Kinetics and mechanisms of arsenic release from amorphous and crystalline arsenic trisulfide

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Abstract

Preventing arsenic release from mine waste materials, i.e., source control, is a preferable option for controlling arsenic discharge to the environment. Designing effective source control strategies requires comprehensive knowledge on the leaching behavior of arsenic from its bearing minerals. To determine the kinetics and mechanisms of arsenic release, we carried out reactor leaching experiments using arsenic trisulfide (As₂S₃) as a model arsenic sulfide mineral. The experimental results show that the arsenic release increased with pH, the dissolved oxygen concentration, and temperature. The speciation analysis indicates that arsenic was present in solution in the form of arsenite (III) and arsenate (V) and that thiosulfate and sulfate were the main soluble sulfur species. A two-step process that involves a series of primary and secondary reactions was proposed to explain the release of different arsenic and sulfur species. The release rates of arsenic and sulfur from crystalline orpiment were always slower than those from amorphous As₂S₃.

Kinetic equations were derived from the leaching data to describe the release rate as a function of the leaching parameters for both amorphous As_2S_3 and crystalline orpiment. The magnitudes of the reaction orders and the activation energy indicate that the surface chemical reaction is limiting the rate of arsenic release from amorphous As_2S_3 . In contrast, both kinetic modelling and the solid surface characterization support that a mixed-control mechanism determines the arsenic release from crystalline orpiment. Namely, the process is controlled by the surface chemical reaction and the diffusion of dissolved oxygen through a product layer on the solid surfaces. The solid surface characterization shows that this product layer is most likely to be an arsenic-deficient phase enriched in elemental sulfur.

Lay Summary

The mining industry is moving towards processing low grade ores, which would result in production of more wastes. Arsenic release from mine waste materials causes serious environmental concerns due to the toxicity and carcinogenic nature of the element. The general objective of this research is to gain a fundamental understanding of the key factors that control arsenic release from arsenic trisulfide (As₂S₃), one of the main arsenic-bearing minerals. The main finding of this research is that arsenic was released to significant extents from As₂S₃ under conditions that can be encountered in waste rock piles. The conditions refer to near neutral to alkaline environment at pH 6 ~ 10, dissolved oxygen concentration up to 8.3 ppm, and temperature from 23 °C to 50 °C. These results provide key information for the future research on the prevention and management of waste rock drainage containing arsenic.

Preface

The original idea of this project was proposed by Dr. Wenying Liu. The objectives were discussed and identified by the author, Seyed Mohamadjavad Mirazimi, with the help of Dr. Wenying Liu. The author, Seyed Mohamadjavad Mirazimi, was responsible for designing and executing the lab experiments, preparing and analyzing the results, and writing the manuscript. Dr. Liu extensively helped with all aspects of the research work.

The journal papers listed below are under preparation from the research work presented in the dissertation. The first article was prepared based on the experimental data in Chapter 5. The majority of the data presented in Chapter 6 was included in the preparation of the second article. The third article used the experimental data in Chapter 7. The fourth article is under preparation based on the experimental data presented in Chapter 8. The fifth article is under preparation based on the experimental data presented in the dissertation and previous research studies on arsenic release from arsenic bearing sulfides.

The author Seyed Mohamadjavad Mirazimi wrote all the original manuscripts. Dr. Wenying Liu contributed to the major suggestions of revisions. All other co-authors provided less contribution to the interpretation and revisions.

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- 5- M. Mirazimi, M. Mohammadi and W. Liu, "Arsenic release from arsenic bearing sulfides: A review". Manuscript in preparation.

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List of Symbols

Symbol	Meaning	Common Unit
K _a	Equilibrium constant	
E_a	Activation energy	kJ/mol
k	Apparent rate constant	1/day
R	Universal gas constant	J/mole/K
t	Time	day
Τ	Temperature	Κ
Tref	Reference temperature	Κ
x	Total arsenic released	_
τ	Timescale	day
$\boldsymbol{\varphi}$	Topological exponent	_

List of Abbreviations

AES	Auger electron spectrometry
AMD	Acid mine drainage
DO	Dissolved oxygen
EDX	Energy dispersive X-ray
GF-AAS	Graphite-furnace atomic absorption spectrometry
GC	Gas chromatography
HPLC	High pressure liquid chromatography
IC	Ion chromatography
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
ORP	Oxidation/reduction potential
RSD	Relative standard deviation
SCM	Shrinking core model
SE	Secondary electron
SEM	Scanning Electron Microscopy
SHE	Standard hydrogen electron
XPS	X-ray photo-emission spectrometry
XRD	X-ray diffraction

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My parents

My sister

and

My lovely wife, Maryam

Chapter 1: Introduction

1.1 Research context and significance

Release of potentially toxic elements, such as heavy metals and metalloids, from wastes produced during mining activities is one of the major challenges for the mining industry. Arsenic is one of the main contaminants present in drainages generated by mine wastes, especially from gold and copper mine operations (Savage et al., 2000). Upon exposure to water and air, minerals and rocks weather, resulting in release of arsenic together with other potentially toxic elements from their bearing minerals (Flora, 2005). Mining and metal extraction processes can completely alter and accelerate the weathering process. The released arsenic accompanied by other potentially toxic elements is mobilized to surface waters and groundwater, posing a serious threat to the environment and human health.

Several methods have been used to treat arsenic-contaminated soils and water. Precipitation/coprecipitation is the most commonly used technique, which involves adding chemical reagents to remove arsenic from water as insoluble solid precipitates (Henke, 2009). Other methods, such as ion exchange, adsorption, and passive treatments have also been implemented to remove or reduce arsenic in receiving waters and soils. Even though they may be effective in certain circumstances, these methods have common drawbacks that limit their use. The major drawbacks are lack of longterm stability of reaction products, slow process, sludge generation, necessity of different pretreatments, and high capital and operating costs (Feenstra and Erkel, 2007; Nidheesh and Anantha Singh, 2017). Given the complexity and costs associated with the common methods aforementioned, a preferable option to manage waste rock drainages is to prevent or control contaminant release at the source, i.e., source control. Different source control strategies have been implemented, with various levels of success. A few examples are separating arsenic bearing minerals from the rest of the wastes (Wang and Ferron, 2003), limiting oxygen and water transport to sulfide minerals to minimize their oxidation (Johnson and Hallberg, 2005), and adding minerals to provide buffering capacity to reduce the dissolution rate of arsenic minerals (Banks et al., 1997).

To implement an effective source control measure, it is essential to understand the major factors that control the rate of arsenic release from its sources, the mechanisms by which arsenic is released, and the speciation of arsenic in aqueous solutions. This knowledge is central to predicting future arsenic concentration, mobility, and fate in mine drainages and receiving waters. This knowledge is also essential to designing effective source control measures that target the principal factors controlling arsenic release.

1.2 Research problem

Arsenopyrite and enargite, the two common arsenic bearing minerals, have been extensively studied with the objective of maximizing copper and gold extraction in hydrometallurgical processes. However, much less is known on the dissolution behavior of orpiment, despite being one of the major arsenic-containing minerals found on some mine sites. Furthermore, there is increased interest in removing arsenic from metallurgical waste streams as arsenic trisulfide, typically in amorphous form, to minimize arsenical waste volume. The long-term stability of this waste must be understood to prevent arsenic remobilization in the environment.

The overall objective of this research is to gain a fundamental understanding of arsenic and sulfur release from amorphous As_2S_3 and crystalline orpiment. We studied the kinetics that relates the arsenic release rate to the key environmental factors, the mechanisms by which arsenic and sulfur are released, and the speciation of arsenic and sulfur in response to the environmental factors.

1.3 Thesis outline

This thesis is divided into 9 chapters to show the current status of research and gaps, the research objectives and methods used, and the research findings obtained by the author.

Chapter 1 introduces the general context of this research and the significance of studying the arsenic release from amorphous As_2S_3 and crystalline orpiment.

Chapter 2 reviews the literature in kinetics and mechanisms of arsenic release from different arsenic sulfide minerals, different methods used to treat arsenic contaminated waters, and the necessity of implementing source control strategies to prevent arsenic release from its sources.

The general and specific research objectives were stated in Chapter 3. The research methods applied to achieve the objectives were described in detail in Chapter 4.

Chapter 5 reports the research findings on the effect of pH, dissolved oxygen concentration, and temperature on the release rates and speciation of arsenic and sulfur from amorphous As_2S_3 . The results obtained were used to propose the possible reaction pathways responsible for the release of arsenic and sulfur species from As_2S_3 .

In Chapter 6, a kinetic equation was derived using the experimental data reported in Chapter 5 to correlate the arsenic release to the three factors investigated. A reaction mechanism was proposed based on the reaction orders and the activation energy derived. Surface properties of the leaching solid residues were characterized by SEM-EDX and XRD to support the proposed mechanism.

Chapters 7 and 8 investigate the effect of the degree of crystallinity on the arsenic and sulfur release using crystalline orpiment as the mineral sample. For the purpose of comparison with the case of amorphous As_2S_3 , the research design and data interpretation were similar to those in Chapter 5 and 6. The effect of the three factors on the release rate and speciation of arsenic and sulfur was quantified, followed by derivation of a kinetic equation and interpretation of reaction mechanisms.

Chapter 9 summarizes the key findings of the present work and the recommendations for future work.

Chapter 2: Literature Review

2.1 Introduction

This chapter reviews the literature of arsenic release and its leaching kinetics from the most common arsenic bearing sulfides. Section 2.2 gives an overview of wastes produced from mining activities and their potential negative impacts on the environment and ecosystems. Then a brief introduction is given on the chemistry and the occurrence of arsenic and sulfur in the environment in Sections 2.3 and 2.4. Section 2.5 reviews the studies on arsenic release from its bearing sulfides and the effect of different parameters on arsenic release kinetics. The importance of studying the arsenic release from orpiment (As_2S_3) as the focus of this study is discussed in Section 2.6. Section 2.7 summarizes the different available options for dealing with the arsenic release problem and the significance of controlling arsenic release at the source.

2.2 Mining wastes

2.2.1 Volume of mine wastes produced

The mining industry plays a key role in the global economic and social development. The global quantity of non-fuel mineral extraction from the earth's crust has grown each year. While demands for metals are increasing, metallic ore grades are falling globally (Norgate and Jahanshahi, 2010). As a consequence, mining activities, from mining to mineral beneficiation to metal extraction, produce increasing amounts of solid, liquid and gaseous wastes.

Figure 2.1 shows the most common types of wastes produced at metal mines. Large volumes of wastes are produced after the small fractions of valuable metals are extracted (Bridge, 2004). There is no precise information regarding the global production of mine wastes. The quantities of metal produced in the yearly reports can provide estimated annual quantities of mine wastes produced globally. For example, in 2006 approximately 50 Mt of metals (As, Be, Co, Cr, Cu, Hg, Nb, Ni, Pb, Sb, Sn, Ta, V, W, Zn) were produced. Assuming that the average ore grade of these metals is 0.5%, a mass of 10,000 Mt of solid wastes was produced by mining, processing and extraction (Lottermoser, 2013).



Figure 2.1 Wastes production in various stages of mining activities (Lottermoser, 2013).

2.2.2 Waste rock drainage

Release of different contaminants into the surrounding environment and ecosystems is one of the major environmental impacts caused by mining activities. Waste rocks are usually stored above ground in large free-draining piles. When exposed to the air and water, they generate drainage that contains heavy metals and other potentially harmful substances, such as selenium, arsenic and mercury. They may be released and mobilized to receiving waters and soils (Figure 2.2), resulting in significant impacts on the aquatic systems and water quality (Al-Abed et al., 2007; McGregor et al., 1998; Schaider et al., 2007).



Figure 2.2 Conceptual process of mining waste rocks and sulfide minerals oxidation and release of toxic elements (Lottermoser, 2013).

Depending on the nature of the rocks, mined ores, minerals and the additives used during mineral processing and metallurgical extraction, effluents containing different elements and compounds can be generated on mine sites (Lottermoser, 2013). Acidic mine drainage (AMD) is the most

common effluent produced during mining activities, which is usually generated from the oxidation of sulfide minerals, such as pyrite. Acidic waters are not the only effluents produced from metal extraction. Neutral to alkaline mine waters are commonly reported that contain carbonate, bicarbonate, metals such as Cu, Cd, Fe, Hg, Mn, Mo, Ni, Pb, Tl, U, and Zn, and metalloids such as As, Sb and Se (Ashley et al., 2003; Carvalho et al., 2009; Cidu et al., 2007; Craw et al., 2004; Day et al., 1998; Desbarats and Dirom, 2007; Lindsay et al., 2009; Rollo and Jamieson, 2006; Wilson et al., 2004; Younger, 2000). These potentially harmful elements released from mine wastes can be mobilized to surface waters, groundwater, soil, and sediments, which may pose serious hazards to human health (Williams et al., 2006).

