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2020
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Feasibility study on the use of imidazolium-based ionic liquids in the extraction of gold

MSc Engineering Dissertation

Prepared by

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Submitted to

The Faculty of Engineering and the Built Environment, University of the Witwatersrand, Johannesburg,

In fulfilment of the requirements for the degree of Master of Science in Engineering

Supervisor(s): Herman Potgieter, Geoffrey Simate, Lizelle van Dyk

January, 2020

Declaration

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

Acknowledgment

I am thankful to the Almighty God for giving me patience and courage to successfully complete the research work. I express my sincere gratitude towards my respected supervisor, Prof. Herman Potgieter, who has been a constant source of motivation and inspiration right from the beginning till the successful completion of my research work.

My special thanks to Prof. Geoffrey S. Simate and Prof. Lizelle D. van Dyk, my co-supervisors for their help and guidance with their experience and knowledge.

In addition, I would like to express my deep appreciation to Prof. Marek Dworzanowski the manager of the project, who generously financially supported me in this research project. Without this financial support, I could not have studied at Wits University.

I would also thank the laboratory experts Mr. Motlatsi Phali and Mrs. Janet Smith for helping, guiding and supporting me with their valuable time and providing many helpful suggestions and technical support when I lagged behind in certain aspects. I am also thankful to all the staff members of the School of Chemical and Metallurgical Engineering who have directly or indirectly helped me during my research work.

I am indebted to my family for their love and support during my research work.

Abstract

The extraction of gold from low grade sulfidic gold ores has been the focus of a great deal of research in recent years. In this study, the feasibility of the oxidative leaching of gold from a refractory sulfidic low-grade gold tailing (pyrite concentrate) with ionic liquids in the presence of thiourea (leaching agent) and ferric ion (oxidant) was investigated. Ionic liquids have many fascinating physicochemical properties, e.g. unmeasurable vapour pressure, low melting point and high thermal stability which allow them remain liquid over a wide temperature range. These features make them promising green solvents for dissolving different types of ores, including extracting gold in a manner that may not pose any threat to the environment.

The influence of operating parameters such as concentration of ionic liquid, pulp density, time and temperature on the extraction of gold was investigated with two imidazolium based ionic liquids, 1-butyl-3-methylimidazolium hydrogen sulphate [$Bmim^+HSO_4^-$] and 1-butyl-3-methylimidazolium trifluoromethansulfonate [$Bmim^+CF_3SO_3^-$]. The influence of these operating parameters were assessed and screened using a half fractional factorial design (2^{5-1}) approach. Results indicated that the concentration of the ionic liquid, pulp density and temperature were significant factors in the extraction of gold from refractory sulfidic low-grade gold tailing ore.

Additional experiments were carried out focusing on the most influential experimental factors. Central composite design (CCD) in conjunction with response surface methodology (RSM) was used to create an optimization design within selected ranges of the statistically significant factors (5%-25% IL [$Bmim^+HSO_4^-$], solid to liquid ratio of 1:10-1:2 and temperature 25-70 °C) in an attempt to find the optimal gold extraction conditions within this range. It was found that the optimum point for the concentration of ionic liquid [$Bmim^+HSO_4^-$] in the aqueous solution was 15% (v/v); pulp density was 15% (w/v) whereas the temperature was 55 °C. An amount of 35.4% gold extraction was achieved under these optimum conditions.

Furthermore, the effect of temperature on the gold extraction from the ore in a range of 20-65 °C in 20% (v/v) [$Bmim^+HSO_4^-$]-water solution, at pH = 1 and shaking speed of 250 rpm was examined for 12 h leaching time intervals. The experimental results generally revealed that the extraction of gold improved by increasing the temperature. The apparent activation energy was calculated based on the Arrhenius theory and it suggests that the kinetic process of ionic liquid gold leaching was limited by diffusion with an activation energy (E_a) of 28.4 kJ/mol. In addition, solid analysis on the ore before and after leaching was performed with SEM, XRD and Raman.

Seminars

Conference Proceeding

1) J. H. Potgieter, S. Teimouri, G. Simate, L. van Dyk, M. Lundstrom and M. Dworzanowski. International Conference on Mechanical, Metallurgy and Materials Science, 28-29 March 2019, Milan, Italy.

2) J. H. Potgieter, S. Teimouri, G. Simate, L. van Dyk, M. Lundstrom and M. Dworzanowski. International Process Metallurgy Symposium, 5-6 November 2019, Espoo, Finland.

Research paper

1) Oxidative leaching of refractory sulphidic gold tailings with an ionic liquid.
   S. Teimouri, J. H. Potgieter, G. S. Simate, L. van Dyk and M. Dworzanowski
   (Submitted to Minerals Engineering).
2) Using response surface methodology (RSM) and experimental design to optimize gold extraction from refractory sulphidic gold tailings with ionic liquids.
   S. Teimouri, G. Mawire, J. H. Potgieter, G. S. Simate, L. van Dyk and M. Dworzanowski
   (Submitted to Journal of the Southern African Institute of Mining and Metallurgy).

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1 Introduction

1.1 Background

In recent years, precious metals have received worldwide attention. In particular, amongst the precious metals, gold has a wide range of high-performance applications in the industry due to its unique physicochemical properties. Gold is also an important metal that significantly contributes to the vibrancy of the modern-day economy and industry. In fact, in view of the immense economic value and unique qualities of gold, it is considered to be one of the most significant noble metals, as well as one of the most important elements in the world. Gold is found in its metallic state in nature and is mined as such (Tong *et al.*, 2013). It is unreactive in air and water and does not interact with either oxygen or sulfur, has high durability in intensive corrosive environments and is highly conductive. It finds application in the production of alloys because of its unique and special characteristic properties that are essential for the long-term resistance and stability of alloys (Nicol *et al.*, 1992).

The demand for gold is increasing with advancements of the industrialized world, but the global reserves of high-grade gold ores in which the metal concentration is relatively high are limited and diminishing. In addition, even though refractory low-grade gold ore reserves exist, traditional techniques such as hydrometallurgical and pyrometallurgical processes are not very effective in recovering gold from it. Refractory gold ore contains micro-disseminated gold particles encapsulated (locked) inside of minerals such as silicates or sulfides. As a consequence, these approaches may require additional chemical reagents and energy to access the locked gold.

Presently, there is a growing interest to extract gold from its sulfide deposits such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$), and arsenopyrite (FeAsS). Pyrite is the most abundant and wide-spread of the earth's iron sulfide minerals. The interest in pyrite destruction and dissolution arises from the fact that it also contains gold and other valuable metals such as copper and zinc locked in its structure (Long & Dixon, 2004).

From a metallurgical perspective, gold ore can be generally classified into free-milling and refractory ores types. In free-milling ores, the gold is readily available to the leaching solution. Approximately 95% of gold in free-milling ores can be extracted by the conventional cyanidation process after 20-30 hours when the ore is ground to a size of 80% passing 75 µm, as is normally applied in the industrial preparation, without requiring excessively high reagent

concentrations. Refractory ores are defined as a type of ore in which the gold is locked into other minerals and has to be made available for leaching by the destruction of the host mineral matrix (Vaughan, 2004). In other words, refractoriness means that there are invisible ultrafine gold particles encapsulated inside the ore matrix. Refractory gold ores typically give low gold recoveries of less than 80% (in some cases much less than 50%) through direct cyanide leaching or give satisfactory gold recoveries only with the use of considerably larger amounts of reagents or more complex treatment processes. Thus, the host mineral matrix should be destroyed through chemical ways such as oxidative methods to liberate the gold and make it accessible in the solution for extraction (La Brooy *et al.,* 1994).

Currently, extraction of the valuable metals from refractory sulfidic low-gold-bearing-ores, such as pyrite and chalcopyrite can be a laborious process involving pyrometallurgy and/or hydrometallurgy. These extraction processes are highly dependent on the chemical and physical properties of the ore, as well as the state of minerals existing inside the ore (Olyaei *et al.,* 2016). For example, pyrometallurgical processes, such as roasting and smelting in a furnace, use high temperatures to convert ore into raw metals and have the undesirable side effect of releasing sulfurous gases which need to be captured and treated (Syed, 2012). Hydrometallurgical methods, on the other hand, consume acids or bases to dissolve these minerals, which is then followed by the extraction and recovery of the desired metal. Hydrometallurgical treatment produces low concentrated aqueous wastes that require additional treatment or else can have extensive impact on the aquatic environment (Abbott *et al.,* 2017). Some of the difficulties involved in processing gold using these traditional methods include low gold extraction, high energy demand, time-consuming and techniques require extensive labour.

Tailings are classified as secondary ores and are materials that have been discharged from plants and they are the left over material after the recovery of the target minerals. DRDGOLD Ltd a specialist in surface retreatment of gold tailings processes. Tailings are considered to be valuable and any further recovery has the potential of financial rewards. Additionally, tailings are an environmental burden and improving recovery is a bonus, hence rekindling the interest in processing tailings. The Ergo plant feed comprise of ore from sand dumps, slime dams and surface tailings left over by mining operations across the Witwatersrand basin. Figure 1.1 displays the location of old dumps processed by DRDGOLD Ltd and the deposition of their process tailings. Sand dumps contain coarse-grained particles which are the consequence of

less efficient stamp-milling process in earlier mining techniques compared to advanced grinding process applying presently. They contain high grades of gold encapsulated in coarse-grained particles. Sand dumps are reclaimed mechanically using front-end loaders, and most of sand dumps have been re-treated using more efficient milling processes. Slime dams are also a result of old treatment methods and contain lower grades of gold. The material from slimes is broken down using monitor guns that spray jets of high pressure water at the target area, and then the slurry is fed to the processing plants (DRDGOLD Limited, 2013).

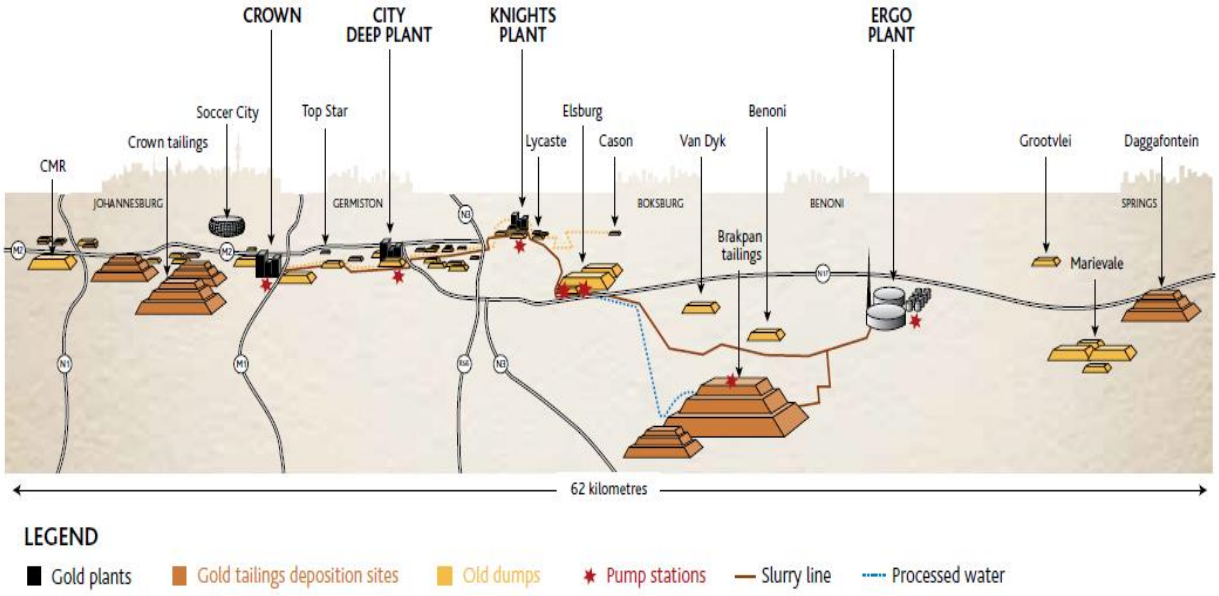


Figure 1.1 DRDGOLD Ltd tailings map (DRDGOLD Limited, 2013)

Currently, gold has been mostly leached from its ores by cyanidation which is considered a standard commercial route for leaching of ores containing gold due to its high efficiency and cost-effectiveness (Olyaei *et al.*, 2016). However, the cyanidation techniques have been recognized as undesirable and environmentally hazardous because of the toxicity of cyanide (Grosse *et al.*, 2003). Therefore, there is a growing interest towards developing alternative techniques for dissolving sulfide gold-containing ores in order to liberate gold during or after sulfide mineral oxidation (Abbott *et al.*, 2015). Some alternative reagent for cyanide with focus on liberation and extraction of gold from ore are thiourea, thiocyanate, thiosulfate leaching during pressure oxidation, high-intensity grinding and halide leaching (Syed, 2012).

Where refractory low-grade gold tailing exist and other techniques cannot be applied efficiently, ionic liquid (IL) leaching has shown potential for application. The use of ionic liquids is an attractive alternative technique for the solubilization of sulfidic ores to liberate

gold (Whitehead *et al.,* 2009). Ionic liquids are considered promising substitutes due to their unique solvent properties such as non-flammability, non-volatile, large chemical and thermal stability ranges, high conductivity and wide electrochemical windows (Lee, 2012). Furthermore, ionic liquids can be easily synthesized and designed for specific functions due to the almost countless combinations of at least two constituents which can be different possible cations and anions. Thus, the term "designer solvents" has arisen in common use (Sowmiah *et al.,* 2009).

The purpose of this work is to examine the feasibility of imidazolium-based ionic liquids to extract gold from refractory sulfidic low-grade gold tailing source from DRD Gold plant, in South Africa. There are gold losses to tailings and opportunities to improve gold processing have rewards. Basically, this particular study concentrates on improving extraction of gold from tailings with low amount of gold.

1.2 Research Problem

Globally growing environmental concerns and the economic downturn have led to conventional gold treatment processes being viewed as undesirable due to the environmental pollution they cause, large quantities of reagents they require and their hazardous operating effluents. These reasons have prompted researchers to investigate new alternative and more environmentally compatible ways to treat minerals for gold extraction. Ideally, the ability to extract gold from refractory low-grade ore requires innovation so as to achieve an efficient and effective yield of gold. For this purpose, ionic liquids (ILs) are proposed to be used as a neoteric solvent for extracting gold. Furthermore, it is theorized that oxidative leaching of refractory sulfidic low-grade tailing ore using ILs/thiourea/iron (III) sulfate can be an environmentally benign process to extract gold. The green character of ILs is mainly associated to their non-volatility or negligible vapour pressure which reduce explosion risk and inability to produce air pollution (Tong *et al.,* 2013).

1.3 Aim and Objectives

The overall aim of this investigation is to study the feasibility of extracting gold from refractory sulfidic low-grade tailing ore using imidazolium-based ionic liquids. As part of this aim, this study endeavors to determine whether two types of imidazolium-based ionic liquids, 1-butyl-3-methylimidazolium hydrogen sulphate [$Bmim^{+}HSO_4^{-}$] and 1-butyl-3-methylimidazolium

trifluoromethansulfonate [$Bmim^{+}CF_3SO_3^{-}$], can be used efficiently for extracting gold from this ore.

The specific objectives of this investigation are as follows:

- Identify the significant factors that influence the extraction of gold in a system containing these ionic liquids by using design of experiments (DOE). The operating parameters that will be looked at are concentration of ionic liquid, pulp density, time and temperature.
- Optimize the selected significant factors within a specified range of operating parameters to maximize the extraction of gold by using DOE and surface response methodology.
- Determining the kinetics of the process and fitting a suitable gold extraction model onto the data.

1.4 Hypothesis

It is feasible to extract gold by oxidative leaching from refractory sulfidic low-grade tailing ore using ILs/thiourea/iron (III) to a larger degree than cyanidation.

1.5 Dissertation Layout

This dissertation comprise of five chapters. The introduction chapter outlines the motivation for this research, the problem statement, and the objectives of this study. Chapter two provides an literature review on the extraction of gold, gold extraction modeling and some theory around experimental design. Chapter three describes the materials used and experimental methods applied to achieve the objectives of this study. The results and analysis of the experimental data are presented in chapter four (results and discussion), and also includes a discussion of the results and the fitting of a gold dissolution model to the data. The final chapter (chapter five) provides a summary of the main conclusions and makes recommendations for future research. Appendices of detailed laboratory test results and other important data are also included.

2 Literature Review

2.1 General Introduction

World demand for gold is strongly influenced by general economic conditions and by high demand from modern growing industries that consume great quantities of gold, such as super alloys and manufacturers of electronic devices. The demand for gold and the simultaneous exhaustion of high-grade gold ore resources and the difficulty associated with the processing of refractory low-grade gold ores which cannot be treated environmentally benign by traditional metallurgical processes, they have created noteworthy challenges in the gold supply market because of decreasing grades. There are, however, large deposits that have yet to be explored using modern technology, so the size of the reserves may be undervalued.

Sulfidic gold ore, which is often considered as a low-grade gold ore consists several kinds of metal elements including iron, copper, arsenic, zinc, lead, silicon, magnesium, manganese and selenium, and thus establishes an attractive alternative source of gold. The aim of this chapter is to briefly describe a general knowledge of sulfide ore containing gold mineralogy and occurrence, as well as, conventional and alternative new metallurgical methods applied for its extraction and recovery from the typical ores. The typical processing means hydrometallurgical methods of leaching, then separation and finally recovery of gold from the pregnant solution.

2.1.1 Gold

It is a well-known fact that gold is a useful and valuable metal. Since the earliest of times, gold has been acknowledged and appreciated throughout the world for its outstanding physical and chemical properties such as high resistance to corrosion, ductility to be molded into any shape and size and its beauty. This renowned precious metal has been used widely in various fields; not only in the decorative and jewelry industries but also in many advanced technologies (Liu *et al.,* 2009). The unique properties of gold also include its excellent electrical conductivity, the fact that it does not tarnish in air or water, thus it can form alloys with different metals. Historically, gold was important as currency around the world, but nowadays it is regarded as an investment tool and an industrial commodity. A major portion of gold is used for jewelry and investment in the form of bullion coins or bars (Syed, 2012). Furthermore, recently there has been an increasing tendency in the applications of valuable metals, especially gold, in new developing applications such as electronic connectors and electrical contacts due to its thermal and electrical conductivity, catalysts, corrosion-resistant materials, as well as using it for

medical and environment applications (Lee, 2012). The industrial demand for gold in the world aroused sustained interest amongst scientists to develop a more effective and environmentally friendly method to extract it from mineral ores and secondary sources (Campos *et al.*, 2008).

2.1.2 Gold mineralogy and occurrence

Gold (atomic number 79, mp 1065 °C) is the noblest metal in the periodic table. It is located in the Ib group in the periodic table in the same classification with silver and copper. It has two common oxidation states: Au^{+} (aurous) and Au^{3+} (auric). The electronic configuration of the element in the ground state is [Xe] $4f^{14}$ $5d^{10}$ $6s^{1}$. The monovalent and trivalent state is [Xe] $4f^{14}$ $5d^{10}$ and [Xe] $4f^{14}$ $5d^{8}$, respectively. The precious metals like gold are characterized by low terrestrial abundance. The average gold concentration in the earth's crust is about 0.005 (g/t), which is noticeably lesser than other valuable metals for instance, silver (0.07 g/t) and copper (50 g/t). Its abundance in seawater and river water is 0.05 and 0.2 µg L^{-1}, respectively (Marsden & House, 2006).

Gold has high tendency to be concentrated as a metallic form in meteorites. It is widespread in very low amounts in various rocks all over the world. Generally, rocks rich in clays and low in carbonates is the best place for accruing gold (Jones & Fleischer, 1969). Gold is commonly found in massive hydrothermal deposits (high temperature), sedimentary beds and placer deposits. Furthermore, it has a high affinity for sulfur and for that reason often occurs as ultrafine particles in sulfide minerals, in which gold is mostly unliberated (locked in sulfide matrix). Further, it exists in considerably lower quantities in the silicate, metamorphic ores and sometimes as an accessory mineral in igneous rocks. Gold occurrence is mostly in the metallic phase and also as different alloys, particularly with silver %15 and to a lesser extent with copper, platinum, palladium, tellurium, selenium, bismuth, iron, mercury and rhodium (Marsden & House, 2006).

2.2 Existing gold-bearing ore processing methods

The fast-growing demand for gold in the industrialized world has led to depletion of high-grade gold ore resources. Thus, nowadays refractory low-grade gold ores which are difficult to process due to their refractoriness have become important in order to obtain gold.

Based on the mineralogical characteristics and mineral processing methods required, gold ores can be categorized into the following types: placer, quartz vein-iode, oxidized, silver-rich,

copper sulfide ore, iron sulfide, arsenic sulfide, antinomy sulfide, bismuth sulfide, telluride and carbonaceous-sulfidic ore (Vaughan, 2004).

Of these sulfidic gold ore has become one of the significant resources for extracting gold in order to fulfill modern world demand. At the moment, extracting gold from low-grade sulfidic ores, such as pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and arsenopyrite (AsFeS), can be a laborious process involving pyrometallurgy and/or hydrometallurgy (Olyaei *et al.*, 2016). Sulfidic ores contain gold locked in its structure. Gold can appear in different forms within pyrite or other sulfide as can be seen in Figure 2.1. Gold can appear as (1) free-milling, (2) along grain boundaries, (3) enclosed in the sulfide matrix, (4) at the boundaries between sulfide grains, (5) along fractures and/ crystal defects, and (6) as colloidal particles or in solid solution in the sulfide mineral. Gold can be invisible as a solid solution within the pyrite grains. To liberate the gold from pyrite demands fine grinding of the material and/or more oxidative conditions (Marsden & House, 2006).

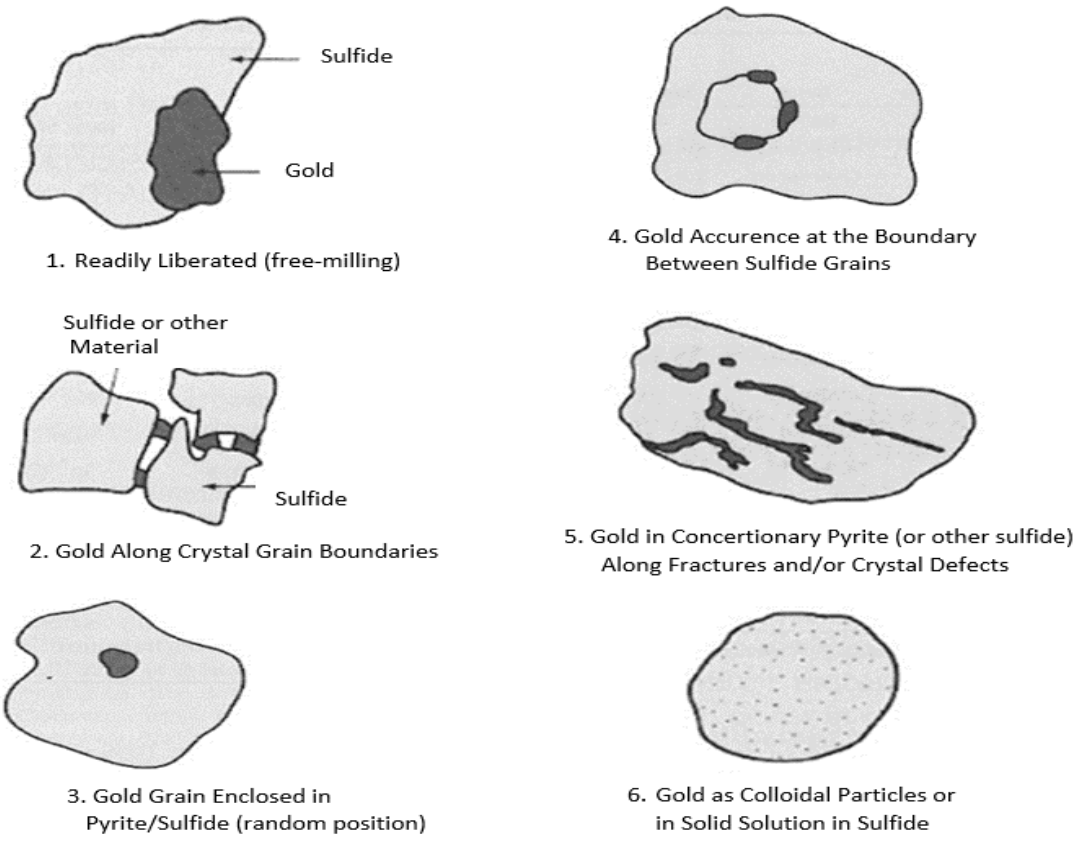


Figure 2.1 The different forms in which gold appears in the sulfide ore structure (Marsden & House, 2006)

Basically, most of the gold–bearing ore are mineralogically and chemically complex, like sulfide minerals in which the gold is unliberated. It should be mentioned that gold is present in the sulfidic ores as a minor constituent of other minerals and, therefore, it is not amenable to concentration through any conventional processing methods. Conventional pyrometallurgical and/or hydrometallurgical processing methods can be time-consuming and energy intensive. Regardless, gold has been mostly leached from its ores by cyanidation for more than one century. It is considered a standard commercial route for leaching of ores containing gold due to its high efficiency (Olyaei *et al.*, 2016). Nevertheless, the cyanidation techniques have been recognized as undesirable and environmentally hazardous because of the severe toxicity of cyanide (Grosse *et al.*, 2003).

