



UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

**EXTRACTION OF GOLD FROM TAILINGS USING
ENVIRONMENTALLY FRIENDLY REAGENTS**

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

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DECLARATION

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

A handwritten signature in black ink, appearing to read 'MAREMA JACK KHUDUWE', written over a horizontal dashed line.

Marema Jack Khuduwe

27th day of January 2025

ABSTRACT

The depletion of high-grade gold ores, the high production costs associated with mining at lower depths, and the high demand for gold have caused the mining industry to search for alternative sources of gold. Additionally, the conventional cyanidation process raises health and environmental concerns. The treatment of waste generated by the cyanidation process to reduce the residual cyanide content before disposal also incurs additional costs. Therefore, this study focuses on the extraction of gold from tailings using environmentally benign reagents such as 1-butyl-3-methyl-imidazolium hydrogen sulfate (BmimHSO₄) ionic liquid (IL), ethaline (mixture of choline chloride and ethylene glycol) deep eutectic solvent (DES), and thiosulfate.

The gold tailings used in this work were obtained from DRD Gold Ergo Mining (Pty) Ltd operations in the Witwatersrand Basin, South Africa. Mineralogical analysis by X-ray diffraction (XRD) showed that the tailings material consisted of quartz (72.13%), muscovite (7.49%), chlorite (2.65%), pyrophyllite (1.50%), clinocllore (1.30%), and other trace minerals. The gold association by mineral liberation analysis (MLA) employing the Sparse Phase Liberation-Dual Zoom (SPL-DZ) method indicated that all the gold was locked in the iron oxide (FeO) matrix. Gold grade analysis by fire assay analysis (FAA) showed that the tailings had a head grade of 0.32 g/t Au.

The leaching of the gold tailings was carried out by employing the use of the design of experiments (DOE) method to identify factors that significantly influence the gold extraction process. The central composite design (CCD) technique in conjunction with response surface methodology (RSM) was used to optimize the identified significant factors to obtain optimum conditions for optimal gold extraction. The effect of particle size and the co-dissolution of Ag, Cu, Fe, and Ni with Au was investigated. Furthermore, the recovery of Au by activated carbon (AC) from leach solutions of the investigated reagents was also investigated

The results from the IL studies indicated that the reagent concentration had a positive and significant influence on the gold extraction process, suggesting that to achieve optimal gold extraction, IL concentration must be kept at a high level. The interaction of temperature, concentration, and pulp density also significantly influenced the gold extraction process in the IL solution. The theoretical optimum conditions established from the statistically-based optimization model were 75 °C leaching temperature, 1.0 M (25% aqueous BmimHSO₄

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mixture) IL concentration, and 10 %w/v pulp density, giving a maximum Au extraction of 45.3%. This low Au extraction is attributed to the inefficiency of ILs in dissolving metals from their solid oxide form, thus unable to liberate the gold for dissolution locked in the metal iron oxide. On the other hand, leaching studies focusing on the use of DES found that pulp density and leaching time had a significant and positive influence on the gold extraction process. This suggests that to achieve maximum gold extraction, pulp density and leaching time must be kept at high levels. The optimum conditions were found to be 30 %w/v pulp density and 7 hrs leaching time. A maximum Au extraction of 76.4% was achieved. This high gold extraction is attributed to the high FeO destruction observed in the study, suggesting that the gold was liberated and amenable to leaching. Lastly, thiosulfate leaching studies identified temperature, time, pulp density, the interaction of temperature and concentration, the interaction of concentration and pulp density, and the interaction of temperature and time as the parameters significantly influencing gold extraction. A maximum Au extraction of 47% was achieved. This low gold extraction is attributed to the low efficiency of thiosulfate in dissolving metal iron oxide and the reagent consumption through silica dissolution, thus reducing the amount of thiosulfate available for gold dissolution.

The results of the effect of tailings particle size results revealed that the IL leaching of bulk tailings (-300 μm , P80 = 75 μm) gave Au extraction of 21.9% while the leaching of smaller particle size tailings (-38 μm) increased Au extraction to 45.3%. The high gold extraction at smaller particle sizes is attributed to the large surface area available for interaction with the leaching agent and the presence of a thin boundary, thus resulting in improved leaching efficiency. On the other hand, DES leaching of bulk tailings resulted in Au extraction of 71.9% and the leaching of smaller particle size tailings gave 76.4% Au extraction, indicating that reduction in particle size did not have a significant impact on gold dissolution. Lastly, thiosulfate leaching of bulk tailings gave a maximum Au extraction of 24% and the leaching of smaller particle size tailings resulted in an increased Au extraction of 47%, indicating that a reduction in particle size in this system had a significant effect.

The study indicated that DES was more efficient in the dissolution of gold tailings compared to the use of IL and thiosulfate. Furthermore, DES gave higher Au extraction (71.6%) compared to cyanide solutions which gave Au extraction of 46.9%. However, cyanide gave a higher Au extraction compared to IL (21.9%) and thiosulfate (24%). These results indicate that ethaline DES is more efficient compared to 1-butyl-3-methyl-imidazolium hydrogen sulfate IL

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and thiosulfate, and thus can be used in the processing of this kind of tailings as an alternative to cyanide.

Moreover, the reagents dissolved more gold compared to other metals in the tailings except for IL which dissolved more Cu (50.4%) and Ni (61.9%) compared to Au (45.3%). Finally, the recovery of gold from the leach solution of the investigated reagents using activated carbon (AC) was found to be possible with the maximum Au adsorption of 84.6% achievable from IL leach solution in 2 hours at AC amount of 60 g/l and 4 hours at AC amount of 120 g/l. The maximum Au adsorption of 75% was achieved from DES leach solution in 4 hours at an AC amount of 120 g/l. The highest Au adsorption of 46.4% was achieved from thiosulfate leach solution in 6 hours. The recovery of Au by AC from leach solutions of IL and DES was high, however, they are not comparable to the 99% gold recovery by AC from cyanide solutions in the industry. This indicates that the recovery of gold from these solutions by alternative adsorbents should form a basis for further investigation.

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PUBLICATIONS AND PRESENTATIONS

Journal Publication

1. Khuduwe, M.J., Shemi, A., & Ndlovu, S., 2024. Extraction of Gold from Tailings Using Ethaline Deep Eutectic Solvent. *Minerals*, 14(12), p.1239.

Conference Presentation

1. Khuduwe, M.J., Shemi, A., & Ndlovu, S., 2024. Extraction of gold from tailings using ethaline deep eutectic solvent: Southern African Institute of Mining and Metallurgy (SAIMM) Hydrometallurgy Conference, Stellenbosch, South Africa, 1st – 3rd September, 2024.

DEDICATION

Dedicated to
my family for their
understanding and unwavering support

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CHAPTER 1

INTRODUCTION

1 Introduction

The high demand for gold, coupled with the depletion of high-grade gold ores and the high production costs associated with mining at lower depths, has ultimately led to a search for alternative sources of gold. Alternative secondary materials identified as possible sources of gold include mine tailings, anode slime, electronic scrap, jewelry, and metal polishing waste. However, most recent research efforts have focused on gold extraction from mine tailings (Gökelma et al., 2016).

In the South African gold mining industry, the cluster of gold mines in the Witwatersrand Basin generates a significant amount of mine tailings (Malatse and Ndlovu, 2015). These tailings are associated with significant levels of sulfides, silicates, and minor levels of valuable metals such as gold.

Gold tailing dumps mostly in the Witwatersrand area are currently being reprocessed by many mining companies using the cyanidation process to recover the gold that is still hosted in the tailings. For example, Pan African Resources utilizes a carbon-in-leach process followed by electrowinning and smelting in their Barberton Tailings Retreatment Project (BTRP) to produce a saleable gold product (Cornish, 2013). Another company, Gold Fields performs size classification of the tailings using a cyclone, where the cyclone overflow gravitates to the dewatering thickeners and the cyclone underflow gravitates to the regrind mill for further particle size reduction (80% passing 75 μm). The thickener underflow slurry is then leached via carbon-in-pulp or carbon-in-leach followed by elution and electrowinning. The residual slurry after gold extraction from a CIP or CIL arrangement is pumped to the Tailings Storage Facilities (TSF) for final tailings disposal (Gold Fields: Mineral Resource and Mineral Reserve Overview 2011 - 6. Projects). DRDGold Limited utilizes carbon-in-leach, elution, zinc precipitation, and smelting to reprocess tailings for gold recovery (M. Gerke, personal communication, July 12, 2023).

The waste generated by the cyanidation process requires treatment to reduce the cyanide concentration before disposal. This is done to avoid damage to the environment and

ecosystems. Cyanide is very toxic to humans and animals. The cyanide solution in waste streams can seep through the soil and contaminate groundwater, causing long-term environmental problems (Gökelma et al., 2016). The effect of cyanide on plants and living things can vary greatly and depends heavily on the amount ingested. If ingested at higher levels it can cause irreversible damage such as inhibition of intracellular respiration and intermediate cell death (Gökelma et al., 2016).

Recently, a significant amount of research has been devoted to the development of alternative non-toxic dissolution reagents that can be used to recover gold from both primary and secondary materials (Xie et al., 2021; Birich et al., 2016; Jenkin et al., 2016). For example, thiocyanate and thiosulfate are used in some of the techniques that have been developed as possible alternatives to cyanidation. However, commercial adoption of these techniques has been hampered by limitations such as high reagent consumption, high reagent costs, and increasing gold production costs (Tian and Liu, 2022). According to Hilson and Monhemius (2006), thiourea leaching has shown considerable promise. Thiourea dissolves gold under acidic conditions to form a cationic complex. The reaction is fast, and gold extraction of up to 99% has been reported (Hilson and Monhemius, 2006). Nevertheless, the use of thiourea has limitations, some of which are restricted working conditions and the inability to treat low-grade ores. The main limitations of thiourea leaching are the expensive oxidants required and the increased consumption of thiourea (Ubalini et al., 1998). Besides thiourea, biodegradable reagents such as thiosulfate, ionic liquids (IL), and deep eutectic solvents (DES) that could offer a new eco-friendly approach to the processing of a variety of ores, have been proposed as alternatives, especially for the difficult-to-treat ores that consume a lot of energy (Abbott et al., 2015).

Thiosulfate has been seriously considered as a substitute for cyanide because it generally causes fewer environmental impacts (Abbruzzese et al., 1995). Gold dissolves slowly in alkaline thiosulfate with the rate of dissolution being influenced by thiosulfate concentration, dissolved oxygen, and temperature, and can be enhanced by the addition of copper ions (Kuzugüdenlí and Kantar, 1999). The thiosulfate leaching process is catalyzed by copper and has several advantages over the traditional cyanidation process such as environmental friendliness and high selectivity in gold dissolution, despite its slow rate (Aylmore, 2001; Ubalini et al., 2019). Acceptable gold leaching rates using thiosulfate are achieved in the presence of ammonia, together with copper (Breuer and Jeffrey, 2000).

Ionic liquids and deep eutectic solvents are considered green solvents and their properties give them the potential to be used as alternatives to traditional reagents (Chen and Mu, 2021). ILs are anhydrous salts that are liquid at room temperature. They are highly effective solvents and electrolytes with the potential for high selectivity in both dissolution and metal recovery processes. These liquids are a relatively new class of solvents that consist entirely of large organic cations and inorganic or organic anions of various sizes, and some of them can be considered environmentally benign. ILs have been applied as alternatives for molecular organic solvents in various fields due to their unique properties such as negligible vapor pressure, large liquidus range, high thermal and chemical stability, wide electrochemical window, and nonflammability (Schoor et al., 2019). They can serve as efficient solvents for the selective oxidative leaching of gold ores (Whitehead et al., 2007).

The study by Whitehead et al. (2007) on the leaching of gold from a synthetic oxidic ore and a natural sulfidic ore in the presence of iron (III) and thiourea at 20 – 50 °C in 1-butyl-3-methyl-imidazolium hydrogen sulfate ([Bmim]HSO₄) ionic liquid showed that gold extraction of greater than 85% from both synthetic ore and natural sulfidic ore can be achieved. The authors also examined the effect of varying the alkyl chain length in the (n-alkyl) methyl-imidazolium cation and of varying the anion in bmim⁺X⁻ liquids (X⁻ = Cl⁻, CH₃SO₃⁻, N(CN)₂⁻, HSO₄⁻) on metal ion recovery from ore and the results showed that the bmim⁺(HSO₄⁻) liquid was the most effective leaching medium.

Teimouri et al. (2020) studied the effect of temperature on gold extraction from a flotation-concentrated refractory gold tailings sample containing pyrite in a solution of 1-butyl-3-methyl-imidazolium hydrogen sulfate with thiourea as a complexing agent and iron (III) sulfate as an oxidant. Their results showed that gold extraction increased with an increase in temperature with the highest gold extraction of 42.6% achieved at 65 °C after 12 hours of leaching.

Whitehead et al. (2004) employed the use of 1-butyl-3-methyl-imidazolium hydrogen sulfate IL with iron (III) sulfate as an oxidant and thiourea as a complexing agent for the extraction of gold and silver. Their results showed that selective extraction of gold (≥85%) and silver (≥60%) from powdered ore of predominantly chalcopyrite, pyrite, pyrrhotite, and sphalerite minerals was achieved at room temperature in 50 h, with other value metals present in the ore (Cu, Zn, Pb, Fe) being extracted to only low percentages.

Deep eutectic solvents are a form of ionic liquids which are mixtures of salts such as choline chloride with hydrogen-bond donors such as urea. DESs are systems formed from a mixture of Lewis or Brønsted acids and bases that can contain a variety of anionic and/or cationic species (Whitehead et al., 2007). They are less harmful to the environment, yet chemically stable (Jenkin et al., 2016). DESs can dissolve many inorganic substances, especially metal oxides (Jenkin et al., 2016). They have selective solubility, combined variability of structure and performance, and are easy to regenerate (Tian and Liu, 2022).

Villemejeanne et al. (2022) studied the recovery of gold and palladium in a one-step electro-leaching-electrochemical deposition process (EL-ECD) using deep eutectic solvents ChCl:EG 1:2 and ChCl:EG 1:3. Their results showed that gold and palladium electro-leaching-electrochemical deposition was successfully achieved in ChCl:EG 1:3 mixture with yields ranging between 85% and 100%. Winardhi et al. (2022) used a particle-based approach to predict the success and selectivity of leaching processes using a deep eutectic solvent. The approach employed a combination of laboratory-based X-ray computed tomography (CT) and scanning electron microscopy-based image analysis (Winardhi et al., 2022a). The authors conducted leaching of Au-Ag-bearing sulfide flotation concentrate by the deep eutectic solvent ethaline with iodine as an oxidizing agent. Their results showed that time-lapse CT provides an accurate estimation of the dissolution rate of pyrite, chalcopyrite, galena, telluride minerals, and gold. The authors then used dissolution rates to simulate the metal recoveries from the sulfide concentrate as a function of leaching time and found that the simulation results were within a 5% variation of metal recoveries obtained by batch leaching experiments. Additionally, it was found that sulfide minerals dissolve in a solution of DES except for pyrite (Winardhi et al., 2022a). According to Jenkin et al. (2016), ILs and DESs can be used to selectively dissolve native gold, tellurium, sulfides, and tellurides.

The tailings reprocessing sector in South Africa has received much attention due to the economic, environmental, financial, and political imperatives affecting new and existing tailings facilities (Singo and Kramers, 2021). On a national level, reprocessing residues into valuable products would reduce the national trade deficit and boost the economy. The physical practice of reprocessing tailings residues would also benefit local communities that are adversely affected by the disposal of mine waste and the consequent reduction in job opportunities (Vitti and Arnold, 2022). The reprocessing of moderate to low-grade gold tailings not only helps to boost the national economy but also provides business opportunities for

mining companies. These tailings reprocessing options further help to improve the quality of life for the surrounding areas as the reclamation process frees up land for other beneficial uses. Furthermore, the use of non-toxic reagents overcomes environmental problems caused by cyanidation. Moreover, less, or non-toxic gold solutions are also more suitable for further lab-scale research (Marsden and House, 2006; Syed, 2012). However, the environmental impact is not the only problem that raises the demand for non-toxic reagents. There are other disadvantages of cyanide leaching, such as big losses in the processing of preg-robbing ores. Additionally, these ores cause a higher demand for cyanide with an associated decrease in the dissolution yield (Göknelma et al., 2016).

This research study aims to evaluate the performance of alternative environmentally friendly leaching reagents in the extraction of gold from tailings. The choice of the selected reagents in this work is influenced by the mineralogical characteristics of the tailings. The tailings used in this work are characterized largely by the presence of silicates and very low levels of oxides and sulfides, with all the gold associated with iron-oxides as shown in Chapter 3.

The three leaching reagents investigated in this work include 1-butyl-3-methyl-imidazolium hydrogen sulfate IL in the presence of ferric sulfate as an oxidant and thiourea as a complexing agent, ethaline DES in the presence of $I_2(s)$ as an oxidant, and thiosulfate in the presence of copper sulfate as a catalyst. DESs have been studied for their ability to dissolve metal oxides, and the solubility of metal oxides in DESs is largely dependent on the nature of the hydrogen-bond donor (HBD) (Smith et al., 2014). ILs have been reported to have the ability to dissolve diverse solids, such as elements, oxides, and sulfides, at moderate temperatures without the need for special conditions (Grasser et al., 2022). Thiosulfate leaching has been reported as efficient in the dissolution of metal oxides and silicates (Celep et al., 2014). The dissolution of sulfide minerals in thiosulfate is effective in the processing of low sulfur content gold-containing materials. This is because high levels of sulfur in the material result in increased reagent consumption (Ubal dini et al., 2014).

1.1 Problem statement

Cyanidation is a dominant leaching process used by the mining industry to recover gold due to its availability, relatively low cost, and ability to achieve high gold recoveries. However, cyanide application in gold processing has been of concern due to its toxicity to the ecosystem. Inevitably, waste arising from the cyanidation process requires expensive treatment before disposal. This has led to the search for non-toxic alternative reagents that can still be comparatively effective in gold dissolution. Additionally, the depletion of high-grade gold ores has also led to the search for alternative sources of gold. As a result, many gold mining companies have shifted from processing primary ore to reprocessing tailings as an alternative source of gold. However, this approach faces significant challenges due to the low gold grade in the tailings, which leads to poor recoveries.

1.2 Research Aims and Objectives

This research study aims to investigate the use of alternative environmentally friendly reagents to extract gold from leach tailings. This aim will be achieved through the following research objectives:

- Investigating the extent of gold extraction from tailings using solvents 1-butyl-3-methylimidazolium hydrogen sulfate IL ([Bmim]HSO₄), ethaline (ChCl: EG) DES, and sodium thiosulfate.
- Identifying and optimizing factors significantly influencing the gold extraction during [Bmim]HSO₄, ethaline, and sodium thiosulfate alternative leaching processes.
- Comparing the gold yields achieved through the investigated alternative leaching processes to those achieved via the well-established cyanidation process.

1.3 Research Questions

The aim and objectives of the study will be met through answering the following questions.

- Can the investigated less toxic alternative reagents achieve gold extractions comparable to the gold extraction achieved using cyanide?
- Which of the investigated process parameters, time, temperature, pulp density, concentration, and particle size have a significant influence on the gold extraction process?
- How selective are the investigated alternative reagents towards gold?

1.4 Research Hypothesis

Ethaline (DES), 1-butyl-3-methylimidazolium hydrogen sulfate (IL), and sodium thiosulfate can be used effectively to extract gold from tailings. These reagents have high selectivity towards gold which can improve the leaching efficiency of gold tailings. The leaching efficiency in DESs and ILs can improve because of their high stability and wide electrochemical window. The extraction of gold in thiosulfate solution can improve when processing low sulfur content material because sulfur species consume thiosulfate.

1.5 Research Methodology

The research methodology for this study includes the following main tasks: literature review, experimental activities, laboratory tests, analysis of the results obtained, conclusions, and recommendations.

1.6 Research Scope

The proposed research is limited to the leaching of gold from gold leach tailings. Leaching of gold tailings is performed using three different reagents, respectively. In all the leaching experiments, the target metal is gold.

1.7 Dissertation Layout

This section provides an overview of the chapters and sections covered in this dissertation. The dissertation consists of five chapters. Each chapter begins with a brief introduction that highlights the areas covered in various sections of the chapter. At the end of each chapter, a summary and conclusion are provided to keep the reader focused and lead them to the following chapters.

Chapter 1 – *Introduction*: This chapter provides the background of the study, the motivation for the study, and the problem statement. In addition, it presents the aim, objectives of the study, the research hypothesis, and the research questions that the study intends to answer.

Chapter 2 – *Literature review*: This chapter provides an overview of the study-related literature. This includes literature on precious metals, their extraction processes, and green solvents such as ionic liquids and DESs and their application in hydrometallurgy. This chapter also includes

general knowledge of gold, mineralogical characterization of gold ores, sources of gold, conventional, current, and proposed alternative gold extraction processes.

Chapter 3 – *Methodology*: This chapter describes the materials and methods used in the study and the rationale for their selection.

Chapter 4 – *Results and Discussion*: This chapter presents the results of the experiments performed in the study. In addition, the observed results are discussed with the aim of providing answers to the research questions.

Chapter 5 – *Conclusion and recommendations*: This chapter summarizes the most important results of the study, points out the limitations, and finally gives recommendations resulting from the study.

1.8 Summary

In this introductory chapter, the background, problem statement, research aim and objectives, research hypothesis, and research questions were discussed. A brief description of the research methodology and scope were highlighted. The next chapter reviews literature associated with this study.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Gold remains a precious metal that contributes to the artistic, cultural, and economic development of mankind. Gold was presumably the first metal used by humans because of its occurrence in the native state in placer deposits, enabling its recovery without the requirement of complex separation techniques. Its use has also been enabled by its malleability and ductility, which meant it could be easily worked with primitive tools. The earliest uses of gold were in the Middle East, during the Neolithic age, where gold was collected from streambeds either manually or by crude gravity concentration methods (Marsden and House, 2009). Finely worked gold ornaments have been found in graves in Mesopotamia originating from about 2700 BC. Similarly, gold mining in Egypt started with alluvial workings. It was followed by shallow underground vein mining in Nubia in about 1300 BC with activity centered around

Extraction of gold from tailings using environmentally friendly reagents

Hammamet, whose mines ran up to 90 m deep and sometimes extending 500 m along veins (Marsden and House, 2009).

In South Africa, the Witwatersrand Basin gold ore deposits are the primary and main source of gold production (Janisch, 1986). However, the high demand for gold (**Figure 2.1**) has led to the depletion of these ores, causing the mining industry to search for alternative sources of gold. Notably, gold tailings have been identified as secondary sources of gold thus, providing an alternative source to the primary reserves.

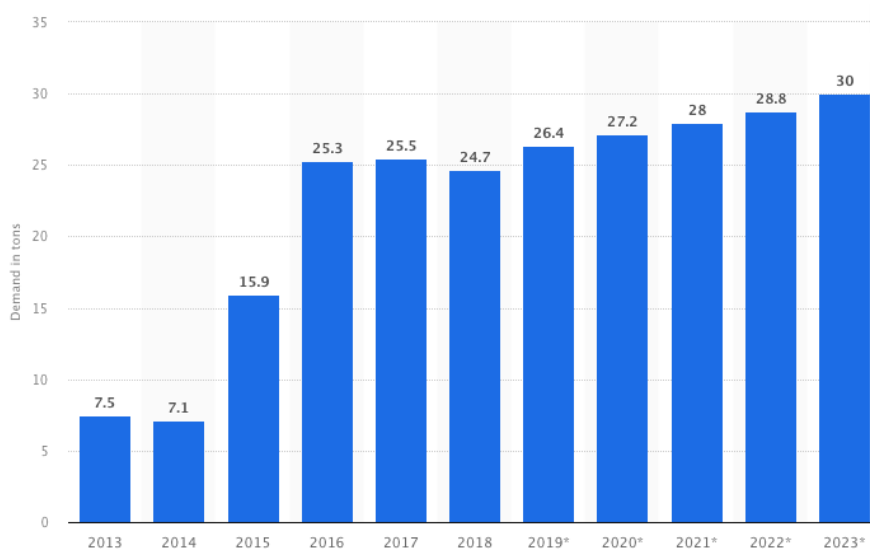


Figure 2.1. South Africa's increasing gold demand from 2013 to 2023 (in metric tons). Source: Statista, 2023

Gold (Atomic Number: 79; Atomic weight: 196.967 u; Density: 19.32 g/cm³; Symbol: Au; Melting Point: 1065 °C; Boiling Point: 2966 °C; Electron Configuration: [Xe]6s¹4f¹⁴5d¹⁰) is the most noble metal on the periodic table (Helmenstine, 2019). It has two common oxidation states: Au⁺ (aurous) and Au³⁺ (auric) and is a yellow-colored, dense, ductile, and malleable metal. It is a good conductor of electricity and heat (Helmenstine, 2019). Gold is not affected by exposure to air or to most reagents. It is inert and a good reflector of infrared radiation. Gold is usually alloyed to increase its strength (Helmenstine, 2019).

Gold is used in coinage and is the standard for many monetary systems (Marsden and House, 2009). Other major uses of gold are well demonstrated by its end-use distribution as presented in **Figure 2.2**. Gold is also used in investment. In some countries, like India for example, gold is considered very precious and can be used as collateral against loans (Fisher, 2018). Furthermore, gold is used in medical treatments (Fisher, 2018).

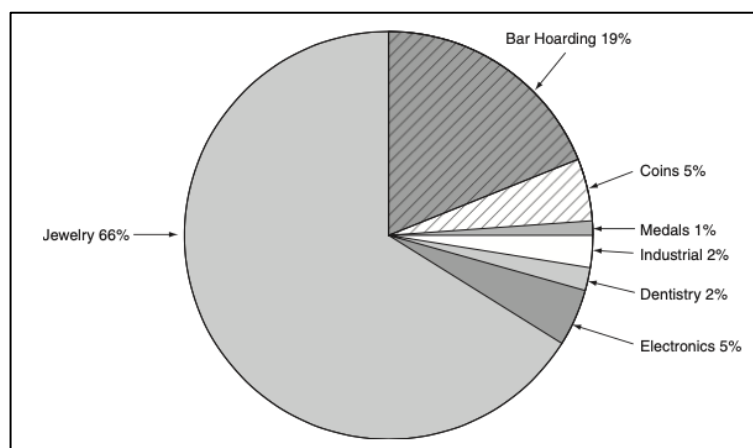


Figure 2.2. Approximate gold distribution by end use in 1989 (Marsden and House, 2009)

This literature review aims to give a general overview of gold tailings mineralogy, occurrence, and processing techniques. The importance of selecting a route for processing gold tailings based on their chemical and physical characteristics is highlighted.

2.2 Gold occurrence and mineralogy

The Witwatersrand is a 2.8-2.9 billion years old sedimentary basin located on the Kaapvaal Craton (**Figure 2.3**) (Kositsin and Krapez, 2004). Sedimentation of the Witwatersrand Supergroup occurred under a reducing Archean atmosphere and modern-style plate tectonics, as evidenced by the presence of detrital pyrite (FeS_2), detrital uraninite (UO_2), and macro-diamonds within the auriferous quartz pebble conglomerates (**Table 2.1**) (England et al., 2002; Smart et al., 2016). The mining of the Witwatersrand conglomerates and their contained gold and associated detrital sulfides dates back to 1885 (Frimmel and Nwaila, 2020). The gold in the basin is largely associated with a series of quartz-pebble conglomerate beds (reefs) that formed during continental sedimentation in alluvial fans and braid-plain depositional environments (Frimmel, 2019). This gold can occur in different forms within the pyrite or other sulfides. It can occur as free milling, along crystal grain boundaries, enclosed in the pyrite/sulfide matrix, at the boundary between sulfide grains, along fractures and/or crystal defects in concretionary pyrite (or other sulfides), and as colloidal particles or in solid solution in the sulfide matrix (**Figure 2.4**). Much of this gold is 'invisible', a loosely-defined term reserved for gold that behaves in a refractory manner to direct cyanidation (Coetzee et al., 2011). The mineralogy of gold ore deposits determines the degree of refractoriness and can be graded and classified according to the amount of gold that can be recovered by normal cyanidation (La Brooy et al., 1994) as presented in **Table 2.2**.

Extraction of gold from tailings using environmentally friendly reagents

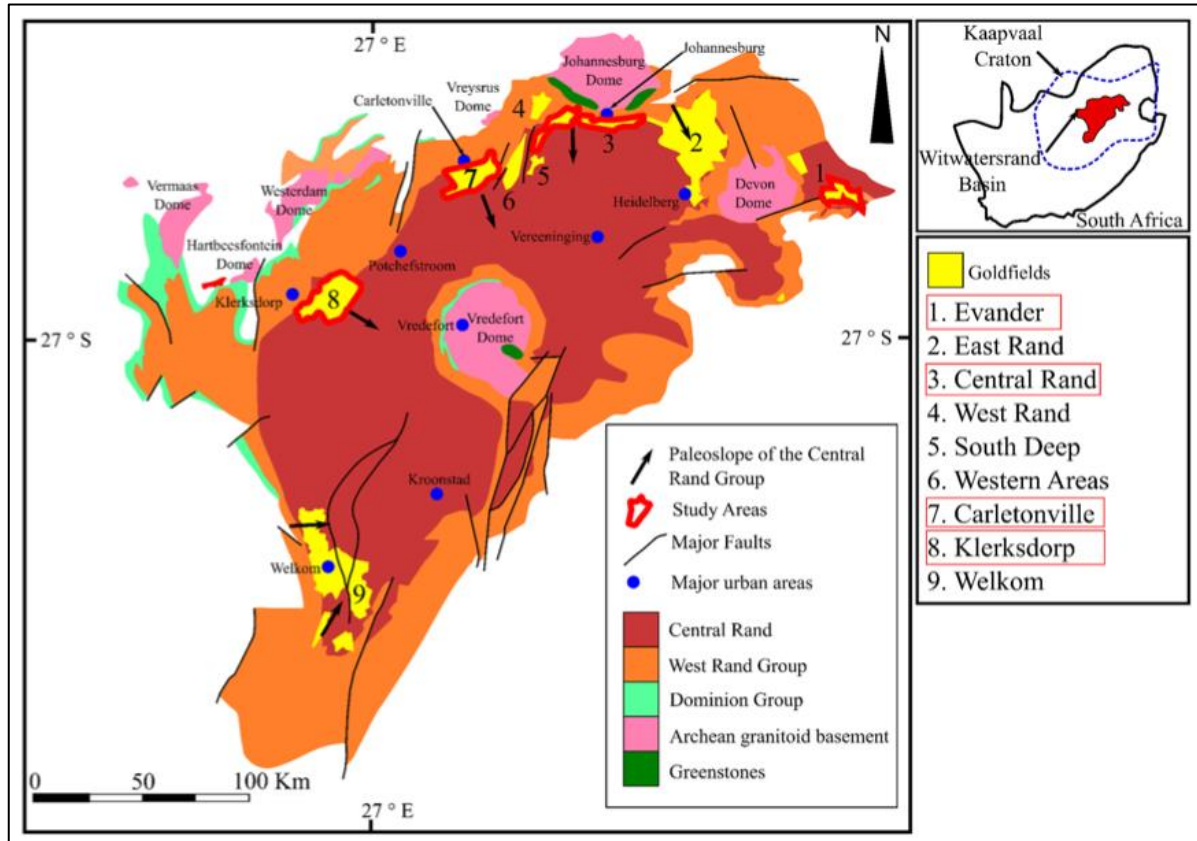


Figure 2.3. A surface geological map of the Witwatersrand basin (Chingwaru et al., 2023b)

Extraction of gold from tailings using environmentally friendly reagents

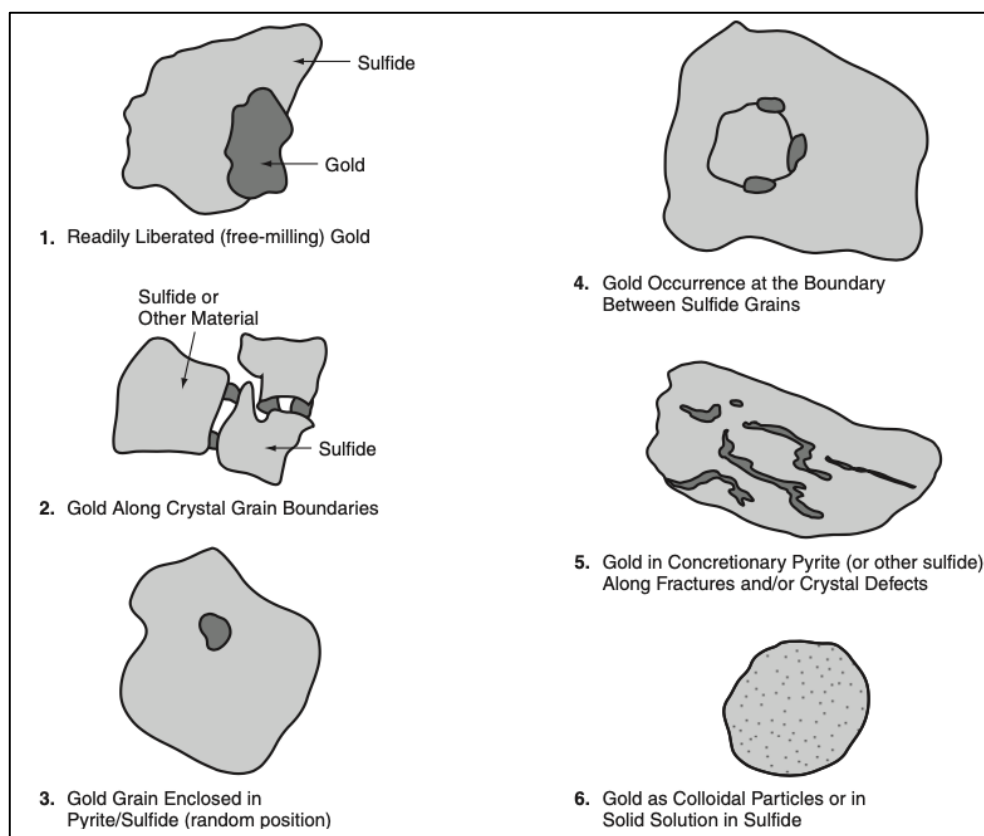


Figure 2.4. Schematic representation of types of gold associations with sulfide minerals (Marsden and House, 2006)

Table 2.1 Typical mineralogical composition of primary gold ore from three Witwatersrand blanket reefs (Marsden and House, 2006)

Component	Vaal	Ventersdorp	Dominion
Gold (ppm)	50	44	202
Silver (ppm)	8	5	-
Uranium oxide (ppm)	870	290	-
Uraninite, thorite (%)	-	-	11,5
Quartz (%)	88,3	88,9	30,6
Chlorite (%)	0,8	4,9	26,2
Muscovite (sericite) (%)	4,4	3,0	0,2
Pyrophyllite (%)	0,1	0,2	-
Zircon (%)	0,1	0,2	1,1
Monazite (%)	-	-	6,0
Chromite (%)	0,2	0,1	0,5
Cassiterite (%)	-	-	0,3
Titanium minerals (%)	0,1	0,1	12,3
Sulfide minerals (%)	6,0	2,6	11,1

Extraction of gold from tailings using environmentally friendly reagents

Table 2.2. Classification of gold ore refractoriness (La Brooy et al., 1994)

Classification	Gold recovery
Highly refractory	< 50%
Moderately refractory	50-80%
Mildly refractory	80-90%
Free Milling	90-100%

2.3 Gold ore processing and generation of tailings

The processing of gold ore begins with size reduction via crushing, followed by milling. The ground ore then undergoes flotation to produce a gold-rich concentrate and tailings. Whilst the tailings are discarded onto tailings dumps, the concentrates are further processed to extract gold using several extraction stages. The gold extraction may involve acidification, pre-treatment, and gold extraction using cyanidation via carbon in pulp (CIP) or carbon in leach (CIL) techniques. The gold adsorbed onto the carbon is then eluted with the strip liquor undergoing electrowinning for the recovery of the gold metal. The electrowon gold metal is then purified through a furnace to produce gold Doré bars ready for sale to the commercial market. An example of a flowsheet for gold ore processing is presented in **Figure 2.5**.