Arsenic (As) and its compounds are known as one of the most toxic pollutants, which can cause severe damages to the environment and human health (Lengke et al., 2009). There are two main sources of arsenic release into the environment: anthropogenic activities, especially mining activities, which will be the focus of this study; and natural sources such as volcano actions (Fendorf et al., 2019; Li et al., 2017; Stuckey et al., 2015). Arsenic release associated with the mining industry is mainly caused by the weathering of arsenic bearing minerals and waste rocks produced during mining activities.

Mine wastes and sediments may contain arsenic in different forms such as absorbed arsenic or associated with arsenic bearing minerals such as arsenopyrite (FeAsS), realgar (AsS) and orpiment (As₂S₃). Leaching of arsenic bearing minerals can release both adsorbed arsenic and arsenic bound within the mineral matrix (Floroiu et al., 2004), mobilizing it to nearby surface watersheds (Henke,

2009). Arsenic concentration found in fresh waters is typically between 10^{-7} to 10^{-5} M, but can be elevated to 10^{-4} M by arsenic release from various sources (Akoitai, 2000a).

2.3 Chemistry of arsenic and its occurrence

2.3.1 Arsenic chemistry

Arsenic is a chemical element with the symbol of As and a member of the 15th group. The atomic number is 33 and the atomic mass is 74.921 atomic mass unit. The most stable isotope of arsenic is ⁷⁵As, in which each atom has 33 protons and 42 neutrons. Arsenic electron configuration can be demonstrated as:

It is a semi-metal and classified as a metalloid with properties between metals and non-metals, such as semi-conductivity (Cullen and Reimer, 1989). It is ranked as 20th in abundance on earth and is mostly found in the core, clay-rich and sulfide-rich portions of the crust (Cullen and Reimer, 1989; Henke, 2009). Arsenic can be found in both organic and inorganic forms in nature. Organic arsenic forms may be produced by biological activities, mostly in surface waters, but are rarely quantitatively important. Organic forms may however occur where waters are significantly impacted by industrial pollutions (Smedley and Kinniburgh, 2002). Table 2.1 summarizes some of the arsenic properties.

group	15
atomic number	33
atomic weight	74.9216
electronegativity	2.1
density (20 °C)	5.72 g/cm ³
melting point (k)	1090
hardness (Mohs' scale)	3.5
oxidation states	-1, 0, +3, +5
isotopes	⁶⁸ As, ⁶⁹ As,, ⁷⁸ As, ⁷⁹ As

Table 2.1 Arsenic properties

2.3.2 Sources of arsenic in the environment

Arsenic is ubiquitous in the atmosphere, soils and rocks, surface and underground waters, and in organisms at different concentrations. The concentration ranges of arsenic found in various environmental media are shown in Figure 2.3. Arsenic can be mobilized and migrated through a combination of natural and anthropogenic processes such as weathering, biological processes, volcanic releases, using of arsenical pesticides, combustion of fossil fuels, and mining activities (Smedley and Kinniburgh, 2002). Arsenic contamination in natural waters is a world-wide problem and has become a serious threat to human health by affecting drinking water quality (Jain and Ali, 2000).



Figure 2.3 Arsenic concentrations in different environmental media (EPA, 2000).

2.3.3 Arsenic toxicity and health effects

Arsenic is being recognized as a toxic element in natural ecosystems and is historically regarded as the "king of poison" (Azeue and Nriagu, 1994; Cullen and Reimer, 1989; Day, 2010; Süß, 2011). It can affect the human blood system by damaging the white blood cells. It also contributes to skin, bladder and other cancers, with reported evidences of affecting the reproductive and renal systems (Akoitai, 2000a; Lengke, 2001).

The average per capita daily total arsenic intake for human is less than 200 µg for both organic and inorganic forms of arsenic. A one-time dose of 1 to 2.5 mg As₂O₃/kg body wt. can be fatal (Andrade, 2006). Elevated concentrations of arsenic in natural waters have been reported at different locations worldwide such as Bangladesh, Chile, India, Indonesia, Vietnam, and USA. Many studies have been conducted to support supply of arsenic-free drinking water (Jain and Ali, 2000; Smedley and Kinniburgh, 2002; Süß, 2011). The recommended limit of arsenic in drinking water was lowered from 50 μ g/L to 10 μ g/L in 1993 by the World Health Organization (WHO), which still poses a residual cancer risk of 1/500 (Mushak et al., 2000). The US Environmental Protection Agency (USEPA) proposed a 5 μ g/L standard in 2000 (USEPA, 2000).

Human body can be exposed to both organic and inorganic arsenic via various ways, such as air, food and water. A wide range of arsenic toxicity and contamination in different locations has been determined (Jain and Ali, 2000). The chemical form of arsenic has a huge effect on its toxicity. Arsenite (III) in both inorganic and organic forms is considered to be the most biologically toxic (Sharma and Sohn, 2009). Inorganic arsenic species are commonly more toxic to human and animals than the organic forms (Meharg and Hartley-Whitaker, 2015; Sharma and Sohn, 2009). Arsenic speciation in environmental samples is gaining increasing importance as its toxicity largely depends on its oxidation state.

2.3.4 Arsenic speciation and detection in aqueous systems

Arsenic is a redox-sensitive element and can form different species with other elements in multiple oxidation states; -3, -1, 0, +3, and +5. Oxidation and reduction of arsenic species mainly depend on the pH and oxidation reduction potential (ORP) of the environment. Its two most abundant inorganic oxidation states are arsenite (III) and arsenate (V). The oxidation state of arsenic plays an important role in the behavior of this element in the aqueous environment. Moreover, the oxidation state of arsenic determines its sorption/desorption behavior and therefore its mobility in aqueous systems (Jain and Ali, 2000). Arsenate (V) tends to be adsorbed on the surface of reactive minerals including iron and aluminum oxide minerals, whereas arsenite (III) is more mobile

(approximately 60 times), more bioavailable, and more toxic than arsenate (V) (Lenhart, 2004; Nazari et al., 2017; Rajaković et al., 2013).

Most toxic metals are present in aqueous environments as cations (e.g. Pb²⁺, Cu²⁺, Ni²⁺, Cd²⁺), which can be removed as insoluble precipitates by increasing the system pH. At near-neutral pH, most toxic metal cations tend to coprecipitate or precipitate in the form of oxide, hydroxide, carbonate or phosphate, or more likely by their strong adsorption to hydrous metal oxides, clay or organic matter (Smedley and Kinniburgh, 2002). However, arsenic ions tend to become less strongly sorbed as pH increases and can present in solution at relatively high concentrations (Dzombak and Morel, 1990). These facts emphasize the importance of arsenic speciation in the aqueous environments.

Figure 2.4 shows the thermodynamically stable arsenic species in water calculated by HSC Software and at two different temperatures. Depending on the aqueous properties (pH and Eh) and the presence of dissolved oxygen, arsenic can be predominant in the form of oxyanions (bounded to oxygen) (Cutter, 1992; Flora, 2005). The pentavalent arsenic (As^{5+}) predominates over a broad range of pH. Under more acidic and oxidizing conditions, $H_3AsO_4^0$ is more stable and more mobile than other charged arsenate (V) species. In the pH range from 2.5 to 6.9 $H_2AsO_4^-$ predominates. HAsO4²⁻ and AsO4³⁻ become more stable at higher pH. Eqs. (2-1)-(2-3) show the dissociation of arsenate (V) at different pH and their corresponding equilibrium constants:

$$H_3AsO_4^0 = H_2AsO_4^- + H^+$$
 $pK_a = 9.2$ (2-1)

$$H_2AsO_4^- = HAsO_4^{2-} + H^+$$
 $pK_a = 12.1$ (2-2)

$$HAsO_4^{2-} = AsO_4^{3-} + H^+$$
 $pK_a = 13.4$ (2-3)



Figure 2.4 Arsenic-water Eh-pH diagram calculated by HSC 7.1 software at 23 °C and 50 °C, 1 atm, and a total dissolved arsenic concentration of 0.002 M.

On the other hand, in more reducing environments different trivalent arsenic species exist at different pH levels. Figure 2.4 shows that the uncharged H₃AsO₃⁰ is the predominant species over a broad range of pH values from acidic to about pH 8. Eqs. (2-4) - (2-6) show the reactions responsible for dissociation of different arsenite (III) oxyanions. The distributions of the arsenate (V) and arsenite (III) species as a function of pH are given in Figure 2.5 and Figure 2.6, respectively.

$$H_3AsO_3^0 = H_2AsO_3^- + H^+$$
 pK_a = 2.24 (2-4)

$$H_2AsO_3^- = HAsO_3^{2-} + H^+$$
 $pK_a = 6.69$ (2-5)


Figure 2.5 Arsenate (V) speciation as a function of pH drawn using Stabcal software at 25 °C.



Figure 2.6 Arsenite (III) speciation as a function of pH drawn using Stabcal software at 25 °C.

Various methods and instruments have been used for determination of arsenic species and the total dissolved arsenic in aqueous solutions. Inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and graphite-furnace atomic absorption spectrometry (GF-AAS) are known as the most commonly used instruments for the total arsenic measurement. Other analysis methods include hydride generation atomic absorption spectroscopy (HG-AAS), ion chromatography and ion exchange resins (IC). High pressure liquid chromatography (HPLC) has been used for determination of arsenic speciation in aqueous solutions (Chen et al., 2014).

2.4 Sulfur speciation and detection in aqueous systems

Most arsenic minerals occur as sulfide minerals. Their weathering and dissolution would result in release of different sulfur species into the aqueous system. The presence of different sulfur species with different oxidation states plays an important role in complexing and transporting arsenic and other toxic elements (Planer-Friedrich et al., 2007; Polack et al., 2009; Webster, 1990). Hence it is important to understand the sulfur species release to the environment from dissolution of arsenic sulfide minerals.

Sulfate (SO₄²⁻) and sulfide (including H₂S, HS⁻ and S²⁻) are known as the most common sulfur species in the natural environment. However, other sulfur intermediate species can be present as a result of incomplete oxidation of sulfide to sulfate species (Kaasalainen and Stefánsson, 2011; Lengke, 2001). Among these species, sulfite (SO₃²⁻), thiosulfate (S₂O₃²⁻), polythionate (S_xO₆²⁻), polysulfides (S_x²⁻) and elemental sulfur (S⁰) are the most stable forms of intermediate sulfur

oxidation states. Table 2.2 shows the common sulfur-water (S-O-H) ions and their corresponding sulfur oxidation states.

Species	S oxidation state	Species	S oxidation state
H_2S_g, HS^-, S^{2-}	-2	$S_xO_6^{2-5} x \ge 3$	+10/x
$H_2S_x, HS_x^-, S_x^{2-} x = 2-9$	-2/x	SO _{2 aq} , HSO ₃ ⁻ , SO ₃ ²⁻	+4
S_8	0	$S_2O_6^{2-}$	+5
$S_2O_3^{2-}$	+2	HSO ₄ ⁻ , SO ₄ ²⁻	+6
S ₂ O ₄ ²⁻	+3	H ₂ S ₂ O ₈ , HS ₂ O ₈ ⁻ , S ₂ O ₈ ²⁻ , H ₂ SO ₅ , HSO ₅ ⁻	S(+6) and O(-1)

Table 2.2 The common sulfur species and their corresponding sulfur oxidation states

Figure 2.7 shows the Pourbaix diagram for the sulfur-water system, which shows that only sulfide, elemental sulfur and sulfate are thermodynamically stable. However, many other sulfur species mentioned above have kinetic stability and can be present as dominant species under certain conditions. Moreover, elemental sulfur is metastable at low temperatures and within a large pH and ORP conditions (sulfur area in Figure 2.7). The oxidation rate of elemental sulfur to sulfate is very slow. Therefore, elemental sulfur produced by oxidation of sulfide minerals remains as S^0 in the environment and can significantly influence the mineral dissolution behavior (Vignes, 2013). Passivation of mineral surfaces as a result of elemental sulfur formation can decrease or stop the dissolution of the solid. Several research studies reported the formation of elemental sulfur layer and their different effects on the leaching reactions (Asta et al., 2010; Conner, 2013; Corkhill and Vaughan, 2009; Ravichandran et al., 1998). It was shown that elemental sulfur can act as a barrier to diffusion when it is formed and accumulated on solid surfaces as a uniform and consistent layer,

thereby inhibiting further oxidation of the solids (Corkhill and Vaughan, 2009; Cruz et al., 1997; Fernandez et al., 1996). In contrast, a non-uniform elemental sulfur layer is unlikely to act as a diffusion barrier and therefore has no effect on the solid oxidation rate (Mcguire et al., 2001; Mikhlin et al., 2006).