Compared to other refractory sulfide minerals that contain gold, pyrite contains less gold than arsenopyrite, but still in significant amounts. The most common refractory sulfide minerals are listed in Table 2.1. Pyrite can contain from 1.087 to 1.5 ppm gold, while arsenopyrite can contain up to 1.7 wt % (17000 ppm) (Ahtiainen & Lundstrom, 2016).

Table 2-1 Gold concentrations in different refractory gold (Ahtiainen & Lundstrom, 2016)

Mineral	Formula	Gold Concentration
Arsenopyrite	AsFeS	< 0.3 ppm – 1.7 wt %
Pyrite	FeS_2	1.087 to 1.5 ppm
Tetrahydride	$Cu_{12}As_4S_{13}$	< 0.25 – 800 ppm
Pyrrhotite	$Fe_{x-1}S$	< 0.25 – 59 ppm
Marcasite	FeS_2	0.006 – 1.8 ppm
Chalcopyrite	$CuFeS_2$	0.05 – 4.1 ppm
Leollingite	$FeAs_2$	0.01 – 20 ppm

Carbonaceous refractory ore are also contains gold. The problem in the carbonaceous refractory ore leaching can be tendency of gold to adsorb on carbon during leaching if present in the ore/concentrate, thereby reducing gold extraction by cyanidation (Ahtiainen & Lundstrom, 2016). This phenomenon is called preg-robbing and these gold ores sometimes require oxidative pre-treatment prior to cyanide leaching (Marsden & House, 2006).

2.2.1 Pyrometallurgical processing of gold

The pyrometallurgical process has been used for gold extraction from its ore since antiquity. Typically, this technique is based on the burning of crushed ore containing gold and scrap and is conducted in a furnace or molten bath with high temperature (1800 - 2000 °C). Impurities in minerals are removed using volatilization. Often slags, which accumulate on the surface of the molten metal, or sludges which sink to the bottom, are formed during pyrometallurgical processing (Marsden & House, 2006). This approach has several drawbacks, including extremely high energy requirements for melting, high capital cost, prolonged separation time and incomplete recovery of the desired metal, especially from low-grade minerals (Syed, 2012).

Roasting refers to the pyrometallurgical oxidation process of sulfide minerals, in which the sulfide phase is broken up to make the gold available. Refractory sulfidic and carbonaceous ores are oxidized in the presence of an oxidizing gas (air or oxygen) at high temperatures. The temperature for roasting varies from 600 to 1000 °C, depending on the process and mineralogy of the ore (Ahtiainen & Lundstrom, 2016). The purpose of roasting is to remove the sulfur in the ore to produce a porous product. The gold in the porous product is highly liberated and easily reachable to the leaching solution and complexing agent (Marsden & House, 2006). Moreover, the reagent consumption and gold-absorbing potential of ore (preg-robbing) is minimized. Roasting was the most used and favored oxidizing method about 25 years ago, but it has started to become less favored due to the strict environmental legislation, and gas phase emissions which can contain arsenic oxide and sulfur dioxide. However, sulfur oxides produced as by-products that can be used to produce sulfuric acid from the exhaust gases (Fleming, 2009).

2.2.2 Hydrometallurgical processing of gold

A hydrometallurgical process envolves principally the dissolution of minerals in an acidic and/or basic aqueous medium and the recovery of selected metals from these solutions. It also includes the selective transition of species from liquid/solid to liquid/liquids systems (Syed, 2012). Currently, there are some hydrometallurgical processes that are either in operation or being piloted or evaluated in the gold mining industry. The most common ones are discussed in the following sections.

Pressure oxidation (POX)

Pressure oxidation (POX) comprises leaching of ore under acidic or basic conditions in the presence of an oxidant at high pressure (4500 kPa) and elevated temperatures (≥250 °C) (Rusanen *et al.*, 2013). This oxidation process is performed in an autoclave to maintain high pressure and temperature. In this procedure, the host minerals are decomposed rapidly at high temperature and pressure using oxygen as the oxidant. The main objective is to destroy the sulfide lattice to liberate gold particles into solution (Marsden & House, 2006).

The gold particles can be extracted through cyanide leaching with >95% recovery, depending on the concentrate mineralogy. The main products of the pyrite oxidation reaction are ferrous sulfate [$FeSO_4$], ferric sulfate [$Fe_2(SO_4)_3$], sulfuric acid [H_2SO_4] and elemental sulfur [S] (Fleming, 2009). The typical pyrite oxidation reaction is presented in Equation 2.1:

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \rightarrow 2\,FeSO_4 + 2\,H_2SO_4 \qquad (2.1)$$

Bio-leaching

Bio-hydrometallurgy is the process of using bacterial microorganisms to recover valuable metals from ores or secondary sources. Since the mid-1950s, the effect of micro-organisms for oxidation reactions have been noticed. The oxidation reactions can be catalyzed with several kinds of bacteria that can be found in nature (Syed, 2012). Thus, bacterial oxidation leaching can be used to extract metals from sulfidic containing gold ores and mineral concentrates. This process is called biomining or mineral bioprocessing (Watling, 2016).

In bioleaching the sulfide and iron is oxidized microbiologically, during which sulfuric acid and ferric iron are produced. This method is used to recover gold from refractory ores in which gold is locked inside the ore, and is due to the fact that microbes oxidize the refractory ore and release the gold (Rawlings *et al.*, 2003). The biooxidation process has been used for gold recovery from sulfidic containing gold ore (Fomchenko *et al.*, 2010), and spent electronic scrap (Natarajan & Ting, 2015) by applying microbially supported oxidation reactions. Bioleaching of sulfide ores is mostly based on the action of aerobic, acidophilic, chemilithotrophic bacteria such as *Thiobacillus ferrooxidans* and/or *Leptospirillum ferrooxidans* (Romero *et al.*, 2003).

There are some environmental advantages in this oxidation process besides economic benefits: (i) the energy consumption compared to a pyrometallurgy process (roasting or smelting) is much lower and (ii) hazardous gases like sulfur dioxide are not formed in bioleaching

(Rawlings, *et al.*, 2003). However, biohydrometallurgical processing often faces the problem of slow kinetics (Rubio & García Frutos, 2002).

Oxidative leaching of sulfidic ores

The oxidative dissolution reactions follow an electrochemical mechanism illustrated in Figure 2.2. The main parts of this mechanism are the oxidation and reduction reactions in which an electron is being transferred between a mineral (M) and an oxidant ($Fe^{3+}_{(aq)}$) in an aqueous solution (Crundwell, 2013).

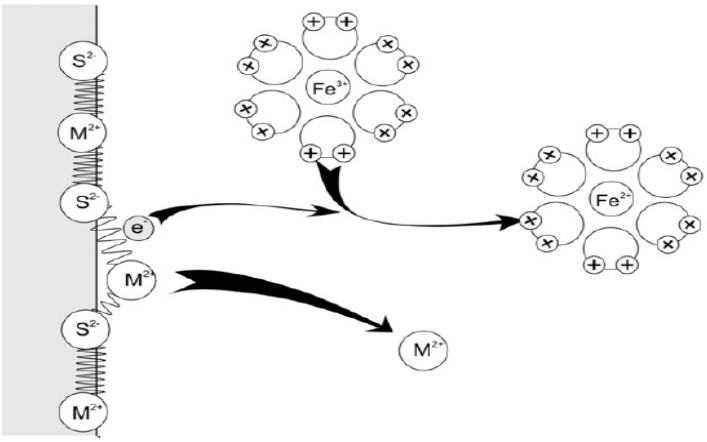


Figure 2.2 The concurrent model of electrochemical dissolution of a mineral (Crundwell, 2013)

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

$$M_{(s)} \rightarrow M^{+}_{(aq)} + e^{-} \quad (2.2)$$

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

$$Fe^{3+}_{(aq)} + e^{-} \leftrightarrow Fe^{2+}_{(aq)} \quad (2.3)$$

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

$$M_{(s)} + Fe^{3+}_{(aq)} \rightarrow M^{+}_{(aq)} + Fe^{2+}_{(aq)} \quad (2.4)$$

Pyrite aqueous oxidation can be done in electrochemically and/or bacterially catalyzed ways. Typically, thiobacillus bacteria like *T. ferrooxidans* and *T. caldus* have been applied to catalysis the pyrite biooxidation reaction as an iron and sulfur oxidizer (Fomchenko *et al.*, 2010).

Scientists have conducted experiments on oxidative pyrite dissolution under various experimental conditions like the type of oxidant (Fe^{3+}, O_2, H_2O_2), pH, Eh, temperature, stirring

speed and particle size of the ore. Moses and Herman (1991) have done various experiments on pyrite dissolution at circumneutral pH by using Fe^{3+} and O_2 as the oxidant. Likewise, these researchers have recommended that pyrite oxidation and dissolution can be controlled by electrochemical processes (Chandra & Gerson, 2010). The electrochemical process of pyrite dissolution was further investigated and improved by work done by Rimstidt and Vaughan (2003). They combined results from other researchers and their own previous studies in order to offer a detailed mechanism that presents fundamental and primary steps of the anodic oxidation of pyrite and the cathodic reduction of oxidants (Fe^{3+} and O_2). They proposed a schematic explanation of the electrochemical mechanism of pyrite oxidation and dissolution with detailed information which is depicted in Figure 2.3 (Rimstidt & Vaughan, 2003).

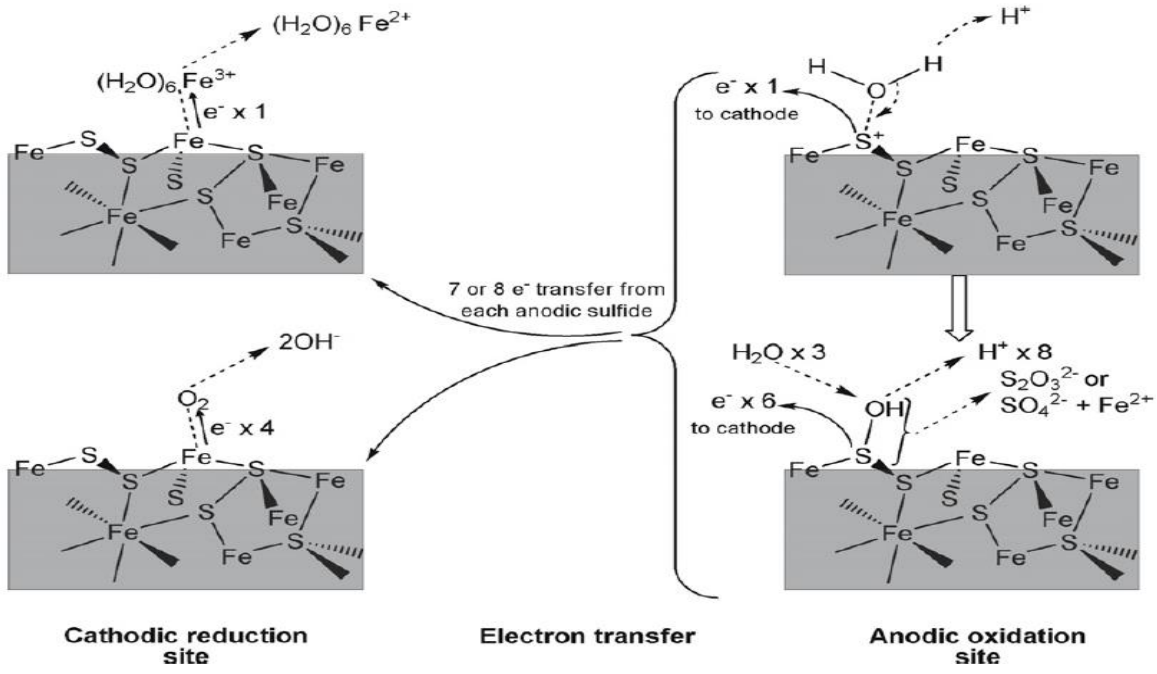


Figure 2.3 Schematic illustration of the electrochemical mechanism of pyrite (Rimstidt & Vaughan, 2003)

From a molecular point of view illustrated graphically in Figure 2.4, the initial step of oxidative leaching is the cathodic reduction of the sulfidic mineral (FeS_2) through removing an electron from the sulfur (S atom), followed by transferring the electron from the anodic site to the cathodic, and ultimately the reduction of oxidants (Fe^{3+} and/or O_2) by accepting the electron. The cathodic and anodic sites can be either in the different surfaces of two pyrite particles or the same particle (Rimstidt & Vaughan, 2003). Therefore, it is an agreed fact that pyrite aqueous oxidation is an electrochemical process which consists of three steps, as demonstrated

clearly in Figure 2.4. The (I) cathodic reaction, (II) electron transfer from anode to cathode, as well as (III) the anodic reaction. These three steps occur simultaneously in the actual oxidation process (Rimstidt & Vaughan, 2003).

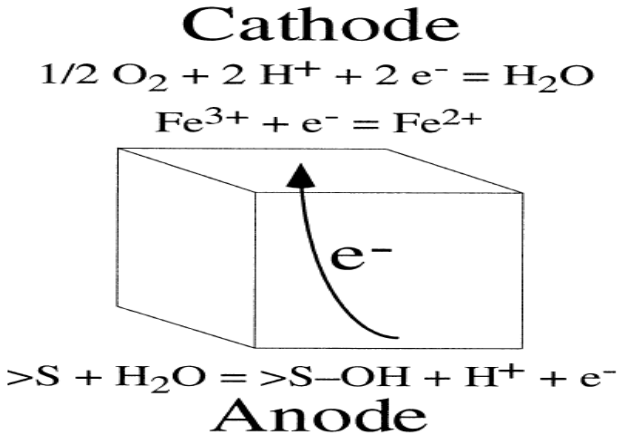


Figure 2.4 Electrochemical process of pyrite oxidation (Rimstidt & Vaughan, 2003)

Oxidative leaching of pyrite can be done by different oxidants such as oxygen (O_2), hydrogen peroxide (H_2O_2) and ferric ion (Fe^{3+}), which produce dissolved iron and sulfuric acid (McKibben & Barnes, 1986). The overall reaction for these three oxidants are shown as follow:

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \quad (2.5)$$

$$FeS_2 + 15/2\ H_2O_2 \rightarrow Fe^{3+} + 2\ SO_4^{2-} + H^+ + 7\ H_2O \quad (2.6)$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16\ H^+ \quad (2.7)$$

It was proposed by Moses et al. (1987) that the rate of pyrite oxidation in the presence of Fe^{3+} was faster than the experimental condition in which oxygen has been used as an oxidant in the medium with a low pH range. Thus, it is more economically favorable to add ferric ion as it is largely accessible in gold treatment routes as the superior oxidant (Moses *et al.*, 1987).

Luther (1987) discussed that the reason why pyrite oxidation through $Fe(III)_{aq}$ is faster in comparison to O_2 oxidation is because of building a direct bond through making a transition intermediate oxidant to the pyrite surface, in which this intermediate act as a bridge to facilitate and assist the electron transition from fully filled molecular orbital of S_2^{2-} to the vacant molecular orbital of Fe^{3+} (Luther, 1987). Ferric ion is stable at pH < 2 and precipitate as hydroxyl species (ferric hydroxide) as the pH increases (Whitehead *et al.*, 2007).

2.3 Leaching methods

Selective removal of the goal metal from the ore through proper reagents to penetrate the gangue mineral can be defined as leaching process. The leaching method is divided into the following groups, depending on the mineralogy of the ore, reaction vessel and operation.

- In-situ Leaching (ISL)
- Heap Leaching (HL)
- Vat Leaching (VL)

In-situ leaching, heap leaching and vat leaching are explained in the following sections.

2.3.1 In-situ leaching

The possibility of in-situ gold leaching was examined for the first time through an underground pilot trial in the 1970s in the United States. The leaching procedure is applied to the ore remaining in the mine after it has been mined out or directly to the underground ore in the mine (Martens *et al.*, 2018). The leach solution is introduced from the top to the ore body and permitted to seep into the ground by gravity, moving through the ore body and then collected at the bottom using a system of sumps. This method is highly dependent on the porous structure of the minerals. It may require inducing cracks by underground explosions if the natural permeability of the rocks is low. For subsequent separation, the pregnant leached solution is pumped to the surface (Martens *et al.*, 2018).

The conventional ISL process is not environmentally and economically acceptable. Excessive caution has to be taken since this leaching system can pose a threat to the surrounding environment due to seeping of toxic lixiviants (cyanide) into the underground water and metal loss into natural groundwater, thus causing pollution (Martens *et al.*, 2018).

2.3.2 Heap Leaching

This method has been started on a large scale in the late 1970s in Nevada and is typically used for leaching of low-grade minerals to extract valuable metal by a cost-effective mean (Marsden & House, 2006). Heap leaching has been broadly used for the extraction of low-grade ores to produce copper, gold, silver, uranium, nickel, zinc and currently platinum group metals and electronic scrap (Ghorbani *et al.*, 2016).

In this process, ore is first crushed into a fine particles size and piled up in heaps. By spraying leaching reagent from the top of the heaps, the ore gradually is leached on a large water resistant pad and the desirable metal extracted into solution. The leach solution is typically sulfuric acid for nickel and/or copper ores, or for minerals containing gold and silver, diluted cyanide solution. The leach solution is distributed over the heap using pipes and then the pregnant leach solution (PLS) is transferred from the bottom of the heap (drainage layer) into the PLS pond before being pumped to the recovery system. The leaching rate can be improved by decreasing the particle size of the ore, which results in high surface area, and also by screening out the fine clay material first (Ghorbani *et al.*, 2016).

At first sight this method appears to be simple in operation, but it rapidly becomes complex when considering the variables involved in the subprocedure. Variables, such as chemical reactions that result in the dissolution of the metal from the gangue, precipitation, oxidation and other solution phase chemical reactions, need to be considered (McBride *et al.*, 2012). Applying micro-organisms resident inside the ore bed may simplify the leaching process especially for the sulphidic gold ores (Ghorbani *et al.*, 2016). A typical heap leaching diagram is depicted in Figure 2.5.

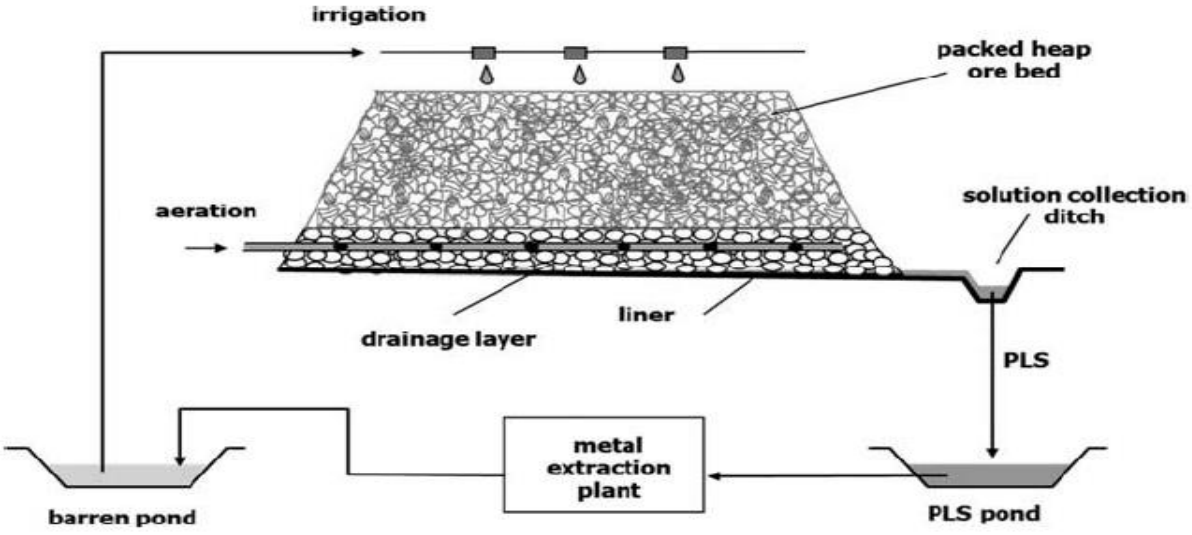


Figure 2.5 Schematic representation of a heap leaching process (Ghorbani *et al.*, 2016)

The main advantage of heap leaching involves economical capital and process costs, because it requires simple operating equipment, is effective for low-grade ores and wastes, and only leaves slight deposits. Despite its advantages heap leaching has some drawbacks: (1) it needs a suitable territory to keep a large amount of solution inside the ore bed which limits the control

of the process, (2) time-consuming, (3) unplanned release of the pregnant solution to the location, (4) slow kinetics of the leaching reaction and (5) loss of water through evaporation (Ghorbani *et al.,* 2016).

2.3.3 Vat leaching

In vat leaching coarse materials are placed in stationary vats without agitation. The lixiviant is pumped through beds of ore at ambient conditions and the metal of interest is leached from the ore into the solution (Hiji & Maganga, 2015). The process is typically operated sequentially to increase the interaction time between the ore and the reagents. In each sequence the leachate is removed from one vat and added to another container which has a newer ore. The extraction happens counter currently, this leads to an increase in the extraction yield. This would be expected, since the fresh reagents react with the leached ore at one end and on the other end the pregnant leachate meets the fresh ore (Sousa *et al.,* 2010).

2.4 Leaching solution

A typical industrial leaching solution contains water, acids (H_2SO_4, HCl), bases (NaOH, NH_4OH), salts solutions or combinations of these. It might be possible to enhance the leaching kinetics by adding oxidizing agents such as H_2O_2, Fe^{3+}, HClO, NaClO, Cl_2 or reducing agents (Fe^{2+}, SO_2) (Niemczewska *et al.,* 2004). Currently, the most commonly used gold leaching reagents include cyanide, thiocyanate, thiourea, and thiosulfate (Smolyaninov *et al.,* 2014).

2.4.1 Cyanide leaching

For over one century, cyanide has been the predominant leaching reagent for extracting gold from ore from mines and secondary resources due to the chemical stability of the cyanide complex formation with gold and the possibility of high yield and dissolution rate (Hilson & Monhemius, 2006). The overall chemical gold (Au) dissolution reaction is illustrated below (Syed, 2012).

$$4\,Au\,(s) + 8\,CN^- + O_2 + 2\,H_2O \rightarrow 4\,Au(CN)_2^- + 4\,OH^- \qquad (2.8)$$

Gold is oxidized and dissolved in alkaline cyanide solution to form the stable anionic gold-cyanide complexes $Au(CN)_2^-$. The optimum pH for gold dissolution is in the basic range of pH=10-10.5 (Hilson & Monhemius, 2006).

Even though cyanide leaching is still industrially a favorable technique, it has some disadvantages, such as toxic waste solutions with poisonous effects on the aquatic and soil environment in the event of an unpredicted spill or tailings dam breach. Besides the inability of the cyanide solution to leach refractory sulphidic gold ores efficiently (Azizi & Ghaedrahmati, 2015).

Even though cyanide can be destroyed by exposing it to sunlight (natural degradation) (Sharma, 2003), and chemicals such as chlorine dioxide (ClO_2), ozone (O_3) (Parga *et al.*, 2003) and ferrate [Fe(VI)] can be used to detoxify cyanide, these methods are not completely successful (Sharma, 2003).

2.4.2 Halide leaching

Halide leaching includes chloride, bromide, or iodide in aqueous solutions. Halides have been used for extracting gold since before cyanidation. Chlorination was a frequently used method in the 1900s and chlorine has been widely used as a leaching solution for extracting gold from its ores. Depending on the chemical and operating conditions of the solution, gold forms both Au(I) and Au(III) complexes with Cl^-, Br^-, and I^- (Syed, 2012).

The general anodic and cathodic electrochemical reaction for gold leaching in halide ion (X^-) solutions are as follow (La Brooy *et al.*, 1994):

$$Au + n\,X^- \rightarrow Au\,X_n^{(n-m)-} + me^- \quad \text{(Anodic reaction)} \tag{2.9}$$

$$Cl_2 + 2\,e^- \rightarrow 2\,C1^- \quad \text{(Chlorination at pH = 1)} \tag{2.10}$$

$$HOBr + 2\,e^- \rightarrow Br^- + OH^- \quad \text{(Bromination at pH = 1-6)} \tag{2.11}$$

$$I_3^- + 2\,e^- \rightarrow 3\,I^- \quad \text{(Iodination at pH = 1)} \tag{2.12}$$

Chlorine can be produced in different ways, e.g., electrolysis of aqueous sodium chloride (NaCl), adding manganese (IV) oxide (MnO_2) to hydrochloric acid (HCl) or mixing hydrochloric acid and nitric acid (ratio 1:3). The mechanism of producing chloride is as follows (Hilson & Monhemius, 2006):

$$NaCl_{(aq)} + H_2O \rightarrow \mathrm{Na}^+_{(\mathrm{aq})} + OH^-_{(\mathrm{aq})} + H_{2(g)} + 0.5\,Cl_{2(g)} \tag{2.13}$$

$$MnO_2 + 4\,HCl \rightarrow MnCl_2 + 2\,H_2O + Cl_{2(g)} \quad (2.14)$$

$$2\,HNO_3 + 6\,HCl \rightarrow 2\,NO + 4\,H_2O + 3\,Cl_{2(g)} \quad (2.15)$$

Chlorine quickly forms complexes with gold,

$$2\,Au + 3\,Cl_2 \rightarrow 2\,AuCl_3 \quad (2.16)$$

Chlorination leaching can be a possible substitute for extracting gold from refractory sulfidic gold minerals. This process can destroy the sulfide mineral matrix and simultaneously leach the gold. It should be noted that higher redox potential and reagent concentrations are required for refractory ores, such as pyrite and arsenopyrite, compared to free-milling ores. Almost all sulfide ores can be leached in chloride solutions (Hilson & Monhemius, 2006). Equation 2.17 represents the oxidation of pyrite in chloride solutions:

$$4\,FeS_2 + O_2 + 2\,H_2O + 8\,Cl^- \rightarrow 4\,[FeCl_2]^+ + 8\,SO_4^{2-} + 4\,H^+ \quad (2.17)$$

Gold leaching is faster in chloride solution than in cyanide. The desired leaching rate in this process can be attained in high chloride and chlorine concentrations in the presence of oxidants such as copper, at a low pH, high temperature, as well as high ore surface areas for gold and silver leaching. Presently, in the existing processes, the concentration of the chloride ions varies between 120-200 g/l and bromide ion between 1-20 g/l.