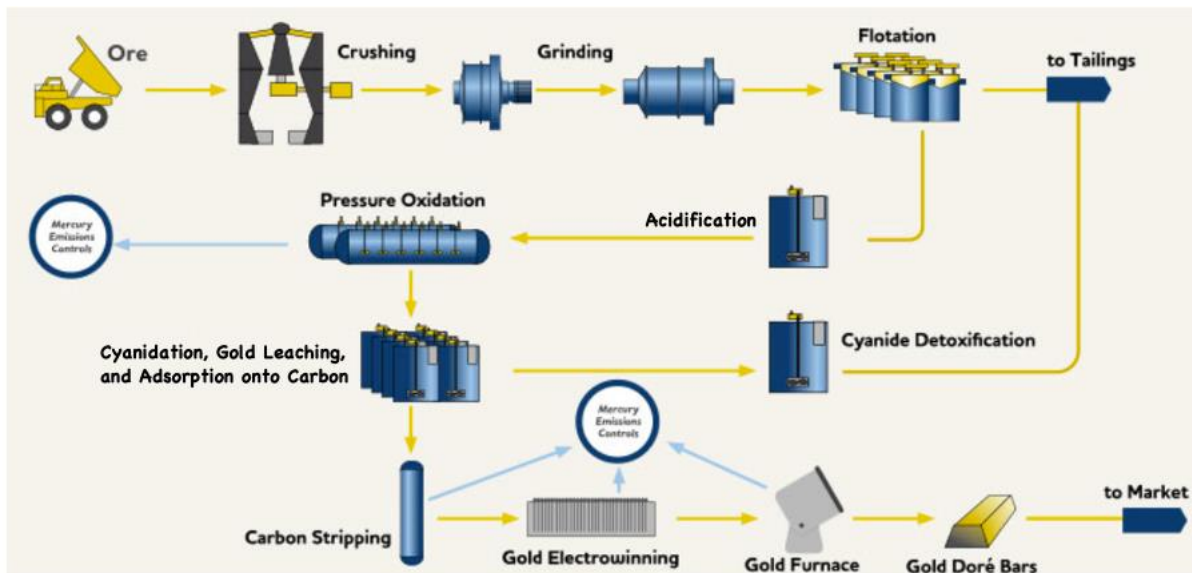


Figure 2.5. Flowsheet example of gold ore processing and beneficiation (Jordan, 2023)

Gold tailings are the residual materials left over after the gold extraction process. Gold tailings dumps are produced from a variety of settings including underground mines, open-pit mines, heap leach pads, and historic mining districts. The extended mining legacy in South Africa and the world has resulted in a massive accumulation of tailings material, approximately 16 billion tons with a recovery potential of 450 million ounces of gold (Clegg, 2023; Chingwaru et al., 2023b). Due to historical processing inefficiencies, these tailings still contain significant amounts of gold, hence, they are currently being reprocessed as a secondary gold resource (Chingwaru et al., 2023b). Huge piles of tailings dams have been produced whilst others are still being produced across South Africa, as 40% of gold reserves are found in South Africa (Ogola, 2018). In South Africa, there are approximately 800 million tons of gold tailings, which contain approximately 30 million ounces of recoverable gold (Clegg, 2023).

2.4 Gold tailings mineralogy and role in processing route selection

The comprehensive characterization of the gold distribution in tailing material presents challenges due to the complexity of the tailings material (Chingwaru et al., 2023a). The diverse mineralogy of gold carriers, for example, hinders accurate identification and quantification of the gold mineralogical distribution (Chryssoulis and Cabri, 1990; Chryssoulis and McMullen, 2005). Furthermore, the fine-grained nature of the tailings mineral particles pose difficulties to traditional gold identification methods (Goodall, 2008; Goodall and Scales, 2007). Additionally, tailings dumps are made up of different sources of tailings material due to the toll dumping from different mines. Therefore, one dump can consist of tailings from different mines which also means variability in the mineralogy within one specific tailings dump. This makes obtaining sample representativity from tailings another challenge, requiring careful sampling for accurate mineralogical characterization (Coetzee et al., 2011).

Moreover, gold tailings undergo oxidation which produces shifts in mineralogy and the remobilization of deleterious elements (Zhang et al., 2023). The complex mineralogy and the additional low grade below 1 g/t Au of tailings, therefore, make the gold extraction process challenging and costly (Janisch, 1986; Fleming, 1998).

Accurate characterization of tailings demands a multidisciplinary approach that integrates mineralogical and metallurgical analytical techniques (Chingwaru et al., 2023a). Some of the techniques used in gold process mineralogical analysis can be classified into two categories: conventional and advanced instrumental techniques (Zhou et al., 2004). Conventional

Extraction of gold from tailings using environmentally friendly reagents

techniques include Fire Assay Analysis (FAA) which determines gold in all forms and can measure gold concentrations from 0.1 to 50 g/t Au, Quadruple Ton One FA-AA Assay (FA-AA) which also determines gold in all forms, and Optical Microscopy (OMS) which is a systematic scan for gold particles, mineral identification, alteration and characteristics study (Zhou et al., 2004). Advanced instrumental techniques include (Zhou et al., 2004):

- Automated Digital Imaging System (ADIS) which scan and measure gold.
- Scanning Electron Microscope (SEM) which can be used for gold scanning, mineral identification, and surface morphological study.
- Quantitative Evaluation of Material by Scanning Electron Microscope (QEMSCAN) which can be used for gold scanning, mineral identification, liberation and surface morphological study.
- Electron Probe Microanalysis (EPMA) used for compositional analysis of gold and other minerals.
- Dynamic Secondary Ion Mass Spectrometry (D-SIMS) which is used for quantification and mapping of gold in sulfides and FeOx.
- Proton-induced X-ray Emission (u-PIXE) used for quantification and mapping of gold in sulfides and silicates.
- Laser Ablation Microprobe Inductively Coupled Plasma Mass Spectroscopy (LAM-ICP-MS) which can be used for quantification of gold in sulfides, silicates, and oxides.
- Time-of-Flight Laser Ion Mass Spectrometry (TOF-LIMS) which is used for quantification of surface gold and analysis of surface chemistry.

The mineralogy of tailings largely depends on the type of ore originally treated, the extraction process followed, the efficiency of the process, and the age of the tailings (Janisch, 1986). This, in turn, determines the processing route to be employed for the extraction of gold. For example, Dehghani et al. (2009) studied the recovery of gold from the Mouteh Gold Mine tailings dam, in Iran. Sulfide minerals and active carbon were identified as the main sources of gold in the tailings. The authors preconcentrated the tailings by flotation. The flotation concentrate obtained was taken for regrinding followed by roasting before cyanidation resulting in gold recovery in the range of 87.8 to 98.4% (Dehghani et al., 2009). Artisanal miners from several mining areas of the Nazca-Ocoña gold belt, in Mid-South Peru, process gold tailings by amalgamation with mercury (Alfonso et al., 2019). The recovery of gold through this process was found to be very inefficient (Alfonso et al., 2019). This was expected because for the amalgamation process to take place, the gold must be liberated from the matrix in which it has

been encapsulated and be in direct contact with mercury (Whitehouse et al., 2006; Hylander et al., 2007; Velásquez-López et al., 2011). Mineralogical analysis revealed that the gold in the tailings was associated with quartz veins, pyrite, tellurides, electrum, and other sulfides (Alfonso et al., 2019). It is, therefore, important to note that residues of a deposit or even a portion of a deposit display unique characteristics that require unique processing steps. This needs to be understood and unique reclamation and processing stages developed where possible (Muir et al., 2005).

The Witwatersrand tailings reservoirs in South Africa is an illustrative case of complex tailings material. The historical Witwatersrand tailings consist of waste products resulting from the mining and metallurgical treatment of Witwatersrand primary ores, which have accumulated over a century of mining (Chingwaru et al., 2023). These historical tailings dumps comprise over 16 billion tons of heterogeneous material, primarily composed of quartz, pyrophyllite, muscovite, chloritoid, and chlorite, along with minor quantities of pyrite, gypsum, apatite, rutile, and secondary iron oxides (Chingwaru et al., 2023; Janse van Rensburg, 2016; Nengovhela et al., 2006). Because of the inherent complexity of the Witwatersrand tailings, the traditional cyanidation employed in current reprocessing operations results in less than 50% gold recovery (Janse van Rensburg, 2016).

The Witwatersrand tailing dumps have further been demonstrated to have a significant amount of invisible gold within the sulfides (Chingwaru et al., 2023b). The gold in these tailings is also associated with slimes (silicate-dominated material) and light mineral fraction (composed of silicate minerals). Understanding the gold distribution within these fractions is critical for optimizing processing routes, as these fractions collectively account for approximately 21-87% of the total gold in the tailings (Chingwaru et al., 2023b). Characterization of gold in complex historical refractory tailings for enhanced process optimization demonstrated that silicates and sulfides collectively encapsulate approximately 33-69% of the gold present in the tailings (Chingwaru et al., 2023a).

2.5 Current processing methods for gold tailings

Gold tailings have been identified as an alternative source of gold because they still have gold (0.2 to 1.1 g/t Au) (Nwagboso, 2022; Cornish, 2013) that can be exploited economically. For example, Chingwaru et al. (2023) reported that detrital auriferous sulfides in the Witwatersrand tailings dump potentially represent a large underexploited economic resource (up to 420 tons

Extraction of gold from tailings using environmentally friendly reagents

of Au). Treating gold tailings has the added advantage of alleviating the growing ramifications of acid mine drainage (AMD) and effluents with deleterious elements, while potentially recovering additional high-demand by-product metals (Chingwaru et al., 2023).

It is important to note that the methods used in the processing of gold tailings are, in most cases, the same as those used in the processing of primary gold ores. Many of the methods currently being used for gold extraction are based on techniques that have been known or established for centuries. Gravity concentration, amalgamation, crushing, milling, cyanide leaching, chlorination, zinc precipitation, and carbon adsorption are all processes that have been used for at least a hundred years, and combinations of these remain the basis for most gold recovery flowsheets (Marsden and House, 2006). However, the environmental impact and limitations of the current gold ores/tailings processing techniques have led to the search for alternative processing techniques. For example, conventional cyanidation is toxic, and ores/tailings may not respond to it for three basic reasons. Firstly, in highly refractory ores, the gold can be locked up in the mineral matrix so that lixivants are unable to reach it. Secondly, in complex ores, reactive minerals in the ore can consume gold lixivants due to side reactions resulting in insufficient cyanide and/or oxygen in the pulp to leach the gold. Thirdly, components of the ore may adsorb or precipitate the dissolved gold cyanide complex so that it is lost from the leach liquor. Some ores may have contributions from each of the three factors, which could influence the processing strategy. Therefore, it is critical to pretreat these ores to remove the materials that cause these challenges before cyanidation. The current methods for the processing of gold tailings processing are discussed in the sections that follow with an overview of the commonly used methods illustrated in **Figure 2.6**.

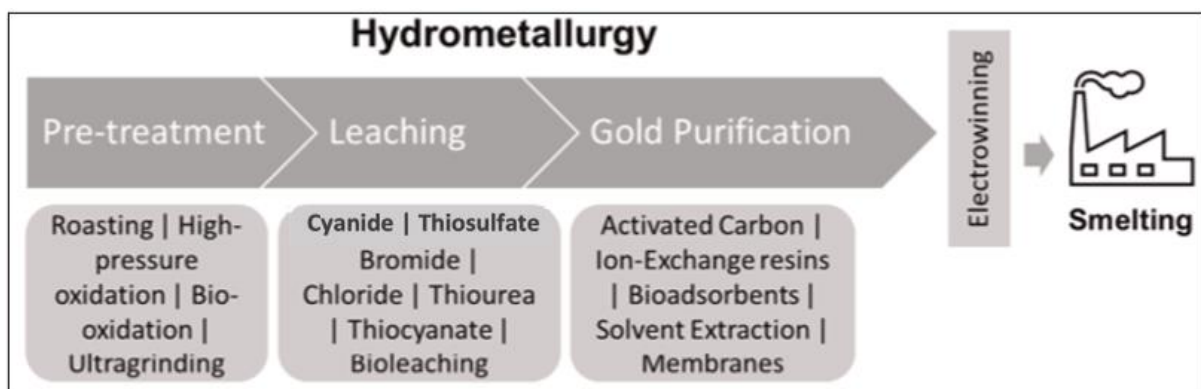


Figure 2.6. Overview of the main hydrometallurgical processes in the extraction of gold from raw materials (Sousa et al., 2022)

2.5.1 Pre-treatment Processes

The pretreatment of gold ores/tailings refers to the removal of unwanted and/or deleterious materials from ores and the breaking down of locking mineral matrices to liberate the gold thus making the gold more amenable to subsequent leaching (Marsden and House, 2006). It is applied when direct treatment by cyanidation gives unacceptably low gold recovery or is uneconomic, due to gold being locked in reactive gangue minerals or gold occurring with reagent-consuming minerals or carbonaceous materials (Marsden and House, 2009). Well-known pretreatment methods in gold ores/tailings processing include grinding, gravity concentration, pre-oxidation/pre-aeration, bio-oxidation, flotation, roasting, pressure oxidation, and chlorination for carbonaceous ores.

Grinding which is a subsequent process to crushing is a process that is employed to further reduce the size of the ore/tailings particles thereby liberating the gold from gangue minerals to facilitate the gold extraction process (Ellis et al., 2003). A benefit of this technique is that the host mineral is not destroyed such as in an oxidative chemical reaction which leads to problems associated with the treatment of the reaction products. However, it has proven to be energy-intensive (Ellis et al., 2003). The ground material can then be preconcentrated by physical processes such as gravity separation to increase gold grade.

Gravity separation utilizes differences in mineral densities to separate gold-bearing minerals from gangue minerals (Burt, 1999). It is suitable for free gold and gold associated with heavier minerals. The advantage of this process is that it avoids the use of chemical reagents. Gravity separation has been employed in gold plants as the primary recovery method or before other downstream processes like flotation and cyanidation since the early days of mineral processing (Adams, 2005).

Flotation is a concentration technique that is commonly applied to sulfidic minerals associated with gold. Flotation separates minerals based on their hydrophobic and hydrophilic physico-chemical properties. The mineralogy of the ore has a profound effect on the reagents used and operational parameters employed (Marsden and House, 2009). Flotation concentrates can further be treated by processes like pressure oxidation and roasting.

Pressure oxidation (POX) of gold ores and flotation concentrates is a commercially proven, effective pretreatment process for liberating refractory gold (Fraser et al., 1991). POX oxidizes sulfides at elevated temperatures and pressure releasing encapsulated gold grains, thus

enhancing subsequent cyanidation (Thomas and Pearson, 2016). The technology is mature, but it is still regarded as a high technology-high capital cost option (Litz and Carter, 1988). Pressure oxidation usually incorporates a pre-oxidation step before autoclaving in which feed is preconditioned by using a combination of dewatering, acid decomposition, and slurry heating (Fraser et al., 1991).

Pre-oxidation is applied to refractory (i.e., sulfidic) gold ores/tailings before cyanidation using an oxidative step. The presence of sulfidic minerals in the cyanidation of gold ore/tailings causes significant consumption of oxygen injected into the system. This results in reduced dissolved oxygen for the oxidative leaching of gold, and consequently reduced optimum gold recovery from the ore (Nunan et al., 2017). Pre-oxidation is applied on these types of gold ores/tailings to convert sulfides into oxides or sulfates. This pretreatment step leads to an increase in dissolved oxygen, reduced cyanide consumption in the cyanidation step, and improved gold recoveries (Nunan et al., 2017).

Roasting has been the traditional method of treating refractory material and conventionally has been used to treat flotation concentrates with high sulfur content (Fraser et al., 1991). Roasting is used to convert sulfides into oxides by heating the material below melting point in the presence of excess air, making them more amenable to subsequent cyanidation (La Brooy et al., 1994). It is one of the most cost-effective processing options, but the cost goes up significantly if sulfur dioxide stack emissions must be controlled (La Brooy et al., 1994).

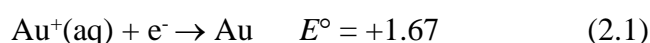
Bio-oxidation, on the other hand, employs microorganisms to decompose sulfide minerals, improving leaching conditions with minimal environmental impact (Sparrow and Woodcock, 1995). However, the slow reaction kinetics associated with this process can be a drawback (Savvaidis, 1998; Fomchenko et al., 2016; Liu et al., 2016).

Unlike sulfide materials, carbonaceous ores are pretreated using chlorine oxidation. Chlorine oxidation refers to the reaction of various metals or metal oxides, sulfides, and other compounds to be extracted with highly chemically active chlorine under certain conditions by adding chlorinating agents (Cl_2 , NaCl , CaCl_2 , etc.) to facilitate the oxidation of the ore (Xinga et al., 2020). All these pretreatment processes can be applied in the processing of gold tailings depending on the grade, mineralogy, and processing costs.

Gold Chemistry

Stability and chemical reactivity

Gold is the only metal that is not attacked in water by either oxygen or sulfur at any temperature. To understand this characteristic of gold, it is useful to consider the redox potentials of gold in the absence of coordinating ligands. Gold must be oxidized for a reaction to occur. For example, gold can be oxidized according to the following reaction (Mortier, 2006):



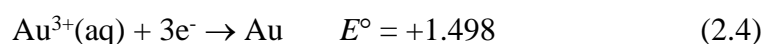
The tendency for this reaction to occur is given by the following Nernst reduction potential equation:

$$E = E^\circ - 2.303 \frac{RT}{F} \log_{10} \frac{[\text{Au}]}{[\text{Au}^+]} \quad (2.2)$$

Where R is the gas constant, F is the Faraday constant, T is the absolute temperature (25 °C or 298 K), and E° is the standard electrode reduction potential for the reaction ($E^\circ = 1.67$ V). If the activity of the Au metal is taken as unity, and if the activity of the dissolved species (Au^+) is assumed to be equal to its molar concentration $[\text{Au}]$, the reaction reduces to:

$$E = 1.67 + 0.059 \log[\text{Au}^+] \quad (2.3)$$

For the alternative oxidation process:

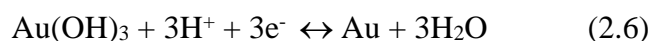


We can similarly write:

$$E = 1.498 + 0.0197 \log[\text{Au}^{3+}] \quad (2.5)$$

In both cases, in **Equation 2.3** and **Equation 2.5**, the positive reduction potentials for Au are indicative of the tendency for Au not to oxidize, hence its stability. It is also evident that, between Au^+ and Au^{3+} , the oxidation state III is the most stable (Mortier, 2006).

When gold is oxidized, it can also interact with its environment according to the following chemical reactions:



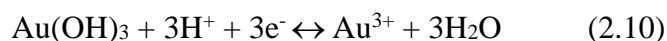
$$E = 1.46 - 0.059\text{pH} \quad (2.7)$$

Extraction of gold from tailings using environmentally friendly reagents



$$E = 2.63 - 0.059\text{pH} \quad (2.9)$$

These reactions can only occur if sufficient strong oxidants are present (Mortier, 2006). The relationship indicating the conditions under which auric hydroxide is in equilibrium with 10^{-4} M auric ions is represented by Finkelstein and Hancock (1974).



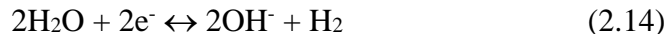
$$\text{pH} = -\frac{1}{3}\log_{10}[\text{Au}^{3+}] - 0.693 \quad (2.11)$$

The reactions in aqueous solution are further restricted by the limits of the stability of water as it can be oxidized to oxygen or reduced to hydrogen. The oxidation of water can be written as follows (Mortier, 2006):



$$E = 1.229 - 0.059\text{pH} \quad (2.13)$$

The reduction of water is the following redox couple:



$$E = 0.0017 - 0.059\text{pH} \quad (2.15)$$

The gold-water system can be expressed graphically in a Pourbaix diagram where the equilibrium potential of each couple is plotted against pH for particular concentrations. A simplified Pourbaix diagram for the gold-water system using a concentration of 10^{-4} M is shown in **Figure 2.7**. The diagram indicates the conditions under which particular species are expected to be formed.

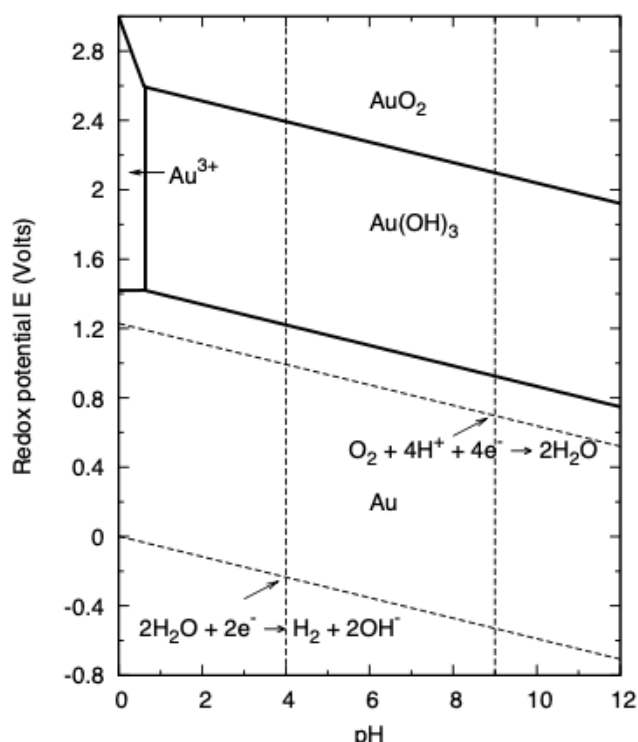
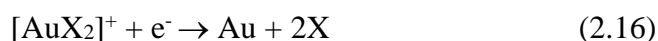


Figure 2.7. Simplified Pourbaix diagram for the gold-water system at 25 °C (Mortier, 2006)

The dotted lines represent the limits of the stability of water. It can be deduced from this diagram that the oxidized forms of gold only exist at potentials significantly greater than the line of the oxidation of water to oxygen. Under these conditions, water is oxidized to oxygen, and the various gold species are reduced to gold metal. This implies that gold is stable in water and cannot be oxidized by dissolved oxygen in the presence of either strong acids or strong alkalis. Gold is the only metal with this property, hence it is the most noble of the metallic elements (Mortier, 2006).

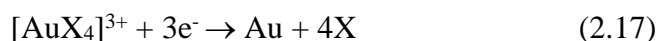
However, gold can dissolve in aqueous solutions containing suitable ligands in the presence of an oxidizing agent. Neither condition alone is sufficient, for example, gold does not dissolve effectively in hydrochloric acid or nitric acid separately, but dissolves readily in aqua regia forming a tetrachloroauric(III) acid ($[AuCl_4]^-$). Similarly, gold dissolves in hydrochloric acid in the presence of hypochlorite or iron(III) as an oxidant (Mortier, 2006). The dissolution of gold in cyanide solutions with air or hydrogen peroxide as an oxidant is another example of this effect (Puddephatt, 1978). The reaction with oxygen as an oxidizing agent occurs by adsorption of oxygen onto the gold surface, followed by the reaction of this surface layer with cyanide to give first AuCN and then $[AuCN_2]^-$ complex which goes into solution (Mortier,

2006). In general, the reaction to oxidize gold to gold(I) in the presence of suitable ligands can be written as follows:

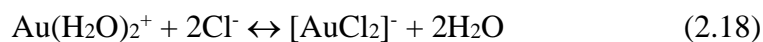


Where X is a ligand.

The reaction to oxidize gold to gold(III) in the presence of suitable ligands can also be written as follows:



The standard potential E° depends on the stability constant for the formation of the complex. In the presence of a suitable ligand, a high value of the stability constant K and a low value of E° is obtained. Au^+ and Au^{3+} ions cannot exist freely in solution but always form complexes with available ligands (Mortier, 2006). In pure water, the ions form the respective aqua ions, and reactions 2.16 and 2.17 are more correctly written in terms of the ions $\text{Au}(\text{H}_2\text{O})_2^+$ and $\text{Au}(\text{H}_2\text{O})_4^{3+}$, respectively. If a stronger ligand than H_2O is present (e.g., chloride) the following equilibria are established (Mortier, 2006):



As a result, **reactions 2.16** and **2.17** reach equilibrium further to the right as can be seen in **Figure 2.8**. The reduction potentials are reduced to more negative values, the metal is oxidized more easily, and the gold dissolution window is widened.

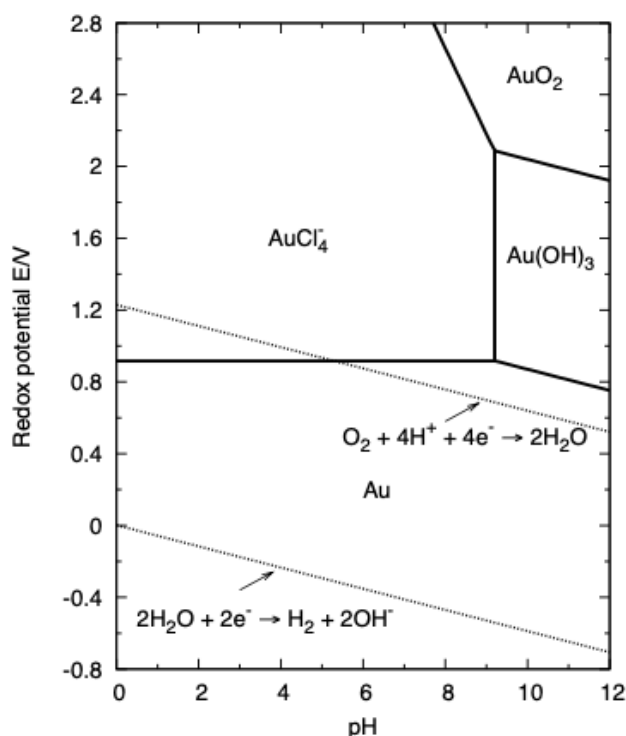


Figure 2.8. Simplified Pourbaix diagram for the gold-water-Cl⁻ system at 25 °C (Mortier, 2006)

Figure 2.8 summarizes the effect of the addition of chloride ions to the gold-water system. In this Pourbaix diagram, drawn for Cl⁻ = 2 M and [Au(III)] = 10⁻² M, the region where the complex [AuCl₄]⁻ is the most stable can be seen clearly. It is important to note from the figure that a part of the domain of stability of [AuCl₄]⁻ falls within the region of stability of water. Therefore, in the presence of chloride ions, gold can exist in an oxidized form in contact with water under acidic conditions. Stronger ligands than chloride will increase the domain of stability of the oxidized species (Mortier, 2006).

Gold complexes

The common gold complexes include gold(I) complexes and gold(III) complexes. Gold complexes can also exist as gold(II) complexes. These complexes are formed with halide ions (i.e., fluoride, chloride, bromine, and iodine ions) (Kauffman and Halpern, 2018). The stability of gold complexes is related to the atom in the ligand which is bound directly to the gold. Gold(I) and gold(III) are class B metal ions (Mortier, 2006). Therefore, the stability of their complexes tends to decrease with increasing electronegativity of the ligand donor atom. Generally, this leads to stability orders of I⁻ > Br⁻ > Cl⁻ > F⁻, whereas the order of electronegativities is F⁻ > Cl⁻ > Br⁻ > I⁻ (Mortier, 2006). For complexes containing a single gold atom, the oxidation states I, II, and III are possible (Stillman, 1960).

Gold(I) complexes

Au⁺ has a closed shell electronic configuration [Xe]4f¹⁴5d¹⁰. Therefore, gold(I) complexes are diamagnetic and the stereochemistry of the halo gold(I) complexes is linear with a coordination number two. The stability of the ions [AuX₂]⁻ increases with the heavier halide ions. These more stable ions can be prepared by the reduction of [AuCl₄]⁻ or [AuBr₄]⁻ in ethanol or acetone solutions according to the following reaction (Mortier, 2006):



Gold(II) complexes

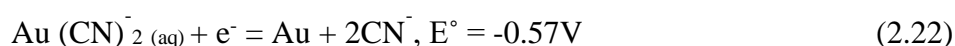
The oxidation state two is the dominant oxidation state for copper, but it is very rare for a gold atom. In gold(II) complexes, the metal atom has a 5d⁹ configuration and such complexes are expected to be paramagnetic. This oxidation state can be established as transient intermediates in redox reactions between the stable oxidation states I and III. The gold (II) oxidation state is not stable (Mortier, 2006).

Gold(III) complexes

Gold dissolves in aqua regia forming tetrachloroauric(III) acid (H[AuCl₄]). In a mixture of hydrobromic and nitric acids, gold dissolves forming tetrabromoauric(III) acid (H[AuBr₄]). These strong acids can then be isolated by evaporation of the solutions with repeated addition of hydrochloric or hydrobromic acid to remove all the nitric acid and nitrogen oxides to generate the hydrated forms H[AuCl₄].3H₂O and H[AuBr₄].xH₂O (Mortier, 2006). The oxidation state III is very important for gold because it is the most stable state. All known gold(III) complexes are diamagnetic with a low-spin 5d⁸ electron configuration and the vast majority of these compounds have the four-coordinate square-planar stereochemistry (Mortier, 2006).

Au-CN-water system

In an aqueous alkaline cyanide solution, gold is oxidized and dissolves to form the Au(I) cyanide complex (Au(CN)₂⁻) according to the following reactions:



Extraction of gold from tailings using environmentally friendly reagents

With the formation of the stable complex of aurocyanide ($\text{Au}(\text{CN})_2^-$), the Eh-pH diagram in **Figure 2.7** changes significantly to the Eh-pH diagram shown in **Figure 2.9**. Under these complexation conditions, the Au reduction reaction has a much lower reduction potential E° at -0.57V compared to the first reduction reaction which has E° at $+1.45\text{V}$. Under the non-complexed conditions, the dissolution of gold is limited by the equilibrium of reduction reaction whereas, under complexed conditions, the Au dissolution window is much wider and occurs at a lower potential.

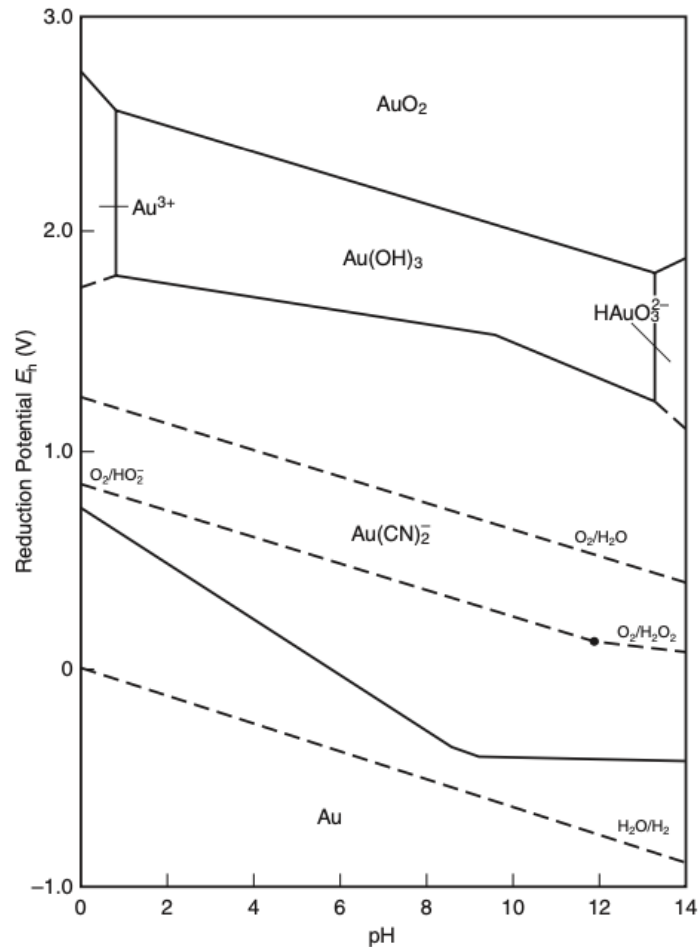


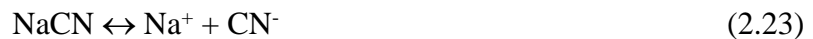
Figure 2.9. Pourbaix diagram for the Au-CN-H₂O system at 25 °C. Concentration of all soluble gold species = 10^{-4} M. $[\text{CN}^-]_{\text{total}} = 10^{-3}$ M, $p\text{O}_2 = p\text{H}_2 = 1$ atm, $\log([\text{H}_2\text{O}_2]/[\text{HO}_2^-]/p\text{O}_2)$ (Marsden and House, 2009)

2.5.2 Gold Leaching

In the context of gold leaching the reaction of primary concern is the dissolution of gold in an aqueous solution, which requires both a complexing agent and an oxidant to achieve acceptable leaching rates (Marsden and House, 2009). This section reviews some of the reagents used for the leaching of gold from solid feed material.

Cyanide Leaching

Cyanide is universally used because of its relatively low cost, and its selectivity for gold and silver over other metals (Marsden and House, 2009). The different processes developed for leaching with cyanide include agitation leaching, heap leaching, and intensive cyanidation. Simple cyanide salts, such as sodium, potassium, and calcium cyanide, dissolve and ionize in water to form their respective metal cation and free cyanide ions, as follows:



All these three salts have been used effectively on a commercial scale as sources of cyanide for leaching. Sodium and potassium cyanide are more readily soluble than calcium cyanide and are generally available in a purer form, which has advantages for the handling and distribution of the reagent in leaching systems. Cyanide ions hydrolyze in water to form molecular hydrogen cyanide (HCN) and hydroxyl (OH^-) ions, with a corresponding increase in pH (Marsden and House, 2009):



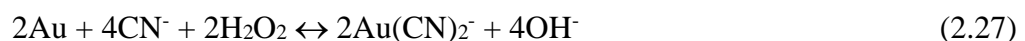
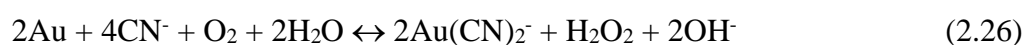
Hydrogen cyanide is a weak acid, which undergoes incomplete dissociation in water as follows (Marsden and House, 2009):



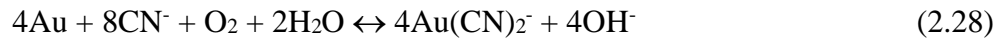
Where:

$$K_a(25\text{ }^\circ\text{C}) = 6.2 \times 10^{-10}, \quad \text{p}K_a = 9.31.$$

The overall dissolution of gold in aerated, alkaline cyanide solutions, considering both the anodic and cathodic half-reactions, is most accurately described by the following reaction equations, which proceed in parallel:



The overall equation proposed by Elsner is as follows (Marsden and House, 2009):



The Eh-pH diagram for the gold cyanide system shown in **Figure 2.9** indicates that the electrochemical driving force for dissolution, that is, the potential difference between the lines representing gold oxidation and oxygen reduction reactions, is maximized at pH values between approximately 9.0 and 9.5. Commonly, cyanide leaching is performed at pH values greater than 9.5 to prevent excessive loss of cyanide by hydrolysis. Low pH cyanide leaching has been investigated as a means to reduce lime consumption and scaling. However, as the pH decreases, the proportion of cyanide present in the solution as hydrogen cyanide increases, and a closed leaching system must be used to prevent excessive loss of cyanide by volatilization of the HCN (Marsden and House, 2009). Consideration of the thermodynamics indicates that HCN should be capable of leaching gold, but investigations have shown that HCN does not leach gold at a sufficiently fast rate to compete with the kinetics of leaching with CN^- (Perry et al., 1999).

