Doctoral Thesis

Ammonium thiosulfate leaching of arsenic-bearing refractory gold ores.

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctorate in Engineering

by

Takunda Joseph Mhandu

Laboratory of Chemical Resources,
Division of Sustainable Resources Engineering,
Graduate School of Engineering,
Hokkaido University, Japan
March 2024

Declaration

I, Takunda Joseph Mhandu hereby declare that, except where specific reference is made in the text, this dissertation is my own research work, and it has never in its entirety or in parts submitted to any university for academic qualification.

Signature: _____

Takunda Joseph Mhandu

Date: 19 February 2024

Abstract

The depletion of free milling gold deposits has made the mining industry depend on refractory gold ores to meet the gold demand. Global statistics have shown that about 2/3 of the gold resources are refractory and the exploitation of these ores is expected to increase in future as the main primary gold deposits.

In refractory gold ores, sulfide-refractory gold ores account for a substantial proportion of the refractory gold ores in which minerals like arsenopyrite and pyrite are commonly associated with gold. Gold is extracted from these ores using the conventional cyanidation process, but it has two major problems: gold recovery is usually less than 50 % due to encapsulation of gold grains in the sulfide matrix and cyanide the reagent used during leaching is toxic to both humans and animals. To address the toxicity of cyanide, several reagents including halides, thiourea and thiosulfate have been proposed to be alternatives to cyanide. Amongst these proposed reagents, thiosulfate is the most lucrative reagent to replace cyanide.

The use of thiosulfate to extract gold from refractory ores is promising because of its non-toxicity and high selectivity but the sulfide minerals (i.e., pyrite, arsenopyrite), refractory gold ores, hinder gold extraction due to the high consumption of lixiviant. To minimize the high reagent consumption, pretreatment techniques such as ultrafine grinding, biological oxidation and roasting are applied to make the ores amenable to thiosulfate leaching. On the other hand, these pretreatment techniques have drawbacks: ultrafine grinding does not remove decomposition effects of sulfide on thiosulfate, arsenic in arsenopyrite is toxic to microbes and roasting generates toxic arsenic oxides, making the pretreatment methods not compatible for arsenopyrite containing refractory gold ores. In this study, a new pretreatment method to improve gold extraction from arsenopyrite/pyrite-bearing gold ores are proposed based on the model experiments using mixture of gold powder and arsenopyrite and pyrite-bearing ore.

Chapter 1 describes the statement of the problem and the objectives of this study.

Chapter 2 reviewed literature on techniques to extract from refractory ores including roasting, ultrafine grinding, bio-oxidation, ultrasound enhanced oxidation, ozone oxidation and chemical oxidation. In addition, the available alternatives to cyanide are also evaluated.

In Chapter 3, model leaching experiments using gold powder and arsenopyrite leaching were conducted to determine the effects of the sulfide minerals on gold extraction. Gold extraction

significantly reduced in the presence of sulfide minerals like arsenopyrite and pyrite. Surface analysis using XPS and SEM-EDS for gold in ammonia thiosulfate solutions showed that a very thin layer containing cuprous sulfide, iron oxyhydroxide and elemental sulfur was formed on gold surface. This layer was formed both in the presence and absence of sulfide minerals, indicating that the layer is not the essential cause of the suppression in gold extraction with sulfide minerals. Solution analysis using UV-Vis showed that the presence of sulfide minerals accelerated the decomposition of thiosulfate. From this, it was concluded that thiosulfate decomposition is the main cause of the suppression in gold extraction in the presence of sulfide minerals like arsenopyrite and pyrite.

In Chapter 4, a novel pretreatment was proposed to enhance the succeeding ammonia thiosulfate leaching of gold. In the proposed pretreatment, sulfide minerals like arsenopyrite and pyrite is decomposed by the oxidation using the solutions containing cupric ammine complex. Model experiments using the mixture of gold powder and sulfide minerals were conducted. The results showed that significant amounts of sulfide minerals were decomposed in the pretreatment, and this suppressed the thiosulfate decomposition in the succeeding ammonia thiosulfate leaching, causing the enhancement of gold extraction.

In Chapter 5, based on the results of model experiments outlined in Chapter 4, the effectiveness of the proposed pretreatment was evaluated using refractory gold ores obtained from Zimbabwe. Without pretreatment, 45% thiosulfate was decomposed and the gold extraction from the ores were less than 5 %, while with pretreatment thiosulfate decomposition was suppressed to 25% and gold extraction was improved to over 45 %.

Chapter 6 summarized the important findings of this dissertation and its implications.

Contents

CHAPTER 1: GENERAL INTRODUCTION

1.1 Background

Gold is a lustrous, yellow metal which is malleable and chemically inert. Over the years, gold has played a pivotal role in humans' economic and social lifestyle as currency and a metal for jewelry, signifying wealth, and power respectively (Mudd et al., 2012). It has also found applications in industries such as electronics, electrical systems and devices, medical treatments, drugs, implants, and this has increased its demand (Corti & Holliday, 2004). Despite the rise in the demand in the use of gold, there is a growing depletion of "free milling ores", making the mining industry rely on processing of refractory ores for gold production (Mudd et al., 2012; Espatia, 2021). Gold ore refractoriness vary with gold mineralization and can also be classified based on the gangue mineral association (Afenya, 1991). In arsenopyrite/ pyrite ores, the refractoriness is from gold (Au) being encapsulated within arsenopyrite (FeAsS)/pyrite (FeS_2) matrix (Zhang et al., 2019), and other characteristic elements which makes it difficult extract it (Xing et al., 2019). Refractory gold ores constitute the largest reserves but are the most difficult from which gold can be extracted from and gold leaching recoveries are often below 50% (Yang, et al., 2005). In conventional cyanidation process arsenopyrite encapsulates gold and prevents interaction of CN^- with gold for leaching to occur. The problem of encapsulation results in low gold extraction and pretreatment of the refractory ores is employed to enhance the gold extraction. The other challenge of extracting gold from the refractory ores is the environmental pollution associated with processing ores containing arsenic. Arsenic is a very toxic metal which causes detrimental effects to both plants and animals if it pollutes the environment. In addition, the use of cyanide as a lixiviant is an environmental hazard as cyanide is also toxic to animals if ingested. To solve the problem of the toxicity of the lixiviant, alternatives have been proposed including halides, thiourea and thiosulfate. Of the proposed cyanide alternatives, thiosulfate is the most promising due to its low toxicity, fast leaching kinetics and high selectivity to gold. It is on this basis that this study investigates the applicability of thiosulfate to leaching of gold in pyrite and arsenopyrite-bearing ores.

1.2 Objective of the research

This research aims to develop an efficient method to recover gold from refractory ore (arsenic-bearing ores).

1.3 Outline of the dissertation

This dissertation is composed of six chapters. The key contents of each chapter are outlined as follows:

Chapter 1 describes the statement of the problem, background of fine particle problems in gold extraction from refractory gold ores.

Chapter 2 reviewed techniques to gold extract from refractory ores including roasting, ultrafine grinding, bio-oxidation, ultrasound enhanced oxidation, oxidation, ozone oxidation and

chemical oxidation.

In chapter 3, model experiments using gold powder and arsenopyrite leaching were conducted to determine the effects of the sulfide minerals on gold extraction and the results were compared to gold powder leached in the absence of sulfide minerals with that in the presence of arsenopyrite and pyrite samples. The mechanism of gold suppression in the presence of arsenopyrite was investigated using thermodynamics calculations and validated by leaching experiments.

In chapter 4, a novel pretreatment stage before thiosulfate leaching was proposed which uses cupric ammine pre-oxidation before thiosulfate leaching to enhance gold extraction. Model experiments using gold powder and arsenopyrite leaching were conducted to determine the effects of a pretreatment stage in the subsequent thiosulfate leaching step.

In chapter 5, the effectiveness of cupric ammine pretreatment before thiosulfate leaching of run-off-mine (ROM) samples obtained from a mine, in Zimbabwe (i.e., sulfide zone ore and transitional zone) ore was conducted. In addition, stability of the pretreated leach residue of the mine samples was assessed to see the effects of the pretreatment of the minimization of acid mine drainage formation.

Chapter 6 summarizes the most essential findings of this dissertation and propose a possible application.

References

Afenya, P. (1991). Treatment of carbonaceous refractory gold ores. *Minerals Engineering, 4*(7), 1043-1055.

Espitia, S. L., & Lapidus, G. T. (2021). Arsenic removal strategy in the processing of an arsenopyritic refractory . *Hydro 203*, 105628.

Mudd, G., Giurco, D., Mohr, S., & Mason, L. (2012). *Gold resources and production: Australia in a global context.* Sydney: The Department of Civil Engineering (MonashUniversity) and the Institute for Sustainable Futures (University of Technology, Sydney).

Xing, W., Sohn, S., & Lee, M. (2019). A Review on the Recovery of Noble Metals from Anode Slimes. *Mineral Processing and Extractive Metallurgy, 41*(2), 130-143.

Yang, Y.; Zhang, X.; Xu, B.; Li, Q.; Jiang, T.; Wang, Y. Effect of arsenopyrite on thiosulfate leaching of gold. *Trans. Nonferrous Met. Soc. China* **2015**, *25*, 3454–3460.

Zhang, Y., Wang, C., Ma, B., Jie, X., & Xing, P. (2019). Extracting antimony from high arsenic and gold containing stibnite ore using slurry electrolysis. *Hydrometallurgy, 186*, 284-291.

.

CHAPTER 2: LITERATURE REVIEWS

2.1 Introduction

The demand for gold is increasing due to its many applications in various industrial sectors jewelry (53%), financial purposes (i.e., investment and central banks) (39%), and electric and electronic equipment (6%), and the remaining 2% in medical and pharmaceutical products. To meet high demand for gold, high-grade gold deposits must be available for exploitation, but currently that is not the case. Wilson et al. (2022) reported that there has been a decrease in the gold grades in global gold deposits from 10 g/t in the 1970s [4] to less than 1.5 g/t [5]. The low-grade ores available for gold extraction are mainly refractory deposits in which gold is difficult to extract using conventional methods. In the refractory ores, gold is associated with sulfide minerals like arsenopyrite (FeAsS), pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and minor sulfides like stibnite (Sb_2S_3). In the case of arsenic-bearing gold ores, gold recovery is usually less than 50 % (Yang, Rao, Liu, Zhang, & Chen, 2017) due to gold being encapsulated by the sulfide matrix and cyanide being consumed by associated gangue elements like copper, zinc (Ubaldini, Massidda, Abbruzzese, Vegliò, & Toro, 1998) (Hammerschmidt, Güntner, Kerstiens, & Charitos, 2016). In addition, the arsenic contained in arsenopyrite is a toxic element which kills microbes and has carcinogenic effects on human beings (Fatoki & Badmus, 2022). Apart from this, cyanide, the lixiviant used in the conventional process is very toxic and poses hazard to the environment. Hence, to extract gold from these refractory gold ores more sustainable, environmentally friendly methods of extracting gold from their primary ores must be developed. This chapter reviews the different techniques used to extract gold from arsenic–bearing gold ores and recent research and developments made in the gold extraction from refractory gold ores.

1.1. Arsenopyrite−bearing refractory gold ores and problems associated with processing of these ores.

In most gold bearing ores, gold occurs as free particles of gold and electrum, incorporated in the sulfide mineral matrix. In some cases, gold is present in ores as compounds, that is, gold tellurides, AuAg tellurides, aurostibnite ($AuSb_2$), maldonite (Au_2Bi),etc., along with characteristic elements such as iron (Fe),copper (Cu), As and Sb (Simon, Huang, Penner-Hahn, Kesler, & Kao, 1999) (Ashley, Creagh, & Ryan, 2000)

(Yang, Rao, Liu, Zhang, & Chen, 2017). Many studies have also confirmed that arsenopyrite and pyrite are the most common sulfide minerals associated with gold, where gold is present as micro-to nanosized inclusions of metallic gold and electrum ,incorporated in the sulfide crystal structure (Simon, Huang, Penner-Hahn, Kesler, & Kao, 1999) (Cabri, et al., 2000) (Merkulova, et al., 2019) (Vikentyev, et al., 2021).

In arsenopyrite–bearing ores, the refractoriness is due to the following reasons: (1) gold is encapsulated in matrix of sulfide minerals like pyrite (FeS_2); (2) characteristic elements like Sb, Fe, Cu, Pb and Zn associated with the ores consume the leaching agents and compete with gold in the leaching process, making it difficult to extract gold; (3) redeposition or adsorption of dissolved gold due to the presence of naturally occurring carbonaceous material within the ore (Xing, Sohn, & Lee, 2019). These factors result in poor gold extraction from these refractory ores as gold is lost to the tailings (Ubaldini, Massidda, Abbruzzese, Vegliò, & Toro, 1998).

For the past century, cyanide leaching has been the most common method for extracting gold from its hypergenic ores (in the weathering crust) (Brooy, Linge, & Walker, 1994). Due to the gradual decrease in the free milling ores, with time, direct cyanidation is proving to be ineffective in extraction of gold from the readily available refractory ores (Mudd, Giurco, Mohr, & Mason, 2012). In addition ,during the leaching of arsenic–bearing ores, high toxicity As, cyanide and its tailings poses health and environmental problems if not properly managed (Ubaldini, Massidda, Abbruzzese, Vegliò, & Toro, 1998) (Aylmore & Muir, 2001) (Jeon, et al., 2021). Hence proper management of these elements during the processing of arsenic–bearing gold ores is required to minimize environmental pollution. Table 2.1 below shows various refractory gold ores and the nature of refractoriness.

Table 2.1: Nature of refractoriness in gold ores around the world.

Nature of refractoriness	**Major minerals chemical & formula**	**Name of Mine and Country**	**Au grade (g/t)**	**References**
	Arsenopyrite (FeAsS), Pyrite	Kibali, Democratic Republic of Congo	2.9	(Resources, 2018)

	(FeS_2), Galena PbS), pyrrhotite (FeO(OH),	Olympiada, Russia	2.07	(Polyus, 2017)
Physical encapsulation and surface passivation	stibnite(Sb_2S_3),	Cam and Motor, Zimbabwe	2.99	(Index, 2020)
	Hematite(Fe_2O_3)($FeSb_2S_4$)Sphalerite(ZnS)	Youanmi, Australia	5.42	(limited, 2020)
		Muruntau, Uzbekistan	3.4	(Wilde.A. & Gilbert, 2000)
		Loulo gounkoto, Mali	5	(RESOURCES, 2018)
	Chalcopyrite ($CuFeS_2$)	Cadia, Australia	1.17	(Limited, 2020)
	Pyrite (FeS_2)	Grasberg, Indonesia	0.64	(Leys, Cloos, New, & MacDonald, 2012)
	Bornite (Cu_5FeS_4),	Kuh-e-Zar, Iran	0.7-3.02	(Karimpour, et al., 2017)
Formation of base metal aurocyanide complexes	Molybdenite (MoS_2)	Pueblo Viejo, Dominican Republic	1.4	(Technology, 2012)
	Sphalerite (ZnS)	Tampakan, Philippines	0.19	(Technology, 2012)
	Malachite ($Cu_2CO_3(OH)_2$			
	Illite(K,H_3O)(Al,Mg,Fe) $_2(Si,Al)_4O10[(OH)_2(H_2O)$	Cripple Creek, USA	2.3	(Kadel-Harder, et al., 2020)
	Arsenopyrite (FeAsS),	Gold strike, USA	3.32	(Bermeo, Penaloza, & Chavez, 2019)
Adsorption of dissolved Au by carbonaceous material.	Pyrite (FeS_2)	Prestea, Ghana	2.24	(Bermeo, Penaloza, & Chavez, 2019)
	Molybdenite (MoS_2)	Batkyrchik, Russia	2.7	(Bermeo, Penaloza, & Chavez, 2019)
	Ullmannite (NiSbS)	Takwa, Ghana	0.9-3.7	(Yang, Liu, Song, & Dong, 2013)
	Tetrahedrite($(Cu,Fe)_{12}Sb_4S_{13}$)	Ashanti, Ghana	1.4	(Yang, Liu, Song, & Dong, 2013)
		Kerr Anderson, Canada	28.35	(Yang, Liu, Song, & Dong, 2013)

2. Recent research and development for arsenopyrite–bearing gold ore processing

2.1. Overview

As discussed in the last section, the major problem associated with arsenic-bearing refractory gold ores is incomplete gold extraction due to encapsulation. This section reviews the available techniques for extracting gold from arsenic–bearing ores and

strategies to overcome the problems are discussed. The complexity of extracting gold from arsenic–bearing ores makes pretreatment processes before leaching imperative. Ultra–fine grinding (Celep & Yazici, 2013), roasting (Dunn & Chamberlain, 1997), pressure oxidation (Gudyanga, Mahlangu, Chifamba, & Simbi, 1998), bacterial oxidation (de Carvalho, da Silva, Giardini, Souza, & Leão, 2019), chemical oxidation, i.e. acid and alkaline pretreatment (Wang Y. , Liu, Yan, & Ye, 2021) (Espitia & Lapidus, 2021) (Karimov, et al., 2021) are some of the common pretreatment techniques being employed to extract gold from arsenic–bearing ores but each method comes with its own short comings.

2.2 Approaches extraction of gold physically encapsulated.

2.2.1 Ultra-fine Grinding

The ultra–fine grinding technique (UFG) is effective for treating gold ores in which gold is physically encapsulated with gold grains (size ranges between 1–2 µm to 20 µm) locked in the sulfide matrix. By applying UFG, the desired degree of liberation of gold grains can be achieved without using chemicals (Corrans & Angove, 1991). UFG does not emit toxic effluents like SO_2 which is generated in a thermal pretreatment process, roasting, discussed later. Thus, the use of UFG is incompliance with the stringent environmental requirements in the mineral processing industry. Examples of industrial plants utilizing the UFG technique include, Kalgoorlie Consolidated Gold Mines, Australia (Ellis & Gao, 2003), Kibali Gold Mine, South Africa (Mahlangu, et al., 2019), Sukari Gold mine , Egypt (Pardey, Osman, & Johnson, 2010) etc.

Fine grinding can be achieved using three types of mills, namely: vibratory mills, stirred mills and jet mills. Stirred mills (i.e., Vertimill, Stirred Media Detritor (SMD) and ISAMill) are used to achieve the size of ground product (d_{80}) around 2–3 µm (Brooy, Linge, & Walker, 1994). The UFG general process flowsheet is shown in Figure 2.1.

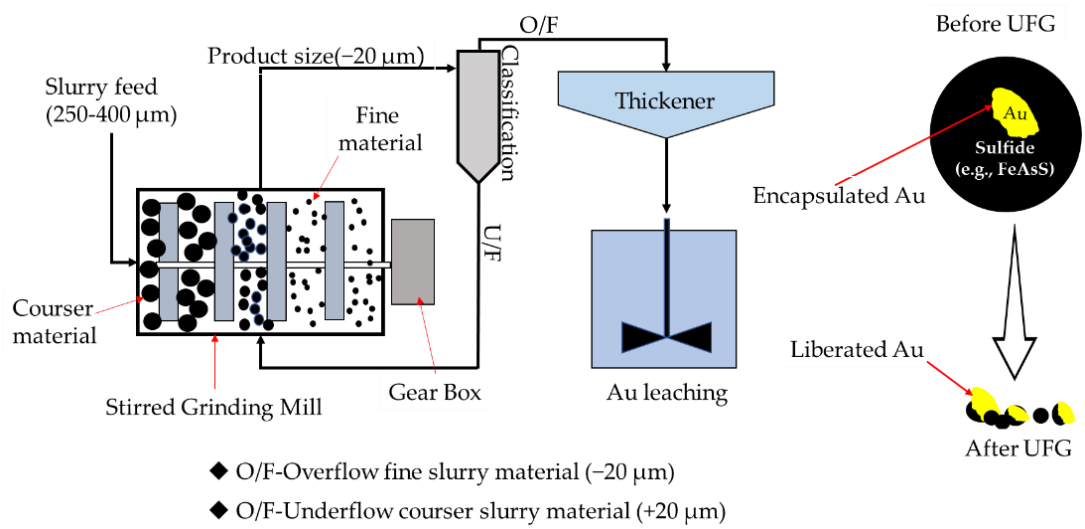


Figure 2.1: General flowsheet of UFG process.

In UFG, the stirring speed, media size and ball charge ratios are the significant parameters which directly affect the fineness of the product, but parameter specifications vary with ore types (Jankovic, 2003) (Celep & Yazici, 2013). The desired product size for any operation is a key factor in selecting the most suitable mill to use during UFG. Table 2.2 gives a summary of the key operating conditions of stirred mills.

Table 1.2: Operation conditions for stirred mills.

Type of mill	Ore type	Grinding media size	Operating speed (m/s)	Power Intensity (KW/m^3)
Vertimill	Sulfidic ore	6.0 mm	3	39
Stirred Media Detriot (SMD)	Pyritic ore	6.5 mm	10−12	243
IsaMill	Pyritic ore	6.5 mm	>15	133

Research done by Celep et al., (2019) on the effect of grinding (using a pin−type vertical stirred media mill) on extraction of gold from a refractory ore containing pyrite by cyanidation revealed that gold extraction in 24 hr of leaching was 40 % without grinding and improved to 66 % after grinding (D_{80} of ground product, –3.7 µm). Apart from improvement of recovery, UFG tends to concentrate gold in the smaller size fraction as reported by a study done by Owusu et al., (Owusu, Agorhom, Fosu, & Arthur, 2020).

In this study, about 60 % of the Au was concentrated in –38 µm size fractions as shown in Figure 4. The major limitation of UFG is that it liberates gold physically locked only, and it is not effective for gold chemically incorporated in sulfides like auro-stibnite ($AuSb_2$). This means that gold can be liberated from the sulfide matrix but the lixiviant for example, cyanide or thiosulfate, can still be consumed by the action of sulfides or other associated mineral composition. Another problem associated with the use of this technique is high energy consumption, stirred mills' energy consumption is 3 times more than the conventional mills (Celep & Yazici, 2013).

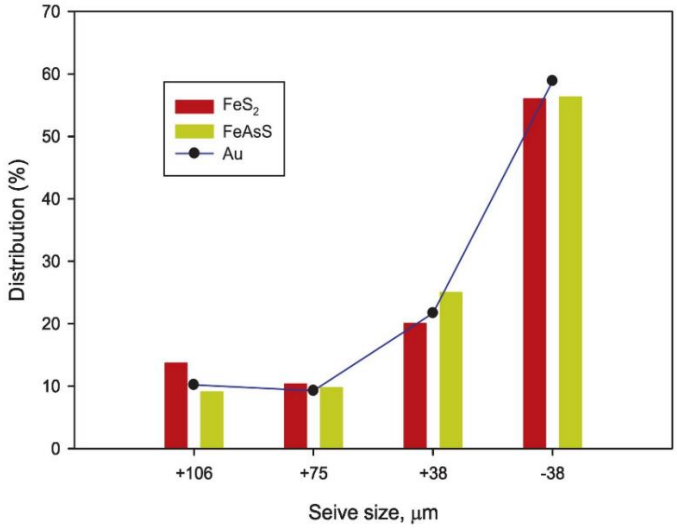


Figure 2.2. Gold, pyrite and arsenopyrite size–by–size deportment (Owusu, Agorhom, Fosu, & Arthur, 2020).

2.2.2 Roasting

Roasting is the traditional way of treating refractory gold ores in which gold is physically encapsulated in the sulfide matrix and it is conducted before cyanidation. There are several variations of gold ore roasting (Nanthakumar, Pickles, & Kelebek, 2007) (Li H. , 2018) (Qin, Xueyi, Qinghua, Dawei, & Zhang, 2021). Oxidizing roasting converts the arsenopyrite to iron oxides, arsenic oxide, sulfur oxides and arsenate (Mikhail, 1992). The calcine is porous and allows lixiviants to access gold grains leading, thus improving the gold extraction. The roasting treatment is performed in rotary kilns or fluidized–bed reactors: at around 450 °C, As is removed as arsenic oxide gas (As_2O_3), then at 600–700 °C, oxidation of the FeAsS occurs as follows:

$$2FeAsS + 3.5O_{2(g)} \rightarrow Fe_2O_3 + 2As_2O_{3(g)} + 2SO_{2(g)} \quad (1)$$

When oxidizing roasting treatment is applied on arsenic–bearing ores, final gold recovery in the following steps (leaching and recovery) is improved to 80–90 %. Table 3 shows examples of mines that employ roasting as a pretreatment technique prior to the cyanidation process. The major technical problem associated with oxidizing roasting is the formation of iron oxide layer, which encapsulate gold grains (secondary encapsulation) and suppress gold leaching (Fraser & Wells, 1991) (Gudyanga, Mahlangu, Chifamba, & Simbi, 1998) (Liu, Chi, Xu, Zeng, & Liang, 2000) (Nunan, et al., 2017). This is because the oxidation of sulfides is exothermic in nature, and it is difficult to control the temperature and extent of the reactions during the roasting process. The environmental problems caused by the roasting process is emission of SO_x gases, causing acid rain (Park, et al., 2021). Moreover, oxidizing roasting of arsenic–bearing ores, generates volatile arsenic trioxide (As_2O_3) in Eq (1), is highly toxic and has acute effects at a small concentration of 20 mg/Kg (Ruan, et al., 2022). This makes the roasting pretreatment not to be compatible for ores with high concentrations of arsenopyrite. Table 2.3 summarizes some of the industrial operations where roasting is utilized as a pretreatment step before leaching gold from refractory ores.

Table 2.3: Application of roasting pretreatment in gold mines around the world (Walker et.al, 2015) (Dunne, Kawatra, & Young, 2019)

Name of Mine	**Country**	**Associated sulfide minerals**	**Roasting Technique**	**Recovery**	**Status**
Giant Mine, Yellowknife, Northwest	Canada	FeS_2 Sb_2S_3	FB	> 80%	Closed
Goldstrike, Nevada	USA	FeS_2 FeAsS	FB	92 %	Operational
Kalgoorlie Consolidated Gold Mines, Western Australia	Australia	FeS_2 $CuFeS_2$	CBF	>90 %	Operational

New Carlin	USA	FeS_2	CBF	> 90 %	Operational
Syama	Mali	FeAsS FeS_2	CBF	>90 %	Operational

2.2.3 Bioleaching

The application of bacteria in leaching processes started in the 1950s to recover copper from low–grade copper ores and commercialized in the 1980s for the treatment of refractory gold ores in South Africa (Nan, Cai, & Kong, 2014). Currently, there are numerous gold mines in the world that are applying bioleaching to recover gold from sulfidic refractory gold ores as shown in Table 2.4. Physically encapsulated gold liberation is achieved by oxidizing the sulfide minerals and elemental sulfur (S) using microbes (Nunan, et al., 2017) (Wang, Faraji, Ramsay, & Ghahreman, 2021). The major advantages of this technique include zero emission toxic gases like SO_2 as compared to oxidizing roasting, relatively lower costs of operation, thus, it is an economically viable method to extract gold from low grade ores (Brooy, Linge, & Walker, 1994) (Ahn, Wu, & Lee, 2019). The process of bacteria oxidation comprises of three stages; (1) cultivation of bacterial culture, (2) bio–catalyzed oxidation for removing As and S, (3) residue pretreatment, that is, neutralizing before cyanidation. Acidophilic bacteria (*Acid thiobacillus−thiooxidants, acidithiobacillus–ferrooxidants* and *leptospirillum–ferrooxidants*) are the most widely used bacteria (Dave, 2018). Acidophilic bacteria survive at pH 1.2–1.8 and temperatures of ranging from 30–35ºC They oxidize Fe^{2+} to Fe^{3+}, Eq (7), S to SO_4^{2-} and H_2SO_4 ,Eq (9) and arsenic to arsenite (AsO_3^{3-}) ,Eq (7) or arsenate (AsO_4^{3-}) resulting in the liberation of Au from the sulfide matrix (Ofori-Sarpong, Osseo-Asare, & Tien, 2011) (Renjie, Jingying, & Zhongying, 2016). The mechanism of bacteria oxidation is illustrated in Figure 2.3.

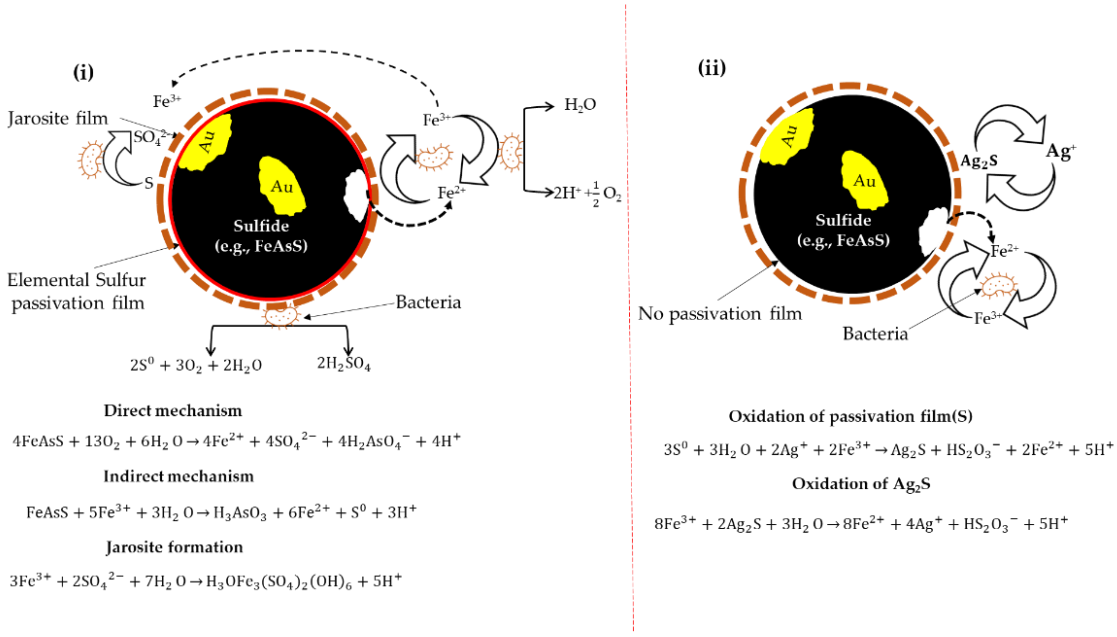


Figure 2.3: Mechanism of bacterial leaching (i) and (ii) with Ag^{+}.