However, the chlorination process has a number of disadvantages compared to cyanide leaching (Syed, 2012):

- The complexes of gold-chloride and gold-bromide are not as stable as gold-cyanide complexes.
- The gold has a tendency to adsorb faster onto carbon i.e., preg-robbing in which less gold is extracted.
- It requires special materials of construction of the leaching reactor (stainless steel and rubber-lined) because of high chloride concentrations, which may cause possible extremely corrosive acidic and oxidizing problems.
- Chlorine gas is highly hazardous, it must be carefully handled to prevent any health threat (Syed, 2012).

2.4.3 Thiourea leaching

Thiourea [$SC(NH_2)_2$] is an organic reagent, and its crystals can form a stable aqueous species in water or in an acidic medium. Thiourea has displayed considerable potential as a leaching agent for extracting gold from its ore and secondary resources. In acidic medium, the aqueous form of thiourea dissolves gold to produce a stable cationic Au-thiourea complex (Hilson & Monhemius, 2006). Figure 2.6 represents the open structure of the Au-thiourea complex (Piro *et al.*, 2002). The anodic electrochemical reaction follows the Equation 2.18:

$$Au + 2\ SC(NH_2)_2 \rightarrow Au(SC(NH_2)_2)_2^{+} + e^{-} \quad (2.18)$$

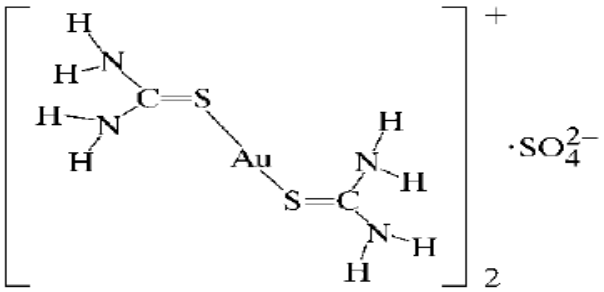


Figure 2.6 The structure of Au-thiourea complex (Piro *et al.*, 2002)

The leaching process is typically conducted in the acidic pH = 1–2 range (in basic solution $SC(NH_2)_2$ decomposes rapidly). This technique can be successful under restricted conditions by controlling pH and redox potential of the leaching solution, concentration of thiourea, and the leaching time (Syed, 2012). Depending on the type of oxidizing reagent (e.g., hydrogen peroxide (H_2O_2) or ferric ion (Fe^{3+})) used in the leaching process, different reduction reactions can happen in the solution (Lacoste-Bouchet *et al.*, 1998):

$$H_2O_2 + 2\ e^{-} \rightarrow 2\ OH^{-} \quad (2.19)$$

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+} \quad (2.20)$$

One of the most effective oxidants for acidic thiourea leaching is the ferric ion. The overall dissolution reaction of gold in the presence of thiourea and ferric ions in an acidic pH = 1-2 solution follows the reaction given by Equation 2.21:

$$Au + Fe^{3+} + 2\ SC(NH_2)_2 \rightarrow Au(SC(NH_2)_2)_2^{+} + Fe^{2+} \quad (2.21)$$

Previous leaching investigations found that the ferric ion as an oxidant can also react with thiourea to form formamidine disulfide (FD) (Lacoste-Bouchet *et al.*, 1998). In other words,

thiourea reforms on its own to produce FD in the presence of oxidizing agents in an acidic aqueous environment which is the key product of thiourea oxidation (Yazici *et al.*, 2014). The corresponding reaction follows Equation 2.22 (Yazici *et al.*, 2014):

$$2\ SC(NH_2)_2 + 2\ Fe^{3+} \rightarrow NH_2(NH)CSSC(NH)NH_2 + 2\ Fe^{2+} + 2\ H^+ \quad (2.22)$$

There are some studies about the product of thiourea oxidation, and also the role of FD in the gold leaching, but the obtained results were contradictory. FD had the ability to oxidize gold in thiourea solution and make the same cationic complex with Au at low pH as thiourea (Lacoste-Bouchet *et al.*, 1998). The electrochemical reaction follows Equation 2.23 (Yazici *et al.*, 2014):

$$2\ Au + 2\ SC(NH_2)_2 + NH_2(NH)CSSC(NH)NH_2 + 2\ H^+ \rightarrow 2\ Au(SC(NH_2)_2)_2^+ \quad (2.23)$$

There are certain benefits in using acidic thiourea leaching compared to cyanide, such as less toxicity, low sensitivity to base metals and remaining sulfur, as well as high gold recovery from refractory sulfidic gold ores such as pyrite, chalcopyrite and carbonaceous ores (Hilson & Monhemius, 2006).

2.4.4 Thiocyanate leaching

The thiocyanate (SCN^-) gold leaching process was suggested in the early-1900s by White, but the work in this field stayed largely undeveloped till Fleming restarted it in 1986. The dissolution of gold with thiocyanate is conducted in aqueous acidic pH = 1-2 in the presences of iron (III) as an appropriate oxidant (Marsden & House, 2006). During the gold leaching process with thiocyanate and ferric ion, SCN^- is oxidized by Fe(III) which itself is reduced to Fe(II) in order to produce some intermediate species, including $(SCN)_3^-$ and $(SCN)_2$ which both can act not only as oxidizing agents but also as complexing agents for gold to create both the Au(I) and Au(III) complexes, depending on the potential of the solution (Gökelma *et al.*, 2016).

$$Au + 2\ SCN^- \rightarrow Au(SCN)_2^- + e^-;\ E^0 = +0.662\ (V) \quad (2.24)$$

$$Au + 4\ SCN^- \rightarrow Au(SCN)_4^- + 3\ e^-;\ E^0 = +0.636\ (V) \quad (2.25)$$

Subsequently, gold can be recovered through carbon adsorbents and ion exchangers from the pregnant solution. According to laboratory scale research results, it has been concluded that the thiocyanate method is comparable to cyanide gold leaching. It also demonstrated noticeably better effectiveness than the thiourea system (Syed, 2012). Thiocyanate gold leaching is a

potentially promising substitute for cyanide since it has fewer effects on the environment, fewer pollution problems, and shows less sensitivity to other cations in the leaching solution. Nonetheless, the consumption of great amounts of reagent renders the thiocyanate systems economically unfavorable in spite of their prospective environmental benefits (Hilson & Monhemius, 2006).

2.4.5 Thiosulfate leaching

Thiosulfate ($S_2O_3^{2-}$), which has been used in photography and the medicinal industry, has been considered as a substitute for gold leaching due to its less toxicity (Hilson & Monhemius, 2006). Thiosulfate leaching is adaptable to refractory gold ores. According to the following reaction thiosulphate forms a stable anionic complex with gold in mildly oxidative conditions in alkaline or neutral solution according to Equation 2.26:

$$2\,Au + 0.5\,O_2 + 4\,S_2O_3^{2-} + H_2O \rightarrow 2\,Au\,(S_2O_3)_2^{3-} + 2\,OH^- \quad (2.26)$$

The leaching process can be enhanced by ammonia and copper to achieve acceptable leaching rates (Syed, 2012). This process is used to treat carbonaceous material or preg-robbing ores with high carbon content (more than %1.44) because the gold thiosulfate complex has low tendency for absorption on carbon. This process is still unaffordable from an economical point of view due to the high amount of reagent consumption (Hilson & Monhemius, 2006).

2.4.6 Ionic liquids

Ionic liquids (ILs) are anhydrous salts which are liquid at ambient temperatures. They are relatively new class of solvents which are entirely composed of large organic cations and inorganic or organic anions of different sizes. Their exceptional properties include non-flammability, non-volatility, thermal and chemical stability, high conductivity, wide electrochemical window and recyclability, which all play an important role to yield durable and environmentally benign solvents (Park *et al.*, 2014). Their application is growing into several fields, such as hydrometallurgical processes, catalytic reactions, separation processes, and electrochemistry (Abbott *et al.*, 2017). ILs can be classified into four kinds based on their cationic portion: 1) alkylammonium-, 2) dialkylimidazolium-, 3) phosphonium- and 4) N-alkylpyridinium-based. Generally, the cations should be bulky, asymmetric and heteroaromatics, with weak intermolecular interactions and low charge densities (Welton, 2004).

Ionic liquids are very ‘‘designable” due to numerous possible cation-anion combinations that can be customized to have desirable and specific properties. This flexibility allows ionic liquids to be deliberately designed for specific end use and has led to the concept of them being ‘‘designer solvents’’ (Earle & Seddon, 2000). Their physicochemical properties like melting point, viscosity, density, and hydrophobicity can be easily adjusted by changing the structure of the ions or through the addition of other ions (Tian *et al.*, 2010). The chemical structures of some cations and anions commonly used to produce ionic liquids are illustrated in Figure 2.7. A summary of the unique properties of ionic liquids are listed in Table 2.2.

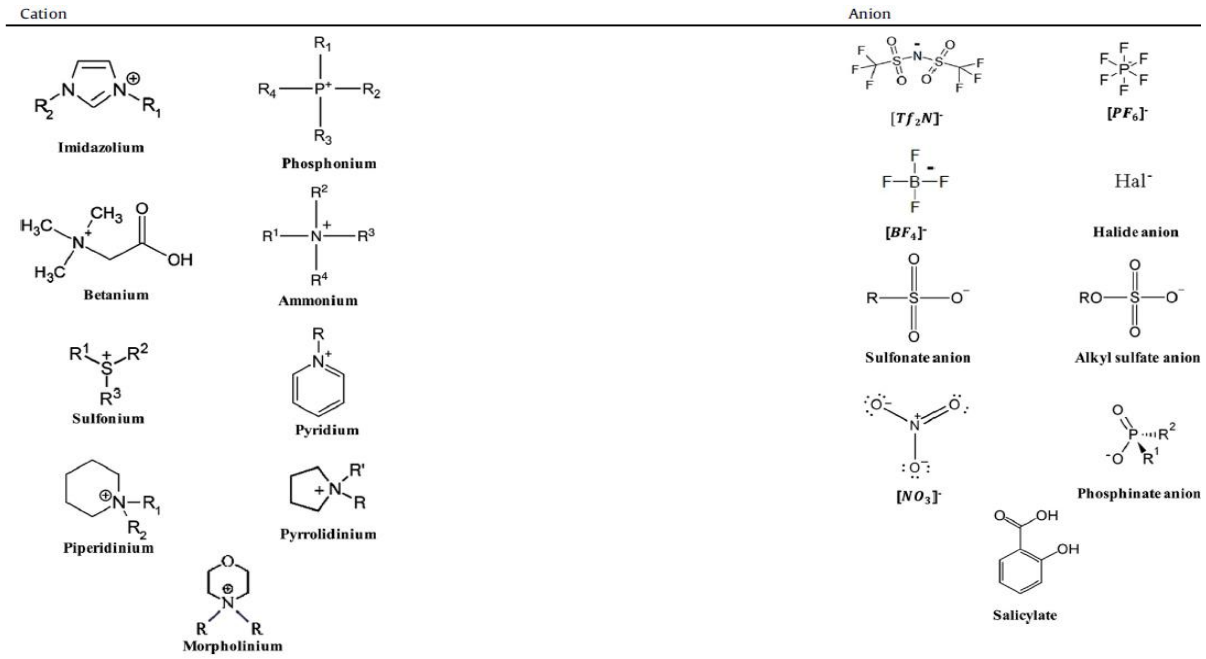


Figure 2.7 Chemical structure of some cations and anions commonly used to produce ionic liquids (Kim *et al.*, 2018)

Table 2-2 Properties of ionic liquids (Park *et al.*, 2014)

Properties	Values
Melting point	Preferably below 100 °C
Liquidus range	Often > 200 °C
Thermal stability	Usually high
Viscosity	Normally < 100 cP, workable
Dielectric constant	Implied < 30
Polarity	Moderate
Ionic conductivity	Usually < 10 mS/cm
Molar conductivity	<10 Scm2/mol
Electrochemical window	Often > 4 V
Vapor pressure	Usually negligible

The first generation of ILs is the deep eutectic solvents (DES) which contain a eutectic mixture of any number of simple quaternary ammonium salts such as choline chloride which is an organic compound (hydrogen-bond acceptor) with urea, glycerol and ethylene glycol which are strong hydrogen-bond donors. The similarities between deep eutectic solvents and ionic liquids are significant. Deep eutectic solvents are now seen as a class of ionic liquids. A eutectic mixture is formed when components are mixed together in a very specific ratio. The interactions between these compounds will be such that intermolecular forces are significantly reduced and the melting point of the mixture is much lower than the normal melting point of its constituents (Jenkin *et al.*, 2016). DESs provide an alternative to traditional metal processing because of the use of environmentally benign and chemically stable components which are commercially available and are cheap. Thus it avoids the production of large volumes of low concentrated aqueous waste (Abbott *et al.*, 2017).

From a sequential point of view, ILs with a discrete anion are the second generation of ILs. The most popular discrete anion involves tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-), bis(trifluoromethylsulfonyl)imide (Tf_2N^-) and hydrogen sulfate (HSO_4^-). Besides, the high stability of the imidazolium ring in electrochemical conditions and low melting points make it a promising cation (Figure 2.8) (Abbott *et al.*, 2011).

In addition, there are some reports about the practical application of imidazolium-based ILs as catalysts for the improved yield and reaction time of several organic reactions (Grosse *et al.*, 2003). Moreover, the hydrophobic or hydrophilic behavior of imidazolium-based ILs, as well as their miscibility with water by using different anions, can be tailored by modifying the number of carbons in the alkyl chains in the dialkyl imidazolium cation (Abbott *et al.*, 2017). Therefore, this cation with an appropriate discrete anion can have distinctive properties to act as an extractant.

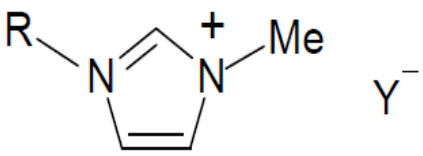


Figure 2.8 Chemical structure of 1-alkyl-3-methylimidazolium ionic liquid (Łuczak *et al.*, 2008)

Increasing the length of alkyl chain in the imidazolium cation can increase the viscosity of the ionic liquid. Whitehead et al. (2007) have investigated the extraction of a sulfidic gold ore with five 1-(n-alkyl)-3-methylimidazolium hydrogen sulfate (n = C4 butyl, C5 pentyl, C6 hexyl, C7 heptyl and C9 octyl) at 50 °C for 48 h. They observed that the gold extraction decreased by increasing the number of carbons from 4 to 9. This is correlated to the viscosity of the IL which can increase by growing the length of the alkyl chain (Whitehead *et al.*, 2007).

In another work by Bhattacharjee et al. (2012) the viscosity of binary mixture of this IL [$Bmim^+HSO_4^-$] with water examined. They observed that the viscosity of the binary mixture decreased by increasing temperature from 303.15 K to 343.15 K which is 30 °C to 70 °C at ambient pressure. It was also found that the viscosity is lower in a water rich mixture. The results for viscosity (η/mPa.s) for [$Bmim^+HSO_4^-$]-water mixture at different temperatures are listed in Table 2.3 (Bhattacharjee *et al.*, 2012).

Table 2-3 Experimental Dynamic Viscosity (η/mPa.s) for [$Bmim^+HSO_4^-$]-water binary mixture at different temperatures (Bhattacharjee *et al.*, 2012)

X_1 Water content	Temperature (K)				
	303.15 K	313.15 K	323.15 K	333.15 K	343.15 K
η/mPa.s					
0.0083	3464.8	1628.4	848.29	479.63	290.47
0.0950	2188.5	1070.2	574.42	333.16	206.27
0.2013	1351.0	686.70	380.33	226.51	143.38
0.3903	516.76	283.25	176.26	105.13	69.710
0.5924	138.81	83.980	53.969	36.546	25.786
0.7934	21.845	15.114	10.938	8.219	6.356
0.8988	5.838	4.375	3.401	2.724	2.234

The capability of 1-butyl-3-methyl-imidazolium hydrogen sulfate [$Bmim^+HSO_4^-$] in an aqueous solution to release [H^+], causes this IL to act as a Brønsted acid (Whitehead *et al.*, 2009). The hydrogen sulfate anion [HSO_4^-] can dissociate, which leads to the release of an [H^+] ion and this possesses substantial acidity to a slution. Hence, the acidity of this imidazolium-based IL can derive from the hydrogen sulfate anion (Whitehead *et al.*, 2007). Regarding the chemical features of 1-butyl-3-methyl-imidazolium IL, the dissociation of the $[Bmim]^+HSO_4^-$ in the presence of water follows the equilibrium presented in Equation 2.27.

$$[Bmim]^+ \ldots\ldots HSO_4^- \leftrightarrow [Bmim]^+ + H^+ + SO_4^{2-} \quad (2.27)$$

$$K = \frac{[\,Bmim]^+\,[\,H^+]\,[SO_4^{2-}]}{[[\,Bmim]^+ \ldots\ldots HSO_4^-]}$$

where K is the dissociate equilibrium constant. Based on Equation 2.27, by increasing the concentration of the ionic liquid, the concentration of $[H^+]$ will rise as well, which leads to higher acidity in the aqueous solution (Crowhurst *et al.*, 2003). It was found that when water was added to this imidazolium-based IL, H-bonding between the hydrogen sulfate anion (HSO_4^-) and the water molecules may affect the dissociation equilibrium (Dong *et al.*, 2009).

Ionic liquids have been utilized in research by Whitehead et al. (2004). They have described ionic liquids as 'green' leach solutions. They investigated the extraction of gold and silver from a sulfidic ore which contains Au (5.65 g/t) and Ag (18.72 g/t), using IL [$Bmim^+$ HSO_4^-] as a nonconventional solvent with thiourea as complexing agent and iron(III) sulfate as the oxidant at pH = 1, solid to liquid ratio of 1:4 in room temperature for 50 hours of leaching time. The comparative dissolution of gold and silver from the ore using an aqueous sulfuric acid H_2SO_4/thiourea/$Fe_2(SO_4)_3$ mixture and [$Bmim^+HSO_4^-$]/thiourea/$Fe_2(SO_4)_3$ have been reported. The results revealed that silver extraction from the ordinary sulfide ore was improved significantly for the ionic liquid (>60%) compared to aqueous sulfuric acid (<10%), but the gold extraction achieved was relatively similar (>85%) with the IL [$Bmim^+HSO_4^-$] and the H_2SO_4 aqueous system.

Furthermore, the recyclability of the IL [$Bmim^+HSO_4^-$] solution with activated carbon at room temperature have been investigated without decomposition or important change in extraction effectiveness (Whitehead *et al.*, 2004). Thus, recyclability and simplicity of synthesis offer a cost-effective method in the recovery of precious metals. Therefore, the application of imidazolium-based ILs in solventometallurgy can potentially offer an effective extraction of gold from sulfidic ores (Abbott *et al.*, 2015).

The IL [$Bmim^+HSO_4^-$] is soluble in water and can accumulate in environment. Thus, the toxicity of this IL has been investigated by El-Harbawi, (2014) on marine and freshwater fish. According to the obtained results by this researcher the IL [$Bmim^+HSO_4^-$] is practically non-toxic (El-Harbawi, 2014).

The extraction of copper from chalcopyrite investigated by McCluskey et al. (2002) with ionic liquid [Bmim]PF_4 and $Fe(BF_4)_3$ as the leaching agent. They used a mixture of [Bmim]PF_4 and

water with the ratio of 1:1, after 8 h an amount of 90% copper extraction achieved at 100 °C. Jenkin et al. (2016) investigated the use of deep eutectic solvents, a type of room temperature ionic liquid, to dissolve electrum by an oxidation and reduction process followed by the recovery of gold by electrodeposition.

Besides the use of ILs as alternative extractants, work has also led to progress in designing functional ILs referred to as "task-specific ionic liquids" which was invented by Davis (Abbott *et al.*, 2011). Task-specific ionic liquids (TSILs) consist of functional groups attached directly to the cation and/or anion structure (Ratti, 2014). The covalent attachment of some functional groups to cations/anions, or both, of an ordinary ionic liquid, imparts on it the capacity to function not only as a green solvent but also as a catalyst and a reagent in many chemical reactions (Ratti, 2014). Some practical functional groups that have been appended to imidazolium rings are listed in Figure 2.9.

Currently, there has been a large number of research reports on the use of ionic liquids, due to their environmentally friendly properties, as well as their variability and flexibility. The use of ionic liquids avoids the need for the strong mineral acids and high temperatures typically required for dissolving ores in conventional metallurgical processes. Thus, ionic liquids do not have the same drawbacks that had been reported in traditional methods, such as the consumption of large volumes of acid, high energy demands, corrosion of equipment and environmental concerns (Abbott *et al.*, 2011).

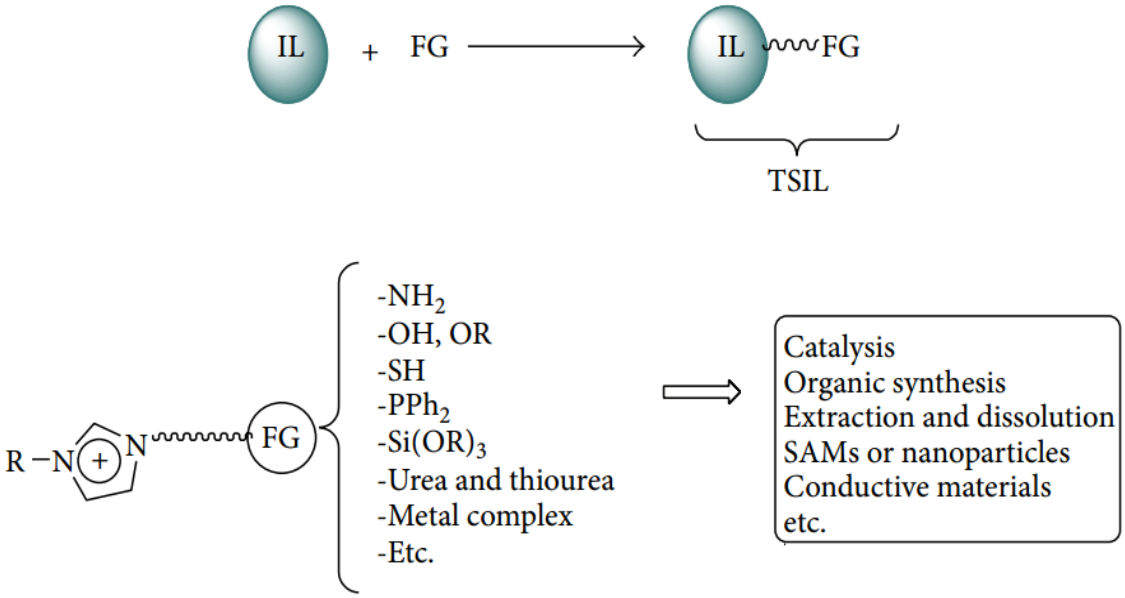


Figure 2.9 Task-specific ionic liquids (TSILs) (Ratti, 2014)

2.5 Recovery of gold from leachant (Pregnant solution)

After leaching, the gold must be recovered from the pregnant solution for further processing into elemental gold. Various techniques have been studied for the recovery of gold solution and these include precipitation, cementation, adsorption, solvent extraction, ion-exchange, and electrowinning processes.

2.5.1 Precipitation

The principle of the precipitation technique is based on the reduction-oxidation reaction between the target metals in the mother leach liquor and the zero valent pulverized base metal as elucidated in Equation 2.28. Typically, the precipitant solid base metal oxidizes to M^{2+} while gold ions reduce to the native state, Au^0 (Grosse *et al.,* 2003). Due to the simplicity, efficiency, and easiness of this method, it has been used commercially to recover gold and silver from leaching solutions. Copper, zinc, iron, and aluminum are the common precipitants which have been employed (Syed, 2012).

$$2\,Au^{+} + M^{0}_{solid} \rightarrow 2\,Au^{0} + M^{2+} \tag{2.28}$$

The process is not ideal, due to the tendency to precipitate other metals from the leach solution such as copper, lead and sulfur (less selectivity), as well as lengthy refining time, disposal problems and labor-intensive processes (Grosse *et al.,* 2003).