The effect of a pH above 9.5 on gold dissolution rate is small and depends on the presence of other solution species and ore constituents, as well as the type of alkali used for pH modification. In some cases, the rate may decrease significantly with increasing pH due to an increase in the rate of interfering reactions, such as the dissolution of sulfides and other reactive species. These effects are generally more severe with calcium hydroxide than with either sodium or potassium hydroxide because of the lower solubility of many of the salts formed (Marsden and House, 2009).

Kaumetova et al. (2022) studied the recovery of gold from ore beneficiation tailings at the Vasilkovsky deposit using direct cyanidation. The preparation of the material for cyanidation consisted of grinding, water washing, and alkaline treatment followed by cyanidation (Kaumetova et al., 2022). The tailings consisted of fine-grained gabbro and medium-grained quartz diorites intersected by quartz-arsenopyrite, quartz, tourmalinic and carbonate veinlets with native gold confined to quartz-arsenopyrite veins and veinlets, and single gold segregations confined to microstructures in quartz and arsenopyrite (Dyachkov et al., 2020; Dyachkov et al., 2021; Stupnik et al., 2014). It was determined that a maximum gold recovery of 97.5% from tailings can be reached at an optimal solids content of 50% in the pulp (Kaumetova et al., 2022). Pan African Resources utilizes a carbon-in-leach process followed by electrowinning and smelting in their Barberton Tailings Retreatment Project (BTRP) to

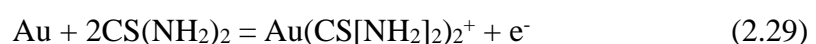
produce a saleable gold product (Cornish, 2013). DRDGold Limited utilizes carbon-in-leach, elution, zinc precipitation, and smelting to reprocess tailings for gold recovery.

Direct cyanide leaching, ammonia leaching as a pretreatment before cyanide leaching, and ammoniacal cyanide leaching of copper-rich gold ore were investigated by Bas et al. (2015). The ore consisted predominantly of quartz (85% SiO₂) and to a small extent, sulfidic minerals (3.14% S in total). The authors observed a strong interference effect from the contained copper sulfides with the cyanide leaching of gold. The copper interference appeared to be linked to the easier dissolution of reactive copper sulfides than gold, hence the depletion of cyanide available by copper (Bas et al., 2015). The maintenance of high levels of cyanide (≥5 g/L NaCN) was required for achieving high extractions (>97%) for gold at the expense of dissolution of up to 79% copper. The pretreatment of the ore by ammonia leaching was found to remove 73% of the reactive copper, leading to 99.8% extraction of gold in subsequent cyanide leaching even at low cyanide levels (1.5 g/L NaCN) (Bas et al., 2015). On the other hand, ammoniacal cyanide leaching was observed to suppress the dissolution of copper and significantly enhanced the leaching of gold with reduced cyanide consumption. The concentration of NH₃ was found to be the most influential factor controlling selectivity and the extent of gold extraction (Bas et al., 2015).

Goldcorp and CanmetMINING evaluated the potential for economic reprocessing of historic tailings at the Aunor A facility located in Timmins, Canada. The tailings were found to contain about 2 g/t of gold with more than 85% recoverable by direct cyanidation and 75-80% using a copper-ammonium thiosulfate leach system. The tailings were found to be highly agglomerated, and to maximize recovery, processing through an attrition mill was necessary to break down the agglomerates before leaching. This was supported by the gold department study showing that 7% of the gold was occluded in agglomerates (Cheng et al., 2019).

Thiourea leaching

During leaching, in acidic conditions, thiourea dissolves gold, to form a cationic complex. The anodic reaction follows the equation:



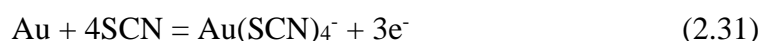
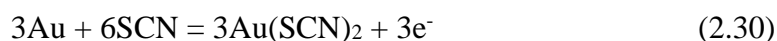
Thiourea, however, must be used under relatively restricted conditions as it is stable thermodynamically in acid and neutral mediums but decomposes rapidly in basic solutions

(Hilson and Monhemius, 2006). Thiourea leaching is usually carried out in the pH range of 1-2, and its effective application is dependent upon cautious optimization and control of pH, redox potential, thiourea concentration, and leaching time. The use of thiourea is an attractive option for treating refractory ores and flotation concentrates, although it is anticipated that with further research, it can be implemented to treat lower-grade ores (Hilson and Monhemius, 2006). Despite the effectiveness of thiourea as a gold leaching reagent, its commercial adoption has been hindered due to its cost being higher than cyanide, high consumption rates, and the fact that the gold recovery from the pregnant leach solution requires more development.

Kaňuchová et al. (2021) investigated the leaching of gold from flotation wastes (Hodruša Hámre tailings pond) using thiourea. The researchers achieved an optimal gold recovery of 83% after 4 hours of leaching the flotation waste. Ahmed et al. (2020) investigated thiourea leaching of gold present in uranium tailings. Sulfuric acid leaching pretreatment was employed to dissolve uranium as well as remove easily leachable metals. The gold dissolution process was performed in a thiourea-sodium sulfite acidic system. The presence of sodium sulfite as an oxidant can significantly reduce thiourea decomposition, accelerate the gold dissolution process, decrease leaching time, and decrease the activation energy of the gold dissolution (Ahmed et al., 2020). The researchers found that the acidic pretreatment of the low-grade uranium ore material with H₂SO₄ was not only advantageous in reducing thiourea consumption, lowering SO₂ requirement, and obtaining improved gold extraction, but also in eliminating the neutralization step and achieving significant economic benefit. The addition of sodium sulfite significantly increased the gold dissolution rate from 45 to 94% in a period of 60 minutes (Ahmed et al., 2020).

Thiocyanate leaching

The thiocyanate ion, SCN⁻, has been reported as an alternative and less harmful leaching reagent to cyanide. Gold in an aqueous thiocyanate solution forms stable Au(I) and Au(III) complexes, as the following reactions show:



Gökelma et al. (2016) and Azizitorghabeh et al. (2021) reported that the best leaching conditions with thiocyanate can be obtained in the presence of a suitable oxidizing agent like ferric iron, a pH level of the solution of about 2, electrochemical potential of 600-700 mV, and

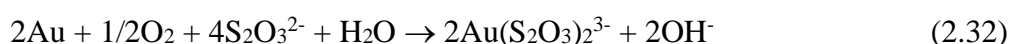
temperatures of around 25 - 40 °C. The ferric ions catalyze the gold extraction by raising the dissolution kinetics and increasing the stability of the thiocyanate ion. Iron(III) is reduced to iron(II) while oxidizing thiocyanate to the intermediate (SCN)₃⁻ and (SCN)₂ species, which are capable of oxidizing gold (Göknelma et al., 2016). At optimal conditions, gold extraction of 95% can be achieved with thiocyanate, while dissolution rates are like those of thiourea (Göknelma et al., 2016).

Yeboah (2019) investigated the dissolution of gold from an oxide gold ore in thiocyanate solutions in the presence of Fe(III) as an oxidant. The highest gold extraction (91.1%) was achieved at a thiocyanate concentration of 0.1 M and Fe(III) of 0.2 M (Yeboah, 2019).

One main reason that the thiocyanate gold leaching process has not yet been commercialized is that the process requires a redox potential higher than that required by the cyanide leaching (Azizitorghabeh et al., 2021).

Thiosulfate leaching

Thiosulfate has also been proposed as a substitute for cyanide (Senanayake, 2005; Panayotov, 1996; Navarro et al., 2002; Duarte, 2015). The reagent dissolves gold slowly under alkaline conditions. The gold dissolution rate is influenced by the concentrations of thiosulfate, dissolved oxygen, and temperature, and can be enhanced by the addition of copper ions. Gold forms a stable anionic complex with thiosulfate according to the following reaction (Hilson and Monhemius, 2006):



In recent years, thiosulfate has been considered seriously as a potential alternative for cyanide because it normally causes fewer adverse environmental impacts (Hilson and Monhemius, 2006) and also has comparable gold leaching rates to that of cyanide (Tanda, 2017). Thiosulfate also experiences less interference from foreign cations and poses fewer pollution concerns. According to Ubaldini et al. (2019), an important characteristic of the thiosulfate leaching process is that it has the best selectivity towards gold; it does not attack the majority of the gangue mineral constituents. Thiosulfate leaching has, however, also been noted to have complex chemistry and requires stability maintenance under variable pH/Eh conditions. This is a critical drawback to its extensive application in the gold industry (Jeffrey and Breuer, 2000). The other major problem with thiosulfate leaching is the high consumption of the

reagent during gold extraction. Furthermore, the process is generally slow, although acceptable leaching rates can be achieved in the presence of ammonia using copper (II) as an oxidant (Hilson and Monhemius, 2006).

Most thiosulfate work has been carried out on complex ores containing copper, carbonaceous ores, or ores containing high concentrations of lead, zinc, or manganese. For example, a mildly refractory gold ore containing pyrite and chalcopyrite was used to determine the feasibility of thiosulfate as an alternative leaching reagent, and gold extraction of 72% was achieved over a period of 50 days (Hilson and Monhemius, 2006). Thiosulfate had its first commercial application at Barrick's Goldstrike operation in Nevada, USA, for the leaching of gold from a preg-robbing ore (Tanda, 2017). However, this process was not cost-effective compared to the cyanidation process and thus, the company switched back to processing their ore with cyanide (Mahlangu, 2023).

The application of thiosulfate in the reprocessing of historic tailings from the Aunor mine in Timmins, Canada was investigated by Cheng et al. (2019). The researchers conducted some preliminary sodium thiosulfate leaching tests on the sulfidic tailings bulk sample with 3 %wt. solids at pH 12 and 25 °C in the presence of copper (II) as an oxidant. It was found that the gold dissolution was somewhat dependent on the copper (II) concentration and the maximum gold dissolution was around 80% in 24 hours (Cheng et al., 2019).

Income et al. (2021) investigated the leaching of gold from copper-gold tailings samples using ammoniacal thiosulfate. Various factors were studied to determine optimum leaching conditions. The researchers found that the most suitable conditions were 0.07 M copper(II) sulfate, 0.5 M ammoniacal thiosulfate, pH 10, 1:10 solid-liquid ratio, 30 °C leaching temperature, 400 rpm agitation speed, and 5 h leaching time. Gold recovery by the ammoniacal thiosulfate leaching method was greater than 90% (Income et al., 2021).

Ubal dini et al. (2019) examined the application of innovative and sustainable technologies for the treatment of auriferous refractory tailings from Romania using thiosulfate leaching followed by purification and recovery (adsorption by activated carbon and electrowinning). The tailings consisted predominately of quartz followed by pyrite and traces of muscovite, albite, chamosite, calcite, and chalcopyrite. The researchers found that gold extraction of 75% was achieved at room temperature. As these results were obtained from thiosulfate leaching of low gold content ore, they may be considered encouraging.

In the work by Munive et al. (2020), thiosulfate was studied for the treatment of mine tailings from a Mexican mine. The system was evaluated by 48 h leaching tests at different solid-to-liquid ratios and showed significant gold recoveries, more than 80% at a solid-to-liquid ratio of 1:1. However, a considerable thiosulfate consumption was also observed (Munive et al., 2020).

The investigation by Feng and van Deventer (2007) on thiosulfate leaching of gold revealed the effect of sulfur species on the thiosulfate leaching. The authors found that the gold dissolution increased at low concentrations of the sulfur species and decreased at high concentrations of the sulfur species (Feng and van Deventer, 2007a). Partial oxidation of the sulfide minerals in gold ore or tailings is beneficial for thiosulfate leaching of gold (Feng and van Deventer, 2010). In the study by Feng and van Deventer (2010), pre-treatment with oxidative ammoniacal solution enhanced the thiosulfate leaching of a sulfidic ore, while the thiosulfate consumption was significantly reduced. The sulfide minerals partially decomposed in the pre-treatment process, exposing gold to the leaching solution. Gold extraction in thiosulfate solution after 24 h increased from 69% without pre-treatment to 81, 84, 90, and 94%, respectively, after 1, 3, 7, and 22 h of pre-treatment (Feng and van Deventer, 2010). These findings enable the thiosulfate leaching of high sulfide-containing gold tailings to be more efficient at lower thiosulfate consumption following the oxidative ammoniacal pre-treatment. The evaluation of the feasibility of thiosulfate leaching for the extraction of gold from a quartz auriferous ore has been conducted and the results revealed about 80.8% gold recovery (Abbruzzese et al., 1995).

Chlorination

Chlorine dissolves gold in aqueous solutions by the formation of soluble Au(I) and the more stable Au(III) chloride complexes. The dissolution of gold occurs in two stages as shown in **equations 2.33 and 2.34**. Au(I) chloride forms during the first stage on the gold surface and then AuCl_2^- forms during the second stage. These chlorides diffuse in solution as AuCl_2^- or oxidize further to AuCl_4^- which is more stable, depending on the oxidizing potential of the solution (Syed, 2012; Kuzugüdenli and Kantar, 1999; Costa, 1997).



A big advantage of chlorination is the high dissolution rate due to the higher solubility of chlorides in water compared to alkaline cyanide leaching. The processing of silver and lead-containing minerals with chlorine is problematic because of the formation of insoluble chloride layers onto the gold surface. This causes a loss in metal recovery. Another disadvantage is the difficulty in handling of the strongly corrosive chlorine solution and the need for a closed reaction container because of the formed chlorine gas (Marsden and House, 2006).

A cleaner chlorination thermal treatment for the recovery of gold from cyanide tailings was investigated in the work of Li et al. (2021). Chlorination thermal treatment was conducted and the results showed that Cl_2 was the main compound participating in the chlorination reaction, and almost no HCl was formed. Under the best conditions, roasting the cyanide tailings with 5 wt.% CaCl_2 at 1273 K yielded close to 90% gold recovery. A toxicity analysis showed that the pollution risk posed by the roasted cyanide tailings was significantly reduced, as the cyanide content in the roasted slag was only 0.77 vol% of that of the raw material, which meets the national emission standards (Li et al., 2021a). In another work by Li et al. (2021), a method for the extraction of gold from cyanide tailings was investigated. Sulfuric acid was used as a pre-treatment leaching solution followed by chlorination leaching (Li et al., 2021). Chlorination leaching, under suitable conditions, resulted in an effective gold recovery, with a leaching rate of 81%.

Bromine and Iodine

Bromine and iodine are two other important halide-leaching reagents with a similar dissolution reaction to chlorine. These reagents are strongly oxidizing and show much higher dissolution rates than cyanide leaching. The dissolution reaction can be summarized in the following equations (Syed, 2012):



Because of the difficulty in handling, high reagent costs, and health issues, bromine, and iodine have not been used industrially (Syed, 2012; Li et al, 2012).

Sousa et al. (2018) performed experimental tests to assess the feasibility of bromine produced in-situ, in the leaching reactor, to dissolve gold using ore samples from the unexploited Portuguese mine of Castromil. The sample of the ore consisted mainly of quartz, reduced and oxidized sulfide, and iron oxides. The authors found that pretreatment of the ore by roasting

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resulted in the highest gold dissolution (86%), although the simultaneous addition of H₂O₂ and FeCl₃ resulted in a similar recovery (80%) with much lower environmental impacts. It was found that the comparison between bromine, cyanide, and thiosulfate leaching for the same ore indicated that bromine is a good technical alternative for leaching this type of gold ore. The bromine leaching process was found to have the following advantages: fast dissolution rate, non-toxic, it does not require the use of a pH regulator, and it can be performed with low quantities of the leaching solution (Sousa et al., 2018).

On the other hand, Batnasan et al. (2018) presented a viable approach for the recovery of precious metals such as gold (Au), silver (Ag), and palladium (Pd) from waste printed circuit boards (WPCBs) via iodine leaching. The authors found that under optimum leaching conditions, almost all (>99%) Au was dissolved in an iodine-iodide solution while the dissolution efficiencies of other precious metals (Ag, Pd) were less than 1 and 6%, respectively. These results indicate that gold can be extracted selectively and economically from WPCBs via iodine leaching.

Table 2.3 gives an overview of the most important properties of gold-leaching reagents regarding their applicability and toxicity.

Table 2.3. Comparison of different leaching reagents (Gökelma et al., 2016)

Reagent	Toxicity	Advantages	Disadvantages
Cyanide	Very high	High dissolution rate	Environmental issues
Aqua regia	High	High dissolution rate	No feasible large-scale applications
Chlorination	Medium	Proven technology. Good efficiency.	No feasible large-scale applications High temperature required
Bromine and Iodine	Low	High dissolution rate	High reagent costs
Thiocyanate	Medium	Recyclable	No feasible large-scale applications Limited availability
Thiosulfate	Medium	Cheap reagent	Detoxification costs High reagent consumption
Thiourea	Medium	Proven technology High dissolution rate and fast kinetics	Dissolution of heavy metals besides gold

2.6 Currently Researched Environmentally Friendly Reagents Alternative to Cyanide

The rising environmental concerns associated with the use of cyanide due to its toxicity have forced the gold mining industry to find alternative leaching reagents that can mitigate the negative impact on the ecosystem as well as reduce operational costs. These reagents must be both environmentally benign and effective. Some of the most promising less toxic reagents proposed as alternatives to the currently commercialized cyanidation process are discussed in the following sections.

2.6.1 Glycine

Amino acids contain an amine group, a carboxylic group, and a sidechain that is specific to each of them. They are well-known as the building blocks of proteins and are particularly important in biochemistry (Sparkman et al., 2011). However, in the recent decade, amino acids have attracted significant interest and attention in extractive metallurgy as “green” lixivants for metal recovery. Among all the amino acids, glycine is the most widely reported, due to its low cost, simplest structure, high affinity for metals, and availability (Li et al., 2023). It is naturally derived from microbes and is the first amino acid isolated from hydrolysis of protein in 1820 by Henri Braconnot (Aliyu and Na’Aliya, 2012). Glycine is a crystalline, non-toxic, non-volatile, non-hygroscopic, and is a recyclable reagent. When dissolved in water, it can exist in three forms, i.e., $\text{H}_2\text{NCH}_2\text{COO}^-$ (glycinate anion), $\text{N}^+\text{H}_3\text{CH}_2\text{COO}^-$ (zwitterion), and $\text{C}_2\text{H}_6\text{NO}_2^+$ (glycinium cation) (Aksu and Doyle, 2001; Li et al., 2023). In aqueous media, glycine is stable in a wide Eh-pH range and has shown high affinities to base and precious metals by complexation (Li et al., 2021b). Using glycine as a lixiviant to extract metals from solid resources can be considered a new “green” approach in hydrometallurgy (Li et al., 2023).

Altinkaya (2021) investigated the extraction of gold from a gold ore and flotation tailings by glycine leaching. The author found that for gold ore, 90% gold extraction was achieved under optimal conditions of 1.25 M glycine concentration, pH = 12, and 60 °C leaching temperature. For flotation tailings, glycine leaching achieved 60% gold extraction under optimal conditions of particle size (d_{80}) = 26 μm , 1.25 M glycine concentration, pH = 12, and 60 °C leaching temperature. Nwagboso (2022) studied the use of alkaline pre-treatment followed by glycine leaching to extract gold from tailings. Silicates were the dominant mineral phase in the tailings. Alkaline pre-treatment of the tailings was performed using sodium hydroxide to break down the silicate matrices encapsulating the microscopic gold. Subsequent leaching was conducted using glycine in the presence of potassium permanganate as an oxidant. The author found that

gold was leached at room temperature, however, increased temperatures proved to be essential for the process (Nwagboso, 2022). Glycine concentration was found to be statistically significant for gold dissolution. At high glycine concentrations and elevated temperatures, there was a possible formation of polypeptides. Up to 52.3% gold dissolution was achieved using 0.05 M glycine solution at 60 °C leaching temperature and 30% pulp density with 1 g/L KMnO_4 oxidant (Nwagboso, 2022).

Godigamuwa and Okibe (2023) combined glycine and thiosulfate to leach Au from printed circuit boards (PCBs). The results revealed that the glycine-thiosulfate system exhibited a synergistic effect on gold leaching, resulting in 93.7% gold extraction at a pH of 9.3 and a leaching temperature of 40 °C, while the gold extractions for the glycine and thiosulfate leaching systems, separately, were 50.7% and 47.1%, respectively (Godigamuwa and Okibe, 2023). The stability of leached Au in the thiosulfate system tends to decrease when operating at lower thiosulfate concentrations. However, the glycine-thiosulfate system maintains the stability of the leached Au. This novel and non-toxic approach could be applied to the leaching of leach other precious metals from various sources such as ores and spent catalysts (Godigamuwa and Okibe, 2023).

2.6.2 Ionic Liquids

Ionic liquids (ILs) have been defined as ionic anhydrous salts or compounds that are liquid below 100 °C, with the most common being liquid at room temperature (Spathariotis, 2020). They consist of an asymmetric organic cation and a smaller inorganic or organic anion (**Figure 2.10**). In contrast with most usual salts, ionic liquids have a non-crystalline structure because of their asymmetric formation, allowing them to be liquids at room temperature (Spathariotis, 2020). This definition of ionic liquids was used traditionally to differentiate between ionic liquids and classical molten salts which melt at higher temperatures, however, ionic liquids are now generally referred to as solvents which consist solely of ions (Smith et al., 2014). The traditional definition was first used to describe chloroaluminate-based ionic liquids (Abbott et al., 2008).

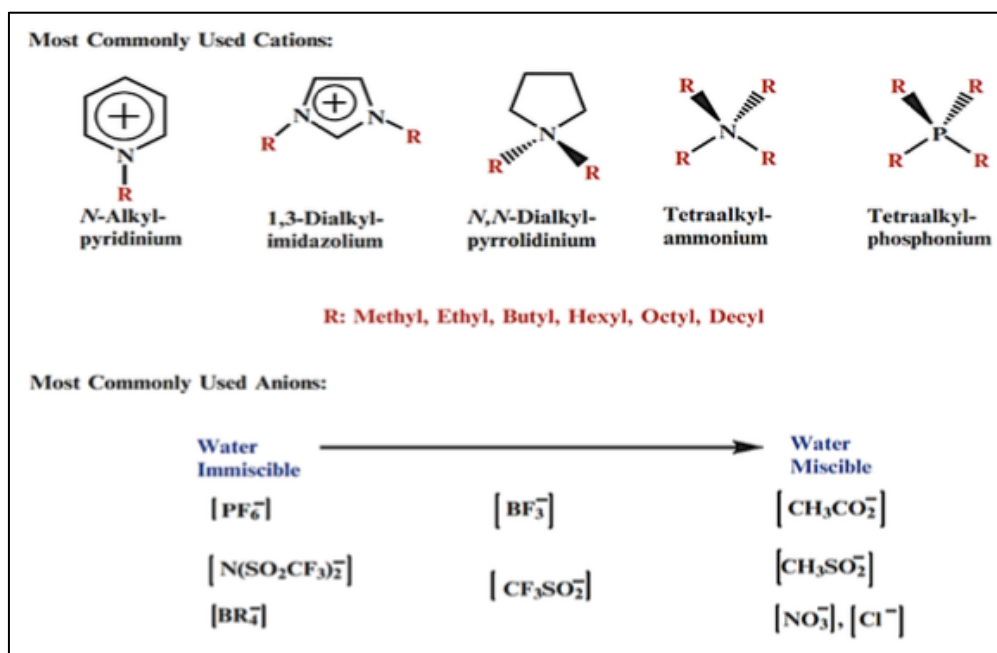


Figure 2.10. Common cations and anions that are used for the formation of ionic liquids (Mohammad and Inamuddin, 2012)

A major limitation of the chloroaluminate ionic liquids is their inherent air and moisture sensitivity, due to the rapid hydrolysis of AlCl_3 upon contact with moisture. The moisture sensitivity of these systems can be somewhat reduced by the replacement of AlCl_3 with more stable metal halides such as ZnCl_2 to form eutectic-based ionic liquids. The ionic liquids formed from organic cations with AlCl_3 and ZnCl_2 are often termed first-generation ionic liquids (Welton, 1999). This class of ionic liquids are fluid at low temperatures due to the formation of bulky chloroaluminate or chlorozincate ions at eutectic compositions of the mixture. This reduces the charge density of the ions, which in turn reduces the lattice energy of the system leading to a reduction in the freezing point of the mixture (Smith et al., 2014).

The second generation of ionic liquids are those that are entirely composed of discrete ions, rather than the eutectic mixture of complex ions seen in the first generation ionic liquids. Wilkes and Zaworotko (1992) working with alkyl-imidazolium salts, discovered that air and moisture-stable liquids could be synthesized by replacing the AlCl_3 used in the eutectic ionic liquids with discrete anions such as the tetrafluoroborate and acetate moieties. Although this second generation of ionic liquids is generally air and moisture-stable, some studies have observed that exposure to moisture affects their chemical and physical properties, with the development of HF as water content increases (Endres and El Abedin, 2006). The stability of this class of ionic liquids can be improved by using more hydrophobic anions such as trifluoromethanesulfonate (CF_3SO_3^-), bis(trifluoromethanesulfonyl)imide $[(\text{CF}_3\text{SO}_2)_2\text{N}]$, and

tris(trifluoromethanesulphonyl)methide $[(CF_3SO_2)C^-]$ (Endres and El Abedin, 2006; Bonhoe et al., 1996; MacFarlane et al., 1999).

Second-generation ionic liquids have the additional benefit of large electrochemical windows, allowing less noble metals, inaccessible from the chloroaluminate liquids to be electrodeposited (Endres and El Abedin, 2006). In summary, the most widely used ionic liquids can be split into two distinct categories, those formed from eutectic mixtures of metal halides (such as $AlCl_3$) and organic salts (generally nitrogen-based and predominantly with halide anions), and those containing discrete anions such as PF_6^- or bis(trifluoromethanesulphonyl)imide. It is estimated that the total number of possible ionic liquids could be in the range of 10^6 distinct systems. Ionic liquids have the potential to be highly versatile solvents, with properties that can be easily tuned for specific uses (Smith et al., 2014). However, for ionic liquids to be successful as viable alternatives to aqueous electrolytes, they must also be simple and economic to synthesize (Beyersdorff et al., 2017).

Compared to cyanide, ILs are environmentally benign reagents that can dissolve many inorganic substances. ILs are known as the most promising alternative reagents for leaching because of their wide liquid temperature range, good solubility, high thermal and chemical stability, very low volatility, low vapor pressure, wide electrochemical window, non-flammability, and eco-friendly character (**Table 2.4**). The application of ILs as reagents in the extraction of gold can provide new alternatives to the traditional cyanidation process and realize a green and clean gold production process (Tian and Liu, 2022). Although ILs are considered environmentally benign and can efficiently dissolve various metals under mild conditions, they are too expensive to be used in an economical way to dissolve base metals (Li and Binnesmans, 2021). However, the high cost of ILs could be justified for the extraction or recovery of precious metals from minerals ores, or secondary resources (Li and Binnesmans, 2021).

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Table 2.4. Properties of ionic liquids (Smith et al., 2014)

Freezing point	Below 100 °C
Liquidus range	Often > 200 °C
Thermal stability	High
Viscosity	Normally < 100 cP, workable
Polarity	Moderate
Conductivity	< 10 mS·cm ⁻¹ , “Good”
Electrochemical window	> 2 V, even 4.5 V, except for Bronsted acidic systems
Vapor pressure	Negligible

One of the key issues concerning the mechanism of metals in ionic liquids is the species that form upon dissolution. Metal ions being generally Lewis acidic will complex with Lewis or Brønsted bases to form a variety of complexes (Abbott et al., 2008). In aqueous-based media the chemistry of H⁺ and OH⁻ dominates the species formed in the solution, the redox properties, and the solubility of the metals (Smith et al., 2014). The study of metal ion speciation in ionic liquids started only very recently. The picture is considerably more complex than that in aqueous solutions because of the differing Lewis basicities of the anions (Abbott et al., 2008). This makes it difficult to explain the dissolution of gold in a solution of ionic liquids as the species that form including the gold complex after leaching is unknown and not reported in literature.

A series of studies have been reported where ILs were used as solvents for the extraction of gold and silver and have shown that they function as efficient solvent systems for the oxidative leaching of gold and silver from complex sulfidic ores (Whitehead et al., 2004; Whitehead et al., 2007; Whitehead et al., 2009). Extraction efficiencies of metals have been studied by varying solvent ILs and oxidizing and complexing agents. Bmim-based ILs with varying anions (N(CN)₂⁻, CH₃SO₃⁻, HSO₄⁻, BF₄⁻, and Cl⁻ were used as solvents for the extraction of gold and silver. Here the ILs were noted to act as solvents and Fe₂(SO₄)₃ as an oxidizing agent (Whitehead et al., 2004). Among all five ILs investigated, only [Bmim][HSO₄] showed high extraction efficiency and selectivity (Whitehead et al., 2004). Thiourea was selected as a complexing agent because of its high selectivity for gold and silver (Whitehead et al., 2004). The system of [Bmim][HSO₄]/thiourea/Fe₂(SO₄)₃ could effectively leach gold and silver over the base metals Cu, Zn, Pb, and Fe in a gold-bearing ore (Whitehead et al., 2004), indicating that the [Bmim][HSO₄]/thiourea/Fe₂(SO₄)₃ system has more selectivity for precious metals

over base metals. The selectivity differences between different anions result from their differences in coordination ability with the metal ions (Li and Binnesmans, 2021).

Constantin et al. (2019) investigated methods for the processing of flotation tailings involving ILs. The work of the researchers involved successive steps of acid leaching to concentrate the tailings. The acids used were H_2SO_4 and HNO_3 , respectively. Their findings showed that preconcentration acid leaching of the tailings led to an increased gold and silver content in the resulting slime. The slime rich in Au and Ag was subsequently processed using ionic liquids for more efficient recovery of the precious metals. These findings by Constantin et al. (2019) suggest that low-grade material should be concentrated before leaching for effective extraction of precious metals such as gold and silver using ILs. However, doing so depends on the mineralogical characteristics of the material and target metal(s) department.

Teimouri et al. (2020) studied the extraction of gold from refractory flotation-concentrated tailings containing pyrite in an ionic liquid $[\text{Bmim}][\text{HSO}_4]$ /thiourea/ferric ion system. Most of the gold was encapsulated in the pyrite (FeS_2) mineral and a low percentage in the quartz (SiO_2) mineral. Their results showed possible dissolution of the pyrite mineral, resulting in over 40% gold extraction. The gold locked in the silica was undissolved due to the inability of silica dissolution in a solution of ionic liquid 1-butyl-3-methyl-imidazolium hydrogen sulfate (Teimouri et al., 2020). It was also shown that gold extraction improved by increasing temperature. It can be concluded that higher temperatures led to improved reaction kinetics, decreased viscosity of the $[\text{Bmim}][\text{HSO}_4]$ -water solution, improved mass transfer or diffusivity in the solution, and ultimately enhanced gold extraction (Teimouri et al., 2020). The results revealed possible dissolution of the pyrite mineral, resulting in over 40% gold extraction. The gold locked in the silica was undissolved due to the inability of silica to dissolve in a solution of ionic liquid 1-butyl-3-methyl-imidazolium hydrogen sulfate (Teimouri, 2020). Whitehead et al. (2007) studied the application of 1-butyl-3-methyl-imidazolium hydrogen sulfate ionic liquid for the leaching of gold from ores. Their results revealed that more than 85% gold extraction was achieved from both sulfidic and oxidic ores. The results found by Teimouri et al. (2020) and Whitehead et al. (2007) show that ILs can be used for the effective extraction of gold from sulfidic and oxidic gold-bearing materials.

2.6.3 Deep Eutectic Solvents

In literature, deep eutectic solvents (DESs) are considered ionic liquid analogues because they have quite similar properties to ILs. For example, they both have low vapor pressure, have a relatively wide liquid range, and are often non-flammable. However, these are two different types of solvents. DESs are obtained by mixing a quaternary ammonium or metal salt (Hydrogen Bond Acceptor – HBA) with a hydrogen bond donor (HBD) such as acids, amides, and alcohols that can complex with the halide anion of the ammonium salt (**Figure 2.11**) (Spathariotis, 2020).

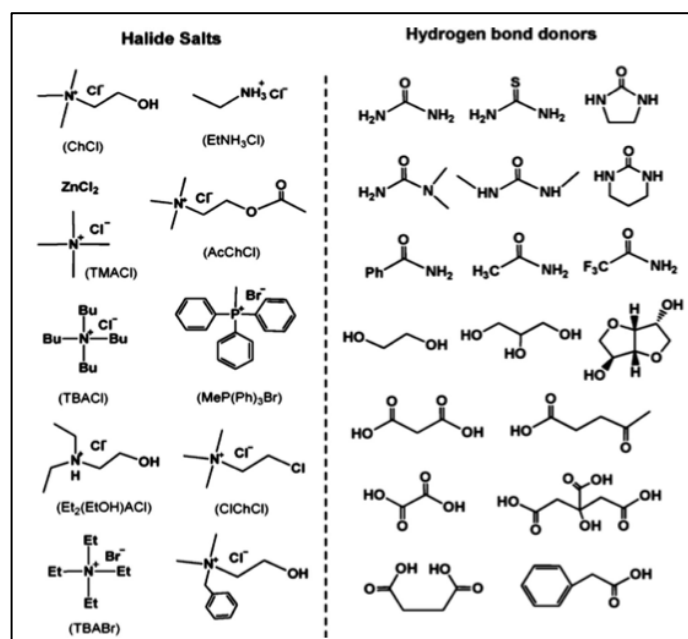


Figure 2.11. Typical structures of HBAs and HBDs used for the synthesis of DESs (Ttaib, 2011)

Deep eutectic solvents can be described by the general formula:



where Cat^+ can be any ammonium, phosphonium, or sulfonium cation, and X is a Lewis base, generally a halide anion. The complex anionic species are formed between X^- and either a Lewis or Brønsted acid Y (z refers to the number of Y molecules that interact with the anion). The majority of studies have focused on quaternary ammonium and imidazolium cations with particular emphasis being placed on more practical systems using choline chloride (hydroxyethyltrimethylammonium chloride), $[\text{ChCl}, \text{HOC}_2\text{H}_4\text{N}^+(\text{CH}_3)_3\text{Cl}^-]$, because choline chloride is a nontoxic and cheap compound (Smith et al., 2014; Li and Binnesmans, 2021).

DESs are largely classified depending on the nature of the complexing agent used (**Table 2.5**) (Smith et al., 2014).

Table 2.5. General formulas for the classification of DESs (Smith et al., 2014)

Type	General formula	Examples of terms
I	$\text{Cat}^+\text{X}^-\text{zMCl}_x$	M = Zn, Sn, Fe, Al, Ga, In
II	$\text{Cat}^+\text{X}^-\text{zMCl}_x\text{yH}_2\text{O}$	M = Cr, Co, Cu, Ni, Fe
III	$\text{Cat}^+\text{X}^-\text{zRZ}$	Z = CONH_2 , COOH , OH
IV	$\text{MCl}_x + \text{RZ} = \text{MCl}_{x-1}^+\text{RZ} + \text{MCl}_{x+1}^-$	M = Al, Zn Z = CONH_2 , OH

DESs formed from MCl_x and quaternary ammonium salts, Type I, can be considered to be of an analogous type to the well-studied metal halide/imidazolium salt systems. Examples of Type I eutectics include chloroaluminate/imidazolium salt metals and ionic liquids formed with imidazolium salts and various metal halides including FeCl_2 (Sitze et al., 2001).