The main bio–oxidation reactions, with respect to FeAsS, occur as follows: Eqs (5)– (8).

$$4FeAsS + 13O_2 + 6H_2O \xrightarrow{\text{Bacteria}} 4Fe^{2+} + 4SO_4^{2-} + 4H_2AsO_4^{-} + 4H^{+} \quad (5)$$

Ferrous sulfate formed in the above reaction, Eq (6) is then oxidized to ferric sulfate**,** which is a strong oxidant to decompose FeAsS Eq (7), and elemental sulfur formed in Eq(7) is oxidized in Eq(8).

$$4Fe^{2+} + O_2 + 4H^{+} \xrightarrow{\text{Bacteria}} 4Fe^{3+} + 2H_2O \quad (6)$$

$$FeAsS + 5Fe^{3+} + 3H_2O \xrightarrow{\text{Bacteria}} H_3AsO_3 + 6Fe^{2+} + S^{0} + 3H^{+} \quad (7)$$

$$2S^{0} + 3O_2 + 2H_2O \xrightarrow{\text{Bacteria}} 2H_2SO_4 \quad (8)$$

The effectiveness of bio-oxidation of arsenic–bearing ores is affected by three factors which are the (i) concentration of As^{3+}, (ii) treatment time and, (iii) temperature. However, the leaching behavior of minerals in the presence of bioleaching systems is also another factor to consider. FeAsS is oxidized at a rate about two times faster than FeS_2 because of its lower electrode potential, hence gold is liberated faster if FeAsS is the main

gold mineral carrier (Abbruzzesse, Ubaldini, Veglio, & Toro, 1994). In a study by Komnitsas et al., (1995), the degree of oxidation was measured for 3 g of FeAsS and FeS_2 concentrates of the same particles size (–0.044 mm) in H_2SO_4 in the presence of T–Ferrooxidans bacteria for 17 days. The degree of FeS_2 oxidation was between 27–40% whilst that FeAsS was 77– 100 %. The following is an in-depth in the factors that affect bioleaching systems:

Effect of As^{3+} concentration on bio-oxidation.

Despite arsenopyrite oxidation rate being faster than pyrite, the bacteria activity is significantly affected by a gradual increase in As^{3+} concentration (Aposhian, Zakharyan, Avram, Sampayo-Reyes, & Wollenberg, 2004) (Cui, Yang, Chen, Zhang, & Li, 2010).

As^{3+} ions toxicity to microorganisms is much higher than that of As^{5+}, hence the oxidation of As^{3+} to As^{5+} must be accelerated to improve the bacterial activity and overall leaching kinetics. An investigation into the effect of As valence to bioleaching by Cui et al., (Cui, Yang, Chen, Zhang, & Li, 2010), revealed that the conversion of As^{3+} to As^{5+} is favored in high Fe:As ratio of 10:1 respectively, attained by addition of FeS_2, thus, reducing the As^{3+} poisoning to the microbes.

As^{3+} poisoning to bacteria is a serious challenge during gold extraction from high arsenic bearing ores. Hence, studies on the development of domesticated, As resistant bacteria to enhance the effectiveness of bioleaching to As bearing Au ores have been carried out. HQ−0211 bacteria have been identified as one of the most As resistant bacteria and effective for bioleaching of high As containing ores (Auwalu & Yang, 2020) (Cui, Yang, Chen, Zhang, & Li, 2010). Auwalu et al., (Auwalu & Yang, 2020) used domesticated HQ−0211 bacteria and Achaean culture to treat high As bearing Au ores before Au leaching. The domesticated strain (HQ−0211) oxidized about 65.5 % As^{3+} to As^{5+}. To segregate the As^{3+} from the solution, separation was done in strong acidic solution with toluene as the As^{3+} extractant while As^{5+} was retained in the aqueous solution.

Effect of treatment time on bio-oxidation

Many studies have reported that Au extraction with increase in bioleaching treatment time of up to 60 day in some cases (Hansford & Chapman, 1992) (Charandraprabh, Modak, Natarajan, & Raichur, 2002) (Marchevsky, Quiroga, Giaveno,

& Donati, 2017) (Huang & Yang, 2021). Observations made by Ubaldini (Ubaldini, Vegliò, Fornari, & Abbruzzese, 2000) and de Carvalho [43] confirmed that bio–oxidation leaching efficiency improves with an increase in leaching time of up to 30 days yielding. Gold extraction of over 90 %, while 37 % of As extracted. The long treatment time is a serious drawback of bioleaching: The causes of long treatment times for arsenic–bearing ores is attributed to formation of Fe, As, S containing intermediates and products such as jarosite (($\mathbf{M}Fe_3(SO_4)_2(OH)_6$), where **M** is K^+, Na^+,H_3O^+, etc.)), goethite (Fe(OH)O) and elemental S that have a passivation effect on the bioleaching process (Figure 3) (Corkhill & Vaughan, 2009) (Marquez, Ospina, & Morales, 2012). Remediations for slow kinetics reported include the use of metal ions like Ag^+, Cu^{2+}, Co^{3+}, Hg^+, Bi^{3+} which act as catalysts and other organic, complexing agents like ethylenediaminetetraacetic acid (EDTA) can be used to improve the leaching kinetics of bioleaching and minimize the effect of passivation (Li, et al., 2021). Zhang et al., (Zhang, Li, & Liu, 2020) used 5 mg/l Ag^+ into the bioleaching system of an As–bearing Au ore and this resulted in an improvement of As removal from about 30 % without additives to over 47 %. In addition, use of Ag^+ ions also shortened the bioleaching time from 19 days to 15 days.

Effect of temperature on bio-oxidation

The leaching temperature is a factor that affects the kinetics of bacteria during the liberation of gold grains from minerals sulfide matrix. It is an established fact that increasing temperatures beyond 35 ºC denatures the bacterial enzymes and kills them (Marquez, Ospina, & Morales, 2012) (Liu, Wu, & Zhang, 2017) (Mubarok, Winarko, Chaerun, Rizki, & Ichla, 2017). Hence, the application of thermophiles, a type of micro-organisms that survive at temperatures of 60−80 ºC was considered for treatment of sulfide minerals with an improvement in the leaching kinetics (Lindstrom, Sandstom, & Sundkvis, 2003). The application of thermophiles at industrial scale is being used in processing plants in the world such as in the BIOX^{TM} process, developed by GENCOR, and the BacTech process, to oxidize refractory gold concentrates (Whincup & Binks, 2004). However, it still takes days to treat sulfide minerals for example the BacTech process has a residence time of 5−6 days treating high As concentrates (Tech, 2011).Table 4 gives example of some notable gold mines that are utilizing bio-leaching as pretreatment to arsenopyrite/pyrite-bearing gold ores.

Table 2.**2**:A summary of commercial BIOX plants in the world (Ndlovu, 2008) (BIOX, 2012) (Walker, Jamieson, Lanzairotti, Hall, & Peterson, 2015) (Exchange, 2022)

Name of Mine	Gold grade	Country	Date of Commissioning	Concentrate treatment capacity. [tpd]	Reactor size [m^3]	Current Status
Fairview	7.29	South Africa	1986	62	340	Operating
Wiluna	5.4	Australia	1993	158	480	Operating
Ashanti	2.78	Ghana	1994	960	900	Operating
Coricancha[d]	5.8	Peru	1998	60	262	Operating
Fosterville	5-10	Australia	2005	211	900	Operating
Suzdal	2.3	Kazakhstan	2005	520	650	Operating
Bogoso/Prestea	2.24	Ghana	2007	820	1500	Operating
Jinfeng	2.76	China	2007	790	1000	Operating
Kokpatas	4	Uzbekistan	2008	2138	2008	Operating
Agnes[d]	5.3	South Africa	2010	20	75	Operating
Obuasi[r]	9	Ghana	2018	2000	274	Operating
Cam and Motor Mine	2.99	Zimbabwe	2022	200	500	Operating

2.3 Strategies to solve high reagent consumption due to decomposition of leaching reagent by coexisting elements in the conventional cyanidation process.

Many publications have reported the ineffectiveness of conventional cyanidation process in extraction gold from refractory ores due to cyanide decomposition by co existing elements in the ores and the huge Au losses during the extraction process

(Abbruzzesse, Ubaldini, Veglio, & Toro, 1994) (Aylmore & Muir, 2000) (Adams, 2005) (Hilson & Monhemius, 2006) (Celep, I brahim, & Deveci, 2011) (Tabelin, et al., 2021) (Qin, Xueyi, Qinghua, Dawei, & Zhang, 2021). In general, cyanide dissolves gold in the presence of oxygen at around pH 10 as shown by the following Eq (10) (Adams, 2005).

$$4Au_{(s)} + 8NaCN_{(aq)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 4NaAu(CN)_{2(aq)} + 4NaOH_{(aq)} \quad (9)$$

During cyanidation of arsenic ores, CN^- react with FeAsS to form thiocyanate, (SCN^-) Eqs (10), (3), arsenite (AsO_3^{3-}), and arsenate (AsO_4^{3-}) (Kyle, Breuer, Bunney, & Pleysier, 2012). Arsenate (AsO_4^{3-}) is also formed in solution due to the oxidation of arsenite AsO_3^{3-})

$$4FeAsS + 28CN^-{}_{(aq)} + 2O_{2(g)} + 2H_2O_{(l)} \rightarrow 4SCN^-{}_{(aq)} + 2AsO_3{}^{3-}{}_{(aq)} + 4Fe(CN)_6{}^{4-} + 4H^+ \quad (10)$$

From Eqs (2) and (3) CN^- ions and O_2 intended for the dissolution of Au in Eq (9) are consumed resulting low Au leaching efficiencies and overall, Au losses to the tailings. Hence to solve this problem, extraction of As, Fe or other elements before cyanidation can be effective in minimizing the Au losses. Acid and or alkaline leaching have been reported to enhance Au extraction from arsenic-bearing ores (Li, et al., 2016) (Karimov, et al., 2021).

2.3.1. Acid pretreatment.

In this technique, arsenic–bearing gold ores are oxidized under elevated temperature and pressure, producing effluents that are more environmentally stable whilst efficiently precipitating toxic elements such as As, etc. During oxidation, arsenic–bearing ores undergo complex reactions that may form hematite (Fe_2O_3), jarosite [$H_3OFe_3(SO_4)_2(OH)_6$], basic ferric sulfate ($Fe_2(SO_4)_3$ (H_2O) n), and a range of possible Fe(II)–AsO_4–SO_4 phases. Arsenic can be selectively removed by pressure oxidative leaching because As is dissolved in an acidic media whilst other characteristic elements like Sb remain in the leach residue (Mahlangu, Gudyanga, & Simbi, 2006)(Li, et al., 2016) (Han, Chao, Wenqing, Fen, & Wenhua, 2017). The phases formed during POX are dependent on the operational parameters such as the temperature, pH, Fe/As ratio, and leaching time. When sulfide minerals are oxidized, they form oxides which have a porous structure that allows dissolved O_2 and any lixiviant to gain access to gold grains. The main reaction for the oxidation of arsenopyrite proceeds as follows:

$$4FeAsS + 13O_2 + 6H_2O \rightarrow 4H_3AsO_4 + 4FeSO_4 \quad (12)$$

$$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 3Fe_2(SO_4)_3 + 2H_20 \quad (13)$$

$$Fe_2(SO_4)_3 + 2H_3AsO_4 \rightarrow 2FeAsO_4 + 3H_2SO_4 \quad (14)$$

There are some notable research studies that have demonstrated the effectiveness of extraction of As before cyanidation and are given as follows:

Case 1: Comparable results were also obtained from a study by Celep et al., (Celep O. , Yazici, Altinkaya, & Deveci, 2019b), in which about 66 % As and 65 % Sb were removed from silver (Ag) concentrates using ferric chloride ($FeCl_3$) acidified in a chloride solution.

Case 2: A research conducted by Karimov et al., (Karimov, et al., 2021) investigated the arsenic deposition process from nitric acid leaching solutions. Results from the study indicate that arsenic removal rates of up to 98% from gold concentrates are achievable, with 95–98% of the dissolved arsenic precipitating as arsenic (II) sulfide, as depicted in Figure 3. In nitric acid leaching, the kinetics of arsenic sulfide dissolution are negatively affected by the formation of elemental sulfur, leading to passivation.

Case 3: Rogozhnikov et al. (Rogozhnikov, Karimov, Shoppert, Dizer, & Naboichenko, 2021), conducted studies on the pretreatment kinetics of refractory sulfide on Au−As concentrates in the presence of Fe(III) ions and FeS_2. Results from the study showed that FeS_2 has a catalytic effect on the FeAsS because it provides an alternative surface for the reduction of nitrate ions in electrical contact with FeAsS ,this reduces the passivation effect of elemental sulfur (Dixon, Mayne, & Baxter, 2008) (Nazari, Radzinski, & Ghahreman, 2017). The main reactions for dissolution of FeAsS and FeS_2 are illustrated by Eq (17−19).

$$FeAsS + 13HNO_3 \leftrightharpoons Fe(NO_3)_2 + 4HAsO_2 + 4H_2SO_4 + 11NO_2 + 5H_2O \quad (17)$$

$$FeS_2 + 8HNO_3 \leftrightharpoons Fe(NO_3)_3 + 2H_2SO_4 + 5NO_2 + 2H_2O \quad (18)$$

The major challenge with pressure oxidation (POX) processes, is that they are energy intensive due to the need to generate high temperature and pressure, therefore not economically viable for low–grade refractory ores (Ahtiainen, Liipo, & Lundström, 2021).

2.3.2. Alkaline Leaching

Alkali pretreatment is performed using sodium hydroxide (NaOH) and/or sodium sulfide (Na_2S) to liberate gold locked in arsenic-bearing containing antimony (Sb). The pretreatment is carried out at ambient conditions, does not emit toxic gases such as SO_x, like the roasting methods and is not corrosive as compared to acid–based pretreatment techniques (Ubaldini, Vegliò, Fornari, & Abbruzzese, 2000) (Espitia & Lapidus, 2021).

Sequential leaching involves the initial leaching of antimony (Sb) using a combination of Na_2S and NaOH to produce sodium thioantimonite, while arsenic (As) remains in the residue, as described by Eq, (20−22). Usually, NaOH is added to inhibit the hydrolysis of Na_2S and improve the solubility of Sb_2S_3 by producing soluble oxothioantimonates and thioantimonites when the concentration of Na_2S in the leaching solution is inadequate (Wu, Feng, Li, Liao, & Wang, 2019).

$$Sb_2S_{3(s)} + 3Na_2S_{(aq)} \leftrightharpoons 2Na_3SbS_{3(aq)} \quad (20)$$

$$Sb_2S_{3(s)} + 2NaOH_{(aq)} \leftrightharpoons NaSbOS_{(aq)} + NaSbS_{2(aq)} + H_2O \quad (21)$$

$$Na_2S_{(aq)} + 2H_2O \leftrightharpoons Na_2S_{(aq)} + 2NaOH_{(aq)} \quad (22)$$

The dissolution of FeAsS in alkaline solutions can be represented by Eq (23).

$$2FeAsS_{(s)} + 10OH^-{}_{(aq)} + 7O_2 \rightarrow Fe_2O_3 + 2AsO_4{}^{3-}{}_{(aq)} + 3SO_4{}^{2-}{}_{(aq)} + 5H_2O \quad (23)$$

In alkaline conditions, the oxidation of FeAsS is thermodynamically favored due to the low potential required for oxidation. However, iron oxide products form on the unreacted FeAsS causing a passivation effect. Therefore, As and Sb can undergo separation using a two-stage alkali pretreatment technique. In the initial step, Sb dissolves by Na_2S and NaOH, whilst As remains in solid state. Subsequently, solid-liquid separation is then conducted to individually isolate the As and Sb respectively. The Sb is dissolved and can be extracted from solution by electrowinning. The As present in the residue can be separated in an acidic medium such as nitric acid, while the leach residue can be neutralized and subjected to cyanidation (Rogozhnikov, Rusalev, Dizer, & Naboychenko, 2018). The major challenges associated with this method include significant reagent consumption and the production of substantial quantities of pyrite/arsenopyrite effluents, which are discharged into the tailings. The problem of arsenic effluent generation has prompted extensive research efforts to mitigate the adverse environmental impacts of arsenic present in arsenopyrite and prevent acid mine drainage (Park, et al., 2019) (Park, et al., 2021). The following table summarizes some notable research that demonstrated alkane pretreatment arsenic bearing refractory gold ores.

Table 2.3: Research using on alkane pretreatment.

Ore characteristic	**Reagents and conditions used**	**Notable results**	**References**

Au–Sb–Ag	Pretreatment conducted for 2 hr with 3 mol/L NaOH at 80 ºC	Au extraction improved from 49.3 % to 85.4 %	(Celep, I brahim, & Deveci, 2011)
Au-FeAsS	As can be removed from the ore by NaOH at high concentration of 3 mol/L	79 % As removed during pretreatment. Gold extraction improved from 40 % to 83 %	(Espatia & Lapidus, 2015) (Espitia & Lapidus, 2021)

2.3.3. Enhanced pretreatment techniques

The conventional pretreatment methods already discussed in the previous section have a lot of problems, e.g., slow leaching kinetics in bioleaching and environmental such as emission of toxic gases in roasting process. To alleviate some of these challenges, novel approaches to pretreatment have been suggested by researchers such as incorporation of ultrasound and ozone during pretreatment process.

(i) Ultrasound enhanced pretreatment processes in gold extraction

Ultrasound technology has been integrated into alkaline pretreatment processes, as depicted in the schematic diagram presented in Figure 2.4. When ultrasound is introduced into a liquid phase, it induces the formation of vibrating cavitation bubbles. These bubbles enhance local micro-mixing of liquids adjacent to solid surfaces, facilitating the delivery of fresh solvent (leaching agent) to the solid surface (Suslick & Price, 1999) (Tiwari B. , 2015). The asymmetric collapse of cavitation bubbles near the solid surface causes a jetting effect that breaks or erodes the solid surface, thus exposing a new metal rich surface (Tiwari B. , 2015) (John, Houwer, Mechelen, & Gevern, 2020). This technique has attracted a lot of research interest due to its enhancements in gold extraction, leaching kinetics, and environmental capabilities as reported by because it improves gold extraction, improves leaching kinetics Swamy & Narayana, (2001). It has been effectively employed in the extraction of copper, lithium, and uranium, leading to increased metal extraction (Avvaru, Roy, Chowdhury, & Pandit, 2008) (Turan, Sari, & Demiraslan, 2019). The following Table 2.4 gives a summary of studies on the application of ultrasound in extraction from refractory gold ores.

Table 2.4: Application of ultrasound in gold extraction

Ore characteristic	**Reagents & experimental conditions**	**Results**	**References**
Au-FeAsS-FeS_2	Ultrasound and chlorination oxidation	Au extraction improved from 45.8 % to 68.55 %	(Fu, Zhang, Wang, Cui, & Peng, 2017)
Au-FeAsS	Ultrasound and alkaline (NaOH) pretreatment	Au extraction improved from 49.3 % to 85.4 %	(Celep, I brahim, & Deveci, 2011)
Au-FeAsS	Ultrasound and alkaline treatment	About 80.5 % Au extraction was attained in 1 hr of pretreatment with ultrasound	(Zhang G. , Wang, Zhang, & Peng, 2016)
Au- As-Sb	Ultrasound and alkaline treatment	Gold extraction improved from to 93.1 whilst 81.2 % Sb was removed in 1 hr at 40 °C during pretreatment.	(Hu, Guo, Wang, & Zhang, 2020)

The findings shown in Table 2.4, have demonstrated that ultrasound can be integrated in the pretreatment arsenic–bearing ores before leaching to enhance gold extraction. Despite the benefits reported from the review, the impediment on application of the ultrasound technique on a large scale has been due to low efficiency in converting electrical energy to acoustic energy (Majid, Nayik, Nanda, & Yildiz, 2015). By using modern piezoelectric transducers, energy conversion can be increased to as high as 80 %. Currently its commercial application is seen in the food industry for emulsification, microbial disinfectant, and cleaning (Vyas & Ting, 2018). It is also important to note that, though the application of ultrasound has a significant improvement in the leaching kinetics, systematic comparative studies are needed to evaluate the enhancement in the of total gold extraction compared to using conventional pretreatment methods.

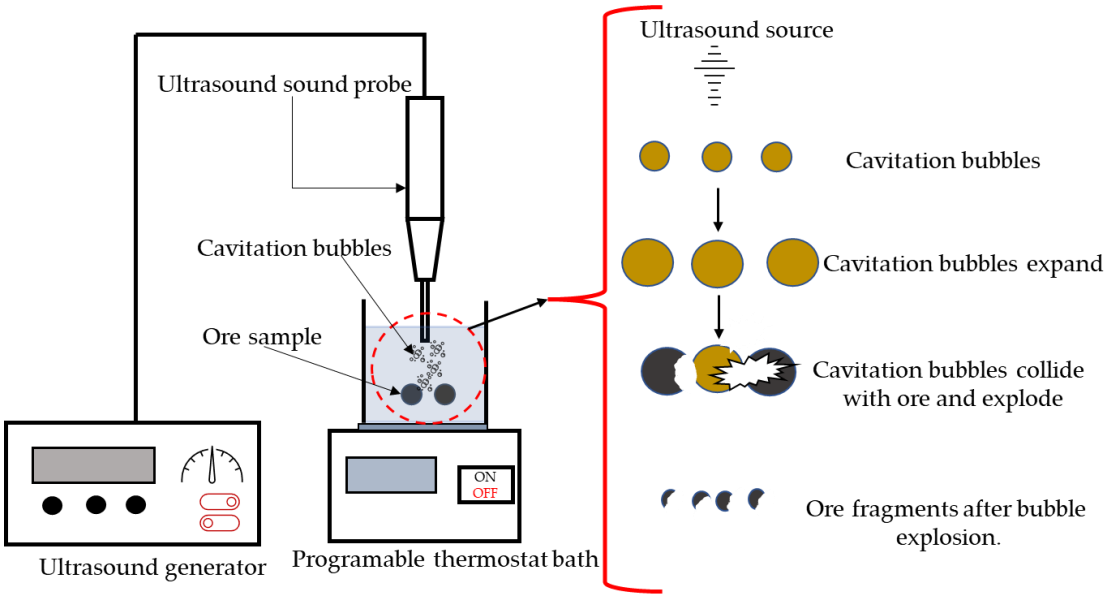


Figure 2.4: Schematic diagram of the ultrasound treatment technique.

(ii) *Ozone oxidation enhanced pretreatment processes in gold extraction*

Ozone is an oxidant used in the hydrometallurgical leaching processes because of its high oxidizing potential (*2 V*), which makes it thermodynamically capable of oxidizing a wide range of metals, sulfides, and arsenides (Li, Li, & Qian, 2009). This technique has several advantages including environmental friendliness, elimination of the passivation layer, primarily composed of the elemental sulfur. Table 2.5 provides an overview of studies showcasing the effectiveness of ozone oxidation in gold extraction from refractory gold ores.

Table 2.5: Application of ozone oxidation in gold extraction from refractory ores.

Ore characteristic	**Techniques used**	**Results**	**References**
Au-FeAsS-FeS_2	Ozone and leaching	Au extraction improved from 19.5 % to 96.5 %	(Li, Li, & Qian, 2009)
Au- Ag-FeS_2	Ozone and leaching	Au extraction increased from 53 % to 88 % and 26 % to 78% for Ag.	(Rodriguez et.al., 2006)
Au- As-Sb	Ozone and Ultrasound	94% Sb was removed from ore 4hr, an improvement from 12hr in ozone only.	(Guo, Xin, Wang, & Tian, 2017)

The drawback of this technique is the low solubility of ozone in aqueous media, that is, about 14 mmol/L of ozone dissolves in water at 20 ºC. As observed in the review, the combined application of ultrasound and ozone treatment enhances gold extraction, leaching kinetics and reduces reagent consumption. However, there is a paucity of information regarding their industrial-scale application.

2.4 Absorption of dissolved Au in solution," preg robbing".

The problem of gangue absorption of dissolved gold by arises from the carbonaceous matter typically found in arsenic-bearing ores, in the form of amorphous carbon, graphite, lignite, and micromolecular hydrocarbon materials (Marsden & House, 2006) (Zhang X. , et al., 2022). Pretreatment techniques such as roasting (Thomas & Cole, 2016), chemical oxidation like NITRO process (Afenya, 1991),and biological oxidation (Chicago,USA Patent No. 12/277,046, 2009) have been utilized to address this of 'preg robbing" problem. Microwave roasting has been applied on arsenic-bearing ores with carbonaceous material, Figure 2.5 depicts the transformation of the ore material post-treatment. A study by Amankwah and Ofori–Sarpong (2020) on microwave roasting of flash flotation Au concentrate containing FeS_2, FeAsS and carbonaceous matter demonstrated that that over 90 % sulfur (S), As and carbonaceous matter can be removed prior to cyanidation. After cyanidation of the calcine, over 95 % of Au was recovered (Amankwah & Ofori-Sarpong, 2020). Vacuum roasting has also been reported, for example Zhanget.al, (2022) applied it to an ore with the following composition: Au (2.9 g/t), FeS_2 (2.04 %), C (5.05 %), SiO_2 (80.61 %) at 700-1200 ℃. The results indicated that after treatment about 73.4 % of Au was liberated, and 88.4% was extracted from the ore after chemical analysis and leaching of the calcine respectively.

Hydrometallurgical methods can also be applied to address the "preg robbing "problem. They can be e classified as chemical and biological, achieving the following

effects (1) chemical oxidation of carbonaceous matter (2) biological oxidation of carbon matter.

Biological oxidation using fungai can be used to decompose carbonaceous materials as demonstrated by Yen et al., (2009), were Trametes versicolor culture media with the fungal tissues on carbon-bearing on a high As refractory ore a led to improvement in Au extraction from 54.1% to 95.25 % after treatment. Konadu et al., (2019) applied thermophilic iron-oxidizing archeaon and fungal crude enzymes treatment to a refractory ore with the following composition: Fe-10.2 %, S-8.56 %, As-1.60 % C-5.86 %, Si-19.3 5. The Au extraction after treatment was approximately 92 %.

As-bearing refractory gold ores containing carbonaceous material, can be directly leaching using thiosulfate owing to the low affinity for the Au-thiosulfate ions to carbon. Chen et.al., (2022) applied thiosulfate leaching to a gold ore concentrate with the following composition: Au−21.3 g/t, copper, total carbon, and organic carbon being 0.015 %,6.22 % and 0.18 % respectively. The dominant gangue minerals present were Al/Mg/Ca silicates and after leaching for 24 hr, the Au extraction was about 73. 69 %. The opportunities for direct leaching of thiosulfate As-bearing ores in general will be discussed in Chapter 3.

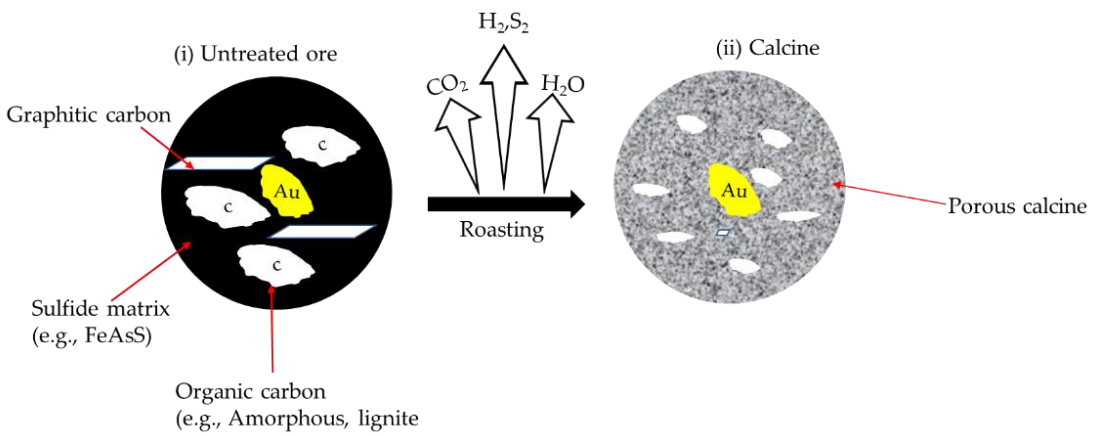


Figure 2.5: Structural transformation of carbonaceous ore material

2.4.1 Summary

Determination of the best pretreatment for the arsenopyrite–bearing gold ores is dependent upon the mineralogy of the ore hence. However, conducting a comparative analysis of the processes, considering both the cost (Capital expenditure (CAPEX) and Operational expenditure (OPEX)) and environmental impact, is essential. Table 2.8 provides comparative analysis of pretreatment techniques applied on pyrite/arsenopyrite–bearing ores.

Table 2.8. Comparative analysis of pretreatment techniques prior to leaching arsenopyrite–bearing ores.

Pretreatment	%Au unlocked	Environmental impact	Cost	Challenges
Physical				
UFG	>80%	Low	Low CAPEX&OPEX	High energy consumption (Celep & Yazici, Ultra fine grinding of silver plant tailings of refractory ore using vertical stirred media mill., 2013)
Pyrometallurgical				
Roasting	>80%	Highly toxic	High CAPEX&OPEX	Toxic gases, secondary encapsulation of Au by oxides (Nunan, et al., 2017) (Nanthakumar, Pickles, & Kelebek, 2007)
Hydrometallurgical				
Bioleaching	>90%	Low	High CAPEX&OPEX	Slow leaching Kinetics (Owusu, Agorhom, Fosu, &

				Arthur, 2020) (Wang, Faraji, Ramsay, & Ghahreman, 2021)
POX (Acid leaching)	>90%.	Medium	High CAPEX&OPEX	High energy consumption. (Hilson & Monhemius, 2006) (Yang, et al., 2015) (Rogozhnikov, Karimov, Shoppert, Dizer, & Naboichenko, 2021)
Alkali leaching	>90%	Medium	High CAPEX&OPEX	High reagent consumption (Celep, I brahim, & Deveci, 2011) (Wang Y. , Liu, Yan, & Ye, 2021) (Espitia & Lapidus, 2021).

2.5. Alternatives to cyanidation

The process flowsheet of gold from refractory gold ores is becoming increasingly complex and lengthy due to numerous pretreatment processes required to render the ore amenable to leaching(cyanidation). This is a clear indication that gold production is becoming more expensive. In section (1.1), the nature of refractoriness in refractory gold ores (arsenic- bearing ores) was discussed and pretreatment techniques reviewed in section 2.2-2.4, demonstrated that they could potentially solve the technical problems associated with gold extraction. However, the ecological impacts on the use of cyanide are challenges researchers need to address to efficiently extract gold from refractory gold ores efficiently while also protecting the environment. The toxicity of cyanide and its tailings has led governments, through environmental groups, to advocate for the total ban of cyanide in gold processing plants. For example, the government of Hungary and Czech Republic have already banned the use of cyanide (Organisations, 2011). In 2010 the European Union parliament discussed the possibility of a total ban

cyanide use completely but later postponed the implementation due to lack of a more developed alternative lixiviant for cyanide (Feng & Deventer, 2010) (Kyle, Breuer, Bunney, & Pleysier, 2012) (Jeon, et al., 2020; Jeon, et al., 2021). Currently there are over 20 reagents suggested to replace cyanide, but the most promising of the reagents to replace cyanide are halides (chlorine), thiourea, thiosulfate (Wang, Faraji, Ramsay, & Ghahreman, 2021).