Figure 2.7 Eh-pH diagram of the S-H₂O system and the presence of metastable region of elemental sulfur at 25 °C, unit activities of solutes and 1 atm pressure (Vignes, 2013).

Sulfide is unstable and can be rapidly oxidized to elemental sulfur and sulfate in the presence of oxygen or other metal ions (Roy and Trudinger, 1970). Sulfite and thiosulfate are known as moderately strong reducing agents. Depending on the system conditions and the presence of oxidants such as oxygen, ferric, cupric, iodine and chlorine, they can undergo oxidation to sulfate

(Greenwood and Earnshaw, 1997). Thiosulfate is very unstable in acidic environment and its stability increases with pH. It disproportionates to sulfite and elemental sulfur at alkaline pH (Peters, 1976). These species are not stable in comparison with sulfide and sulfate ions and will eventually convert to more stable sulfur species. However, the rate of oxidation reactions is very slow, which makes the sulfur intermediates kinetically stable under suitable conditions. Therefore, to include the stability regions for more sulfur intermediates in the sulfur-water diagram, sulfate should be excluded. Figure 2.8 shows the metastability of different sulfur intermediates at different pH and ORP values.



Figure 2.8 Eh-pH diagram of the S-H₂O system and the presence of metastable intermediate sulfur species at 25 °C, unit activities of solutes and 1 atm pressure (Peters, 1976).

There are various techniques for measurement of total dissolved sulfur and different sulfur species in aqueous systems, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), gas chromatography (GC), and ion chromatography (IC). Each technique has its own advantages and drawbacks with different levels of sensitivity, detection limit, and selectivity for different sulfur species (Lengke, 2001). ICP-AES and IC have been used for total sulfur and speciation measurement in the solutions obtained from leaching experiments, respectively. The main advantages of ICP-AES and IC are simultaneous detection of sulfur and arsenic, requirement of minimal sample volume, short measurement time, and less sample pretreatments.

2.5 Arsenic and sulfur release from arsenic bearing sulfides

2.5.1 Arsenic-bearing minerals

Arsenic can be found as a major constituent in more than 200 minerals, including elemental arsenic, arsenides, sulfides, oxides, arsenates and arsenites. Crystals of native arsenic are found in nature, which are crystallized in a hexagonal system, whereas arsenolamprite and paraarsenolamprite have the same properties but in an orthorhombic shape. The affinity of arsenic to other elements causes this great diversity of arsenic bearing minerals and makes it rarely found as a native element (Day, 2006). Arsenic can bond easily to a variety of ligands and other elements, which strongly affects its chemical behavior. Table 2.3 shows the arsenic mineral groups and the common arsenic minerals found in the environment.

Group	Mineral	Formula
	Native arsenic	As
Elemental arsenic	Arsenolamprite	As
	Paraarsenolamprite	As
	Arsenopyrite	FeAsS
	Cobaltite	CoAsS
	Orpiment	As_2S_3
Arsenic suindes	Realgar	AsS/As ₄ S ₄
	Gersdorffite	NiAsS
	Enargite	Cu ₃ AsS ₄
	Domeykite	Cu ₃ As
	Lollingite	FeAs ₂
Motol organidad	Nickeline or niccolite	NiAs
wietai arseniues	Rammelsbergite	NiAs ₂
	Sperrylite	PtAs ₂
	Safflorite	CoAs ₂
	Arsenolite	As ₂ O ₃
	Claudetite	As_2O_3
Amonito (III)	Sodium arsenite	NaAsO ₂
Arsenne (111)	Leiteite	ZnAs ₂ O ₄
	Reinerite	$Zn_3(AsO_3)_2$
	Gebhardite	$Pb_8(As_2O_5)_2OCl_6$
	Johnbaumite	Ca5(AsO4)3(OH)
	Mimetite	Pb ₅ (AsO ₄) ₃ (Cl)
Arsenates (V)	Austinite	CaZn(AsO ₄)(OH)
	Scorodite	FeAsO4·2H2O
	Erythrite	Co ₃ (AsO ₄) ₂ ·8H ₂ O

Table 2.3 Arsenic mineral groups and examples of common minerals (Day, 2006; Sand et al., 2001)

Arsenic dissolution from arsenic-bearing minerals through natural weathering and mining activities are known to be an important source for arsenic release into the environment (Plant et al., 2003; Smedley and Kinniburgh, 2002; Suess and Planer-Friedrich, 2012a). Environmental factors, such pH, temperature, and microorganisms can significantly affect the stability and dissolution behavior of arsenic-bearing minerals (Al-Abed et al., 2007; Corkhill and Vaughan, 2009; Vink, 1996). Various studies have been conducted to investigate the effect of different parameters on arsenic release from its sulfides. The release kinetics and the speciation of arsenic and other ions in solution are reviewed below.

2.5.2 Arsenic release from arsenopyrite

Different studies have been done on the dissolution-oxidation of arsenic-rich pyrite and arsenopyrite, the two most common arsenic minerals (Asta et al., 2010; Basu and Schreiber, 2013; Corkhill and Vaughan, 2009; McKibben et al., 2008; Pokrovski et al., 2002). The leaching kinetics of pyrite in acidic to neutral and oxidative environments has been studied extensively over the past two decades (McKibben et al., 2008). In contrast, the oxidative release of arsenic from arsenopyrite under conditions similar to the geological conditions came to attention more recently (Walker et al., 2006; Yu et al., 2007).

Arsenopyrite oxidation produces acid, causing a decrease in the environment pH. The oxidation of arsenopyrite is much faster in acidic media than in neutral or alkaline environment, producing such species as Fe (III), arsenite (III), arsenate (V), SO_3^{2-} and SO_4^{2-} (Corkhill and Vaughan, 2009). Different studies have been done regarding the kinetics of arsenopyrite oxidative dissolution, with emphasis on Fe (III) and dissolved oxygen as the main oxidants. McKibben et al. (2008) reported

that Fe (III) ions were the predominant inorganic agents for arsenopyrite oxidation in acidic media; oxidation by Fe (III) was much faster than by dissolved oxygen. In the absence of Fe (III) ions, almost no arsenite (III) was released from arsenopyrite into solution (Breed et al., 1997).

Rimstidt et al. (1994) derived a kinetic model describing the oxidation rate of arsenopyrite with Fe (III) in acidic media and calculated an activation energy of 18 kJ/mol. They assumed that arsenic can be released from arsenopyrite by the reduction of Fe (III) ions according to Eq. (2-7) as the overall reaction. However, later studies on arsenic species released from arsenopyrite dissolution show that arsenic was first released as arsenite (III), which was slowly oxidized to arsenate (V) (Walker et al., 2006; Yunmei et al., 2004).

$$FeAsS + 13Fe^{3+} + 8H_2O = 14Fe^{2+} + SO_4^{2-} + 13H^+ + H_3AsO_4$$
(2-7)

Yunmei et al. (2004) reported that the arsenopyrite oxidation rate increased with increasing concentration of ferric ion and temperature in acidic media. The major arsenic species resulting from the oxidation process was arsenite (III), which was slowly converted to arsenate (V). They also concluded that Cl⁻ could accelerate the release of arsenic from arsenopyrite in an acidic environment. Asta et al. (2010) studied arsenopyrite dissolution in an aqueous environment with varying pH from 1 to 9, temperature from 25 °C to 70 °C, and dissolved oxygen from 0.2 to 8.7 ppm. The authors showed that the dissolution of arsenopyrite under acidic conditions was more affected by dissolved oxygen than by temperature and pH. A sulfur-enriched surface layer on the solid particles was observed to form during dissolution. However, this layer did not exert any passivating effect and thereby the reaction was able to reach steady state. Conversely, in alkaline leaching, precipitation of iron phases was observed, which coated the surface of the particles. A

steady state could not be attained because the diffusion of aqueous species was prevented by the coating formed on the surface. The experimental results were used to derive a leaching kinetic model as Eq. (2-8):

$$R = 10^{-7.41} a_{0_2}^{0.76} a_{H^+}^{0.12}$$
(2-8)

where a_{0_2} and a^{H^+} are the activities of hydrogen ions and dissolved oxygen, respectively. The reaction orders with respect to dissolved oxygen and hydrogen ions were estimated by multiple linear regression of the dissolution rates. The apparent activation energy for the arsenopyrite oxidation by dissolved oxygen was calculated to be 18.5 kJ/mol in the temperature range studied (Asta et al., 2010).

Walker et al. (2006) suggested that arsenopyrite oxidation in a near neutral environment proceeded via a series of oxidation reactions that converted arsenite (III) to arsenate (V): arsenopyrite was oxidized by oxygen, producing ferrous and arsenous acid according to Eq.(2-9); ferrous ions and arsenous acid are then oxidized to form ferric hydroxide and arsenic acid according to Eqs.(2-10) -(2-13). Eq. (2-9) shows that this reaction will not change the pH of the environment. However, depending on the environment pH, Fe²⁺ is oxidized to Fe³⁺ in the absence and presence of microbes. At pH values above 5, Fe³⁺ undergoes hydrolysis to precipitate as hydrous ferric oxide, as shown in Eq. (2-11), which is an acid generating reaction. The oxidation of dissolved arsenite (III) to arsenate (V) also generates protons, as shown in Eqs. (2-12) and (2-13) (Yu et al., 2007).

$$4\text{FeAsS} + 11\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe}^{2+} + 4\text{H}_3\text{AsO}_3 + 4\text{SO}_4^{2-}$$
(2-9)

$$4Fe^{2+} + O_2 + 10H_2O \rightarrow 4Fe(OH)_3 + 8H^+$$
(2-10)

$$FeAsS + 3O_2 + 4H_2O \rightarrow Fe(OH)_3 + H_3AsO_3 + SO_4^{2-} + 2H^+$$
 (2-11)

$$2H_3AsO_3 + O_2 \rightarrow 2HAsO_4^{2-} + 4H^+$$
 (2-12)

$$2H_3AsO_3 + O_2 \rightarrow 2H_2AsO_4 + 2H^+$$
 (2-13)

2.5.3 Oxidation of enargite

Different studies have been conducted on enargite dissolution, a copper sulfide mineral (Cu₃AsS₄), to maximize the extraction of copper or remove arsenic in the copper leaching process (Filippou et al., 2007; Parada et al., 2014). The rate of enargite dissolution has been shown to be higher in the presence of *Thiobacillus ferrooxidans* bacteria than that in chemical leaching in acidic ferric sulfate media (Escobar et al., 1997). Waste rocks and deposits containing enargite usually produce acidic drainage because of enargite oxidation by dissolved oxygen (Eq. (2-14)) (Lattanzi et al., 2008). In the presence of ferric iron produced from pyrite oxidation, arsenate (V) is released from enargite oxidation according to Eq. (2-15). Despite several studies being conducted on copper dissolution from enargite, release of arsenic from enargite from an environmental point of view has not been studied in detail.

$$4Cu_{3}AsS_{4} + 35O_{2} + 10H_{2}O \rightarrow 12Cu^{2+} + 4AsO_{4}^{3-} + 16SO_{4}^{2-} + 20H^{+}$$
(2-14)

$$Cu_{3}AsS_{4} + 35Fe^{3+} + 20H_{2}O \rightarrow 3Cu^{2+} + 35Fe^{2+} + HAsO_{4}^{2-} + 4SO_{4}^{2-} + 39H^{+}$$
(2-15)

2.5.4 Oxidation of realgar

Oxidation of natural realgar in alkaline media was studied by Lengke and Tempel (2003) by varying temperature and the concentration of dissolved oxygen. arsenite (III) and arsenate (V) were observed in the solution with arsenite (III) being the predominant species. The following chemical reaction (Eq. (2-16)) has been proposed for the oxidation of realgar with dissolved oxygen as the main oxidant:

$$4AsS + 11O_2 + 10H_2O \rightarrow 4HAsO_4^{2-} + 4SO_4^{2-} + 16H^+$$
(2-16)

The kinetic study showed that the oxidation is controlled by a surface chemical reaction and the activation energy was calculated to be 64.2 kJ/mol. The oxidation rate of realgar was significantly affected by the concentration of dissolved oxygen in the leaching environment and the kinetic equation was reported as Eq. (2-17) (Lengke and Tempel, 2003):

$$R = 10^{-9.63} [D0]^{0.51} [H^+]^{-0.28}$$
(2-17)