The range of non-hydrated metal halides with a suitably low melting point to form Type I DESs is limited; however, the scope of DESs can be increased by using hydrated metal halides and choline chloride (Type II DESs). The relatively low cost of many hydrated metal salts coupled with their inherent air and moisture insensitivity makes their use in large-scale industrial processes viable (Smith et al., 2014).

Type III eutectics, formed from choline chloride and hydrogen bond donors have been of interest due to their ability to solvate a wide range of transition metal species, including chlorides and oxides (Abbott et al., 2003). These liquids are simple to prepare and relatively unreactive with water. The wide HBDs available mean that this class of DESs is particularly adaptable. The physical properties of the liquid are dependent upon the hydrogen bond donor and can be easily tailored for specific applications. Although the electrochemical windows are significantly smaller than those for some of the imidazolium salt-discrete anion ionic liquids, they are sufficiently wide to allow the deposition of metals such as Zn with high current efficiencies (Smith et al., 2014). This class of DESs is particularly versatile, with a wide range of possible applications investigated including the removal of glycerol from biodiesel (Abbott et al., 2007), the processing of metal oxides (Abbott et al., 2006), and the synthesis of cellulose derivatives (Abbott et al., 2006).

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Most DESs that are fluid at room temperatures are formed using an organic cation, generally based around ammonium, phosphonium, and sulfonium moieties. Inorganic cations generally do not form low melting point eutectics due to their high charge density; however, previous studies have shown that mixtures of metal halides with urea can form eutectics with melting points below 150 °C (Gambino et al., 1987). Abbott et al. (2007) have built upon this work and shown that a range of transition metals can be incorporated into room temperature eutectics, and these have now been termed Type IV DESs. It would be expected that these metal salts would not normally ionize in non-aqueous media; however, $ZnCl_2$ has been shown to form eutectics with urea, acetamide, ethylene glycol, and 1,6-hexanediol (Abbott et al., 2007).

Although DESs share many characteristics and properties with ILs, they are easier to prepare out of relatively inexpensive, biodegrade, and recyclable components, giving them the potential for large industrial use. However, their use has sometimes been limited by their increased viscosity (Smith et al., 2014). DESs' viscosity depends upon the size of the ions, the bonding, and the space available for the solvent molecules or ions to move into. Lower mobility of free species in the liquid results in high viscosities due to strong bonding. Most DESs have a viscosity range above 100 cP at 25 °C. However, it has been observed that temperature changes can alter the viscosity in an Arrhenius-like manner, with increased temperatures leading to a decrease in the viscosity of the DESs (Spathariotis, 2020). Besides the chemical composition of the solvent, the water content also plays a significant role in the viscosity of the liquid (Smith et al., 2014; Fischer, 2015).

Although the physical properties of DESs are similar to other ILs, their chemical properties suggest application areas that are significantly different (**Figure 2.12**).

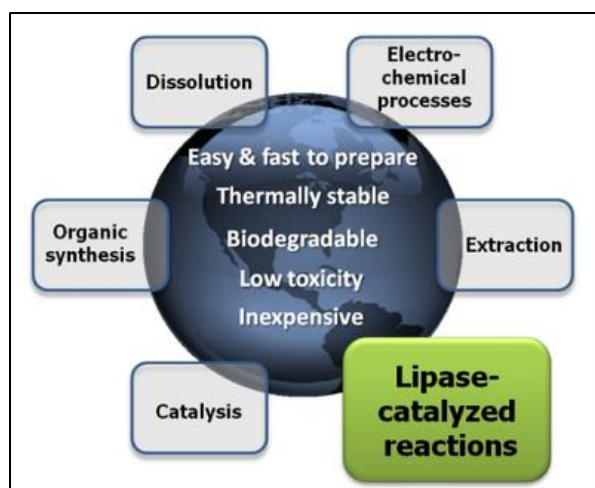


Figure 2.12. Properties and application of deep eutectic solvents in different fields (Smith et al., 2014)

Generally, DESs have no oxidizing power themselves, so they are often used as solvents for metal dissolution either with the aid of an oxidizing agent or as an electrolyte for the electrooxidation of metals (electrolytic dissolution). Iodine in DESs (e.g., in ethaline which is a mixture of choline chloride and ethylene glycol in a 1:2 molar ratio) shows strong oxidizing power which can be used for leaching of gold from gold-bearing ores (Abbott et al., 2011; Jenkin et al., 2016). Iodine in DESs used for metal dissolution is similar to the halogens in organic solvent systems since DESs and organic solvents are both used as solvents for halogens and the formed metal salts. The difference is that most DESs have components that can act as ligands, whereas most organic solvents are much less coordinating. For example, the chloride ions in ethaline can complex with gold to form $[\text{AuCl}_4]^-$, and this complex can dissolve in DESs easily by interacting with the counterion choline (Li and Binnesmans, 2021).

A deep eutectic solvent (DES) was applied in the dissolution and recovery of the precious metals from a material consisting of galena, electrum, chalcopyrite, pyrite, and tellurobismuthite (Jenkin et al., 2016). The results revealed that electrum, galena, chalcopyrite, and tellurobismuthite were soluble in DES through oxidative leaching. Pyrite was notably insoluble by an oxidative leach in DES. DESs have high selectivity and are generally suitable for the processing of metal oxides (Abbott et al., 2006).

2.7 Recovery

Following leaching, gold ions remain dissolved in the solution together with other elements. It is necessary to recover gold ions from this solution by separating them from the other dissolved metals present (Sousa et al., 2022). Gold ion adsorption onto activated carbon (AC) is one of the most common methods used to recover gold from leaching solutions.

Activated Carbon

Activated carbon is an effective adsorbent for the removal of organic and inorganic elements dissolved in aqueous media. Activated carbon is a porous, amorphous carbonaceous material with a large internal surface area – characteristics that facilitate the transfer (by adsorption) of the gold ions into the AC. Gold adsorption that involves AC is widely applied in cyanidation processes; it can also be employed in alternative reagent systems (Sousa et al., 2022). When AC is employed at the leaching stage, it is put into contact with the leachate in large, agitated adsorption tanks and the two processes occur simultaneously (i.e., leaching and adsorption) (Tahli and Wahyudi, 2017).

Selecting the most suitable AC for gold recovery is imperative because any losses of AC result in a reduction in gold output. Modifying (physical/chemical treatment and impregnation) the AC to enhance its adsorption properties is common. After adsorption, gold must be eluted from the AC. This is accomplished through incineration or by using eluents such as methanol, ethanol, acetone, chloroform, and dimethyl acrylamide solutions. The most common reagents used in gold elution from loaded activated carbon are NaOH and NaCN. This process is widely applied at the industrial level (Sousa et al., 2022).

2.8 Summary

This chapter discusses gold, its occurrence and mineralogy, its secondary sources, and different processing methods. This chapter shows the environmental challenges associated with the current gold processing techniques and thus, the need to look at alternative non-toxic dissolution reagents. This chapter has also demonstrated that ionic liquids and deep eutectic solvents have become very promising low-temperature environmentally friendly solvents for the processing of metals from various sources. Because of their wide liquid temperature range, low vapor pressure, low melting point, good thermal and chemical stability, and adjustable properties and functions, they have great potential applications in mineral processing. They can be used to efficiently dissolve many inorganic substances and release the locked gold for dissolution in their solutions. However, the dissolution mechanism is unclear and needs to be studied and reported. The next chapter discusses the materials and methods used in this study.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter discusses the preparation of materials as well as experimental and analytical methods employed in the study. Justification for the selection and implementation of methods employed is also presented in this chapter. The experimental procedure followed in this study is diagrammatically presented in **Figure 3.1**.

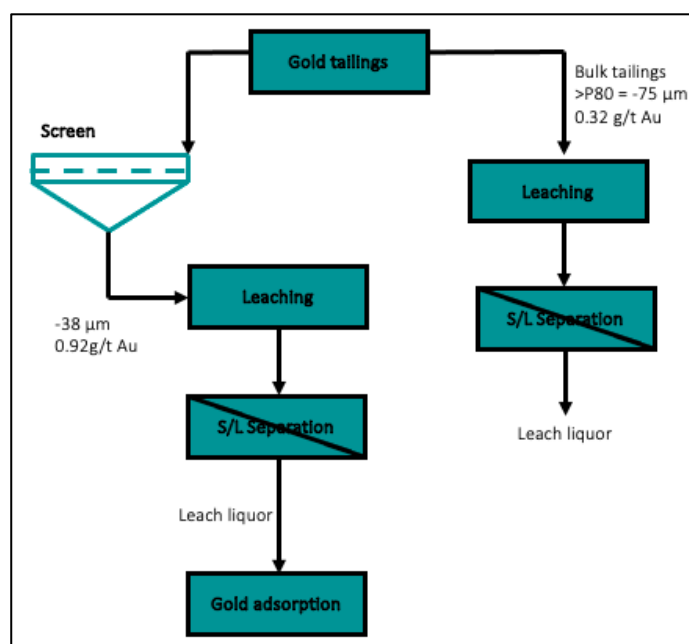


Figure 3.1. The experimental approach followed in this research study

3.2 Materials Preparation

The gold tailings material used in this study was provided by DRDGold Pty (Ltd). The tailings sample was collected from the tailings processing stream just before the CIL stage (**Figure 3.2**). The gold tailings sample was received in a fine slurry form and did not need further size reduction. The slurry was filtered using a filter press. The filtered solids were dried in an oven for 24 hours at 50 °C to remove the remaining moisture. The dried material was thoroughly homogenized, and a representative sample was obtained using a riffler splitter (Model 15A, Eriez). Characterization of the sample material was carried out using XRD (Bruker D2 Phaser, Bruker Corporation, Karlsruhe, Germany), Fire Assay Analysis (FAA) (SC-144DR, LECO, St. Joseph, MI, USA), Tescan Integrated Mineral Analyzer (TIMA), and MLA (FEI MLA 650F,

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FEI Company, Hillsboro, OR, USA) employing the Sparse Phase Liberation-Dual Zoom (SPL-DZ) method.

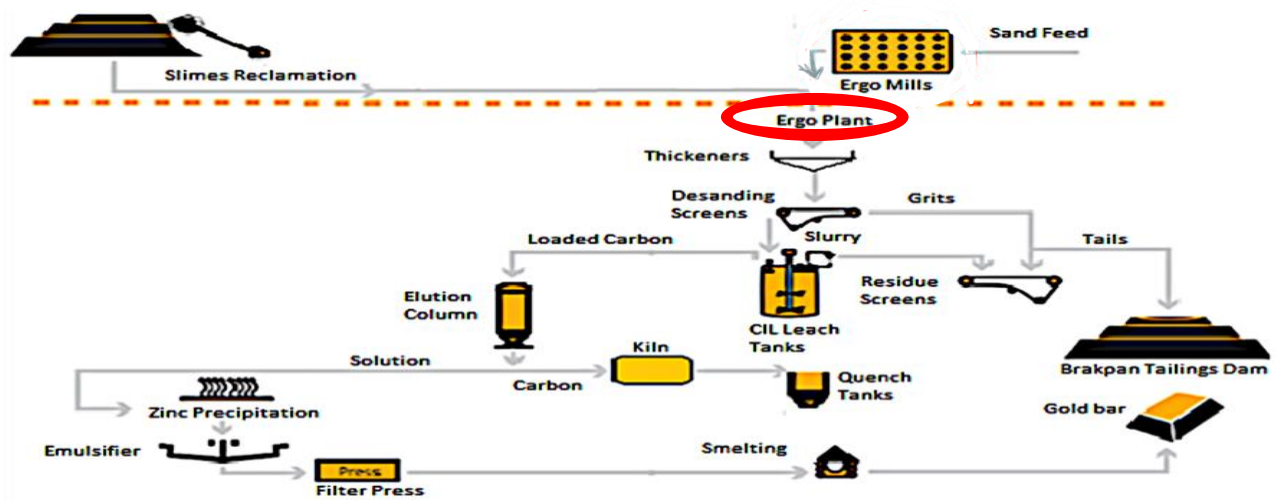


Figure 3.2. Process steps followed in reprocessing gold tailings at DRDGold Limited. Gerke, M. (2023) DRDGold Ergo Mining (Ltd) Pty Operations [PowerPoint slides]

The remaining bulk material was characterized for particle size distribution (PSD) using an electronic sieve shaker (Model ES200, Mark IV, Endecotts Ltd., London, UK). The material was homogenized and classified into size fractions of -38, -53+38, -75+53, -106+75, -150+106, -212+150, and +212 μm . A representative sample was obtained from each of the size fractions and analyzed for gold. The entire material preparation procedure before leaching is illustrated in **Figure 3.3**.

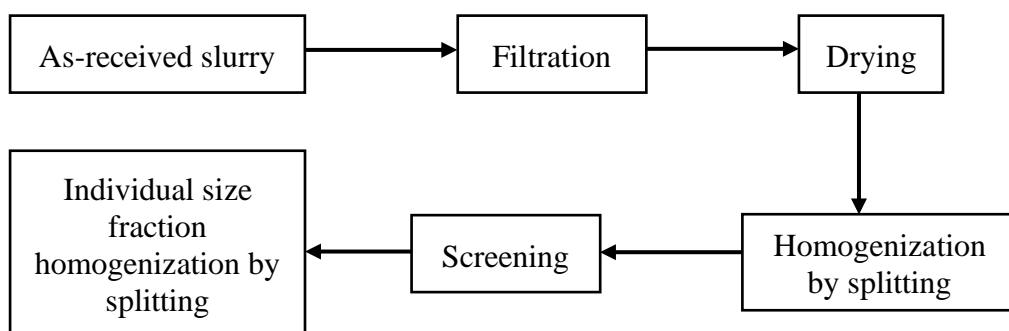


Figure 3.3. Flow diagram showing the material preparation procedure followed in this work

3.3 Reagents

All reagents used in this study were of analytical grade. The reagents were purchased from C.C. IMELMANN and Associated Chemical Enterprises (ACE) and were used as received without further purification. Deionized water, 1-butyl-3-methyl-imidazolium hydrogen sulfate

($\geq 95\%$ w/w), ferric sulfate, thiourea, iodine, ethylene glycol, choline chloride ($\geq 98\%$ w/w), sodium hydroxide, sodium thiosulfate, copper sulfate, and sodium cyanide were used in the experiments. Deep eutectic solvent ethaline was prepared by mixing choline chloride with ethylene glycol and heated at $50\text{ }^{\circ}\text{C}$ in a reciprocal shaking bath (Model 207, MERCK) until a homogeneous and transparent liquid was formed.

3.4 Experimental

3.4.1 Design of Experiments

Design of experiments (DOE) is a statistical method employed to examine the relationship between multiple input variables (factors) and key output variables (responses). DOE is a powerful data collection and analysis tool that can be used in a variety of experimental situations.

DOE enables the manipulation of multiple input factors to assess their influence on the desired output (response). By manipulating inputs at the same time, DOE can identify significant interactions that may be missed when experimenting with one factor at a time (Bower, 2024). This approach allows for the investigation of all possible combinations can be investigated (full factorial) or only a portion of the possible combinations (fractional factorial).

A strategically planned and executed experiment may provide substantial information about the influence of one or more factors on the response. Many experiments involve keeping certain factors constant and varying the levels of another variable, known as the “one factor at a time” (OFAT) approach. However, the OFAT method is less efficient compared to simultaneously changing multiple factor levels (Bower, 2024).

Fundamental principles in designing an experiment include blocking, randomization, and replication (Telford, 2007).

- **Blocking:** When randomizing a factor is impossible or too costly, blocking allows restricted randomization by carrying out all of the trials with one setting of the factor and then all the trials with the other setting.
- **Randomization:** This involves randomizing the order in which the experimental trials are performed, helping to eliminate the effects of unknown or uncontrolled variables.
- **Replication:** This is the repetition of the entire experimental treatment, including the setup.

A repetitive approach to gaining knowledge is recommended, usually involving the following sequential steps (Bower, 2024):

1. A screening design that reduces the number of variables being investigated.
2. A “full factorial” design that examines the response of every combination of factors and factor levels, aiming to identify a range of values where the process is close to optimization.
3. A response surface designed to model the response.

3.4.1.1 Screening – identification of significant factors

Two key objectives of this study were to identify and optimize factors that significantly influence gold extraction from tailings during leaching. To do this, a statistical DOE method was employed as a tool to develop an experimental plan for determining the factors that significantly affect gold tailings leachability using IL, DES, and thiosulfate, respectively. The significance of each factor and interactive effects were evaluated using a two-level four-factor full factorial statistical design of experiments (2^4) and gold extracted was taken as the measured response. Identification of influential factors is critical for process optimization and cost control (Shemi, 2013).

A statistical DOE method was employed because it simultaneously studies multiple process variables which, when combined, results in a better understanding of the process (Barrentine, 1999). The application of DOE early in process development can result in improved process yields, reduced variability, closer conformance to target requirements, reduced development time, and reduced overall costs (Montgomery, 2012). An experimental design matrix was used in order to change multiple factors in a systematic way to ensure a reliable and independent study of the main factors and their interactions. This stage of the study focused on identifying factors with a significant influence on IL, DES, and thiosulfate leaching of gold tailings. The main objective was to find the factors resulting in the maximum dissolution of gold using IL, DES, and thiosulfate, respectively. A statistical analysis of the experimental results was employed to evaluate the significance of the factors using the normal probability plot and the Pareto chart. Leaching experiments were carried out at low and high factor levels represented by codified values of -1 and +1, respectively. The factors investigated included reagent concentration, leaching time, pulp density, and leaching temperature.

The normal probability plot is a statistical method that is used to evaluate the significance of factors. It is a plot of the effect of the actual value evaluations against their accumulative normal

probabilities. All the non-significant effects are distributed normally alongside the straight line on the plot, with mean zero and variance (σ^2) whereas the significant effects will have non-zero means and not located alongside the straight line. The more significant the effect, the further away it will be from the straight line on the plot (Montgomery, 2012).

The Pareto chart provides an alternative and equally effective way of helping with the selection of significant factors. The Pareto chart is a type of chart that contains both bars and line graphs, where individual values are illustrated by bars in descending order from left to right and the cumulative total is represented by a line. The first bar on the left-hand side is the highest bar compared to other bars and shows the most significant variable of the chart (Wilkinson, 2006). Variances are arranged in descending order to identify the largest improvement opportunities and separate the ‘critical few’ from the trivial many. The horizontal line in the Pareto chart indicates the minimum statistically significant effect magnitude for a 5% significance level, while the vertical column lengths are proportional to the degree of significance for each effect. Any effect or interaction that goes above the horizontal line is reflected as significant (Wilkinson, 2006).

Factors and Levels in Experimental Runs

The choice of factors and levels was based on the knowledge of parameters that influence the leaching process of tailings. This study was designed to determine the influence of some of these parameters in the leaching of gold tailings using alternative reagents and quantify them to make sure that their influence is both measurable and predictable. In this work, the agitation rate, thiourea, ferric sulfate, and iodine concentrations were held constant, and other factors were categorized as controlled factors. The controlled factors selected for investigation are presented in **Tables 3.1, 3.2, and 3.3**. The pulp density used in thiosulfate leaching is slightly higher than in IL and DES leaching because according to Abbruzzese et al. (1995), high gold extractions in a thiosulfate solution are obtained at high solid-to-liquid ratios.

Table 3.1. Controlled experimental factors and levels for IL leaching

Controlled factors	Level 1	Centre point	Level 2
IL concentration (M)	0.1	0.6	1.0
Leaching temperature (°C)	25	50	75
Leaching time (hours)	3	5	7
Pulp density (%w/v)	10	20	30

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Table 3.2. *Controlled experimental factors and levels for DES leaching*

Controlled factors	Level 1	Centre point	Level 2
DES concentration (ChCl: EG)	1:2	1:3	1:4
Leaching temperature (°C)	25	50	75
Leaching time (hours)	3	5	7
Pulp density (%w/v)	10	20	30

Table 3.3. *Controlled experimental factors and levels for thiosulfate leaching*

Controlled factors	Level 1	Centre point	Level 2
Thiosulfate concentration (M)	0.1	0.6	1.0
Leaching temperature (°C)	25	50	75
Leaching time (hours)	3	5	7
Pulp density (%w/v)	20	30	40

3.4.1.2 Optimization

Optimization of factors was carried out after screening for significant factors. The central composite design (CCD) technique in conjunction with response surface methodology (RSM) was used to carry out optimization tests. RSM is a useful statistical and mathematical method that is used for modeling and analysis of problems (Shemi, 2013). Its main objective is to optimize the response surface that is influenced by various process parameters. The RSM quantifies the relationship between the controllable input parameters and the response surface (Tripathy and Murthy, 2012).

The optimization experiments were designed using the CCD and the optimal set of factors was determined mathematically. The CCD consists of a 2^k factorial with n_f factorial runs, $2k$ axial or star runs, and n_c center runs. The practical deployment of a CCD often arises through sequential experimentation, that is, a $2k$ has been used to fit a first-order model, this model has exhibited a lack of fit, and the axial runs are then added to allow the quadratic terms to be incorporated into the model. The CCD is a very efficient design for fitting the second-order model. There are two parameters in the design that must be specified: the distance α of the axial runs from the design center and the number of center points n_c (Montgomery, 2012). The choice of these two parameters is discussed below.

Rotatability

It is important for the second-order model to provide good predictions throughout the region of interest. The model should have a reasonably consistent and stable variance of the predicted response at points of interest \mathbf{x} (Montgomery, 2012). A second-order response surface design should be rotatable. This means that the variance is the same at all points \mathbf{x} that are at the same distance from the design center. That is, the variance of the predicted response is constant on spheres (Box et al., 1978). The contours of the constant standard deviation of the predicted response should be concentric circles. A design with this property will leave the variance unchanged when the design is rotated about the center $(0, 0, \dots, 0)$, hence the name *rotatable* design (Montgomery, 2012). Rotatability is a reasonable basis for the selection of a response surface design. Because the purpose of RSM is optimization and the location of the optimum is unknown prior to running experiments, it makes sense to use a design that provides equal precision of estimation in all directions (Montgomery, 2012).

A CCD is made rotatable by the choice of α . The value of α for rotatability depends on the number of points in the factorial portion of the design; in fact, $\alpha = (n_f)^{1/4}$ yields a rotatable central composite design where n_f is the number of points used in the factorial portion of the design (Montgomery, 2012). Rotatability is a spherical property; that is, it makes the most sense as a design criterion when the region of interest is a sphere. However, it is not important to have exact rotatability to have a good design. For a spherical region of interest, the best choice of α from a prediction variance viewpoint for the CCD is to set $\alpha = \sqrt{k}$. This design is called a spherical CCD and it puts all the factorial and axial design points on the surface of a sphere of radius \sqrt{k} (Myers et al., 2009).

Factors used in this study were investigated using codified values $(-\alpha, -1, 0, +1, +\alpha)$. **Table 3.4** shows a relationship between the coded values and actual values for the five levels of each factor.

Table 3.4. Relationship between coded and actual values of the variable (Shemi, 2013)

Coded	Actual value of a factor
$-\lambda$	ξ_{\min}
-1	$(\xi_{\max} + \xi_{\min})/2 - (\xi_{\max} - \xi_{\min})/2\lambda$
0	$(\xi_{\max} + \xi_{\min})/2$
+1	$(\xi_{\max} + \xi_{\min})/2 + (\xi_{\max} - \xi_{\min})/2\lambda$
$+\lambda$	ξ_{\max}

ξ_{\max} and ξ_{\min} are the minimum and maximum values of the natural variables respectively,

$$\lambda = 2^{(k-q)1/4}$$

Where,

λ is the distance of an axial point from the centre

K is the number of factors studied

q is a fraction of the number of factors. For a full factorial design, $q = 0$

The levels of each factor shown in actual and coded values calculated using the relationships in **Table 3.4** are shown in **Tables 3.5, 3.6, and 3.7**.

3.4.2 Ionic liquid leaching of gold tailings

The 1-butyl-3-methyl-imidazolium hydrogen sulfate ionic liquid was used as a gold dissolution lixiviant during the leaching experiments. The IL leaching experiments were carried out under acidic conditions ($\text{pH} \leq 1.0$) (Teimouri et al., 2020) and lower electrochemical potentials (0.51 to 0.57 V) in the presence of 1 g/kg tailings of ferric sulfate as an oxidant and 20 g/kg tailings of thiourea as a complexing agent. ILs liquids have a wide pH stability range, maintaining their liquid state over a broad pH spectrum. This allows for their use in both acidic and basic conditions, providing flexibility in operating pH range conditions. Furthermore, ILs have wide electrochemical windows, meaning that they can withstand a broad range of voltages without undergoing decomposition. Therefore, the Eh conditions employed in this work are suitable for the 1-butyl-3-methylimidazolium hydrogen sulfate IL leaching conditions. The 1-butyl-3-methylimidazolium hydrogen sulfate/ferric/thiourea leaching system has a good gold selectivity (Whitehead et al., 2009) which is essential for efficient gold extraction and minimizing the consumption of the reagents. Additionally, ILs remain stable even at high temperatures (Whitehead et al., 2004). The use of ferric sulfate as an oxidant during gold leaching in IL systems offers several advantages in comparison to traditional cyanidation processes such as environmental friendliness (Whitehead et al., 2009). Thiourea was used to serve as a complexing agent because of its high gold complexation capacity from the pregnant leach solutions (Ubalini et al., 1998).

All leaching experiments were carried out in 250 ml Erlenmeyer flasks. Leaching experiments comprised adding weighted gold tailings samples to Erlenmeyer flasks containing a mixture of ferric sulfate, thiourea, and 1-butyl-3-methyl-imidazolium hydrogen sulfate. The resulting

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slurry was agitated in a constant temperature platform shaking incubator. Separate samples were used for each given leaching condition. After leaching, the residual tailings were separated from the solution by filtration using vacuum filtration, filter press, or syringe filtration. The obtained leach liquor was analyzed for gold by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The resulting solids were dried and analyzed using SEM.

Table 3.5. IL leaching experimental layout and runs for the three-factor central composite design

Random Run	Standard Run	Factor levels					
		Coded			Actual		
		A (Temp)	B (Conc)	C (Pulp density)	A Temp (°C)	B Conc (M)	C Pulp density (%w/v)
5	1	-1	-1	+1	25	0.2	30
1	2	-1	-1	-1	25	0.2	10
17	3	0	0	0	50	0.6	20
4	4	+1	+1	-1	75	1	10
16	5	0	0	0	50	0.6	20
7	6	-1	+1	+1	25	1	30
18	7	0	0	0	50	0.6	20
19	8	0	0	0	50	0.6	20
8	9	+1	+1	+1	75	1	30
12	10	0	+1.682	0	50	1.273	20
9	11	-1.682	0	0	7.95	0.6	20
2	12	+1	-1	-1	75	0.2	10
11	13	0	-1.682	0	50	-0.073	20
14	14	0	0	+1.682	50	0.6	36.817
15	15	0	0	0	50	0.6	20
6	16	+1	-1	+1	75	0.2	30
20	17	0	0	0	50	0.6	20
3	18	-1	+1	-1	25	1	10
10	19	+1.682	0	0	92.04	0.6	20
13	20	0	0	-1.682	50	0.6	3.182

3.4.3 Deep eutectic solvent leaching of gold tailings

Ethaline was used as a gold-leaching lixiviant for the deep eutectic solvent (DES) leaching experiments. The DES leaching experiments were carried out under acidic conditions ($3 < \text{pH} < 6$, $0.287 \leq \text{Eh} \leq 0.392$) in the presence of 5 g/kg tailings of iodine. DESs are known as ionic liquid analogs and therefore share similar properties, advantages, and operating conditions with the ILs (Spathariotis, 2020). Leaching experiments were conducted in a similar way as IL leaching experiments with the obtained leach liquor analyzed for gold by Inductively Coupled

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Plasma-Mass Spectrometry (ICP-MS) and the resulting dry solids analyzed using SEM. The role of iodine is to catalyze the gold ions according to the following reaction (Jenkin et al., 2016):



Iodine in ethaline shows strong oxidizing power which can be used for the leaching of gold from gold-bearing ores (Abbott et al., 2011; Jenkin et al., 2016).

The chloride ions in ethaline can complex with gold to form $[AuCl_4]^-$, and this complex can dissolve easily by interacting with the counteraction choline (Li and Binnesmans, 2021).

Table 3.6. DES leaching experimental layout for the two-factor central composite design

Standard run	Run	Factor levels			
		Coded		Actual	
		A (Pulp density)	B (Time)	A Pulp density (%w/v)	B Time (hours)
1	10	-1	-1	10	3
2	3	+1	-1	30	3
3	11	-1	+1	10	7
4	6	+1	+1	30	7
5	7	-1.414	0	5.858	5
6	4	+1.414	0	34.142	5
7	5	0	-1.414	20	2.172
8	12	0	+1.414	20	7.828
9	8	0	0	20	5
10	9	0	0	20	5
11	2	0	0	20	5
12	13	0	0	20	5
13	1	0	0	20	5

3.4.4 Thiosulfate leaching of gold tailings.

Sodium thiosulfate was used as a reagent for the thiosulfate gold tailings leaching experiments. The experimental setup was also similar to that of IL leaching experiments. However, the leaching experiments were carried out under basic conditions (pH = 8–10.5, Eh = 0.15–0.2 V) in the presence of copper sulfate. The resulting leach liquor was also analyzed for gold by ICP-MS and the solids were analyzed using SEM. Thiosulfate gold leaching is reported as a slow alkaline process in the absence of a suitable catalyst. Cu(II) was used because it is a very effective catalyst for this reaction (Marsden and House, 2009). The aurothiosulfate complex is

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the most stable gold-bearing soluble species in the leaching system between pH 8.5-10.5 (Abbruzzese et al., 1995). For effective gold dissolution, an oxidation potential of 0.15-0.2 V with reference to a standard hydrogen electrode (SHE) is required (Abbruzzese et al., 1995). Metallic gold is stable in reducing conditions of Eh less than -0.1 V, in which case the leaching of gold does not occur at all (Smith and Martell, 2015; Zipperian et al., 1988). Cu(II) is added into the leaching system to act as a catalyst and to oxidize metallic gold to gold (I). Only a few oxidizing agents such as copper ions are adequate in thiosulfate solutions. For example, gaseous oxygen seems not to be effective for metallic gold oxidation (Abbruzzese et al., 1995).

Table 3.7. Thiosulfate leaching experimental layout and runs for the three-factor central composite design

Standard run	Run	Factor levels					
		Coded			Actual		
		A (Temp)	B (Pulp density)	C (Conc)	A Temp (°C)	B Pulp density (%w/v)	C Conc (M)
19	1	0	0	0	50	30	0.6
15	2	0	0	0	50	30	0.6
4	3	+1	+1	-1	75	40	0.2
2	4	+1	-1	-1	75	20	0.2
17	5	0	0	0	50	30	0.6
20	6	0	0	0	50	30	0.6
16	7	0	0	0	50	30	0.6
1	8	-1	-1	-1	25	20	0.2
6	9	+1	-1	+1	75	20	1
9	10	-1.682	0	0	7.95	30	0.6
18	11	0	0	0	50	30	0.6
12	12	0	+1.682	0	50	46.82	0.6
11	13	0	-1.682	0	50	13.18	0.6
7	14	-1	+1	+1	25	40	1
13	15	0	0	-1.682	50	30	-0.073
5	16	-1	-1	+1	25	20	1
3	17	-1	+1	-1	25	40	0.2
10	18	=1.682	0	0	92.04	30	0.6
14	19	0	0	+1.682	50	30	1.273
8	20	+1	+1	+1	75	40	1

3.4.5 Model prediction and fitting

DOE is used to design and analyze experiments to predict and fit models. Below is an overview of the steps involved in DOE model prediction and fitting.

Step 1: Defining the Problem

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- Identification of the response variable(s) and the factors that influence it (Montgomery, 2017).

Step 2: Selecting an Experimental Design

- Selection of a suitable design (e.g., full factorial, fractional factorial, Plackett-Burman, etc.) based on the number of factors and available resources (Box et al., 2005).

Step 3: Conducting Experiments

- Experiments are carried out according to the design, measuring the response variable(s) for each run (Anderson and Whitcomb, 2015).

Step 4: Data Analysis

- This step involves the use of statistical software (e.g., Python, JMP, Design Expert, etc.) to analyze the data and fit a model (e.g., linear, quadratic, etc.) (Kutner et al., 2005).

Step 5: Model Prediction

- In this step, the fitted model is used to predict the response variables(s) for new, unseen combinations of factors (Myers et al., 2016).

Step 6: Model validation

- The model is validated by checking its accuracy (Cawse, 2017).

Step 7: Optimization

- This step makes use of the fitted model to determine the optimal combination of factors that maximize the response variable(s) (Del Castillo, 2017).

3.4.6 Confirmatory tests

Optimum parameters obtained for the IL, DES, and thiosulfate leaching processes were used to run confirmatory experiments. After leaching, the residual tailings were separated from the solution by filtration. The leach liquor was analyzed for gold and other metals such as Cu, Fe, Ni, and Ag by ICP-MS to assess the co-dissolution of other metals with the target metal. The gold results were compared with those predicted by the model. The fresh and leach residual tailings were analyzed by SEM to observe surface morphology and phase changes before and after leaching.

3.4.7 Gold adsorption onto activated carbon

Gold adsorption experiments were carried out with the IL, DES, and thiosulfate solutions coming from the leaching of the gold tailings, respectively. The experiments were carried out under the conditions of 25 °C at 150 rpm agitation speed. The experiments were carried out by varying adsorption time while keeping activated carbon (AC) addition constant at 12 g/L, 60 g/L, and 120 g/L respectively. This was conducted to investigate the adsorption of gold onto the AC (an established gold recovery process) from leach solutions of these reagents and thus gold recovery from solution.

3.4.8 Cyanide leaching of gold tailings.

Detailed cyanide leaching was not investigated in this study and was only conducted for comparison purposes. Leaching experiments were conducted by adding 0.2 kg/t of cyanide into a glass reactor containing 49 % w/v pulp density of gold tailings slurry at ambient temperature at 450 rpm agitation rate. pH was controlled within a range of 10.5 - 11.5 using NaOH. These test conditions were based on the current cyanide-leaching operating conditions at DRDGOLD Limited. AC (12 g/l) was used for gold adsorption in the reactor. Oxygen was fed into the reactor at a flow rate of 10 ml/min to give a dissolved oxygen (DO) content of 12 - 20 mg/l. After leaching, the slurry was filtered. The leach residue was analyzed using the aqua regia digestion method.

3.5 Data analysis

The data was obtained as described in the preceding sections of this chapter. The data obtained was used to determine relationships between gold extraction and the parameters tested as well as the performance of reagents investigated. The experimental results and the relationships are discussed in the chapters that follow. The gold extractions were calculated as a percentage of the gold in the leach liquor to that in the as-received gold tailings material.

CHAPTER 4

RESULTS AND DISCUSSION

4 Introduction

This chapter presents and interprets the experimental results obtained from the research work with the aim of answering the research questions. This chapter first presents and discusses the characterization of the material used in the study. The chapter is divided into three parts: part 1: ionic liquid gold leaching; part 2: deep eutectic solvent gold leaching; and part 3: thiosulfate gold leaching. Therefore, this chapter further presents the comparison and discussion of the results obtained from the three parts.