2.5.1 Thiourea

Application of thiourea to gold extraction started in 1906 by Moir (Brooy, Linge, & Walker, 1994), and gold is leached as follows: Eq (24).

$$\mathrm{Au} + 2\mathrm{NH_2CSNH_2} + \mathrm{Fe^{3+}} \rightarrow (\mathrm{Au(NH_2CSNH_2)_2})^{+} + \mathrm{Fe^{2+}} \quad (24)$$

The advantages of thiourea (TU) include faster leaching kinetics (4−6 hrs.), high Au selectivity and minimum environmental impacts. However, its disadvantages include instability in both alkaline and acidic conditions, which makes it costly to use and is a carcinogen (Marsden & House, 2006). Direct leaching of sulfidic refractory ores in general by TU results in Au recoveries less than 20 % due to the decomposition of TU (Zhang, Ritchie, & LaBrooy, 2004). In acidic conditions, TU readily transforms to formamidine disulfide (FDS, $(NH_2)_2CSSC(NH_2)_2^{+}$), as shown in Eq (25), leading to the formation of a passivating elemental sulfur layer that lowers gold extraction (Qin, Gua, Tian, & Zhang, 2021).

$$2\mathrm{CS(NH_2)_2} \rightarrow \mathrm{NH_2CSSC(NH_2)_2}^{2+} + \mathrm{e^-} \quad (25)$$

Sulfidic minerals like FeAsS and FeS_2 exacerbate the decomposition of TU, with around 90 % of the TU to be decomposing during leaching of refractory gold ores (Qin, Gua, Tian, & Zhang, 2021). To effectively leach gold from the refractory ores, pretreatment is usually conducted before leaching. Amongst the commonly used pretreatment methods including, roasting, pressure oxidation and bio-oxidation: bacterial oxidation is widely used in TU leaching systems (Zhang, Ritchie, & LaBrooy, 2004). Recent studies on the use of TU to extract Au from As–bearing Au ores showed that more than 80 % of Au can be extracted when the ore is pretreated by bioleaching, but this is associated with high consumption of TU as TU is readily oxidized by ferric ions in acidic solution (Hilson & Monhemius, 2006) (Xu R. , et al., 2020)

In TU leaching system, Au is recovered from solution using adsorption techniques (activated carbon and ion exchange resins), cementation (using iron powder

or aluminum) and electrowinning (Ubaldini, Massidda, Abbruzzese, Vegliò, & Toro, 1998). Ion exchange resins activated carbon and organic absorbents are the most used methods to recover Au from TU pregnant leach solutions due to their recyclability making the recovery cost-effective. However, the major challenge with adsorption methods is low Au selectivity of adsorption as other metal species compete for adsorption sites with Au (Zhang, Ritchie, & LaBrooy, 2004). After the adsorption stage, gold is usually electrowon as follows:

$$\mathrm{Au(CS(NH_2)_2)_2}^{2+} + \mathrm{e}^- \leftrightharpoons \mathrm{Au} + 2\mathrm{CS(NH_2)}_2 \tag{26}$$

$$\mathrm{(CS(NH_2)(NH))_2} + 2\mathrm{H}^+ + 2\mathrm{e}^- \leftrightharpoons 2\mathrm{CS((NH_2)}_2) \tag{27}$$

The gold electrowinning stage in TU systems is also associated with additional problems such as low selectivity due to similar reduction potentials co-existing ions in solution, which co-deposit with gold. Another problem is dissolution of Au back into solution by the action of TU; for example, when there is excess leachate in solution, the formamidine disulfide is generated, which can be reduced back to thiourea as shown by Eq (27). Additionally, the evolution of the hydrogen gas at the cathode and oxygen reduction lead to low gold recovery; oxygen reduction at the cathode becomes dominant in the presence of low concentration of gold in solutions, further hindering Au deposition. To improve gold recovery, there must be (1) high gold concentration in solution, (2) high corrosive resistance material for the electrodes, and (3) ease of removing the product from the cathode.

The following equations illustrate the side reactions that occur on the cathode during Au electrowinning in thiourea solutions:

$$2\mathrm{H}^{2+} + 2\mathrm{e}^- \leftrightharpoons \mathrm{H}_2 \tag{28}$$

$$\mathrm{O_2} + 4\mathrm{H}^+ + 4\mathrm{e}^- \leftrightharpoons 2\mathrm{H_2O} \tag{29}$$

Cementation is another method that can be applied to extract Au from TU pregnant leaching solution where metal species like Cu, Zn, Ni, Al, and Fe can be used as electron donors (Lee, Kim, & Oh, 1997). Eq (30) is an illustration of the cementation using Fe as an oxidant (Zhang & Dreisinger, 2002)

$$\mathrm{Fe} + (\mathrm{Au(NH_2CSNH_2)_2})^+ \rightarrow \mathrm{Fe}^{2+} + \mathrm{Au} + 4(\mathrm{CS(NH_2)_2} \tag{30}$$

Recovery of gold from TU pregnant leach solutions is attained using many approaches, but its stability in both acidic and alkaline conditions seems to overshadow all those advantages.

2.5.2 Chloride Leaching

The use of chlorine in the extraction of Au started before cyanide was used in which chloride leaching systems were the most dominant used (Brooy, Linge, & Walker, 1994). The major advantages of the chloride system over cyanide are faster leaching kinetics and ability to leach gold in the presence of sulfide minerals, without the need for pretreatment like roasting and pressure oxidation (Marsden & House, 2006) (Li H. , 2018). On the other hand, the challenges associated with halide leaching systems include their relatively poor selectivity for gold, instability of gold chloride complex and their highly corrosive nature, thus, increasing the cost related to construction materials on industrial scale (Hilson & Monhemius, 2006) (Marsden & House, 2006). In chloride systems, cupric and ferric ions are commonly used as oxidants in acidic conditions (pH< 3) to avoid precipitation of oxidants (Kim, 1995). In arsenic-bearing refractory ores, leaching is typically conducted at elevated temperature and pressure in autoclaves at 170–200 °C and oxygen pressures between 700–1000 kPa to achieve complete oxidation (Adams, 2005) (Fu, Zhang, Wang, Cui, & Peng, 2017) (Pangum & Browner, 1996) (Ahtiainen, Liipo, & Lundström, 2021) (Zhang Y. , Wang, Baozhong, Jie., & Peng, 2019). In this process, two major reactions regimes dominate: (1) oxidation of FeAsS and (2) complexion of Au as follows: (Pangum & Browner, 1996).

$$2\mathrm{FeAsS} + 3\mathrm{H_2}0 + 6.5\mathrm{O_2} \rightarrow 2\mathrm{H_3AsO_4} + 2\mathrm{FeSO_4} \quad (31)$$

$$4\mathrm{Au} + 3\mathrm{O_2} + 12\mathrm{HCl} + 4\mathrm{NaCl} \rightarrow 4\mathrm{NaAuCl_4} + 6\mathrm{H_2O} \quad (32)$$

$$\mathrm{Au} + 3\mathrm{FeCl_3} + \mathrm{NaCl} \rightarrow \mathrm{NaAuCl_4} + 3\mathrm{FeCl_2} \quad (33)$$

The oxidation of FeAsS to ferric arsenate ($FeAsO_4$), Eq (31), allows for the simultaneous Au liberation from the sulfide matrix and its dissolution. Gold extraction from arsenic-bearing refractory ore can be as high as 80, as demonstrated by a study by Ahtiainen et al., (Ahtiainen, Liipo, & Lundström, 2021) using a chloride–bromine leaching system was used on high As–bearing ores.

The commonly used methods to recover Au from halides systems is using solvent extraction (Xing, Lee, & Senanayake, 2018), ion exchange resins, activated carbon and electrowinning. The use of absorbents (ion exchange resins, activated carbon)

is a well-developed technology but due to the poor selectivity of halides during leaching, selective adsorption of Au is affected. Thus, applicability of halide systems to arsenic-bearing Au ores can be possible, but the major issue that still needs to be addressed by research including stabilization of Au chloride complexes, the corrosiveness of the halide solutions and their impact to cost on construction materials.

2.5.3 Ammonium thiosulfate Leaching

Ammonium thiosulfate leaching system has received a lot of attention by researchers as the alternative lixiviant to cyanidation due to its selectivity to Au during dissolution less toxicity and is cheap (Aylmore & Muir, 2001) (Feng & Deventer, 2010) (Zhang & Senanayake, 2016) (Jeon, et al., 2020) (Espitia & Lapidus, 2021). Thiosulfate can selectively leach Au in the presence of a wide range of metals from both secondary and primary resources including As and Sb (Feng & Deventer, Thiosulphate leaching of gold in the presence of ethylenediaminetetraacetic acid (EDTA, 2010). In this technique, Au is oxidized by cupric tetra–ammine complex [Cu $(NH_3)_4^{2+}$] in the presence of thiosulfate ion ($S_2O_3^{2-}$) (Aylmore & Muir, 2000). The role of NH_3 is to stabilize copper ions via chelation and prevent the decomposition of the thiosulfate (Muir, 2011) (Zhang & Senanayake, 2016). The dissolution of Au is illustrated by Eqs. (34)– (37) as follows: (Aylmore & Muir, 2000) (Rivera, Patiño, Roca, & Cruells, 2015).

$$\mathrm{Au} + 5\mathrm{S_2O_2}^{2-} + \mathrm{Cu(NH_3)_4}^{2+} \rightarrow \mathrm{Au(S_2O_3)_2}^{3-} + 4\mathrm{NH_3} + \mathrm{Cu(S_2O_3)_3}^{5-} \quad (34)$$

$$\mathrm{Au} + \mathrm{Cu(NH_3)_4}^{2+} \rightarrow \mathrm{Au(NH_3)_2}^{+} + \mathrm{Cu(NH_3)_2}^{+} \quad (35)$$

$$4\mathrm{Cu} + 8\mathrm{S_2O_3}^{2-} + 2\mathrm{H_2O} + \mathrm{O}_2 \rightarrow 4\mathrm{Cu(S_2O_3)_2}^{3-} + 4\mathrm{OH}^{-} \quad (36)$$

$$4\mathrm{Cu} + 8\mathrm{NH_3} + 2\mathrm{H_2O} + \mathrm{O_2} \rightarrow 4\mathrm{Cu(NH_3)_4}^{2+} + 4\mathrm{OH}^{-} \quad (37)$$

Many researchers have confirmed the high leaching efficiencies of thiosulfate during extraction of Au from refractory ores (Aylmore & Muir, 2000) (Brooy, Linge, & Walker, 1994) (Celep, Altinkaya, Yazici, & Deveci, 2018) (Espitia & Lapidus, 2021) (Xu, et al., 2017). Sulfides in general have detrimental effects on the decomposition of thiosulfate; sulfides function as catalyst to decompose thiosulfate. The rate of thiosulfate decomposition in the presence of sulfides follows this order: pyrite > arsenopyrite > chalcopyrite > galena > sphalerite. Moreover, the Au dissolution rate decrease in the order of sphalerite > arsenopyrite > pyrite > galena ≈ chalcopyrite (Xu, et al., 2017). Apart from increasing the decomposition of thiosulfate, FeAsS inhibits the dissolution of gold by

forming a passive layer on the gold grains during thiosulfate leaching: sulfide ions are released from FeAsS, and they are deposited to form an elemental S layer on gold grains (Yang, et al., 2015).

In order to minimize the decomposition of thiosulfate by sulfides during Au leaching, use of pretreatment(roasting, pressure oxidation, alkaline leaching etc.),inorganic, and organic additives including ethylenediaminetetraacetic (EDTA) (Feng & Deventer, Thiosulphate leaching of gold in the presence of ethylenediaminetetraacetic acid (EDTA, 2010) (Celep, Altinkaya, Yazici, & Deveci, 2018), carboxymethyl cellulose (CMC) (Yang, et al., 2015), phosphate/polyphosphates and sodium citrate (Puente-Siller, Fuentes-Aceituno, & Nava-Alonso, 2014) have been reported. EDTA is a widely used complexing agent and it forms stable complexes with Cu (II), thus, preventing the decomposing of thiosulfate by Cu (II). In addition to stabilizing the Cu (II) ions, CMC changes the semiconductor characteristic of FeAsS surfaces which inhibits the negative effects of FeAsS on thiosulfate decomposition (Feng & Deventer, Thiosulphate leaching of gold in the presence of ethylenediaminetetraacetic acid (EDTA, 2010). The following Table 2.9 gives recent studies on leaching arsenic–bearing gold ores using thiosulfate.

Table 2.9: Case studies of extraction of gold from refractory ores using thiosulfate

Case Study	Materials and experimental conditions
1	Xu et al., (Xu B. , et al., 2016) used thiosulfate after alkaline pressure oxidation pretreatment on a gold concentrate with 90 % particle size passing 48 µm containing Au (31.1 g/t), S (6.15 %) and C, As, Sb being 3.61 %, 1.7 % and 0.98 % by weight respectively. Most of the S, As and Sb were from arsenopyrite and stibnite respectively. <u>Key experimental conditions</u>: Alkaline pressure oxidation treatment conditions: T−220 ℃,O_2 partial pressure−0.8 MPa, Ca $(OH)_2$−0.2 M, Time−3 hr. Leaching conditions: $Na_2S_2O_3$−0.2 M, $CuSO_4$−0.012 M, NH_3−1.2 M, time−5 hr.

Results: 83 % and 86 % after leaching treated residue by cyanidation and thiosulfate respectively.

2 Espitia et al., (Espitia & Lapidus, 2021) applied thiosulfate after alkaline pretreatment of a Au concentrate with the following assay values: 52 % FeAsS, 33 %FeS_2,8% ZnS, 2% PbS and 18 g/t Au.

Key experimental conditions

Alkaline treatment conditions: Temp−25 ℃,solid−liquid composition−40 g/l, 3M NaOH, time−48 hr.

Thiosulfate leaching conditions: $Na_2S_2O_3$−0.2 M, EDTA−0.025 M, $CuSO_4.5H_2O$−0.05 M, $NH_4H_2PO_4$−0.1 M, time−7 hr, pH−10, Temp−25 ℃.

Results:63 % and 81 % gold recovery of the treated residue by cyanidation and thiosulfate respectively.

3 Feng and Deventer (Feng & Deventer, Thiosulphate leaching of gold in the presence of ethylenediaminetetraacetic acid (EDTA, 2010) applied thiosulfate on a pretreated gold ore from Newcrest gold mine with the following composition: Au−4.3 ppm, Fe−5.27 %, S−2.9 %, As−383 ppm, Cu−0.07 %.

Key experimental conditions:

Alkaline treatment conditions: The ore was oxidized in cupric ammoniacal solutions with the following conditions: NH_3−0.8, Cu^{2+}− 6 mM, time−22 hrs.

Thiosulfate leaching conditions: $Na_2S_2O_3$−0.25 M, 1 M−NH_3 and Cu^{2+}−12 mM 24 hr

Results: 94 % gold extraction

4	Yu et al, (Yu, et al., 2018) applied thiosulfate leaching on acid pressure oxidation treated refractory gold ore with the following composition: Au−22.3 g/t, Fe−13.12 %, As−1.14 %, S−15.94 %; Al_2O_3−4.76 %, MgO−13.9 %. Key experimental conditions Acid treatment conditions: pH−1, Temp−200 ℃, stirring speed 500 rpm, T−7 min. Thiosulfate leaching conditions: $Na_2S_2O_3$−505 mM, 1 M−NH_3, sodium humate (HA)−0.5 mM and Cu^{2+}−34.77 mM, for 24 hr Results: About 86.21% Au was extracted from the concentrate.
5	Wang et al., (Wang, Wang, Dong, Fu, & Xie, 2019) leached a refractory Au concentrate calcine after a microwave roasting treatment with the following composition: Au−21.9 g/t, Fe 1.72 %, S−0.51%, C−6.64 %, SiO_2−43.43 %, CaO−17.11 %, MgO−7.85 %. Key experimental conditions Roasting conditions: microwave power−2.5 Kw, roasting time−30 min, Temp−500 ℃. Leching conditions: 0.01 mol/L Cu^{2+}, 0.5 mol/L $NH_3 \cdot H_2O$, 0.1 mol/L $S_2O_3^{2-}$, initial pH 11.0 and leaching time for 5.0 hr, Temperature−50 °C. Results: Au extraction 90.2 %.

The difficulty to extract gold from thiosulfate leaching systems has been reported by many researchers and activated carbon has low affinity for gold–thiosulfate complex which makes the process more expensive as well (Hilson & Monhemius, 2006) (Aylmore & Muir, 2000) (Feng & Deventer, Thiosulphate leaching of gold in the presence of ethylenediaminetetraacetic acid (EDTA, 2010) (Jeon, et al., 2020). The other lucrative methods of extraction gold from thiosulfate leach solutions are ion–exchange resins. Resins are easy to use, does not require complex regeneration stages, have high Au extraction of up to 99 % (Xu B. , et al., 2019) and the functional groups of the resins can

transform to selectively adsorb the gold thiosulfate ions in solution. These advantages have attracted researchers to focus on them to recover Au from thiosulfate pregnant leach solutions (Xu, et al., 2017). Many studies conducted were on weak–base and strong–base resin and they revealed that weak–base resins have low adsorption capacity of 2 kg Au/t, and their capacities further decrease with increase in pH especially around pH 8–11 (Zhang & Dreisinger, The adsorption of gold and copper onto ion-exchange resins from ammoniacal thiosulfate solutions, 2002) (Zhang, et al., 2021) (XIE, CHEN, & WANG, 2021). Strong base resin was found to have higher adsorption capacities of 10–25 kg Au/t and independent of the pH but have very low selectivity to Au; ions such as $[Cu(S_2O_3)_3]^{2-}$ and will have preferential adsorption over $[Au(S_2O_3)]^{3-}$ (Jeffrey, Hewitt, Dai, & Brunt, 2010). On an industrial scale, ion exchange resins have been applied at Goldstrike mine, but it has many stripping, washing and regeneration stages which complicates the whole process (Jeon, et al., 2021) (Young, 2019).

Cementation is a gold recovery technique that can be considered as an alternative to extract Au from thiosulfate solutions. The traditional Merrill−Crowe Zn method used in the cyanidation systems, is ineffective due the presence of oxygen which: re–dissolved the gold precipitates, passivates the Zn surface and high Zn consumption (Aylmore & Muir, 2001). Recently, a novel technique of using zero-valent aluminum (ZVAl) and activated carbon to extract Au–thiosulfate complexes from solution was developed in our laboratory, yielding up to 99 % Au recovery from printed circuits boards (PBCs) (Jeon, et al., 2020). The mechanism of this technique is illustrated by Figure 2.6:

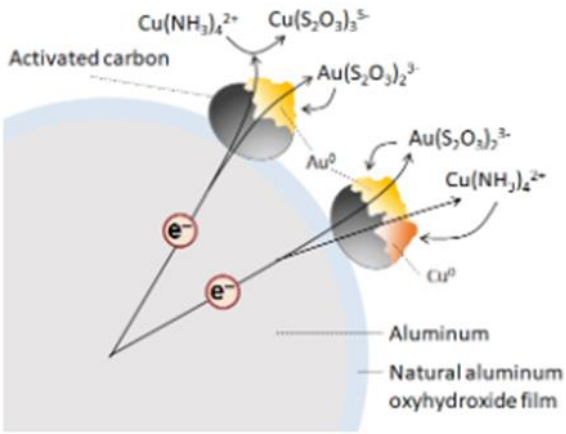


Figure 2.6: Schematic diagram of the Au recovery form thiosulfate solutions (Jeon, et al., 2021)**.**

From Figure 9, the zero valent aluminum (ZVAl) acts as the primary electron donor, whilst the attached activated carbon is the electron pathway from ZVAl to Au thiosulfate complex hence the galvanic interactions generated facilitate the cementation of the dissolved Au (Jeon, et al., 2020). This technique has assessed on Au pregnant leach solutions containing Cu, Fe, Co, Ni and Zn ion coexisting in solution resulting in Au recoveries above 90 % (Jeon, et al., 2021). The challenge with this method is that the cementator used ZVAl, is more electronegative (-1.66 V) and selectivity improves when the difference in potential is small. Thus, other elements like Cu, can deposit on the activated carbon before Au does depending on the concentration in solution. This technique has not been applied to recover Au from As/Sb bearing Au ores, which is a study the authors are investigating to fill the knowledge gap.

2.5.4 Summary on alternatives to cyanide

The extraction of Au from refractory ores, arsenic–bearing ores has been reported to be complex, generating toxic effluents. Hence in order to replace cyanide, which has received a lot of criticism on an environmental basis and its effectiveness to treat arsenic–bearing ores, the alternative must have the following attributes: (1) inexpensive and recyclable (2) highly selective to gold; (3) non–toxic and (4) easy to manage in downstream process (Hilson & Monhemius, 2006) (McNulty, 2001). Table 2.91 shows the summary of the extent of research and applicability of the alternatives of cyanide in the leaching of refractory ores.

Table 2.91. Alternatives to cyanide (Hilson & Monhemius, 2006).

Lixiviant	**pH range**	**Au Extraction (%)**	**Environmental Impact**	**Research Level**	**Extent of commercialization**
Thiourea	1–2	>80	Low	Fairly popular	New England Antimony Mine, Australia (Hilson & Monhemius, 2006)
Chlorine	1–3	>80	Medium	Extensive	Not reported

Thiosulfate	9–10	>80	Low	Extensive	Goldstrike Mine, USA (Jeon, et al., 2021) (Aylmore & Muir, 2000)

2.6. Chapter Summary

This chapter has examined strategies that can be used to effectively extract Au from As–bearing ores. As free–milling ore reserves diminish, refractory ores are expected to become the primary sources of gold in the future. However, conventional methods of extracting Au are not suitable to the refractory Au ores because of the low gold recoveries. To address this issue, pretreatment techniques such as ultra–fine grinding, roasting, bioleaching, and alkaline pretreatment, are being used before cyanidation. For arsenic–bearing ores, ultra–fine grinding is effective in liberating the physically encapsulated Au in the sulfide matrix but cannot liberate gold chemically locked (i.e., in stibnite ($AuSb_2$)). Additionally, ultra-fine grinding does not eliminate the negative effects of characteristic elements on the leaching reagent. Roasting generates highly toxic effluents containing arsenic oxide gases making it unsuitable for pretreating arsenic–bearing ores before leaching. Although bioleaching is cost-effective, it has longer leached cycles and the toxicity of arsenic species (As^{3+} and As^{5+}) outweighs its benefits. Chemical pretreatments (acidic and alkaline) are highly effective but lead to high reagent consumption. Both biological and chemical treatments are susceptible to surface passivation of gold grains, but using techniques like ultrasound and ozone oxidation during treatment improves treatment times and gold extraction.

From both an environmental and technical standpoint, extracting gold from arsenic-bearing ores results in effluents with high arsenic levels. In addition, using cyanide as a lixiviant exacerbates the risks of environmental pollution. The most favorable solution to this problem is to use an environmentally friendly, non-cyanide leaching agent. Thiourea, chlorine, and ammonium thiosulfate are potential alternatives, but further development is needed to meet industrial requirements. Thiosulfate is more developed compared to other alternatives and is currently being used at an industrial scale at Goldstrike, Nevada, USA. The successful industrial application of thiosulfate can be achieved by using a pretreatment method before ammonium thiosulfate leaching to minimize thiosulfate consumption. To select the most suitable pretreatment method before ammonium thiosulfate leaching, understanding the mechanism of ammonium thiosulfate consumption in the presence of sulfide minerals is imperative.

References

Abbruzzesse, C., Ubaldini, S., Veglio, F., & Toro, L. (1994). Preparatory bioleaching to the conventional cyanidation of arsenical gold ores. *Miner.Eng.*, 49-60.

Adams, M. (2005). *Advantages in Gold Ore Processing, 1st ed.* Perth, Australia: Elsevier B.V.

Afenya, P. (1991). Treatment of carbonaceous refractory gold ores. *Minerals Engineering, 4*(7), 1043-1055.

Ahn, J., Wu, J., Ahn, J., & Lee, J. (2019). Comparative investigation on sulfidic gold ore Processing:A novel bioxidation process option. *Minerals Engineering., 140*(10.1016/j.mineng.2019.105864).

Ahtiainen., R., Liipo, J. .., & Lundström, M. (2021). Simultaneous sulfide oxidation and gold dissolution by cyanide-free leaching from refractory and double refractory gold concentrates. *Min.Eng. Vol 170*, 107042.

Alguacil, F. (2006). *The chemistry of gold extraction (2nd edition).* Littleton, Colorado, USA: John O Marsden and CIain house SME.

Amankwah, R., & Ofori-Sarpong, G. (2020). Microwave roasting of flash flotation concentrate containing pyrite, arsenopyrite and carbonaceous matter. *Minerals Engineering , Vol 151*, 106312.

Aposhian, H., Zakharyan, R., Avram, M., Sampayo-Reyes, A., & Wollenberg, M. (2004). A review of the enzymology of arsenic metabolism and a new potential role of hydrogen peroxide in the detoxication of the trivalent arsenic species. *Toxicology and Applied Pharmacology, 198*(3), 327-355.

Ashley, P. M., Creagh, C., & Ryan, C. (2000). Invisible gold in ore and mineral concentrates from the Hillgrove gold-antimony deposits,NSW,Australia. *Mineralium Deposita, 35*, 285-301.

Auwalu, A., & Yang, H. (2020). As(III)-Domesticate HQ0211 Mix of Bacterial and Archaeal Culture in Pretreatment of Arsenic -bearing Refractory Gold ore. *Transactions of the Indian Instituite of Metals , 73*(10.1007/s266-019-01803-z), 65-71.

Avvaru, B., Roy, S., Chowdhury, S., & Pandit, A. (2008). Enhancement of the leaching rate of Uranium in the presence of ultrasound. *Ind.Eng.Chem.Res., 45*, 7639-7648.

Aylmore, M., & Muir, D. (2001). Thiosulfate leaching of gold. *Miner. Eng, 14*, 135-174.

BIOX. (2012). *BIOX ASTER*. (GOLD FEILDS) Retrieved 2012, from http://overendstudio.co.za/websites/gold_fields_biox/biox/operations.html#

Brooy, S., Linge, H., & Walker, G. (1994). Review of gold extraction from ores. *Min. Eng. Vol 7(10)*, 1231-1241.

Cabri, L., Newville, M., Gordon, R., Daryl Crozier, E., Sutton, S., Mcmahon, G., & Jiang, D. (2000).

Chemical speciation of gold in arsenopyrite. *Canadian Mineralogist, 38*, 1265-1281.

Celep, O., & Yazici, E. Y. (2013). Ultra fine grinding of silver plant tailings of refractory ore using vertical stirred media mill. *Trans. Nonferrous Met. Soc. China 23*, 3412-3420.

Celep, O., Altinkaya, P. .., Yazici, E. Y., & Deveci, H. (2018). Thiosulphate leaching of silver from an arsenical refractory ore. *Minerals Engineering*, 285-295.

Celep, O., I brahim, A., & Deveci, H. (2011). Improved gold and silver extraction from a refractory antimony ore by pretreatment with alkaline sulphide leach. *Hydrometallurgy Volume 105*, 234-239.

Celep, O., Yazici, E., Altinkaya, P., & Deveci, H. (2019b). Characterization of a refractory arsenical silver ore by mineral liberation analysis (MLA) and diagnostic leaching. *Hydrometallurgy, 189*, 105106.

Celep, O., Yazici, E., Kuzu, M., & Deveci, H. (2019). Effect of Ultra-Fine grinding on Extraction of Gold and Silver from a refractory flotation tailings by cyanide. *IMCET 2019.* ANTALYA, TURKEY: IMCET.

Charandraprabh, M., Modak, J., Natarajan, K., & Raichur, A. (2002). Strategies for efficient start-up of contiouns biooxidation process for refractory gold ores. *Minerals Engineering, 15*, 751-753.

Chen, J., Xie, F., Wang, W., Fu, Y., & Wang, J. (2022). Leaching of a carbonaceous gold concentrate in copper-tartrate-thiosulfate solutions. *Minerals Engineering, 183*, 107605.

Corkhill, C., & Vaughan, D. (2009). Arsenopyrite oxidation-A review. *Appl.Geochem.*, 2342-2361.

Corrans, I., & Angove, J. .. (1991). Ultra fine milling for the recovery of refractory gold. *Minerals Engineering*, 763-776.

Cui, R., Yang, H., Chen, S., Zhang, S., & Li, K. (2010). Valence variation of arsenic in bioleaching of arsenic-bearing gold ore. *Trans.Nonferrous.Met.Soc.China., 20*, 1171-1176.

Dave, S. (2018). Microbial technology for metal recovery from e-waste printed boards. *JBMOA*, 241-247.

de Carvalho, L., da Silva, S. R., Giardini, R. M., Souza, L. C., & Leão, V. (2019). Bio-oxidation of refractory gold ores containing stibnite and gudmundite. *Enviro. Tech& Innov*, 100390.

Deng, T., & Liao, M. (2002). Gold recovery enhancement from a refractory flotation concentrate by sequential bioleaching and thiourea leach. *Hydrometallurgy*, 249-255.

Dixon, D., Mayne, D., & Baxter, K. (2008). GalvanoxTM- a novel galvanically- assisted atmospheric leaching of technology for copper concentrates. *Can. Metall.Q., 47*, 327.

Duan, L., Li, X., Jiang, Y., Lei, M., & Dong, Z. (2017). Arsenic transformation behaviour during thermal decomposition of P.vittata, and arsenic hyperaccumulator. *J.Anal.Appl.Pyrolysis*, 584-591.

Dunn, J., & Chamberlain, A. (1997). The recovery of gold from refractory arsenopyrite concentrates

by pyrolysis-oxidation. *Minerals Engineering*, 919-928.

Dunne, R., Kawatra, K., & Young, C. (2019). *Sme Mineral Processing and Extractive Metallurgy Handbook.* Englewood,Colorado,USA: Society for Mining Metallurgy.

Ellis, S., & Gao, M. (2003). Development of ultrafine grinding at Kalgoorlie Consolidated Gold Mines. *Mining, Metallurgy and Exploration, 20*, 171-177.

Espatia, S., & Lapidus, G. (2015). Pretreatment of a refractory arsenopyritic gold ore using hydroxyl ion. *Hydrometallurgy, 153*, 106-113.

Espitia, S. L., & Lapidus, G. T. (2021). Arsenic removal strategy in the processing of an arsenopyritic refractory . *Hydro 203*, 105628.

Exchange, T. (2022, May 2). *Further Africa*. (Further Africa) Retrieved 6 13, 2022, from https://furtherafrica.com/2022/05/02/riozim-commissions-biox-plant-for-gold-mining-efficiency/

Feng, D., & Deventer, J. (2010). Thiosulphate leaching of gold in the presence of ethylenediaminetetraacetic acid (EDTA. *Minerals Engineering*, 143-150.

Feng, D., & Van Deventer, J. (2002). The role of heavy metal ions in gold dissolution in the ammoniacal thiosulfate system. *Hydrometallurgy*, 231-246.

Fleming, C., McMullen, J., Thomas, K., & Wells, J. (2001). Recent advances in the development of an alternative to the cyanidation process:Thiosulfate leachingand resin in pulp. *Min.Met .Explor*, 1-9.

Fraser, K. W., & Wells, J. (1991). Processing of refractory gold ores. *Minerals Engineering, Vol. 4*, 1029-104.

Fu, L., Zhang, L., Wang, S., Cui, W., & Peng, J. (2017). Synergistic extraction of gold from the refactory gold ore via ultrasonic and chlorination - oxidation. *Ultrasonics Sonochemistry, 37*(10.1016/j.ultsonch.2017.02.008), 471-477.