2.6 Orpiment as an important form of arsenic sulfide – the focus of this research

Orpiment (As_2S_3) is a naturally occurring arsenic sulfide mineral found at different mine locations. It is generally found in carbonate rocks and associated with stibnite (Sb_2S_3), calcite (CaCO₃), barite (BaSO₄) and gypsum (CaSO₄.2H₂O) (Lengke et al., 2009). The presence of amorphous form of As_2S_3 has been reported in different deposits at different mine locations (Eary, 1992; Webster, 1990). Precipitation of amorphous As_2S_3 is known as a common method to remove dissolved arsenic from waste streams (Hu et al., 2019; Yao et al., 2019). As_2S_3 can precipitate from contaminated solutions with H_2S gas through Eq. (2-18), which is known as the sulfidization process (Nazari et al., 2017):

$$2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$$
(2-18)

Amorphous As_2S_3 can also be formed as a product of chemical reaction between arsenic trioxide, sodium sulfide and hydrochloric acid (Eq. (2-19)) (Li, 2013):

$$As_2O_{3(s)} + 3Na_2S_{(aq)} + 6HCl_{(aq)} \rightarrow As_2S_{3(s)} + 6NaCl_{(aq)} + 3H_2O_{(l)}$$

$$(2-19)$$

 As_2S_3 has been reported to be insoluble in acidic environments, whereas the solubility is shown to change significantly in response to pH increase (Darban et al., 2011). Eqs. (2-20) – (2-21) were obtained as the main reactions for arsenite (III) release from orpiment when the oxygen is removed from the environment (Floroiu et al., 2004; Webster, 1990). In anoxic solutions and in the presence of sulfide ions, formation of thioarsenite species has been proposed and supported by thermodynamic calculations (Eary, 1992; Helz and Tossell, 2008).

$$As_2S_3 + 6H_2O \rightarrow 2H_3AsO_3 + 3HS^- + 3H^+$$
 (2-20)

$$3As_2S_3 + 3HS^- + H^+ \rightarrow 2H_2As_3S_6^- \tag{2-21}$$

Oxidative dissolution of amorphous and natural orpiment was conducted in a mixed flow reactor with leaching parameters including pH, dissolved oxygen, and temperature (Lengke and Tempel, 2002, 2001). Orpiment was shown to be oxidized by dissolved oxygen, releasing arsenic acid into the aqueous solution according to Eq. (2-22). The amorphous orpiment is shown to have a higher dependency on pH than the natural orpiment. Eqs. (2-23) and (2-24) were derived as the rate laws of natural and amorphous orpiment oxidation. The oxidation rate of the amorphous orpiment was higher than that of the natural one by a factor of 1.2-2.1 under similar conditions.

$$As_2S_3 + 6O_2 + 6H_2O \rightarrow 2H_3AsO_3 + 3SO_4^{2-} + 6H^+$$
(2-22)

$$R_{As_2S_3(natural)} = 10^{-11.77} [D0]^{0.36} [H^+]^{-0.47}$$
(2-23)

$$R_{As_2S_3(\text{amorphous})} = 10^{-16.77} [D0]^{0.42} [H^+]^{-1.26}$$
(2-24)

Based on the thermodynamic data, the oxidation of orpiment in the presence of oxygen was calculated to produce arsenate (V) as the predominant species of arsenic via Eqs. (2-25) and (2-26). However, oxidation of arsenite (III) to arsenate (V) is slow and the oxidation of orpiment may not proceed to completion. Arsenite (III) and intermediate sulfur species have been shown to be the predominant arsenic and sulfur species in the aqueous phase as a result of orpiment oxidation (Yu et al., 2007). The formation of thioarsenite and arsenite (III) ions is also reported in alkaline leaching of orpiment in Eq. (2-27) (Zhang, 2004). The presence of microbes is also shown to accelerate arsenic release from orpiment (Ehrlich, 1963).

$$As_2S_3 + 10O_2 + 6H_2O \rightarrow 2HAsO_4^{2-} + 3SO_4^{2-} + 10H^+$$
(2-25)

$$As_2S_3 + 10O_2 + 6H_2O \rightarrow 2H_2AsO_4^- + 3SO_4^2^- + 8H^+$$
(2-26)

$$As_2S_3 + 6OH^- = AsS_3^{3-} + AsO_3^{3-} + 3H_2O$$
(2-27)

2.7 Water treatment for arsenic removal

The concentration of dissolved arsenic in waste waters such as mining effluents and the stability of arsenic bearing wastes are continuously monitored and governed by regulatory agencies (Nazari et al., 2017). The mining industry has applied several effective approaches, including physical, chemical and biological processes, to remove arsenic from water (Lee et al., 2005; Lottermoser, 2013). The most commonly used methods include precipitation, adsorption, reverse osmosis, ion exchange and membrane filtration (Kartinen and Martin, 1995).

• Precipitation

Precipitation of arsenic refers to addition of chemical reagents to remove arsenic as insoluble solid precipitates. (Henke, 2009). Precipitation/coprecipitation has been the most commonly used technique to treat arsenic contaminated waters. Arsenic precipitation can reduce the concentration of dissolved arsenic to less than 10-50 ppb (EPA, 2002). Regardless of the method applied, the majority of arsenic must be in the form of arsenate (V). Different oxidizing agents have been used to oxidize arsenite (III) to arsenate (V), including hydrogen peroxide (Molnár et al., 1994), ozone (Khuntia et al., 2014), permanganate (Sorlini and Gialdini, 2010), and ultraviolet (UV) assisted oxidation process (Emett and Khoe, 2001; Yoon et al., 2008).

Lime precipitation is a common simple method to remove arsenite (III) and arsenate (V) from hundreds of ppm down to 1-5 ppm in the form of calcium arsenite or calcium arsenate at elevated pH values. However, the structure and stability of the arsenical products are significantly dependent on the pH, temperature, ageing time, and calcium to arsenic ratio (Moon et al., 2004; Zhu et al., 2006). Despite being a relatively economic process, the arsenical products must be kept in designated hazardous landfills due to its poor long-term stability (Nazari et al., 2017).

Arsenate (V) can be removed from aqueous solutions by adsorption to iron oxides or precipitates as hydrated ferric arsenate, the crystalline form of which is known as scorodite (FeAsO_{4.2}H₂O). Several studies have been conducted on different methods to remove arsenic from aqueous solutions as scorodite (Nazari et al., 2017). High temperature pressure oxidation (HTPO) is a technique in which ferric sulfate is added to a solution containing arsenite (III) at 150-230 °C and an oxygen pressure of 2000 kPa in an autoclave. This method is common in pretreatment of gold refractory ores to remove arsenic as scorodite, liberating gold (Demopoulos et al., 1995; Laboratories and Canada, 1988). The main drawback of this method is the capital costs associated with high pressure and temperature conditions in autoclaving. Scorodite is stable at pH 4 and below. At pH above 4, arsenic may be remobilized into the environment (Lottermoser, 2013).

In some cases, arsenate (V) can be reduced to arsenite (III), which is then removed as arsenic sulfides, such as AsS and As_2S_3 (Younger et al., 2002), via supplying sodium sulfide or hydrogen sulfide (Nazari et al., 2017). This process is much more expensive than lime precipitation, but the product has a higher concentration of arsenic and therefore a much lower volume (Yao et al., 2019).

$$2HAsO_{2 (aq)} + 3H_{2}S_{(g)} = As_{2}S_{3 (s)} + 4H_{2}O_{(aq)}$$
(2-28)

• Ion exchange

Strong base anion-exchange resins can be used to remove dissolved arsenic from contaminated waters. This technique can significantly reduce the arsenic concentration down to drinking water regulation levels. It is more effective for arsenic removal when arsenic is in the form of arsenate (V). Therefore, an initial oxidation of arsenite (III) to arsenate (V) is necessary for application of this method. On the other hand, competition between different ions such as sulfate, nitrate and chloride, which are common in mine effluents, and arsenic oxyanions for the resin surfaces can significantly affect the process efficiency (Korngold et al., 2001). Furthermore, the capacity of ion exchange resins to uptake arsenic ions from aqueous phase is considered as one of the main drawbacks for using this method (Bissen and Frimmel, 2003).

• Passive treatment

Conventional arsenic treatment technologies are costly and generate sludge (Cohen, 2006). Passive treatment uses natural processes to remove toxic elements such as arsenic from the contaminated zone. Constructed wetland is one of the most commonly used passive treatment methods to remove metals and metalloids, including arsenic (Lizama et al., 2011; Ye et al., 2003). Wetlands are distinct ecosystems which are flooded by water to provide an oxygen removed environment with plants that prefer slightly acidic to moderately acidic environments (Egiebor and Oni, 2007). In wetlands, sulfate is reduced to sulfide by anaerobic sulfate-reducing bacteria. The sulfide produced reacts with metal cations, including arsenic ions (mostly arsenite (III)), to form insoluble sulfide precipitates (Cohen, 2006; Egiebor and Oni, 2007). The long stability of reaction products is also of major concern.

2.8 Source control

Water treatment in general has the following disadvantages: generation of sludges, the necessity of different pre-treatments, and high capital and operating costs. Given the complexity, costs, and duration associated with water treatment, a preferable option to manage waste rock drainage is to control and prevent contaminant release at the source, i.e. source control. The release process is complex and can be controlled by a combination of physical, chemical, and biological factors.

• Physical control

One typical source control strategy currently applied is to separate the arsenic bearing minerals from the rest of the waste by different methods, such as flotation and gravity separation. The separated arsenic minerals are then sent to tailings or sent back to the mine if the arsenic concentration is low (Wang and Ferron, 2003). Flooding and sealing of underground mines to prevent oxygen transport has been reported on some abandoned mines (Johnson and Hallberg, 2005). Similarly, covering waste rock piles with a layer of organic materials, sediment or clay and soil compaction is reported as another method to reduce the contact of waste rock with oxygen and water (Pozo-Antonio et al., 2014). However, these physical techniques are unable to completely prevent the arsenic release from its sources.

• Chemical control

A range of complex geochemical reactions occurs in waste rock environment, from sulfide oxidation, to acid neutralization, to formation of iron and aluminum secondary minerals. Acid neutralization by calcite and dolomite affects the dissolution behavior of arsenic minerals (Banks

et al., 1997). Secondary mineral phases formed can coat the surfaces of arsenic bearing minerals and decrease the reaction rate. Addition of different reagents to microencapsulate pyrite has been used to reduce sulfide oxidation (Li et al., 2018). Several studies show the possibility of reducing sulfide oxidation at neutral pH by coating with iron oxyhydroxide (Huminicki and Rimstidt, 2009).

• Biological control

Release of arsenic and other toxic elements from mine wastes is influenced by the presence of microorganisms in the environment. Oxidation of pyrite, arsenopyrite and orpiment have been shown to be influenced by the presence of iron and sulfur oxidizing bacteria (Ehrlich, 1963; Tu et al., 2017). Addition of chemicals such as bactericides and anionic surfactants has been tested to reduce the activity of microorganisms (Kleinmann, 1990; Li et al., 2018). Biological activities can reduce the mobility of metals by adsorption or precipitation (Lim et al., 2014).

2.9 Summary

To implement effective source control, it is essential to attain knowledge on the fundamental processes that determine the dynamics of arsenic release from its bearing minerals and waste rock. Such fundamental processes include waste rock hydrology, geochemical reactions, and microbial activities. This research is focused on the geochemical reactions associated with arsenic release, with a general objective of advancing knowledge in the key factors that control the kinetics and pathways of arsenic release from mine waste rock. This body of knowledge would eventually assist with the design of the most effective source control strategies.

Chapter 3: Research gaps and objectives

3.1 Research gaps

• Rate and pathways of arsenic and sulfur release from arsenic trisulfide (As₂S₃)

The literature review shows that there are abundant studies on arsenic and sulfur release from dissolution of arsenopyrite and pyrite, the two most common arsenic-bearing sulfides. However, arsenic sulfides and sulfosalts, rather than arsenian pyrite, are shown to be the principal sources of arsenic release in different mine locations (Kim et al., 2000). In addition, there is increased interest in removing arsenic from metallurgical waste streams as arsenic trisulfide and stabilizing it for long-term disposal in the environment. Therefore, it is essential to determine the key factors affecting the leaching kinetics and to develop rate laws to predict arsenic release from arsenic trisulfide as a function of environmental factors.

• Speciation of arsenic and sulfur in aqueous solutions

Concentrations of arsenic and sulfur detected in the environment are generally reported as total arsenic and sulfur (Cheng et al., 2009). However, the mobility, toxicity and reaction mechanisms responsible for arsenic and sulfur release from their bearing minerals depend on the arsenic and sulfur species present in the system. Fewer studies have been focused on the speciation of arsenic and sulfur released from arsenic trisulfide (As_2S_3) dissolution under the conditions that could be encountered in a mine waste rock environment. It is essential to identify arsenic and sulfur species for understanding the possible pathways responsible for their release from arsenic trisulfide.