MATERIAL CHARACTERIZATION

The PSD of the tailings material was found to be over 80% passing 75 μm as shown in **Figure 4.1**. The results of the PSD show that the overall size of the as-received tailings material was finely suitable for leaching and required no further size reduction. Therefore, the tailings material was leached as received without further size reduction because it already had a PSD of 80% passing 75 μm , which is the typical size used for gold ore leaching (Stange, 1999). The mineralogical characterization of the tailings material showed the predominant existence of quartz (SiO_2) (**Table 4.1**). Quartz was found to be the predominant mineral in both the bulk and -38 μm tailings as presented in **Figure 4.2** and **Figure 4.3**. The smallest particle size fraction (-38 μm) was found to have a higher gold concentration and higher gold weight percent as can be seen in **Table 4.2**. In addition to having a higher gold content, smaller size particles lead to faster leaching kinetics since finer particles have a larger surface area. Therefore, for research purposes, both smaller particle size and bulk tailings were investigated in the study. The mineral liberation analysis (MLA) employing the Sparse Phase Liberation-Dual Zoom (SPL-DZ) method based on the bright phase search identified two native/nugget gold grains comprising 100 wt.% of Au (**Table 4.3**). The distribution for both Au grains was found to be less than 1.75 μm and less than 25% liberated by area (essentially locked), suggesting that the tailings material is refractory. These gold grains were both found to be locked within Fe-oxides (**Figure 4.4**). This implies that the reagents used in the study must break down the Fe-oxide matrix to release and dissolve the gold into solution. According to ICP-OES results, the bulk

and – 38 μm tailings contained about 6.57 wt.% and 7.76 wt.% Fe respectively, as shown in **Table 4.4**.

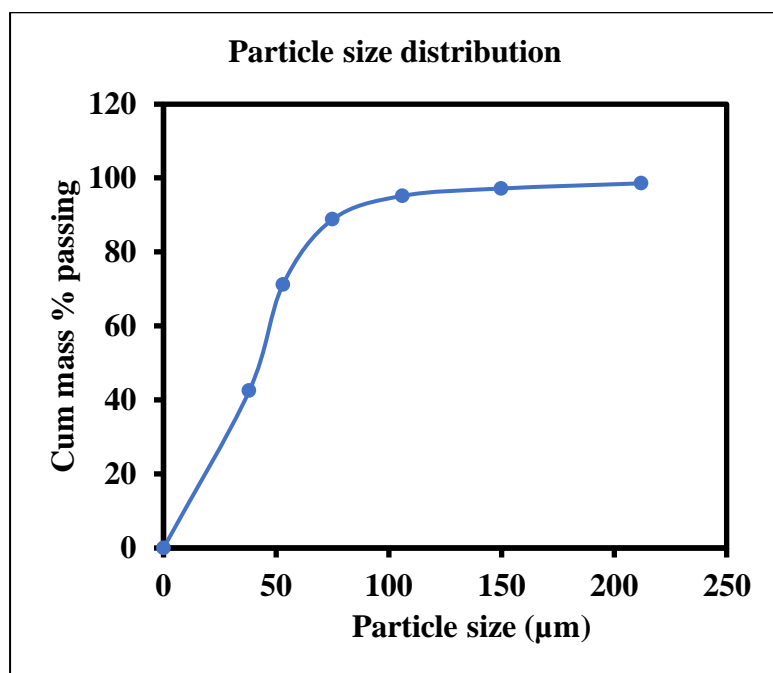


Figure 4.1. Particle size distribution (PSD) of the as-received material

Table 4.1. XRD mineralogical analysis of the gold tailings used in this study

Mineral	Chemical formulae	Mass%
Quartz	SiO_2	72.13
Muscovite	$\text{KAl}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH}, \text{F})_2$	7.49
Chlorite	$\text{Mg}_{2.5}\text{Fe}_{1.65}\text{Al}_{1.5}\text{Si}_{2.2}\text{Al}_{1.8}\text{O}_{10}$	2.65
Pyrophyllite	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$	1.50
Clinochlore	$(\text{Mg}, \text{Fe})_6(\text{Si}, \text{Al})_4\text{O}_{10}$	1.30
Hematite	Fe_2O_3	1.00
Magnetite	Fe_3O_4	0.88
Pyrrhotite	Fe_9S_{10}	0.10
Rutile	TiO_2	0.19
Marcasite	FeS_2	0.10
Biotite	$\text{K}_2(\text{Fe}_{2.786}\text{Mg}_{2.321}\text{Ti}_{0.550})(\text{Al}_{2.413}\text{Si}_{5.587}\text{O}_{20})(\text{OH})_4$	0.54
Diopside	$\text{CaMgSi}_2\text{O}_6$	0.18
Other		11.94
Total		100

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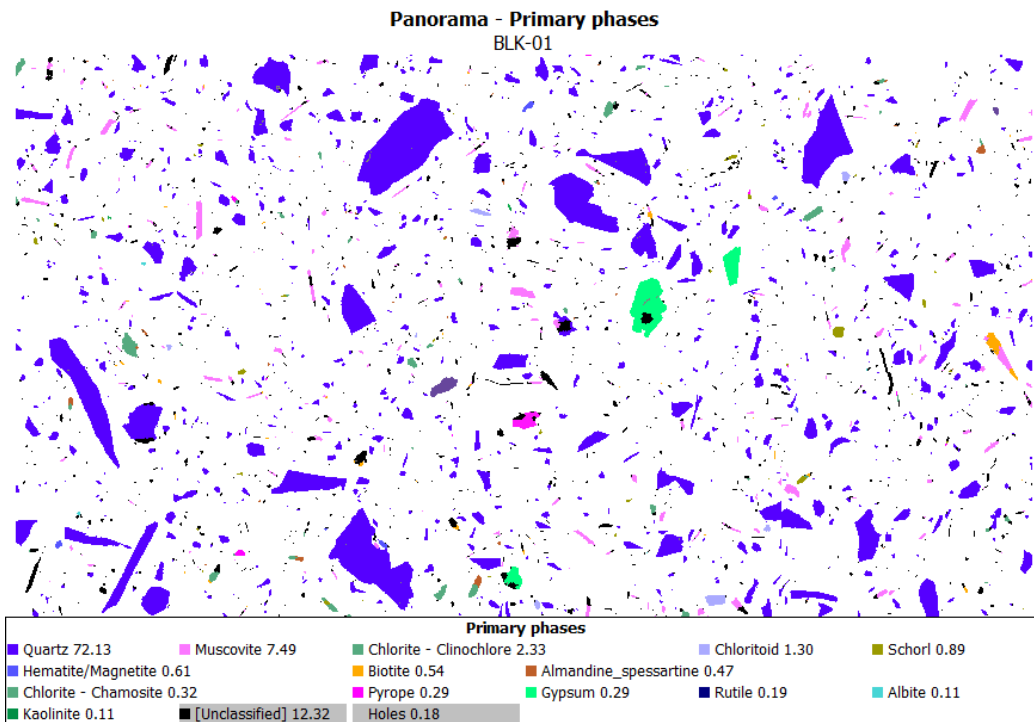


Figure 4.2. Mineral liberation of the as-received bulk gold tailings material

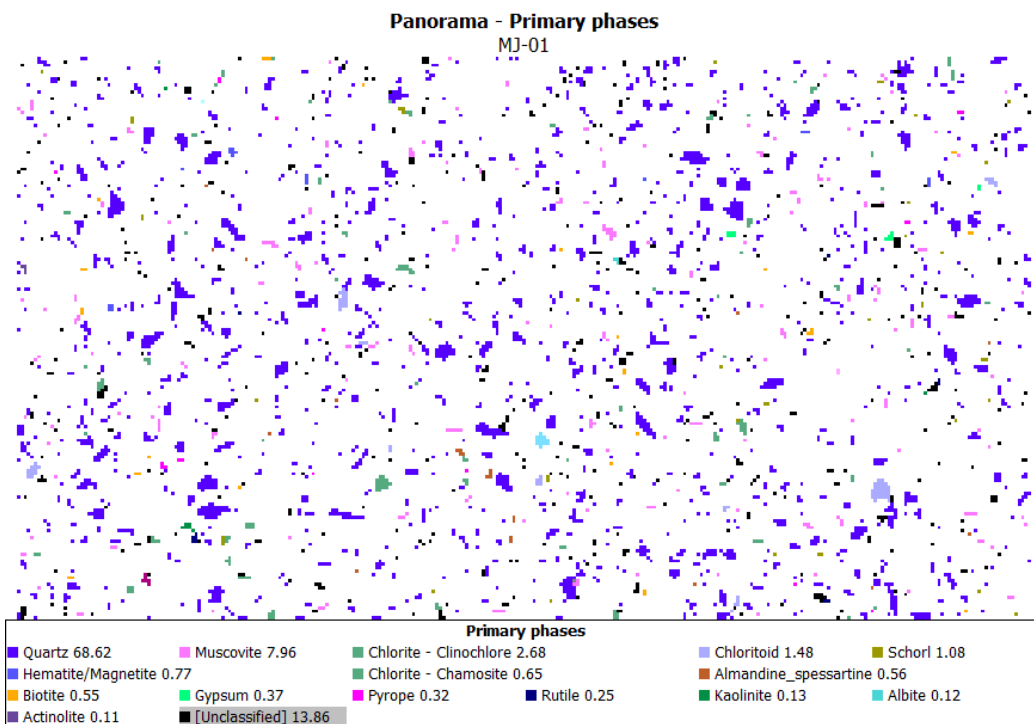


Figure 4.3. Mineral liberation of smaller particle size (~38 μm) gold tailings

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Table 4.2. Size fractions and gold analysis by FAA of the as-received tailings

Size fraction (µm)	Au (g/t)	% (w/w)
+212	0.44	4.012
-212 + 150	0.42	7.15
-150 + 106	0.50	19.09
-106 + 75	0.28	12.73
-75 + 53	0.40	16.10
-53 + 38	0.40	18.18
-38	0.92	22.73
Total	0.32	100.00

Table 4.3. Gold mineral association of the tailings by MLA

Mineral	Gold (wt.%)	Fe-oxide composition	
		Fe	O
Electrum	0.00		
Base metal sulfides	0.00	75.07	24.03
Feldspar	0.00	73.31	26.69
Mica	0.00		
Aluminosilicates	0.00		
Carbonates	0.00		
Fe oxides	100.00		
Other silicates	0.00		
Mn Oxide	0.00		
Sulfates	0.00		
Phosphate	0.00		
Uranium oxides	0.00		
Others	0.00		

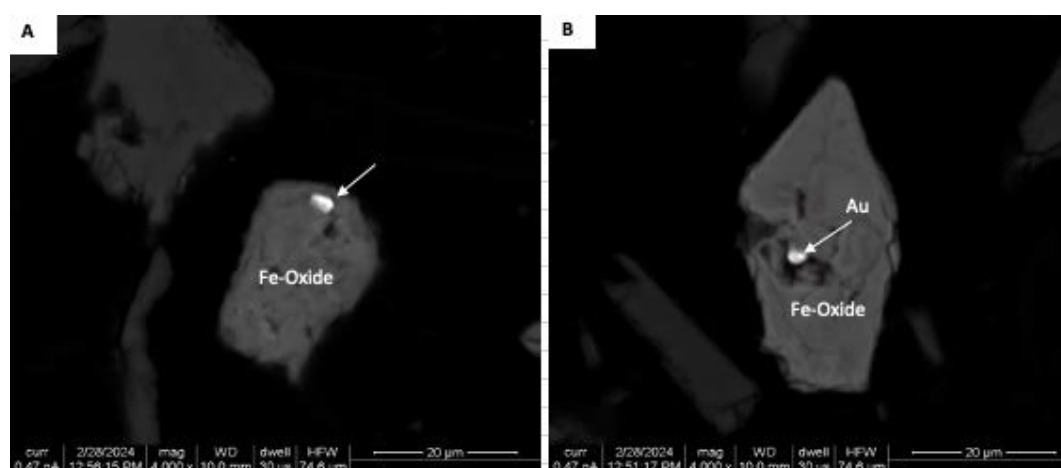


Figure 4.4. BSE images obtained by MLA employing SPL-DZ method showing gold grains enclosed with the Fe-oxide matrix. Gold grains size less than 1.75 µm

Extraction of gold from tailings using environmentally friendly reagents

Table 4.4. Chemical composition of the tailings material used in the study

Chemical composition	Percent	
	-38 μm tailings	Bulk tailings
Silicon dioxide, SiO_2	64.6	65.2
Aluminium dioxide, Al_2O_3	11.2	9.84
Iron, Fe(tot)	7.76	6.57
Titanium oxide, TiO_2	0.407	0.369
Calcium oxide, CaO	0.30	0.28
Magnesium oxide, MgO	0.97	0.843
Potassium oxide, K_2O	2.37	2.05
Manganese oxide, MnO	0.084	0.070
Phosphorus, P	<0.05	<0.05
Barium, Ba	0.04	0.032
Cobalt, Co	0.005	0.005
Chromium, Cr	0.043	0.038
Copper, Cu	0.010	0.017
Nickel, Ni	0.016	0.015
Lead, Pb	0.004	0.003
Strontium, Sr	0.006	0.005
Vanadium, V	0.006	0.005
Zinc, Zn	0.012	0.012

PART 1: IONIC LIQUIDS GOLD LEACHING**4.1 Identification of Significant Factors**

Gold extraction results from ionic liquid (IL) leaching experimental runs for the 2⁴ full factorial design with codified values are given in **Table 4.5**. The gold extraction was calculated as a percentage of the gold in the leach liquor to that in the Witwatersrand gold tailings.

Table 4.5. IL gold extraction results for the 2⁴ full factorial design

Random run order	Standard run order	Controlled factors				% Au extraction
		A	B	C	D	
14	1	-1	-1	-1	-1	85.7
2	2	1	-1	-1	-1	67.7
21	3	-1	1	-1	-1	75.8
7	4	1	1	-1	-1	95.0
17	5	-1	-1	1	-1	57.6
22	6	1	-1	1	-1	81.5
11	7	-1	1	1	-1	69.7
3	8	1	1	1	-1	84.5
12	9	-1	-1	-1	1	59.4
20	10	1	-1	-1	1	69.9
16	11	-1	1	-1	1	96.4
1	12	1	1	-1	1	63.7
5	13	-1	-1	1	1	65.6
10	14	1	-1	1	1	78.6
19	15	-1	1	1	1	87
4	16	1	1	1	1	69.7

The experimental data in **Table 4.5** was used to estimate the main effects and interactions presented in **Figure 4.5**. The actual factor levels coded as values of -1 and +1 in the table are as follows:

A (Leaching temperature): 25 °C (-1) and 75 °C (+1); B (IL concentration): 0.2 M (-1) and 1.0 M (+1); C (Leaching time): 3 h (-1) and 7 h (+1); D (Pulp density): 10 %w/v (-1) and 30 %w/v (+1)

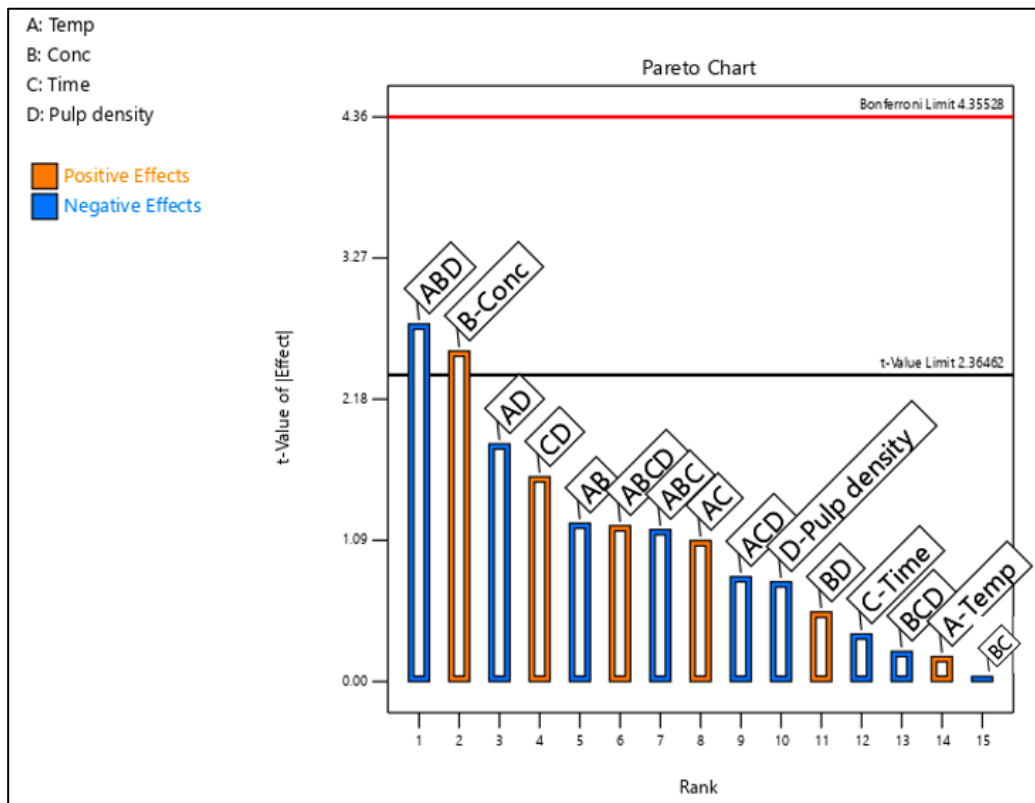


Figure 4.5. The Pareto chart showing the main significant and interactive effects of leaching temperature (A), IL concentration (B), leaching time (C), and pulp density (D)

In **Figure 4.5**, the Bonferroni limit represents the threshold above which the effects that emerge are strongly significant. The effects emerging above the t-limit but below the Bonferroni limit are moderately significant. The combination of factors, ABD, AD, CD, AB, ABCD, ABC, AC, ACD, BD, BCD, and BC are interactive effects.

Analysis of the Pareto chart (**Figure 4.5**) showed that only one individual factor (B), representing IL concentration, was statistically significant since its bar on the chart exceeds the critical value line (t-value limit line) and had a positive effect on the response (gold extraction). Consequently, to maximize gold extraction, IL concentration will need to be kept at a high level. The effect of the other individual factors namely, leaching time, leaching temperature, and pulp density were found to be statistically insignificant as they fell below the critical value line. Among the interactive effects, the interaction of temperature (A), IL concentration (B), and pulp density (D) had a statistically significant effect on the gold extraction process. However, the ABD interaction had a negative effect on the gold extraction process. The experimental data in **Table 4.4** was also used to estimate the main and interaction effects on the normal probability plot of effects presented in **Figure 4.6**.

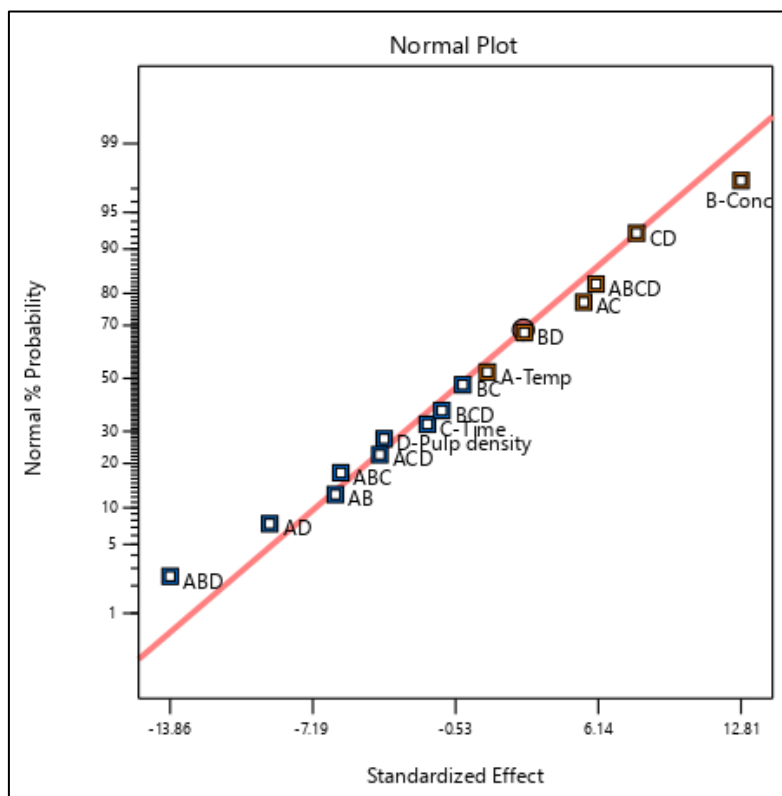


Figure 4.6. The normal plot of effects of main factors and factor interactions from the 2^4 full factorial design using IL. A, B, C, and D are the main factors: A-temperature, B-IL concentration, C-time, and D-pulp density. CD, ABCD, AC, BD, BCD, ACD, ABC, AB, AD, and ABD are factor interactions

Analysis of the individual factors on the probability plot showed that IL concentration (B) was the only factor of statistical significance because it was far from the normal distribution line. Leaching temperature (A), leaching time (C), and pulp density (D) were not statistically significant because they were distributed on the normal distribution line. The normal plot of effects (**Figure 4.6**) also showed that there was only one statistically significant interaction (ABD) because it was distributed far from the normal distribution line. All the other factor interactions were statistically insignificant because they were distributed on or close to the normal distribution line. As expected, results from the normal probability plot of effects were in good agreement with findings from the Pareto chart.

Findings by Teimouri (2020) also indicated that factors significantly influencing the leaching of gold using ionic liquid 1-butyl-3-methyl-imidazolium hydrogen sulfate include IL concentration. Whitehead et al. (2007) also showed that an increase in IL concentration had a significant influence on copper, gold, and silver extraction from both a synthetic oxidic ore and a natural sulfidic ore.

Extraction of gold from tailings using environmentally friendly reagents

The gold extraction results for center points for the 2^4 full factorial design are presented in **Table 4.6**.

Table 4.6. IL gold extraction results for centre point replicates

Runs	Controlled factors				% Au extraction
	A	B	C	D	
1	0	0	0	0	66.0
2	0	0	0	0	82.6
3	0	0	0	0	87.0
4	0	0	0	0	95.7
5	0	0	0	0	65.4
6	0	0	0	0	69.4

The actual factor levels coded as values of (0) in the table are center point values and are as follows: A (leaching temperature): 50 °C (0); B (IL concentration): 0.6 M (0); C (leaching time): 5 h (0); D (pulp density): 20 %w/v (0).

Center points were used as a basis for checking the presence or absence of curvature. However, the model was found to be non-significant, indicating the absence of curvature. Therefore, curvature was removed to simply the model.

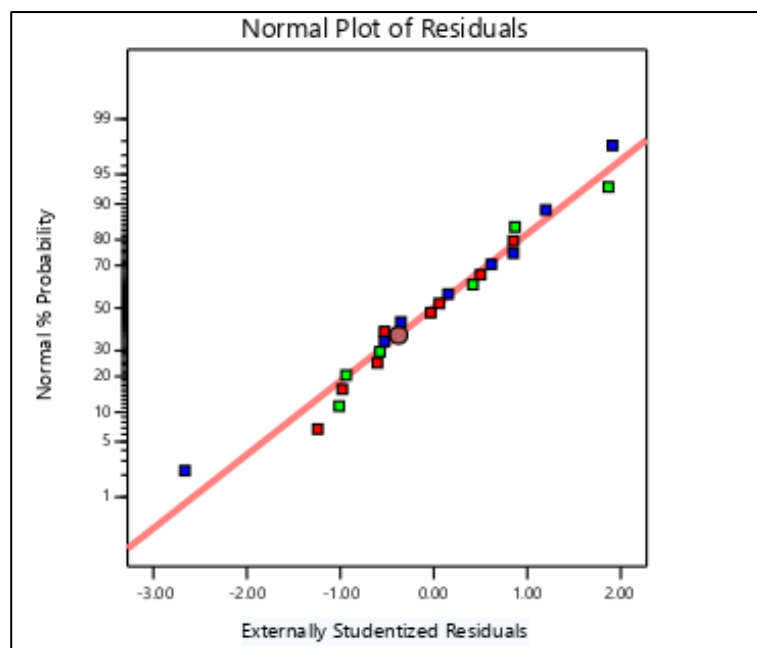


Figure 4.7. Normal plot of residuals

Extraction of gold from tailings using environmentally friendly reagents

The normal plot of residuals illustrated in **Figure 4.7** shows that all the residues lie close to the straight line with a high linear correlation, which indicates that the residuals were distributed normally. The normal plot of residuals helps to ensure reliable regression results. The normal distribution of residuals implies that the model is adequate.

4.1.1 Influence of significant factors on gold extraction

Effect of IL concentration

The effect of IL concentration on gold extraction is presented in **Figure 4.8**. The figure shows gold extraction from tailings at 0.2 M (5% aqueous Bmim[HSO₄] mixture) and 1 M (25% aqueous Bmim[HSO₄] mixture) which are low and high IL concentration levels respectively. The figure shows that higher gold extraction was achieved at high IL concentration whereas lower concentration resulted in low gold extraction. The increase in gold extraction with the increase in IL concentration can be related to the increasing acidity of the (Bmim[HSO₄]) solution. Bmim[HSO₄] acts as an acid when present in an aqueous solution, due to the dissociation of hydrogen sulfate anion which releases H⁺ ions into the solution (Whitehead et al., 2007). However, it should be noted that increasing the concentration to 100% Bmim[HSO₄] will result in reduced gold extraction because at 100% Bmim[HSO₄], the ability of the hydrogen sulfate anion to dissociate and act as an acid is reduced as proton hydration does not occur in pure ionic liquids (Whitehead et al., 2007).

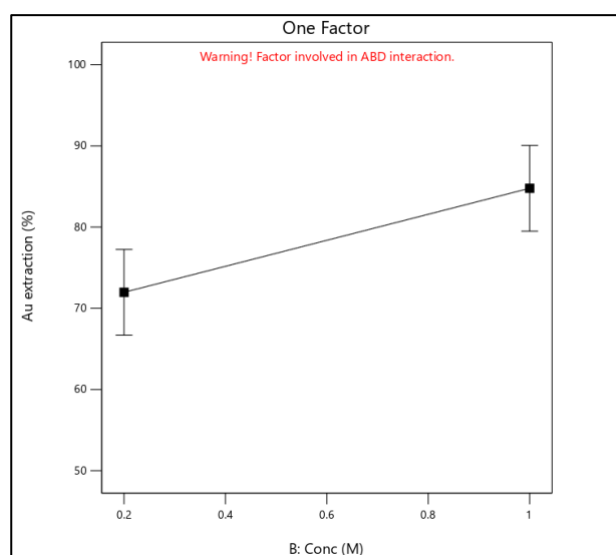


Figure 4.8. The effect of ionic liquid concentration on the gold extraction process

Pure ILs are usually viscous, especially Bmim[HSO₄] (900 mPa), hence water was added to reduce the viscosity of the IL (Whitehead et al., 2007), thus improving the transport properties

of the cations and anions in the system (Mawire and van Dyk, 2018). The increase in gold extraction with an increase in IL concentration (i.e., viscosity) suggests that the mass transfer of the system was not affected under the tested conditions.

Factor interactions.

In the range studied, the ABD factor interaction had a significant effect on the gold extraction process. However, the effect was negative as can be seen in **Figures 4.5 and 4.6**. The effect of factor interaction (ABD) on gold extraction is demonstrated in **Figure 4.9**.

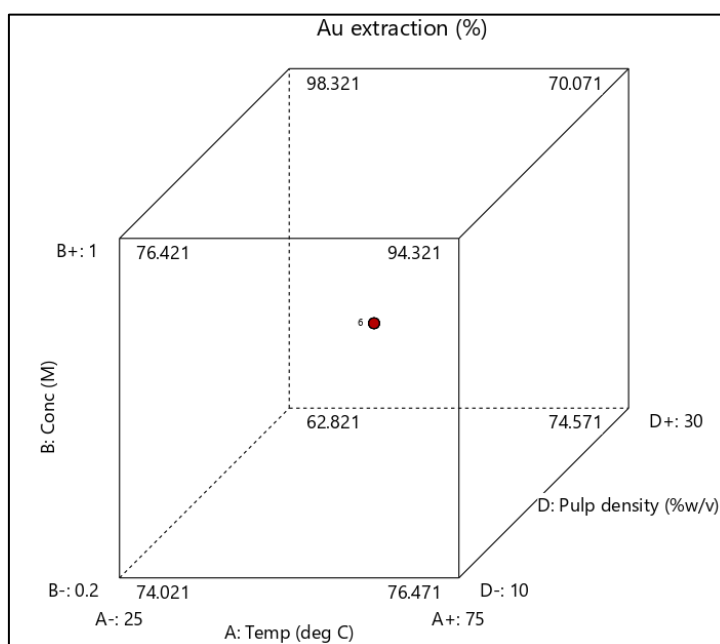


Figure 4.9. The effect of the interaction of temperature, concentration, and pulp density (ABD) on the gold extraction process in IL solution

Figure 4.9 shows that an increase or decrease of all the factors at the same time results in low gold extraction. However, the figure shows that the highest gold extraction can be achieved at low temperature (A), high IL concentration (B), and high pulp density (D) while the lowest gold extraction is obtained at low temperature, low concentration, and high pulp density. From both the Pareto chart and the normal probability plot of effects, it is clear that IL concentration is the key driving factor, which is required to be kept at a high level in order to maximize gold extraction. Similarly, the effect of factor interaction (ABD) in **Figure 4.9** shows that for high gold extraction to occur, IL concentration (B) needs to be at a high level while temperature (A) and pulp density should be kept at inversely related levels. This means, at a high IL concentration, if temperature is at a low level, pulp density should be kept at a high level, and if temperature is at a high level, pulp density should be kept at a low level. This phenomenon

could be attributed to the effect of temperature on the viscosity of ionic liquids. At low temperatures, ionic liquids are known to be less viscous whereas at high temperatures they become more viscous due to moisture loss caused by evaporation (Mohammad and Inamuddin, 2012). This high viscosity can lead to poor mass transfer and thus low extraction efficiencies.

4.2 Optimization of significant factors

The interaction of temperature (A), IL concentration (B), and pulp density (D) was identified as a significant interaction. IL concentration was identified as an individual significant factor as shown in **Figure 4.5**. Therefore, all three factors were incorporated and used to optimize the gold extraction process. The optimization experiments were carried out to determine the optimal conditions for leaching of gold from tailings using IL.

4.2.1 Derivation of the model

The experimental results for the gold extraction are presented in **Table 4.7**. The coefficients of the regression model were estimated by fitting the experimental (obtained) values using Design Expert[®] 13 software.

Table 4.7. Obtained values for IL gold extraction

Standard Run	Factor levels						% Au extraction (Obtained)
	Coded			Actual			
	A (Temp)	B (Conc)	C (Pulp density)	A Temp (°C)	B Conc (M)	C Pulp density (%w/v)	
1	-1	-1	-1	25	0.2	10	32.2
2	+1	-1	-1	75	0.2	10	19.8
3	-1	+1	-1	25	1.0	10	34.8
4	+1	+1	-1	75	1.0	10	40.0
5	-1	-1	+1	25	0.2	30	30.0
6	+1	-1	+1	75	0.2	30	30.4
7	-1	+1	+1	25	1.0	30	33.0
8	+1	+1	+1	75	1.0	30	38.4
9	-1.682	0	0	7.95	0.6	20	4.5
10	+1.682	0	0	92.0	0.6	20	33.0
11	0	-1.682	0	50	0.073	20	14.5
12	0	+1.682	0	50	1.3	20	40.1
13	0	0	-1.682	50	0.6	3.2	7.2
14	0	0	+1.682	50	0.6	36.8	30.2
15	0	0	0	50	0.6	20	34.8
16	0	0	0	50	0.6	20	30.4
17	0	0	0	50	0.6	20	26.1
18	0	0	0	50	0.6	20	30
19	0	0	0	50	0.6	20	29.1
20	0	0	0	50	0.6	20	30.9

Extraction of gold from tailings using environmentally friendly reagents

The fit model was obtained as:

$$\text{Au extraction (coded)} = 28.47 + 3.41*A + 5.63*B + 3.20*C \quad (4.1)$$

$$\text{Au extraction (actual)} = 6.82 + 0.14*A + 14.1*B + 0.32*C \quad (4.2)$$

where, A is leaching temperature, B is IL concentration, and C is pulp density.

The equation in terms of coded factors can be used to make predictions about the response (gold extraction) for given levels of each factor. The high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

The equation in terms of actual factors can be used to predict the response for given levels of each factor. Here, the levels are specified in the original units for each factor. The equation in terms of actual factors, however, cannot be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

The fit summary in **Table 4.8** shows the suggested fit model.

Table 4.8. Fit summary

Source	Sequential p-value	Lack of Fit p-value	Adjusted R ²	Predicted R ²	
Linear	0.0382	0.0065	0.2877	-0.0787	Suggested
2FI	0.7238	0.0042	0.2052	-1.0002	
Quadratic	0.7332	0.0023	0.0859	-2.5269	
Cubic	0.3224	0.0008	0.2283	-47.9540	

4.2.2 Checking the adequacy of the developed model.

The adequacy of the fitted (linear) model was carried out using the analysis of variance (ANOVA) given in Table 4.9.

Table 4.9. ANOVA for linear model

Source	Sum of squares	Degree of freedom	Mean Square	F-value	p-value	
Model	730.75	3	243.58	3.56	0.0382	Significant
A-Temperature	158.54	1	158.54	2.32	0.1476	
B-Concentration	432.50	1	432.50	6.32	0.0230	
C-Pulp density	139.71	1	139.71	2.04	0.1724	
Residual	1095.49	16	68.47			
Lack of Fit	1055.75	11	95.98	12.07	0.0065	Significant
Pure Error	39.75	5	7.95			
Cor Total	1826.24	19				

The Model F-value of 3.56 implies the model is significant. There is only a 3.82% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, concentration (B) is a significant model term. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 12.07 implies the Lack of Fit is significant. There is only a 0.65% chance that a Lack of Fit F-value this large could occur due to noise. However, a significant lack of fit is bad because the model should fit.

The fit statistics are presented in Table 4.10. A negative Predicted R² in Table 4.10 implies that the overall mean may be a better predictor of the response than the fitted linear model. In some cases, a higher-order model may also predict better. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 6.612 in Table 4.10 indicates an adequate signal. Therefore, the fitted linear model can be used to navigate the design space.

Table 4.10. Fit statistics

Standard Deviation	8.27		R²	0.4001
Mean	28.47		Adjusted R²	0.2877
C.V. %	29.06		Predicted R²	-0.0787
			Adeq Precision	6.6116

4.2.3 IL gold leaching optimum conditions

As stated, the major objective of the study is to determine the conditions that maximize gold extraction from tailings. Therefore, after the model was checked for adequacy of fit in the region defined by the coordinates of the design and was found to be adequate, the model was used to locate the points of maximum gold extraction. Thus, the optimum gold extraction conditions from tailings using ionic liquid were 1.0 M (25% Bmim[HSO₄]) IL concentration, 75 °C leaching temperature, 10 %w/v pulp density, and 5 hours leaching time.

4.2.4 Confirmatory experiments

The optimal gold extraction prediction is shown in **Table 4.11**. Confirmatory tests were carried out under the identified optimum conditions in section 4.2.3 to confirm the model-predicted gold extraction.