Gamino-Arroyo, Z., Pareau, A., Buch, F., Gomez-Castro, L., Sachez-Cadena, M., Stambouli, J., & Avila-Rodriguez, M. (2021). Design of Multistage Extraction System for Simultaneous Separation of Silver and Gold from Thiourea Solutions. *Chemical Engineering and Processing-Processing Intensification., 164*, 108391.

Grosse, A., Dicinoski, G., Shaw, M., & Haddad, P. (2003). Leaching and recovery of gold using ammoniacal thiosulfate leach liqours. *Hydrometallurgy*, 1-21.

Gudyanga, F., Mahlangu, T., Chifamba, J., & Simbi, D. (1998). Reductive-Oxidative Pretreatment of Stibnite Flotation Concentrate:Thermodynamic and Kinetic Consideration. *Miner. Eng. Vol 11(6)*, 563-580.

Guo, X., Xin, Y., Wang, H., & Tian, Q. (2017). Mineralogical characterisation and pretreatment of antimony extraction by ozone of antinomy refractory gold concentrates. *Transactions of nonferrous metals society of China, 27*(8), 1888-1895.

Hammerschmidt, J., Güntner, J., Kerstiens, B., & Charitos, A. (2016). Roasting of gold ore in the circulating fluidized-bed technology. In *Gold Ore Processing (Second Edition)* (pp. 393-409). Oberursel, Germany: Outotec GmbH & Co. KG.

Han, J., Chao, L., Wenqing, Q., Fen, J., & Wenhua, L. (2017). Pretreatment of tin anode slime using alkaline pressure oxidative leaching. *Seperation and Purification Technology, Volume 174*, 389-395.

Hansford, G., & Chapman, J. (1992). Batch and Continuos bio-leaching kinetics of a refractory gold-bearing pyrite concentrate. *Minerals Engineering, 6*, 597-612.

Hilson, G., & Monhemius, A. (2006). Alternatives to cyanide in the gold mining industry: what prospects for the future? *Journal of Cleaner Production , Vol 14*, 1158-1167.

Hu, Y., Guo, P., Wang, S., & Zhang, L. (2020). Leaching Kinetics of Antimony from Refractory Gold ore in Alkaline Sodium Sulfide under Ultrasound. *Chemical Engineering Research and Design, 164*(10.1016/jcherd.2020.09.029), 219-229.

Huang, Z., & Yang, T. (2021). Comparative study on Refractory Gold Concentrate Kinetics and Mechanisms by Pilot Scale Batch and Continous Bio-Oxidation. *Minerals, 11*(10.3390/min11121343), 1343.

Index, M. (2020, May 2). *Mining Index*. (Infinity Mining Possibilities) Retrieved May 2, 2020, from https://www.miningindex.co.zw/2020/05/07/riozim-re-embarks-on-a-us17-million-biox-plant-construction/

Jankovic, A. (2003). Variables affecting the fine grinding of minerals using stirred mills. *Minerals Engineering*, 337-345.

Jeffrey, M., Hewitt, D., Dai, X., & Brunt, S. (2010). Ion exchange adsorption and elution for recovering gold thiosulfate from leach solutions. *Hydrometallurgy Vol (100)*, 136-143.

Jeon, S., Chinosengwa, S. B., Park, I., Tabelin, C. B., Ito, M., & Hiroyoshi, N. (2021). The Effects of Coexisting Copper, Iron, Cobalt, Nickel, and Zinc Ions on Gold Recovery by Enhanced Cementation via Galvanic Interactions between Zero-Valent Aluminum and Activated Carbon in Ammonium Thiosulfate Systems. *MDPI:Metals Volume 11*, 1352.

Jeon, S., Tabelin, C. B., Takahashi, H., Ilhwan, P., Ito, M., & Hiroyoshi, N. (2020). Enhanced cementation of gold via galvanic interactions using activated arbon and zero-valent aluminum: A novel approach to recover gold ions from ammonium thiosulfate medium. *Hydrometallurgy*, 105165.

John, J., Houwer, V., Mechelen, D., & Gevern, T. (2020). Effect of ultrasound on leaching of lead from landfilled metallurgical residues. *Ultrasonics Sonochemistry, 69*(1350-4177), 105239.

Kadel-Harder, I., Spry, P., Layton-Matthews, D., Voinot, A., Handt, A., & McCombs, A. (2020). Paragenetic relationships between low- and high-grade gold mineralization in the Cripple Creek Au-Te deposit, Colorado: Trace element studies of pyrite. *Ore Geology Reviews,*

127, 103847.

Karimov, K., Rogozhnikov, D., Kuzas, E., Dizer, O., Golovkin, D., & Tretiak, M. (2021). Deposition of arsenic from nitric acid leaching solutions of gold-arsenic sulphide concentrates. *Metals, 11*(6), 889.

Karimpour, M., Shafaroudi, A., Bajestani, A., Schader, R., Farmer, l., & Sadeghi, M. (2017). Geochemistry, geochronology, isotope and fluid inclusion studies of the Kuh-e-Zar deposit, Khaf-Kashmar-Bardaskan magmatic belt, NE Iran: Evidence of gold-rich iron oxide–copper–gold deposit. *Journal of Geochemical Exploration, 183*, 58-78.

Kim, Y. (1995). *Studies on Gold dissolution and loss of Gold due to gangue minerals in chloride solutions.* Sydney: University of New South Wales, Australia.

Konadu, K., Huddy, R., Harrison, S. T., Osseo-Asare, K., & Sasaki, K. (2019). Sequential pretreatment of double refractory gold ore (DRGO) with a thermophilic iron oxidizing archeaon and fungal crude enzymes. *Minerals Engineering, 138*, 86-94.

Kyle, J., Breuer, .., P.L., Bunney, K., & Pleysier, R. (2012). Review of trace toxic elements (Pb, Cd, Hg, As, Sb, Bi, Se, Te) and their deportment in gold processing: Part II: Deportment in gold ore processing by cyanidation. *Hydro , Vol 111-112*, 10-21.

Lee, H., Kim, S., & Oh, J. (1997). Cementation behaviourof gold and silver onto Zn,Al and Fe powders. *Can Metall, 36*, 149-155.

Leys, C., Cloos, M., New, B., & MacDonald, G. (2012). opper-Gold ± Molybdenum Deposits of the Ertsberg-Grasberg District, Papua, Indonesia. *Society of Economic Geologists, 16*, 215-235.

Li, H. (2018). Investigation on the recovery of gold and silver from cyanide tailings using chlorination roasting process. *J. Alloys and Compounds 763*, 241–249.

Li, Q., Li, D., & Qian, F. (2009). Pre-oxidation of high-sulfur and high-arsenic refractory gold concentrate by ozone and ferric ions in acidic media. *Hydrometallurgy, 97*(1-2), 61-66.

Li, Q., Luo, J., Xu, R. Y., Xu, B., Jiang, T., & Yin, H. (2021). .Synergistic enhancement effect of Ag+and organic ligands on the bioleaching of arsenic-bearing gold concentrate. *Hydromeatllurgy*, 105723.

Li, Y., Liu, Z., Li, Q., Liu, F., & Zhiyong, L. (2016). Alkaline oxidative pressure leaching of arsenic and antimony bearing dusts. *Hydrometallurgy*, 41-47.

Limited, N. M. (2020). Cadia Operations New South Wales, Australia NI 43-101 Technical Report. New South Wales ,Australia: Newcrest Mining Limited.

Limited, V. M. (2020, 1 20). *Venus Metals* . (Venus Metal Corpotation limited) Retrieved 6 22, 2022, from https://www.venusmetals.com.au/our-projects/youanmi-gold-project.

Lindstrom, E., Sandstom, A., & Sundkvis, J. (2003). A sequancial two stepprocess using moderately and extremely thermophilic cultures for biooxidation of refractory gold concentrates.

Hydrometallurgy, 71(1-2), 21-30.

Liu, J., Chi, R., Xu, Z., Zeng, Z., & Liang, J. (2000). Selective arsenic-fixing roast of refractory gold concentrate . *Metallurgical and Materials Transactions*, 1163–1168.

Liu, J., Wu, W., & Zhang, X. (2017). Adhersion properties and factors influencing Leptospirillum Ferriphilum in the Biooxidation of Refractory gold-bearing pyrite. *Hydrometallurgy, 160*, 39-46.

Luptakova, A., Macingova, E., Ubaldini, S., Fornari, P., & Abbruzzese, C. (2008). Bioleaching of antimony minerals by bacteria Acidithiobacillus ferrooxidans and Desulfovibrio desulfuricans. *Environ.Chem.Technol, 102*, 409-411.

Madkour, L., & Salem, I. (1996). Electrolytic recovery of antimony from natural stibnite ore. *Hydrometallurgy, 43*, 265-275.

Mahlangu, T., Gudyanga, F., & Simbi, D. (2006). Reductive leaching of stibnite (Sb2S3) flotation concentrate using metallic iron in a hydrochloric acid medium I: Thermodynamics. *Hydro, Vol 84*, 192-203.

Mahlangu, T., Sumaili, F., Ayizi, D., Sindini, B., Mande, P., Toit, G., . . . Lotz, P. (2019). Kibali Gold Mine sulphide concentrate treatment – understanding the preoxidation of sulphide concentrates. *Mineral Processing and Extractive Metallurgy, 129*(1), 74-86.

Majid, I., Nayik, G., Nanda, V., & Yildiz, F. (2015). Ultrasonication and food technology: A review. *Cogent Food & Agriculture, 1*(1), 107102.

Marchevsky, N., Quiroga, M., Giaveno, A., & Donati, E. (2017). Microbial oxidation of refractory gold sulfide concentrate by a native. *Trans.Nonferrous Met.Soc.China., 27*, 1143-1149.

Marquez, M., Ospina, J., & Morales, A. (2012). New insights about the bacterial oxidation of arsenopyrite:A mineralogical scope. *Miner.Eng*, 248-254.

Marsden, J., & House, C. (2006). *The chemistry of gold extraction.* Littleton, Colorado: Society for Mining,Metallurgy and Exploration.

McNulty, T. (2001). Cyanide subsitutes. *Mining Magazine, 184(5)*, 256-261.

Mubarok, M., Winarko, R., Chaerun, S., Rizki, I., & Ichla, J. (2017). Improving gold recovery from refractory gold ores through biooxidation using iron-sulfur-oxidizing mixotrophic bacteria. *Hydrometallurgy, 168*, 69-75.

Mudd, G., Giurco, D., Mohr, S., & Mason, L. (2012). *Gold resources and production: Australia in a global context.* Sydney: The Department of Civil Engineering (MonashUniversity) and the Institute for Sustainable Futures (University of Technology, Sydney).

Muir, D. (2011). A review of the selective leaching of gold from oxidised copper gold ores with ammonia-cyanide and new insights for plant control and operations. *Minerals Engineering*, 576-582.

Nan, X., Cai, X., & Kong, J. (2014). Pretreatment process on Refractory Gold ores with As. *ISIJ Vol ,54,*

54(10.2355), 543-547.

Nanthakumar, B., Pickles, C., & Kelebek, S. (2007). Microwave pretreatment of a double refractory gold ore. *Minerals Engineering*, 1109-1119.

Nazari, A., Radzinski, R., & Ghahreman, A. (2017). Review of arsenic metallurgy treatmentof arsenical minerals and immobilization of arsenic. *Hydrometallurgy, 174*, 258-281.

Ndlovu, S. (2008). Biohydrometallurgy for sustainable development in the African minerals industry. *Hydrometallurgy, 91*(1-4), 20-27.

Nunan, T., Viana, L., Peixoto, G., Ernesto, H., Verster, D., & Pereira, J. (2017). Improvements in gold ore cyanidation by pre-oxidation with hydrogen peroxide. *Minerals Engineering*, 67-70.

Ofori-Sarpong, G., Osseo-Asare, K., & Tien, M. (2011). Fungal pretreatment of sulfides in refractory gold ores. *Minerals Engineering*, 499-504.

Organisations, E. N. (2011). *Banning of cyanide from Mining in the European Union.* Brno, Czech Republic.: European Netwrok of Environmental Law Organisations.

Owusu, C., Agorhom, E., Fosu, S., & Arthur, E.-B. (2020). Adsorption studies of sulphidic refractory gold ore. *Powder Technology*, 310-316.

Pangum, L., & Browner, R. (1996). Pressure chloride leaching of refractory gold ore. *Min. Eng. , Vol 9(5)*, 547-556.

Pardey, A., Osman, R., & Johnson, N. (2010). *Mineral Resource and Reserve Estimate for the Sukari Gold Project, Egypt.* Marsa Alam, Red Sea Governorate, Egypt: Sukari Gold Mines,CENTAMIN.

Park, I., Ryota, T., Yuto, T., Tabelin, C. B., Phengsaart, T., Jeon, S.,Hiroyoshi, N. (2021). A novel arsenic immobilization strategy via a two-step process: Arsenic concentration from dilute solution using schwertmannite and immobilization in Ca–Fe–AsO4 compounds. *Journal of Environmental Management*.

Park, I., Tabelin, C., Seno, K., Jeon, S., Inano, H., Ito, M., & Hiroyoshi, N. (2020). Carrier-microencapsulation of arsenopyrite using Al-catecholate complex nature of oxidation products, effects on anodic and cathodic reactions, and coating stability under simulatated weat6hering condition. *Heliyon*, 03189.

Park, I., Tabelin., C. B., Sanghee, J., Xinlong, L., Kensuke, S., Ito., M., & Hiroyoshi, N. (2019). A review of recent strategies for acid mine drainage prevention andmine tailings recycling. *Chemosphere*, 588-606.

Polyus, P. (2017). *Competent Person's Report – Mineral Assets PJSC Polyus* . Moscow , Russia: PJSC Polyus .

Puente-Siller, D., Fuentes-Aceituno, J., & Nava-Alonso, F. (2014). Study of thiosulfate leaching of silver sulfide in the presence of EDTA and sodium citrate. Effect of NaOH and NH4OH. *Hydrometallurgy*, 1-11.

Qin, H., Gua, X., Tian, Q., & Zhang, L. (2021). Recovery of gold from refactory gold ores: Effect of pyrite on the stability of thiourea leaching systems. *International Journal of Minerals,Metallurgy and Materials, 28*(6), 956-964.

Qin, H., Xueyi, G., Qinghua, T., Dawei, Y., & Zhang, L. (2021). Recovery of gold from sulfide refractory gold ore: Oxidation roasting pretreatment and gold extraction . *Minerals Engineering* , 106822.

Renjie, L., Jingying, L., & Zhongying, G. (2016). Review on Chromobacterium violaceum for gold bioleaching from e-waste. *Procedia Environmental Sciences, 31*, 947-953.

Resources, R. (2018). *Technical Report on the Kibali Gold Mine, Democratic Republic of the Congo.* Toronto , Canada: Barrick Gold.

RESOURCES, R. (2018). *Technical Report on the Loulo-Gounkoto Gold Mine Complex, Mali.* London, United Kingdom: Randgold Resources Limited.

Rivera, I., Patiño, F., Roca, A., & Cruells, M. (2015). Kinetics of metallic silver leaching in the O_2–Thiosulfate system. *Hydrometallurgy*, 63-70.

Rodriguez, E., Nava-Alonso, F., Jara, J., & Lara-Valenzuela, C. (2006). Treatment of pyritic matrix gold–silver refractory ores by ozonization–cyanidation. *Minerals Engineering, 19*(1), 56-61.

Rogozhnikov, D., Karimov, K., Shoppert, A., Dizer, O., & Naboichenko, S. (2021). Kinetics and mechanism of arsenopyrite leaching in nitric acid solutions in the presence of pyrite and Fe(III) ions. *Hydrometallurgy, 199*, 105525.

Rogozhnikov, D., Rusalev, R., Dizer, O., & Naboychenko, S. (2018). Nitric acid loosening of rebellious sulphide concentrates containing precious metals. *Tsvetnye Metally*(10.1758/tsm), 38-44.

Ruan, S., Qiu, D., Wang, C., Jie, X., Zhang, Y., Yao, Z., & Chen, Y. (2022). Microwave pyrolysis pretreatment of Hing Arsenic Refractory Gold Sulfide Concentrates in Nitrogen Atmosphere: Process Optimization and Mechanism. *JOM, 74*(10.1007/s11837-021-05000-6), 167-177.

Salinas-Rodríguez, E., Hernández-Ávila, J., Cerecedo-Sáenz, E., Arenas-Flores, A., Veloz-Rodríguez, M., Toro, N.,Acevedo-Sandoval, O. A. (2022). Leaching of Copper Contained in Waste Printed Circuit Boards, Using the Thiosulfate—Oxygen System: A Kinetic Approach. *Materials, 15*(7), 2354.

Seisko, S., Aromaa, J. J., & Lundström, M. (2020). Effect of redox potential and OCP in ferric and cupric chloride leaching of gold. *Hydrometallurgy, Volume 195*, 105374.

Simon, G., Huang, H., Penner-Hahn, J., Kesler, S., & Kao, L. (1999). Oxidation state of gold -bearing arsenian pyrite. *American Mineralogist, 84*, 1071-1079.

Suslick, K., & Price, G. (1999). Application of Ultrasound to Materials Chemistry. *Annu.Rev.Mater.Sci,*

29, 295-326.

Swamy, K., & Narayana, K. (2001). Intensification of leaching process by dual frequency ultrasound. *Ultrasonics Sonochemistry, 8*(4), 341-346.

Tabelin, C., Park, I., Jeon, S., Phengsaart, T., Villacorte-Tabelin, M., Alonzo, D., . . . Hiroyoshi, N. (2021). Copper and critical metals production from porphyry ores and E-wastes: A review of Resource Availability, Processing/recycling Challenges, Socio-environmental Aspects, and Sustainability Issues. *Resources, Conservation and Recycling, 170*(105610).

Tech, B. (2011). *A new approach to the reclamation of historic mine tailings.* Toronto,Canada: Bac Tech Environmental Corporation.

Technology, M. (2012, September 9). *Mining Technology*. (Verdict) Retrieved June 21, 2022, from https://www.mining-technology.com/projects/pueblo-viejo-gold-mine/

Thomas, K., & Cole, A. (2016). Chapter 23 - Roasting Developments – Especially Oxygenated Roasting. In *Gold ore processing (Second Edition)* (pp. 373-392). Oakville,ON, Canada: Elsevier Science.

Tiwari, B. (2015). Ultrasound: A clean, green extraction technology. *Trends in Analytical Chemistry., 71*, 100-109.

Turan, M., Sari, Z., & Demiraslan, A. (2019). Ultrasound-assisted leaching and kinetic study of blended copper slag. *Metall. Mater. Trans, 50*, 1-8.

Ubaldini, S., Massidda, R., Abbruzzese, C., Vegliò, F., & Toro, L. (1998). Gold recovery from finely disseminated ore by use of cyanidation and thioureation. *Hydrometallurgy*, 113-124.

Ubaldini, S., Vegliò, F., Fornari, P., & Abbruzzese, C. (2000). Process flow-sheet for gold and antimony recovery from stibnite. *Hydrometallurgy*, 187-199.

Vikentyev, I., Vikent'eva, O., Tyukova, E., Nikolsky, M., Ivanova, J., Sidorova, N., . . . Spirina, A. (2021). Noble Metal Speciations in Hydrothermal Sulphides. *Minerals, 11*(10.3390/min 11050488), 488.

Vyas, S., & Ting, Y. (2018). A Review of the Application of Ultrasound in Bioleaching and Insights from Sonication in(Bio)Chemical Processes. *Resources, 7*(3).

Walker, S., Jamieson, H., Lanzairotti, A., Hall, G., & Peterson, R. (2015). The effect of ore roasting on arsenic oxidation state and solid phase speciation in gold mine tailings. *Geochemistry: Exploration, Environment, Analysis, 15*, 273-291.

Wang, J., Faraji, F., Ramsay, J., & Ghahreman, A. (2021). A review of biocyanidation as a sustainable route for gold recovery from primary and secondary low-grade resources. *Journal of Cleaner Production*, 126457.

Wang, J., Wang, W., Dong, K., Fu, Y., & Xie, F. (2019). Research on leaching of carbonaceous gold ore with copper-ammonia-thiosulfate solutions. *Minerals Engineering, 137*, 232-240.

Wang, Y., Liu, X., Yan, J., & Ye, S. (2021). Selective extraction of arsenic and antimony from gold-

bearing sludge using two-stage alkaline leaching . *Resources, Conservation & Recycling 167*, 105388.

Whincup, P., & Binks, M. (2004). A case study of the development , engineering and construction of pyrite-arsenopyrite gold ore. *Bac-Min Conference,pp 191-202.* Bedigo, Australia.

Wilde.A., & Gilbert, D. (2000). Setting of the giant Muruntau Gold Deposit:Implications for ore genesis. *Journal of The Virtual Explorer*, 103809.

Wu, H., Feng, Y., Li, H., Liao, S., & Wang, H. (2019). Basic theory and optimization of gold containing antimony concentrate leaching by alkaline sulfide. *Physicochem. Probl. Miner. Process., 55*(1), 248-257.

Xie, F., Chen, J.-n., & Wang, J. (2021). Review of gold leaching in thiosulfate-based solutions. *Transactions of Nonferrous Metals Society of China, 31*(11), 3506-3529.

Xing, W., Lee, M., & Senanayake, G. (2018). Recovery of metals from chloride leach solutions of anode slimes by solvent extraction. Part I: Recovery of gold with Cyanex 272. *Hydrometallurgy, 180*, 58-64.

Xing, W., Sohn, S., & Lee, M. (2019). A Review on the Recovery of Noble Metals from Anode Slimes. *Mineral Processing and Extractive Metallurgy, 41*(2), 130-143.

Xu, B., Li, K., Dong, Z., Yang, Y., Li, Q., Liu, X., & Jiang, T. (2019). Eco-friendly and economical gold extraction by nickel catalyzed ammoniacal thiosulfate leaching-resin adsorption recovery. *Cleaner Production*, 1475-1485.

Xu, B., Wenhao, K., Qian, L., Yongbin, Y., Tao, J., & Liu, X. (2017). A Review of Thiosulfate Leaching of Gold: Focus on Thiosulfate Consumption and Gold Recovery from. *MDPI: Metals, 7*, 222.

Xu, B., Yang, Y., Li, Q., Jiang, T., & Li, G. (2016). Stage leaching of a Complex Polymetallic Sulfide Concentrate: Focus on the extraction of Ag and Au. *Hydrometallurgy, 159*, 87-94.

Xu, B., Yang, Y., Li, Q., Jiang, T., Liu, S., & Li, G. (2016). The Development of an Environmentally Friendly Leaching Process of a High C, As and Sb bearing sulfide gold concentrate. *Minerals Engineering, 89*, 138-147.

Xu, R., Li, Q., Meng, F., Yongbin, Y., Bin, X., Huaqun, Y., & Tao, J. (2020). Bio-Oxidation of a Double Refractory Gold Ore and Investigation of Preg-Robbing of Gold fromThiourea Solution. *MDPI-Metals 2020, Vol 10*, 1261.

Yang, H., Liu, Q., Song, X., & Dong, J. (2013). Research status of carbonaceous matter in carbonaceous gold ores and bio-oxidation pretreatment. *Trans. Nonferrous Met. Soc. China , 23*, 3405-3411.

Yang, T., Rao, S., Liu, W., Zhang, D., & Chen, L. (2017). A selective process for extracting antimony from refractory gold ore. *Hydrometallurgy*, 571-575.

Yang, Y., ZHANG, X., Bin, X., Qian, L., Tao, J. .., & Ya-xuan, W. (2015). Effect of arsenopyrite on

thiosulfate leaching of gold. *Trans. Nonferrous Met. Soc. China, Vol 25*, 3454-3460.

Yen, W., Amankwah, R., & Choi, Y. (2009, June 25). *Chicago,USA Patent No. 12/277,046.*

Young, A. (2019). *SME Mineral Processing & Extractive Metallurgy Handbook.* Englewood,Colorado,USA: Society for Mining ,Metallurgy and Exploration.

Yu, L., Li, S., Liu, Q., Deng, J., Luo, B., Liang, Y., . . . Lai, H. (2018). Gold recovery from refractory gold concentrates by pressure oxidation pre-treatment and thiosulfate. *Physicochemical Problems of Mineral Processing, 55*(2), 537-551.

Zhang, G., Wang, S., Zhang, L., & Peng, J. (2016). Ultrasound- intensified leaching of gold from a refractory ore. *ISIJ International, 56*(4), 714-718.

Zhang, H., & Dreisinger, D. (2002). The adsorption of gold and copper onto ion-exchange resins from ammoniacal thiosulfate solutions. *Hydrometallurgy ,Vol(66)*, 67-76.

Zhang, H., Ritchie, I., & LaBrooy, S. (2004). The adsorption of thiourea complex onto activated carbon. *Hydrometallurgy, 72*, 291-301.

Zhang, X., & Senanayake, G. (2016). A Review of Ammoniacal Thiosulfate Leaching of Gold: An Update Useful for Further Research in Non-cyanide Gold Lixiviants. *Mineral Processing and Extractive Metallurgy Review*, 385-411.

Zhang, X., Kou, J., & Sun, C. (2019). A comparative study of the thermal decomposition of pyrite under microwave and conventional heating with different temperatures. *Analytical and Applied Pyrolysis, 138*(165), 41-53.

Zhang, X., Song, Y., Wu, L., Dong, P., Zhou, M., & Liu, G. (2022). Improvement of the leach efficiency of carbonaceous gold concentratesusing reduction roasting pretreatment technology. *Advanced powder technology, 33*, 103387.

Zhang, X., Song, Y., Yin, N., Jin, B., & Li, Y. (2022). Unraveling the dissociation mechanism of gold in carbonaceous gold ore during vacuum roasting pretreatment: Effect of pyrite. *Minerals Engineering, 184*, 107658.

Zhang, Y., Yang, Y., Liu, X., Jiang, T., & Lyu, X. (2021). Hexaamminecobalt(III) catalyzed thiosulfate leaching of gold from a concentrate calcine and gold recovery from its pregnant leach solution via resin adsorption. *Minerals Engineering, 171*(1), 107079.

Zhang, Y., Li, Q., & Liu, X. (2020). Role of Ag+ in the Bioleaching of Arsenopyrite by Acidithiobacillus ferrooxidans. *MDPI:Metal 2020*, 10030403.

Zhang, Y., Wang, C., Baozhong, M., Jie., X., & Peng, X. (2019). Extracting antimony from high arsenic and gold-containing stibnite ore using slurry electrolysis. *Hydrometallurgy*, 284-291.

Zhang, Y., Wang, C., Ma, B., Jie, X., & Xing, P. (2019). Extracting antimony from high arsenic and gold containing stibnite ore using slurry electrolysis. *Hydrometallurgy, 186*, 284-291.

Zhao, P., Liu, C., Srinivasakannan, C., Zhang, L., Wang, F., & Gao, J. (2021). Basic research on the

microwave absorbing properties and microwave roasting mechanism of stibnite concentrate. *Powder Technology, 379*, 630-640.

Zhao, Y., Zhao, H., Abashina, T., & Vainshtein, M. (2021). Review on arsenic removal from sulfide minerals: An emphasis on enargite and arsenopyrite. *Miner. Eng. Vol, 172*, 107133.

Zhu, T., Lu, X., Liu, H., Li, J., Zhu, L., Lu, J., & Wang, R. (2014). Quantitative X-ray photoelectron spectroscopy-based depth profiling of bioleached arsenopyrite surface by Acidithiobacillus ferrooxidans. *Geochimica et Cosmochimica Acta, 127*, 120-139.

CHAPTER 3: AMMONIUM THIOSULFATE LEACHING OF GOLD IN THE PRESENCE OF PYRITE AND ARSENOPYRITE: UNDERSTANDING OF THE MECHANISM OF GOLD EXTRACTION BY ARSENOPYRITE.

3.1. Introduction

In the preceding chapter, the applicability of thiosulfate in gold extraction from arsenic-bearing gold ores was examined. The industrial application of thiosulfate is still limited due to its excessive consumption. It is worth noting that Goldstrike Mine, Nevada, USA, is using thiosulfate as a leaching reagent to extract gold from refractory gold ores (Xu, et al., 2017) (Jeon, et al., 2020). To develop the most effective method to extract gold from arsenic-bearing gold ores, a thorough understanding of the mechanism by which gold extraction is suppressed is important. Several authors have reported on the causes of low gold extraction in the presence of arsenopyrite, suggesting that the decomposition of thiosulfate and passivation of gold are further accelerated when sulfide minerals (e.g., arsenopyrite and/or pyrite) are present in the refractory ore (Feng & Deventer, 2010) (Feng & Van Deventer, 2002). The suppression of gold extraction by arsenopyrite is not well understood. Chen et al 2008, reported that arsenopyrite does not significantly contribute much to thiosulfate decomposition but adversely affects gold extraction compared to pyrite. Yang et al., (2015) found that arsenopyrite suppresses gold extraction by formation of a passivation layer (i.e., cuprous sulfide (Cu_2S), sulfur (S)) on the gold surface, which acting as a barrier between thiosulfate ions and gold grains (Yang, et al., 2015). Consequently, this chapter will focus on the understanding of the mechanism of gold suppression in the presence of arsenopyrite which is one of the minerals commonly associated with gold. Leaching experiments for gold powder were conducted with model samples high bearing arsenopyrite sulfide (HAsBS) samples.

3.2 Materials and Methods

3.2.1 Materials

A high arsenic sample was supplied by Kitabita Mine, Yamaguchi Prefecture, Japan. Table 3.1 shows the chemical composition of the HAsBS sample determined using the X-ray fluorescence spectrometer (XRF, EDXL300, Rigaku Corporation, Tokyo, Japan). Quantitative X-ray diffraction (XRD, Multiplex, Rigaku Corporation, Tokyo, Japan) analysis result (Figure 3.1) showed that the HAsBS sample was composed of arsenopyrite, chalcopyrite, pyrite, pyrrhotite, and quartz.

The ore sample was crushed using a jaw crusher (1023-A, Yoshida Manufacturing Co., Ltd., Sapporo, Japan) with a sieve (an aperture size of 1 mm), and ground using a Retsch RS 200-disc mill (Retsch Inc., Hean, Germany) to sizes of 80% less than 38 μm. Leaching experiments were conducted using gold powder (99.99%),

sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), ammonium sulfate ($(NH_4)_2SO_4$), ammonia water ($NH_4(OH)$, 31%), and cupric sulfate ($CuSO_4$ $5H_2O$), which were all obtained from Wako Pure Chemical Industries, Ltd., Japan. To characterize the surface of gold during leaching, a gold foil (thickness 0.127 mm and 99.99% purity) obtained from Sigma-Aldrich, Corporation, St. Louis, MO, USA, was used.

Table 3.1. Chemical composition of arsenopyrite sample.