2.5.2 Cementation

Cementation is a special case of precipitation. Since 1890 the recovery of gold from cyanide pregnant leach liquor has been achieved with zinc cementation through a bedframe of zinc. Besides Zn, there are other metals that have been considered as cementing agents such as Fe, Cu, Mg, and Al (Lee *et al.,* 1997). Basically, there are two electrochemical half-reactions that occurres on the zinc particle's surface; 1) the cathodic deposition of gold and 2) the anodic decomposition of zinc powder (Syed, 2012). The cathodic and anodic half-reactions have been described respectively as follows:

$$2\,Au(CN)_2^{-} + 2\,e^{-} \rightarrow 2\,Au + 4\,CN^{-} \tag{2.29}$$

$$Zn + 4\,CN^{-} \rightarrow Zn(CN)_4^{-} + 2\,e^{-} \tag{2.30}$$

In this method the coexistence of other cations in the solution such as nickel, copper, lead, sulfur, arsenic, and antimony can have a deleterious effect on gold recovery due to utilizing the reagent (Wang *et al.,* 2007).

2.5.3 Adsorption (activated carbon)

One of the most popular adsorbents for the removal of desired metals from solution is activated carbon (AC). In 1951 adsorption on activated carbon (AC) was discovered by McQuiston and Chapman for the recovery of gold complexes with cyanide from pregnant solution. The recovery of precious metals through low cost activated carbon has been used broadly (Syed, 2012). Fundamentally, adsorption is an equilibrium separation means in which an adsorbate (target metal) is dispersed between the liquid and solid phase, which are the sample solution and adsorbent, respectively. The adsorbate can attach to the surface of adsorbent either chemically and/or physically. In chemisorption a chemical reaction between the surface and the adsorbate can happen, in which an electronic structure of bonding molecules or atoms is changed and new chemical bonds are generated at the adsorbent surface. While, in physical adsorption an electronic structure of molecules or atoms is scarcely altered in adsorption (Mckay, 1983).

Activated carbons have distinctive porous appearance and characteristics which make them a beneficial adsorbent. Their well-built permeable structure consists of not only hydrophobic graphitic construction layers on surface, but also hydrophilic functional groups. Moreover, AC has high adsorption capability because of the internal pore structure (Marsden & House, 2006). As a result, adsorption on AC has been recognized as one of the favorable recovery methods because of its advantages including easiness of operation, flexibility, simplicity, cost-effectiveness and technical applicability (Soleimani & Kaghazchi, 2008). Despite the benefits that this recovery method has it is not typically selective specifically for valuable metals. The adsorption of gold complexes on the AC can be affected by other base metals, especially copper probably through competitive adsorption (Soleimani & Kaghazchi, 2008).

2.5.4 Solvent extraction

Solvent extraction is a recovery process in which extractants are utilized in the removal of metals from the aqueous solution. Gold is one of the main metals to which the solvent extraction technique is applied as a separation method, in order to achieve high purity of the

precious metal from leach solutions (Katsuta *et al.*, 2016). Generally, it uses two immiscible solvents -the pregnant leach liquor and an appropriate organic solvent.

The primary mechanism of this technique is the transfer of a low polarity gold complex from the leach liquor to a water-immiscible organic solvent (Grosse *et al.,* 2003). The subsequent selective stripping of the extracted precious metal complex from the organic phase into a small volume of the aqueous phase can also improve the separation factor (Aly & Hamza, 2013). Kordosky et al. (1992) have reported on solven extraction of gold from cyanide solution. The recovery of gold was 86% with N,N-bis(2-ethyl hexyl), 18 h running time at pH = 9. The advantages of this method include high selectivity, high purity, complete metal recovery, and low capital costs (Won *et al.*, 2014).

2.5.5 Ion-exchange

Ion-exchange resins are employed for the separation of noble metals from solution (Schoeman *et al.*, 2012). These resins have multiple similarly charged functional groups that can be exchanged from the leach liquor with the target metal ions that are of opposite charge (counterions). Generally, ion-exchanging resins are synthetic polymers in which hydrocarbon groups make up a permeable three-dimension structure. This 3-D construction allows ions in the leach liquor to move freely through the polymeric network. They mainly have two parts: an organic structural component and functional groups bound to the organic framework (Syed, 2012). The functional groups can be altered to provide selectivity for specific ions or complexes. Typically ion-exchanging resins are categorised based on the type of ions they can exchange. Positively charged ions can be exchanged by cationic resins, whereas, negatively charged ions can be exchanged by anionic resins, and they include:

- Strong acid cation resin which employs functional groups like sulphonate (SO^{-}_{3}).
- Weak acid cation resin which has carboxylic acid ($RCOO^{-}$) as functional groups.
- Strong base cation resin which contains quaternary amine as its functional group.
- Weak base cation resin which has amine functional groups (Aly & Hamza, 2013).

The cyanide complexes with gold(III) have a negative charge, thus a strong basic resin with a crosslinked polystyrene matrix and a quaternary amine as its functional group have been investigated. An amount of (>80%) gold recovery was achiveved from the cyanide leach solution after 48 h (Schoeman *et al.*, 2012).

After the extraction, ion-exchange resins can be stripped chemically from desired adsorbed ions by using acid, base, salts or complexing agents. This step has been called elution. The elution process by inexpensive ions like chloride and carbonate, as well as the fully eluted polymer, can be recycled up to for four times with high yield (Grosse *et al.,* 2003). Low energy requirements, rapid adsorption kinetics, high equilibrium loadings, reusability and low impact on the environment are the main advantages of this technique (Schoeman *et al.,* 2012). However, these resins have low selectivity for removing gold, low sorption capacity , and also have high costs that include the synthesis/purchase of a polymeric matrix and the introduction of special functional groups which are not economically and environmentally desirable (Cyganowski *et al.,* 2017).

2.5.6 Electrowinning

Recovery of metal ions from the pregnant leach liquor by applying an electric current to an electrolytic unit is known as electrowinning. Electrochemical technology offers an efficient and selective means for gold recovery from leach liquor. The process is based on migration of metal ions from an electrolyte solution to the cathode to form a metallic deposition (Grosse *et al.,* 2003). The reduction of metal ions M^{n+} to a metallic state $M_{(s)}$ at the cathode can be represented by Equation 2.31.

$$M_{(aq)}^{n+} + ne^- \rightarrow M_{(s)} \tag{2.31}$$

Cathodic removal of gold offers safety and versatility by using simple equipment such as an electroplating bath, an insoluble anode and an appropriate cathode to deposit metal on (Paul *et al.,* 2005). The electrochemical treatment of metal ions has several advantages as it provides high selectivity, good environmental compatibility, better enrichment efficiency, low operating cost and lower chemical reagents consumption than the conventional chemical precipitation method (Marsden & House, 2006). The electrochemical method can be challenging in low-grade gold solutions along with existence of large amounts of undesirable cations such as Cu(I) and Cu(II). These unwanted cations can be deposited on the cathode which leads to a polluted and depreciated metallic product (Grosse *et al.,* 2003).

2.6 Gold dissolution models

Leaching is a reaction between solid particles and liquid which is defined as a heterogeneous reaction. The reaction occurs at the interface of the fluid and solid (ore particle) phase. A diffusion layer is established at the separation line between the solid and liquid parts, presented in Equation 2.32 (Koleini *et al.*, 2010).

$$aA_{(\text{fluid})} + bB_{(\text{particle})} \rightarrow product \tag{2.32}$$

Leaching of precious metal(s) from the mineral grains (solid phase) takes place through a number of distinct reaction steps as shown in Figure 2.10.

1) Diffusion of a reagent in the bulk fluid through the diffusion layer surrounding the particle to the surface of the solid,
2) Adsorption of the reagent onto the surface of the mineral (solid),
3) Chemical or electrochemical reaction between the reagent and the mineral grains involving dissolution reactions,
4) Desorption of the product from the mineral surface,
5) Transmission of the product through the diffusion layer or product layer formed as a result of reaction with the reagent (Baba *et al.*, 2012).

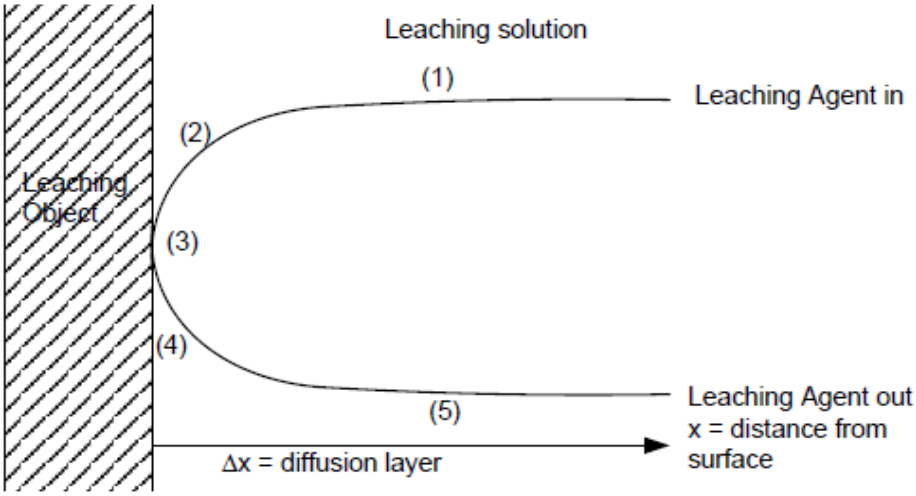


Figure 2.10 Basic sketch of a leaching process (Baba *et al.*, 2012)

The rate of a leaching reaction can be enhanced through mixing the solid/liquid mixture and raising the concentration of the active reagents in the leaching solution. Moreover, by reducing the ore particle size it increases the exposed contacting surface area of the mineral to the liquid

part. In a well-mixed system, reducing particle size may lead to an increase in the reaction rate (Baba *et al.*, 2012). Furthermore, the solid to liquid ratio or pulp density can have an effect on the thickness of the solution, which also influences gold leaching or the kinetics of the reaction. It has been found that either too high or too low pulp densities can affect the gold leaching performance in an undesirable way. It is obvious that excessively dense pulps (solids) hinder mass transfer, whilst dilute pulps results in a loss of ore leaching residence time, as well as high reagent addition rates (Koleini *et al.*, 2010).

In hydrometallurgy, the use of the shrinking core model for the solid-liquid systems has been extensively examined (Dicinoski *et al.*, 2000). Thus, previous research acknowledges that kinetics of the gold leaching follow the shrinking core model in leaching experiments using gold-bearing ore and concentrated gold ore (Senanayake, 2004).

The dissolution rates of a sulfidic gold ore can therefor be examined on the basis of the shrinking core model under the hypothesis that the ore consists of homogeneous spherical solid particles that react with the fluid (reagent) isothermally. The essential premises of the shrinking core model are that the rate of reaction can be controlled by diffusion of a dissolved reagent or product from (or to) the bulk fluid to (or from) the solid-solution interface through a boundary layer; the rate can be controlled by some chemical reaction taking place at the solid-solution interface; the rate can be controlled by diffusion of a dissolved reactant or product through the product layer of inert mineral or solid product formed during the reaction.

Mathematical models for dissolution with the hypothesis of a shrinking core model can be expressed as follows:

If the rate of the chemical reaction at the boundary phase is considerably larger than the diffusion rate of reagent through the boundary phase, diffusion of the oxidant through the product layer is the rate determining step and Equation 2.33 can be applied (Koleini *et al.*, 2010).

$$1-3(1-X)^{2/3}+2(1-X) = k_d\, t \qquad (2.33)$$

On the contrary, if the rate of the chemical reaction at the boundary phase is by far slower than the diffusion rate of reagent through the boundary phase, the reaction rate is controlled by a chemical surface reaction and Equation 2.34 can be applied.

$$1-(1-X)^{1/3} = k_r\, t \qquad (2.34)$$

where X is the fractional conversion; t is time, k_d and k_r are rate constants for the diffusion and chemical reaction, respectively. Generally, the rate of a reaction can be limited by the slowest step of the model and be controlled by it (Koleini *et al.*, 2010).

Dong et al. (2009) studied kinetics of copper extraction by IL [$Bmim^+HSO_4^-$]-water solution 20% (v/v) from chalcopyrite. The results in the range of temperatures from 40 to 90 °C revealed that the apparent activation energy was 69.4 kJ/mol (Dong *et al.*, 2009). According to Arrhenius theory the high activation energy of 69.4 kJ/mol, suggested that the copper leaching was controlled by diffusion through a product layer followed by electrochemical surface reaction. In another study by Aguirre et al. (2016), the kinetics of chalcopyrite leaching to extract copper was investigated in a 20% (v/v) IL [$Bmim^+HSO_4^-$]-water solution in the temperature range of 30–90 °C. The activation energy was determined to be E_a = 60.4 kJ/mol. The magnitude of E_a indicates that the reaction was limited by chemical reaction. Moreover, a kinetic study for gold leaching from concentrate pyrite with acid thiourea medium was reported by Gabra (1984). The effect of temperature in the range of 20-60 °C was examined. The activation energy was determined as E_a = 8.53 kJ/mol. Low activation energy revealed that the kinetics of leaching gold from pyrite in this system was controlled by diffusion (physical process) (Li & Miller, 2006).

In another work, the kinetics of gold dissolution in acidic thiourea medium in pH range of 1-2 with ferric sulfate as the oxidant investigated by Li and Miller (2007). They observed that under surface reaction the rate of the dissolution reaction was one-fourh and minus one-fifth with respect to thiourea concentration and hydrogen ion concentration, respectively. The reaction was independent of ferric ion concentration. The apparent activation energy was 58.1 kJ/mol and the empirical kinetic described by the rate expression as: $dC_{Au} / dt = k [Tu]^{0.25} [H^+]^{-0.2}$ (Li & Miller, 2007).

It is therefore propose to use the shrinking core model to fit data from the gold extraction studies.

2.7 Design of experiment

Design of experiments (DOE) is a statistical means to improve the investigation plan to maximize the overall knowledge and understanding of the process using a minimum of resources. Generally, DOE can examine several factors at the same time in a systematic manner. Recently, DOE has been applied extensively in the modern industrial processes, as

well as various scientific and engineering fields in order to develop new products/procedures like manufacturing, management processes and engineering designs in a cost-effective and assured manner (Montgomery, 1984).

In this statistically designed method, the initial stage is screening, followed by central composite design (CCD) in conjunction with response surface methodology (RSM). In screening, several operating factors can be considered in factorial design to discover factors that have considerable effect on the measured response. In fact, the significance of each variable and their probable interactive effects were examined using normal probability plot and pareto chart.

Normal probability plot of effects

The process of screening (finding statistically significant studied factors) in which unreplicated factorial design has been applied, occasionally yielding high order interactions. In order to estimate the important effects according to their amounts and calculating their growing probabilities, normal probability plot was constructed based on the coefficient effects (Daniel, 1959). A normal probability plot is a plot of the effect of the actual value evaluations versus their accumulative normal probabilities. All the non-significant effects that are negligible usually dispersed normally alongside the straight line on the plot, with mean zero and variance (σ^2). Contrary, the important effects have nonzero means and are not located alongside the straight line. It should be mentioned that the more important the effect, the further away it from the straight line on the plot (Montgomery, 1984).

Pareto chart

Pareto chart, named after Vilfredo Pareto, is a type of chart by frequencies 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 the line. The first incarnation on the left-hand side has the highest bar compare to other bars and shows the most significant variable of the chart (Wilkinson, 2006). Variances are arranged in their descending order to identify the largest opportunities for improvement and to separate a 'critical few' from the trivial many. The horizontal line in the Pareto diagram indicates the minimum statistically significant effect magnitude for 5% significance level, while the vertical column lengths are proportional to the degree of significance for each effect. Any effect or interaction that go above the horizontal line is reflected significant (Wilkinson, 2006).

There are two types of optimization methods: the standard one variable at a time (OVAT) and multivariate statistically based method entitled response surface methodology (RSM). In the OVAT approach, only a unique factor is varied while others are kept constant. Its main disadvantage is that it ignores the probable interaction between different independent factors that would otherwise have affected the response. Moreover, it requires more experiments which leads to consumption of more chemical reagents. Consequently, this technique is often laborious, expensive, inefficient and time-consuming (Candioti *et al.*, 2014). The restrictions of conventional methods can be overcome by applying a multivariate statistical technique.

RSM is a statistically designed method in which several independent variables are simultaneously varied in a defined number of combined treatments. The ultimate objective of RSM is to consider any plausible interaction between the controlled variables and also to gain the optimum operating condition by the least number of experiments. Hence, there are several advantages of RSM over OVAT, such as that it is fast to implement and cost-effective (Candioti *et al.*, 2014). At the time when the significantly influential factors are identified, they can then be optimized by RSM (Candioti *et al.*, 2014). Figure 2.11 presents the flow chart which illustrates the sequential steps in DOE.

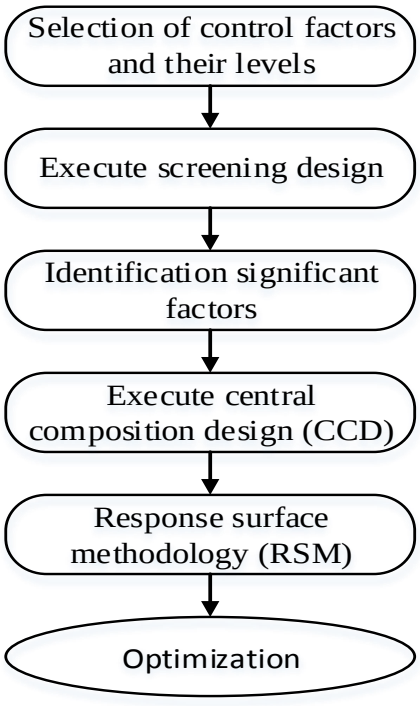


Figure 2.11 A flow chart which illustrates the sequential steps in DOE

2.8 Literature overview

In this review, the chemistry of gold, the important parts of main gold processing were evaluated, including leaching methods and different lixiviants used for gold extraction and their limitations were also discussed. The possibility of using ionic liquids as an emerging solvent to extract gold was assessed. The gold recovery strategies were evaluated. A brief description of design of experiment and response surface methodology was presented which is a potential alternative to the classical approach of varying one factor a time while others are held constant.

3 Materials and Experimental Methods

This chapter describes the materials used, as well as the experimental and analysis techniques employed in this study.

3.1 Materials

3.1.1 Refractory sulphidic gold ore

The ore used in this study was low grade gold tailings, rich in sulphides and refractory in nature obtained from the Ergo Mine (DRDGOLD Limited, 2013). The Ergo process reprocesses gold mine tailing dumps in the Witwatersrand basin. Figuir 3.1 illustrates the metallurgical process employed at the Ergo plant. The sample used was collected from the flotation concentrate before additional milling and subsequent cyanide leaching.

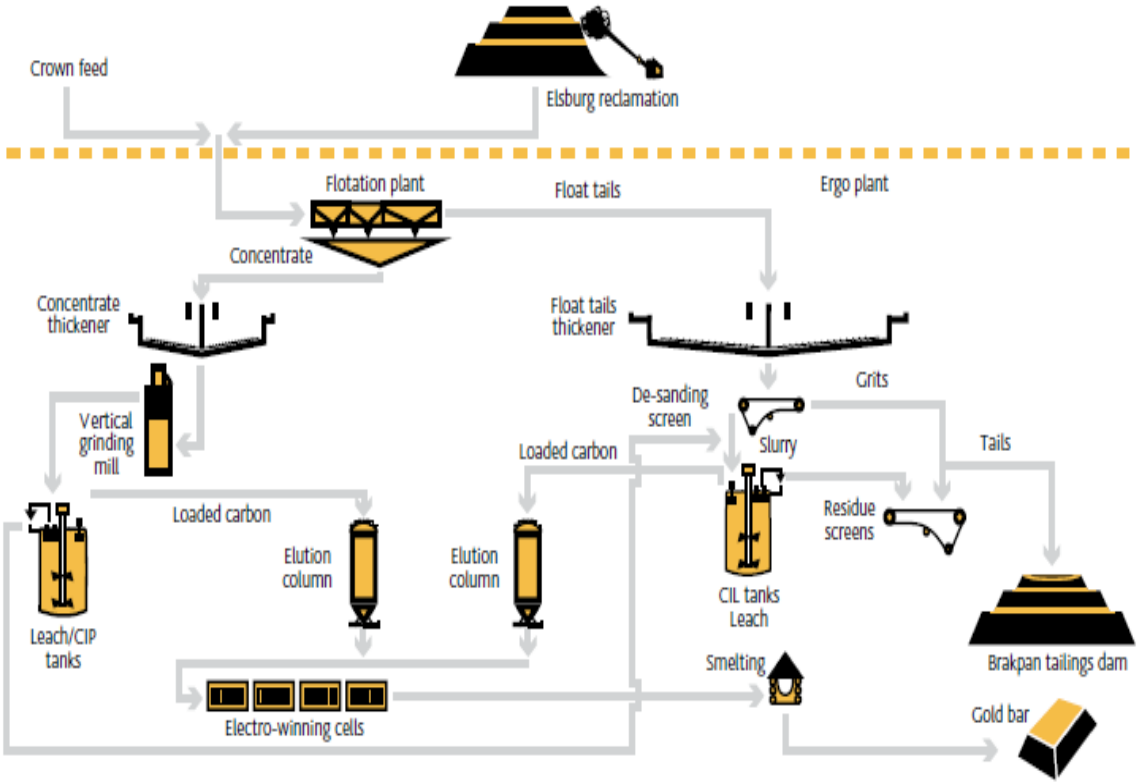


Figure 3.1 Metallurgical process employed at the Ergo plant (DRDGOLD Limited, 2013)

The as-received material were hard lumps of solids and was dry milled in a roller ball mill to break up the conglomerates. The fine material was subsequently dried in an oven for 1 h at 105 °C to remove any moisture. The dried sample was blended and classified into different size fractions using an electronic sieve shaker (Model ES 200) with stainless steel sieves. The finest

size fraction (-45 µm) was used in the leaching experiments due to greater exposed surface area for the experiments, and this contributed approximately 10% of the mass of the original sample.

The collected flotation concentrate ore were characterised using X-ray diffraction (XRD) by Mintek (Dworzanowski, 2018) and the minerology of this refractory sulphidic gold ore is presented in Table 3.1.

Table 3-1 Mineralogy of refractory sulphidic gold ore (Dworzanowski, 2018)

Mineral	Chemical Formulae	Mass%
Quartz	SiO_2	45.13
Pyrite	FeS_2	36.33
Muscovite	$KAl_2(Si_3Al)O_{10}(OH,F)_2$	5.34
Chlorite	$(Mg,Fe^{2+})_5AlSi_3Al_2O_{10}(OH)_8$	4.11
Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$	4.07
Goethite	$Fe^{3+}O(OH)$	2.01
Rutile	TiO_2	0.67
Biotite	$K(Mg,Fe^{++})_3[AlSi_3O_{10}(OH,F)_2$	0.46
K-feldspar	$KAlSi_3O_8$	0.28
Plagioclase	$(Na,Ca)(Si,Al)_4O_8$	0.41
Diopside	$CaMgSi_2O_6$	0.18
Chalcopyrite	$CuFeS_2$	0.38
Arsenopyrite	FeAsS	0.33

Particle-size distribution plays an important role in most metallurgical processes. This is because the mineral composition has been known to vary with particle sizes. The mineralogical variance within an ore affects its reactions and behavior in different acidic or basic media. This arises due to the differences in the acid/base-mineral interactions of the individual minerals existing within the ore. Knowing the chemical composition of the component minerals within the ore and the particle size distribution would, therefore, be beneficial in the understanding of the amount of metals dissolved during the leaching process (Dworzanowski, 2018).

The sample provided by DRD Gold (Ergo Mine) contained 2.38 g/t of gold in the flotation concentrate and the gold content per size fraction is given in Table 3.2 (Dworzanowski, 2018).

Table 3-2 Assay by size analysis of gold (Dworzanowski, 2018)

Size fraction (µm)	Mass (%) Feed	Flotation Feed (Au g/t)	Flotation Concentrate (Au g/t)
+45	55.66	0.27	3.04
+25	14.08	0.26	2.73
+10	20.98	0.35	2.31
-10	9.27	0.42	2.05

The difficulty in treating refractory sulfidic low grade gold ore is that the ultrafine particles of gold are encapsulated and distributed inside the ore matrix. Figure 3.2 shows the locked gold in a pyrite particle. Moreover, Figure 3.3 confirm that most of the gold is locked inside the ore structure.