Table 4.11. Gold extraction at optimum IL leaching conditions

Parameters	Temp (°C)	Conc (M)	Pulp density (%w/v)	Au extraction (%)
Model	75	1.0	10	40.1
Confirmatory tests	75	1.0	10	45.3

The maximum gold extraction predicted by the model (40.1%) is in close agreement with the experimental value (45.3%) as can be seen in **Table 4.11**. This verifies the fitting of experimental data and the fitness of the model. However, gold extraction of +45% achieved via IL leaching is low. The low gold extraction can be attributed to the low efficiency of ILs in dissolving metal iron oxide (Kim et al., 2018) enclosing the gold in the tailings. Studies have also shown that the dissolution of iron oxide samples using ionic liquids requires longer residence time, and the dissolution efficiency is poor (Kim et al., 2018).

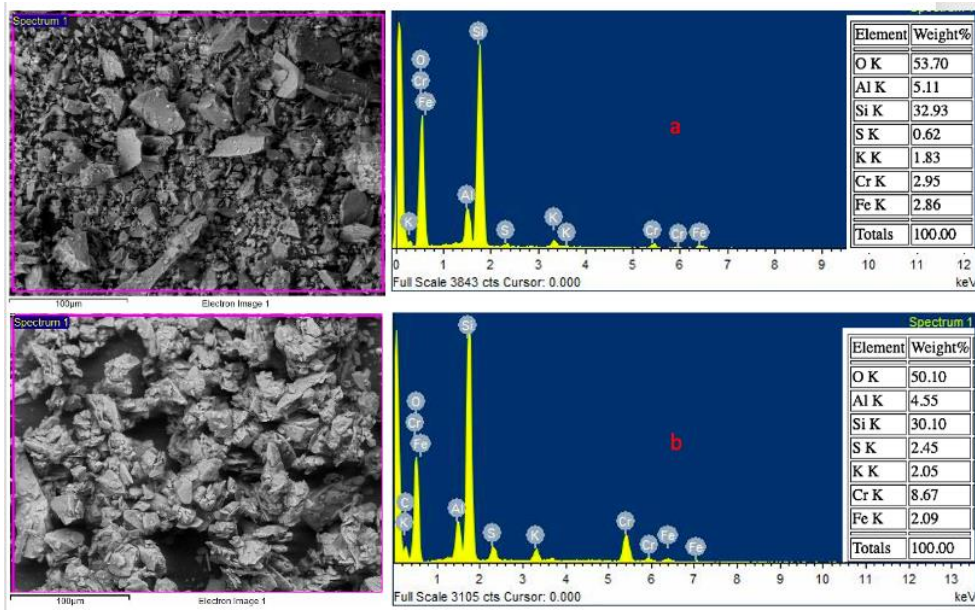


Figure 4.10. SEM-EDS images of gold tailings before (a) and after (b) IL leaching

Furthermore, it has been reported that iron oxides such as FeO, Fe₂O₃, and Fe₃O₄ require longer dissolution times than Fe ions (De Los Ríos et al., 2012). In general, ILs can be used to dissolve metals in specific ionic states with relatively high efficiency in a short period. However, it is more difficult to dissolve metals from their solid oxide form (Kim et al., 2018).

4.3 Effect of particle size on the leaching of gold from tailings using IL

The effect of particle size on gold extraction from tailings using 1-butyl-3-methyl-imidazolium hydrogen sulfate ionic liquid was investigated. Leaching experiments were carried out using the bulk (-300 μm, 80% passing 75 μm) and smaller size (-38 μm) gold tailings under optimum conditions discussed in sub-section 4.2.3. The effect of particle size on the extraction of gold from tailings during IL leaching is illustrated in **Figure 4.11**. The figure shows that the reduction in particle size of the tailings had a significant effect on gold extraction, increasing it by 23.4%. This is attributed to smaller particle sizes having a larger surface area available for interaction with the leaching agent and the presence of a thin boundary layer, thus improving leaching efficiency. The enhanced gold extraction implies that at smaller gold tailings particle size, liberation of the gold is improved, thereby accessible for leaching

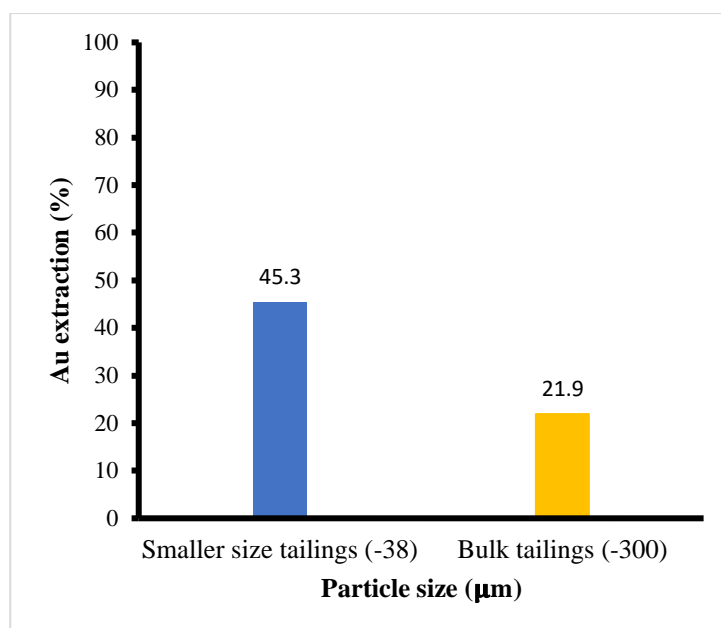


Figure 4.11. The effect of particle size on the gold extraction process from tailings during IL leaching

4.4 Co-dissolution of other metals with Au in a solution of IL

The co-dissolution of other metals in the tailings interfering with the dissolution and extraction of Au in a BmimHSO₄ solution was investigated. Metals investigated include silver (Ag), iron (Fe), copper (Cu), and nickel (Ni). The results of this investigation are shown in **Figure 4.12**. The figure shows that Ag, Cu, Fe, and Ni were extracted together with Au, indicating that Au experienced competitive dissolution during BmimHSO₄ leaching. Kim et al. (2018) reported that IL BmimHSO₄ can also be used in the dissolution and extraction of Fe, Cu, and Ni. Whitehead et al. (2007) reported the extraction of Ag from a sulfidic ore using BmimHSO₄ in the presence of thiourea and iron (III) as an oxidant. **Figure 4.12** shows that the IL was more efficient in the dissolution of Ni (61.9%) and Cu (50.4%) compared to Au (45.3%). As mentioned in sub-section 4.2.4, the low dissolution of Fe (**Figure 4.12**) is attributed to the difficulty of ILs in dissolving metals from their solid oxide form (i.e., FeO).

Extraction of gold from tailings using environmentally friendly reagents

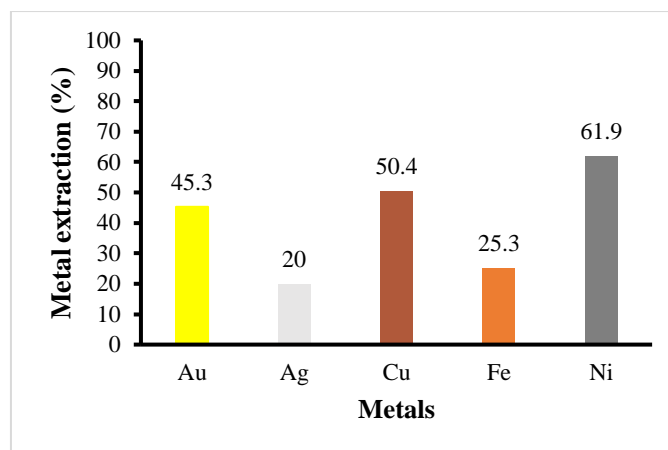


Figure 4.12. Competitive dissolution between Au and other metals in the tailings during IL leaching

In addition to gold being locked, the low extraction of 45.3% can be attributed to most of the BmimHSO₄ being used up in the dissolution of other untargeted metals, reducing the amount of BmimHSO₄ necessary for maximum Au dissolution. The high extraction of Ni and Cu compared to Au can also be an indication of the suitability of IL in the processing of Cu and Ni, however, this will depend on the type of ore and the liberation of the metals.

PART 2: DEEP EUTECTIC SOLVENT GOLD LEACHING**4.5 Identification of Significant Factors**

Gold extraction results from DES leaching experimental runs for the 2⁴ full factorial design with codified and actual values are given in **Table 4.12**. The results for the extraction of gold from tailings using deep eutectic solvent are presented in **Table 4.12**. The results were calculated as a percentage of gold in the leach liquor to that in the unprocessed tailings.

Table 4.12. DES gold extraction results for the 2⁴ full factorial design

Standard run order	Random run order	Controlled factors				% Au extraction
		A	B	C	D	
1	4	-1	-1	-1	-1	57.6
2	16	1	-1	-1	-1	69.6
3	13	-1	1	-1	-1	43.5
4	8	1	1	-1	-1	71.7
5	9	-1	-1	1	-1	51.1
6	6	1	-1	1	-1	66.3
7	1	-1	1	1	-1	60.9
8	5	1	1	1	-1	57.6
9	10	-1	-1	-1	1	76.8
10	14	1	-1	-1	1	56.5
11	3	-1	1	-1	1	83
12	7	1	1	-1	1	53.6
13	2	-1	-1	1	1	70.7
14	15	1	-1	1	1	89.1
15	11	-1	1	1	1	85.9
16	12	1	1	1	1	89.1

The actual factor levels coded as values of (-1) and (+1) in the table are as follows:

A (Temperature): 25 °C (-1) and 75 °C (+1); B (DES concentration (ChCl: EG)) 1:2 (-1) and 1:4 (+1); C (Time): 3hrs (-1) and 7hrs (+1); D (Pulp density): 10 %w/v (-1) and 30 %w/v (+1)

Extraction of gold from tailings using environmentally friendly reagents

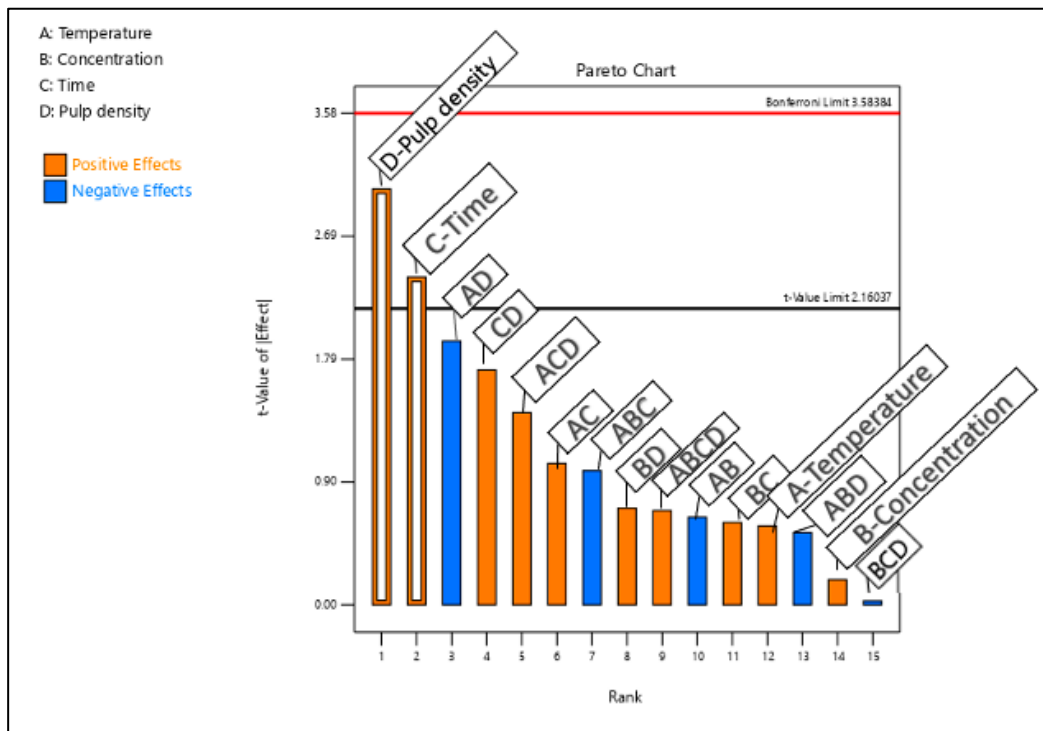


Figure 4.13. Pareto chart showing the significance of main and interactive effects of temperature (A), DES concentration (B), leaching time (C), and pulp density (D)

The combination of factors AD, CD, ACD, AC, ABC, BD, ABCD, AB, BC, ABD, and BCD are interactive effects.

Analysis of the individual factors on the Pareto chart (**Figure 4.13**) showed that pulp density and leaching time were statistically significant since they exceeded the critical line. Temperature and concentration were found to be statistically insignificant. The Pareto chart also shows that the identified significant factors had a positive effect on the response (gold extraction). Factor interaction was found to be insignificant.

Extraction of gold from tailings using environmentally friendly reagents

The experimental data given in **Table 4.12** was also used to estimate the main and interaction effects presented in **Figure 4.14**.

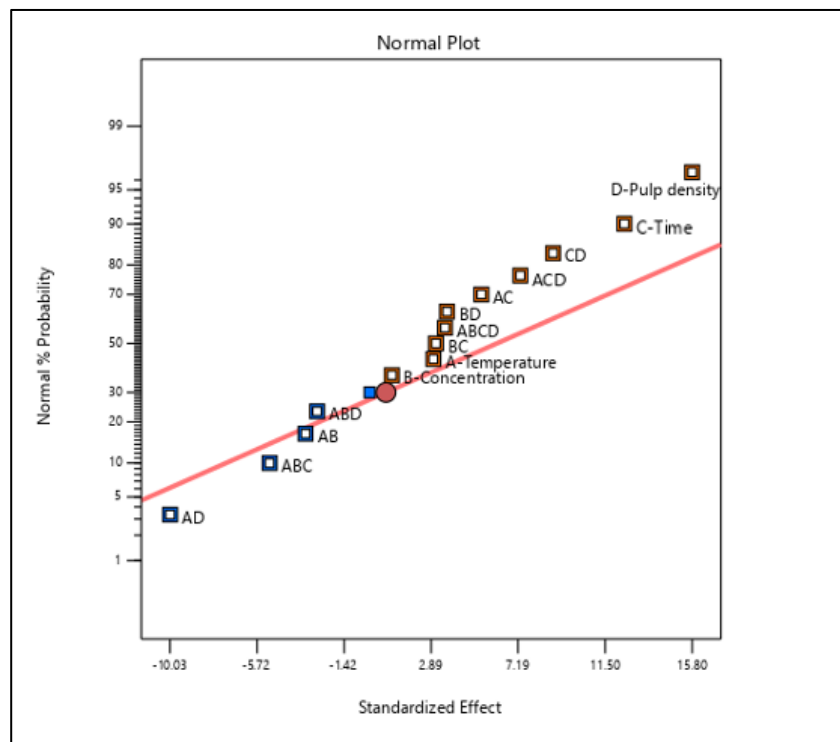


Figure 4.14. The normal plot of effects of main factors and factor interactions from the 24 full factorial design in DES. A, B, C, and D are the main factors: A-temperature, B-DES concentration, C-time, and D-pulp density. CD, ACD, AC, BD, ABCD, BC, ABD, AB, ABC, and AD are factor interactions

The normal probability plot of effects presented in **Figure 4.14** was used to determine the significant effects. Analysis of the individual factors on the probability plot showed that time (C) and pulp density (D) were statistically significant since they were distributed far from the normal distribution line. DES concentration (B) and temperature (A) are not statistically significant because they are within the normal distribution. There was no significant interaction among the factors since all the interactions were distributed close to or on the distribution line.

The significance of pulp density and leaching time compared to other factors refers to the acceptability of the effect considering the statistical data. This means that the effect of the two factors has a strong influence on the extraction process. Although the other factors may be statistically insignificant, they are scientifically important (Shemi, 2013), hence relevant to the process.

Extraction of gold from tailings using environmentally friendly reagents

The gold extraction results for center points for the 2⁴ full factorial design are presented in **Table 4.13**.

Table 4.13. DES gold extraction results for centre point replicates

Runs	Controlled factors				% Au extraction
	A	B	C	D	
1	0	0	0	0	64.7
2	0	0	0	0	87.5
3	0	0	0	0	69.0
4	0	0	0	0	73.4
5	0	0	0	0	92.4
6	0	0	0	0	80.0

The actual factor levels coded as values of (0) in the table are center point values and are as follows: A (Temperature): 50 °C (0); B (DES concentration): ChCl: EG (1: 3) (0); C (Time): 5hrs (0); D (Pulp density): 20 %w/v (0)

The center points were used as a basis for checking the presence or absence of curvature in the model. The model was found to be non-significant when curvature was checked, indicating the absence of curvature. Therefore, curvature was removed to simplify the model.

The normal plot of residuals illustrated in **Figure 4.15** shows that all the residues lie close to the straight line with a linear correlation, which indicates that the residuals were distributed normally.

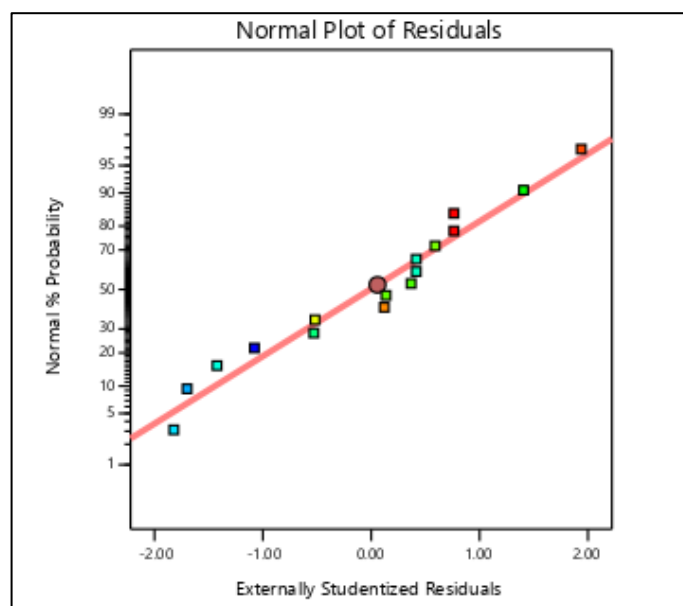


Figure 4.15. Normal plot of residuals

4.5.1 Influence of significant factors on gold extraction

Effect of pulp density

The effect of pulp density on gold extraction using DES is presented in **Figure 4.16**. The figure shows gold extraction from tailings at 10 %w/v and 30 %w/v which are low and high pulp density levels respectively. In most cases, gold dissolution increases with a decrease in pulp density because of reduced mass transfer resistance, however, in this case, as shown in **Figure 4.16**, gold extraction increases with an increase in pulp density. This effect can be attributed to the increased presence of tailings particles (i.e., gold) in the leach solution as pulp density increases, resulting in more gold dissolution. Furthermore, the results indicate that increasing the pulp density from 10 %w/v to 30 %w/v did not significantly impact mass transfer resistance. This suggests that the pulp density threshold, beyond which mass transfer would become challenging and reduce dissolution efficiency, was not reached.

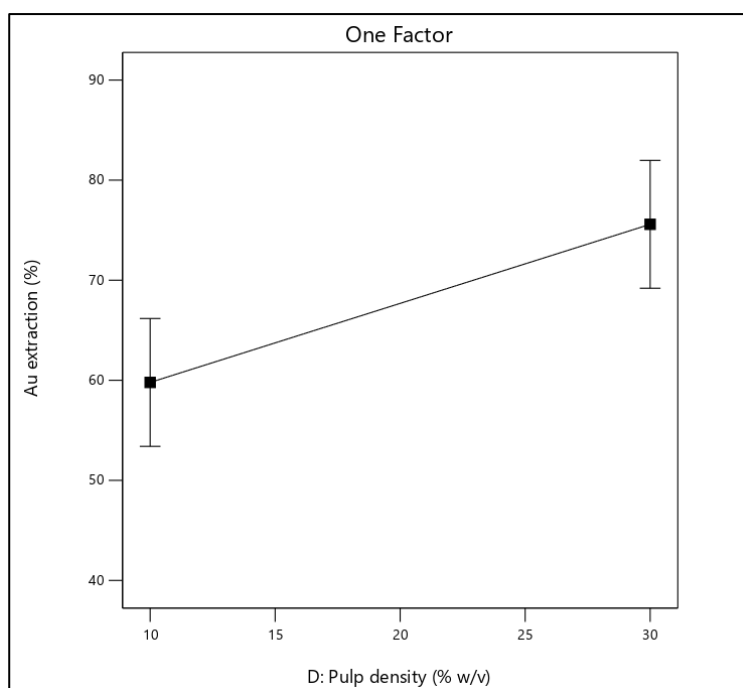


Figure 4.16. The effect of pulp density on the gold extraction process during DES leaching

Effect of leaching time

The effect of leaching time on gold extraction using DES reagent is shown in **Figure 4.17**. The figure illustrates gold extractions from tailings at 3hrs and 7hrs which are low and high levels of leaching time respectively. It can be seen in the figure that gold extraction increases with increasing leaching time. The higher gold extraction observed with longer leaching times indicates increased dissolution of gold over extended periods. This is because longer leaching times provide more opportunity for the lixiviant to interact with the gold-bearing material, resulting in higher dissolution rates (Marsden and House, 2006; Adams, 2005; Kappes, 2005).

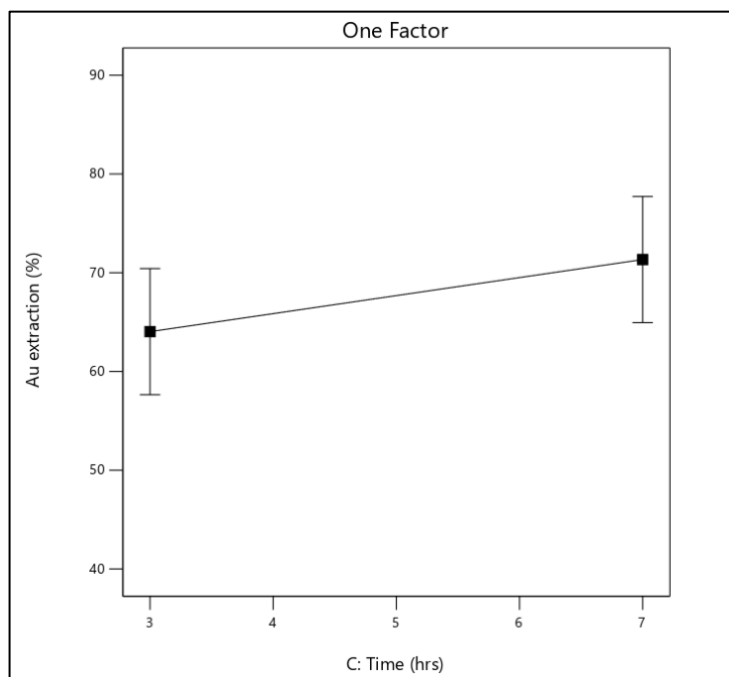


Figure 4.17. The effect of leaching time on the gold extraction process during DES leaching

Factor interactions.

Factor interaction among the various variables, in the range studied, was found to be insignificant. All the interaction effects were normally distributed about the zero mean and fitted on a straight line as illustrated in **Figure 4.14**.

4.6 Optimization of significant factors

The significant factors, pulp density and leaching time, identified in section 4.6 were incorporated and used to carry out optimization experiments. The optimization experiments were carried out to determine the optimal conditions for leaching gold from tailings using DES.

4.6.1 Derivation of the model

The experimental results for the gold extraction are presented in **Table 4.14**. The coefficients of the regression model were estimated by fitting the experimental (obtained) values using Design Expert[®] 13 software.

Table 4.14. Obtained values for DES gold extraction

Standard run	Factor levels				% Au extraction (Obtained)
	Coded		Actual		
	A (Pulp density)	B (Time)	A Pulp density (%w/v)	B Time (hours)	
1	-1	-1	10	3	14.4
2	+1	-1	30	3	48
3	-1	+1	10	7	14.4
4	+1	+1	30	7	43.2
5	-1.414	0	5.858	5	24.5
6	+1.414	0	34.142	5	84.7
7	0	-1.414	20	2.172	65
8	0	+1.414	20	7.828	72.1
9	0	0	20	5	72.1
10	0	0	20	5	50.4
11	0	0	20	5	57.7
12	0	0	20	5	43.2
13	0	0	20	5	65

The fit model was obtained as follows:

$$\text{(Coded equation) Au extraction} = 50.36 + 18.44*A + 0.655*B \quad (4.3)$$

$$\text{(Actual equation) Au extraction} = 11.84 + 1.84*A + 0.33*B \quad (4.4)$$

where, A = pulp density and B = leaching time

The equation in terms of coded factors can be used to make predictions about the response (gold extraction) for given levels of each factor. The high levels of the factors are coded as +1

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and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

The equation in terms of actual factors can also be used to predict the response (gold extraction) for given levels of each factor. Here, the levels are specified in the original units for each factor. This equation, however, cannot be used to determine the relative impact of each factor because the coefficients are scaled to accommodate the units of each factor and the intercept is not at the center of the design space.

The fit summary in **Table 4.15** suggests the fit model.

Table 4.15. Fit summary

Source	Sequential p-value	Lack of Fit p-value	Adjusted R ²	Predicted R ²	
Linear	0.0475	0.1248	0.3476	-0.0630	Suggested
2FI	0.9021	0.0966	0.2764	-1.0256	
Quadratic	0.4693	0.0703	0.2505	-1.6220	
Cubic	0.9141	0.0175	-0.0123	-20.5126	

4.6.2 Checking the adequacy of the developed model.

The adequacy of the fitted model was carried out using the analysis of variance (ANOVA) given in **Table 4.16**.

Table 4.16. ANOVA for the fitted (linear) model

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	p-value	
Model	2724.28	2	1362.14	4.20	0.0475	significant
A-pulp density	2720.85	1	2720.85	8.38	0.0160	
B-time	3.43	1	3.43	0.0106	0.9201	
Residual	3245.83	10	324.58			
Lack of fit	2721.64	6	453.61	3.46	0.1248	Not significant
Pure error	524.19	4	131.05			
Cor Total	5970.11	12				

The Model F-value of 4.20 implies that the model is significant. There is only a 4.75% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case, pulp density (A), with a P-value of 0.016, is a significant model term. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit F-value of 3.46 and P-value of 0.1248, implies the Lack of Fit is not significant relative

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to the pure error. There is a 12.48% chance that a Lack of Fit of F-value this large could occur due to noise. Non-significant lack of fit is good because the model should be fit.

The fit statistics are presented in **Table 4.17**. A negative Predicted R^2 implies that the overall mean may be a better predictor of the response (gold extraction) than the fitted linear model. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. The ratio of 6.027 given in **Table 4.17** indicates an adequate signal. Therefore, the fitted linear model can be used to navigate the design space.

Table 4.17 Fit statistics

Std. Dev.	18.02		R^2	0.4563
Mean	50.36		Adjusted R^2	0.3476
C.V. %	35.77		Predicted R^2	-0.0630
			Adeq Precision	6.0270

4.6.3 DES gold leaching optimum conditions

As stated earlier, the major objective of the study was to determine the conditions that maximize gold extraction from tailings. Therefore, after the model was checked for adequacy of fit in the region defined by the design coordinates and was found to be adequate, the model was used to locate the points of maximum response. The optimum leaching conditions were found to be 30 %w/v pulp density, 7 hours leaching time, 50 °C leaching temperature, and 1 (ChCl): 2 (EG) concentration.

4.6.4 Confirmatory experiments

The optimum gold extraction predicted by the design expert software is shown in **Table 4.18**. Confirmatory tests were conducted using the optimum conditions to confirm the predicted gold extraction.

Table 4.18. Gold extraction at optimum DES leaching conditions

Parameters	Pulp density (%w/v)	Time (hrs)	% Au extraction
Model	30	7	70.0
Confirmatory tests	30	7	76.4

The results in **Table 4.18** show that the actual gold extraction is higher than but comparable to the predicted gold extraction, hence verifying the fitting of experimental data and the fitness of

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the model. The high gold extraction of 76.4% suggests that the DES destroyed the metal iron oxide enclosing the gold, allowing the gold to be accessible for leaching. Literature has shown that DESs are generally suitable for the processing of metal oxides (Abbott et al., 2006; Jenkin et al., 2016). The SEM-EDS results illustrated in **Figure 4.18** further show a reduction in the Fe-oxide after leaching, indicating Fe-oxide dissolution.

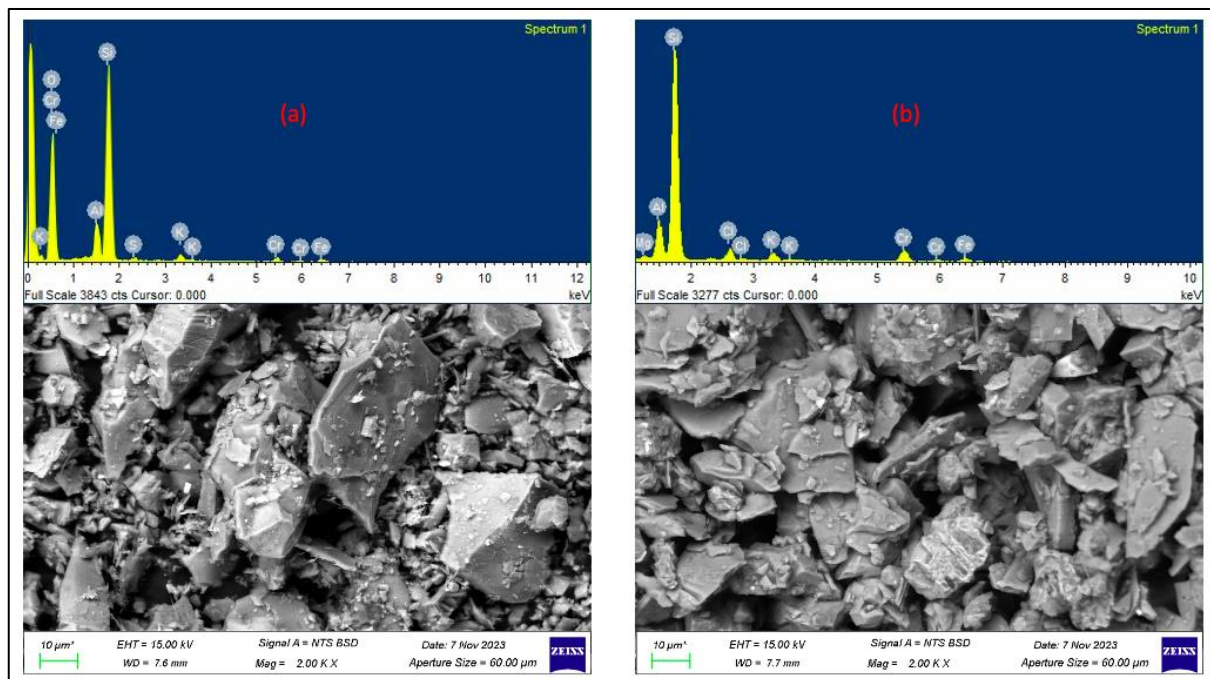


Figure 4.18. SEM-EDS images of gold tailings before (a) and after (b) leaching

4.7. Effect of particle size on gold leaching of tailings using DES

The effect of particle size on gold extraction from tailings using ethaline DES was investigated. Leaching experiments were carried out using the bulk (-300 μm , 80% passing -75 μm) and smaller size (-38 μm) gold tailings under similar optimum conditions. The effect of particle size on the extraction of gold from tailings during ethaline leaching is illustrated in **Figure 4.19**. The figure shows that the reduction in particle size increased gold extraction by only 4.5%. Gold extraction was expected to increase with a reduction in tailings particle size because smaller particle sizes have more surface area exposed for leaching, thus resulting in an increased dissolution rate. However, **Figure 4.19** shows that particle size reduction did not have a significant effect on gold extraction from tailings suggesting that the gold dissolution reaction mechanism was chemical reaction controlled. This is because the effect of particle size is significant when the leaching rate is under diffusion control and minor if the leaching rate is chemical reaction controlled (Faraji et al., 2022).

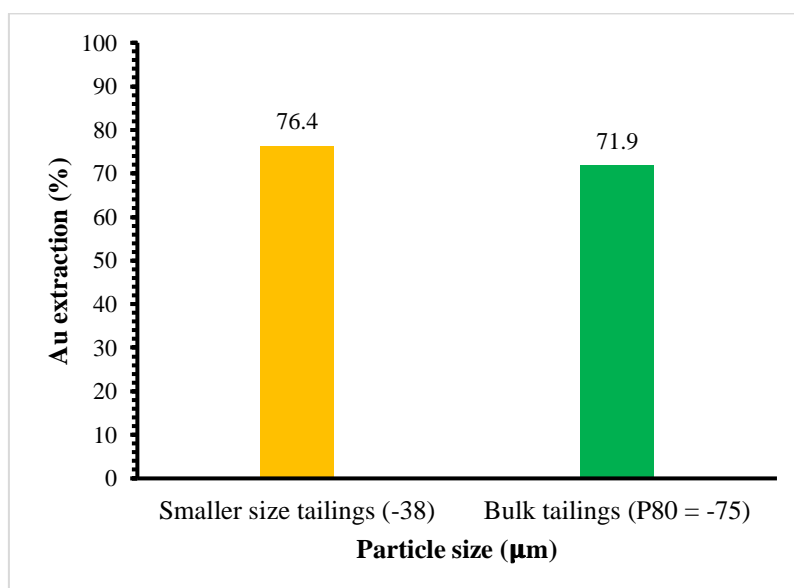


Figure 4.19. Effect of particle size on the gold extraction process during DES leaching

4.8 Co-dissolution of other metals with Au in a DES solution

The co-dissolution of Ag, Cu, Fe, and Ni with Au was also studied in a solution of DES ethaline. The results are presented in **Figure 4.20**. The figure shows the selectivity of DES over all the other metals.

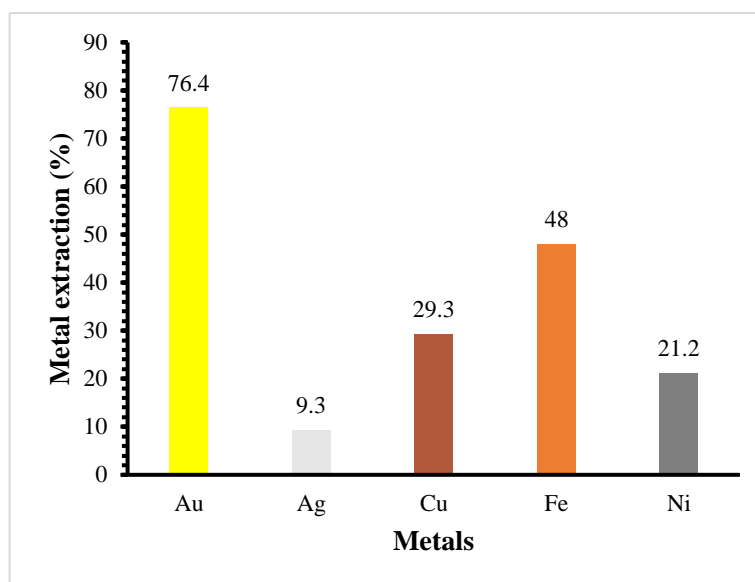


Figure 4.20. Competitive dissolution between Au and other metals in the tailings during DES leaching

The high gold extraction (**Figure 4.20**) in comparison to Ag, Cu, Fe, and Ni shows that the DES has more affinity for gold dissolution over the other metals. However, the extractions of Cu, Fe, and Ni are quite high, suggesting competitive dissolution with gold. This indicates that these impurities need to be removed for efficient processing of gold using DES. The removal of these impurities will lead to reduced reagent consumption caused by the dissolution of untargeted metals, resulting in more DES available for gold dissolution.