Elements	Fe	As	S	O	Mg	Si	Cu	Br	Zn	Sb	Others
wt.%	29.2	25.1	15.4	14.5	11.5	3.9	0.24	0.1	0.03	0.01	0.02

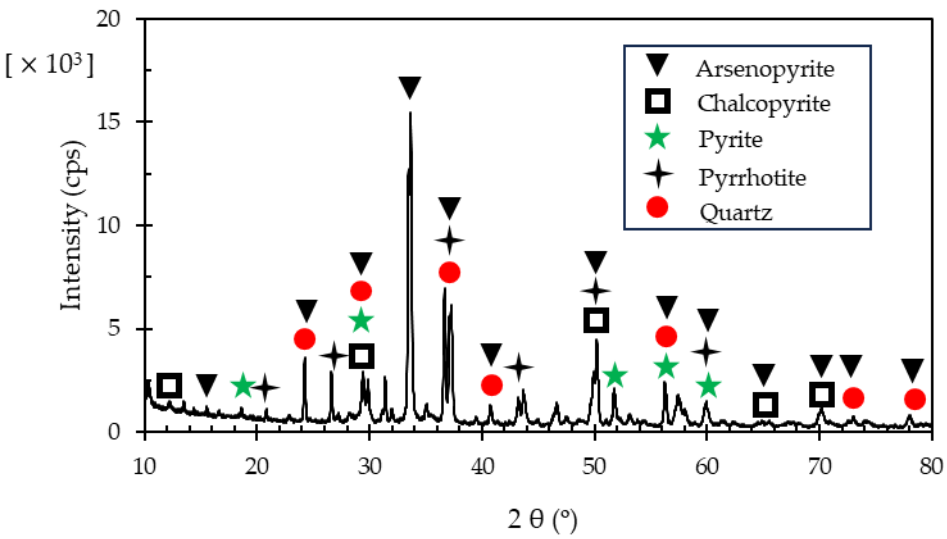


Figure 3.1. The X-ray powder diffraction (XRD) patterns of HAsBS ore.

3.2.2 Leaching Experiments

Batch leaching experiments were carried out in 50 mL Erlenmeyer flasks containing a known amount of HAsBS (1 g) and 10 mg of gold powder in 10 mL of ammonium thiosulfate solution consisting of 1 M $Na_2S_2O_3 \cdot 5H_2O$, 0.25 M $(NH_4)_2SO_4$, 0.5 M NH_4OH, and 10 mM $CuSO_4 \cdot 5H_2O$. The flasks were shaken in a thermostat water bath shaker at 25 °C for 24 h with a constant shaking amplitude and frequency of 40 mm and 120 min^{-1}, respectively. The effects of leaching time (2–24 h), solid-to-liquid ratio (1–20%), $CuSO_4$ concentration (0.1–15 mM), $Na_2S_2O_3$ concentration (0.1–2 M) on gold dissolution were investigated in the leaching experiments. After leaching, the suspensions were filtered using 0.2 µm membrane filters (Sartorius AG, Germany), and the filtrates were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP–AES 9820, Shimazu Corporation Japan (margin of error ±2%)) to measure the concentration of dissolved elements and by ultraviolet-visible spectroscopy (UV–Vis, UV–970, Japan

Spectroscopic Co., Ltd., Japan) to analyze the thiosulfate and sulfur species. The residues were washed thoroughly with deionized (DI) water, dried in a vacuum drying oven at 40 °C, and analyzed by XRF, X-ray photoelectron spectroscopy (XPS, JPS–9200, JEOL Ltd., Akishima, Japan), and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX, JSM–IT200, JEOL Ltd., Tokyo, Japan) for chemical and surface characterization, respectively.

To determine the amount of dissolved metal in the leaching experiments of gold powder in ammonium thiosulfate solutions, the metal extraction was calculated using the following equation.

$$\text{Metal extraction} = \frac{C_m \times V}{m \times M} \times 100\%, \quad (1$$

where C_m is the concentration of dissolved metal in mg/L, V is the volume of leaching solution in L, m is the mass of the sample (g), and M the metal content in the sample (mg/g), respectively. In addition, thermodynamic calculations using Geochemist's Workbench (GWB) software were carried out for the Fe–As–S–H_2O and Fe–S–H_2O systems to predict the dissolution behavior of the metal species in the HAsBS ore for the conditions used in the leaching experiments.

3.2.3. Characterization of the Passivation Layer on Gold Surface

Batch leaching experiments were conducted to characterize the passivation layer formed on the gold grains in ammonium thiosulfate solutions. Leaching was conducted using 4 mm × 4 mm gold foil, 1 g HAsBS, and 10 mL of ammonium thiosulfate solution, all of which were put in 50 mL flask and shaken (i.e., a thermostat water bath shaker at 25 °C; amplitude 40 mm; shaking speed 120 min^{-1}) for 24 h. The residues were washed thoroughly with DI water, dried in a vacuum drying oven at 40 °C, and analyzed by XRF, XPS, and SEM–EDX for chemical and surface characterization.

3.2.4.Evaluation of thiosulfate consumption due to the presence of pyrite and arsenopyrite.

To evaluate the effect of pretreatment on thiosulfate decomposition, leaching experiments were carried out by mixing 4 g of HAsBS (i.e., pretreated, and untreated) with 40 mL of thiosulfate solution (1 M $Na_2S_2O_3$, 0.5 M NH_3, 0.5 M NH_4Cl) with and without 10 mM $CuCl_2$ in a 50 mL Erlenmeyer flask using magnetic stirring. A 2 mL suspension was collected at regular time intervals (20 min) and the filtrate was analyzed by UV–Vis.

3.3 Results and Discussion

3.3.1 Effect of HAsBS Ore on Gold Dissolution

The suppression mechanism of gold extraction from refractory ores is classified into two phenomena: one is the physical encapsulation of gold grains in the

sulfide matrix, which prevents the contact of the lixiviant with the gold grains. The second is a chemical suppression mechanism that includes thiosulfate decomposition and passivation of the gold grains. The suppressive effect of physical encapsulation can be overcome by ultra-fine grinding to expose the gold grain to the lixiviant, but chemical suppression remains even after ultra-fine grinding is conducted. As a first step in the present study, the chemical suppressive effects of sulfide minerals on gold extraction were evaluated by leaching experiments using the mixture of gold powder and HAsBS ore (Figure 2). In the absence of HAsBS, over 90% of gold was extracted within 8 h, and more than 99% gold extraction was attained after 24 h. This fast-leaching kinetics matches with previous studies (Fleming, McMullen, Thomas, & Wells, 2001) (Grosse, Dicinoski, Shaw, & Haddad, 2003) (Zhang & Senanayake, 2016).

The dissolution reaction of gold in ammonium thiosulfate has been reported by many authors (Equation (2)) (Aylmore & Muir, 2001) (Grosse, Dicinoski, Shaw, & Haddad, 2003) (Duan, Li, Jiang, Lei, & Dong, 2017) (Salinas-Rodríguez, et al., 2022) and is summarized as:

$$\mathrm{Au} + 2\mathrm{S_2O_3}^{2-} + \mathrm{Cu(NH_3)_4}^{2+} \rightarrow \mathrm{Au(S_2O_3)_2}^{3-} + \mathrm{Cu(NH_3)_4}^{+} \qquad (2)$$

In Equation (2), gold is oxidized by the cupric ammine complex ($Cu(NH_3)_4^{2+}$), and the extracted gold (Au^+) is stabilized by forming a water soluble complex with thiosulfate anions (i.e., $Au(S_2O_3)_2^{3-}$). The cuprous ammine complex ($Cu(NH_3)_4^+$) formed in Equation (2) is then oxidized to a cupric ammine complex ($Cu(NH_3)_4^{2+}$) with dissolved oxygen in Equation (3). The overall reaction of gold dissolution from Equations (2) and (3) is summarized by Equation (4).

$$4\mathrm{Cu(NH_3)_4}^{+} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow 4\mathrm{Cu(NH_3)_4}^{2+} + 4\ \mathrm{OH}^- \qquad (3)$$

$$4\mathrm{Au} + 8\mathrm{S_2O_3}^{2-} + \mathrm{O_2} + 2\mathrm{H_2O} \rightarrow 4\mathrm{Au(S_2O_3)_2}^{3-} + 4\ \mathrm{OH}^- \qquad (4)$$

In the overall reaction of gold dissolution (Equation (4)), copper ammines ($Cu(NH_3)_4^{2+}$/($Cu(NH_3)_4^+$) do not appear, and they are considered to be a catalyst for gold extraction. In the solution phase, the decomposition of thiosulfate occurs; that is, thiosulfate ions are oxidized by the cupric ammine complex to form tetrathionate ($S_4O_6^{2-}$) as follows (Alguacil, 2006):

$$2\mathrm{Cu(NH_3)_4}^{2+} + 2\mathrm{S_2O_3}^{2-} \rightarrow 2\mathrm{Cu(NH_3)_4}^{+} + \mathrm{S_4O_6}^{2-} \qquad (5)$$

Because of this reaction (Equation (5)), thiosulfate ions, needed to extract gold, are decomposed, but as Figure 3.2 shows, more than 99% of gold was extracted in the absence of the HAsBS ore; this implies that the effects of thiosulfate decomposition can be considered negligible.

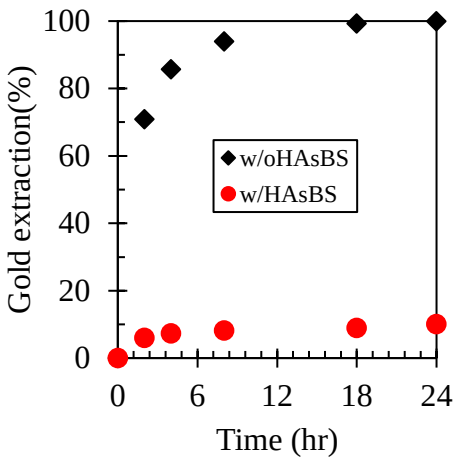


Figure 3.2. The effects of HAsBS ores on gold extraction in ammonium thiosulfate solutions.

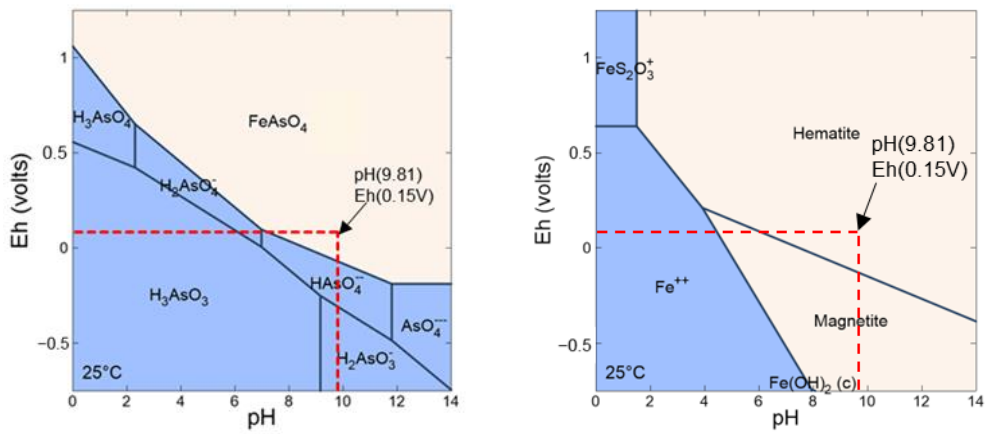
In the presence of HAsBS, a maximum of 10% gold extraction was attained after 24 h, which was much lower compared to the absence of HAsBS where over 99% extraction was obtained. There are two possible reasons that can explain the drastic reduction in gold extraction in the presence of HAsBS, which are: (1) the formation of a passivation layer on the surface of gold that retarded the dissolution of gold (Yang, et al., 2015), and (2) the accelerated decomposition of thiosulfate by associated sulfide minerals (Feng & Van Deventer, 2002). In the following sections, the above hypotheses are discussed based on the experimental results.

3.3.2 Oxidation of arsenopyrite and pyrite ore in Ammonium Thiosulfate Solution

During gold leaching in ammonium thiosulfate solutions, arsenopyrite and pyrite, the major sulfide minerals in HAsBS ore (Figure 1), are oxidized by the cupric ammine complex. Thermodynamic calculations performed using GWB software for the Fe–As–S–H_2O and Fe–S–H_2O systems (Figure 3) showed that iron arsenate ($FeAsO_4$) and hematite (Fe_2O_3) are the stable phase for the iron and arsenic species at the observed pH (9.8) and Eh (0.15 V) conditions in the leaching experiments, shown as the cross point of the red dotted lines in Figure 3.3. Based on this, the possible reactions for arsenopyrite and pyrite oxidation are assumed to be:

$$\mathrm{FeAsS} + 14\ \mathrm{Cu(NH_3)_4}^{2+} + 8\mathrm{H_2O} \rightarrow \mathrm{FeAsO_4} + \mathrm{SO_4}^{2-} + 14\mathrm{Cu(NH_3)_4}^{+} + 16\mathrm{H}^{+} \quad (6)$$

$$2\mathrm{FeS_2} + 12\mathrm{Cu(NH_3)_4}^{2+} + 7\mathrm{H_2O} \rightarrow \mathrm{Fe_2O_3} + 4\mathrm{SO_4}^{2-} + 12\mathrm{Cu(NH_3)_4}^{+} + 14\mathrm{H}^{+} \quad (7)$$



(a) (b)

Figure 3.3. Eh–pH diagram of the (a) Fe–As–S–H_2O system, (b) Fe–S–H_2O system. (Concentrations of Fe, As, and S were taken to be 0.001 mg/L, 0.001 mg/L, and 0.1 mg/L.)

To confirm the proposed oxidation reactions for arsenopyrite and pyrite, soluble Fe, As, and S concentrations during the leaching experiments with HAsBS were analyzed (Figure 3.4). The dissolved sulfur concentration increased from 39 to 47 g/L in the first 6 h of leaching, Figure 3.4b. This is consistent with reaction (6) and (7), where sulfate ions are released by the oxidation of HAsBS. After 6 h, the soluble sulfur concentration started to decrease, and the concentration reached 36 g/L at 24 h. The decline in soluble sulfur concentration indicates that precipitation of the sulfur species occurs during the leaching. This may be interpreted by assuming the decomposition of thiosulfate due to the presence of an excess amount of dissolved oxygen. According to Rodriguez et al. 2022, an excess amount of dissolved oxygen favors the oxidation of thiosulfate and its complexation with Cu; oxygen causes the oxidation of Cu(I) to Cu(II), at the same time decomposing thiosulfate to form $(S_2O_3)_3^{5-}$, sulfite(SO_3^{2-}), sulfate(SO_4^{2-}), and elemental sulfur(S) as shown in Equations (8) and (9) (Aylmore & Muir, 2001). In addition, the rate of oxidation of Cu(I) to Cu(II) is slower than the reduction of Cu(II) by thiosulfate, which may result in the formation of Cu(I)-sulfide precipitates, thus causing a reduction in the sulfur concentration.

$$3S_2O_3{}^{2-} + 6H_2O \rightleftharpoons 2SO_4^{2-} + 4S^0 + 2OH^- \quad (8)$$

$$3S_2O_3{}^{2-} + 6OH^- \rightleftharpoons 4SO_3{}^{2-} + 2S^{2-} + 3H_2O \quad (9)$$

$$S_2O_3{}^{2-} \rightarrow SO_3{}^{2-} + S^0 \quad (10)$$

As shown in Figure 3.4a, the extraction of Fe and As was very low with about 0% and less than 0.4% after 24 h of leaching, respectively. This indicates that both Fe and As species are not stable in the aqueous phase under the leaching conditions, and they are precipitated, probably, as ferric arsenate, hematite, or ferric hydroxides. Such precipitates

might affect the gold extraction; they may cover the surface of gold powder, suppressing gold extraction, and this is discussed in detail in the next section, Section 3.3.3

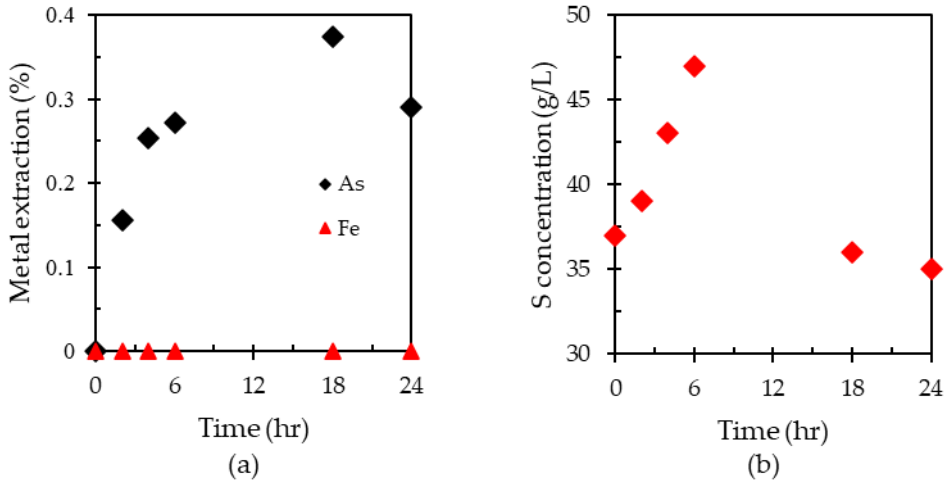


Figure 3.4. The dissolution behavior of HAsBS during gold leaching: (a) extraction of Fe and As, and (b) change in S concentration with time.

3.3.3 Effects of the Passivation Layer on Gold Extraction

As highlighted in Section 3.3.2, the second possible reason that can cause the reduction in gold extraction in the presence of HAsBS is the formation of a passivation layer. A passivation layer covers the surface of the gold and prevents interaction between the gold and the lixiviant, resulting in low gold extraction. In a study by Yang et al. (2015), characterization of the passivation layer after ammonium thiosulfate leaching in the presence of arsenopyrite revealed that the passivation layer was comprised of cuprous sulfide (Cu_2S), elemental sulfur (S), iron oxyhydroxide (FeOOH), and iron arsenate ($FeAsO_4$) species on the surface of gold. To confirm the presence of these materials, this study analyzed the surface of the leached gold foils using SEM–EDX and XPS. Figure 3.5 shows the results of SEM–EDX analysis for gold foil before and after leaching with HAsBS ores.

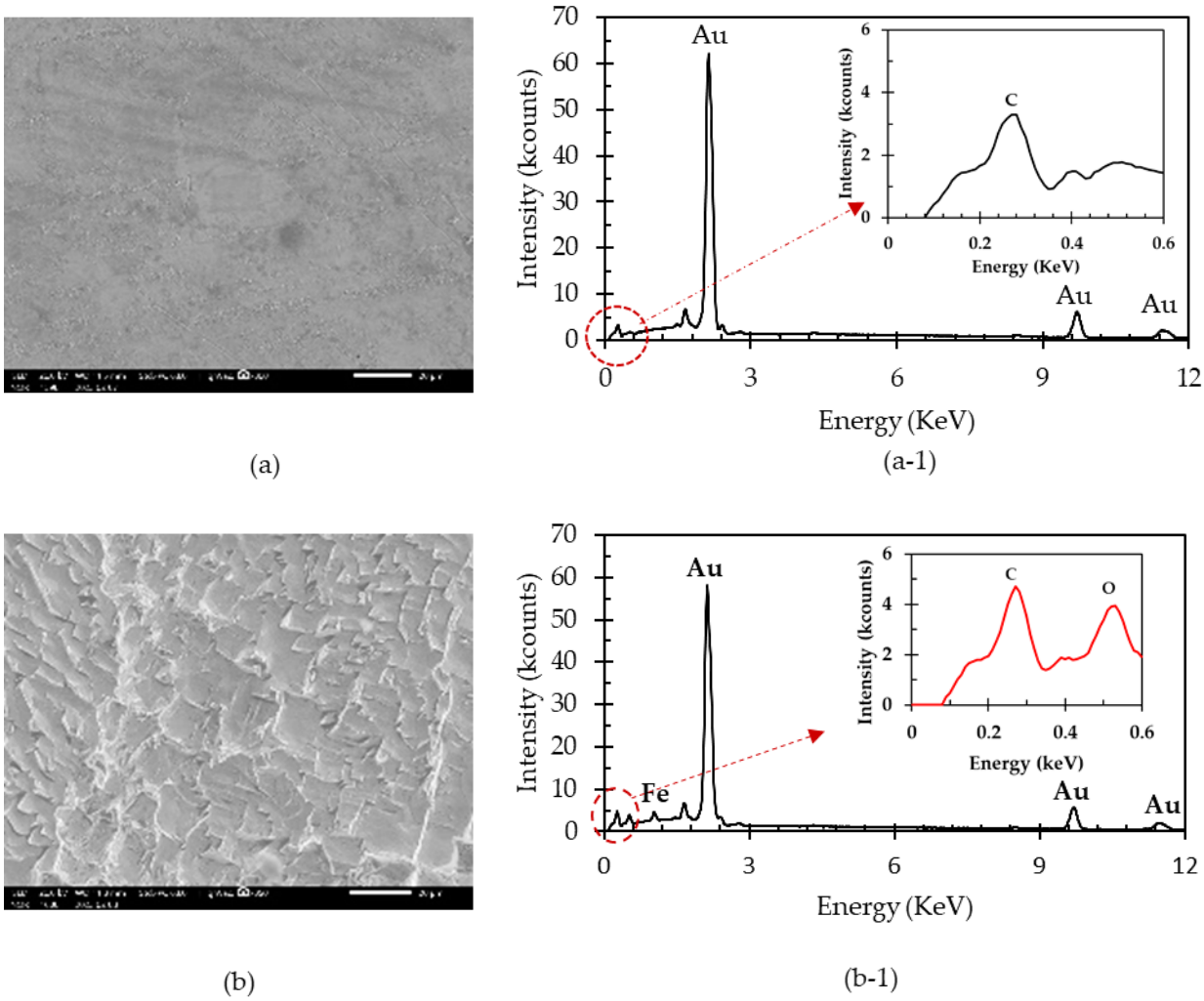


Figure 3.5. SEM–EDX photomicrographs of gold foil (a) before leaching and the corresponding EDX spectrum (a-1), (b) gold foil after leaching and the subsequent EDX spectrum (b-1).

The SEM–EDX images (Figure 3.5) and EDX spectrum (Figure 3.5(a-1, b-1)) did not detect any sulfur, arsenic, or copper species but showed the presence of oxygen and iron on the surface of gold after leaching. This may be because the amounts of the passivating materials on the gold surface were below the detection limit of SEM–EDS analysis. To detect a small amount of passivating materials, XPS was used to characterize the gold surface in the presence (i) and absence (ii) of HAsBS, (Figure 3.6).

As shown in Figure 3.6, in the XPS spectrum, signals from Cu, Fe, As, S, and O were detected on the surface of the gold foil leached in the presence of HAsBS (i). In the deconvolution results for the Cu 2p3/2 spectrum, Figure 3.6a, a strong peak at 932.5 eV was assigned to Cu(I) bound to a sulfur species as Cu_2S (Yang, et al., 2015), and minor peaks at 934.5 eV and 936.0 eV corresponding to Cu(II)-oxide and Cu(II)-sulfate were

detected, respectively (Nakai, Sugitani, Nagashima, & Niwa, 1978). In the deconvoluted spectrum of S 2p3/2, peaks were detected at 163.0 eV and 161.7 eV and were assigned to disulfide and monosulfide sulfur species combined with copper species, respectively (Mielczarski & Minni, 1984), and at 165.5 eV corresponding to elemental sulfur. In addition, satellite peaks were observed at 167.3 eV and 167.9 eV, which could be S associated with the sulfate species (Wagner C.D., 1979). In the case of oxygen, the O 1s deconvoluted peaks at 531.9 eV and 534.3 eV were observed and were all attributed to oxygen in hydroxyl ions of Fe(III) hydroxide (Park, et al., 2020) while another small peak at 536.0 eV was assigned to the oxygen of water molecules. The iron spectrum showed peaks at 706.8 eV and 710.0 eV corresponding to Fe(II)-AsS and Fe(III)-AsS in the bulk FeAsS, respectively. The other iron peaks detected were at 711.7 eV corresponding to Fe(III)–hydroxide and at 713.7 eV attributed to similar Fe(III)-SO_4 species (Park, et al., 2021). In addition, there were satellite iron peaks observed at 715.8 eV and 715.1 eV, which were assigned to hydrated Fe(III) oxide (Can, et al., 2017). The arsenic spectra exhibited strong peaks at 41.3 eV and 45.5 eV, assigned to arsenic in the bulk FeAsS and As(III)-oxide, respectively. Furthermore, a peak at 46.2 eV was detected and assigned to (As(V)-O) species. The results from the XPS validated the presence of a passivation layer for the gold foil leached in the presence of HAsBS ore and were consistent with the work conducted by Yang et al. (2015) but did not give a clear indication of the source of elemental sulfur that formed on the surface of the gold foil.

To determine the source of the sulfur species observed on the gold foil, XPS characterization was undertaken for the gold foil leached in the absence of the HAsBS (ii) and the results are outlined in Figure 3.6(aii–eii). The XPS spectrum of Cu 2p3/2 (Figure 3.6(aii)) showed a peak centered at 933.5 eV assigned to Cu(II) oxide, while peaks observed at 931.9 eV and 935.6 3 eV were assigned to Cu(II) sulfide and hydrated Cu(II) sulfate, respectively (Nakai, Sugitani, Nagashima, & Niwa, 1978). For the sulfur spectrum (Figure 3.6(bii)), two peaks at 161.9 eV and 164.1 eV were shown and assigned to S^{2-} and elemental sulfur (S), respectively. Oxygen peaks at 533.9 eV and 531.3 eV were assigned to the hydroxide ion (OH^-), and peaks at 532.4 eV and 536.2 eV were attributed to the oxygen of water and Cu(II) species, respectively (Yang, et al., 2015). These results show that even in the absence of HAsBS, elemental sulfur was formed on the gold surface. This indicates that the major source of sulfur in the passivation layer may be formed by the decomposition of thiosulfate.

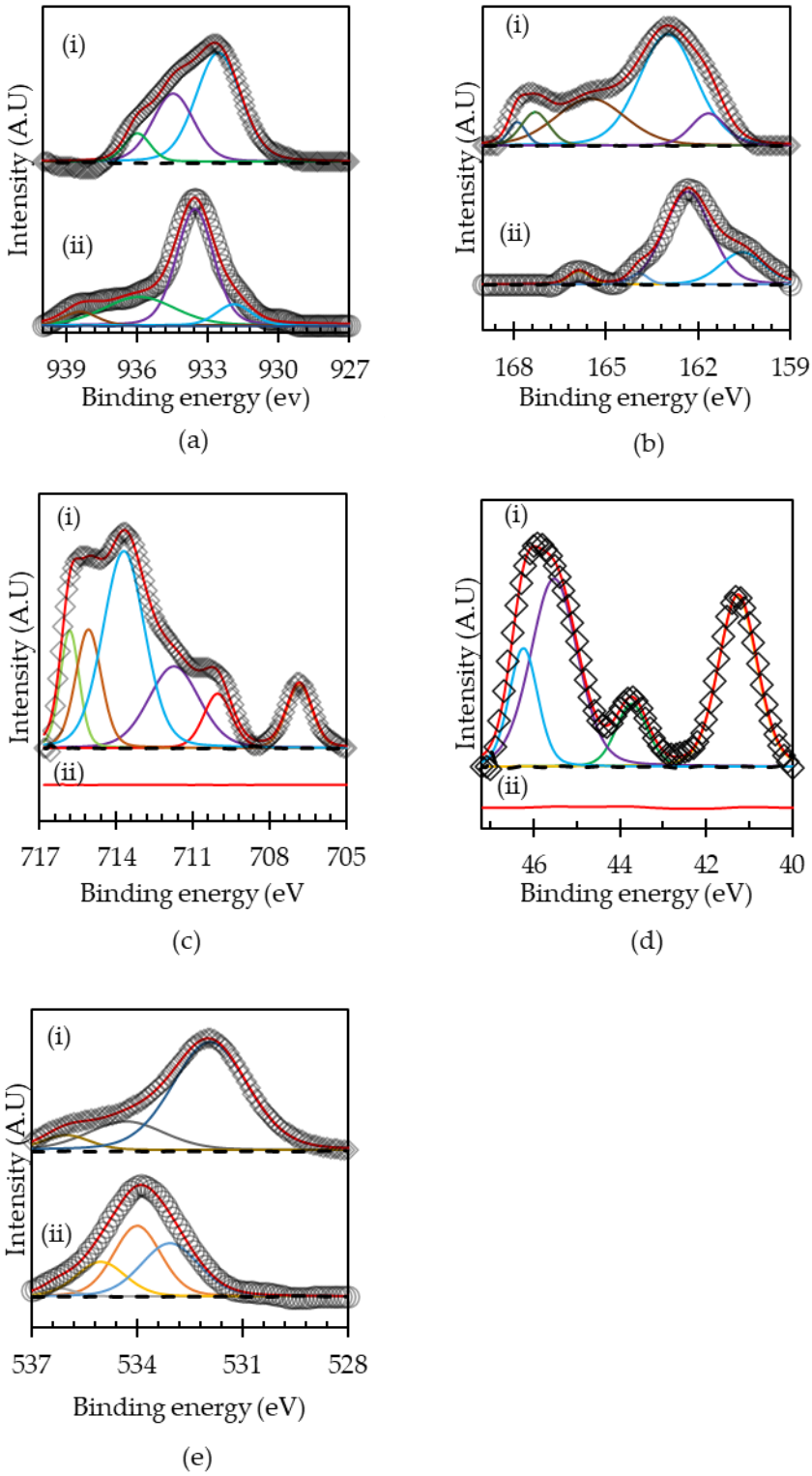


Figure 3.6. XPS spectra of gold foil residue leached in the presence of HAsBS (i) and without HAsBS (ii): (a) Cu 2p, (b) S 2p, (c) Fe 2p (d) As 3d, (e) O 1 s.

The XPS analysis established that during gold leaching, the major passivating species on

the gold surface are elemental sulfur, Cu_2S/Cu_2O, and Fe(III)−O. The following Table 3.2 gives a summary of the assignments used to interpret the XPS spectra for the surface of the gold in the presence and absence of HAsBS.

Table 3.2. XPS peak parameters for Fe 2p, As 3d, S 2p, O1 s, and Cu 2p spectra.