• The role of crystallinity on arsenic and sulfur release

Arsenic trisulfide can be present in both amorphous and crystalline forms in mine sites. They have the same formula as As_2S_3 , but different unit structures and interatomic bonds, which can affect their dissolution behavior. The effect of crystallinity on reaction kinetics and pathways must be studied to develop appropriate kinetic equations to predict the rate of arsenic and sulfur release.

3.2 Research Objectives

To address the research gaps outlined above, the overall objective of this research is to gain a fundamental understanding on the arsenic and sulfur release from amorphous As_2S_3 and crystalline orpiment. This knowledge could eventually serve as useful tools for pinpointing the key factors that can be manipulated to prevent arsenic release from mine waste materials. The general objective is broken down into three specific objectives:

- Objective I: To investigate the behavior of arsenic and sulfur release from amorphous As₂S₃:
 I-a: quantify the effect of different factors on the rates of total arsenic and sulfur release;
 I-b: determine the influence of different factors on arsenic and sulfur speciation;
 I-c: propose reaction pathways responsible for the release of arsenic and sulfur species.
- **Objective II:** To determine the rate law and reveal the mechanism of arsenic release from amorphous As₂S₃:

II-a: derive a kinetic equation to describe arsenic release as a function of different factors;II-b: interpret the reaction mechanism using the reaction orders and the activation energy;II-c: support the proposed reaction mechanism by characterizing the solid surface properties.

• **Objective III:** To assess the effect of the degree of crystallinity on the dissolution of arsenic trisulfide:

III-a: quantify the effect of various factors on the rate and speciation of arsenic and sulfur release from crystalline orpiment;

III-b: identify the rate limiting step and uncover the reaction mechanism for arsenic release from crystalline orpiment.

III-c: compare the kinetics and mechanism of arsenic and sulfur release from amorphous and crystalline arsenic trisulfide.

Chapter 4: Research methods

4.1 Introduction

This Chapter outlines the research and experimental methods applied to achieve the research objectives. For objective I, which is to investigate the behavior of arsenic and sulfur release from amorphous As_2S_3 , the experimental design and the research method were described in detail in Section 4.2. For objective II, which is to determine the rate law and reveal the mechanism of arsenic release from amorphous As_2S_3 , the research methodology was explained in Section 4.3. Section 4.4 explains the research methodology for achieving objective III, which is to assess the effect of the degree of crystallinity on the dissolution of arsenic trisulfide.

4.2 Research methods for Objective I

4.2.1 Experimental design

To quantify the effect of different factors on the rates of total arsenic and sulfur release from amorphous As_2S_3 (Objective I-a), a series of reactor leaching experiments were designed and carried out under different conditions. The independent variables studied were pH, DO concentration, and temperature, the ranges of which are shown in Table 4.1. The dependent variables measured were the total dissolved arsenic and the total dissolved sulfur, the ratio between which was then calculated. In addition, the effect of carbonate/bicarbonate ions on the arsenic release was investigated by performing reactor leaching tests with the same experimental design as shown in Table 4.1 but with sodium carbonate for pH control during leaching. The one-factorat-a-time method was used in the experimental design to facilitate the development of the kinetic model. It should be noted that this design method has limitations and could not be used to investigate the parameter interactions, for which a factorial design method should be used. Both amorphous and crystalline arsenic trisulfide have a soft solid structure with a Mohs hardness of 1.5 to 2. Using magnetic stirrer and stir bars resulted in changes in the particle size during the experiments. Therefore, particle size was not included as an independent variable.

To determine the influence of different factors on arsenic and sulfur speciation (Objective I-b), the aqueous samples collected on day 5 and day 30 were analyzed for the concentrations of different arsenic and sulfur species. Based on the results obtained from Objective I-a and I-b, the reaction pathways responsible for the release of different arsenic and sulfur species were proposed (Objective I-c).

Variable	pН	DO, ppm	Т, °С
рН	6	8.3	23
	7	8.3	23
	8	8.3	23
	9	8.3	23
	10	8.3	23
	8	0.0	23
Dissolved owner	8	2.0	23
Dissolved oxygen	8	5.0	23
	8	8.3	23
	8	8.3	23
Tomoroustan	8	8.3	30
remperature	8	8.3	40
	8	8.3	50

Table 4.1 Experimental design of the leaching tests to investigate the effect of different parameters on arsenic and sulfur release from amorphous As_2S_3

4.2.2 Safe handling of arsenical materials in the laboratory

Arsenic and its compounds are toxic and carcinogenic (Flora, 2005). Personal protective equipment (PPE) including safety glasses, gloves and lab coat must be worn during the laboratory experiments. For both amorphous and crystalline arsenic trisulfide systems, mortar and pestle grinding and sieving were conducted under a well-ventilated fume hood. During the leaching experiments, the solution ORP was continuously monitored to prevent the formation of toxic arsine gas (AsH₃) in a reducing environment (Figure 2.4). At the end of the leaching experiments, solid residual removal from solution and preparation of solid samples for surface analysis were done under a well-ventilated fume hood.

4.2.3 Materials

Amorphous As₂S₃ used was supplied by Alfa Aesar Co. (arsenite (III) sulfide, 99.9% metal basis). The chemicals used in the experiments were of reagent grade. They included sodium hydroxide (NaOH, Sigma-Aldrich), sodium carbonate (Na₂CO₃, Sigma Aldrich), sodium bicarbonate (NaHCO₃, Sigma Aldrich), sodium thiosulfate (Na₂S₂O₃, Sigma Aldrich), sodium sulfite (Na₂O₃S, Sigma Aldrich), sulfuric acid (H₂SO₄, 98%, Anachemia), hydrogen peroxide (H₂O₂ 30%, VWR), nitric acid (HNO₃, 68-70%, VWR), hydrochloric acid (HCl, 37%, VWR), arsenic standard solution (1000 mg/L, Sigma Aldrich), arsenic (III) IC standard solution (1000 mg/L, Sigma Aldrich), arsenic (V) IC standard solution (1000 mg/L, Sigma Aldrich), sulfur standard solution (1000 mg/L, Sigma Aldrich), saturated potassium chloride (KCl, LabChem) for refilling pH electrodes, 4M potassium chloride saturated with silver chloride (KCl, Fisher Scientific) for refilling the ORP electrodes. All

solutions were prepared with deionized water. Nitric acid was mixed with hydrochloric acid in a molar ratio of 1:3 to provide aqua regia solution to digest the arsenic trisulfide sample.

4.2.4 Solid sample preparation and characterization

• Sample preparation

The solid As_2S_3 sample was ground using a mortar and pestle and screened to obtain a particle size of -75+53 µm under a well-ventilated fume hood. The surface area of the As_2S_3 particles was not measured. To remove fine and pre-oxidized particles from the solid surfaces, the sample was washed with 10% sulfuric acid for 1 h followed by washing in ethanol in an ultrasonic bath. The washing process was repeated until the solution was clear. The sample was then dried and stored in a vacuum desiccator until use for the leaching experiments.

• As₂S₃ characterization by XRD

Amorphous As_2S_3 sample was ground to an optimum grain size range for quantitative X-ray analysis (<10 µm) by milling under ethanol in a vibratory McCrone Micronizing Mill for 10 minutes. XRD analysis was performed using a Bruker D8 Advance Bragg-Brentano diffractometer equipped with an Fe monochromator foil, 0.6 mm (0.3°) divergence slit, incident- and diffractedbeam Soller slits and a LynxEye-XE detector. Step-scan X-ray powder-diffraction data were collected over a range 3-80 °20 with CoK α radiation. The long fine-focus Co X-ray tube was operated at 35 kV and 40 mA, using a take-off angle of 6°. The X-ray diffractogram was analyzed using the International Centre for Diffraction Database PDF-4 and Search-Match software by Bruker. X-ray powder-diffraction data of the sample were refined with Rietveld program Topas 4.2 (Bruker AXS).

• Surface elemental composition analysis by SEM/EDX

To characterize the surface of the amorphous As_2S_3 sample prior to leaching, the solid sample was examined using a scanning electron microscope (SEM) coupled with energy dispersive X-ray spectroscopy (FEI Quanta 650 SEM/EDX). EDX analysis was used to determine the arsenic to sulfur ratio on the surface of the solid sample.

• Chemical composition by ICP-OES

Wet chemical analysis was used to verify the chemical composition of the As₂S₃ sample and to support the arsenic to sulfur ratio obtained from other methods. The sample was digested in aqua regia solution (a mixture of nitric acid and hydrochloric acid in a molar ratio of 1:3) using a microwave digestion system (Ethos Up), followed by the solution analysis using an inductively coupled plasma optical emission spectroscopy (ICP-OES Agilent 5100). This method needs a minimal sample volume, a short measurement time, and less sample pretreatment. It has a detection limit of about 30 ppb (Rajakovic and Rajakovic-Ognjanovic, 2016).

4.2.5 Leaching test procedure

Figure 4.1 shows the schematic of the experimental apparatus setup. The leaching tests were carried out in a 500 mL jacketed glass reactor, into which 250 mL of leaching solution was introduced. The solution temperature was kept constant by using a water bath to circulate water at

a constant temperature through the jacket wall. A thermometer was immersed in the leaching solution to continuously measure the solution temperature. A mass of 50 mg of solid samples was added into the reactor. A Teflon-coated magnetic stirring bar was used to keep the solid particles fully suspended and the agitation speed was maintained at 600 rpm.

The pH, ORP, and the concentration of dissolved oxygen in the leaching solution were measured and controlled in the course of leaching. The solution ORP was continuously monitored to prevent the formation of toxic arsine gas in a reducing environment. The pH and ORP control were achieved using a controller (HACH SC200 Universal Controller) with two metering pumps attached to it (Iwaki, Hi-Resolution Pump), one for pH and the other for ORP adjustment. Specifically, the controller compares the pH and ORP values measured by the pH (Accumet pH/ATC Electrode from Fisher Scientific) and ORP probes (Accumet Platinum ORP Electrode from Fisher Scientific) with the set points. If the measured values deviate from the set points, the controller sends signals to the metering pumps to supply NaOH/Na₂CO₃ for pH adjustment and hydrogen peroxide (0.3% v/v) for ORP adjustment.

However, after some initial experiments, it was shown that hydrogen peroxide directly participated as an oxidant in the dissolution rate of As_2S_3 . Therefore, hydrogen peroxide was not added to maintain the ORP of the leaching solutions for the rest of the experiments. Pure oxygen and nitrogen gases were introduced continuously at different flow rates to the leaching system to achieve a constant concentration of dissolved oxygen. The concentration of dissolved oxygen was measured by a DO probe (Oakton Dissolved Oxygen).



Figure 4.1 A schematic of the leaching experimental setup.

4.2.6 Analysis of aqueous samples collected from the leaching tests

• Analysis of total arsenic and sulfur concentration

In the course of leaching, 1 mL of aqueous samples were taken at specific time intervals and filtered by a 0.45 µm filter. The filtrate was analyzed for the total concentrations of dissolved arsenic and dissolved sulfur by conducting three replicated analyses using an inductively coupled plasma optical emission spectroscopy ICP-OES (Agilent 5100). The arsenic and sulfur standard solutions used for the analysis were prepared from a single element standard stock solution

containing 1000 mg/L of the element. The calibration curve for arsenic or sulfur was established by plotting the linear relationship between the peak intensities against the concentration of the element in the standard solutions. The calibration curves were obtained each time prior to analyzing a batch of aqueous samples. To ensure the method accuracy, a calibration check was done every 10 samples by measuring a known standard solution. The method has a detection limit of approximately 5 μ g/L for arsenic and 30 μ g/L for sulfur. The matrix of the eluent solution (mobile phase) was the same as that used in the leaching experiments.

The reported results for the total dissolved arsenic and sulfur were the average of the three replicated analyses. The relative standard deviation (RSD) was calculated by dividing the standard deviation by the average of the three replicates. The RSD was consistently negligible for arsenic measurement. But the RSD for sulfur was occasionally high, and a re-calibration had to be performed. To increase the accuracy of the sulfur detection, the argon gas purging time before starting the analysis was doubled and the rinsing time after each reading was increased.

• Determination of arsenic and sulfur speciation

The aqueous samples collected on day 5 and 30 under different leaching conditions were also analyzed by ion chromatography (Dionex ICS-1100, Thermo Fisher Scientific, USA) to determine the concentrations of different arsenic and sulfur species. The IC used was equipped with an electrical suppressor, an analytical column (Dionex IonPac AS22 Fast column-Thermo Fisher Scientific, USA), a guard column. The separated arsenic and sulfur species were detected by an electrical conductivity detector (DS6 Heated Conductivity Cell), which measures the conductance of each ions. The eluent solution (mobile phase) was made by diluting 0.45 M carbonate and 0.14 M bicarbonate (Thermo Fisher Scientific, USA) by 100 times and used at a flow rate of 1.2 mL·min⁻¹. The instrument detection limit was 10 μ g/L. Prior to each analysis, the sample was filtered using a 0.45 μ m syringe filter.