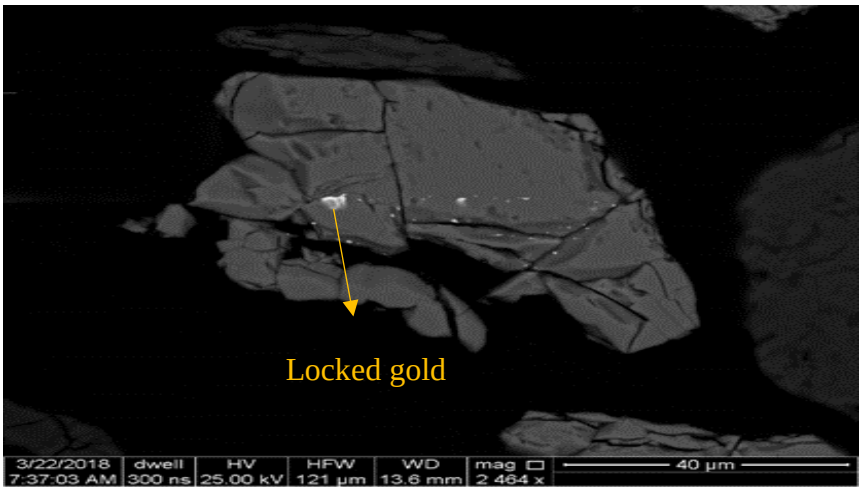


Figure 3.2 Gold locked in pyrite particle (Dworzanowski, 2018)

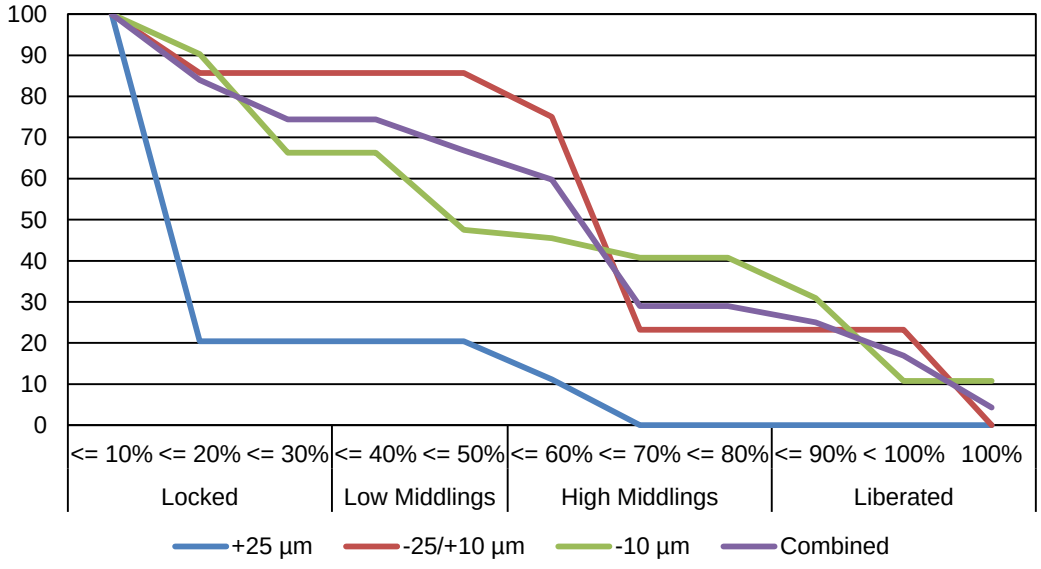


Figure 3.3 Ergo flotation concentrate gold liberation by fraction size (Dworzanowski, 2018)

3.1.2 Chemical reagents

All required chemicals and reagents were purchased from Merck and Sigma Aldrich. The reagents used were all of analytical grade. They were used as received without further purification. Imidazolium ionic liquids, 1-butyl-3-methyl-imidazolium hydrogen sulfate [$Bmim^+HSO_4^-$] and 1-butyl-3-methylimidazolium trifluoromethansulfonate [$Bmim^+CF_3SO_3^-$], were used as solvents with thiourea $SC(NH_2)_2$ in the presence of ferric sulfate $Fe_2(SO_4)_3$, as oxidant for gold extraction from the refractory sulfidic low-grade gold ore described above. The pH of the IL solution was controlled using sodium hydroxide and/or hydrochloric acid.

3.2 Gold leaching experiments

The oxidative leaching experiments envolved extracting gold from the refractory sulfidic low grade gold ore (pyrite concentrate) in an aqueous solution of ILs as leaching solvent in the presence of $Fe_2(SO_4)_3$ as an oxidant, using thiourea as a complexing agent. In order to investigate the effect of the type of discrete anion in dialkylimidazolium cation, different anions such as (HSO_4^-) and ($CF_3SO_3^-$) were evaluated to determine the effect of the anion in the IL for gold extraction. The IL was mixed with deionized water to make solutions with different IL concentrations. The IL-water mixture has added benefit, e.g., the high viscosity of pure IL (100%) decreased in the mixture solution. Thereafter, according to the solid to liquid ratio, the desired amount of the ore sample, thiourea and ferric ions were added to the IL-water solution in 50 ml schott bottles. The solution was shaken for a specific time and at a set temperature in an incubator shaker. After the set time elapsed, the samples were filtrated and the leach liquor was analyzed for its gold content using atomic absorption spectroscopy (AAS) and the extraction was calculated (Appendix A).

3.2.1 Determining the influence of operating parameters on gold extraction: Factorial design

To identify the factors that have considerably large effect on gold extraction and the interactions amongst them, a half fractional factorial design of 2^{5-1} was performed. All the controlled factors were evaluated at three levels, low level, centre point (the mid-point between high and low level of the factor) and high level which are represented as -1, 0 and +1, respectively. The experimental design factors and their levels are tabulated in Table 3.3.

Table 3-3 Experimental factors and levels for operating parameters

Factors	Parameter	Low level (-1)	Centre point (0)	High level (+1)
A	IL type	[$Bmim^+SF_3SO_3^-$]	[$Bmim^+HSO_4^-$]	[$Bmim^+HSO_4^-$]
B	IL Conc.	33% IL	55.5% IL	78% IL
C	S:L ratio	1:8 (12.5%)	1:6 (18.7%)	1:4 (25%)
D	Temperature	35 °C	55 °C	65 °C
E	Time	17 h	27.5 h	38 h

In each experiment, an appropriate amount of the refractory sulfidic low grade gold ore (fraction size -45 µm), 20 g/kg ore of thiourea as complexing agent and 1 g/kg ore of iron (III) sulphate as oxidant were added to 10 ml mixed solution of different concentration of ILs with deionized water to obtain the required solid to liquid ratio of 1:4, 1:6 and 1:8 in the 50 ml schott bottles. The solid contained the ore, thiourea and $Fe_2(SO_4)_3$ and the liquid was IL-water solution with different concentrations of the ILs. The ore sample was thoroughly homogenised and it was re-homogenised for each test. This was done to ensure the representative samples corresponded to each other for every test. The pH of the leaching mixture was adjusted to pH = 1 by adding sodium hydroxide and/or hydrochloric acid. The bottles were then incubated in a platform shaking incubator at 250 rpm shaking speed, and the temperatures were adjusted based on the experimental design (Table 3.4).

The acidic pH = 1 was chosen because of the reagents, thiourea (complexing agents) and ferric ion (oxidant) used in this study. To avoid rapid thiourea degradation, as well as ensuring the stability of thiourea, an acidic solution is required. In acidic medium, the aqueous form of thiourea act as a ligand to form a stable cationic complex with gold. Moreover, ferric ions are stable at pH< 2 and precipitate as hydroxyl species (ferric hydroxide) as the pH increases (Whitehead *et al.*, 2007).

Table 3-4 Factorial design for experimental runs

Runs	level of variabls				
	A IL type	B IL% Conc.	C S:L ratio	D Temp. (°C)	E Time (h)
1	$BmimSF_3SO_3$	33	1:8	35	38
2	$BmimHSO_4$	33	1:8	35	17
3	$BmimSF_3SO_3$	78	1:8	35	17
4	$BmimHSO_4$	78	1:8	35	38
5	$BmimSF_3SO_3$	33	1:4	35	17
6	$BmimHSO_4$	33	1:4	35	38
7	$BmimSF_3SO_3$	78	1:4	35	38
8	$BmimHSO_4$	78	1:4	35	17
9	$BmimSF_3SO_3$	33	1:8	65	17
10	$BmimHSO_4$	33	1:8	65	38
11	$BmimSF_3SO_3$	78	1:8	65	38
12	$BmimHSO_4$	78	1:8	65	17
13	$BmimSF_3SO_3$	33	1:4	65	38
14	$BmimHSO_4$	33	1:4	65	17
15	$BmimSF_3SO_3$	78	1:4	65	17
16	$BmimHSO_4$	78	1:4	65	38
17	$BmimHSO_4$	55	1:6	55	27.5
18	$BmimHSO_4$	55	1:6	55	27.5
19	$BmimHSO_4$	55	1:6	55	27.5
20	$BmimHSO_4$	55	1:6	55	27.5

3.2.2 Experimental description for central composite design

Central composite design (CCD) was used to design the experiments to gather results for fitting a second order response to obtain response surface plots. The design for CCD consists of the following three parts:

- Factorial points: 2^k factorial design whose factors' levels are coded as $-1, +1$.
- Axial points: An axial portion consisting of $2k$ points arranged so that two points are chosen on the axis of each control variable at a distance of λ from the design centre.
- Centre point n_c.

Hence, the total number of design points in CCD design can be calculated using Equation 3.1:

$$n = 2^k + 2k + n_c \quad (3.1)$$

where k is the number of factors, and n_c is the number of centre point replications (Obeng *et al.*, 2005).

The number of centre point replications, n_c, for the three factors studied (k = 3) was calculated using the following Equation (n_c= 6) (Montgomery, 1984):

$$n_c \cong 0.8385\ (2^{k/2} + 2)^2 - 2^k - 2k \quad (3.2)$$

α-values depend on the number of variables to be tested and can be calculated from Equation 3.3,

$$\lambda = (2^k)^{1/4} \quad (3.3)$$

For instance, in this case, the number of tests for the CCD for k = 3, $\lambda = \sqrt{3}$, n_c = 6 is 20 runs**.**

For the three variables under consideration, a second-order polynomial regression model has been proposed, with Equation 3.4 as follows:

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j + \varepsilon \quad (3.4)$$

where y is the predicted response, β_0, β_i, β_{ii}, and β_{ij} are the coefficients for intercept, coefficient of linear effect, coefficient of quadratic effect and coefficient of interaction effect, respectively, ε is the term that represents other sources of variability not accounted for by the response function, and X_i and X_j are coded independent variables.

Based on the result of the initial factorial design (screening stage) it was noticed that the lowest concentration of IL (33% IL) achieved the higher gold extraction. Therefore, in CCD design the IL concentration were lowered even further to 5, 10, 15, 20, 25% IL to examine whether even more gold extraction could be achieved or not. All factors studied (-1, +1, 0, - λ, + λ) are presented in Table 3.5.

Table 3-5 Design levels for the CCD analysis

Variable		Level of variable				
		Lowest - λ	Low -1	Centre 0	High +1	Highest + λ
IL% Conc.	X_1	5%	10%	15%	20%	25%
S:L ratio	X_2	1:10	1:8	1:6	1:4	1:2
Temperature	X_3	25 °C	35 °C	48 °C	60 °C	70 °C

An appropriate mixture amount (determined by S:L) of the ore (fraction size -45 µm), thiourea (20 g/kg ore) and iron(III) sulphate (1 g/kg ore), was added to a 10 ml mixture solution of IL [$Bmim^+HSO_4^-$] and deionized water in the 50 ml schott bottles in each experimental run. The pH of the mixture was adjusted at pH = 1 by adding 2 M sodium hydroxide, since the initial IL [$Bmim^+HSO_4^-$]-water solution pH was less than 1. The bottles were then shaken in a platform incubator at 250 rpm shaking speed, and the desired temperature was adjusted according to the experimental design for 24 hours leaching time (Table 3.6). Both studied ILs could extract gold, for the follow-up experiments the IL 1-butyl-3-methyl-imidazolium hydrogen sulfate [$Bmim^+HSO_4^-$] was chosen since it was cheaper than the other IL [$Bmim^+CF_3SO_3^-$], and 24 hours as an arbitrary convenient experimental period. The samples were analysed for its gold content as previously described.

Table 3-6 Central composite design: Experimental runs

Coded level of variables			Actual level of variables		
A IL Conc.	B S:L ratio	C Temperature	A IL% Conc.	B S:L ratio	C Temp. (°C)
Factorial points					
-1	-1	-1	10	1:8	35
+1	-1	-1	20	1:8	35
-1	+1	-1	10	1:4	35
+1	+1	-1	20	1:4	35
-1	-1	+1	10	1:8	60
+1	-1	+1	20	1:8	60
-1	+1	+1	10	1:4	60
+1	+1	+1	20	1:4	60
Axial points					
-1.68	0	0	5	1:6	48
+1.68	0	0	25	1:6	48
0	-1.68	0	15	1:10	48
0	+1.68	0	15	1:2	48
0	0	-1.68	15	1:6	25
0	0	+1.68	15	1:6	70
Centre points					
0	0	0	15	1:6	48
0	0	0	15	1:6	48
0	0	0	15	1:6	48
0	0	0	15	1:6	48
0	0	0	15	1:6	48
0	0	0	15	1:6	48

3.2.3 Fitting of a gold leaching model

In order to determine the kinetics of the gold leaching, time extraction experiments were performed and the data fitted to the shrinking core models. In each experiment, 1.25 g of the ore (fraction size -45 µm), 20 g/kg ore of thiourea and 1 g/kg ore of iron (III) sulphate were used. These were added to a 10 ml mixture solution of IL [$Bmim^{+}HSO_4^{-}$] with deionized water (20% v/v IL) with a solid to liquid ratio of 1:8 at pH = 1. The bottles were then shaken in a platform incubator at 250 rpm, in the temperature range of 20–65 °C. A bottle of each sample were removed at different time intervals (20 min, 40 min, 1 h, 3 h, 5 h, 7 h and 12 h) throughout the experiment. The pregnant solution was filtered and analysed as described before.

Additionally, the ore and the solid residue were analysed using scaning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy to observe changes before and after leaching.

4 Results and discussion

The feasibility of using ionic liquids in the extraction of gold from refractory sulfidic low-grade tailing ore was investigated using design of experiments for screening followed by response surface methodology and additional experiments to determine the kinetics.

4.1 Identification of significant operating parameters on gold extraction

Different experimental parameters were tested in half-fractional factorial design, including ionic liquid type and concentration, solid to liquid ratio, temperature and leaching time to identify significant operating parameters and their effect on extraction. The experimental results given in Table 4.1 were used to evaluate the main and interaction effects of the process parameters.

Table 4-1 Results of half-fractional factorial design experimental runs of gold extraction

Runs	[c] Control Factors					% Au Extraction
	A IL type	B IL% Conc.	C S:L ratio	D Temp. (°C)	E Time (h)	
1	$BmimSF_3SO_3$	33	1:8	35	38	27.8
2	$BmimHSO_4$	33	1:8	35	17	26.7
3	$BmimSF_3SO_3$	78	1:8	35	17	10.4
4	$BmimHSO_4$	78	1:8	35	38	5.7
5	$BmimSF_3SO_3$	33	1:4	35	17	18.7
6	$BmimHSO_4$	33	1:4	35	38	14.7
7	$BmimSF_3SO_3$	78	1:4	35	38	4.8
8	$BmimHSO_4$	78	1:4	35	17	2.6
9	$BmimSF_3SO_3$	33	1:8	65	17	43.7
10	$BmimHSO_4$	33	1:8	65	38	44.1
11	$BmimSF_3SO_3$	78	1:8	65	38	23.5
12	$BmimHSO_4$	78	1:8	65	17	25.2
13	$BmimSF_3SO_3$	33	1:4	65	38	28.3
14	$BmimHSO_4$	33	1:4	65	17	32.2
15	$BmimSF_3SO_3$	78	1:4	65	17	18.0
16	$BmimHSO_4$	78	1:4	65	38	10.1

[c] The actual factor levels, coded as values of -1 and +1 in the table were as follows: for type of ILs (A): $BmimSF_3SO_3$ (-1) and $BmimHSO_4$ (+1); IL concentration (B): 33% IL (-1) and 78% IL (+1); S:L ratio (C): 1:8 (-1) and 1:4 (+1); temperature(D): 35 °C (-1) and 65 °C (+1); time (E): 17 h (-1) and 38 h (+1).

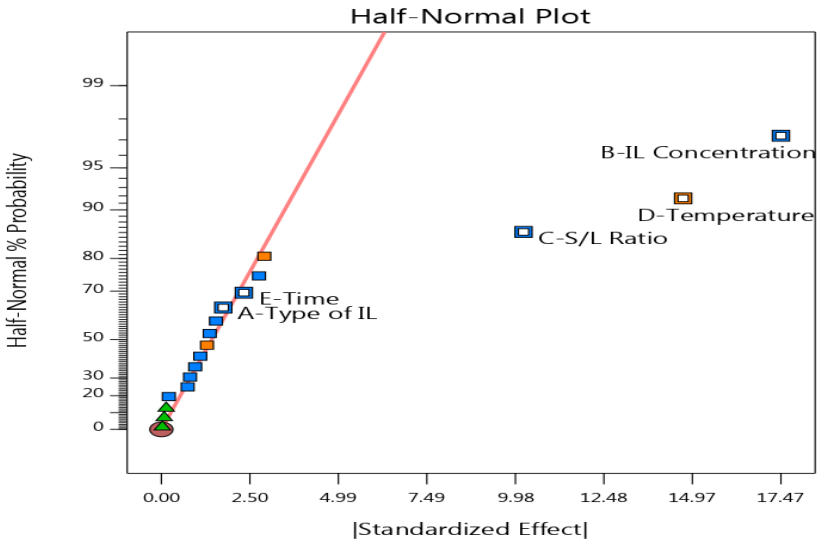


Figure 4.1 Half-Normal plot of effects of the main and two-factor interactions; A, B, C, D, E are main factors

The evaluation of the main effects of the studied factors and their interaction terms at the same time is illustrated on a half-normal probability plot of the gold extraction (Figure 4.1). All the unimportant effects are typically spread with mean zero and variance σ^2 and tend to lie along the straight line on the plot. Significant effects are situated far away from the straight line with non-zero means. The greater the significant effect, the further away it is from the straight line. From this statistical analysis, the observed significant effects are the following main factors: concentration of IL (B), solid to liquid ratio (C), and temperature (D).

A normal first-order polynomial model (fitted model) between significant factors and the response was developed to depict the dependence of the response on the significant factors in Equation 4.1.

The model is expressed below as:

R = (overall constant) + (linear effects)

The final Equation in terms of coded factors is:

$$R\ (\text{Au Yield}) = +\ 21.02 - 8.48\ B_b - 4.86\ C_c + 7.11\ D_d \qquad (4.1)$$

where R is the measured response which is yield of gold, B_b, C_c, and D_d are the coefficients constants (+1 and -1) for the studied factors B (concentration of IL), C (solid to liquid ratio), and D (temperature), respectively.

In Equation 4.1 the positive sign of contrast for the main factor D (temperature) indicate the synergistic effects on %E, while the negative sign of the coefficient for the main factors B

(concentration of IL) and C (solid to liquid ratio) represents an antagonistic effect. In other words, the negative signs in the variables of the prediction model equation have an opposite relation with the studied response, which means in order to maximize the gold extraction, these factors must be maintained at low levels. The positive signs have a direct relation, which means that these factors must be kept at high levels. In addition, the size of the regression coefficients in the equation denotes the degree of significance of each independent variable in the order of descending significance with respect to the influence on the desired measured response %E, which is concentration of IL (B) > temperature (D) > solid to liquid ratio (C).

The results obtained from the half-normal probability plot of effects (Figure 4.1) are confirmed with a Pareto chart as shown in Figure 4.2. The purpose of the Pareto chart is to highlight the most important among a set of factors. 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 exceeds the horizontal line (Bonferroni limit) is considered significant. The sequence of the significant main and interaction effects with respect to decreasing influence on the desired measured response %E was in agreement with that obtained from the half-normal probability plot of standardized effects, namely concentration of IL (B) > temperature (D) > solid to liquid ratio (C). Analysis of the individual factors on the Pareto chart also confirmed that the IL concentration, solid to liquid ratio and temperature were statistically significant since they exceeded the critical value line.

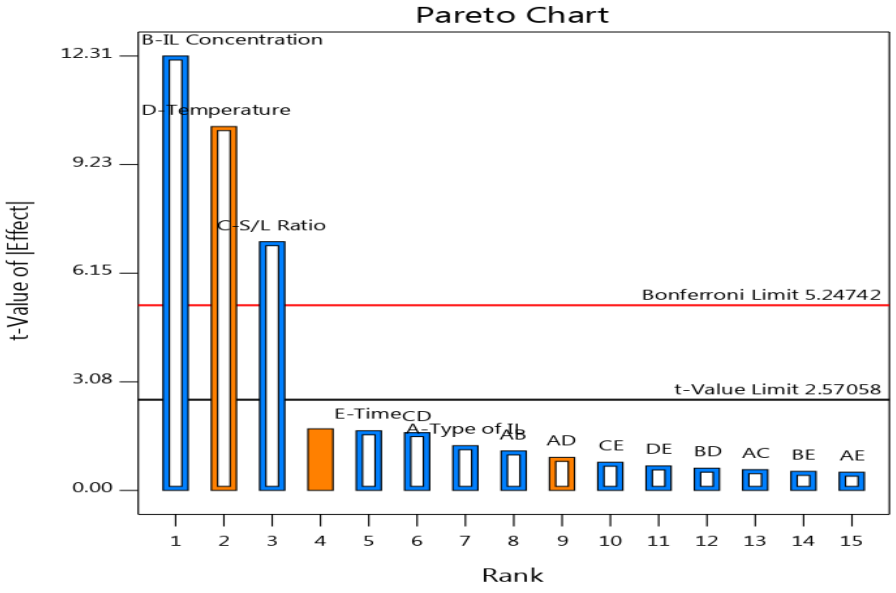


Figure 4.2 Pareto chart illustrating significance of main and interactive effects of A: Type of IL, B: IL Concentration, C: S/L ratio, D: Temperature, E: Time, the interactions: AB, AD, CE, DE, BD, AC, BE, AE.

Test for curvature using centre points

The response conforming to the treatments at precisely the middle of the high and low level of the controlled factors is the centre points (Table 4.2). Conducting multiple repeats at this point is required to study the curvature or nonlinearity in the model. Curvature is only meaningful for quantitative factors. Therefore, this test is to examine whether the fitted model is either linear or nonlinear (Montgomery, 1984). The estimate of the curvature effect is calculated according to Equation 4.2 as follows:

$$E_{(curvature)} = Y_i - Y_c \quad (4.2)$$

In this Equation Y_i is the average examinations of all the factorial treatments (16 runs), and Y_C is the average of the observations of the centre points (4 runs). If the difference of average response at the centre point and the factorial treatments is small, it proves that the centre points lie on or nearby the plane passing through the factorial points and hence, there is no quadratic effect or curvature. If the ratio is considerably large, then a quadratic curvature is present.

Table 4-2 Centre point replicates for a half fractional factorial design for gold extraction

Runs	**Control Factors**					**% Au Extraction**
	A IL type	B IL% Conc.	C S:L ratio	D Temp. (°C)	E Time (h)	
1	$BmimHSO_4$	55.5	1:6	45	27	9.8
2	$BmimHSO_4$	55.5	1:6	45	27	10.5
3	$BmimHSO_4$	55.5	1:6	45	27	12.7
4	$BmimHSO_4$	55.5	1:6	45	27	9.1

In this study, the experimental gold extraction at the four center points were 9.8%, 12.7%, 9.1% and 10.5%. The average of these four centre points is 10.5%; with a coefficient of variation (CV) of 12.7%. The average of the 16 factorial runs for the base design (Table 4.1) is 21.0%. Thus, according to Equation 4.2, the difference between them is 10.5 and also, the sum of squares for pure quadratic modeling from Equation 4.1 is 352.4. The ratio of the sum of the pure quadratic (SSPE) value and the error (σ^2) is 2.0. It means that if the difference is greater than 2, it is assumed that a curvature exists. It appears to be the test for nonlinearity, however, does not tell which factor(s) contain the curvature, it only represents the fact that it exists (Barrentine, 2014).

Based on the results two ionic liquids, namely [$Bmim^+ HSO_4^-$] and [$Bmim^+ CF_3SO_3^-$] were used as categorical factors in factorial design could extract gold, but no ionic liquid performed significantly better than the other. Figure 4.3 illustrates the chemical structure of ILs [$Bmim^+ CF_3SO_3^-$] and [$Bmim^+ HSO_4^-$]. The highest gold extractions achieved by [$Bmim^+ HSO_4^-$] and [$Bmim^+ CF_3SO_3^-$] was 44.1 % after 38 h and 43.7 % after 17 h respectively, which shows that both ionic liquids could extract gold from the ore. In this work the selected reagents, thiourea (complexing agent) which is an organic compound and ferric ions as the oxidant were soluble in the studied ionic liquids. Knowing that the oxidative dissolution of concentrate pyrite ore is an exothermic reaction therefore using these ILs could be suitable since they possess non-flammability and negligible vapour pressure when applied as solvent.



Figure 4.3 The chemical structure of two ILs, (A) [$Bmim^+CF_3SO_3^-$] and, (B) [$Bmim^+HSO_4^-$]

4.1.1 Single factor effect on extraction

Effect of IL concentration

The effect of IL concentration on gold extraction illustrated in Figure 4.4. The ratio of 33% IL and 78% IL in aqueous solution, which were the low and high levels of this studied factor respectively, examined. The results demonstrate that higher extraction of gold was obtained at a lower IL concentration under the conditions tested. It should be noted that some of the ILs have high viscosity, especially [$Bmim^+HSO_4^-$] (900 mPa) when it compared to water (1 mPa) (Whitehead *et al.*, 2007). Thus, there was added value in a mixed solution of ILs with deionized water in which viscosity can be lowered. In the IL-water solution the cations and anions are freer in water rich mixtures than in water poor solutions (Bhattacharjee *et al.*, 2012). Therefore, higher extraction of gold in the 33% IL solution can possibly be attributed to the lower viscosity of this IL-water mixture solution compared with the poor extraction in the 78% IL solution. This is in an agreement to the work by Aguirre et al. (2016), in which a low concentration of [$Bmim^+HSO_4^-$] with 20% IL (v/v) extract higher copper from chalcopyrite ore (Aguirre *et al.*, 2016).