Spectral Peak	Binding Energy	FWHM	Line Shape	Chemical Species	Content (at. %)	References
Fe $2p_{3/2}$ [a]	706.8	1.2	GL (20)	Fe(II)-AsS	7.8	(Park, et al., 2020)
Fe $2p_{3/2}$ [a]	710.0	2.4	GL (20)	Fe(III)−AsS	7.3	(Park, et al., 2020)
Fe $2p_{3/2}$ [a]	711.7	0.9	GL (20)	Fe(III)−O	19.9	(Chen, Xie, Wang, Fu, & Wang, 2022)
Fe $2p_{3/2}$ [a]	713.7	1.3	GL (20)	Fe(III)−SO_4^{2-}	39.5	(Zhu, et al., 2014)
As $3d_{5/2}$ [a]	41.3	1.1	GL (20)	As(O)	31.6	(Park, et al., 2020)
As $3d_{5/2}$ [a]	43.7	0.9	GL (20)	As(I)-O	9.5	(Park, et al., 2020)
As $3d_{5/2}$ [a]	45.5	1.3	GL (20)	As(III)-O	42.6	(Hollinger G., 1994)
As $3d_{5/2}$ [a]	46.2	0.8	GL (20)	As(V)-O	16.4	(Hollinger G., 1994)
S $2p_{3/2}$ [a]	161.7	1.3	GL (20)	Monosulfide(S^{2-})	9.3	(Park, et al., 2020)
S $2p_{3/2}$ [a]	163.0	2.2	GL (20)	Disulfide(S_2^{2-})	52.7	(Park, et al., 2020)
S $2p_{3/2}$ [a]	165.5	2.7	GL (20)	Elemental (S)	27.0	(Park, et al., 2020)
S $2p_{3/2}$ [a]	167.9	0.7	GL (20)	Thiosulfate (SO_3^{2-})	3.5	(Park, et al., 2020)
S $2p_{3/2}$ [a]	167.3	1.1	GL (20)	Thiosulfate (SO_3^{2-})	7.6	(Park, et al., 2020)
S $2p_{3/2}$ [b]	160.6	1.7	GL (20)	Monosulfide(S^{2-})	22.8	(Park, et al., 2020)
S $2p_{3/2}$ [b]	162.3	1.77	GL (20)	Disulfide(S_2^{2-})	69.6	(Park, et al.,

						2020)
S $2p_{3/2}$ [b]	163.9	0.68	GL (20)	Elemental sulfur(S^0)	3.0	(Zhu, et al., 2014)
S $2p_{3/2}$ [b]	165.9	0.81	GL (20)	Sulfate (SO_4^{2-})	4.52	(Park, et al., 2020)
Cu $2p_{3/2}$ [a]	932.5	2.3	GL (20)	Cu(I)-S	57.9	(Bilal, et al., 2022)
Cu $2p_{3/2}$ [a]	934.5	2.1	GL (20)	Cu(II)−O	33.5	(Wang, Wang, Dong, Fu, & Xie, 2019)
Cu $2p_{3/2}$ [a]	936.0	1.3	GL (20)	Cu(II)−sulfate.	8.8	(Nakai, Sugitani, Nagashima, & Niwa, 1978)
Cu $2p_{3/2}$ [b]	931.9	1.9	GL (20)	Cu(I)-S	57.5	(Bilal, et al., 2022)
Cu $2p_{3/2}$ [b]	933.5	3.6	GL (20)	Cu(II)−O/$Cu(OH)_2$	26.8	(Wu, Feng, Li, Liao, & Wang, 2019)
Cu $2p_{3/2}$ [b]	935.9	1.7	GL (20)	$Cu(OH)_2$	6.1	(Wu, Feng, Li, Liao, & Wang, 2019)
Cu $2p_{3/2}$ [b]	938.4	1.7	GL (20)	Cu(II)−sulfate.	9.5	(Wu, Feng, Li, Liao, & Wang, 2019)
O 1s [a]	531.9	2.5	GL (20)	Hydroxyl oxygen (OH^-)	73.9	(Park, et al., 2021)
O 1s [a]	534.3	1.6	GL (20)	(O)attached to water	6.5	(Wagner C.D., 1979)
O 1s [a]	536.0	2.6	GL (20)	(O)attached to water	19.6	(Wagner C.D., 1979)
O 1s [b]	533.1	1.9	GL (20	Hydroxyl oxygen (OH^-)	36.6	(Biesinger, Lau, Gerson, & Smart, 2010)
O 1s [b]	534	1.6	GL (20)	(O)attached to water	39.7	(Biesinger, Lau, Gerson, & Smart,

						2010)
O 1s [b]	535.0	1.7	GL (20)	(O)attached to water	20.1	(Biesinger, Lau, Gerson, & Smart, 2010)
O 1s [b]	536.3	1.1	GL (20)	(O)attached to water	3.5	(Biesinger, Lau, Gerson, & Smart, 2010)

Keys: a—gold foil leached with HAsBS, b—gold foil leached without HAsBS.

Using the data in Table 2, the presence of a layer composed of Cu_2S, S, and FeOOH was confirmed on the gold surface in the presence of HAsBS by XPS analysis. The formation of passivation materials (Cu_2S and S) was, however, also observed even without HAsBS, indicating that the major source of sulfur in the passivation materials comes from the decomposition of thiosulfate. Considering these results, the effects of the passivation layer were limited and may not cause low gold extraction in the presence of HAsBS ore as used in this study but could be caused by thiosulfate decomposition.

3.3.4 Effect of HAsBS on Thiosulfate Consumption.

In the previous section, the formation of a passivation layer on gold with HAsBS and its effects were discussed. Another possible mechanism for the low gold extraction is thiosulfate decomposition induced by sulfide minerals. Therefore, the stability of thiosulfate in the presence of HAsBS was evaluated using UV–Vis spectral analysis to confirm thiosulfate decomposition by HAsBS. The UV–Vis spectral analyses for 0.5 M NH_4Cl/0.5 M NH_3 buffer solutions containing 100 μM of sodium thiosulfate or sodium sulfate are shown in Figure 3.7. Thiosulfate gave a strong absorbance peak at 214–216 nm, which is in line with previous reports (Chen, Xie, Wang, Fu, & Wang, 2022). The absorbance for sulfate ions was very low in the measured range (190–290 nm), and thus it can be assumed that absorbance at 215 nm (Abs_{215}) corresponds to thiosulfate.

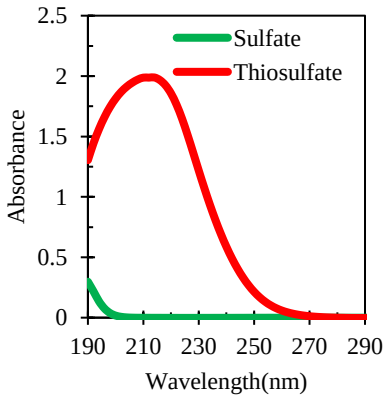


Figure 3.7. UV–Vis spectra of sulfate (SO_4^{2-}) and thiosulfate ($S_2O_3^{2-}$).

The stability of thiosulfate in 0.5 M NH_4Cl/0.5 M NH_3 buffer solutions containing 100 μM of sodium thiosulfate was assessed with and without HAsBS (Figure 3.8). The effects of HAsBS addition with time on the absorbance at 215 nm (Abs_{215}), corresponding to thiosulfate, were measured (Figure 3.9). The vertical axis of Figure 3.9 shows Abs_{215} at t min normalized with initial, at t = 0 min, $Abs_{215}(0)$, given by the ratio $Abs_{215}(t)/Abs_{215}(0)$. Without HAsBS, the normalized absorbance slightly decreased with time, indicating that thiosulfate tends to self-decompose (Xu, et al., 2017). Even with the self-decomposition, the normalized absorbance remained over 0.60 after 80 min, suggesting that about 65% of thiosulfate remains in the experiments. The decreasing rate of the normalized absorbance was strongly affected by the addition of HAsBS. With HAsBS, the normalized absorbance rapidly decreased to 0.20 at 20 min, and it reached 0.05 at 80 min. This suggests that thiosulfate decomposition was accelerated by HAsBS. Xu et al. (2017) reported that thiosulfate decomposition is mainly due to the oxidation on semiconductor sulfide minerals (Figure 3.10); thiosulfate ions are oxidized on the anodic sites of the mineral surface and electrons are transferred through the semiconductor minerals to a cathodic site where the reduction of oxidizing agents such as oxygen and $Cu(NH_3)_4^{2+}$ occurs. In a study by Chen et al. (2008), it was established that pyrite, pyrrhotite, and arsenopyrite can result in thiosulfate decomposition. Based on the mineralogical analysis conducted in this study, HAsBS contains arsenopyrite, pyrite, and pyrrhotite (Figure 3.11). From this, it can be assumed that the rapid decomposition of thiosulfate with HAsBS is mainly due to the sulfide minerals in the ore. This allowed us to hypothesize that thiosulfate decomposition in the presence of HAsBS may be the dominant mechanism for the suppression of gold extraction. Based on this assumption, a method to enhance the extraction of gold associated with HAsBS is proposed in the next chapter.

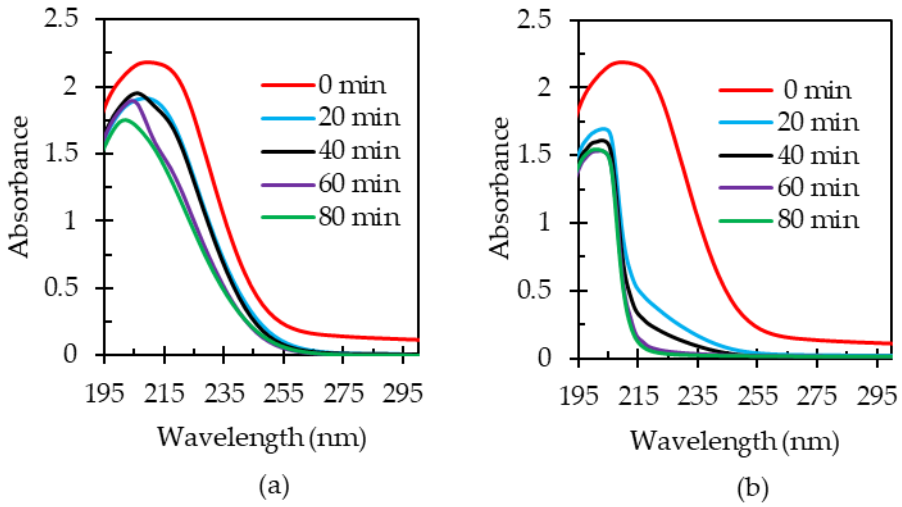


Figure 3.8. UV−Vis spectra of thiosulfate (a) in the absence of HAsBS ore, (b) in the presence of HAsBS ore.

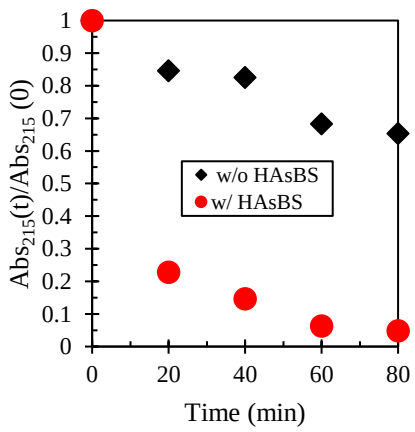


Figure 3.9. UV−Vis spectra thiosulfate decay of the (Abs_{215}) absorbance for thiosulfate with and without HAsBS.

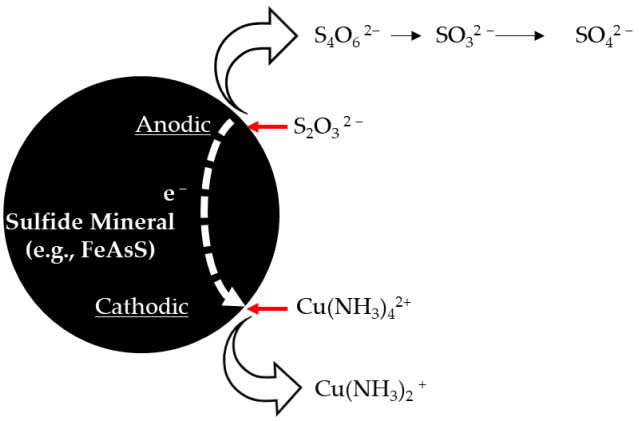


Figure 3.10. Schematic diagram of the decomposition of thiosulfate on the surface of

sulfide minerals (Xu, et al., 2017).

3.4 Summary

The following is the summary of the finding obtained in the study conducted in this Chapter:

- ✓ The mechanism for gold extraction proposed in the previous studies was confirmed to be passivation of the gold particles and thiosulfate decomposition.
- ✓ Thiosulfate was decomposed with sulfide minerals because sulfides are semiconductors and provide anode and cathode sites for oxidizing thiosulfate with cupric ions. Thiosulfate is decomposed to sulfate, the most stable sulfide species under the experimental conditions used.
- ✓ In arsenic-bearing gold refractory ores passivation is not entirely the main cause of gold extraction suppression as suggested by previous authors, but rather, the decomposition of thiosulfate in the presence of sulfide minerals is the primary cause of the suppression of gold extraction, as indicated by UV-Vis and XPS results presented in this study.
- ✓ XPS analysis confirmed the presence of a layer comprising of Cu_2S, S, and FeOOH on the gold surface in the presence of HAsBS and in the absence of HAsBS elemental sulfur, Cu_2S/Cu_2O were identified.
- ✓ To improve the gold extraction in the presence of sulfide minerals, oxidizing the of the surface of sulfides minerals can minimize thiosulfate decomposition.

References

Alguacil, F. (2006). *The chemistry of gold extraction (2nd edition).* Littleton, Colorado, USA: John O Marsden and CIain house SME.

Aylmore, M., & Muir, D. (2001). Thiosulfate leaching of gold. *Miner. Eng, 14*, 135-174.

Biesinger, M., Lau, L., Gerson, A., & Smart, R. (2010). Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides:Sc, Ti, Cu and Zn. *Appl.Surf.Sci*, 887-898.

Bilal, M., Ito, M., Akashino, R., Bu, X., Hassan, F., Park, I., . . . Hiroyoshi, N. (2022). Heterogenous carrier flotation technique for recovering finely ground chalcopyrite particles using coarse pyrite particles as a carrier. *Minerals Engineering., 180*, 107518.

Can, F., Demirci, O., Dumoulin, F., Erhan, E., Arslan, L., & Ergenekon, P. (2017). Iron porphyrin-modified PVDF membrane as a biomimetic material and its effectiveness on nitric oxide binding. *Appl.Surf.Sci*, 625-630.

Chen, J., Xie, F., Wang, W., Fu, Y., & Wang, J. (2022). Leaching of a carbonaceous gold concentrate in copper-tartrate-thiosulfate solutions. *Minerals Engineering, 183*, 107605.

Duan, L., Li, X., Jiang, Y., Lei, M., & Dong, Z. (2017). Arsenic transformation behaviour during thermal decomposition of P.vittata, and arsenic hyperaccumulator. *J.Anal.Appl.Pyrolysis*, 584-591.

Fatoki, J., & Badmus, J. (2022). Arsenic as an environmental and human health antagonist: A review of its toxicity and disease initiation. *Journal of Hazardous Materials Advances, Volume 5*, 100052.

Feng, D., & Deventer, J. (2010). Thiosulphate leaching of gold in the presence of ethylenediaminetetraacetic acid (EDTA. *Minerals Engineering*, 143-150.

Feng, D., & Van Deventer, J. (2002). The role of heavy metal ions in gold dissolution in the ammoniacal thiosulfate system. *Hydrometallurgy*, 231-246.

Fleming, C., McMullen, J., Thomas, K., & Wells, J. (2001). Recent advances in the development of an alternative to the cyanidation process:Thiosulfate leachingand resin in pulp. *Min.Met .Explor*, 1-9.

Grosse, A., Dicinoski, G., Shaw, M., & Haddad, P. (2003). Leaching and recovery of gold using ammoniacal thiosulfate leach liqours. *Hydrometallurgy*, 1-21.

Hollinger G., S. -K. (1994). Oxides on GaAs and InAs surfaces: An x-ray-photoelectron-spectroscopy study of reference compounds and thin oxide layers. *Physical Review, 49*(15), 11159 .

Jeon, S., Tabelin, C. B., Takahashi, H., Ilhwan, P., Ito, M., & Hiroyoshi, N. (2020). Enhanced cementation of gold via galvanic interactions using activated arbon and zero-valent aluminum: A novel approach to recover gold ions from ammonium thiosulfate medium. *Hydrometallurgy*, 105165.

Mielczarski, J., & Minni, E. (1984). The adsorption of diethyldithiophosphate on cuprous sulphide . *Surf.Interface.Anal*, 221.

Mudd, G., Giurco, D., Mohr, S., & Mason, L. (2012). *Gold resources and production: Australia in a global context.* Sydney: The Department of Civil Engineering (MonashUniversity) and the Institute for Sustainable Futures (University of Technology, Sydney).

Nakai, I., Sugitani, Y., Nagashima, K., & Niwa, Y. (1978). X-ray photoelectron spectroscopic study of copper minerals. *J.Inorg.Nucl.Chem.*, 789-791.

Nan, X., Cai, X., & Kong, J. (2014). Pretreatment process on Refractory Gold ores with As. *ISIJ Vol ,54, 54*(10.2355), 543-547.

Park, I., Ryota, T., Yuto, T., Tabelin, C. B., Phengsaart, T., Jeon, S. .., . . . Hiroyoshi, N. (2021). A novel arsenic immobilization strategy via a two-step process: Arsenic concentration from dilute solution using schwertmannite and immobilization in Ca–Fe–AsO4 compounds. *Journal of Environmental Management*.

Park, I., Tabelin, C., Seno, K., Jeon, S., Inano, H., Ito, M., & Hiroyoshi, N. (2020). Carrier-microencapsulation of arsenopyrite using Al-catecholate complex nature of oxidation

products, effects on anodic and cathodic reactions, and coating stability under simulatated weat6hering condition. *Heliyon*, 03189.

Park, I., Tabelin., C. B., Sanghee, J., Xinlong, L., Kensuke, S., Ito., M., & Hiroyoshi, N. (2019). A review of recent strategies for acid mine drainage prevention andmine tailings recycling. *Chemosphere*, 588-606.

Salinas-Rodríguez, E., Hernández-Ávila, J., Cerecedo-Sáenz, E., Arenas-Flores, A., Veloz-Rodríguez, M., Toro, N., Acevedo-Sandoval, O. A. (2022). Leaching of Copper Contained in Waste Printed Circuit Boards, Using the Thiosulfate—Oxygen System: A Kinetic Approach. *Materials, 15*(7), 2354.

Tabelin, C., Park, I., Jeon, S., Phengsaart, T., Villacorte-Tabelin, M., Alonzo, D., . . . Hiroyoshi, N. (2021). Copper and critical metals production from porphyry ores and E-wastes: A review of resource availability, processing/recycling challenges, socio-environmental aspects, and sustainability issues. *Resources, Conservation and Recycling, 170*(105610).

Wagner C.D., R. W. (1979). *Handbook of X-Ray Photoelectron Spectroscopy.* Eden Prairie: Perkin-Elmer Corporation, Physical Electronics Division,Minn. 55344.

Wang, J., Wang, W., Dong, K., Fu, Y., & Xie, F. (2019). Research on leaching of carbonaceous gold ore with copper-ammonia-thiosulfate solutions. *Minerals Engineering, 137*, 232-240.

Xu, B., Wenhao, K., Qian, L., Yongbin, Y., Tao, J., & Liu, X. (2017). A Review of Thiosulfate Leaching of Gold: Focus on Thiosulfate Consumption and Gold Recovery from. *MDPI: Metals, 7*, 222.

Zhang, X., & Senanayake, G. (2016). A Review of Ammoniacal Thiosulfate Leaching of Gold: An Update Useful for Further Research in Non-cyanide Gold Lixiviants. *Mineral Processing and Extractive Metallurgy Review*, 385-411.

Zhu, T., Lu, X., Liu, H., Li, J., Zhu, L., Lu, J., & Wang, R. (2014). Quantitative X-ray photoelectron spectroscopy-based depth profiling of bioleached arsenopyrite surface by Acidithiobacillus ferrooxidans. *Geochimica et Cosmochimica Acta, 127*, 120-139.

CHAPTER 4: APPLICABILITY OF CUPRIC AMMINE PRETREATMENT TO IMPROVE GOLD EXTRACTION IN THE PRESENCE OF ARSENOPYRITE.

4.1. Introduction

As discussed in the previous chapter, the primary cause of low gold extraction in the ammonium thiosulfate leaching in the presence of mineral sulfides like pyrite and arsenopyrite is the decomposition of thiosulfate on the mineral surface. To enhance the gold extraction in the ammoniacal thiosulfate leaching system, roasting has been the predominant technique used to oxidize refractory sulfide gold ores before leaching (Nie, et al., 2021). By roasting, dense sulfide minerals are oxidized and converted to porous oxides, which increases the contact between gold and the lixiviant, and minimizes thiosulfate decomposition, resulting in enhanced gold extraction. However, in the case of high arsenic bearing sulfide (HAsBS), roasting generates toxic gases containing sulfur oxide gases (SOx) and arsenic oxides (As_2O_3 or As_2O_5) making it an unsuitable technique for treating HAsBS (Bowell, Alpers, Jamieson, Nordstrom, & Majzlan, 2014) (Yang, Shi, Zhang, Sasaki, & Endo, 2023). These toxic emissions can lead to leaks of arsenic and potential incidents of exposure, highlighting the unsuitability of roasting for HAsBS ores (Duan, Li, Jiang, Lei, & Dong, 2017) (Schlesinger, Klein, & Vengosh, 2022).

To prevent toxic arsenic-containing gases, arsenic-bearing sulfide minerals in refractory gold ores can be pre-oxidized in low-temperature processes to minimize thiosulfate decomposition in the same manner as high-temperature roasting. Pre-oxidation/pretreatment of sulfide minerals using ammonium solutions containing cupric ions can be considered as a pretreatment process for refractory gold ores at ambient temperature and pressure conditions. Thus, ammonium thiosulfate leaching will be carried out in a two-step process for gold: (1) the pre-oxidation of HAsBS using an ammonia solution containing cupric ions, and (2) ammonium thiosulfate leaching of the pretreated ore to extract gold.

In the first step (1), sulfide minerals are oxidized by cupric ions (or cupric amine complexes), and associated metal species such as copper in the sulfide minerals are extracted into aqueous phase by forming soluble complexes with ammonium, while iron, the dominant metal in the sulfide minerals, is precipitated as metal oxyhydroxides on the surface of sulfide grain. This may minimize thiosulfate decomposition due to sulfide minerals in the subsequent gold extraction process using ammonium thiosulfate.

In this chapter, demonstration experiments using a model ore composed of gold powder and ground HAsBS were conducted to evaluate the effect of the pre-oxidation on gold extraction.

4.2 Materials and Methods

4.2.1 Materials

In these experiments, the HAsBS sample was supplied by Kitabita Mine, Yamaguchi Prefecture, Japan. The chemical composition of the sample was characterized in Chapter 3. Leaching experiments were conducted using gold powder (99.99%), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), ammonium chloride ((NH_4Cl), ammonia water ($NH_4(OH)$, 31%), and cupric chloride ($CuCl_2$), which were all obtained from Wako Pure Chemical Industries, Ltd., Japan. To characterize the surface of gold during leaching, a gold foil (thickness 0.127 mm and 99.99% purity) obtained from Sigma-Aldrich, Corporation, St. Louis, MO, USA, was used.

4.2.2. Pre-oxidation of HAsBS and Its Effect on Gold Leaching procedure

Pre-oxidation experiments were carried out by mixing 10 mg gold powder, 1 g HAsBS, and 10 mL of solution containing 0.5 M NH_3, 0.5 M NH_4Cl, and 10 mM CuCl2 in a 50 mL Erlenmeyer flask and shaking in a thermostat water bath shaker at 25 °C (amplitude 40 mm; shaking speed 120 min^{-1}) for 24 h. After 24 h, shaking was stopped for decantation and 5 mL of supernatant was taken for analysis. Subsequent gold leaching was carried out by adding 5 mL of 2 M $Na_2S_2O_3$ solution containing 0.5 M NH_3, 0.5 M NH_4Cl, and 10 mM $CuCl_2$ to the flask and shaking the flask for another 24 h. After gold leaching, solutions and solid residues were collected by filtration, and analyzed by ICP-AES and SEM–EDX, respectively. Control experiments (gold leaching experiments without pre-oxidation) were carried out by shaking 10 mg gold powder, 1 g HAsBS, and 10 mL of solution containing 1 M $Na_2S_2O_3$, 0.5 M NH_3, 0.5 M NH_4Cl, and 10 mM $CuCl_2$ in 50 mL Erlenmeyer flask at 25˚C for 24 h. The effect of pretreatment temperature and leaching conducted were conducted in 500 ml glass reactor by adding 100 mg of gold powder with 100 ml of cupric ammine solution at a temperature range:(30 ˚C, 35 ˚C, 40 ˚C, 50 ˚C), maintained by using a Thermo Fisher PID controlled heating mantle.

To evaluate the effect of pretreatment on thiosulfate decomposition, leaching experiments were carried out by mixing 4 g of HAsBS and pyrite (i.e., pretreated, and untreated) with 40 mL of thiosulfate solution (1 M $Na_2S_2O_3$, 0.5 M NH_3, 0.5 M NH_4Cl) with and without 10 mM $CuCl_2$ in a 50 mL Erlenmeyer flask using magnetic stirring. A 2 mL suspension was collected at regular time intervals (20 min) and the filtrate was analyzed by UV–Vis. In addition, the concentration of thiosulfate in the pregnant leaching solution determined by ion chromatography with a Dionex Integration RFIC System (Thermo Fisher K.K, Tokyo Japan).

4.3 Results and Discussion

4.3.1 Pretreatment of HAsBS using ammonia solution containing cupric ions.

A pre-oxidation experiment using ammonia solution containing cupric ions were conducted for the model samples composed of gold powder and HAsBS. From Equations (6) and (7) in chapter 3, it is expected that iron and arsenic species are precipitated during the oxidation of HAsBS. As shown in Figure 4.1, after 24 h of pretreatment in an ammonium solution containing cupric ions, about 25% of the sulfur were dissolved, but almost no iron and arsenic species were detected in the solution as expected. This suggests the precipitation of iron and arsenic species. Because the solution used in the pre-oxidation did not contain thiosulfate, gold extraction in the pre-oxidation step was small (about 1%).

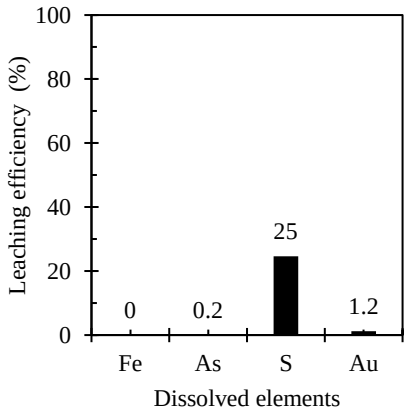


Figure 4.1. Effects of cupric ammine oxidation on the leaching of HAsBS ore.

The SEM–EDX analysis to evaluate the insulating layer formation on HAsBS after pretreatment for 24 h is shown in Figure 4.2. The morphology of the HAsBS before and after pre-oxidation shows that the HAsBS surface changed from smooth to "pitted", and it was also confirmed that precipitates were attached to the HAsBS surface after pre-oxidation. From EDX mapping for the residue, Fe, As, S, and O were evenly distributed on the mineral grain. The intensity of oxygen in the EDX spectrum (Figure 4.3) was higher in the residues as compared to the HAsBS particles before leaching. The stronger oxygen peak for the residue may be attributed to the formation of $FeAsO_4$ adsorbed on the ferric oxyhydroxides precipitated from the oxidation of HAsBS (Equation (8) in chapter 3). Weak copper signals were also detected on the HAsBS leach residues, which might indicate the formation of Cu(I)-sulfide precipitates on the mineral surface as shown in Figure 4.2(b-5).

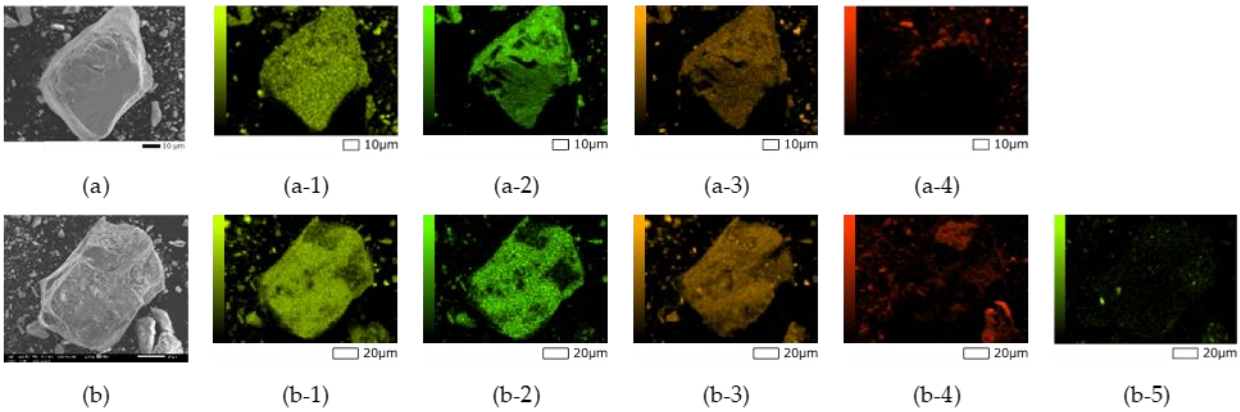


Figure 4.2. SEM–EDX photomicrographs of (a) HAsBS before treatment and the subsequent elemental maps, (a-1) Fe, (a-2) As, (a-3) S, (a-4) O; (b) pre-oxidized HAsBS; (b-1) Fe, (b-2) As, (b-3) S, (b-4) O and (b-5) Cu.

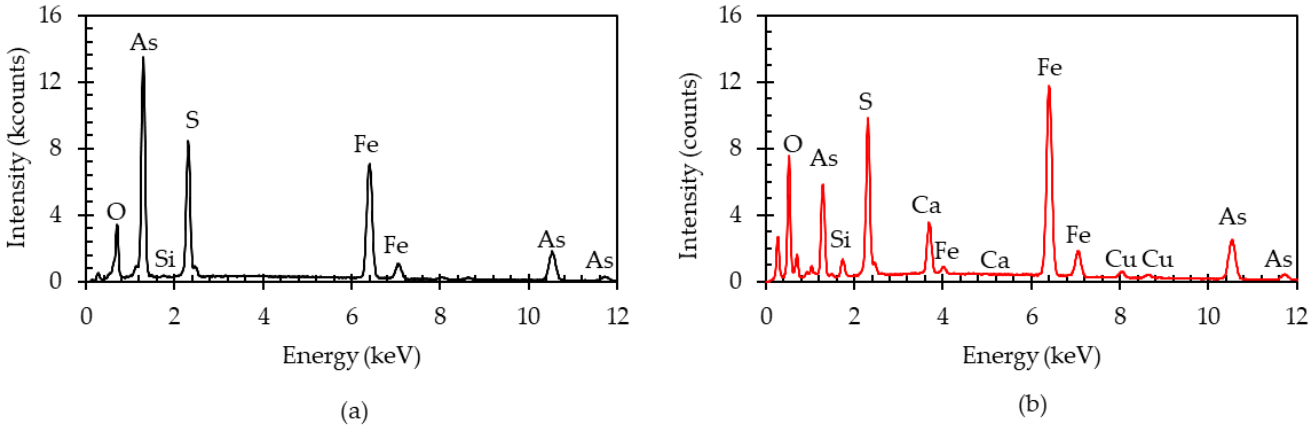


Figure 4.3. EDX-energy elemental spectra of (a) untreated HAsBS, and (b) pre-oxidized HAsBS.