The arsenic species detected were arsenite (III) and arsenate (V). The sulfur species detected were thiosulfate ($S_2O_3^{2-}$), sulfite (SO_3^{2-}), and sulfate (SO_4^{2-}). The standard solutions for each species were prepared from a single ion standard stock solution containing 100 mg/L of the species. The calibration curve for each species was constructed by plotting the linear relationship between the peak area against the concentration in the standard solution. Blank and standard solutions were analyzed at the beginning and end of each batch of samples to ensure the accuracy of the method.

The retention times for sulfite and sulfate in the standard solutions were very close on the IC chromatogram, both of which were at about 5.6-5.8 minutes. Because of the similar retention times, all attempts to separate their peaks by changing the analysis parameters failed. Only one peak at 5.6-5.8 minute was obtained in almost all chromatograms. Sulfite is unstable and difficult to determine due to its rapid oxidation to sulfate (Druschel et al., 2003; Fernandez et al., 1996; Greenwood and Earnshaw, 1997). Therefore, the concentrations calculated from this retention time were assigned to sulfate.

4.3 Research methods for Objective II

4.3.1 Experimental design

To derive a kinetic equation to describe arsenic release as a function of different factors (Objective II-a), a kinetic model was applied to fit the experimental data collected from the leaching

experiments shown in Table 4.1. The kinetic equation derived was used to relate the rate of arsenic release from amorphous As_2S_3 to pH, dissolved oxygen concentration, and temperature. The ratelimiting steps were then revealed by analysis of reaction orders with respect to each parameter and the activation energy (Objective II-b). To support the proposed mechanism (Objective II-c), the evolution of the solid surface properties during leaching, in particular, the formation of elemental sulfur on the solid surfaces, was investigated using SEM-EDX. In addition, the presence of elemental sulfur on the solid surfaces was verified by CS_2 washing of the solids.

4.3.2 Kinetics modeling

The progressive-conversion and shrinking core models (SCMs) are the most common kinetic models used for modelling leaching kinetics (Levenspiel, 1999; Wen, 1968). However, these models are not always suitable to describe the leaching kinetic data. A general model applied by (Bouffard and Dixon, 2007) was used in the present study to relate the fraction of arsenic released from As_2S_3 as a function of leaching time.

The general model is expressed as Eq. (4-1) in a differential form

$$\frac{\mathrm{dx}}{\mathrm{dt}} = \frac{(1-x)^{\varphi}}{\tau} \tag{4-1}$$

By integrating this equation, the model can be expressed as Eq. (4-2).

$$1 - x = \begin{cases} \exp\left(\frac{-t}{\tau}\right) & @ \varphi = 1 \\ \\ \left(1 - (1 - \varphi)\frac{t}{\tau}\right)^{\frac{1}{1 - \varphi}} & @ \varphi \neq 1 \end{cases}$$

$$(4-2)$$

In Eqs. (4-1) and (4-2), x is the weight fraction of the total arsenic released from As_2S_3 and t (days) is the leaching time. φ is a topological exponent, one of the model parameters that need to be determined. τ (days) is the timescale of the reaction, which is given by Eq. (4-3).

$$\frac{1}{\tau}t = kt = \frac{1 - (1 - x)^{(1 - \varphi)}}{1 - \varphi}$$
(4-3)

Where k is defined as the apparent rate constant, which is a function of proton concentration ($[H^+]$ in mol/L), dissolved oxygen concentration ($[O_2]$ in ppm), and temperature (T in kelvin). This function is shown in Eq. (4-4), where a and b are the reaction orders with respect to proton concentration and dissolved oxygen concentration, k_{ref} is the reaction rate constant at the reference temperature T_{ref} , and E_a is the activation energy of the leaching reaction calculated using the Arrhenius equation. Finally, the kinetic equation is expressed as Eq. (4-5)., which relates the cumulative arsenic released (x, ranging from 0 to 1) to the proton concentration, the dissolved oxygen concentration, and temperature.

$$k = \frac{1}{\tau} = k_{(ref)} \exp\left(\frac{E_a}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right) [H^+]^a [D0]^b$$
(4-4)

$$x = 1 - \left\{1 - (1 - \phi)k_{ref} \exp\left[\frac{E_a}{R}(\frac{1}{T_{ref}} - \frac{1}{T})\right](H^+)^a (DO)^b t_{days}\right\}^{(\frac{1}{1 - \phi})}$$
(4-5)

Overall, the kinetic equation contains five parameters that need to be determined: k_{ref} , two reaction orders (a and b), the activation energy (Ea), and the topological exponent (ϕ). They were determined by the method of non-linear least squares regression. Starting from a set of initial values and by iteration, the method finds the optimal set of parameters by minimizing the sum of the squared difference between an observed extraction value and the fitted value provided by Eq. (4-5). The method was applied using the Solver feature of Microsoft Excel in this study. For any non-linear regression problem, it is possible that the method does not converge or converge to a local minimum instead of the global minimum. Therefore, the choice of initial values is crucial. In this study, the classic shrinking core models were used to obtain these initial values (more details in the result chapters).

4.3.3 Characterization of solid surface properties

• Analysis of solid surfaces by SEM-EDX

To study the surfaces of the leaching residues by SEM-EDX, dried powder samples collected from the leaching experiments were placed on pin-type stubs with double-sided carbon adhesive. The samples were then coated with carbon/gold by means of a high-vacuum thermal evaporation technique to make the surface conductive and minimize surface charging. The images were taken using the secondary electron (SE) imaging mode with a FEI Quanta 650 SEM-EDX. The equipment was operated at 20 kV to obtain sufficient secondary electrons for imaging and the working distance was maintained at 10 mm.

• Elemental sulfur removal by CS2

To further verify the presence of elemental sulfur on the leaching residue surfaces and evaluate its influence on the solid dissolution behavior, a leaching test was conducted at pH 8.0, DO 8.3 ppm and 50 °C using the same amorphous As_2S_3 sample described in Section 4.2.2. The test was paused at about 60% of arsenic extraction. The solid residue was collected, dried and washed with CS_2 (99.9%, Sigma-Aldrich) for 1 h at room temperature to remove any possible elemental sulfur formed. The washed solid residue was dried and then placed back into the leaching reactor for resumed leaching. The results on arsenic release were then compared with the case without CS_2 washing.

4.4 Research methods for Objective III

The degree of crystallinity is considered to be a major factor influencing the arsenic and sulfur release behavior. To assess the effect of the degree of crystallinity on the dissolution of arsenic trisulfide, the natural crystalline form of arsenic trisulfide, known as orpiment, was used in the leaching experiments. The mineral was supplied by Ward's Science in Nevada. The same reagent grade chemicals mentioned in Section 4.2.2 were used in the experiments.

For comparison purposes, the experimental design and execution, the data collection and interpretation, and the reporting of research findings are structured in a similar way to the case of the amorphous arsenic trisulfide (As_2S_3) mentioned in Sections 4.2 and 4.3. Firstly, a series of

leaching tests was carried out to quantify the effect of various parameters on the rate and speciation of arsenic and sulfur release from crystalline orpiment (Objective III-a). The experimental design was the same as shown in Table 4.1. Then the experimental data from the leaching experiments were analyzed to derive a kinetic equation, from which the reaction mechanism was revealed (Objective III-b). Finally, the kinetics and mechanisms of arsenic release from amorphous and crystalline orpiment were compared to show their different dissolution behavior (Objective III-c)
Chapter 5: Release behavior of arsenic and sulfur from amorphous As₂S₃

5.1 Introduction

This chapter aims to investigate the effects of various parameters affecting the arsenic and sulfur release from amorphous As_2S_3 . Reactor leaching experiments were carried out to determine the effect of pH, concentration of dissolved oxygen and temperature on the release rate of arsenic and the ratio of the total dissolved arsenic to the total dissolved sulfur. The speciation of arsenic and sulfur under different leaching conditions were analyzed, based on which the possible reaction pathways responsible for the As_2S_3 dissolution were proposed. In addition, the possible effect of carbonate/bicarbonate ions on the arsenic release from As_2S_3 was investigated by performing reactor leaching tests using sodium carbonate for pH control during leaching. The findings enhance our understanding of the key factors controlling the release of arsenic and sulfur and their speciation.

5.2 Leaching parameter control and test method reproducibility

5.2.1 Sample characterization

Figure 5.1 shows the amorphous As_2S_3 particles prepared for the leaching experiments. A representative sample was taken and characterized by X-ray diffraction. Figure 5.2 demonstrates the X-ray diffraction pattern of the solid sample. The presence of a broad peak confirmed the amorphous characteristic of the solid. The chemical composition of the amorphous As_2S_3 sample was obtained by digesting the solid in aqua regia solution in a microwave digestion system, followed by analysis of arsenic and sulfur content by ICP-OES. Table 5.1 shows the average sulfur

and arsenic content obtained from three replicated analyses with the relative standard deviation (RSD). RSD was calculated by dividing the standard deviation by the average of the three replicates. In general, the RSD of the arsenic content was consistently low and therefore the analysis method was deemed precise and reliable. But the RSD of the sulfur content was occasionally high, and a re-calibration had to be performed. The accuracy of sulfur detection by ICP-OES was improved by increasing the argon gas purging time and increasing the rinsing time after each reading.

An SEM image of the raw sample is shown in Figure 5.3. The EDX elemental analysis was used to obtain the arsenic to sulfur weight ratio. Table 5.2 shows that the arsenic to sulfur weight ratios (As/S) obtained by ICP and EDX methods agreed with the theoretical value calculated using the atomic weight of arsenic and sulfur.



Figure 5.1 A sample of amorphous As_2S_3 particles prior to leaching.



Figure 5.2 X-ray diffraction pattern of the amorphous As_2S_3 sample prior to leaching.



Figure 5.3 An SEM image showing the morphology of the amorphous As_2S_3 sample.

Element	Symbol	Content analyzed, %	RSD, %
Arsenic	As	62.21	1.23
Sulfur	S	37.79	1.19
Arsenic/Sulfur	As/S	1.62	-

Table 5.1. Chemical composition of the amorphous As₂S₃ sample analyzed by ICP-OES. RSD represents relative standard deviation derived from three repeated measurements

Table 5.2. Comparison of the arsenic to sulfur weight ratio of As₂S₃ obtained by ICP and EDX method with the theoretical value

Method	ICP	EDX	Theoretical
Arsenic/Sulfur	1.63	1.55	1.56

5.2.2 Reproducibility of the leaching test method

Before conducting the leaching experiments to study the amorphous As₂S₃ dissolution behavior, the reproducibility of the leaching test method was evaluated by running one test in triplicates under the following conditions: pH 8.0, a dissolved oxygen concentration of 8.3 ppm, and 23 °C. Figure 5.4 shows the average percentage of arsenic released from As₂S₃ for the three replicates with the error bars representing the standard error. The standard error of the percentage of arsenic released was obtained by calculating the standard deviation of the three replicates divided by the square root of the number of repeats performed. The average standard error was calculated to be 0.74%. This value was considered to be small and therefore the leaching method was considered to be reproducible. This value was also used as the benchmark for statistically assessing the leaching data. Only an observed difference greater than 0.74% was considered statistically significant.



Figure 5.4 The average percentage of arsenic released from As₂S₃ for the three replicates carried out under the following conditions: pH 8.0, DO 8.3 ppm and 23°C. The error bars represent standard errors calculated from three replicates.

5.2.3 Effect of controlled ORP on arsenic release

ORP was observed to decrease during leaching, which may affect the subsequent interpretation of the reaction kinetics. Therefore, the use of hydrogen peroxide was considered as an option to maintain a constant potential during leaching. Figure 5.5 shows the effect of hydrogen peroxide (H₂O₂) addition on the arsenic release from amorphous As₂S₃. The ORP was maintained at 250 mV, which is within the typical range that could be encountered in a mine waste rock environment. A diluted hydrogen peroxide (3% by volume) solution was used in an attempt to prevent hydrogen peroxide from directly participating in the arsenic release reactions. However, the much higher arsenic release rate in the presence of hydrogen peroxide indicated that it was very likely that the hydrogen peroxide added directly participated as the oxidant in the leaching reaction. Therefore, all subsequent kinetic leaching experiments were conducted without ORP control to avoid any

interference of an added oxidant to the arsenic release kinetics. Other parameters, including pH, DO, and temperature, were fully controlled. Figure 5.6 shows an example of pH, DO and temperature control in the course of leaching. These parameters could be maintained at a constant value during leaching.