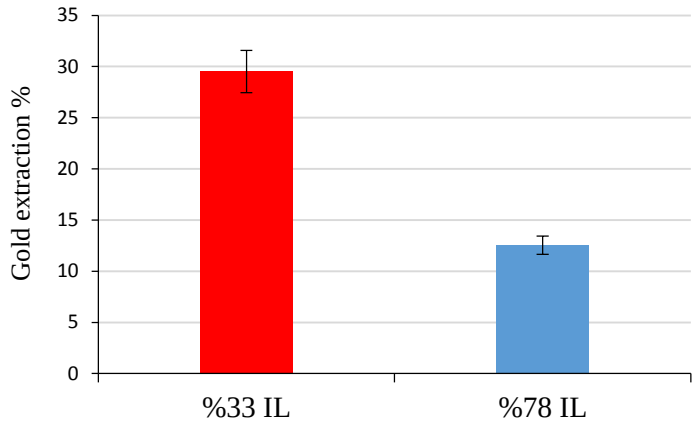


Figure 4.4 Effect of IL concentration on gold extraction

Effect of solid to liquid ratio

The pulp density's effect or solid to liquid ratio on gold extraction is illustrated in Figure 4.5. In the range of experimental conditions, the figure shows that lower extraction of gold was obtained at higher pulp density, which in this case was the solid to liquid ratio of 1:4 (25% w/v). The reduction in the gold extraction from the ore at higher solid to liquid ratio can be attributed to the high thickness of the mixture which leads to ineffective mass transfer and finally low extraction yield. In contrast, the reverse was true at low solid to liquid ratio, i.e., high gold extraction obtained at a solid to liquid ratio of 1:8 (12.5% w/v). Thus, gold extraction influenced by solid to liquid ratio and higher gold was extracted in lower solid to liquid ratio. This can be confirmed with the investigation by Ubaldini, et al. (1998) to extract gold in an acidic thiourea leaching with ferric ion as an oxidant from a refractory gold-bearing ore. The effect of pulp density was examined at 20, 40, and 60% (w/v) and it was found that more gold extracted in the low pulp density of 20% (w/v).

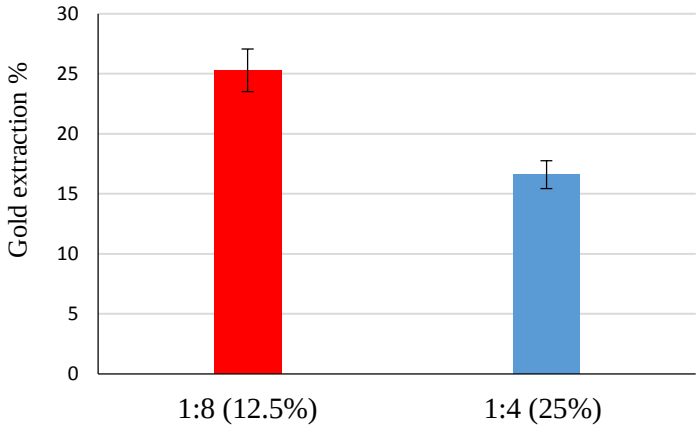


Figure 4.5 Effect of solid to liquid ratio on gold extraction

Effect of temperature

The effect of temperature on gold extraction through IL-water/thiourea/ferric ion mixture demonstrated in Figure 4.6. It shows that a higher extraction of gold was obtained at a higher temperature under the conditions tested. The temperature has impact on viscosity of the IL and/or its mixture with water as well as on the extraction kinetics of gold using thiorea. Higher gold extraction at higher temperature can be expected since thiourea has faster kinetics for gold dissolution which is in agreement with work by Örgül and Atalay (2002) using thiourea and ferric ion for gold extraction from a micro-disseminated gold-bearing ore. Additionally, the viscosity of the IL-water system decrease with an increase in temperature and as mentioned earlier, high viscosity adversely affects extraction in this system. Likewise, by increasing temperature more operative collisions occur between reactant molecules with adequate energy during the oxidation reaction. Thus, the gold leaching enhanced at high temperature.

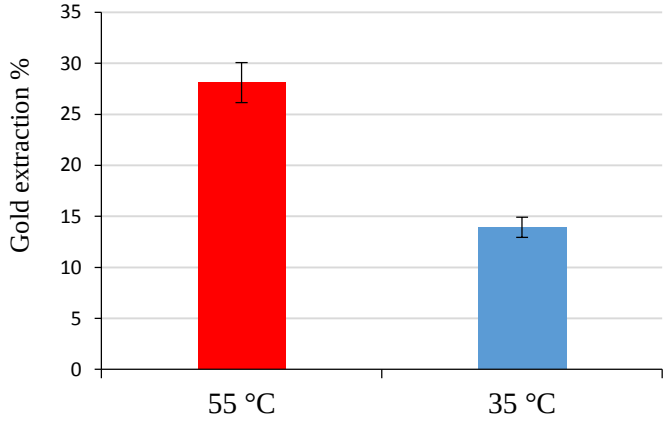


Figure 4.6 Effect of temperature on gold extraction

4.2 Application of response surface methodology to identify best extraction conditions

After conducting the experiments in the CCD design an empirical equation was developed to create surfaces of response and also predict the gold extraction. The second order regression model with the variable terms (the main factors, quadratic and interactions) that were significant at greater or equal to 95% confidence level was obtained as:

$$y = +30.71 - 1.65\,X_1 - 3.06\,X_2 + 0.52\,X_3 - 1.42\,X_1^2 - 2.78\,X_2^2 + 1.49\,X_3^2 - 1.65\,X_1X_2 + 1.40\,X_1X_3 - 1.60\,X_2X_3 \quad (4.3)$$

where X_1, X_2, and X_3 are the coded levels of process variables, namely IL concentration, pulp density and temperature respectively, within the predictor variable limits: $-\lambda \leq x_i \leq \lambda+$; $i = 1,2,3$; and $\lambda = (2^k)^{1/4} = 1.682$ is the distance of the star points from the centre of the CCD that gives the limits of the valid region under experimentation. Experimental results and predicted values obtained using the fitted models are given in Table 4.3. As can be seen from Figure 4.7, the predicted values are reasonably comparable to the experimental values, with the linear correlation coefficient (R^2) of 0.97.

Table 4-3 Observed and predicted values for gold extraction

Runs	Actual level of variables			Au Yield Observed	Au Yield Predicted
	A IL% Conc.	B S:L ratio	C Temp. °C		
1	10	1:8	35	28.4	27.36
2	20	1:8	35	19.21	18.71
3	10	1:4	35	28.40	27.51
4	20	1:4	35	25.23	24.81
5	10	1:8	60	23.80	23.07
6	20	1:8	60	19.60	19.36
7	10	1:4	60	29.60	28.94
8	20	1:4	60	32.40	31.85
9	5	1:6	48	26.76	27.62
10	25	1:6	48	21.17	21.45
11	15	1:10	48	15.00	15.46
12	15	1:2	48	27.00	27.69
13	15	1:6	25	23.82	24.62
14	15	1:6	70	25.88	26.49
15	15	1:6	48	32.15	30.71
16	15	1:6	48	31.76	30.71
17	15	1:6	48	28.82	30.71
18	15	1:6	48	30.88	30.71
19	15	1:6	48	30.30	30.71
20	15	1:6	48	29.71	30.71

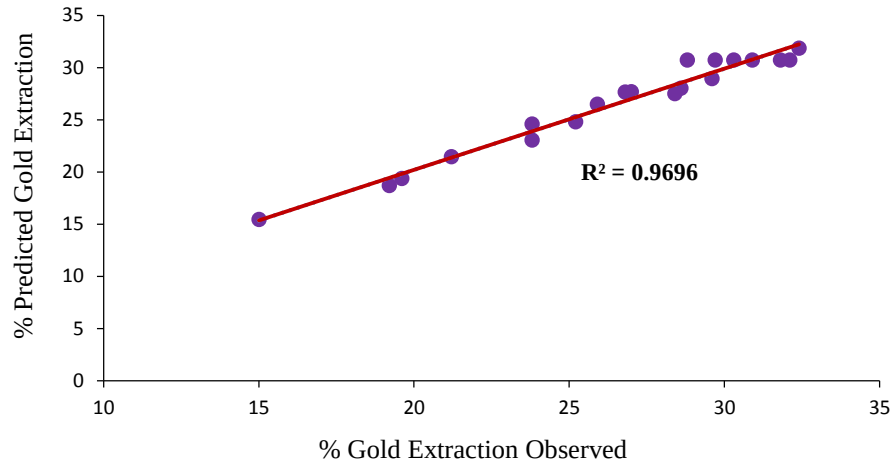


Figure 4.7 Relationships between experimental and predicted values for gold extraction

Checking the adequacy of the developed model

The adequacy of the model has been tested by the F-value, P-value and R-squared value through the software design expert. The results for the analysis of variance (ANOVA) for the fitted model are tabulated in Table 4.4.

Table 4-4 ANOVA for the fitted model

Source	Sum of Squares	df	Mean Square	F-value	P-value	
Model	420.00	9	46.67	23.55	0.0001	significant
A-IL Concentration	43.69	1	43.69	22.04	0.0008	significant
B-Pulp density	131.17	1	131.17	66.18	0.0001	significant
C-Temperature	3.98	1	3.98	2.01	0.0118	significant
AB	21.78	1	21.78	10.99	0.0078	significant
AC	15.78	1	15.78	7.96	0.0181	significant
BC	20.51	1	20.51	10.35	0.0092	significant
A^2	51.93	1	51.93	26.20	0.0005	significant
B^2	121.90	1	121.90	61.50	0.0001	significant
C^2	39.01	1	39.01	19.68	0.0013	significant
Residual	19.82	10	1.98			
Lack of Fit	11.90	5	2.38	1.50	0.3330	not significant
Pure Error	7.92	5	1.58			
Total	439.82	19				

The significance of the fitted regression model was examined using the probability (P-value) value for regression model significance. The model's F-value of 23.55 indicates that the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. In terms of the P-value evaluation, the value of less than 0.0500 indicates that the model terms are significant, while values greater than 0.1000 indicate that the model terms are not significant. Thus, in this case A, B, C, AB, AC, BC, A^2, B^2, C^2 were significant model terms. In which A, B, C were IL concentration, pulp density and temperature, respectively and AB, AC, BC were the interactions between them. As well as, A^2, B^2, C^2 were the quadratic effect of IL concentration, pulp density and temperature, respectively on the gold extraction.

Furthermore, ANOVA study demonstrate that a large F-value and a low P-value (typically less than 0.05) are desired to indicate that the model term is significant. In this study, the F-value and P-value for "Lack of Fit" were 1.50 and 0.33, respectively which reveals that the "Lack of Fit" is not significant. It is expected to have an insignificant lack of fit for having a fitting model.

Table 4-5 Fit Summary Statistics

Std. Dev.	1.41	R-Squared	0.9549
Mean	26.52	Adj R-Squared	0.9144
C.V.%	5.31	Pred R-Squared	0.7626
		Adeq Precision	15.5807

From the fit summary statistics presented in Table 4.5, the low standard deviation value of 1.41 and high R-squared value of 0.95 show that the model is statistically likely to define the accurate performance of the experimental system. "Adeq Precision" measures the signal to noise ratio. Thus, the ratio of 15.58 is an adequate signal as a ratio of greater than 4 is desirable.

Response surface methodology plots

Once the experimental area was confined, the IL concentration (factor A), pulp density (factor B) and temperature (factor C) were fine-tuned using the response surface methodology (RSM) to find a relationship between them.

Figure 4.8 shows response surface (3D) and contour plots (2D), where gold extraction was represented by varying simultaneously the IL [$Bmim^+HSO_4^-$] concentration from 10% to 20% (v/v) and pulp density from 12.5 to 25 (w/v) at constant temperature at 50 °C. The lines of contour plots represent the values of gold extraction for different IL concentration and pulp

density at extraction time of 24 hours. The optimum condition was found as the red shaded area which converge the values from 14% to 16% (w/v) for solid to liquid ratio and also from 14% to 16% (v/v) for the IL [$Bmim^+HSO_4^-$] concentration in the aqueous sample. In other words to obtain a higher gold extraction, the leach solution should be prepared at around the centre point of IL concentration (15% v/v) and the pulp density of (15% w/v). It can be seen from the graph the gold extraction increased with the decrease in pulp density. There were low thickness and effective homogeneous mixing of solids and liquid at low pulp density leading to better mass transfer and hence increased gold extraction.

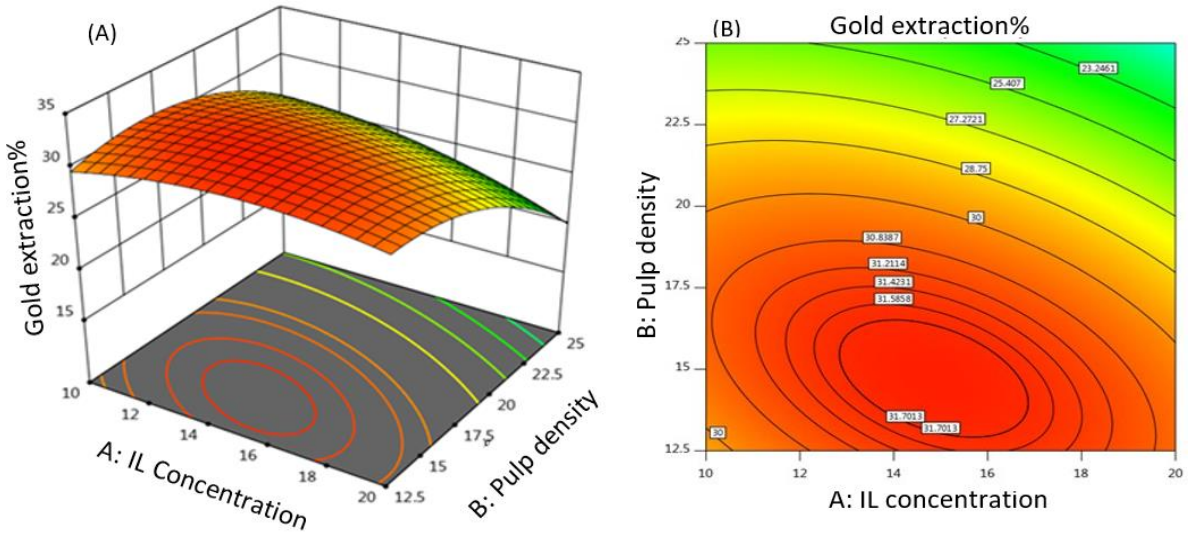


Figure 4.8 (A) Surface and (B) counter plots showing the effects of interaction of IL [$Bmim^+HSO_4^-$] concentration of 10-20% (v/v) and pulp density of 12.5-25% (w/v) on gold extraction at 50 °C, pH = 1, 250 rpm

Figure 4.9 shows response surface and contour plots on the effect of IL concentration and temperature on gold extraction at 15% (w/v) pulp density for 24 hours leaching time. The IL [$Bmim^+HSO_4^-$] concentration was varied from 10% to 20% (v/v) and at the same time, the temperature varied from 35 to 60 °C. From both the counter plot and the response surface, gold extraction increases with a slight decrease in IL concentration at an elevated temperature in the range of 55-60 °C. The viscosity of the aqueous solution of the IL [$Bmim^+HSO_4^-$] with water reduced at high temperature, as well more operative collisions between reactant molecules which leads to better gold extraction in the interaction of temperature and the IL concentration. Besides, at high temperature reaction kinetics of thiourea is faster for extracting gold in the system (Örgül & Atalay, 2002).

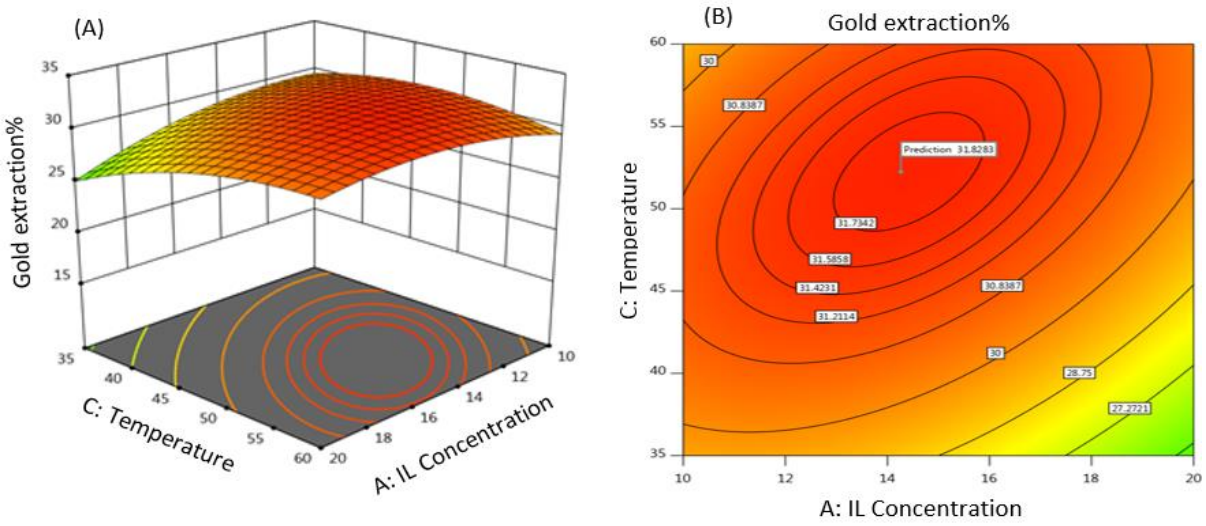


Figure 4.9 (A) Surface and (B) counter plots showing the effects of interaction of IL [Bmim$^+$HSO$_4^-$] concentration of 10-20% (v/v) and temperature range of 35-60 °C on gold extraction at 15% (w/v) pulp density, pH = 1, 250 rpm

Figure 4.10 shows the effect of pulp density and temperature on gold extraction at constant IL concentration at centre points (15% v/v) in response surface and contour plots. As the figure show, gold extraction increases with a decrease in pulp density at elevated temperature. The optimum condition is found as the shaded area which converges at the values from 13% to 15% (w/v) for the S/L ratio and around 55 °C for temperature at extraction time of 24 hours. Therefore, better extraction of gold in the combination of high temperature and low pulp density can possibly be attributed to the lower viscosity of this IL-water mixture solution, enhanced interaction between reactant molecules, faster reaction kinetics of thiourea, as well as low thickness of the mixture.

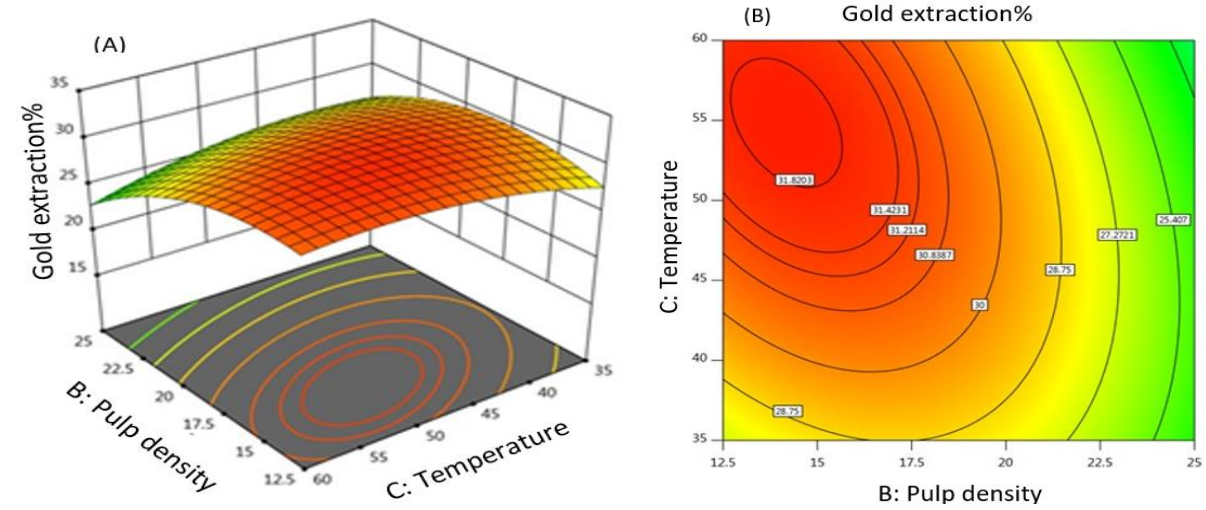


Figure 4.10 (A) Surface and (B) counter plots showing the effects of interaction of pulp density in the range of 12.5-25% (w/v) and temperature in the range of 35-60 °C on gold extraction at 15% (v/v) [Bmim$^+$HSO$_4^-$] concentration, pH = 1, 250 rpm

Determining stationary points

Afterward the fitted 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 coordinates for the stationary points to check the response surface plots (Kleijnen, 2015). To obtain the stationary points, the fitted second order model with k variables was written in matrix notation (Appendix B) (Myers *et al.,* 2016). Equation 4.4 was employed to determine the conditions at the stationary points X_s.

$$X_s = -\frac{\beta^{-1}\, b}{2} \tag{4.4}$$

where in this study, $b = \begin{bmatrix} -1.65 \\ -3.06 \\ +0.52 \end{bmatrix}$, $\beta = \begin{bmatrix} -1.42 & 0 & 0 \\ 0 & -2.78 & 0 \\ 0 & 0 & -1.49 \end{bmatrix}$

and, $\beta^{-1} = \begin{bmatrix} -0.704 & 0 & 0 \\ 0 & -0.359 & 0 \\ 0 & 0 & -0.671 \end{bmatrix}$

The stationary points X_s have been calculated by substituting the values for β^{-1} and b in the Equation 4.5 and then solved it by the online software "Octave". The obtained conditions in coded units for the stationary points are x_{1s} = - 0.58, x_{2s} = -0.55 and x_{3s} = + 0.17. The calculated stationary points lie within the limits of the region of interest in this study, $-1.682 \leq x_i \leq +1.682$; i = 1, 2, 3; where, x_i are the coded levels of process variables.

The coded units were converted to actual uncoded variables by using Equation 4.5, which accordingly give the following variables: %IL [$Bmim^+HSO_4^-$] concentration = 12.5% (v/v), pulp density = 15.3 (w/v), and temperature = 50 °C. The acquired uncoded variables are in good agreements with the obtained optimum conditions in the shaded area of the contour plots and response surface plots.

$$X_i = X_{iH} - \frac{(X_{iH} - X_{iL})(x_{iH} - x_i)}{(x_{iH} - x_{iL})} \quad , i = 1, 2, 3 \tag{4.5}$$

where X_{iL} and X_{iH} are the actual low and high levels of X_i, respectively, x_{iL} and x_{iH} are the coded low and high levels of X_i, respectively, and x_i is the coded variable that is being converted to actual variables.

Confirmatory experiments

Confirmatory experiments were carried out with the level of the parameters suggested by the response surface methodology to test the validity of the obtained condition. The conditions used in the confirmatory experiment were as follows: IL [$Bmim^+HSO_4^-$] concentration 15% (v/v), pulp density (15% w/v), and temperature 55 °C.

The extracted gold after a leaching time of 24 hours were; 35.7%, 34.8%, and 35.5%. The average of these three tests was 35.4% gold extraction, which was consistent with the predicted model value of 35.2%. The model can, therefore, be considered to fit the experimental data very well under these experimental conditions. Table 4.6 tabulated the results for the model confirmation by the design expert (software version 11) for gold extraction at optimal conditions at a 99.9% confidence level. Therefore, it can be concluded that the formulated model is acceptably valid.

Table 4-6 Model confirmation by design expert for gold extraction

Response	Predicted Mean	Observed	Std Dev.	n	99.9% PI low	Data Mean	99.9% PI high
Au Yield	30.7	35.0	1.4	3	26.1	35.0	35.2

In the initial screening stage of the factorial design (Section 4.1) the lowest concentration of IL [$Bmim^+HSO_4^-$] (33% IL) achieved the higher gold extraction of 44.1%. It was postulated that by reducing the IL:water ratio more could lead to an increase in extraction. However, based on the results in confirmatory tests, where the optimum gold extraction was found within the range of conditions, it can be seen that this was not the case (35.4% instead of 44.1%). For this IL to function efficiently there is a specific concentration of it in a solution. Thus, the chosen levels of IL concentration was low in the CCD design.

4.3 Gold extraction kinetics and modeling

The gold extraction kinetics were studied in a mixture of IL [$Bmim^+HSO_4^-$]-water solution/thiourea/ferric ion at a solid to liquid ratio of 1:8, IL concentration of 20% (v/v) at different temperatures and the shinking core model was fitted to the data. The ore and the solid residue were also analysed using SEM, XRD and Raman spectroscopy to observe changes before and after leaching.