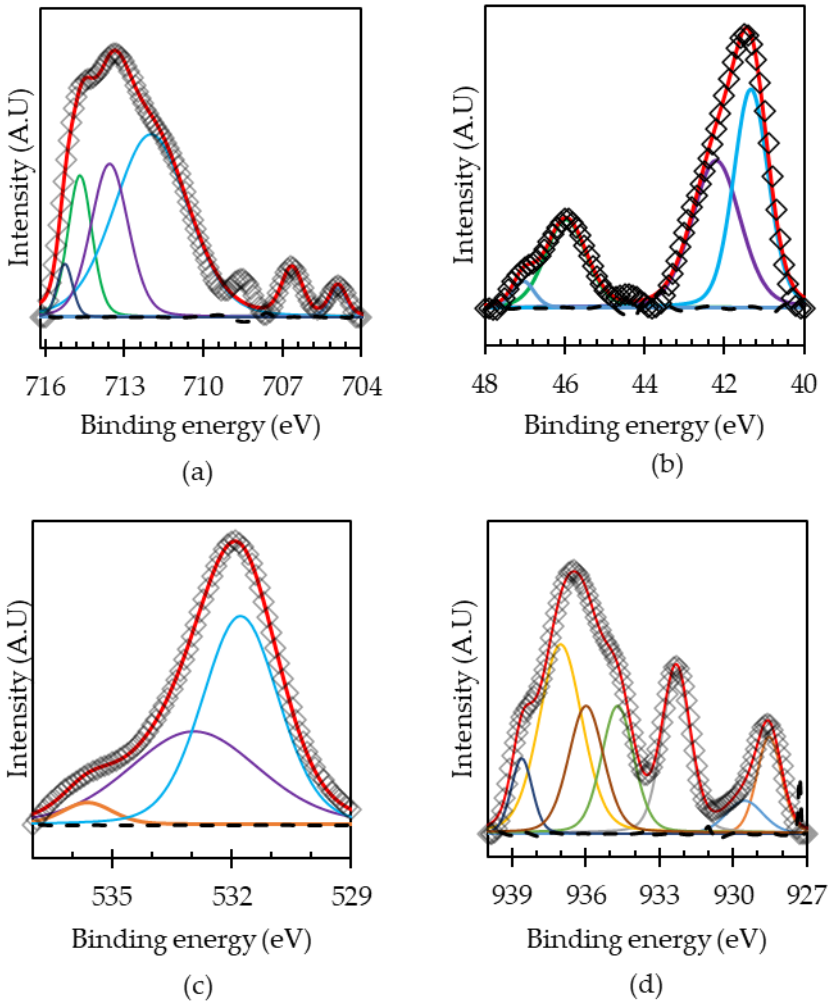
Figure 4.4 shows the XPS results for the residue from pre-oxidation. In the Fe $2p_{3/2}$ spectrum, Figure 4.4a shows two peaks at 708.2 eV and 711.4 eV, and both were assigned to Fe(III)−O [55]. In the deconvoluted results of the As $3d_{5/2}$ spectrum, (Figure 4.4b), two peaks were detected at 45.6 eV and 47.3 eV, corresponding to As(III)−O and As(V)−O, respectively. In the O 1s spectrum, Figure 4.4 d, on the treated HAsBS, a peak at 532.3 eV, which corresponds to the hydroxyl oxygen (OH^-), was detected. These results are consistent with the hypothesis that ferric arsenate ($FeAsO_4$) and ferric oxyhydroxide (FeOOH) are present as oxidation products of arsenopyrite and pyrite.

In the deconvoluted S 2p spectrum, Figure 4.4e, strong peaks at 162.5 eV and 164.1 eV were dominant and assigned to disulfide (S_2^{2-}) attached to Cu(I) species [38], S^{2-} attached to Cu(II) species [56], and elemental sulfur (S) [57], respectively. At higher

energy levels, satellite peaks for sulfur were observed at 166.5 eV, 168.6 eV, and 169.8 eV, which are due to sulfate species.

The XPS analysis also confirmed that strong Cu signals appeared after pre-oxidation. In the Cu 2p3/2 spectrum for the residue after pre-oxidation (Figure 4.4c), a dominant peak was observed at 932.3 eV and this was assigned to Cu(I), which could have originated from Cu_2S or $Cu(S_2O_3)_3^{5-}$ [58]. This may suggest that during the pre-oxidation, copper ions in the solution phase reacted with sulfide minerals in HAsBS ore and formed copper sulfides on the surface. A peak at 934.7 eV corresponded to Cu(II)-oxide species. In addition, the Cu 2p3/2 spectrum had satellite peaks at higher energy levels; that is, 936.0 eV, 937.0 eV, and 938.6 eV, which were assigned to Cu(II)-sulfate species.

The results of surface analyses (SEM–EDX and XPS) confirm that the HAsBS surface is covered by passivating materials such as $FeAsO_4$ and FeOOH after the pre-oxidation step.



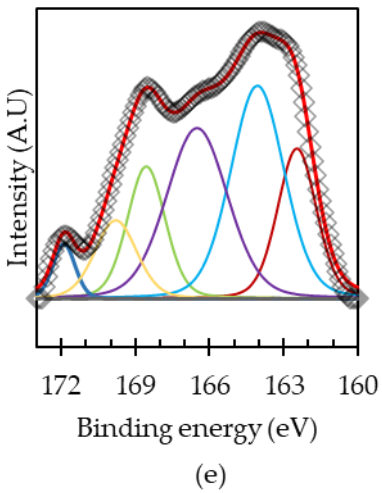


Figure 4.4. XPS results: (a) Fe 2p, (b) As 3d, (c) O 1s, (d) Cu 2p, (e) S 2p spectra.

4.3.2. Effect of Pre-oxidation of HAsBS on Thiosulfate Decomposition

The effects of pre-oxidation were assessed in the previous section (Section 4.3.1), and it was found that a passivating layer, which comprised of oxidation products, formed on the surface of HAsBS. In this section, the effect of the pretreatment (pre-oxidation) of HAsBS on thiosulfate decomposition was evaluated using UV–Vis analysis (Figure 4.5). From the UV–Vis spectra of the thiosulfate solution, which had reacted with untreated HAsBS, the adsorption at 215 nm (Abs_{215}) decreased drastically with time, while the rate of decrease became slower when the thiosulfate solution was reacted with pretreated HAsBS. The decay of absorbance with pretreated HAsBS was almost the same as that without HAsBS. These results confirmed that pre-oxidation of HAsBS, forming a passivating layer on its surface, was effective to minimize the decomposition of thiosulfate.

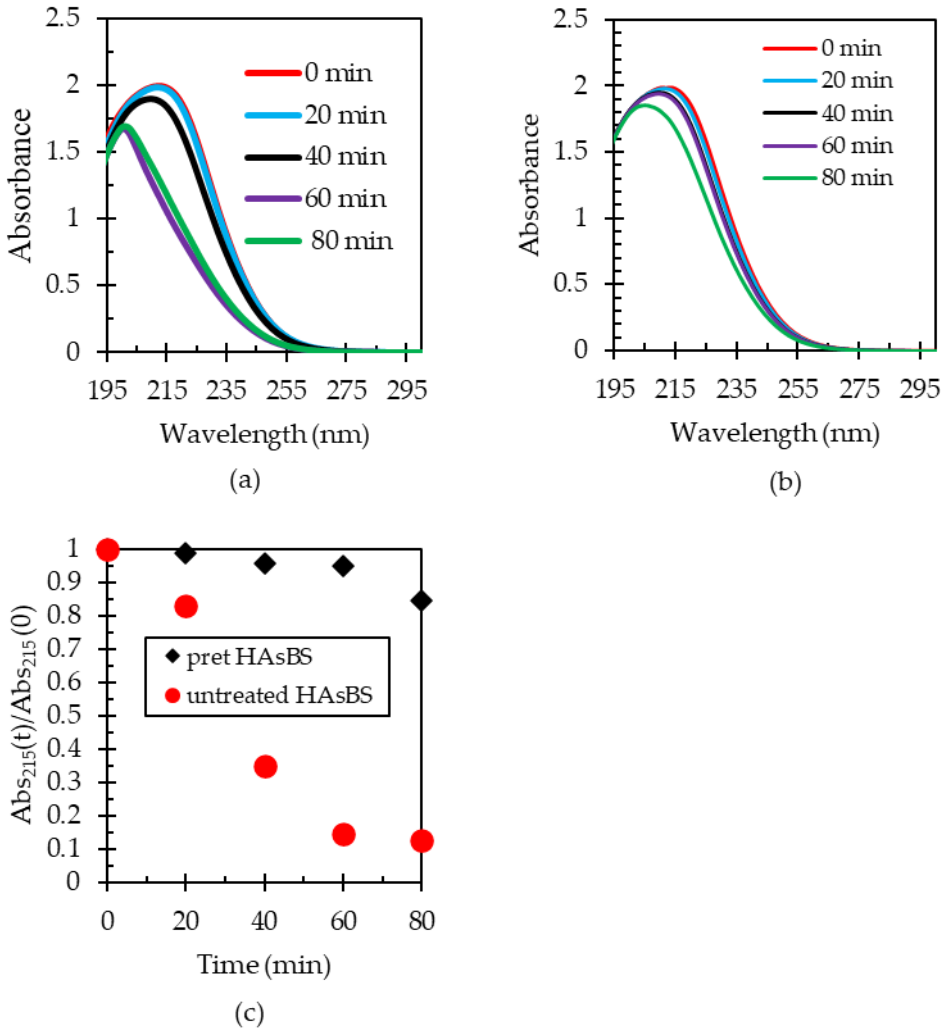


Figure 4.5. UV–Vis spectra for thiosulfate in the presence of (a) untreated HAsBS, (b) with pre-oxidized (pret) HAsBS, and (c) decay of Abs_{215} value with time.

4.3.3. Effect of Pre-oxidation of HAsBS on Gold Extraction

Figure 4.6 shows the effects of the pre-oxidation of HAsBS on the subsequent gold leaching using ammonium thiosulfate solutions, and the results show that gold extraction was significantly improved after pre-oxidation for 24 h; that is, gold extraction was 10% without pre-oxidation, while it increased to 79% when pre-oxidation was applied. The ICP-AES results indicate that passivation of the HAsBS surface was enough to suppress thiosulfate decomposition in the subsequent gold leaching step. When the surface of the HAsBS is oxidized, the oxidation products cover the surface of the sulfides and prevent the transfer of electrons from the thiosulfate ions to the cupric ammine complex as shown in Figure 10, thus minimizing thiosulfate decomposition.

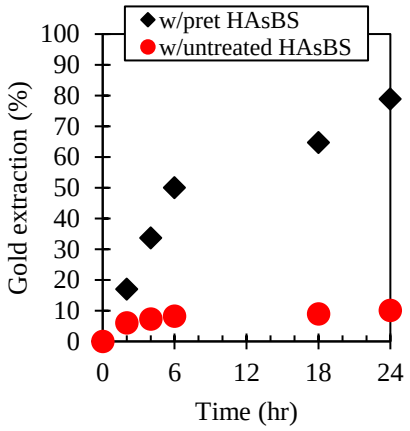
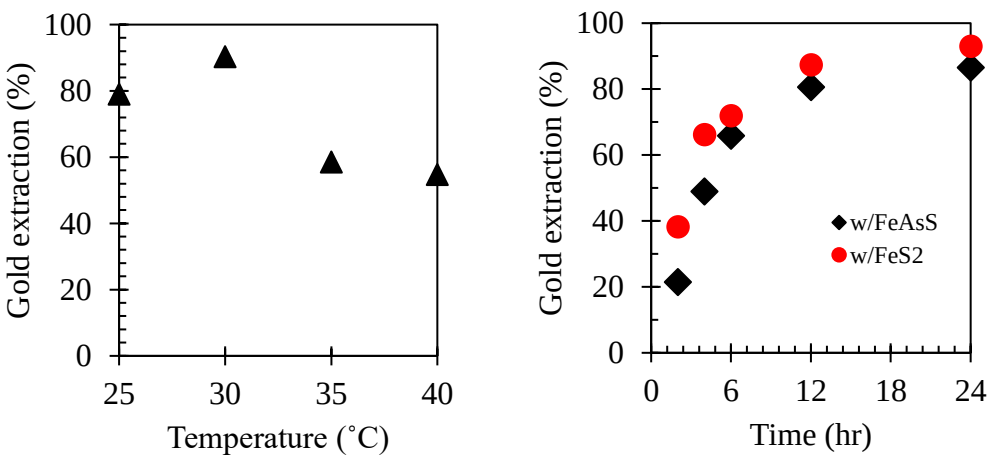


Figure 4.6. The effect of pre-oxidation of HAsBS on gold extraction.

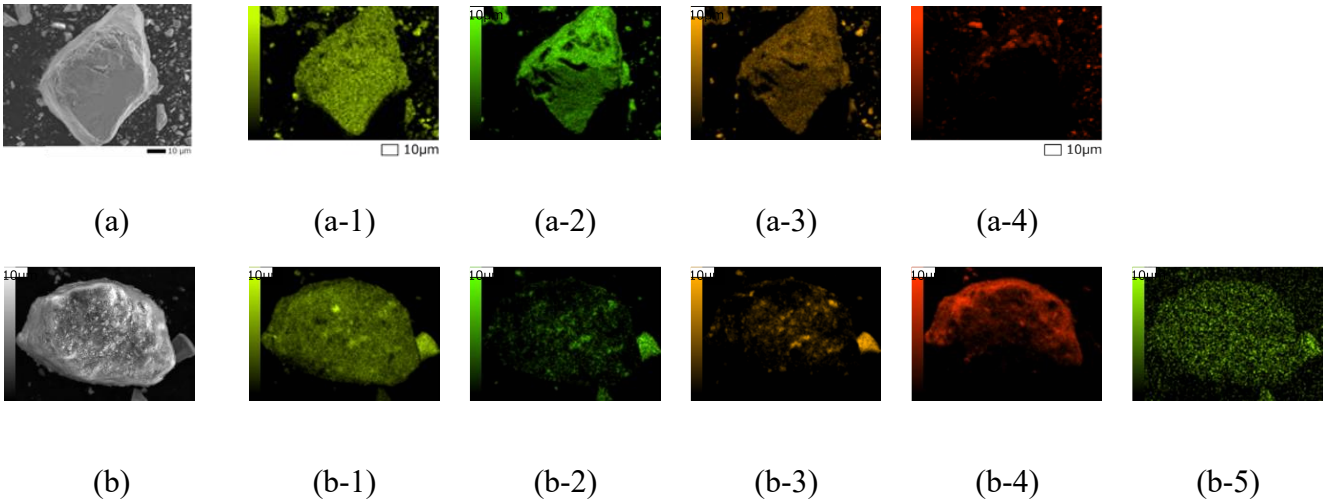
4.3.4 The effect of pretreatment temperature on gold extraction.

The effect of temperature was investigated into two parts (1) the pretreatment temperature was the same as the subsequent leaching temperature, (2) pretreatment temperature was varied but the leaching temperature was kept constant at 30 ˚C. As show in Figure 4.7 below, it is expected that the gold extraction should increase as the temperature is increased but the gold extraction decreases after 30˚C. The reason that can explain the low gold extraction at high temperatures: high temperature increases cause an increase in the redox potential in the system, making the leaching solution to be highly oxidative and in turn result in high thiosulfate decomposition (Seisko, Aromaa, & Lundström, 2020). Figure 4.8 illustrates the morphological changes of pretreated high arsenic bearing sulfide particles which show a cracky surface covered with oxidation products.



(a) (b)

Figure 4.7: Effect of pretreating and leaching temperature on gold extraction



(a) (a-1) (a-2) (a-3) (a-4)

(b) (b-1) (b-2) (b-3) (b-4) (b-5)

Figure 4.8: Effects of pretreatment at elevated temperatures on the morphology of sulfide mineral particles (a) before leaching, (b) after pretreatment and ammonium thiosulfate leaching.

4.4 Summary

The effects of HAsBS on gold extraction in ammonium thiosulfate were investigated by leaching experiments using a model ore composed of gold powder and ground HAsBS. The results showed that during ammonium thiosulfate leaching of the gold/HAsBS mixture, HAsBS having semiconductor properties facilitated the oxidation of the thiosulfate by the cupric ammine complex, resulting in the decomposition of thiosulfate, which is needed for gold extraction. As a result, gold extraction was suppressed in the presence of HAsBS. The thiosulfate decomposition can be minimized by applying a pre-oxidation treatment of HAsBS in cupric ammonium solutions, which results in passivation of the mineral surface with oxidation products. When the pre-oxidation was applied before ammonium thiosulfate leaching, gold extraction was improved from 10% to 79% for HAsBS. The thiosulfate consumption significantly reduced from 60 % before treatment to 23 % after pretreatment for HAsBS, respectively.

Increasing in the pretreatment and leaching temperature resulted in the reduction in gold extraction at temperatures above 30˚C due to the instability thiosulfate decomposition. Therefore, to maintain high gold extraction after pretreatment at high temperatures, an optimum temperature of 30˚C was maintained for all the ammonium thiosulfate leaching experiments. It is further noted that this approach minimizes reagent consumption as the copper (II) ions used in the pretreatment stage can be reused in the

subsequent thiosulfate leaching.

References

Ortego, A.; Calvo, G.; Valero, A.; Iglesias-Émbil, M.; Valero, A.; Villacampa, M. Assessment of strategic raw materials in the automobile sector. *Resour. Conserv. Recycl.* **2020**, *161*, 104968.

Moore, J.; James, C. Recent progress and applications of gold nanotechnology in medical biophysics using artificial intelligence and mathematical modeling. *Nano Express* **2021**, *2*, 022001.

WorldGoldCouncil. World Gold Council, GOLDHUB. 1 November 2022. Available online: https://www.gold.org/goldhub/data/gold-supply-and-demand-statistics (accessed on 23 January 2023).

Schodde, R. Recent trends in gold discovery. In Proceedings of the 2011 NewGenGold Conference, Perth, Australia, 22–23 November 2011.

MetalsFocus. Gold Focus 2020. MetalsFocus. 25 June 2020. Available online: https://www.metalsfocus.com/wp-content/uploads/2020/11/GOLD-FOCUS-2020.pdf (accessed on 14 February 2023).

Mudd, G.; Giurco, D.; Mohr, S.; Mason, L. Gold Resources and Production: Australia in a Global Context. The Department of Civil Engineering (Monash University) and the Institute for Sustainable Futures. University of Technology Sydney, Sydney, Australia, 2012.

Tabelin, C.; Park, I.; Jeon, S.; Phengsaart, T.; Villacorte-Tabelin, M.; Alonzo, D.; Yoo, K.; Ito, M.; Hiroyoshi, N. Copper and critical metals production from porphyry ores and E-wastes: A review of resource availability, processing/recycling challenges, socio-environmental aspects, and sustainability issues. *Resour. Conserv. Recycl.* **2021**, *170*, 105610.

Vikentyev, I.; Vikent, O.; Tyukova, E.; Nikolsky, M.; Ivanova, J.; Sidorova, N.; Tonkacheev, D.; Abramova, V.; Blokov, V.; Spirina, A. Noble Metal Speciations in Hydrothermal Sulphides. *Minerals* **2021**, *11*, 488.

Donoghue, S.; Young, M. *Environmental Assessment Report*; Dargues reef gold mine modification 3 (10_0054 MOD 3); NSW Government, Department of Planning & Environment: New South Wales, Australia, 2016.

Xiao, L.; Wang, Y.; Qian, P. Advances in non-cyanide process for gold smelting. *Gold Sci. Technol.* **2019**, *27*, 292–301.

Adams, C.R.; Porter, C.P.; Robshaw, T.J.; Bezzina, J.P.; Shields, V.R.; Hides, A.; Bruca, R.; Ogden, M.D. An alternative to cyanide leaching of waste activated carbon ash for gold and silver recovery via synergistic dual-lixiviant treatment. *J. Ind. Eng. Chem.* **2020**, *92*, 120–130.

Zhang, Y.; Cui, M.; Wang, J.; Liu, X.; Lyu, X. A review of gold extraction using alternatives to cyanide: Focus on status and prospects of the novel eco-friendly synthetic gold lixiviants. *Miner. Eng.* **2022**, *176*, 107336.

Brooy, S.; Linge, H.; Walker, G. Review of gold extraction from ores. *Miner. Eng.* **1994**, *70*, 1231–1241.

Celep, O.; Altinkaya, E.; Yazici, Y.; Deveci, H. Thiosulfate leaching of silver from arsenical refractory ore. *Miner. Eng.* **2018**, *122*, 63–70.

Jeon, S.; Ito, M.; Tabelin, C.B.; Pongsmrankul, R.; Kitajima, N.; Park, I.; Hiroyoshi, N. Gold recovery from shredder light fraction of E-waste recycling plant by flotation-ammonium thiosulfate leaching. *Waste Manag.* **2018**, *77*, 195–202.

Xie, F.; Chen, J.; Wang, J. Review of gold leaching in thiosulfate-based solutions. *Trans. Nonferrous Met. Soc. China* **2021**, *31*, 3506–3529.

Xu, B.; Wenhao, K.; Qian, L.; Yongbin, Y.; Tao, J.; Liu, X. A Review of Thiosulfate Leaching of Gold: Focus on Thiosulfate Consumption and Gold Recovery from refractory ores. *Minerals* **2017**, *7*, 222.

Jeon, S.; Tabelin, C.B.; Takahashi, H.; Ilhwan, P.; Ito, M.; Hiroyoshi, N. Enhanced cementation of gold via galvanic interactions using activated arbon and zero-valent aluminum: A novel

approach to recover gold ions from ammonium thiosulfate medium. *Hydrometallurgy* **2020**, *191*, 105165.
Feng, D.; Van Deventer, J. Leaching behaviour of sulphides in ammoniacal thiosulphate systems. *Hydrometallurgy* **2002**, *63*, 5–13.
Feng, D.; Van Deventer, J. The role of heavy metal ions in gold dissolution in the ammoniacal thiosulfate system. *Hydrometallurgy* **2002**, *64*, 231–246.
Yang, Y.; Zhang, X.; Xu, B.; Li, Q.; Jiang, T.; Wang, Y. Effect of arsenopyrite on thiosulfate leaching of gold. *Trans. Nonferrous Met. Soc. China* **2015**, *25*, 3454–3460.
Park, I.; Higuchi, K.; Tabelin, C.; Jeon, S.; Ito, M.; Hiroyoshi, N. Suppression of arsenopyrite oxidation by microencapsulation using ferric-catecholate complexes and phosphate. *Chemosphere* **2021**, *269*, 129413.
Nie, Y.; Chen, J.; Wang, Q.; Zhang, C.; Shi, C.; Zhao, J. Use of dry grinding process to increase the leaching of gold from a roasted concentrate containing hematite in the thiosulfate system. *Hydrometallurgy* **2021**, *201*, 105582.
Bowell, R.; Alpers, C.; Jamieson, H.; Nordstrom, D.; Majzlan, J. The environmental geochemistry of arsenic- an overview. *Rev. Mineral. Geochem.* **2014**, *79*, 1–16.
Yang, D.; Shi, M.; Zhang, J.; Sasaki, A.; Endo, M. Reductive roasting of arsenic-contaminated red mud for Fe resources recovery driven by johnbaumite-based arsenic thermostabilization strategy. *J. Harzadous Mater.* **2023**, *452*, 131255.
Schlesinger, W.H.; Klein, E.M.; Vengosh, A. The Global Biogeochemical Cycle of Arsenic. *Glob. Biogeochem. Cycles* **2022**, *36*, e2022GB007515. https://doi.org/10.1029/2022GB007515.
Duan, L.; Li, X.; Jiang, Y.; Lei, M.; Dong, Z. Arsenic transformation behaviour during thermal decomposition of P. vittata, an arsenic hyperaccumulator. *J. Anal. Appl. Pyrolysis* **2017**, *124*, 584–591.
Fleming, C.; McMullen, J.; Thomas, K.; Wells, J. Recent advances in the development of an alternative to the cyanidation process: Thiosulfate leaching and resin in pulp. *Min. Met. Explor.* **2001**, *20*, 1–9.
Grosse, A.; Dicinoski, G.; Shaw, M.; Haddad, P. Leaching and recovery of gold using ammoniacal thiosulfate leach liquors. *Hydrometallurgy* **2003**, *69*, 1–21.
Zhang, X.; Senanayake, G. A review of ammoniacal thiosulfate leaching of gold: An update useful for further research in non-cyanide gold lixiviants. *Miner. Process. Extr. Metall. Rev.* **2016**, *37*, 385–411.
Ter-Arakelyan, K. On technological expediency of sodium thiosulfate usage for gold extraction from raw material. *Izv. V. U. Z. Tsvetn. Metall.* **1984**, *12*, 72–76.
Alguacil, F. *The Chemistry of Gold Extraction*, 2nd ed.; John O Marsden and CIain House SME: Littleton, CO, USA, 2006.
Salinas-Rodríguez, E.; Hernández-Ávila, J.; Cerecedo-Sáenz, E.; Arenas-Flores, A.; Veloz-Rodríguez, M.; Toro, N.; Gutiérrez-Amador, M.; Acevedo-Sandoval, O.A. Leaching of Copper Contained in Waste Printed Circuit Boards, Using the Thiosulfate—Oxygen System: A Kinetic Approach. *Materials* **2022**, *15*, 2354.
Aylmore, M.; Muir, D. Thiosulfate leaching of gold-A review. *Miner. Eng.* **2001**, *14*, 135–174.
Robert, T.; Bartel, M.; Offergeld, G. Characterization of oxygen species adsorbed on copper and nickel oxides by X-ray photoelectron spectroscopy. *Surf. Sci.* **1972**, *33*, 123–130.
Nakai, I.; Sugitani, Y.; Nagashima, K.; Niwa, Y. X-ray photoelectron spectroscopic study of copper minerals. *J. Inorg. Nucl. Chem.* **1978**, *40*, 789–791.
Mielczarski, J.; Minni, E. The adsorption of diethyldithiophosphate on cuprous sulphide. *Surf. Interface Anal.* **1984**, *6*, 221.
Wagner, C.; Riggs, W.; Davis, L.; Moulder, J.; Muilenberg, G. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation, Physical Electronics Division: Eden Prairie, MI, USA, 1979.
Hitchcook, A.; Brion, C. K-shell excitation spectra of CO, N_2 and O_2. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 1–21.

Nefedov, V.; Gati, D.; Dzhurinskii, B.; Sergushin, N.; Salyn, Y. A qualitative and quantitative study of the oxides of aluminum and silicon using AES and XPS. *Russ. J. Inorg. Chem.* **1975**, *35*, 1279.

Can, F.; Demirci, O.; Dumoulin, F.; Erhan, E.; Arslan, L.; Ergenekon, P. Iron porphyrin modified PVDF membrane as a biomimetic material and its effectiveness on nitric oxide binding. *Appl. Surf. Sci.* **2017**, *420*, 625–630.

Rajumon, M.; Prabhakaran, K.; Rao, C. Adsorption of oxygen on (100), (110) and (111) surfaces of Ag, Cu and Ni: An electron spectroscopic study. *Surf. Sci.* **1990**, *233*, 233–242.

Park, I.; Tabelin, C.; Seno, K.; Jeon, S.; Inano, H.; Ito, M.; Hiroyoshi, N. Carrier-microencapsulation of arsenopyrite using Al-catecholate complex: nature of oxidation products, effects on anodic and cathodic reactions, and coating stability under simulated weathering condition. *Heliyon* **2020**, *6*, 03189.

Chen, M.; Zhang, Z.; Hu, X.; Tian, J.; Wang, J.; Wan, R.; Zhou, X.; Shen, P.; Liu, D. Oxidation mechanism of the arsenopyrite surface by oxygen with and without water: Experimental and theoretical analysis. *Appl. Surf. Sci.* **2022**, *573*, 151574.

Zhu, T.; Lu, X.; Liu, H.; Li, J.; Zhu, L.; Lu, J.; Wang, R. Quantitative X-ray photoelectron spectroscopy-based depth profiling of bioleached arsenopyrite surface by Acidithiobacillus ferrooxidans. *Geochim. Et Cosmochim. Acta* **2014**, *127*, 120–139.

Feng, X.; Liu, Q.; Wang, S.; Cen, L.; Li, H. Arsenopyrite weathering in acid rain: Arsenic transfer and environmental implications. *J. Hazard. Mater.* **2021**, *420*, 126612.

Hollinger, G.; Kabban, I.S.; Gendry, M. Oxides on GaAs and InAs surfaces: An x-ray-photoelectron-spectroscopy study of reference compounds and thin oxide layers. *Phys. Rev.* **1994**, *49*, 11159.

Bilal, M.; Ito, M.; Akashino, R.; Bu, X.; Hassan, F.; Park, I.; Jeon, S.; Aikawa, K.; Hiroyoshi, N. Heterogenous carrier flotation technique for recovering finely ground chalcopyrite particles using coarse pyrite particles as a carrier. *Miner. Eng.* **2022**, *180*, 107518.

Wang, X.; Wang, J.; Zhang, X.; Tian, Q.; Liu, M.; Cai, N.; Xue, Y.; Chen, W.; Li, W.; Yu, F. Nitrogen-Doped Cu_2S/MoS_2 Heterojunction Nanorod Arrays on Copper Foam for Efficient Hydrogen Evolution Reaction. *ChemCatChem* **2018**, *11*, 1143–1373.

Wu, C.; Yin, M.; O'Brien, S.; Koberstein, J. Quantitative Analysis of Copper Oxide Nanoparticle Composition and Structure by X-ray Photoelectron Spectroscopy. *Chem. Mater.* **2006**, *18*, 6054–6058.

Biesinger, M.; Lau, L.; Gerson, A.; Smart, R. Resolving surface chemical states in XPS analysis of first row transition metals, oxides, and hydroxides: Sc, Ti, V, Cu and Zn. *Appl. Surf. Sci.* **2010**, *257*, 887–898.

Khan, S. UV-ATR Spectroscopy Study of the Speciation in Aqueous Polysulfide Electrolyte Solutions. *Int. J. Electrochem. Sci.* **2012**, *7*, 561–568.

Pappoe, M.; Bottaro, C. Systematic optimization of pyromellitic acid background electrolyte for capillary electrophoresis with indirect UV-Vis detection and online pre-concentration analysis of thiosalt anions in treated mine tailing. *Anal. Methods* **2014**, *6*, 9305–9312.

Liu, X.; Li, Q.; Zhang, Y.; Jiang, T.; Yang, Y.; Xu, B.; He, Y. Electrochemical behavior of the dissolution and passivation of arsenopyrite in 9K culture medium. *Appl. Surf. Sci.* **2020**, *508*, 145269.

de Jong, A.B.H.; Van Ijzendoorn, L.; Soudant, V.; de Beer, V. Preparation, Structure and Surface Chemical Properties of Hydrotreating Model Catalysts: A Surface Science Approach. *J. Phys. Chem.* **1993**, *97*, 6477.

Yu, X.-R.; Liu, F.; Wang, Z.-Y.; Chen, Y. Auger parameters for sulfur-containing compounds using a mixed aluminum-silver excitation source. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *50*, 159–166.