Figure 5.5 Comparison of total arsenic release from As_2S_3 leaching between two systems: without ORP control and with ORP controlled by adding diluted hydrogen peroxide (3% by volume) solution. Other parameters: pH 10, DO 8.3 ppm, and 23 °C.



Figure 5.6 An example of pH, DO and temperature control in the course of amorphous As₂S₃ leaching. The leaching conditions were pH 8.0, DO 8.3 ppm, and 23 °C.

5.3 Behavior of arsenic and sulfur release from amorphous As₂S₃ at varying pH

5.3.1 Effect of pH on arsenic and sulfur release rate

• Arsenic release rate

The effect of pH on arsenic release from As₂S₃ was investigated by carrying out a series of leaching tests at different pH. The pH value was adjusted from 6 to 10 by adding sodium hydroxide to the leaching solution. Figure 5.7-A shows the percentage of arsenic dissolved from amorphous As₂S₃ over time at different pH. The arsenic release strongly depended on pH of the leaching media. Increasing pH had a positive effect on the arsenic release. Approximately 25% of arsenic was released after about 30 days of leaching at pH 6, compared with 37% when pH was increased to 7. Moreover, a stronger effect of pH was observed in the more alkaline pH range. By increasing pH from 7 to 8, the arsenic release increased by 15% in comparison with a 37% increase from pH 8 to 9. The most pronounced effect was observed at pH 10, at which 90% of arsenic was dissolved after about 20 days of leaching.

The release of arsenic ions from the attack of As_2S_3 surface by hydroxyl groups has been reported in the literature. As_2S_3 is shown to have a layered S-As-S structure, where arsenic atoms are located in the interlayer space between sulfur atoms (Mamedov and Mikhailov, 1997). As a result of hydration and the presence of hydroxide ions in the environment, hydroxyl groups can be developed on the surface of the arsenic sulfide. Mamedov and Mikhailov (1997) proposed a solidliquid interaction between As_2S_3 surface and OH⁻ groups through a fast intermediate stage of adsorption of hydroxide groups. The adsorption of hydroxide ions onto the solid surface sites renders the solid surface more negatively charged (Hsieh and Huang, 1991). As a result of bond polarization, arsenic-sulfur interstitial bonds become weaker (Furrer et al., 1986) (Eq. (5-1)). Then a slower chemical reaction on the solid surfaces results in arsenic release as arsenite (III) ions (AsO_3^{3-}) into the environment (Eq. (5-2)) (Darban et al., 2011). This may explain the observed effect of pH on the arsenic release (Figure 5.7-A). Increasing the leaching pH resulted in a higher concentration of OH⁻ groups, thereby accelerating the dissolution of As₂S₃.

$$OH^{-} + As_2S_3 \xrightarrow{Fast} OH^{-}...As_2S_3$$
(5-1)

$$As_2S_3 + 6OH^- \rightarrow AsO_3^{3-} + AsS_3^{3-} + 3H_2O$$
 (5-2)

Total dissolved arsenic to total dissolved sulfur ratio

The stoichiometry of a reaction reveals key information on the leaching mechanism. The ratio of the total dissolved arsenic to the total dissolved sulfur was calculated from the ICP-OES results and compared with the theoretical arsenic to sulfur ratio in the As_2S_3 structure. Figure 5.7-B demonstrates the total dissolved arsenic to the total dissolved sulfur ratio at different pH for the amorphous As_2S_3 dissolution. The arsenic to sulfur ratio was larger than the stoichiometric value of 1.6 when pH was at 8 and below. Further increases in pH to above 8 resulted in the arsenic to sulfur ratios being closer to the theoretical value.



Figure 5.7 Effect of pH on A) total arsenic released from amorphous As₂S₃ orpiment and B) the ratio of total dissolved As to total dissolved S released from 0 amorphous As₂S₃ at DO 8.3 ppm, and 23 °C. Dashed line represents the stoichiometric As/S ratio in As₂S₃.

When the calculated ratio was different from the theoretical value of 1.6, incongruent leaching was considered to have occurred. Incongruent dissolution of arsenic minerals has been reported previously, where the ratio of arsenic to other elements, such as sulfur, iron and copper, in aqueous solution was different from their theoretical ratios in the mineral structure (Eary, 1992; Smedley and Kinniburgh, 2002; Weissberg et al., 1966). Incongruent dissolution is usually attributed to the formation of secondary phases and/or precipitates as the reaction products (Rimstidt et al., 1994). Chemical zonation, nonhomogeneous defects or impurities within the solid have also been proposed as the reasons for incongruent leaching (Cama et al., 2000).

5.3.2 Arsenic and sulfur speciation at different pH

• Arsenic species

Speciation of arsenic in the aqueous phase resulting from mineral leaching will give valuable information in those regards (Suess and Planer-Friedrich, 2012a). Arsenite $(AsO_3^{3-}, +3 \text{ oxidation})$

state) and arsenate (AsO4³⁻, +5 oxidation state) are the commonly known inorganic arsenic species. A range of more complex species can predominate in aqueous sulfidic systems, such as thioarsenite and thioarsenate species (Fisher et al., 2008; Suess and Planer-Friedrich, 2012). They can be mono- (AsO_3S^{3-}) , di- $(AsO_2S_2^{3-})$, and trithioarsenate (AsOS3³⁻), produced as a result of arsenic sulfides leaching at near neutral to more alkaline conditions (Stauder et al., 2005).

To determine the effect of pH on the arsenic and sulfur speciation in the aqueous phase, amorphous As₂S₃ leaching was carried out at varying pH (DO 8.3 ppm and 23 °C). Aqueous sampling was done on day 5 and day 30 to assess the effect of leaching time on arsenic and sulfur speciation. Figure 5.8-A shows the predominant arsenic species detected on day 5 of leaching at increasing pH. The corresponding total arsenic released was also plotted for reference. At pH 6, arsenite (III) was the only arsenic species present in the aqueous phase. By increasing pH towards more alkaline conditions, both arsenite (III) and arsenate (V) were detected. The proportion of arsenate (V) increased at higher pH values.

Figure 5.8-B shows the predominant arsenic species detected on day 30 of leaching at increasing pH. For all pH tested, increasing the leaching time from 5 to 30 days increased the proportion of arsenate (V). For example, at pH 6, arsenate (V) was absent in the leachate on day 5 but accounted for 15% of the total arsenic released on day 30. More importantly, similar to the results for day 5, the proportion of arsenate (V) increased at increasing pH. This could be attributed to a faster oxidation of arsenite (III) to arsenate (V) with increasing pH, which is consistent with the published results.



Figure 5.8 Total arsenic dissolved and proportion of different arsenic species released from leaching of amorphous As₂S₃ at different pH, DO 8.3 ppm and 23 °C: A) on day 5 day of leaching; B) on 30 day of leaching.

Studies on the oxidation of orpiment, realgar and arsenopyrite at various pH have shown the significant dependency of arsenic speciation on pH (Lengke and Tempel, 2001, 2002, 2003; Suess and Planer-Friedrich, 2012b). In the pH range of 6.8 to 8.2, arsenite (III) oxyanions were reported as the predominant species from orpiment oxidative dissolution (Lengke and Tempel, 2002). The dominance of arsenate (V) was observed in the alkaline leaching of arsenopyrite and orpiment (Suess and Planer-Friedrich, 2012a). The oxidation of arsenite (III) to arsenate (V) was accelerated by increasing the system pH (Süß, 2011).

• Sulfur Species

The previous studies have shown that the oxidation of pyrite and arsenopyrite in different leaching conditions produces elemental sulfur and a range of intermediate sulfur species (Asta et al., 2010; Corkhill and Vaughan, 2009; Suess and Planer-Friedrich, 2012a; Tu et al., 2017). Similarly, a diversity of intermediate sulfur species, along with elemental sulfur, has also been detected in the oxidation of other sulfide minerals, such as chalcopyrite, pyrite, and sphalerite (Asta et al., 2010;

Rimstidt et al., 1994; Suess and Planer-Friedrich, 2012a). These intermediates include sulfide (HS⁻), thiosulfate ($S_2O_3^{2^-}$), sulfite ($SO_3^{2^-}$), polythionates ($S_nO_6^{2^-}$), and sulfate ($SO_4^{2^-}$) (Druschel et al., 2003; Floroiu et al., 2004; Lengke, 2001; Suess and Planer-Friedrich, 2012a). Identification of intermediate sulfur species is important for understanding how these reactions proceed to release the final products to the surrounding environment.

The sulfur speciation in the aqueous leachates obtained from the amorphous As_2S_3 dissolution at different pH (DO 8.3 ppm, 23 °C) was analyzed using ion chromatography (IC). The retention times for sulfite and sulfate in the standard solutions were very close on the IC chromatogram, both of which were at about 5.6-5.8 minutes. Because of the similar retention times, all attempts to separate their peaks by changing the analysis parameters failed. Only one peak at 5.6-5.8 minute was obtained in almost all chromatograms. Sulfite was assumed to be unstable and was rapidly oxidized to sulfate. Therefore, the concentrations calculated from this retention time were assigned to sulfate.

Figure 5.9-A demonstrates the effect of pH on the total dissolved sulfur and the proportion of different sulfur species on day 5 of leaching. The total dissolved sulfur increased with increasing pH; the magnitude of the increase was more pronounced at higher pH. For all pH tested, thiosulfate and sulfate were the predominant sulfur species, with the latter having a much lower proportion. The proportion of the two species did not seem to change with pH. Figure 5.9-B shows the total dissolved sulfur and the proportion of different sulfur species on day 30 of leaching. Increasing the leaching time from 5 to 30 days led to a decrease in the proportion of thiosulfate and an increase in the proportion of sulfate, suggesting a conversion of thiosulfate to sulfate. However, the

conversion pathways were expected to depend on the solution conditions and may involve a series of other sulfur intermediates. The possible chemical reaction pathways responsible for the release and formation of different sulfur intermediates were subsequently proposed.



Figure 5.9 Total sulfur dissolved and proportion of different sulfur species released from leaching of amorphous As₂S₃ at different pH , DO 8.3 ppm, and 23 °C: A) on day 5 of leaching; B) on 30 day of leaching.

5.4 Proposed reaction pathways for amorphous As₂S₃ dissolution

5.4.1 Primary arsenic and sulfur release reaction

Arsenic and sulfur speciation analysis showed that arsenite (III) and arsenate (V) were the arsenic species and that thiosulfate and sulfate ions were the main sulfur species produced from As_2S_3 dissolution. We proposed a two-step process that involves a series of primary and secondary reactions leading to the production of different arsenic and sulfur species. The proposed primary reactions are shown as Eq. (5-3) and Eq. (5-4). Via the primary reactions, arsenic is released as arsenite (III) and sulfur is released as thiosulfate.

$$2As_2S_3 + 6O_2 + 9H_2O = 4H_3AsO_3 + 3S_2O_3^{2-} + 6H^+$$
(5-3)

$$2As_2S_3 + 6O_2 + 9H_2O = 4H_2AsO_3^{-} + 3S_2O_3^{2-} + 10H^+$$
(5-4)

Eq. (5-3) was proposed for the dissolution of As_2S_3 in more acidic to neutral environments, where H_3AsO_3 is the predominant arsenite (III) species based on the Pourbaix diagram (Figure 2.4). Eq. (5-4) shows that by increasing the basicity of the system, $H_2AsO_3^-$ would be the predominant arsenite (III) species. For both reactions, the proton concentration would increase as a result of the reactions. To observe the pH trend during leaching, a leaching experiment was conducted at an initial pH of 6.0 with no pH control during leaching (DO 8.3 ppm and 23 °C). Figure 5.10 shows a pH drop during As_2S_3 dissolution, indicating that acid was generated. pH eventually decreased to a level at which arsenic release ceased.



Figure 5.10 pH change as a function of time in amorphous As₂S₃ dissolution, initial pH 6.0, DO 8.3 ppm and 23 °C.