PART 3: THIOSULFATE GOLD LEACHING**4.9 Identification of Significant Factors**

Gold extraction results from thiosulfate leaching experimental runs for the 2⁴ full factorial design with codified and actual values are given in **Table 4.19**. The gold extraction in the thiosulfate leaching of tailings presented in **Table 4.19** was also calculated as a percentage of gold in liquor to that in the unprocessed tailings.

Table 4.19. Thiosulfate gold extraction results for the 2⁴ full factorial design

Standard run order	Random run order	Controlled factors				% Au extraction
		A	B	C	D	
1	8	-1	-1	-1	-1	27.6
2	20	1	-1	-1	-1	41.4
3	14	-1	1	-1	-1	29.9
4	21	1	1	-1	-1	45.2
5	9	-1	-1	1	-1	23
6	13	1	-1	1	-1	52.9
7	6	-1	1	1	-1	38.3
8	12	1	1	1	-1	55.2
9	3	-1	-1	-1	1	23.4
10	5	1	-1	-1	1	45.2
11	18	-1	1	-1	1	26.1
12	11	1	1	-1	1	37.9
13	2	-1	-1	1	1	23.4
14	19	1	-1	1	1	48.7
15	17	-1	1	1	1	27.2
16	7	1	1	1	1	39.7

The actual factor levels coded as values of (-1) and (+1) in the table above are as follows:

A (Temperature): 25 °C (-1) and 75 °C (+1); B (Thiosulfate concentration): 0.2 M (-1) and 1.0 M (+1); C (Time): 3hrs (-1) and 7hrs (+1); D (Pulp density): 20 %w/v (-1) and 40 %w/v (+1)

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The experimental data given in **Table 4.19** was used to estimate the main and interaction effects presented in **Figure 4.21**.

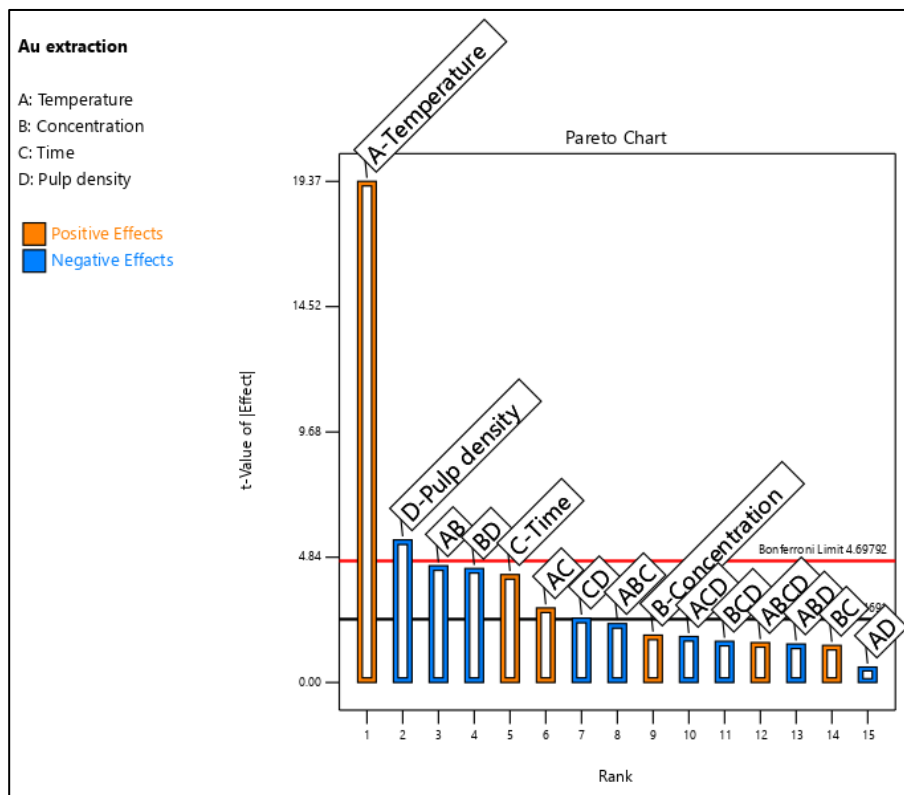


Figure 4.21. Pareto chart showing the significance of the main and interactive effects of temperature (A), thiosulfate concentration (B), leaching time (C), and pulp density (D)

The combination of factors AB, BD, AC, CD, ABC, ACD, BCD, ABCD, ABD, BC, and AD are interactive effects.

Analysis of the individual factors on the Pareto chart showed that temperature and pulp density were strongly significant because they exceeded the Bonferroni limit line. Leaching time was moderately significant since it exceeded the critical line but fell below the Bonferroni limit line suggesting that leaching time was less significant than temperature and pulp density. The concentration of thiosulfate was found to be insignificant. The Pareto chart also shows that temperature and leaching time have a positive effect on the response (gold extraction) while pulp density has a negative effect. The analysis of factor interactions showed that AB, BD, and AC interactions were significant since they exceeded the critical line. However, AB and BD interactions had a negative effect on gold extraction while AC interaction had a positive effect as shown in **Figure 4.21**. The experimental data in **Table 4.19** was also used to estimate the main and interactive effects presented in **Figure 4.22**.

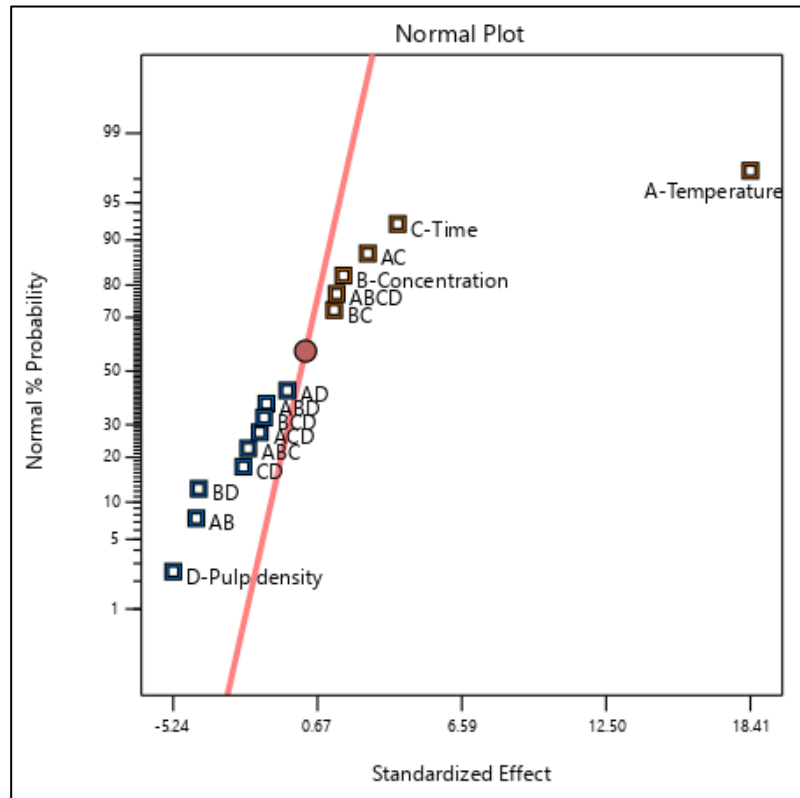


Figure 4.22. The normal plot of effects of main factors and factor interaction from the 2^4 full factorial design in thiosulfate. A, B, C, and D are the main factors: A-temperature, B-thiosulfate concentration, C-time, and D-pulp density. AC, ABCD, BC, AD, ABD, BC, ACD, ABC, CD, BD, and AB are factor interactions

The normal probability plot of effects presented in **Figure 4.22** was used to determine the significant effects. Analysis of the individual factors on the normal plot showed that temperature (A), time (C), and pulp density (D) were statistically significant. Also, analysis of factor interactions showed that AC, BD, and AB were significant.

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The gold extraction results for center points for the 2⁴ full factorial design are presented in **Table 4.20**.

Table 4.20. Thiosulfate gold extraction results for centre point replicates for the 2⁴ full factorial design

Runs	Controlled factors				% Au extraction
	A	B	C	D	
1	0	0	0	0	35.8
2	0	0	0	0	39.3
3	0	0	0	0	34.2
4	0	0	0	0	34.2
5	0	0	0	0	36.3
6	0	0	0	0	36.8

The actual factor levels coded as values of (0) in the table above are center point values and are as follows: A (Temperature): 50 °C (0); B (Thiosulfate concentration): 0.6 M (0); C (Time): 5hrs (0); and D (Pulp density): 30 %w/v (0)

The center points were included to account for the presence of curvature. However, curvature appeared insignificant and therefore, was removed to produce a simpler model.

4.9.1 Influence of significant factors on gold extraction

Effect of temperature

The effect of temperature on gold extraction using thiosulfate reagent is presented in **Figure 4.23**.

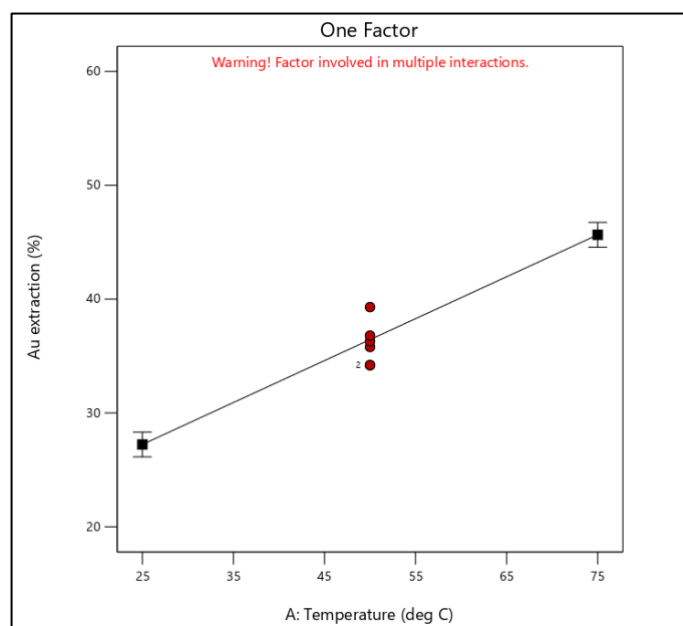


Figure 4.23. The effect of temperature on the gold extraction process in thiosulfate solution

Figure 4.23 shows gold extraction from tailings at 25 °C and 75 °C which are low and high temperature levels respectively. The figure shows that increasing temperature enhanced gold extraction under the studied conditions. This is because higher temperatures affect the kinetics of leaching by accelerating the rate of chemical reaction (Coker, 2001; Habashi, 1999; Navarro et al., 2007; Tavakoli and Dreisinger, 2014). Generally, the effect of temperature on the rate of leaching can be presented by the Arrhenius equation (Missen et al., 1999) as follows:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (4.5)$$

where k is the leaching rate constant, E_a is the activation energy, T is the absolute temperature, R is the universal gas constant and k_0 is the pre-exponential factor.

Temperature can affect the leaching rate strongly or weakly depending on the value of the activation energy. The activation energy of a chemically controlled reaction is typically greater than that for a diffusion or product layer reaction, which is a physical phenomenon. Therefore, the chemical reaction is much more sensitive to temperature than diffusion (Habashi, 1999; Levenspiel, 1999). Thiosulfate solutions are more reactive at higher temperatures and the solubility increases with temperature (Cotton et al., 1999; Lide, 2004). The reaction rate between thiosulfate and copper ions (Cu^{2+}) also increases with increasing temperature (Kumar et al., 2017). Additionally, thiosulfate solutions oxidize more readily at higher temperatures (Cotton et al., 1999). Furthermore, the mixed potential of gold leaching at a steady state decreases with increasing temperature suggesting that the dominant effect of temperature is to enhance the gold oxidation half-cell reaction (Breuer and Jeffrey, 2000).

Effect of pulp density

The effect of pulp density on gold extraction using thiosulfate reagent is presented in **Figure 4.24**.

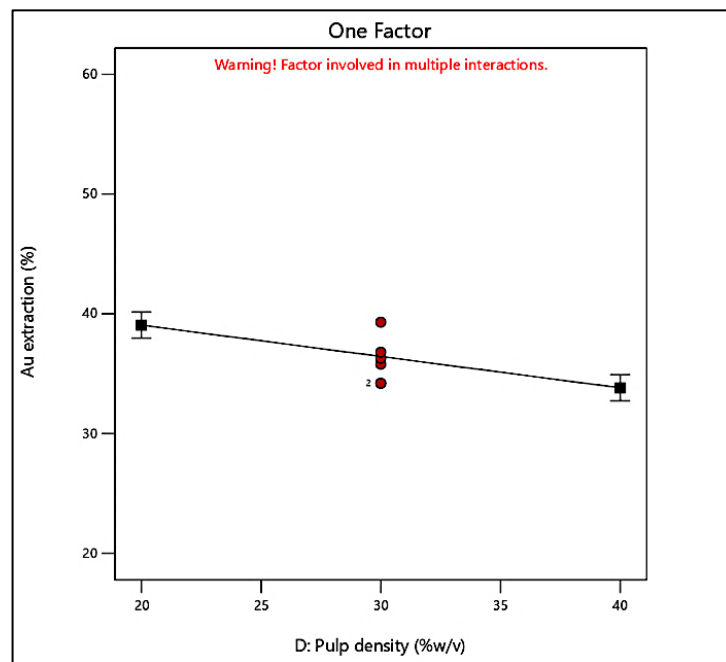


Figure 4.24. Effect of pulp density on the gold extraction process in thiosulfate solution

Figure 4.24 illustrates gold extraction from tailings at 20 % (w/v) and 40 % (w/v) which are low and high pulp density levels respectively. The figure shows that gold extraction decreases with an increase in pulp density, meaning that lower pulp density is beneficial for the extraction of gold due to the availability of a larger quantity of thiosulfate per unit weight of tailings particles. Gold tends to be more greatly leached at lower pulp density under the same concentration of $S_2O_3^{2-}$ due to the high contact probability between $S_2O_3^{2-}$ and gold tailings particles (Cao et al., 2018). This means that, at lower pulp densities, the diffusion resistance of $S_2O_3^{2-}$ is reduced. Additionally, the low gold extractions obtained at high pulp densities can be attributed to the need for greater thiosulfate amounts as pulp density increases (Navarro et al., 2002; Tripathi et al., 2012). Generally, using a high volume of lixiviant increases the leaching rate (i.e., shorter leaching time) (Gharabaghi et al., 2013; Kocan and Hicsonmez, 2019).

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Effect of leaching time

The effect of time on gold extraction is shown in **Figure 4.25**. The figure shows gold extraction from tailings at 3hrs and 7hrs which are low and high levels of leaching time respectively. The figure shows that gold extraction increases with increasing leaching time. However, the increase is not significant. This is because copper (II) sulfate was added as a catalyst/oxidant, which leads to most of the leaching in a thiosulfate system occurring rapidly (Hilson and Monhemius, 2006; Bae et al., 2020). Thus, an increase in leaching time has an insignificant increase in gold extraction because most of the leaching occurred in the early stages.

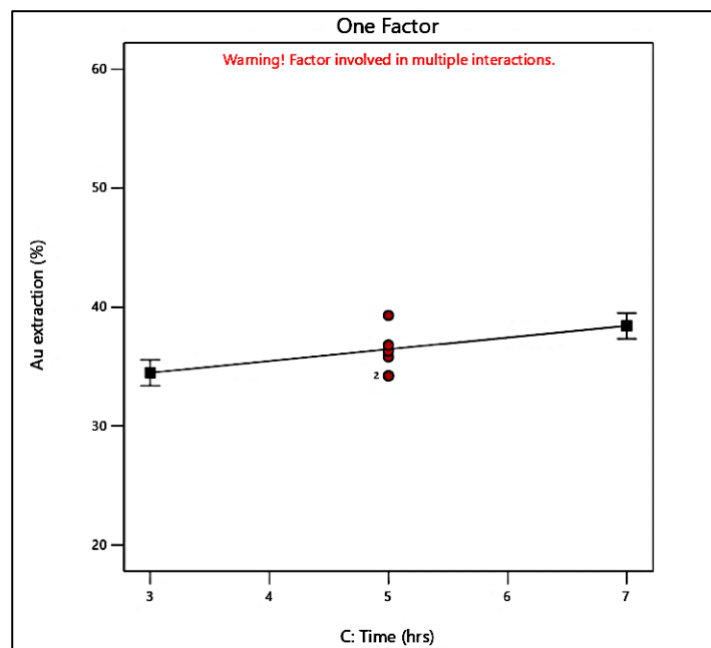


Figure 4.25. Effect of leaching time on the gold extraction in thiosulfate solution

Factor interactions.

Factor interactions AB, BD, and AC were found to be significant among the various factor interactions as shown in **Figure 4.21**. The effect of the significant factor interactions on gold extraction is illustrated in **Figures 4.26, 4.27, and 4.28**.

Extraction of gold from tailings using environmentally friendly reagents

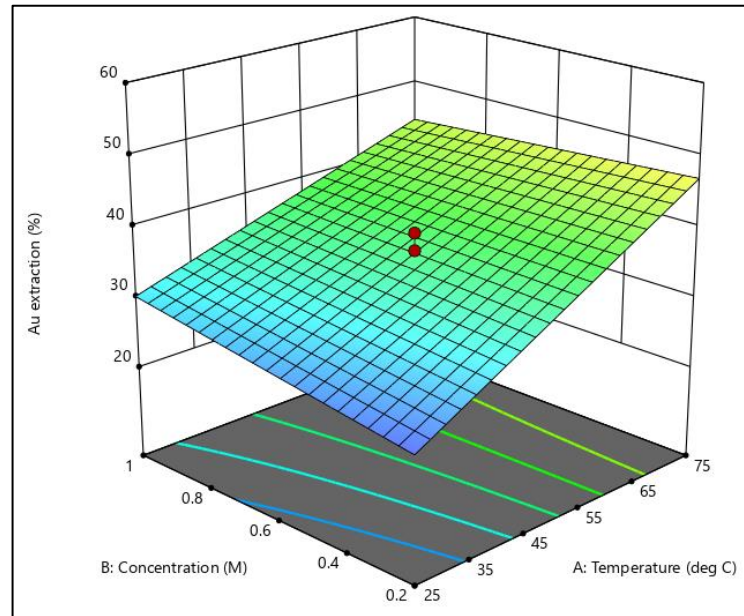


Figure 4.26. The effect of temperature and concentration (AB) interaction on the gold extraction in thiosulfate solution

Figure 4.26 shows that gold extraction is high when the leaching temperature is high, and the thiosulfate reagent concentration is low compared to when they are both high. It also shows that gold extraction is high when concentration is high, and temperature is low compared to when both temperature and concentration are low. Therefore, this shows that high gold extraction can be obtained when thiosulfate concentration is kept at a high level and temperature at a low level or vice versa. Studies have shown that at lower thiosulfate concentrations, the kinetics of gold extraction are slow, and high gold extractions are not reached (Abbruzzese et al., 1995).

The interaction of concentration and pulp density as illustrated in **Figure 4.21** shows a negative effect on gold extraction. This is better expressed in **Figure 4.27** which shows that gold extraction is low when both concentration and pulp density are at their highest levels compared to when they are at their lowest. It can also be seen that gold extraction is high at high thiosulfate concentration and low pulp density compared to when they are both high. The figure shows that to have high gold extraction during thiosulfate leaching of tailings, thiosulfate concentration must be kept at a high level while keeping pulp density at a low level. According to Zipperian et al., 1988, it is important that leaching is carried out with a proper thiosulfate concentration so that the dissolution of gold occurs rapidly, and maximum extraction is quickly achieved. Additionally, as already discussed in this section, lower pulp density enhances gold extraction (Tripathi et al., 2012).

Extraction of gold from tailings using environmentally friendly reagents

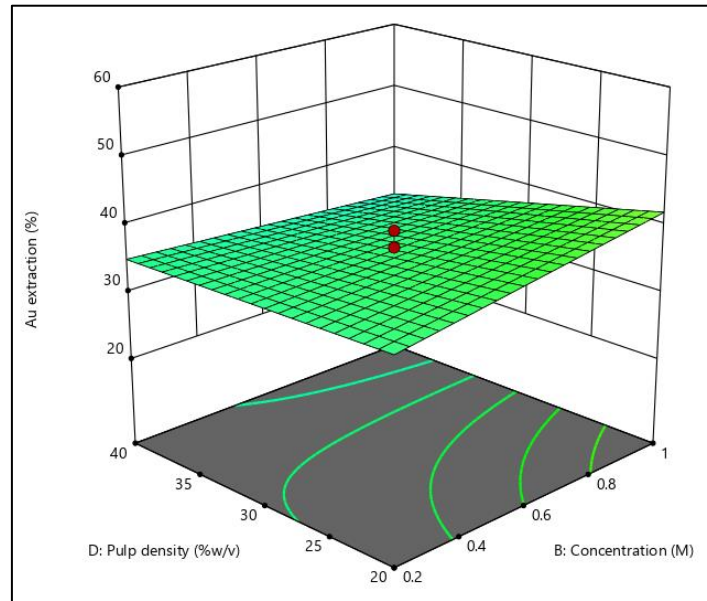


Figure 4.27. The effect of concentration and pulp density (BD) interaction on the gold extraction using thiosulfate

The interaction of temperature and time as illustrated in **Figure 4.21** shows a positive effect on gold extraction from tailings. **Figure 4.28** shows that increasing temperature and leaching time gave a high extraction of gold. Therefore, this indicates that an increase in both leaching time and temperature is favorable for the leaching of gold tailings using thiosulfate. As mentioned above increasing temperature improves the leaching kinetics by accelerating the rate of chemical reaction. Moreover, longer leaching time allows more opportunity for the thiosulfate reagent to interact with the gold-bearing material. Therefore, increased leaching time and temperature result in improved gold extraction.

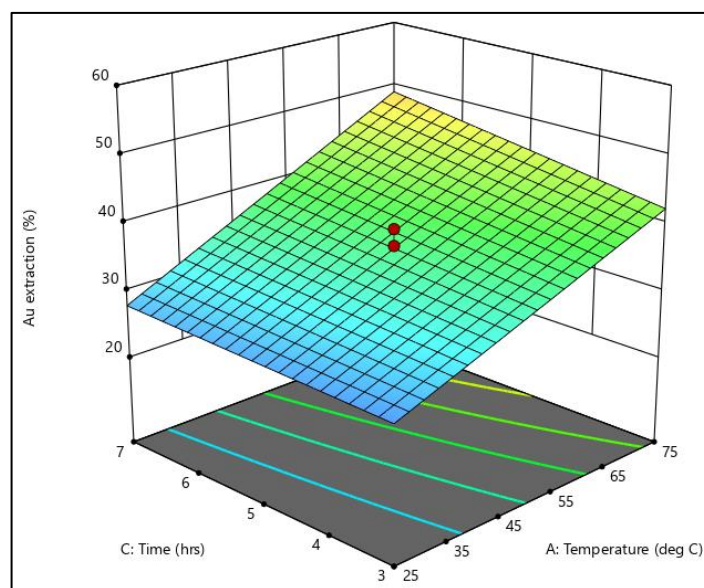
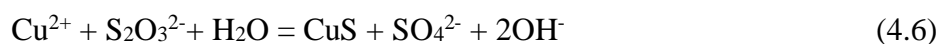


Figure 4.28. The effect of temperature and time (AC) interaction on the gold extraction process using thiosulfate

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It was observed in this study that increasing the leaching temperature to more than 60 °C leads to a decrease in gold extraction (**Figure 4.29**). This is because thiosulfate oxidation is excessive at temperatures above 60 °C (Ji et al., 2003). Additionally, gold extraction decreases at higher temperatures above 60 °C because of passivation due to cupric sulfide formed by the thermal reaction between Cu(II) ions and thiosulfate (Abbruzzese et al., 1995):



Furthermore, higher temperatures above 60 °C facilitate the loss of thiosulfate by decomposition to sulfur compounds, thus only a small fraction of the added thiosulfate remains available for gold complexation (Sitando et al., 2018; Bagdasaryan et al., 1983):

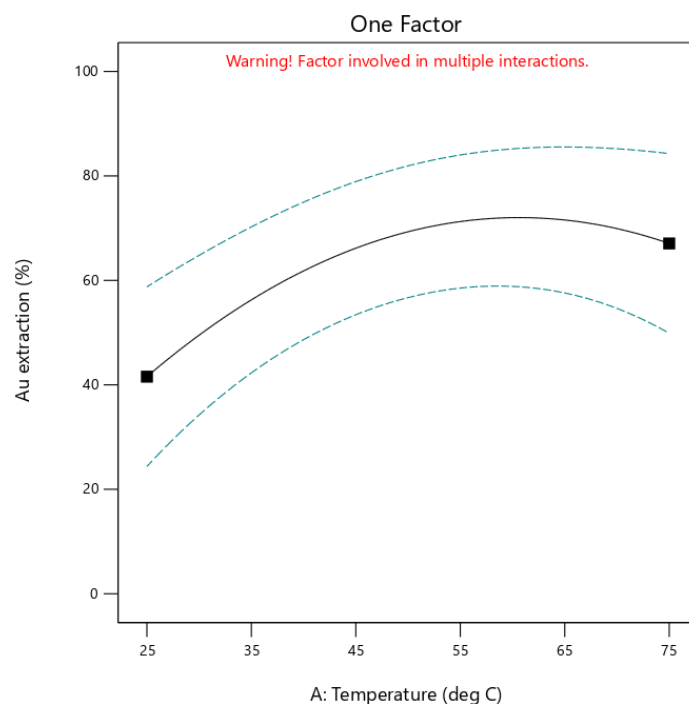
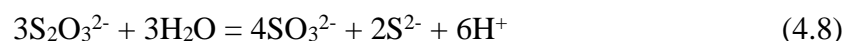
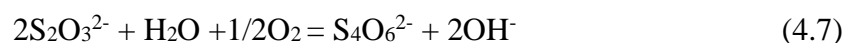


Figure 4.29. Diagram showing a peak in gold extraction as temperature increases above 60 °C

4.10 Optimization of significant factors

Temperature (A), leaching time (C), and pulp density (D) were identified as significant individual factors. The interaction of temperature and concentration (AB), concentration and pulp density (BD), and temperature and time (AC) were also found to be significant. However, temperature, pulp density, temperature-concentration interaction, and concentration-pulp density interaction were more significant than leaching time (**Figure 4.21**). Therefore, temperature, pulp density, and concentration were chosen for optimization experiments, while leaching time was fixed at the highest level due to its positive effect on the response (**Figure 4.21**). The optimization experiments were carried out to determine the optimal conditions for the thiosulfate leaching of gold tailings.

4.10.1 Derivation of the model

The experimental results for the gold extraction are presented in **Table 4.21**. The coefficients of the regression model were estimated by fitting the experimental (obtained) values using Design Expert[®] 13 software.

Table 4.21. Obtained values for thiosulfate gold extraction

Standard Run	Factor levels						% Au extraction (Obtained)
	Coded			Actual			
	A (Temp)	B (Pulp density)	C (Conc)	A Temp (°C)	B Pulp density (% w/v)	C Conc (M)	
1	-1	-1	-1	25	20	0.2	21.9
2	+1	-1	-1	75	20	0.2	40.8
3	-1	+1	-1	25	40	0.2	36.0
4	+1	+1	-1	75	40	0.2	67.3
5	-1	-1	+1	25	20	1.0	28.7
6	+1	-1	+1	75	20	1.0	75.6
7	-1	+1	+1	25	40	1.0	45.7
8	+1	+1	+1	75	40	1.0	61.9
9	-1.682	0	0	7.95	30	0.6	8.0
10	+1.682	0	0	92.0	30	0.6	31.1
11	0	-1.682	0	50	13.2	0.6	44.1
12	0	+1.682	0	50	46.8	0.6	70.2
13	0	0	-1.682	50	30	0.073	1.20
14	0	0	+1.682	50	30	1.3	61.0
15	0	0	0	50	30	0.6	67
16	0	0	0	50	30	0.6	74.1
17	0	0	0	50	30	0.6	75.3
18	0	0	0	50	30	0.6	71.7
19	0	0	0	50	30	0.6	59.8
20	0	0	0	50	30	0.6	71.7

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The fit model was obtained as:

$$\text{Au extraction (coded)} = 69.5 + 11.1*A + 6.4*B + 10.7*C - 2.2*AB + 1.6*AC - 4.6*BC - 15*A^2 - 1.7*B^2 - 11*C^2 \quad (4.9)$$

$$\text{Au extraction (actual)} = -118 + 3*A + 2.8*B + 136*C - 0.009*AB + 0.16*AC - 1.2*BC - 0.02*A^2 - 0.017*B^2 - 68.2*C^2 \quad (4.10)$$

Where, A is leaching temperature, B is pulp density, and C is thiosulfate concentration.

The fit summary in **Table 4.22** suggests the fit model.

Table 4.22. Fit summary

Source	Sequential p-value	Lack of Fit p-value	Adjusted R ²	Predicted R ²	
Linear	0.0524	0.0028	0.2565	0.0249	Suggested
2FI	0.9174	0.0016	0.1187	-0.2887	
Quadratic	0.0032	0.0153	0.6958	-0.1509	Suggested
Cubic	0.2383	0.0087	0.7730	-11.3013	

4.10.2 Checking the adequacy of the developed model.

The adequacy of the fitted model was conducted using ANOVA as illustrated in **Table 4.23**.

Table 4.23. ANOVA for the fitted (quadratic) model

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	8603.93	9	955.99	5.83	0.0055	Significant
A-Temperature	1695.08	1	1695.08	10.33	0.0093	
B-Pulp density	564.40	1	564.40	3.44	0.0933	
C-Concentration	1570.92	1	1570.92	9.58	0.0114	
AB	41.86	1	41.86	0.2552	0.6244	
AC	20.80	1	20.80	0.1268	0.7292	
BC	173.91	1	173.91	1.06	0.3274	
A ²	3239.31	1	3239.31	19.75	0.0012	
B ²	41.60	1	41.40	0.2536	0.6255	
C ²	1715.03	1	1715.03	10.45	0.0090	
Residual	1640.40	10	164.04			
Lack of Fit	1476.71	5	295.34	9.02	0.0153	Significant
Pure Error	163.69	5	32.74			
Cor Total	10244.33	19				

The Model F-value of 5.83 implies that the model is significant. There is only a 0.55% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model

Extraction of gold from tailings using environmentally friendly reagents

terms are significant. In this case, A, C, A², C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The Lack of Fit of F-value of 9.02 implies that the Lack of Fit is significant. There is only a 1.53% chance that a Lack of Fit of F-value this large could occur due to noise. However, a significant lack of fit is bad because it is required for the model be fit.

The fit statistics are presented in **Table 4.24**. A negative Predicted R² implies that the overall mean may be a better predictor of the response than the fitted quadratic model. Adeq Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. A ratio of 7.424 shown in **Table 4.24** indicates an adequate signal. Therefore, the fitted quadratic model can be used to navigate the design space.

Table 4.24. Fit statistics

Std. Dev.	12.81		R ²	0.8399
Mean	50.66		Adjusted R ²	0.6958
C.V. %	25.28		Predicted R ²	-0.1509
			Adeq Precision	7.4244

4.10.3 Thiosulfate gold leaching optimum conditions

After the model was checked and confirmed for adequacy of fit in the region defined by the coordinates of the design, the model was used to locate the points of maximum gold extraction. The optimum conditions for the extraction of gold from tailings using thiosulfate were found to be 60 °C leaching temperature, 20 %w/v pulp density, 1.0 M thiosulfate concentration, and 7 hours leaching time.

4.10.4 Confirmatory experiments

The optimal gold extraction prediction is shown in **Table 4.25**. Confirmatory tests were conducted under the identified optimum conditions to confirm the predicted gold extraction.

Table 4.25. Gold extraction at optimum thiosulfate leaching conditions

Parameters	Temp (°C)	Conc (M)	Pulp density (%w/v)	Au extraction (%)
Model	60	1.0	20	76.1
Confirmatory tests	60	1.0	20	47

Table 4.25 shows that actual gold extraction obtained at optimum leaching conditions was low and not comparable to predicted gold extraction. This suggests a lack of fitting of experimental

data and the fitness of the model. The low actual gold extraction can also be attributed to the low efficiency of thiosulfate in dissolving metal iron oxide (Feng and van Deventer, 2007b) which encloses the gold. The SEM images depicted in **Figure 4.30** show the formation of silica flakes after leaching indicating that silica was dissolved in thiosulfate solution, reducing the amount of thiosulfate available for gold dissolution.

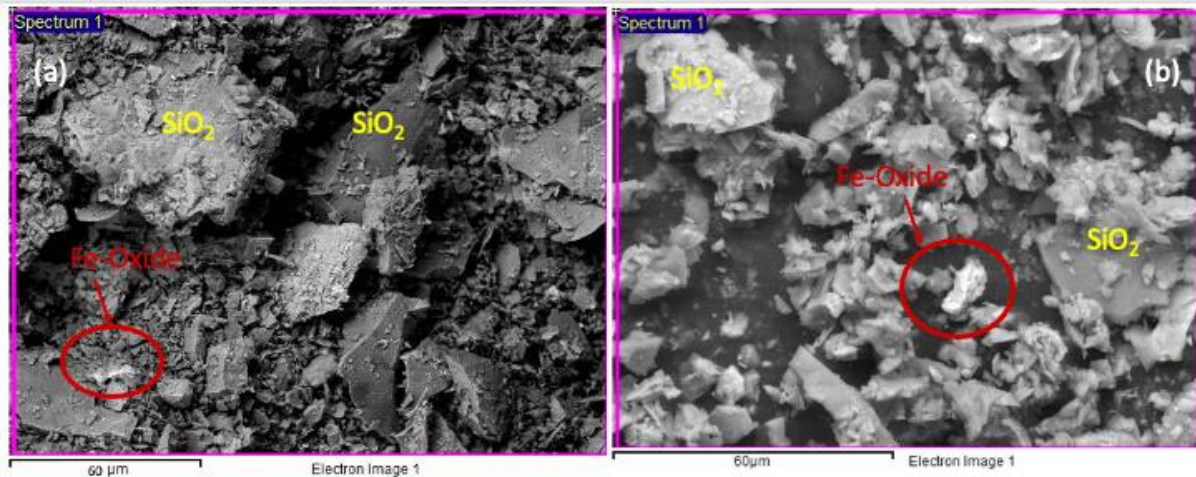
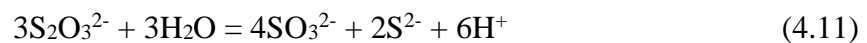


Figure 4.30. SEM-images of the gold tailings before (a) and after (b) thiosulfate leaching

Additionally, **Figure 4.30** shows that FeO was exposed due to the removal of the dominant silica by dissolution. However, the surface of the FeO after leaching still appears to be smooth indicating inefficient dissolution. Furthermore, the low gold extraction can also be attributed to the slurry pH decrease below pH 8 which was observed as leaching progressed. This can be attributed to the presence of hydrogen ions (H^+) in the system formed as thiosulfate decomposes according to the following reaction (Sitando et al., 2018; Bagdasaryan et al., 1983):



Studies have shown that pH control is critical as thiosulfate becomes unstable in acidic solutions (Zhang and Jeffrey, 2008), resulting in poor leaching efficiency.