Contini, G.; Laajalehto, K.; Suoninen, E.; Marabini, A. 5-Methyl-2-mercaptobenzoxazole adsorbed onto chalcocite (Cu_2S): An XPS and X-AES study. *J. Colloid Interface Sci.* **1995**, *171*, 234–239.

Feng, D.; Van Deventer, J. The effect of sulfur species on thiosulfate leaching of gold. *Miner. Eng.* **2007**, *20*, 273–281.

CHAPTER 5: APPLICABILITY OF CUPRIC AMMINE PRETREATMENT ON GOLD EXTRACTION OF MINE SAMPLES FROM ZIMBABWE.

5.1 Introduction

Refractory gold ores are gradually becoming the main primary gold deposit for gold production around the world (Bermeo, Penaloza, & Chavez, 2019) (Huang & Yang, 2021). However, extraction of gold from theses ores is very complex due to gold being encapsulated in sulfide matrix, co-existence of sulfide minerals containing arsenic, heavy metals and organic carbon which have negative impacts on gold extraction as discussed in the previous chapters. To extract gold from primary resources, pretreatment is conducted to improve the gold extraction from the refractory gold ores (Amankwah & Ofori-Sarpong, 2020) (Celep O. , Yazici, Altinkaya, & Deveci, 2019b) (Chen, Xie, Wang, Fu, & Wang, 2022). In the case of arsenic-bearing sulfide minerals, this study has proposed a novel method of using cupric amine pretreatment before thiosulfate leaching.

In chapter 4, model experiments have demonstrated the effectiveness of the pretreatment in extracting gold in the presence of high arsenic bearing sulfide (HAsBs). To implement cupric ammine technique at industrial-scale, the pretreatment method must be assessed using "naturally occurring", run-off-mine samples. This chapter will focus on testing the effectiveness of the cupric ammine pretreatment to improve gold extraction with ammonium thiosulfate leaching and evaluate the stability of the leach residues to minimize arsenic pollution when the tailings are disposed.

5.2. Materials and Methods

5.2.1. Materials

In the leaching experiments conducted, the run of mine (ROM) samples obtained from a mine in Kadoma, Zimbabwe were used. The chemical composition and mineralogical composition of the samples are shown in Table 5.1 and Figure 5.1 respectively. Leaching experiments were carried out using sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$), ammonium chloride ((NH_4Cl), ammonia water (NH4(OH), 31%), and cupric chloride ($CuCl_2$), which were all obtained from Wako Pure Chemical Industries, Ltd., Japan.

Table. 5 1. Chemical composition of sulfide zone ore sample.

Elements	Al	Si	S	Fe	Cu	Zn	As	Sb	Au	Pb
wt.%	15.67	33.70	12.43	5.43	0.02	0.03	0.61	32.10	0.001	0.01

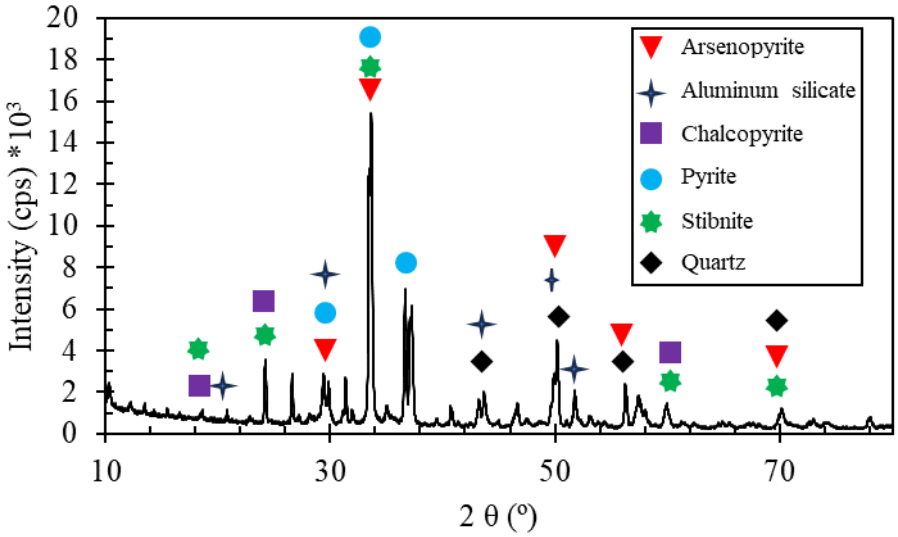


Figure 5.1. XRD of the runoff mine ore samples from Kadoma, Zimbabwe.

5.2.2. Leaching experiments procedures.

Pre-oxidation experiments were conducted by combining 10 g of gold powder with a 100 mL solution comprising 0.5 M NH_3, 0.5 M NH_4Cl, and 10 mM $CuCl_2$. The mixture was subjected to pre-oxidation process in a 500 mL glass reactor, with 100 ml of cupric ammine solution at 30 ˚C using a Thermo Fisher PID controlled heating mantle, maintaining an agitation speed of 400 rpm for 24 hours. After this period, agitation ceased for decantation, and 50 mL of the supernatant was extracted for subsequent analysis.

Gold leaching followed, with the introduction of 50 mL of 2 M $Na_2S_2O_3$ solution containing 0.5 M NH_3, 0.5 M NH_4Cl, and 10 mM $CuCl_2$ to the flask, followed by shaking for an additional 24 hours. Post-gold leaching, both solutions and solid residues were obtained through filtration and subjected to analysis using ICP-AES and SEM–EDX, respectively. Thiosulfate consumption was determined through ion chromatography using a Dionex Integration RFIC System (Thermo Fisher K.K, Tokyo, Japan).

5.3. Results and Discussion

5.3.1. Effects of pretreatment of ROM samples using cupric ammine solutions.

In Chapter 4, pretreatment of model sample (mixture of gold powder and FeAsS) revealed oxidation of the arsenopyrite as indicated by the sulfur dissolution: 25 % sulfur was dissolved, was sufficient to enhance gold extraction. In this chapter, the ROM samples were oxidized using the same parameters applied on the model samples. After 24hr of pre-oxidation of the ROM, about 36 % of sulfur was oxidized as shown in Figure

5.3.1. About 0.4 % As, 0% Fe were recorded in solution which indicates that the Fe and As species would have precipitated on the surface of the ROM ore sample. These results were consistent with the results obtained using the model samples. Due to the high antimony content in the samples used (32 %), about 4% was extracted into the solution. There was no gold detected in solution during the pre-oxidation stage, as compared to the model sample where about 1 % was extracted, this id due to the low gold concentration in the samples used.

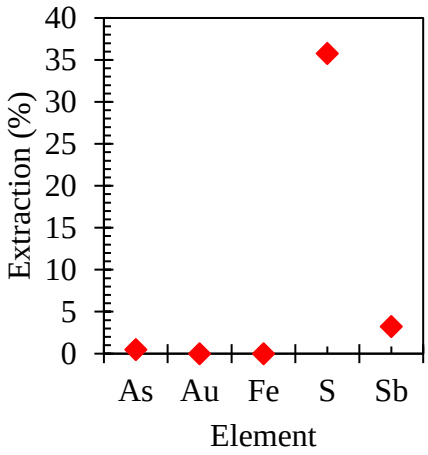


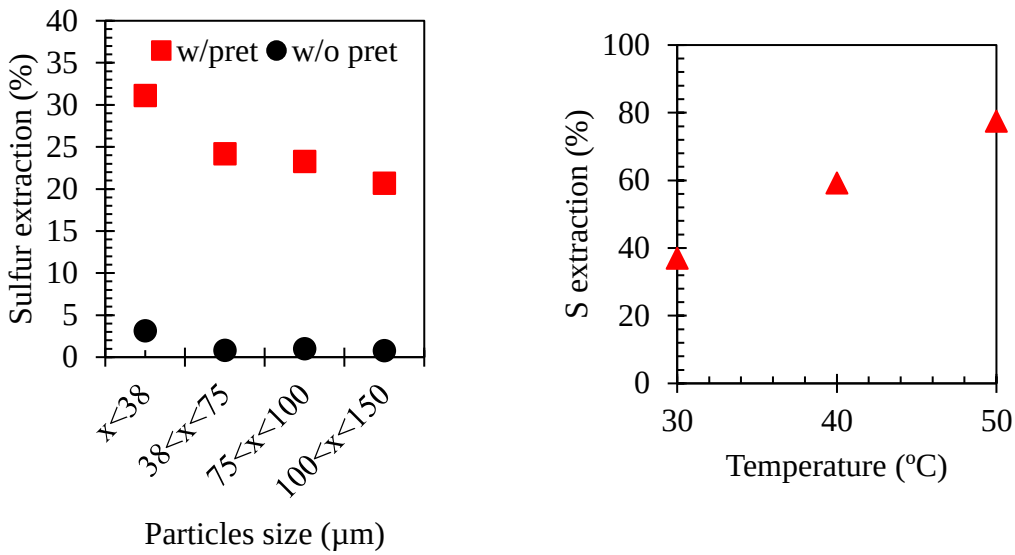
Figure 5.3.1: Effect of pretreatment on the ROM sample

To further evaluate the effectiveness of the pre-oxidation step of the ROM sample sulfur dissolution was assessed a function of particle size and temperature in Figure 5.3.2 (a) and (b). In most chemical reactions, particle size is an important parameter because as the particle size decreases, the larger the surface area (Barriga, 2022). In the pretreatment of the ROM, reduction of the particle size not only improves the efficiency of sulfides oxidation but physically liberates gold particles from the gangue minerals (Celep O. , Yazici, Kuzu, & Deveci, 2019). In Figure 5.3.2 (a) the S extraction was maximum at particles below 38 µm, yielding an extraction of 33 % sulfur dissolution. Consequently, the decline in the S concentration in the larger size fractions can be attributed to the reduction in the surface area and sulfur content.

In most industrial operations, the major cost for the operation is due to the energy consumption in the grinding operation, hence as an optimal grind to implement for the treatment of the ROM ore sample, if the 80 % of the product size after grinding is less than the 75 µm, maximum oxidation of the sulfides can be attained using cupric ammine pretreatment.

The other parameter that was used to assess the effectiveness of the pretreatment process of the ROM was temperature. As shown, in Figure 5.3.2(b), high

temperature favors the oxidation of the sulfide minerals contained in the ROM sample. A maximum of 77 % of the sulfur was oxidized at a pretreatment temperature of 50 ºC. There are reports that have confirmed that, increasing the temperature in cupric ammonia systems increasing the leaching efficiency to a certain extent, about 55 ºC (Rath, Hiroyoshi, Tsunekawa, & Hirajima, 2003). Beyond this point the ammonia in the system will start to evaporate, in this study we did not show the extend of sulfur dissolution of the sulfide minerals beyond 50 ºC. Based on the results in Figure 5.3.2(b), pretreatment temperature of 50 ºC was adopted as the best temperature to effectively oxidize the sulfide mineral in the ROM sample.



(a) S dissolution as a function of particle size (µm)

(b) S dissolution as a function of temperature

Figure 5.3.2: The effects of grinding and temperature on the oxidation of ROM samples

5.3.2. Effects of pretreatment on the thiosulfate consumption.

In the preceding section (5.3.1), it was observed that the oxidation of sulfide minerals was promoted by a combination of small particle size and high temperature, resulting in a 77% sulfur extraction when the ROM sample underwent cupric ammine pretreatment. This section assesses the impact of the pretreatment on thiosulfate consumption, determined by quantifying the remaining thiosulfate ions in solution using an ion chromatography machine, the Dionex Integration RFIC System (Thermo Fisher K.K, Tokyo, Japan). Figure 5.3.3 illustrates the influence of pretreatment on thiosulfate

consumption.

Thiosulfate consumption during the leaching of gold ore without pretreatment was observed to be 65%, whereas after pretreatment, it reduced to 25%, as depicted in Figure 5.3.3. This indicates the effectiveness of the pretreatment method in minimizing thiosulfate consumption by oxidizing the surface of sulfide minerals. In the model experiments outlined, in chapter 4, the enhanced stability of thiosulfate post-pretreatment is anticipated to improve gold extraction. This improvement comes from the increased availability of free thiosulfate ions in the solution for gold extraction. This implies that effective liberation of gold from gangue minerals, particularly sulfide minerals, can enhance gold extraction.

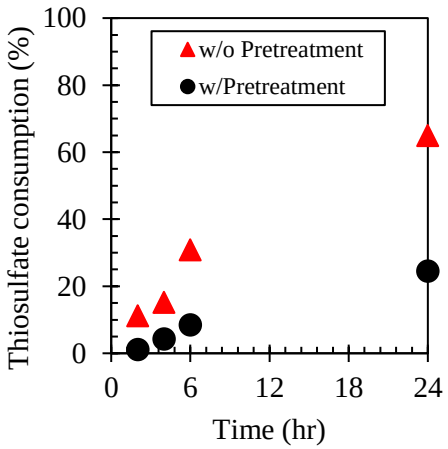


Figure 5.3.3: The effects of pretreatment on thiosulfate consumption

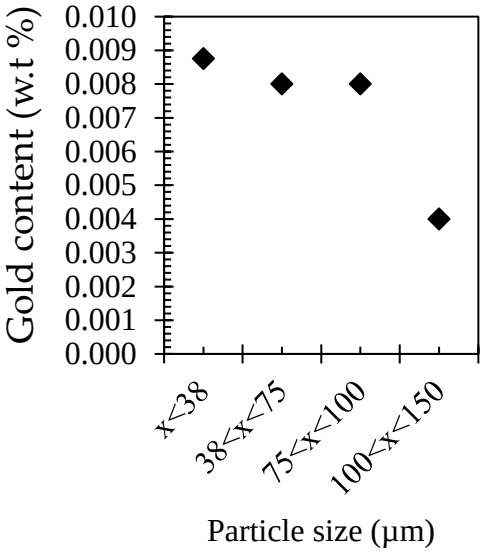
5.3.3. Effects of pretreatment on gold extraction.

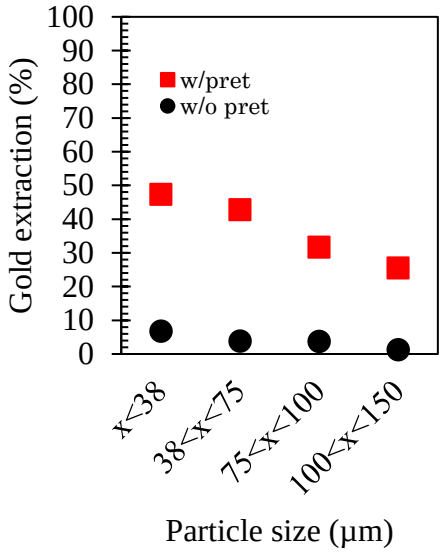
In the previous section (*5.3.4*), cupric ammine pretreatment was effective in the reduction in the thiosulfate consumption from 66% to about 25 %, indicating the availability of more thiosulfate ions in solution for gold extraction. In this section, the effect of pretreatment on gold extraction will be discussed. Based on the model experiments conducted in Chapter 4, when the model samples (mixture of gold powder and arsenopyrite) underwent pretreatment and subsequently ammonium thiosulfate leaching at 30 ºC, gold extraction improved from 10 % without pretreatment to about 83 %. Figure 5.3.4 shows the effect of the pretreatment and subsequent ammonium thiosulfate leaching at 30 ºC had on the gold extraction.

When the ROM samples were leached in ammonium thiosulfate without pretreatment, gold extraction was very low (about 3 %). Pretreatment improved the gold

extraction, but gold extraction was still limited to about 9%, and this value is far from expectation (in Figures 5.3.4(a)). There are numerous reasons that can cause this low gold extraction even after (1) gold might still be encapsulated in the sulfide matrix or silica, due to the presence of high silicate minerals as shown in the XRD analysis((Figure 5.1)) : unlike in the model experiments where free gold was introduced into the system, the gold in the sample is naturally occurring and would be more complex to access: (Xu, et al., 2017) ,(2) the passivation of the gold grains (Yang, et al., 2015).

To evaluate the assumption that gold might not be fully liberated in the ore matrix, causing low gold extraction, leaching of ground ROM sample was conducted at different size fractions ($x > 38\ \mu m$, $38 < x < 75\ \mu m$; $75\ \mu m < x < 100\ \mu m$, and $100\ \mu m < x < 150\ \mu m$, where x represents particle size). The ROM samples were pre-oxidized in an ammonia solution containing $CuCl_2$ for and subsequently leached in ammonium thiosulfate solution at 30ºC for 24 hours respectively. Gold is more contained in smaller size fractions, with a concentration mainly below 38 µm with about 0.01 %wt. gold content. This suggests that grinding effectively liberates encapsulated gold from the sulfide matrix. Consequently, gold extraction is observed to significantly increase with a decrease in particle size, as smaller gold particles are liberated and can interact more effectively with the leaching agent. When pretreatment was conducted at different size fractions, gold extraction improved from 3 % to 45% achieved when particles less than 38m were leached. This might be due to the increase in the concentration of the gold making the lixiviant to effectively interact with the gold. This confirms that fine grinding is required to liberate for two reasons (1) maximum oxidation of the sulfide minerals and (2) liberation of the gold particles.





(a) Gold content changes with particle size

(b) Gold extraction with particles size

Figure 5.3.4: Effect of grinding on gold extraction

Although the gold extraction improved when grinding was applied, there are some factors that can contribute to low gold extraction such as slow leaching kinetics (Mohammadi & Pourabdoli, 2019). Hence, the ground ore with a P_{80} of 18 µm was leached at different temperatures to check the effectiveness of the pretreatment and ammonium thiosulfate leaching respectively. From Figure 5.3.4, there was an improvement of gold extraction from 4.5 % to about 49 % gold extraction achieved after pretreatment at 50ºC and ammonium thiosulfate at 30 ºC. For the ROM samples without pretreatment gold extraction decreased as temperature increased, this was due to the instability of ammonium thiosulfate. As temperature increases, the leaching solution becomes more oxidative and accelerates thiosulfate decomposition.

The enhancement of gold with cupric ammine pretreatment is very significant but the gold extraction is still less that that expected at industrial level, that is 80 % gold extraction. The reason for this might be attributed to passivation of the gold particles, unlike in model experiments were gold in the form of gold powder was liberated with relatively larger particles size (visible gold); the gold in the naturally occurring ores will be submicroscopic and passivation becomes more pronounced at those smaller size fractions.

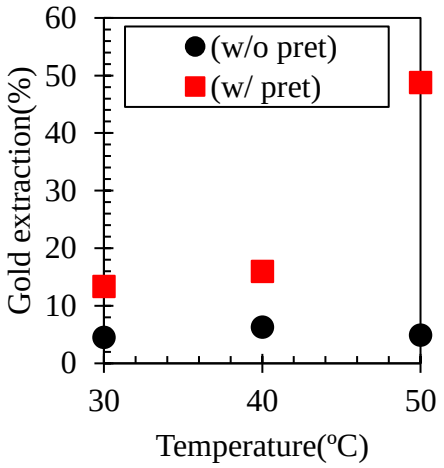


Figure 5.3.5: Effect of temperature on gold extraction

Based on the results obtained when the ROM sample was subjected to leaching at different grind size and temperature respectively. For effective gold extraction using the cupric ammine pretreatment followed by ammonium thiosulfate leaching, the best conditions under which gold extraction can be enhance are pretreatment temperature of 50 ºC, ammonium thiosulfate leaching at 30 ºC, targeting a grind size of P_{80} passing 75 µm. It was also proven that cupric ammine pretreatment effectively oxidizes the sulfide minerals. The ROM sample used in this study has significant amounts of As and Sb which are highly toxic elements. When the leach residues are disposed into the tailings dam, these metals must be kept stable to protect the environment. Therefore, the next section (*section 5.3.4*) focuses on evaluating the effects of pretreatment on the stability of the leach residues.

5.3.4. Effects of pretreatment on the stability of leach residues

After any mineral extraction process, the unwanted material (tailings) is always disposed in a certain place on the mining site but if the waste material is not stable, there will be formation of acid mine drainage (Park, et al., 2021), contamination of ground water and nearby water bodies by the heavy metals contained in the waste material.

In this study, the mine residue samples (residues from the ammonium thiosulfate leaching without pretreatment and residues from the pretreated ROM samples) were leached in deionized water. 1 g of the pretreated residue and untreated residue, respectively, mixed with 10 ml of deionized water, shaken in a thermostat water bath shaker at 25 °C for 24 h with a constant shaking amplitude and frequency of 40 mm and

120 min^{-1}. During the water leaching process, samples were collected at certain time intervals, filtered and the filtrate was analyzed for dissolved metals using ICP-AES. The results of analysis of the filtrates are shown in Figure 5.3.6 below. About 0.2 mg/L arsenic and 0.5 mg/L antimony were dissolved from the pretreated leach residue after 24 hr whilst for the untreated leach residues 12.5 mg/L and 15.3 mg/L were recorded. This indicates that the pretreated leach residues are very stable because they are covered by a layer of oxidation products. According to World Health Organization, the concentration of arsenic in drinkable water As: 0.01 mg/L but industrial waste effluents 0.2 mg/L is still acceptable for industrial effluents (Soda & Nguyen, 2023). In the case of Sb the maximum the allowed in the drinkable water is 0.01 mg/l and for soils should be in the range of 0.3mg/L to 8.6 mg/L. Based on the results obtained for the pretreated leach samples, the concentrations of As, and Sb are within the acceptable levels. However, there is need to evaluate the stability of the residues over a prolonged period like month to assess the longevity of the oxide layer formed after cupric ammine pretreatment.

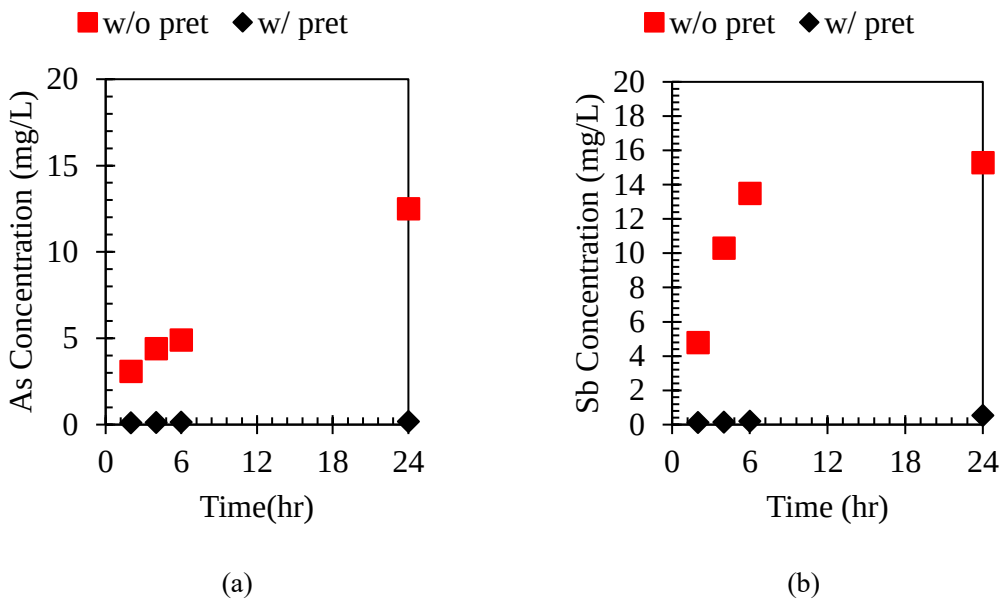


Figure 5.3.6: The effect of pretreatment on the stability of leach residues (a) As, (b) Sb concentration.

5.4. Summary

This chapter focused on testing the effectiveness of the proposed pretreatment process to real mine ore samples. The following is a summary the finding obtained in this study:

- ✓ Pretreatment at 50 ºC and ammonium thiosulfate leaching at 30 ºC reduced the thiosulfate consumption in the subsequent ammonium thiosulfate leaching from 65 % to 25 % before and after pretreatment respectively. This made the gold extraction improve from 3% to 45%.
- ✓ Pretreatment is effective in the production of more stable leach residues. The ICP-AES results of the pretreated residues show that about 0.2 mg/L of As was only dissolved after agitation in deionized water for 24 hr. This means that the pretreatment not only enhances the gold extraction but also stabilizes the leach residues.

References

Amankwah, R., & Ofori-Sarpong, G. (2020). Microwave roasting of flash flotation concentrate containing pyrite, arsenopyrite and carbonaceous matter. *Minerals Engineering , Vol 151*, 106312.

Bermeo, P., Penaloza, I., & Chavez, J. (2019). Treatment for gold ores with high content of carbonaceous matter. *SciELO Analytics*.

Celep, O., & Yazici, E. Y. (2013). Ultra fine grinding of silver plant tailings of refractory ore using vertical stirred media mill. *Trans. Nonferrous Met. Soc. China 23*, 3412-3420.

Celep, O., Altinkaya, P. .., Yazici, E. Y., & Deveci, H. (2018). Thiosulphate leaching of silver from an arsenical refractory ore. *Minerals Engineering*, 285-295.

Chen, J., Xie, F., Wang, W., Fu, Y., & Wang, J. (2022). Leaching of a carbonaceous gold concentrate in copper-tartrate-thiosulfate solutions. *Minerals Engineering, 183*, 107605.

Espatia, S., & Lapidus, G. (2015). Pretreatment of a refractory arsenopyritic gold ore using hydroxyl ion. *Hydrometallurgy, 153*, 106-113.

Mohammadi, E., & Pourabdoli, M. (2019). Effect of Mechanical Activation on the Kinetics of Ammonioum Thiosulfate Leaching of a Refractory Oxide Gold Ore. *Iranian Journal of Materials Dcience and Engineering, Vol. 16, No.2*, 2-11.

Park, I., Ryota, T., Yuto, T., Tabelin, C. B., Phengsaart, T., Jeon, S. .., . . . Hiroyoshi, N. (2021). A novel arsenic immobilization strategy via a two-step process: Arsenic concentration from dilute solution using schwertmannite and immobilization in Ca–Fe–AsO4 compounds. *Journal of Environmental Management*.

Rath, R., Hiroyoshi, N., Tsunekawa, M., & Hirajima, T. (2003). Ammoniacal thiosulphate leaching of gold ore. *The European Journal of Mineral Processing and Environmental Protection,Vol.3, No.3, 1303-0868*, pp. 344-352.

Soda, S., & Nguyen, T. (2023). Classification of Mine Drainages in Japan Based on Water Quality:

Consideration for Constructed Wetland Treatments. *MDPI:Water*, 1258.

Xu, B., Wenhao, K., Qian, L., Yongbin, Y., Tao, J., & Liu, X. (2017). A Review of Thiosulfate Leaching of Gold: Focus on Thiosulfate Consumption and Gold Recovery from. *MDPI: Metals, 7*, 222.

Yang, Y., Zhang, X., Bin, X., Qian, L., Tao, J. .., & Ya-Xuan, W. (2015). Effect of arsenopyrite on thiosulfate leaching of gold. *Trans. Nonferrous Met. Soc. China, Vol 25*, 3454-3460.

CHAPTER 6: GENERAL CONCLUSION

Refractory gold ores are going to be the main primary gold ore deposit and extraction of gold from arsenic-bearing gold ores a novel and environmentally friendly way was demonstrated in this study. Here are the summaries of the study:

Chapter 1 described the statement of the problem, background of fine particle problems in flotation and objectives of this study.

Chapter 2 reviewed techniques available in extracting gold from refractory ores which contain arsenic including ultrafine grinding, bio-oxidation, chemical oxidation, use of ultrasound enhanced chemical oxidation and ozone pretreatment are detailed and discussed.

Chapter 3 investigated the mechanism for suppression of thiosulfate gold leaching in the presence of a high arsenic bearing sulfide model sample. Previous studies have established that the most dominant mechanism is passivation of the gold grains by the oxidation products of arsenopyrite and thiosulfate decomposition. This study confirmed the existence of oxidation products on gold grains in the presence of sulfide minerals where gold extraction was above 99.99% and in the presence of a sulfide mineral where gold extraction was about 10 %. Based on these results it was concluded that passivation is not necessarily the dominant mechanism of suppression of gold extraction but thiosulfate decomposition by sulfide minerals was the most dominant mechanism for gold suppression as confirmed by Uv-Vis results. Therefore, for improvement of gold extraction, minimization of thiosulfate decomposition was proposed as the best solution to improve gold extraction.

In Chapter 4, a novel pretreatment technique was prosed in which high arsenic bearing sulfide mineral and gold powder mixture was pretreated in an ammonia solution containing cupric (Cu^{2+}) ion before ammonium thiosulfate leaching was proposed. The results from the pretreatment in 100mM Cu^{2+} followed by ammonium thiosulfate leaching improved gold extraction from 10% to 79 %. This was due to the stability of thiosulfate ions because of the oxidation of the surface of sulfide minerals. XPS analysis of the pretreated sulfide minerals showed that a mixture iron oxyhydroxide (FeOOH) precipitates and ferric arsenate ($FeAsO_4$) precipitated covered the surface of the sulfide mineral. Increasing the pretreatment and leaching temperature increased the gold extraction to over 80 % at 30 ºC but beyond that, the gold extraction decreased to the instability of the thiosulfate. Therefor the optimum leaching and pretreatment temperature was taken to be 30 ºC.

In Chapter 5, the effectiveness of pretreatment using ammonia solution containing Cu(II) was assessed on refractory runoff mine gold samples ions was conducted. Direct leaching of the mine samples using ammonium thiosulfate at 30 ºC resulted in gold extraction of less than 5 % percent and improved to about 48 % after pretreatment at 50 ºC. The gold extraction improved but it is still below the expected at commercial scale; 80 %. In addition, agitation of the leach residues with deionized water for 24hr showed that about 0.2 mg/L of As and 0.01 mg/L Fe were only dissolved indicating that the cupric ammine pretreatment results in more stable leach residues.

Finally, chapter 6 gives the general conclusions of this study.

ACKNOWLEDGEMENT

Foremost, I would like to acknowledge my supervisor, Prof. Naoki Hiroyoshi, for his kindness and all the support during my doctoral program. Above all I am very grateful for being given an opportunity to tap into the vast wisdom and knowledge he has acquired over the years in the field of Extractive Metallurgy, it was truly an honor to be his student. Outside of the academic life, he provided the moral support and the motivation I needed to manage my academic life in Japan.

I would like to express my gratitude to Prof. Mayumi Ito, for the support, advise, constructive criticism during my evaluation and moral support during my study. I greatly appreciated that.

My sincere thanks are extended to Assoc. Prof. Ilhwan Park, for his kind suggestion on the paper writing, advise on conducting experiments, providing moral support in daily life during my study. I was always encouraged by your positive feedback and encouragement even when I encountered rejections of my manuscripts. Thank you very much for your time and effort.

I also extend my gratitude to Assoc Prof Sanghee Jeon for your support in writing the paper, encouragement to write more papers. Thank you very much for your advice, time, and support.

I would also like to thank my lab mates from Mineral Processing and Resources Recycling, Chemical Resources for the support, feedback, and advice during my study. It was an hour getting to know you guys and sharing a part of my life with you.

Finally, I am forever grateful to my wife Rosinah and my two daughters for their endurance, love, and support. I could not have made it this far if it was not for your love.