs

[Bmim⁺HSO₄⁻], [Bmim⁺Cl⁻] and [Bmim⁺NO₃⁻] with anionic parts ([SO₄²⁻], [Cl⁻], and [NO₃⁻]) similar to the commonly used acids were selected for the DFT calculations. The ΔG for different complexes were calculated to determine which of the ligands ([SO₄²⁻], [Cl⁻] or [NO₃⁻]) will most likely form the most stable complex with In and Ga. The IL [Bmim⁺HSO₄⁻] proved to form the most likely and stable complex, since it possesses [SO₄²⁻] O-donor ligand, resulting in the dimer complex of [In₂(SO₄)₃] and [Ga₂(SO₄)₃] with the lowest ΔG and the largest HOMO–LUMO gap (Figure 8.6).

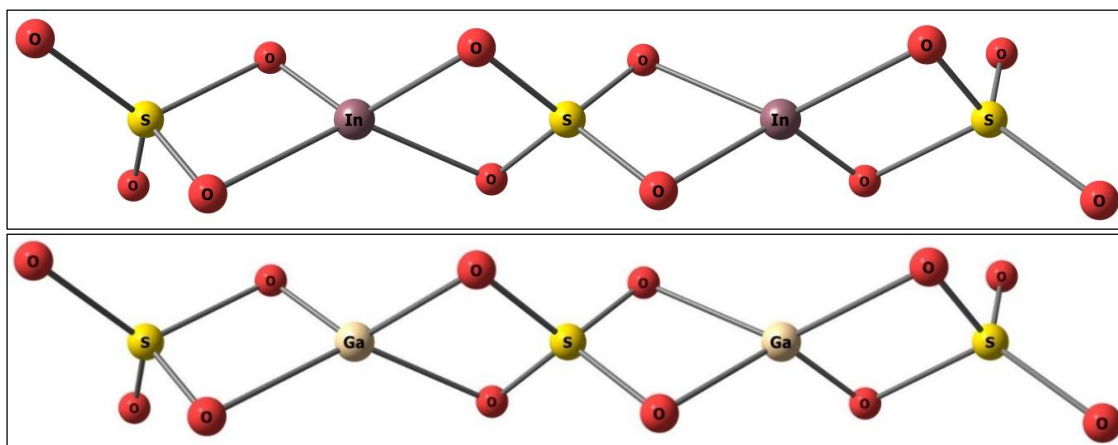


Figure 8.6: The dimer complex of [In₂(SO₄)₃] and [Ga₂(SO₄)₃] as the most probable and stable complexes to form.

Suggestions and recommendations for further research

This research lays the foundation for further research applying the above findings and methods to a broader range of metals found in other forms of secondary metal-containing waste. Questions and feedback from attendees at the author's presentation of this research at the European Metallurgical Conference 2023 showed industrial interest in the use of novel solvents and secondary waste recovery as secondary income streams from existing metal production operations. Other areas in this line of research worth exploring include (1) recovery of the extracted metals from the IL leaching solution via precipitation, solvent extraction and electrowinning (depending on the metals), and (2) investigating how many times the IL can be reused, with stripping taking place between each use, with negligible effect on its extraction efficiency.

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