4.11 Effect of particle size on gold leaching of tailings using thiosulfate

The effect of particle size on gold extraction from tailings during thiosulfate leaching was investigated. Leaching experiments were carried out using the bulk and smaller-size gold tailings under optimum conditions discussed in sub-section 4.10.3. The results are illustrated in **Figure 4.31**.

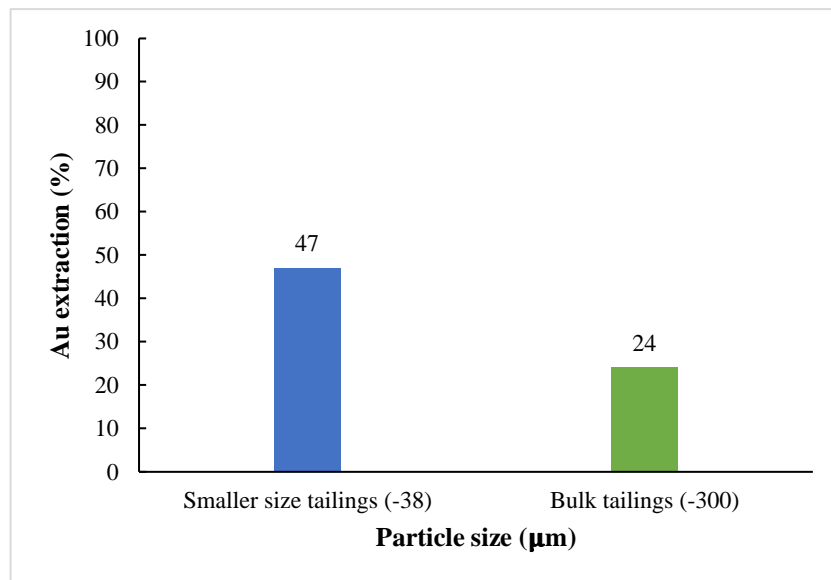


Figure 4.31. Effect of particle size on the gold extraction process in thiosulfate

Figure 4.31 shows that reducing the particle size of the tailings had a significant effect on gold extraction, resulting in a 23% increase in gold extraction. This is attributed to an increase in surface area available for interaction with thiosulfate solution with a reduction in particle size, thus resulting in faster leaching rates.

4.12 Co-dissolution of other metals with Au in thiosulfate solution

The co-dissolution of Ag, Cu, Fe, and Ni with Au in thiosulfate solution under optimum gold thiosulfate leaching conditions was investigated. Results are presented in **Figure 4.32**.

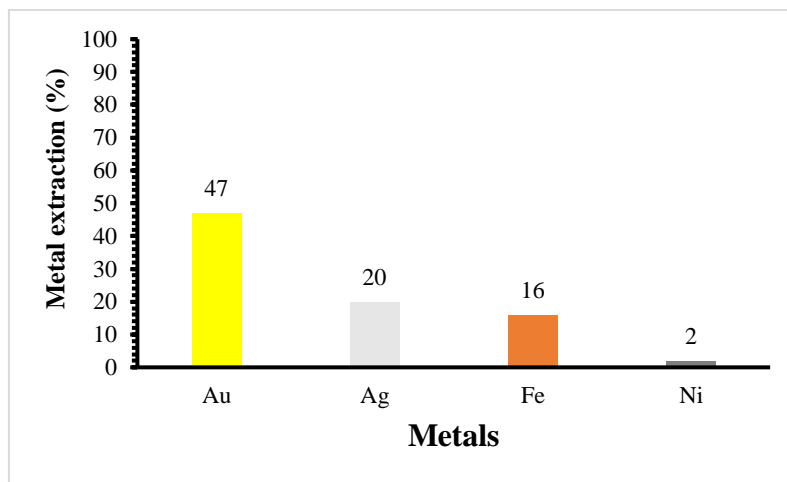


Figure 4.32. Competitive dissolution between Au and other metals in the tailings during thiosulfate leaching

Figure 4.32 shows that most of the gold was dissolved in comparison to Ag, Fe, and Ni, indicating that thiosulfate has more affinity for gold dissolution, followed by silver. This trend is also reported in literature (Zipperian et al., 1988; Chen et al., 2022). The low extraction of Fe and Ni suggests that the application of thiosulfate is more suitable for gold and silver processing. The extraction of Cu was found to be more than 100% because of more Cu being in solution compared to the amount of Cu in the tailings, hence it was not shown in **Figure 4.32**. The only plausible explanation for this is that the Cu found in solution was a combination of dissolved Cu from the tailings and Cu from copper sulfate which was added as an oxidant. This increased the total amount of Cu ions in the solution, giving more than 100% in Cu extraction.

4.13 Cyanidation experiment

Detailed cyanide leaching test work and analysis were not done in this study and tests were only conducted for comparison purposes. The experimental procedure was conducted as reported in Chapter 3. Leaching experiments were conducted by adding 0.2 kg/t of cyanide into a glass reactor containing 49 %w/v pulp density of gold tailings slurry at ambient temperature at 450 rpm agitation rate and pH of 10.5 - 11.5. This experimental procedure was an imitation of large-scale operations from the industry (i.e., DRDGOLD Limited). Results obtained

revealed gold extraction of 46.9% which is comparable to gold extraction of around 51% achieved at DRDGold Limited. Literature has shown that low gold recovery is achieved in the current reprocessing operations of the Witwatersrand tailings due to their inherent complexity (Janse van Rensburg, 2016).

4.14 Summary and Overall Discussion

The work presented above focused on investigating the feasibility of leaching gold from tailings using environmentally friendly reagents, namely IL BmimHSO₄, DES ethaline, and thiosulfate compared to the traditional cyanide reagent. Significant factors influencing the leaching of gold in each of the reagents were investigated and optimized to achieve maximum gold extraction. The effect of particle size and the co-dissolution of Ag, Cu, Fe, and Ni during gold leaching was also investigated for each of the reagents.

The significant factors influencing the leaching of gold from tailings using IL were found to be IL concentration and the interaction of temperature, IL concentration, and pulp density. IL concentration was identified as a significant factor due to the significant increase in gold extraction with an increase in IL concentration. The increase in gold extraction with the increase in IL concentration is related to the increasing acidity of the IL (Bmim[HSO₄]) solution which enhances the leaching efficiency. The factors of significant influence during the leaching of gold from tailings using DES were found to be leaching time and pulp density. The increase in both time and pulp density had a positive influence on gold extraction from tailings. This is because the increase in leaching time provided more opportunity for the DES to interact with the gold-bearing material, thus improving the dissolution rate. The increase in gold extraction with an increase in pulp density suggests that the pulp density threshold, beyond which mass transfer would become challenging and reduce dissolution efficiency, was not reached. The factors significantly influencing the leaching of gold from tailings using thiosulfate were identified as temperature, time, pulp density, the interaction of temperature and concentration, the interaction of concentration and pulp density, and the interaction of leaching temperature and time. The leaching temperature was identified as a significant factor because thiosulfate leaching is a temperature-sensitive process, an increase in temperature makes chemical reaction occur faster than diffusion. Pulp density had a significant influence on gold extraction, a decrease in pulp density increased gold extraction, indicating that lower pulp density is beneficial for the extraction of gold due to the availability of a larger quantity of thiosulfate per unit weight of tailings particles and that more gold is greatly leached at lower

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pulp density due to the high contact probability between $S_2O_3^{2-}$ and gold tailings particles, which further indicates that, at lower pulp densities, the diffusion resistance of $S_2O_3^{2-}$ is reduced.

The identified significant factors were optimized to achieve optimum leaching conditions for each reagent. The optimum conditions for IL leaching were 1.0 M (25%) IL concentration, 75 °C leaching temperature, 10 %w/v pulp density, and 5 hours leaching time. The optimum conditions for DES were found to be 30 %w/v pulp density, 7 hours leaching time, 50 °C leaching temperature, and 1 (ChCl): 2 (EG) DES concentration. On the other hand, thiosulfate optimum leaching conditions were identified as 60 °C leaching temperature, 20 %w/v pulp density, 1.0 M thiosulfate concentration, and 7 hours leaching time. The optimum leaching conditions of IL, DES, and thiosulfate gave maximum gold extractions of 45.3%, 76.4%, and 47%, respectively, after being applied on -38 μm particle size tailings. The same optimum conditions of IL, DES, and thiosulfate gave maximum gold extractions of 21.9%, 71.9%, and 24%, respectively, after being applied on the leaching of 80% passing 75 μm particle size tailings (**Figure 4.33**).

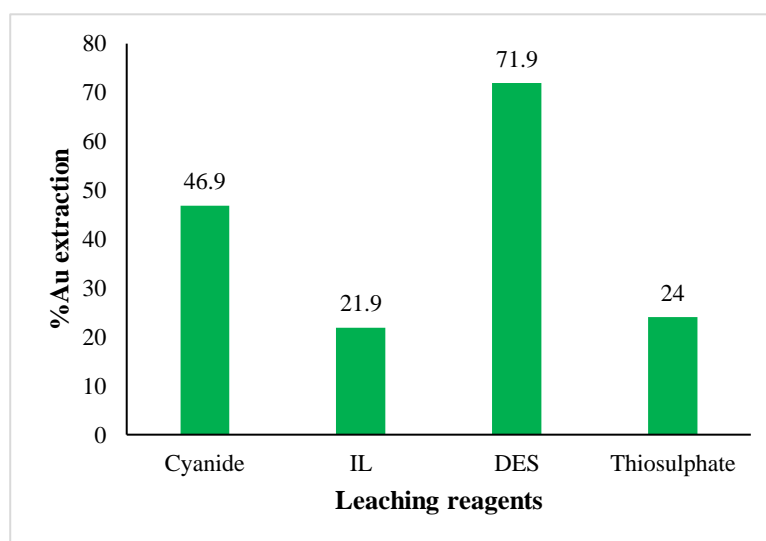


Figure 4.33. Gold leaching efficiency of the investigated reagents from tailings in comparison to cyanide ($P_{80}=75\mu\text{m}$)

The dissolution of metal iron oxide (FeO) to liberate the enclosed gold using ionic liquids is inefficient, hence the low gold extraction achieved via IL 1-butyl-3-methyl-imidazolium hydrogen sulfate leaching. Furthermore, it is more difficult for ionic liquids to dissolve metals from their solid oxide form. The dissolution efficiency of metal iron oxides (i.e., FeO, Fe_2O_3 , and Fe_3O_4) using ILs is poor even at longer residence time. Hence, the gold leaching efficiency

from the FeO compound was low. The low gold extraction achieved via thiosulfate leaching is also attributed to the inefficiency of thiosulfate in dissolving metal iron oxide. Moreover, the SEM results revealed that most of the thiosulfate lixiviant was used to dissolve silica, which is dominant in the tailings, thus reducing the amount of thiosulfate available for gold leaching. The inefficiency of IL and thiosulfate in gold leaching observed in this work shows that the application of these reagents is not feasible in the processing of this kind of tailings in which gold is associated with metal iron oxide compound. Additionally, the gold leaching efficiency of IL (21.9%) and thiosulfate (24%) was lower than that of the traditional cyanidation process (46.9%). However, DES ethaline, on the other hand, achieved higher gold extraction (71.9%) compared to that achieved by the cyanidation process (**Figure 4.33**). This can be attributed to the selectivity of DESs towards gold, leaving gangue minerals undissolved. For example, the dominant quartz mineral in the tailings remains inert in a DES solution (Abbott et al., 2004; Winardhi et al., 2022). This suggests that less DES is consumed by gangue minerals during gold dissolution, resulting in more DES being available for gold dissolution. This indicates that this DES can be applied in the processing of this kind of gold tailings as a cyanide alternative. Furthermore, DESs are less toxic compared to cyanide, cheap, and easy to prepare. The effect of particle size was significant during the processing of gold tailings in IL and thiosulfate solutions and insignificant in DES solution. The co-dissolution results indicated that Au was dissolved with other metals with more Ni and Cu dissolved than Au during IL leaching. DES showed higher dissolution of Au in comparison to all the other metals investigated. This suggests that DES is more suitable for application in the processing of gold compared to silver, copper, iron, or nickel. Thiosulfate showed selective dissolution of Au and Ag with Ni and Fe extracted to low levels.

4.15 Gold adsorption

The recovery of gold from leach solutions of IL BmimHSO₄, DES ethaline, and thiosulfate was investigated by adsorption onto AC. While there is no available evidence in literature of gold recovery from leach solutions of deep eutectic solvents and ionic liquids, results obtained in this work show that it is possible to recover gold from these solutions by activated carbon. The results of gold adsorption onto AC from BmimHSO₄ solution are presented in **Figure 4.34**.

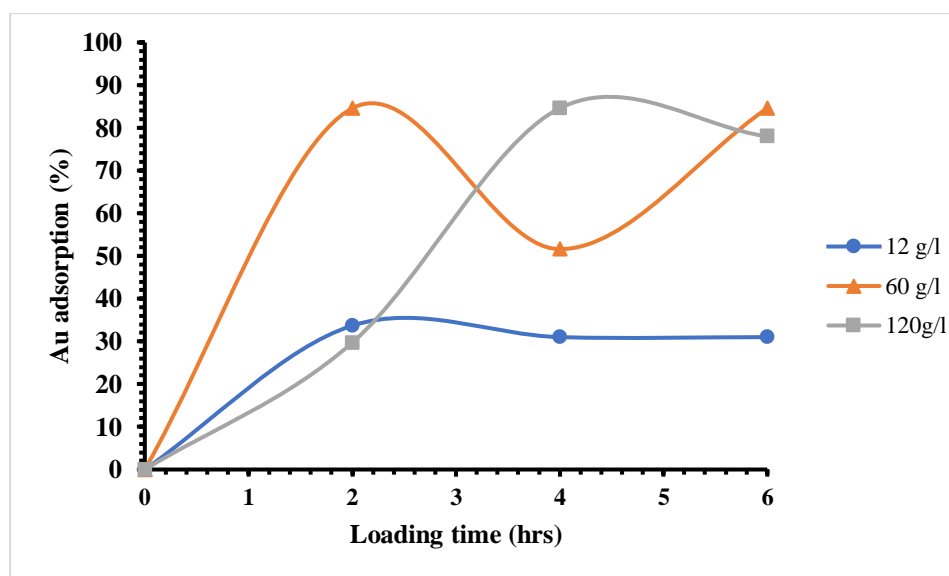


Figure 4.34. Gold recovery by activated carbon from IL leach solution

The results obtained as illustrated in **Figure 4.34** show that gold recovery from BmimHSO₄ solution through adsorption onto AC is achievable and gold adsorption onto AC can be increased with an increase in AC addition. **Figure 4.34** shows that 12 g/l and 60 g/l AC can achieve maximum Au adsorption of 33.7% and 84.6% within 2 hours, respectively. It takes 2 hours for 12 g/l and 60 g/l AC to reach maximum loading capacity because a further increase in adsorption residence time results in a decrease in Au adsorption (**Figure 4.34**), indicating that the two AC concentrations can no longer load any more Au ions onto the surface and instead desorption occurs. Thus, decreasing the overall Au adsorption. This indicates that the maximum loading capacity was reached and the extended time of the experiment led to the desorption of the gold. However, **Figure 4.34** shows that for 60 g/l AC, Au was re-adsorbed giving the same maximum Au adsorption of 84.6%. This indicates that the gold elution that occurred freed the surface of the AC for adsorption, hence the eluted gold was re-adsorbed after 6 h. In contrast, it takes 4 hours for 120 g/l AC to achieve maximum adsorption (84.6%), after which, Au adsorption begins decreasing. A 120 g/l AC takes longer to reach its maximum

loading capacity because there is more surface available for adsorption. However, 60 g/l AC achieves the same amount of Au adsorption as 120 g/l in a short period. This indicates that 60 g/l AC is more feasible for Au recovery from IL BmimHSO₄ solution because increasing AC concentration above 60 g/l results in the same amount of Au adsorption.

The results of gold adsorption onto AC from DES ethaline solution are illustrated in **Figure 4.35**. The figure shows that it is probable to recover gold from a DES solution by adsorption onto AC. It also shows that gold adsorption onto AC increases with an increase in the amount of AC added.

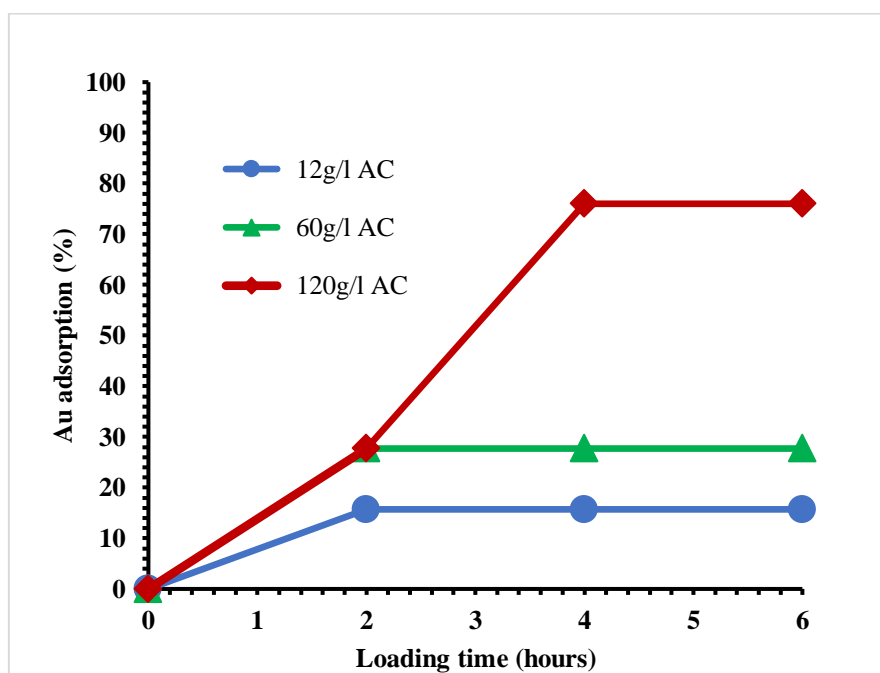


Figure 4.35. Gold recovery by activated carbon from DES leach solution

Figure 4.35 shows that 12 g/l and 60 g/l AC can achieve maximum Au adsorption of 15.7% and 27.7%, respectively. Furthermore, maximum gold loading of 12 g/l and 60 g/l can be achieved in 2 hours because any further increase in loading time does not result in any increase in Au adsorption (**Figure 4.35**), indicating that maximum loading capacity has been reached. However, 120 g/l AC achieves its maximum Au adsorption (75%) in 4 hours with Au adsorption remaining constant beyond 4 hours. The addition of 120 g/l AC in a DES ethaline solution results in higher Au adsorption compared to 12 g/l and 60 g/l AC due to more surface being available for adsorption.

The results of gold adsorption onto AC from thiosulfate solution as depicted in **Figure 4.36**, also display that it is possible to recover gold from thiosulfate solution by adsorption onto AC.

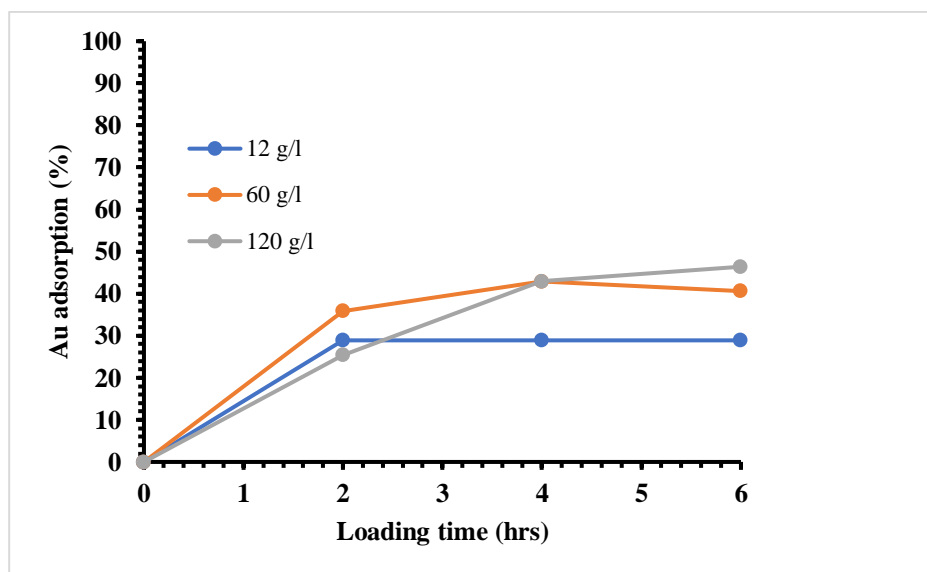


Figure 4.36. Gold recovery by activated from thiosulfate leach solution

Figure 4.36 shows that 12 g/l AC reaches maximum Au adsorption (28.9%) in 2 hours while 60 g/l AC reaches maximum Au adsorption of 42.9% in 4 hours. Gold adsorption remains constant in 12 g/l AC even with an increase in loading time, indicating that the AC has reached its maximum loading capacity and thus increasing the loading time has no effect. On the other hand, 60 g/l AC achieved 35.9% Au adsorption in 2 hours. This increased after 4 hours of loading time to a maximum Au adsorption of 42.9%, as shown by the peak on the graph (**Figure 4.36**). Allowing a loading time of more than 4 hours results in a decrease in Au adsorption, indicating that the adsorbed gold is starting to be dissolved back into solution, thus decreasing the overall Au absorbed.

Additionally, **Figure 4.36** shows that 120 g/l AC reached the highest Au absorption of 46.4% in 6 hours. However, there is no peak (**Figure 4.36**). This indicates that 46.4% is not the maximum Au adsorption for 120 g/l AC and that more loading time is necessary for 120 g/l AC to reach its maximum gold loading efficiency from a thiosulfate solution.

Overall, **Figure 4.36** shows low gold adsorption onto AC from a thiosulfate leach solution, achieving only the highest recovery of 46.4% at the highest amount of AC (120 g/l) added to the solution. This is because aurothiosulfate ($[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$) is very difficult to be adsorbed by AC (Gallagher et al., 1990). The low affinity of AC for $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ may be attributed to the high negative charge and large size of this ion and weak interaction between carbon active sites and ionic ligand of $\text{S}_2\text{O}_3^{2-}$ (Alymore and Muir, 2001).

4.16 Summary and Overall Discussion

The recovery of gold on AC from solutions of the three investigated reagents was found to be possible and increased with an increase in loading time and amount of AC added. It has been shown that the addition of 60 g/l and 120 g/l AC in IL leach solution can both achieve maximum gold recovery of 84.6% in 2 and 4 hours respectively. However, the addition of 60 g/l AC would be the best option for gold recovery from an IL leach solution because it achieves equal maximum gold recovery as 120 g/l AC and in a shorter period. Furthermore, adding 60 g/l AC will reduce the additional costs of adding 120 g/l AC.

A maximum gold recovery of 75% was reached from DES leach solution in 4 hours using 120 g/l of added AC. Added AC of 12 g/l and 60 g/l reached low gold recoveries of 15.7% and 27.7% respectively, indicating low loading capacity.

Added AC of 12 g/l achieved a maximum gold recovery of 28.9% in 2 hours while 60 g/l added AC achieved a maximum gold recovery of 42.9% from thiosulfate leach solution. The highest gold recovery of 46.4% from a thiosulfate leach solution was achieved in 6 hours using 120 g/l of added AC. However, this was not the maximum gold recovery due to the absence of a peak in the graph (**Figure 4.36**), indicating that a longer loading time is required for 120 g/l AC to reach its maximum loading capacity. Less than 47% gold recovery was achieved from a thiosulfate leach solution even at a high amount of added activated carbon. The low gold recovery by activated carbon from thiosulfate leach solution is attributed to the difficulty of aurothiosulfate ($[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$) adsorption onto AC due to the high negative charge and large size of this ion and weak interaction between carbon active sites and ionic ligand of $\text{S}_2\text{O}_3^{2-}$.

Gold recovery by AC from leach solutions of the investigated reagents showed that higher gold recovery (84.6%) was achieved from the ionic liquid 1-butyl-3-methyl-imidazolium hydrogen sulfate leach solution with 60 g/l added AC compared to recovery from deep eutectic solvent ethaline (75%) and thiosulfate (46.4%) leach solutions. However, this recovery rate (84.6%) is lower than the 99% gold recovery achieved in the industry (i.e., DRDGold Limited) from cyanide leach solution with 8-12 g/l added AC. This indicates that gold recovery by AC from cyanide leach solutions is more efficient than from leach solutions of the tested reagents. Therefore, the type of gold complexes that are formed with these reagents and their interaction with AC need to be studied and well-understood in order to attempt to improve gold recovery from their solutions. Additionally, alternative adsorbents used for gold recovery can be investigated.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

This research study focused on investigating the use of alternative environmentally friendly reagents IL 1-butyl-3-methyl-imidazolium hydrogen sulfate, DES ethaline, and thiosulfate in the extraction of gold from tailings. A review of literature has shown that gold can be extracted by leaching using these reagents.

To investigate the use of these reagents in gold extraction, the objectives were defined as to:

- Investigate the extent of gold extraction from tailings using solvents ionic liquid 1-butyl-3-methylimidazolium hydrogen sulfate ([Bmim]HSO₄), deep eutectic solvent ethaline (ChCl:EG), and sodium thiosulfate.
- Identify and optimize significant factors influencing the gold extraction process during the leaching process.
- Compare the gold yields achieved through the investigated alternative leaching processes to those achieved via the well-established cyanidation process.
- Analyzing the co-dissolution of other metals with gold.
- Study the gold adsorption onto activated carbon from leach solutions of the investigated reagents.

A statistical Design of Experiments (DOE) method was employed as a research tool to develop an experimentation strategy to identify factors that have a significant influence on the gold extraction process. Factors investigated included: leaching temperature, reagent concentration, pulp density, and leaching time. The significance of each factor and associated interactive effects were evaluated using a two-level, four-factor full factorial statistical design (2⁴), and dissolved gold was taken as the measured response.

For IL leaching, IL concentration was found to be statistically significant while leaching temperature, leaching time, and pulp density were found to be statistically insignificant. This means that leaching time, temperature, and pulp density did not significantly influence gold extraction while IL concentration had a significant influence on the gold extraction process. The results also indicated that gold extraction was maximized at higher IL concentrations. This means that to achieve optimal gold extraction, IL concentration needs to be kept at a high factor

level. The interaction of temperature, concentration, and pulp density was found to be statistically significant.

For DES leaching, pulp density and leaching time were statistically significant and had a positive response while leaching time and concentration were found to be statistically insignificant. This means that to achieve optimal gold extraction during DES leaching, pulp density and leaching time need to be kept at high factor levels. The interaction of parameters among the variables was found to be statistically insignificant.

For thiosulfate leaching, temperature, time, and pulp density were found to be statistically significant individual factors. However, pulp density had a negative response. The gold extraction response decreased at temperatures beyond 60 °C. This means that to achieve optimal gold extraction via thiosulfate leaching, temperature must be kept at 60 °C, time and pulp density must be kept at high and low levels respectively. The interaction of temperature and concentration, concentration and pulp density, and temperature and time were found to be statistically significant.

Optimization using a statistically based approach called response surface methodology (RSM) was employed following the screening experiments to determine optimum conditions for the significant factors. The data for fitting the model was collected by using central composite design (CCD) and a fitted predictive model was developed as a mathematical expression of gold extraction from tailings.

From the prediction model, an optimal IL gold extraction efficiency of 40.1% was obtained at optimum conditions of 75 °C temperature, 1.0 M IL concentration, and 10 %w/v pulp density. Confirmatory tests showed an extraction efficiency of 45.3%. The results are comparable to each other hence verifying the fitting of experimental data and the fitness of the model. Whilst ILs have high selectivity towards gold, it is however, difficult for ILs to dissolve the FeO mineral (i.e., FeO) enclosing the gold. Hence, low gold extraction was obtained because the gold is unliberated. This suggests that the reprocessing of gold tailings using ILs requires pretreatment of the tailings to liberate the gold before leaching in order to improve the process efficiency. On the other hand, an optimal DES gold extraction efficiency of 70% was predicted at optimum conditions of 30 %w/v pulp density and 7 h leaching time. Confirmatory tests showed an extraction efficiency of 76.4. For thiosulfate leaching, an optimal gold extraction efficiency of 76.1% was predicted at optimum conditions of 60 °C temperature, 1.0 M

thiosulfate concentration, and 20 % w/v pulp density. Confirmatory tests showed an extraction efficiency of 47% which is not comparable with the model-predicted efficiency, hence showing a lack of fitting of experimental data and the fitness of the model. Thiosulfate has also been reported to have a high affinity for gold, however, the reagent achieved low gold extraction in this work. This is attributed to the pH decreasing to acidic conditions during leaching, as gold dissolution in thiosulfate solution occurs under alkaline conditions. Furthermore, the undesired dissolution of silica in the tailings consumed thiosulfate, leaving less thiosulfate available for gold dissolution, which also contributed to the low gold extraction. This suggests that separating silica from the tailings before thiosulfate leaching, and monitoring the pH of the leach solution could improve the process efficiency.

The effect of particle size was significant in the leaching of gold from tailings using IL and thiosulfate and insignificant during DES leaching. IL showed high co-dissolution of Ni and Cu with Au while DES showed high dissolution of Au over Cu, Fe, and Ni. Thiosulfate showed selective dissolution of gold and silver. The leaching of gold tailings in cyanide resulted in a low gold extraction efficiency of 46.9% which was higher than that of 1-butyl-3-methylimidazolium hydrogen sulfate IL (21.9%) and thiosulfate (24%) but lower than the leaching efficiency of ethaline DES (71.9%). This suggests that ethaline DES can be applied as an alternative to cyanide in the processing of gold tailings in which gold is locked within metal iron oxides. Gold adsorption onto AC from leach solutions of the investigated reagents was found to be efficient with the highest maximum Au adsorption efficiency of 84.6% achieved from IL leach solution onto 60 g/l and 120 g/l AC in 2 and 4 hours respectively. The highest maximum Au adsorption efficiency of 75% was achieved from DES leach solution onto 120 g/l AC in 4 hours. The highest Au adsorption efficiency of 46.4% was achieved from the thiosulfate leach solution in 6 hours onto 120 g/l AC although more loading time was required to achieve maximum loading efficiency. Gold recovery by activated carbon from the leach solutions of the tested reagents was lower than the 99% gold recovery achieved by activated carbon from cyanide solution. The recovery of gold by activated carbon from IL and DES solution is not reported in literature. The low gold recovery by activated carbon from the thiosulfate leach solution is because aurothiosulfate ($[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$) is very difficult to be adsorbed by AC. The low affinity of AC for $[\text{Au}(\text{S}_2\text{O}_3)_2]^{3-}$ is attributed to the high negative charge and large size of this ion and weak interaction between carbon active sites and ionic ligand of $\text{S}_2\text{O}_3^{2-}$. The type of gold complexes formed with these reagents need to be studied in order to understand their interaction with activated carbon adsorbent.

5.2 Recommendations

With the knowledge gained from this work, the following can be recommended for further study:

The mineralogical characterization of the tailings used in this work showed the predominant existence of quartz. However, all the gold in the tailings was found to be enclosed in the iron oxide matrix. Further study should thus focus on pre-concentration of the tailings to remove the silica gangue material before leaching. This will upgrade the head grade of the tailings and reduce reagent consumption. For example, during thiosulfate leaching, most of the reagent was used up in the undesired dissolution of the silica mineral, reducing the amount of the reagent for gold dissolution.

Since the tailings are refractory, a detailed study and investigation should be conducted to unlock the enclosed gold from the tailings and increase the efficiency of the reagents. To release the locked gold from the iron oxide matrix, techniques such as ultrasonic oxidative leaching, microwave-assisted leaching, and/or cavitation should be implemented to induce cracks on the surface of the iron oxide compound encapsulating the gold.

Additionally, further study should extend the range of levels of parameters to obtain more significant optimum conditions for gold leaching. For example, an increase in pulp density resulted in an increase in gold extraction during DES leaching, indicating that the pulp density threshold beyond which mass transfer would become a challenge was not reached. Further study should also investigate the influence of other factors such as agitation speed, oxidizing and complexing agent dosages. Literature has shown that oxygen is one of the factors influencing the leaching efficiency of thiosulfate, thus further study can conduct investigations on the leaching of gold in the presence of oxygen. However, the study should investigate the leaching of thiosulfate at low temperatures (less than 60 °C) due to passivation that occurs at high temperatures. The CuSO_4 oxidant should also be part of the parameters to investigate and optimize because too much increase in copper (oxidant) concentration can negatively affect the dissolution of gold due to the increased consumption of thiosulfate.

This work has shown that more gold can be leached from the refractory tailings by DES leaching compared to cyanide leaching. This can be extended to a comparative study of the economic aspects associated with DES leaching and cyanide leaching. In particular, the study

can look at economic aspects such as reagent consumption, reagent cost, energy consumption, and processing time by doing a cost-benefit analysis. Further economic assessment is required to see if the 4.5% increase in gold extraction from 71.9 to 76.4% from leaching of bulk (P80 = 75 μm) and smaller size (-38 μm) tailings respectively, is economically feasible.

Further work should investigate the gold complexes formed during DES and IL leaching to help understand the gold dissolution mechanism and the interaction of these gold complexes with activated carbon. Further work should also investigate gold recovery from thiosulfate leach solution at longer contact times, for example, literature has shown that high gold adsorption can be achieved at a longer contact time of 6 h (Abbrusses et al., 1995). Further work can also investigate gold adsorption at high thiosulfate concentrations as literature suggests that more gold can be recovered by activated carbon at high thiosulfate concentrations e.g., 2M (Ubal dini et al., 2019).

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APPENDICES

APPENDIX A

Gold extraction calculations

In order to determine the initial gold concentration in the tailings sample, 100 g of gold tailings sample was analyzed by fire assay analysis (FAA).

Basis of calculation:

Au concentration in the sample = $0.92 \frac{g}{t}$ or (mg/l) or (ppm)

Weight of gold tailings sample = 10 g

Volume of solution = 50 ml = 0.05 l

Example: Run 2 (Table 4.21)

Before leaching

*Weight of Au in the sample = $\frac{0.92 \times 10^{-4}}{100} * 10 \text{ g} = 0.0000092 \text{ g}$*

After leaching

Au concentration in solution = 0.075 mg/l = 0.000075 g/l

*Weight of Au in solution = Au concentration * volume of solution*

*∴ Weight of Au in solution = $0.000075 \frac{g}{l} * 0.05 \text{ l} = 0.00000375 \text{ g}$*

Calculation of Au extraction (%)

*Au extraction = $\frac{\text{Weight of Au in solution}}{\text{Weight of Au in sample}} * 100$*

*∴ Au extraction = $\frac{0.00000375 \text{ g}}{0.0000092 \text{ g}} * 100 = 40.8\%$*

APPENDIX B

Gold adsorption calculations

$$R = \frac{C_i - C_f}{C_i} * 100$$

Where R is gold adsorption (%), C_i is the initial gold concentration before adsorption (mg/l), and C_f is the final gold concentration after adsorption (mg/l).

For example: Gold adsorption from ionic liquid leach solution by activated carbon (60 g/l).

$$C_i = 0.0455 \text{ mg/l}$$

$$C_f = 0.007 \text{ mg/l}$$

$$R = \frac{0.0455 - 0.007}{0.0455} * 100$$

$$R = \frac{0.0385}{0.0455} * 100$$

$$R = 0.846 * 100$$

$$R = 84.6\%$$

$$\therefore \text{Au adsorption} = 84.6\%$$