4.3.1 Gold extraction kinetics

Figure 4.11 shows the Au concentration (mg/l) vs time (h) and Figure 4.12 shows the gold extraction profiles %gold extraction vs time (h) at different temperatures during the leaching period under study. It can be seen from these that the rate of gold extraction increased as the temperature increased from 20 to 65 °C, which is in line with results obtained from the surface response analysis experiments. It also confirms that higher temperatures favours extraction. Furthermore, the extraction rate (slope of the curve) is quicker in the first three hours than the rest of the leaching reaction period till 12 hours. In general, from the graphical illustration in Figure 4.6, the rate of gold extraction is faster initially and then it decreases with increasing the leaching time. Possible reasons for this can be reducing the amount of gold that can be extracted from the refractory sulfidic low-grade gold ore, and the reagents get consumed as well which may lead to decreasing the rate of gold extraction.

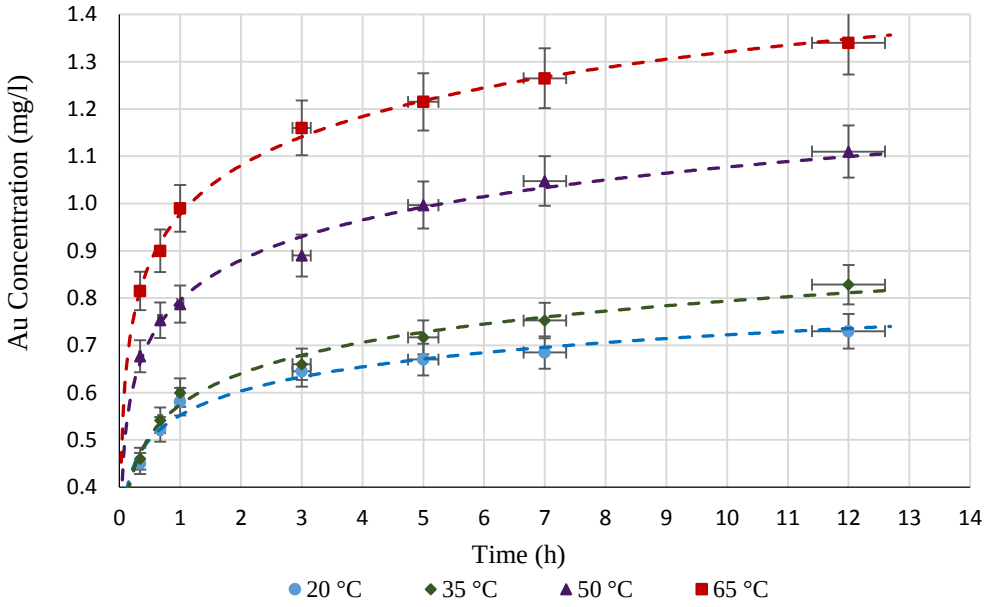


Figure 4.11 Effect of temperature on the gold extraction (Au concentrtion) ([Bmim$^+$HSO$_4^-$]-water solution (20% v/v), S:L 1:8 (w/v), pH = 1, 250 rpm)

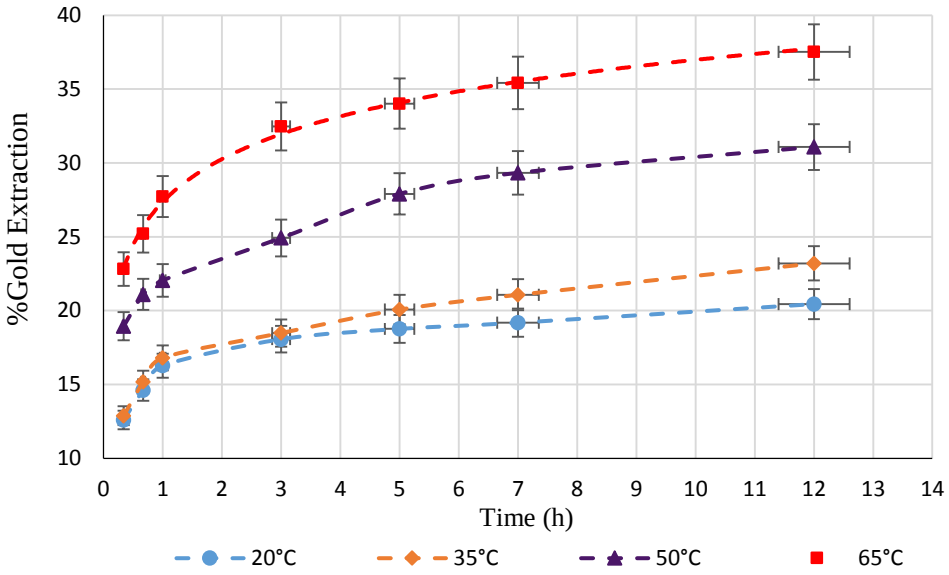


Figure 4.12 Effect of temperature on the gold extraction (%Au extraction) ([Bmim$^+$HSO$_4^-$]-water solution (20% v/v), S:L 1:8 (w/v), pH = 1, 250 rpm)

In order to verify whether the influence of time on the extraction kinetics were negligible, longer extraction experiments were performed. The gold extraction from the refractory sulfidic gold ore by IL [Bmim$^+$HSO$_4^-$]-water solution/thiourea/ferric ion was conducted at longer extraction times of 1 day, 2 days, 3 days and 5 days at pH = 1, temperature 60 °C and shaking speed of 250 rpm. Figure 4.13 demonstrates the gold extraction in longer leaching time and it shows that the gold extraction slightly increased and then reached a plateau. The magnitude of changes in the percentage of the extraction was trivial and an additional 3% increase was observed after 5 days of extraction. It can therefor be concluded that most of the extraction took place during the first day of extraction and that thereafter very little gold extraction occurred.

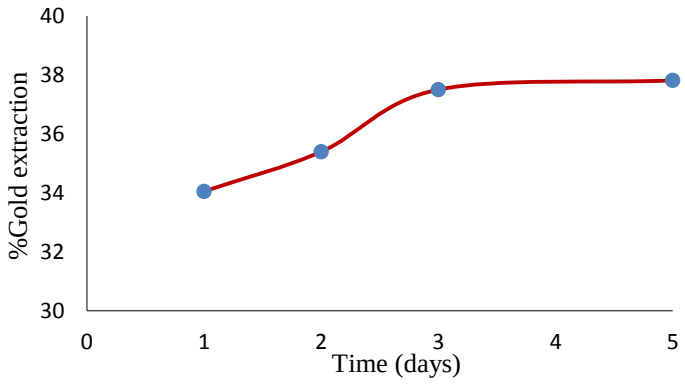


Figure 4.13 Effect of time on the gold extraction ([Bmim$^+$HSO$_4^-$]-water solution (20% v/v), S:L 1:8 (w/v), pH = 1, 250 rpm)

4.3.2 Gold extraction modeling

The kinetic data of the gold dissolution were analyzed using the shrinking core model. In order to examine the rate controlling step, the experimental results at different temperatures were plotted in terms of the standard Equations for difiusion and chemical reaction of the shrinking core model (Section 2.6). Shrinking core model has been used in solid-liquid reaction system. Figure 4.14 and 4.15 shows the data plotted for the diffusion controlled and the chemical reaction controlled kinetics models and the fitted models, respectively. X is the fraction of gold extracted at any time (t).

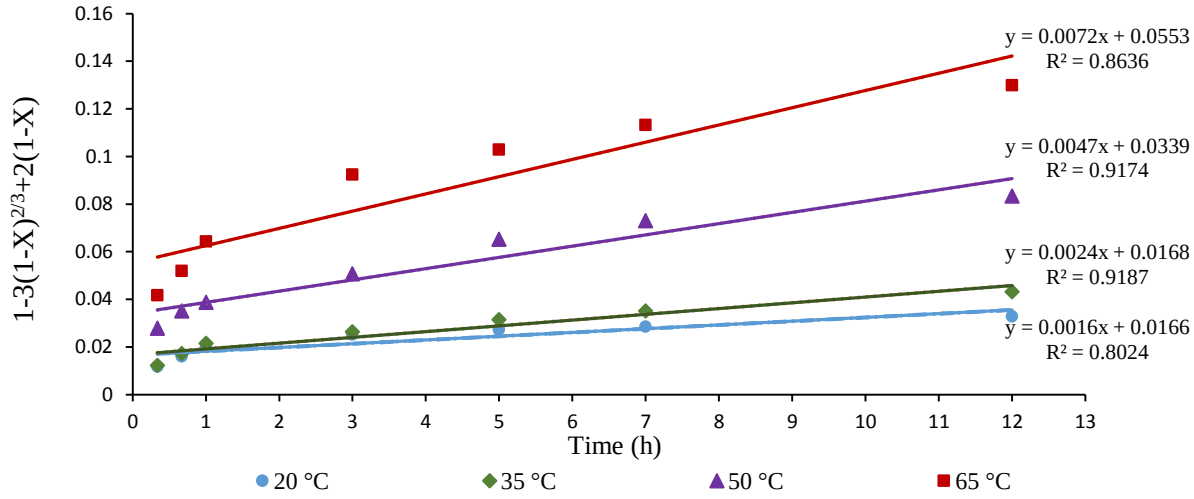


Figure 4.14 Shrinking core diffusion rate control plot of gold extraction at different temperatures ([Bmim$^+$HSO$_4^-$]-water (20% v/v), S:L 1:8 (w/v), pH = 1, 250 rpm)

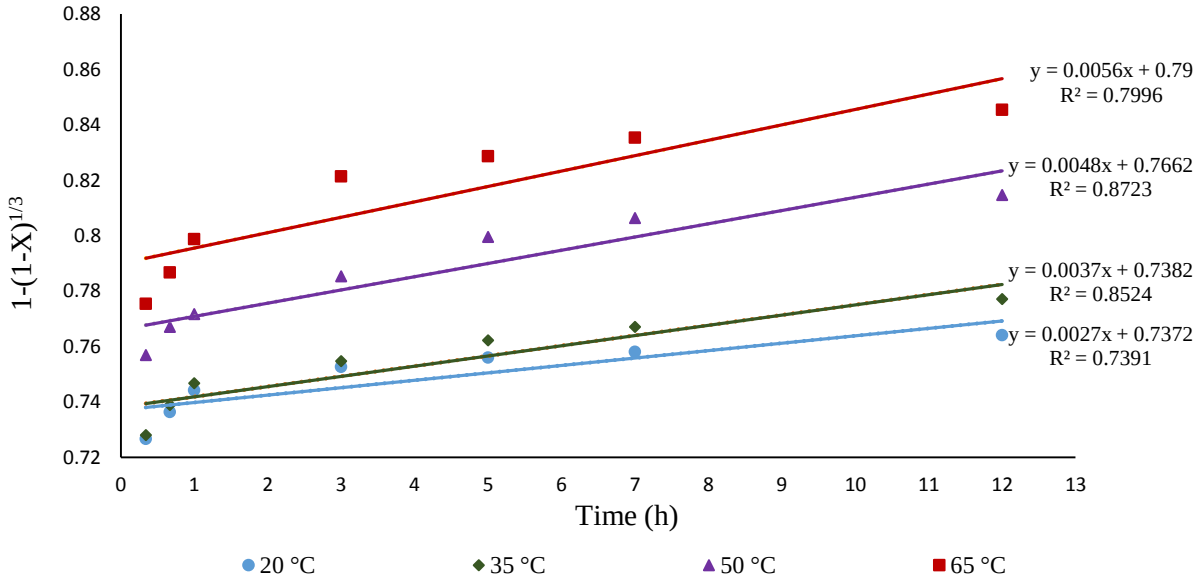


Figure 4.15 Shrinking core chemical kinetics rate control plot of gold extraction at different temperatures ([Bmim$^+$HSO$_4^-$]-water (20% v/v), S:L 1:8 (w/v), pH = 1, 250 rpm)

Based on the graphs the values for the correlation coefficient (R^2) suggest that the leaching rate of gold from low grade sulfidic ore was diffusion controlled, because the correlation coefficients (R^2) are closer to one (the linearity) in Figure 4.14 than for those fits in Figure 4.15. Therefore, the kinetic model based on diffusion through the product layer was assumed to control the rate of reaction for the extraction of gold from the low grade sulfidic ore using the IL [$Bmim^+HSO_4^-$]-water solution/thiourea/ferric ion in the range of the studied temperatures from 20 to 65 °C.

The apparent rate constant *k* was obtained from the slopes of the straight lines in Figure 4.14 and was used to determine the activation energy. By means of the Arrhenius Equation 4.6, the natural logarithm of *(ln k_d)* was plotted against the inverse of their respective temperatures (*1/T*) as depicted in Figures 4.16.

$$k = Ae^{-Ea/RT} \tag{4.6}$$

In the Arrhenius Equation, *k* is the apparent reaction rate constant (hrs^{-1}), *A* is the frequency factor (hrs^{-1}) a temperature-independent constant, E_a is the activation energy ($Jmol^{-1}$), *R* is the universal gas constant (8.314 $JK^{-1}\,mol^{-1}$) and T is the reaction temperature (K). Thus, the slope of this plot gives *($-E_a/R$)* in which E_a can be calculated. According to the slope of the straight line in Figure 4.16, the magnitude of the activation energy for the product layer diffusion was obtained as E_a= 28.4 kJ/mol.

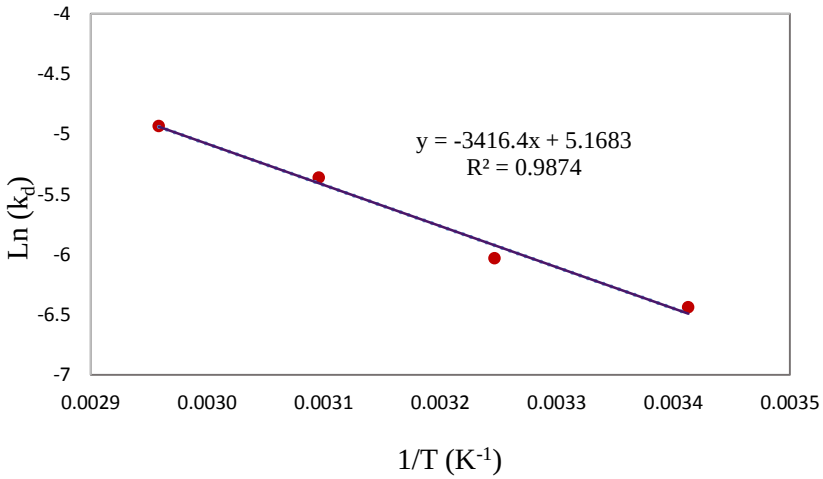


Figure 4.16 Arrhenius plot for gold dissolution from the ore ([$Bmim^+HSO_4^-$]-water (20% v/v), S:L 1:8 (w/v), pH = 1, 250 rpm)

In order to understand the kinetic and model fiting results, analyses of the solid material before and after leaching were conducted using SEM, XRD and Raman spectroscopy.

4.3.3 Solid analyses

The refractory sulfidic gold ore before and after leaching by IL [$Bmim^{+}HSO_4^{-}$]-water solution/thiourea/ferric ion were studied by scanning electron microscopy backscattered electrons (SEM-BSE). Images are shown in Figure 4.17. As can be seen from the SEM micrographs the surface of the ore before leaching looks smoother with a few defects. However, after leaching surface looks rough and shows some pores, pits, and corners appeared on the pyrite surface. This may be due to the dissolving of the pyrite in which gold is "trapped" during the oxidative leaching process during the 12 h leaching time. Moreover, the oxidation reactions happens at those pyrite surface with more edges, defects, and corners which represent areas with high surface energy.

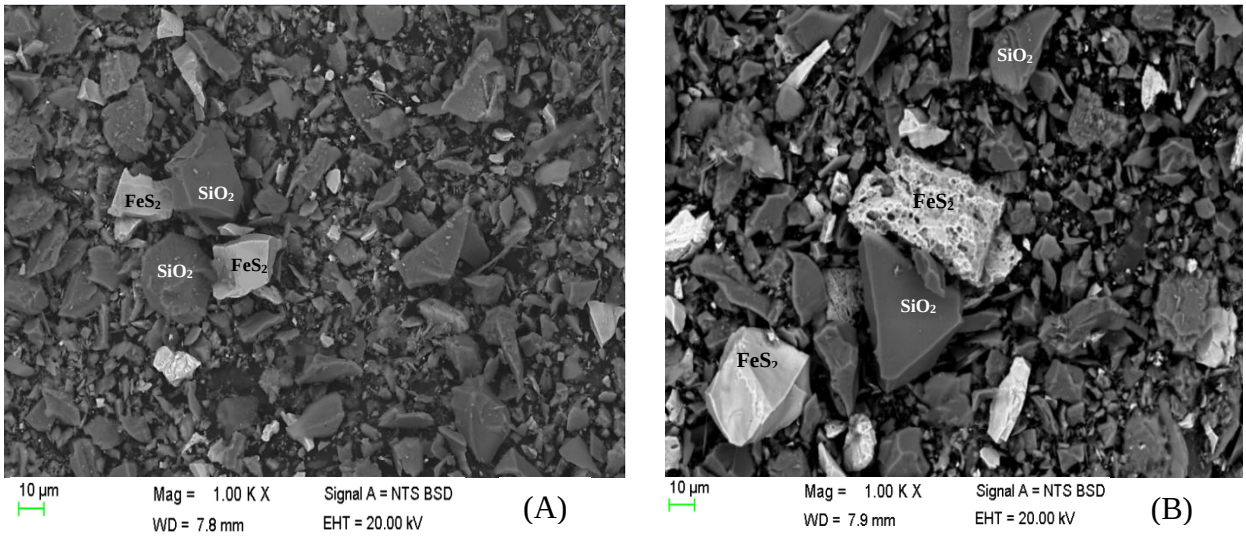


Figure 4.17 Backscattered electron image (BEI) of the sulfidic mineral, (A) Before leaching and (B) After leaching by %20 (v/v) [$Bmim^{+}HSO_4^{-}$]

Figure 4.18 represents the X-ray diffraction (XRD) patterns of the initial ore (before leaching) and the solid residue after 12 h leaching with 20% (v/v) IL [$Bmim^{+}HSO_4^{-}$]-water solution/thiorea/ferric ion. As can be seen, the quartz (SiO_2) is present as the most dominant mineral and pyrite as the second major one. The gold phase could not be detected with the XRD, which can be due to the fact that the gold is either encapsulated or invisible in the pyrite sample or the amount of gold present is lower than the detection limit of XRD. As revealed from the XRD patterns, there were small differences in the intensity of the pyrite peak sizes before and after leaching.

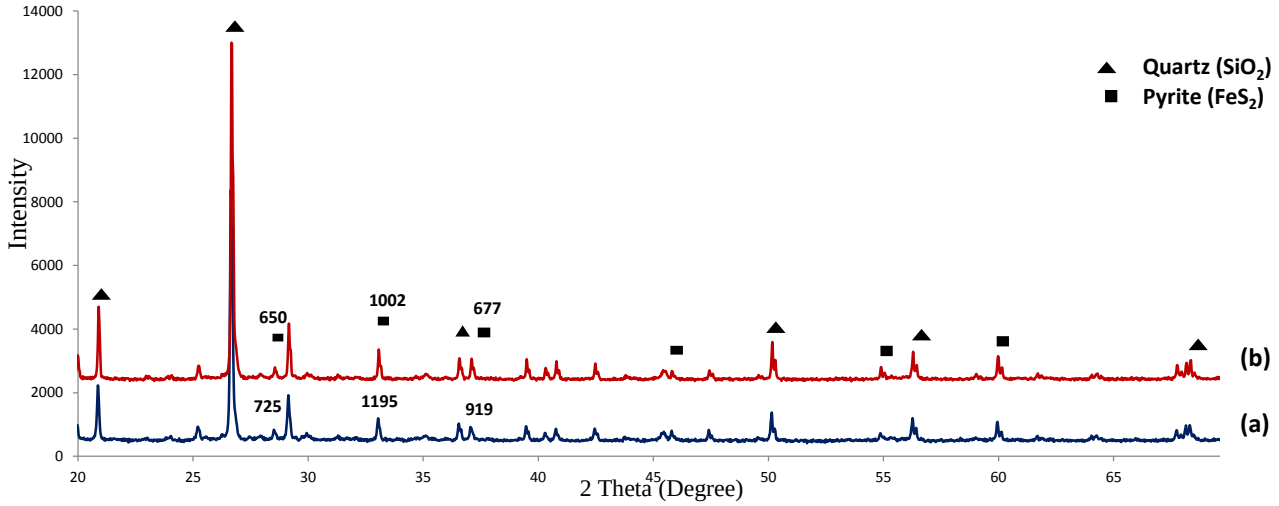


Figure 4.18 XRD pattern of (a) the ore (before leaching), (b) the solid residue (after leaching) after 12 h leaching with 20% (v/v) [$Bmim^+HSO_4^-$]-water solution

Figure 4.19 represents the spectra for a Raman analysis for the sulfidic gold ore before and after oxidative leaching with 20% (v/v) IL [$Bmim^+HSO_4^-$]-water solution/thiorea/ferric ion. As can be seen in the spectra, it detects three peaks for the pyrite (FeS_2) centered at frequencies about 342.8, 379.1 and 430.5 cm^{-1}. The experimentally observed peaks for the pyrite in this study are compared with the pyrite peaks in a geology investigation work on some important and commonly occurred sulfidic mineral by Mernagh and Trudu (1993) to make sure these peaks belong to the pyrite. The results for the pyrite peaks frequencies in cm^{-1} are tabulated in Table 4.7. Additionally, there was an indication of a potential decrease in the species after leaching occurred since the intensity of the peaks declined.

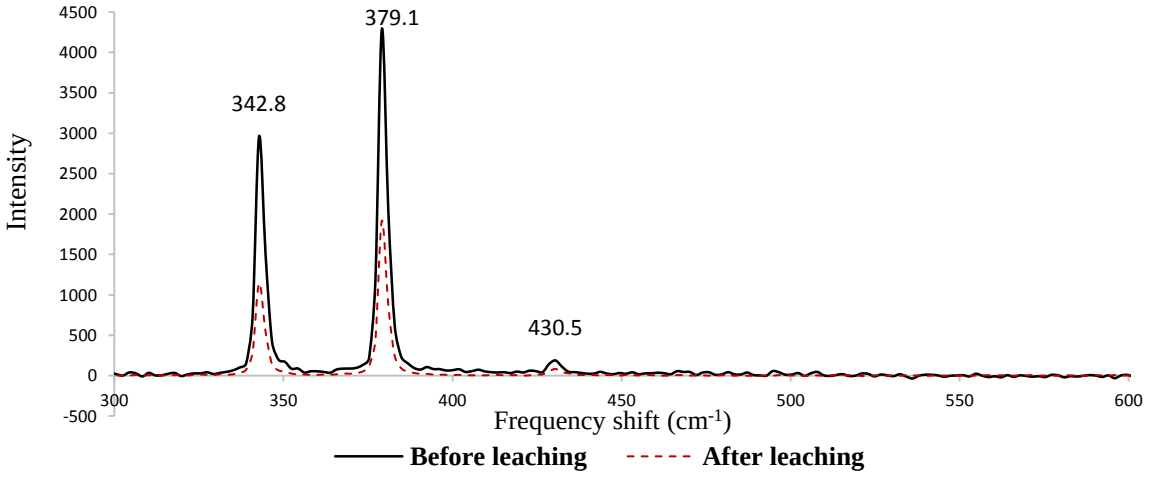


Figure 4.19 Raman spectra of the ore before and after oxidative leaching with 20% (v/v) [$Bmim^+HSO_4^-$]-water solution in 12 h leaching time

Table 4-7 Raman frequencies (in cm^{-1}) for pyrite in this work and the reference

Pyrite peaks (FeS_2)	342	379	430	(This work)
Pyrite peaks (FeS_2)	342	377	428	(Mernagh & Trudu, 1993)

Additionally, Figure 4.20 depicts the sulfur peaks which showed up in the residue spectra, after the oxidative leaching of the sulfidic gold ore. There are three peaks for the elemental sulfur centered at approximately 153, 219 and 470 cm^{-1} in the spectra. These peaks can provide the confirmation for the presence of the elemental sulfur in the solid residue after oxidative leaching. The observed results in the experimental analysis with Raman spectroscopy in order to detect the elemental sulfur peaks in this work are compared with the work by Mycroft et al. (1990) (Table 4.8).

Table 4-8 Raman frequencies (in cm^{-1}) for sulfur in the residue of the sulfidic ore (pyrite) in this work and the reference

Sulfur peaks	153	219	474	(This work)
Sulfur peaks	150	218	469	(Mycroft *et al.*, 1990)

Unfortunately there is no clear evidence for IL gold leaching from refractory sulfidic ore that prove the formation of sulfur. But in this study, this Raman spectra can indicate that sulfur could have formed in oxidative leaching of pyrite at pH = 1 in the presence of ferric ion as the oxidant and it can be possible because of the following reaction in Equation 4.7 (Garrels and Thompson, 1960):

$$FeS_2 \rightarrow Fe^{2+} + 2S^0 + 2e^- \quad (4.7)$$

This could possibly explain why diffusion through a product layer was the rate controlling step in this study.

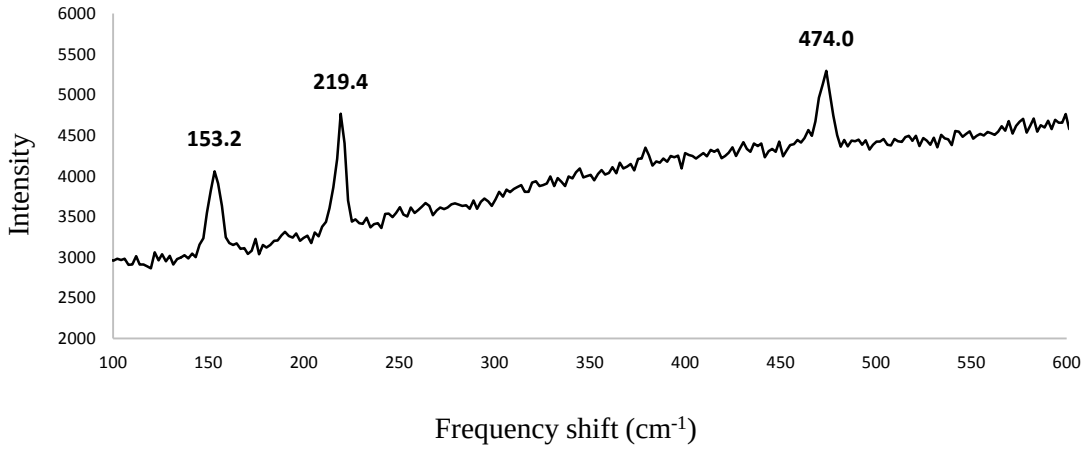


Figure 4.20 Raman spectra of the solid residue with 20% (v/v) [Bmim$^+$HSO$_4^-$]-water in 12 h leaching time

4.4 Comparison of cyanide and IL gold extraction

Cyanide leaching on the same ore in an optimized DRD Gold process with pulp density of 50% (w/v), pH = 11 and 24 h leaching time achieves on average 65% extraction of gold from the low grade sulphidic ore. In this investigation, the extracted of gold with IL [Bmim$^+$HSO$_4^-$] /thiourea/ferric ion with S:L 1:8 (w/v), pH = 1 and 24 h leaching time in confirmatory tests was 35.4%. This could have been increased to 44.1% if the optimization were carried out within the original operating range.

At first glance it appears as if the cyanide process performs better, but one must consider the following facts which may contribute to these differences (i) only the -45 µm fraction of the flotation concentrate were used in this study where Table 3.2 clearly shows that at +45 µm fraction the amount of gold is more and the cyanidation process uses the whole ore sample and (ii) the flotation concentrate on the plant is also subjected to additional milling to particles +25, +10 and -10 µm in size which allows for additional liberation of gold and smaller pyrite particles to digest. In addition even though the ionic liquid mixture does not appear to extract more gold than the cyanidation process is does offer the advantage of a possible safer process since IL [Bmim$^+$HSO$_4^-$] is non-volatile would be the preferable option to extract gold from sulfidic gold ore, with fewer disadvantages. Therefore, further detailed work on the leaching of refractory sulfidic ore containing gold using ILs needs to be undertaken to identify the factors that can achieve higher gold extraction.

5 Conclusion and Recommendation

5.1 Conclsions

The purpose of this work was to examine the feasibility of extracting gold from refractory sulfidic gold tailing ore with imidazolium-based ionic liquids, 1-butyl-3-methylimidazolium hydrogen sulphate [$Bmim^+HSO_4^-$] and 1-butyl-3-methylimidazolium trifluoromethansulfonate [$Bmim^+CF_3SO_3^-$]. This section describes the proposed objectives and their outcomes and findings.

5.1.1 Objective 1: Identify the significant factors that influence the extraction of gold in a system containing ionic liquids

To identify the factors that have considerably large effect on gold extraction a half fractional factorial design of 2^{5-1} was performed. Thus, concentration of ionic liquid, solid to liquid ratio, time and temperature were investigated for two ionic liquids, [$Bmim^+HSO_4^-$] and [$Bmim^+CF_3SO_3^-$] on the extraction of gold. After the evaluation of the experimental results, it was found that within the chosen operating range IL concentration, solid to liquid ratio and temperature had a significant effect on the leaching efficiency. High amounts of extracted gold were observed at low ionic liquid concentration and solid to liquid ratio, and high temperature was necessary.

5.1.2 Objective 2: Optimizing the selected significant factors within a specified range of operating parameters to maximize the extraction of gold using surface response methodology

For this central composite design (CCD) and response surface methodology (RSM) applied in an attempt to determine the optimal conditions of the IL concentration, solid to liquid ratio and temperature for gold extraction. Since both studied ionic liquids could extract the gold, one of the ILs was used for conducting further experiments in the optimization stage. The IL [$Bmim^+HSO_4^-$] was preferred due to being cheaper than the other IL [$Bmim^+CF_3SO_3^-$], the price for 1 L of [$Bmim^+HSO_4^-$] and [$Bmim^+CF_3SO_3^-$] were R5900 and R18660, respectively and 24 hours for the follow-up experiments as an arbitrary convenient experimental period.

Additionally, in the screening stage of the factorial design the lowest concentration of IL [$Bmim^+HSO_4^-$] (33% IL) achieved the higher gold extraction of 44.1%. Therefore, in CCD

design the IL concentration lowered even further to 5, 10, 15, 20, 25% IL to examine whether even more gold extraction could be achieved or not. After conducting the optimization experiments the optimum point were as follows: IL concentration 15% (v/v), pulp density 15% (w/v), and temperature 55 °C. Based on the results in confirmatory tests the gold extraction was 35.4% which was lower. Thus, the chosen levels of IL concentration was too low in the CCD design.

5.1.3 Objective 3: Determining the kinetics of the process and fitting a suitable gold extraction model onto the data

In this study, based on shrinking core model an examination of the plot of the standard equation for diffusion, i.e., $1-3(1-X)^{2/3}+2(1-X)$ versus the leaching time (t), displayed a reasonably good straight line fit with a correlation coefficient R^2 close to one. It indicates that the extraction of gold from the low grade sulfidic ore using the IL [$Bmim^+HSO_4^-$]-water solution/thiourea/ferric ion was controlled by diffusion through a product layer with E_a = 28.4 kJ/mol. The rate of gold extraction increased as the temperature increased from 20 to 65 °C within 20 min till 12 h intervals, thus indicating the need for moderately high temperature. In addition, extraction of gold in longer time from 1 day up to 5 days revealed that the magnitude of the changes in the percentage of the gold extraction was trivial. It can therefor be concluded that most of the extraction took place during the first day of extraction and that thereafter very little gold extraction occurred.

The solid analysis implemented on the ore sample before and after leaching by SEM-BSE, XRD and Raman analysis. In the SEM-BSE image on the solid residue some pores appeared on the pyrite particles in the residue. In XRD there were small differences in the intensity of the peaks before and after leaching which can be due to IL/thiourea/Fe^{3+} leaching. The Raman spectra indicated sulfur shifts in the recorded spectra which can support the speculation of the kinetic model which was limited by diffusion through a product layer.

The comparison between the cyanide leaching in an optimized DRD Gold process and the acidic IL/thiourea/Fe^{3+} on the same ore revealed that cyanide leaching extract more gold that IL leaching. However, a direct comparison is not as simple as the initial physical properties of the ores differ and so additional experiments are proposed. The IL does, however, potentially offer a safer process as since IL [$Bmim^+HSO_4^-$] is non-volatile and not as toxic as cyanide.

5.2 Recommendations and future work

Based on the knowledge acquired in this study, the following recommendations for further study are proposed.

In refractory sulfidic gold ores, since most of the gold is locked in gangue minerals such as pyrite and silicates, a more detailed study and investigations should be conducted in order to unlock the incapsulated gold from the ore. In order to find an approach to reach the locked gold inside the sulfidic ore matrix or release the gold, one way could be by inducing cracks on the surface of the ore by implementing microwave-assisted and/or ultrasonic-assisted oxidative leaching. Moreover, ultrafine grinding of a refractory sulfidic gold ore can increase the exposed surface area, or possibly expose more free gold to enhance the gold extraction yield.

This work was devoted to establishing the feasibility of extracting gold from a concentrated pyrite ore through imidazolium-based ionic liquids. For further study, it is recommended to examine:

- Recovering the extracted gold electrochemically from a pregnant solution using different concentration of gold.
- Examining the recyclability of ionic liquids to make the leaching process economically favorable.
- Applying different approaches such as electrolysis, ultrasonic and microwave radiation to introduce/induce cracks on surface of the sulfidic mineral.
- Applying additional/different oxidants and complexing agents for extracting gold to enhance the yield.

In conclusion, further detailed study on the oxidative leaching of refractory sulfidic ore containing gold needs to be undertaken and the aspect of gold recovery required to be investigated to identify the factors that can contribute to high gold extraction and recovery.

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Appendix A

Sample calculations

Leaching test

In order to obtain an initial concentration of Au in the pyrite sample, 1 gr of pyrite sample was measured and dissolved in the Aqua Regia (20 ml).

Basis of calculation:

Pyrite ore weight = 1 g

Volume of Aqua Regia = 20 ml

After Leaching:

Au in leach liquor (AAS analysis) = 0.92 ppm or (mg/l)

0.92 (mg/l) * 0.02 L = 0.0184 mg Au

The solid residue of the pyrite sample again was dissolved in the Aqua Regia (20 ml).

After Leaching:

Au in leach liquor (AAS analysis) = 0.08 ppm or (mg/l)

0.08 (mg/l) * 0.02 L = 0.0016 mg Au

The initial Au concentration = 0.0184 + 0.0016 = 0.02 mg Au in 1 gr ore

Calculation of %Extraction of Au

Example: *Run 12 (Table B1)*

Au in leach liquor (AAS analysis) = 0.63 ppm or (mg/l)

Solid to liquid ratio (-1), (1:8); 2.5 gr ore in 20 ml IL-water solution

$$\%Extraction\ of\ Au = \frac{0.63\left(\frac{mg}{l}\right)*(0.02\ l)}{0.02\left(\frac{mg}{gr\ ore}\right)*(2.5\ gr\ ore)}*100 = 25.2\ \%$$

Elemental analyses ogold in the pregnant leach solutions were done with the Varian SpectrAA-200 atomic absorption spectrophotometer (AAS) with an air/acetylene flame. The stock standards solution for AAS were 1000 ppm and were diluted using distilled water to the

required concentrations of 2, 4, 8 and 10 ppm for calibration of the atomic absorption spectrophotometer (AAS).

Table A1. Working conditions for gold analysis by AAS

Metal	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Standard Range (ppm)
Gold	242.8	1.0	4	2-10

Design of Experiments

Main Effect

An effect is the difference in response averages that are applicable to the levels of the factor. The effect of factor A on the response can be obtained by taking the difference between the average response when A is in the high level (+1) and the average response when A is in low level (-1).

Effect of factor A = Average response at A high level – Average response at A low level

Example

Average response at factor B at high level (+1), is given by averaging the results obtained by running experiments 1,2, 5, 6, 9, 10, 13 and 14, and average response at factor B at low level (-1) by averaging the results obtained from running experiments 3, 4, 5, 7, 8, 11, 12, 15 and 16.

Average extractions at factor B at high level (+1) =
(10.43+5.65+4.78+2.61+23.48+25.22+18.04+10.11)/8= 12.54

Average extractions at factor B at low level (-1) =
(27.83+26.68+18.71+14.76+43.65+44.10+28.26+32.17)/8= 29.52

Thus the Effect of factor B = -16.98

Interaction Effect

An interaction is a cross product of two or more factors. The net sign of the interaction is also a cross product of the individual signs of the factors. The identity of interaction comes from the identity of the individual factors involved in the cross product. Across product of factor A and factor, B yields a two-factor interaction AB. An interactive effect is a difference in response

averages that are applicable to the levels of the interaction. The interactive effect of interaction AB on the response can be obtained by taking the difference between the average response when AB is high and the average response when AB is low. The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The intercept in an orthogonal design is the overall average response of all the runs. The coefficients are adjustments around that average based on the factor settings.

Table A2. Main and interactive coefficients and effects

Terms	Coefficient	Effect
A-Type of IL	-0.8725	-1.745
B-IL Concentration	-8.48	-16.96
C-S/L Ratio	-4.86	-9.72
D-Temperature	7.10	14.2
E-Time	-1.16	-2.32
AB	-0.7700	-1.54
AC	-0.4050	-0.81
AE	-0.3550	-0.71
BD	-0.4325	-0.865
BE	-0.3713	-0.7426
CD	-1.13	-2.26
CE	-0.5488	-1.0976
DE	-0.4775	-0.955

Modeling the significant effects of extraction prediction

The model or prediction equation is useful for predicting the outcome for future validation experiments. A model is an equation that uses only significant effects. If an interaction effect is significant, the terms for the main effects are also included. This is due to the hierarchy rule for defining a model (Barrentine, 1999). From the normal probability plot, it is found that the significant factors are B, C, and D. Therefore,

Recovery, R = $\acute{R} + \frac{E(B)}{2} B + \frac{E(C)}{2} C + \frac{E(D)}{2} D$,

where $\acute{R}$ represents the average of all the data for the runs (i.e average of all the recoveries) and B, C and D are the contrast constants (i.e +1 or -1), E(B), E(C), and E(D) are effects as indicated.

The coefficients that appear in the ets are half the calculated effects because a change from x = -1 to x = +1 is a change of two units along the x-axis. Therefore,

$$R = +21.02 + \frac{(-16.96)}{2} B + \frac{(-9.72)}{2} C + \frac{(14.2)}{2} D$$

Predicted recovery, R = + 21.02 - 8.48 B - 4.86 C + 7.11 D

The predicted recovery is calculated by substituting an appropriate contrast constant in a particular run.

Example: *Run 12 (Table B1)*

The predictor variables are, B = -1, C = -1, D = -1

Predicted recovery, R = 21.02 – 8.48 (+1) – 4.86 (-1) + 7.11(+1) = 24.51%

Note that the negative signs in some of the variables of the prediction model equation indicate that in order to maximize the oxidative leaching of pyrite to extract gold, these factors must be kept at low levels. The positive signs mean the factors must be kept at high levels.

Residual

This is the difference between the actual recovery and the predicted recovery for each run.

Example

Run 12 (Table B1)

Actual recovery = 25.21, Predicted recovery = 24.51

Residual = 25.21 – 24.51 = 0.7

Appendix B

Central composite design

In case of a second order model for the three factors under consideration, a quadratic polynomial regression model can be represented as follows:

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{3} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j + \varepsilon$$

where y is the predicted response, β_0, β_i, β_{ii} and β_{ij} are the coefficients for intercept, coefficient of linear effect, coefficient of quadratic effect and coefficient of interaction effect, respectively, ε is the term that represents other sources of variability not accounted for by the response function, and X_i and X_j are coded independent variables.

In general, this Equation can be written in matrix form:

$$y = X\beta + \varepsilon$$

where y is defined to be a matrix of measured values and X to be a matrix of independent variables. The matrices b and ε contain the coefficients and errors, respectively (Kwak, 2005).

$$\boldsymbol{y} = \boldsymbol{X}\boldsymbol{\beta} + \boldsymbol{\varepsilon}$$

$$\begin{bmatrix} 28.6 \\ 19.2 \\ 28.4 \\ 25.2 \\ 23.8 \\ 19.6 \\ 29.6 \\ 32.4 \\ 26.8 \\ 21.2 \\ 15 \\ 27 \\ 23.8 \\ 25.9 \\ 32.1 \\ 31.8 \\ 28.8 \\ 30.9 \\ 30.3 \\ 29.7 \end{bmatrix} = \begin{bmatrix} 1 & -1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 & 1 & -1 & -1 & 1 \\ 1 & -1 & 1 & -1 & 1 & 1 & 1 & -1 & 1 & -1 \\ 1 & 1 & 1 & -1 & 1 & 1 & 1 & 1 & -1 & -1 \\ 1 & -1 & -1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 \\ 1 & 1 & -1 & 1 & 1 & 1 & 1 & -1 & 1 & -1 \\ 1 & -1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & -1.682 & 0 & 0 & 2.828 & 0 & 0 & 0 & 0 & 0 \\ 1 & 1.682 & 0 & 0 & 2.828 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & -1.682 & 0 & 0 & 2.828 & 0 & 0 & 0 & 0 \\ 1 & 0 & 1.682 & 0 & 0 & 2.828 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & -1.682 & 0 & 0 & 2.828 & 0 & 0 & 0 \\ 1 & 0 & 0 & 1.682 & 0 & 0 & 2.828 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} \beta_0 \\ \beta_1 \\ \beta_2 \\ \beta_3 \\ \beta_{11} \\ \beta_{22} \\ \beta_{33} \\ \beta_{12} \\ \beta_{13} \\ \beta_{23} \end{bmatrix} + \begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \\ \varepsilon_7 \\ \varepsilon_8 \\ \varepsilon_9 \\ \varepsilon_{10} \\ \varepsilon_{11} \\ \varepsilon_{12} \\ \varepsilon_{13} \\ \varepsilon_{14} \\ \varepsilon_{15} \\ \varepsilon_{16} \\ \varepsilon_{17} \\ \varepsilon_{18} \\ \varepsilon_{19} \\ \varepsilon_{20} \end{bmatrix}$$

The normal Equations are,

$$X^TX \qquad \beta = X^TY$$

$$\begin{bmatrix} 20.0 & 0 & 0 & 0 & 13.7 & 13.7 & 13.7 & 0 & 0 & 0 \\ . & 13.7 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ . & . & 13.7 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ . & . & . & 13.7 & 0 & 0 & 0 & 0 & 0 & 0 \\ . & . & . & (Symetric) & 24.0 & 8.0 & 8.0 & 0 & 0 & 0 \\ . & . & . & . & . & 24 & 8.0 & 0 & 0 & 0 \\ . & . & . & . & . & . & 24.0 & 0 & 0 & 0 \\ . & . & . & . & . & . & . & 8.0 & 0 & 0 \\ . & . & . & . & . & . & . & . & 8.0 & 0 \\ . & . & . & . & . & . & . & . & . & 8.0 \end{bmatrix} \begin{bmatrix} \beta 0 \\ \beta 1 \\ \beta 2 \\ \beta 3 \\ \beta 11 \\ \beta 22 \\ \beta 33 \\ \beta 12 \\ \beta 13 \\ \beta 23 \end{bmatrix} = \begin{Bmatrix} 530.1 \\ -23.4 \\ 92.2 \\ -40.2 \\ 342.4 \\ 325.6 \\ 347.4 \\ -34.4 \\ 58.8 \\ 12.8 \end{Bmatrix}$$

The solutions to the normal Equation are:

$$\beta = (X^TX)^{-1} X^TY$$

$$\begin{bmatrix} 30.73 \\ -1.6 \\ 2.9 \\ 0.52 \\ -1.55 \\ -2.29 \\ -1.6 \\ 1.65 \\ 1.4 \\ 1.6 \end{bmatrix} = \begin{bmatrix} 0.166 & 0 & 0 & 0 & -0.056 & -0.056 & -0.056 & 0 & 0 & 0 \\ . & 0.073 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ . & . & 0.073 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ . & . & . & 0.073 & 0 & 0 & 0 & 0 & 0 & 0 \\ . & . & . & (Symetric) & 0.069 & 0.007 & 0.007 & 0 & 0 & 0 \\ . & . & . & . & . & 0.069 & 0.007 & 0 & 0 & 0 \\ . & . & . & . & . & . & 0.069 & 0 & 0 & 0 \\ . & . & . & . & . & . & . & 1.25 & 0 & 0 \\ . & . & . & . & . & . & . & . & 1.25 & 0 \\ . & . & . & . & . & . & . & . & . & 1.25 \end{bmatrix} \begin{bmatrix} 530.1 \\ -23.4 \\ 92.2 \\ -40.2 \\ 342.4 \\ 325.6 \\ 347.4 \\ -34.4 \\ 58.8 \\ 12.8 \end{bmatrix}$$

Relationship between coded and actual values of a variable (Obeng *et al.*, 2005)

Code	Actual value of the variable
-β	χ_{min}
-1	$[(\chi_{max} + \chi_{min})/2] - [(\chi_{max} - \chi_{min})/2\beta]$
0	$[(\chi_{max} + \chi_{min})/2]$
+1	$[(\chi_{max} + \chi_{min})/2] + [(\chi_{max} - \chi_{min})/2\beta]$
+β	χ_{max}

χ_{max} and χ_{min} = maximum and minimum values of x, respectively; k= number of variables (in this study k=3). $\pm\beta = (2^{k-q})^{1/4}$ for CCD, -q = fraction of the number of factors (in this study q=0)

Experimental layout for the central composite design

Standard Runs	*Coded values of variables*			*Actual values of variables*		
	IL concentration	S:L ratio	Temperature	IL concentration	S:L ratio	Temperature
Factorial points						
1	-1	-1	-1	10	1:8	35
2	+1	-1	-1	20	1:8	35
3	-1	+1	-1	10	1:4	35
4	+1	+1	-1	20	1:4	35
5	-1	-1	+1	10	1:8	60
6	+1	-1	+1	20	1:8	60
7	-1	+1	+1	10	1:4	60
8	+1	+1	+1	20	1:4	60
Axial points						
9	-1.68	0	0	5	1:6	48
10	+1.68	0	0	25	1:6	48
11	0	-1.68	0	15	1:2	48
12	0	+1.68	0	15	1:10	48
13	0	0	-1.68	15	1:6	25
14	0	0	+1.68	15	1:6	70
Centre points						
15	0	0	0	15	1:6	48
16	0	0	0	15	1:6	48
17	0	0	0	15	1:6	48
18	0	0	0	15	1:6	48
19	0	0	0	15	1:6	48
20	0	0	0	15	1:6	48

Appendix C

The effect of temperature was studied at four different temperature values (20, 35, 50 and 65°C) for extracting gold from the concentrated pyrite in 10 ml IL-water solution (15% v/v), with a solid to liquid ratio 1:8, and at pH= 1. The following tables represent the concentration of extracted gold obtained at a different temperature within specific intervals.

In the tables, X is the conversion of the gold and $1-3(1-X)^{2/3}+2(1-X)$ and $1-(1-X)^{1/3}$, are the standard equation for diffusion and chemical reaction based on shrinking core model, respectively.

Time (h)	Au Conc. (mg/l) 20 °C	X (Conversion)	$1-3(1-X)^{2/3}+2(1-X)$
0.34	0.45	0.18	0.012
0.67	0.52	0.21	0.016
1	0.58	0.23	0.020
3	0.65	0.26	0.025
5	0.67	0.27	0.027
7	0.69	0.27	0.029
12	0.73	0.29	0.033

Time (h)	Au Conc. (mg/l) 35 °C	X (Conversion)	$1-3(1-X)^{2/3}+2(1-X)$
0.34	0.46	0.18	0.012
0.67	0.54	0.22	0.017
1	0.60	0.24	0.022
3	0.66	0.26	0.026
5	0.72	0.29	0.032
7	0.75	0.30	0.035
12	0.83	0.33	0.043

Time (h)	Au Conc. (mg/l) 50 °C	X (Conversion)	$1-3(1-X)^{2/3}+2(1-X)$
0.34	0.68	0.27	0.028
0.67	0.75	0.30	0.035
1	0.79	0.32	0.039
3	0.89	0.36	0.051
5	1.00	0.40	0.065
7	1.05	0.42	0.073
12	1.11	0.44	0.084

Time (h)	Au Conc. (mg/l) 65 °C	X (Conversion)	$1-3(1-X)^{2/3}+2(1-X)$
0.34	0.82	0.33	0.042
0.67	0.90	0.36	0.052
1	0.99	0.40	0.064
3	1.16	0.46	0.092
5	1.22	0.49	0.103
7	1.27	0.51	0.113
12	1.34	0.54	0.130

Time (h)	Au Conc. (mg/l)	X (Conversion)	$1-(1-X)^{1/3}$ 20 °C
0.34	0.45	0.18	0.73
0.67	0.52	0.21	0.74
1	0.58	0.23	0.74
3	0.65	0.26	0.75
5	0.67	0.27	0.76
7	0.69	0.27	0.76
12	0.73	0.29	0.76

Time (h)	Au Conc. (mg/l)	X (Conversion)	$1-(1-X)^{1/3}$ 35 °C
0.34	0.46	0.18	0.73
0.67	0.54	0.22	0.74
1	0.60	0.24	0.75
3	0.66	0.26	0.75
5	0.72	0.29	0.76
7	0.75	0.30	0.77
12	0.83	0.33	0.78

Time (h)	Au Conc. (mg/l)	X (Conversion)	$1-(1-X)^{1/3}$ 50 °C
0.34	0.68	0.27	0.76
0.67	0.75	0.30	0.77
1	0.79	0.32	0.77
3	0.89	0.36	0.79
5	1.00	0.40	0.80
7	1.05	0.42	0.81
12	1.11	0.44	0.81

Time (h)	Au Conc. (mg/l)	X (Conversion)	$1-(1-X)^{1/3}$ 65 °C
0.34	0.82	0.33	0.78
0.67	0.90	0.36	0.79
1	0.99	0.40	0.80
3	1.16	0.46	0.82
5	1.22	0.49	0.83
7	1.27	0.51	0.84
12	1.34	0.54	0.85