5.4.2 Secondary arsenic oxidation and sulfur transformation reactions

We proposed that arsenite (III) produced from the primary reactions is partially converted to arsenate (V) via the secondary oxidation reactions (Eqs. (5-5), (5-6) and (5-7)). These reactions are the same as proposed by Yu et. al (2007). The extent to which these reactions occur depends on the leaching conditions. The speciation results (Figure 5.8) showed that at all pH tested, the proportion of arsenate (V) increased as the leaching time was extended, suggesting the gradual oxidation of arsenite (III) to arsenate (V) during leaching. For the same leaching time, the presence of a higher proportion of arsenate (V) in the leachate at higher pH was indicative of a faster oxidation of arsenite (III) to arsenate (V) in more alkaline environments.

$$2H_3AsO_3 + O_2 \rightarrow 2H_2AsO_4^- + 2H^+$$
 (5-5)

$$2H_3AsO_3 + O_2 \rightarrow 2HAsO_4^{2-} + 4H^+$$
(5-6)

$$2H_2AsO_3^- + O_2 \rightarrow 2HAsO_4^{2-} + 2H^+$$
(5-7)

• Sulfur transformation

Thiosulfate was released from As_2S_3 as the initial kinetically stable sulfur intermediate. However, thiosulfate is thermodynamically unstable and would subsequently convert to different sulfur species. The conversion was proposed to occur via two pathways: oxidation (Eqs. 5-8a-d) and disproportionation (Eq. (5-9)), depending on the solution conditions. When the experimental pH was above 8, the total arsenic to total sulfur ratio in the aqueous phase was the same as the stoichiometric value in the As_2S_3 structure (Figure 5.7-B). This result suggested that the dissolved

arsenic and sulfur remained in the aqueous phase as soluble species and that no solid elemental sulfur was produced. Therefore, we proposed that thiosulfate conversion occurred via the oxidation pathway. In other words, thiosulfate underwent a series of oxidation reactions to polythionates $(S_nO_6^{2-})$ and finally to sulfate, the thermodynamically most stable species. These oxidation reactions have been proposed by other researchers (Lengke and Tempel, 2001; Xu and Schoonen, 1995). The unidentified sulfur species shown in Figure 5.9 may include a diversity of sulfur intermediates that we were unable to measure.

$$4S_2O_3^{2-} + O_2 + 2H^+ \rightarrow S_4O_6^{2-} + H_2O$$
(5-8a)

$$S_4O_6^{2-} + S_2O_3^{2-} \rightarrow S_5O_6^{2-} + SO_3^{2-}$$
 (5-8b)

$$S_5O_6^{2-} + S_2O_3^{2-} \rightarrow S_6O_6^{2-} + SO_3^{2-}$$
 (5-8c)

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$$
 (5-8c)

In contrast, when the experimental pH was at 8 and lower, the total arsenic to total sulfur ratio in the aqueous phase was higher than the stoichiometric value in the As_2S_3 structure. The ratio deviated further from the stoichiometric value when pH was lowered. In other words, more elemental sulfur was produced and precipitated out of the solution onto the mineral surfaces, which reduced the total amount of soluble sulfur present in the leachates. This result suggested that the disproportionation pathway is favored at lower pH. In this pathway, thiosulfate generated from the primary reaction disproportionated into sulfite and elemental sulfur in the presence of protons, as shown by Eq. (5-9). Sulfite was rapidly oxidized to sulfate in the presence of oxygen. This process has been reported by Basu and Schreiber (2013).

$$S_2O_3^{2-} + H^+ = HSO_3^{-} + S^0$$

5.5 The role of oxygen in the arsenic and sulfur release from amorphous As₂S₃

5.5.1 Effect of DO on arsenic and sulfur release rate

Based on the primary reactions proposed above, arsenic release in the form of arsenite (III) ions would be accelerated by increasing dissolved oxygen (DO) concentration. Further oxidation of arsenite (III) to arsenate (V) would also be accelerated via the secondary reactions proposed. To determine the dependency of arsenic and sulfur release on the DO concentration, a series of leaching experiments was carried out at different DO levels at pH 8 and 23 °C. pH 8 was chosen because the behavior of sulfur and arsenic is more complex at this pH value. The DO level was adjusted from 0 to 8.3 ppm by varying the ratio of pure oxygen to nitrogen gases. A DO meter was used to continuously measure the DO concentration during leaching.

• Arsenic release rate

Figure 5.11-A shows the total arsenic released from amorphous As_2S_3 versus leaching time at different levels of DO. Higher levels of arsenic release were observed at elevated concentrations of dissolved oxygen. From the primary and secondary reactions proposed, increasing DO concentration would drive the reaction in the forward direction. The total arsenic release reached approximately 28% after about 30 days of leaching at 2.0 ppm of dissolved oxygen. When DO was increased to 8.3 ppm, 50% of arsenic was released. Lengke and Tempel (2003, 2001) reported

that the dependency of arsenic release on DO concentration in the oxidative dissolution of orpiment and realgar.



Figure 5.11 Effect of DO on A) total arsenic released from amorphous As₂S₃ and B) the ratio of total dissolved As to total dissolved S released from amorphous As₂S₃ at pH 8, and 23 °C. Dashed line represents the stoichiometric As/S ratio in As₂S₃.

However, the system in which oxygen was removed also showed the release of arsenic from As_2S_3 . It has been reported that arsenic can be dissolved from As_2S_3 under N_2 sparging or in anoxic conditions, such as in groundwaters (Floroiu et al., 2004; Kim et al., 2000). Floroiu et al. (2004) suggested H_3AsO_3 and $H_2As_3S_6^-$ as the possible species produced in anoxic systems (Eqs.(5-10)) and (5-11)). The presence of dissolved arsenic mainly as arsenite (III) in groundwaters where oxygen concentration is usually close to anaerobic conditions has been reported in different studies (Akoitai, 2000b; Andrade, 2006).

$$As_2S_3 + 6H_2O \rightarrow 2H_3AsO_3^0 + 3HS^- + 3H^+$$
 (5-10)

$$2As_2S_3 + 3H_2O = H_3AsO_3 + H_2As_3S_6 + H^+$$
(5-11)

Total dissolved arsenic to total dissolved sulfur ratio

Figure 5.11-B shows the ratio of the total dissolved arsenic to the total dissolved sulfur versus time at different DO levels. The ratio was above the theoretical value of 1.6 in the experiments with dissolved oxygen, suggesting that elemental sulfur was produced and precipitated out of the solution. By increasing the DO level, the ratio moved closer to the theoretical value, indicating that the production of elemental sulfur occurred to a lesser extent. As shown previously in Eq. (5-9), thiosulfate disproportionation produces elemental sulfur. By decreasing the DO concentration, this disproportionation reaction was more favored than the oxidation pathway, leading to more elemental sulfur being generated. This can explain the total dissolved arsenic to total dissolved sulfur ratio deviating more from the theoretical value when the DO concentration was lowered. In other words, the oxidation pathway (Eqs. (5-8a-d)) became increasingly important with increasing DO concentration, resulting in the total arsenic to total sulfur ratio approximating the theoretical value.

5.5.2 Arsenic and sulfur speciation at different DO

• Arsenic species

Figure 5.12-A shows the arsenic speciation at increasing levels of dissolved oxygen on day 5 of leaching. The total arsenic released was also plotted for comparison. In the absence of dissolved oxygen, arsenite (III) was observed as the dissolved arsenic species and no arsenate (V) was detected in the solution. Arsenite (III) and arsenate (V) were detected as the soluble arsenic species in the presence of DO, with the latter present in higher proportions with increasing DO

concentration. This could simply be explained by the arsenic secondary reaction being driven in the forward direction at higher DO concentrations (Eqs. (5-5), (5-6) and (5-7)), resulting in more arsenite (III) being oxidized to arsenate (V). When the leaching time was extended from 5 to 30 days (Figure 5.12-B), at all DO levels tested, the proportion of arsenate (V) increased. This could be attributed to more arsenite (III) being oxidized to arsenate (V) when the leaching time was extended.



Figure 5.12 Total arsenic dissolved and proportion of different arsenic species released from leaching of amorphous As₂S₃ at different DO, pH 8.0 and 23 °C: A) on day 5 day of leaching; B) on 30 day of leaching.

• Sulfur species

Figure 5.13-A shows the concentration of total dissolved sulfur and the proportion of different soluble sulfur species on day 5 of leaching at different DO levels. An increase in the DO concentration caused more sulfur to be released into the aqueous phase, supporting the role of oxygen as the oxidant for oxidative dissolution of As_2S_3 . Thiosulfate was shown to be the dominant sulfur species at all DO levels. Sulfate was detected in small proportion at the highest DO level tested. However, by increasing the leaching time to 30 days (Figure 5.13-B), sulfate was detected

at all DO levels, with the highest proportion at the highest DO level. These experimental results agree with the proposed secondary sulfur transformation reactions (Eqs. (5-8a-d)), which support that increasing DO concentration is favorable for thiosulfate oxidation to sulfate. For the oxygen removed test, a very small amount of sulfate was also detected to be present in the solution. This could be caused by the introduction of a small amount of DO in the sample dilution and IC analysis process, both performed in an environment open to the atmosphere. In the absence of dissolved oxygen, the total dissolved arsenic to total dissolved sulfur ratio was approximately the stoichiometric value, suggesting that no elemental sulfur was formed.



Figure 5.13 Total sulfur dissolved and proportion of different sulfur species released from leaching of amorphous As₂S₃ at different DO, pH 8.0 and 23 °C: A) on day 5 of leaching; B) on 30 day of leaching.

5.6 Behavior of arsenic and sulfur release from amorphous As₂S₃ at varying temperature

5.6.1 Effect of temperature on arsenic and sulfur release

• Arsenic release rate

The effect of temperature on the dissolution of amorphous As_2S_3 was investigated by conducting the leaching experiments at different temperature (pH 8 and DO 8.3 ppm). Figure 5.14-A shows

that an increase in temperature accelerated arsenic release from As_2S_3 . Approximately 42% of arsenic was dissolved at 23 °C after 25 days of leaching in comparison with a near complete dissolution at 50 °C over the same leaching period. The significant effect of temperature on arsenic release with oxygen as the oxidant has been observed in the oxidative leaching of different arsenic sulfide, such as arsenopyrite (McKibben et al., 2008; Yu et al., 2007), enargite (Lattanzi et al., 2008), orpiment (Lengke and Tempel, 2002), and realgar (Lengke and Tempel, 2003). A surface reaction mechanism has been used to explain the effect of temperature on the arsenic release behavior. Increasing the leaching temperature results in an increase in the attack of As_2S_3 surface by leaching reactants (here as OH⁻), thereby accelerating the chemical reactions on the solid surfaces (Brady and Walther, 1990; Floroiu et al., 2004).



Figure 5.14 Effect of temperature on A) total arsenic released from amorphous As₂S₃ and B) the ratio of total dissolved As to total dissolved S released from amorphous As₂S₃ at pH 8, and DO 8.3 ppm. Dashed line represents the stoichiometric As/S ratio in As₂S₃.

Total dissolved arsenic to total dissolved sulfur ratio

Figure 5.14-B shows the total dissolved arsenic to the total dissolved sulfur ratio for amorphous As_2S_3 dissolution versus time at different leaching temperature. At all temperatures tested, the ratio

was higher than the theoretical value of 1.6. This result could be explained by the disproportionation of thiosulfate to elemental sulfur (Eq. (5-9)), which precipitated out of the aqueous phase, leading to a decrease in the concentration of the total dissolved sulfur. Furthermore, an increase in temperature was associated with a further deviation from the theoretical value. This suggests that thiosulfate disproportionation to elemental sulfur occurred to a greater extent at a higher temperature.

5.6.2 Arsenic and sulfur speciation at different temperatures

• Arsenic species

Figure 5.15-A demonstrates the effect of leaching temperature on arsenic speciation in the leaching solution. The total dissolved arsenic was plotted for reference. On day 5 of leaching, arsenite (III) and arsenate (V) were detected as the soluble arsenic species, with the former accounting for a larger percentage. Arsenite (III) released from the primary reactions was partially oxidized to arsenate (V) via the secondary reactions (Eqs. (5-5), (5-6) and (5-7)). However, the percentage of arsenite (III) decreased at higher temperatures, indicating that the oxidation of arsenite (III) to arsenate (V) was enhanced by increasing the temperature. Figure 5.15-B shows that extending the leaching time from 5 to 30 days resulted in a higher proportion of arsenate (V) at the same pH, indicating that more arsenite (III) was oxidized to arsenate (V).



Figure 5.15 Total arsenic dissolved and proportion of different arsenic species released from leaching of amorphous As₂S₃ at different T, pH 8.0 and DO 8.3 ppm: A) on day 5 day of leaching; B) on 30 day of leaching.

• Sulfur species

Total dissolved sulfur concentration and sulfur speciation were also analyzed for all temperatures tested. Figure 5.16-A shows that over a 5-day leaching period increasing the leaching temperature resulted in a higher concentration of sulfur released from As₂S₃ to the aqueous phase. Thiosulfate was detected as the main sulfur species. As temperature was increased, an increasing proportion of sulfate was also detected. Sulfate was generated from the thiosulfate disproportionation reaction, which was accelerated by increasing the leaching temperature. For the same temperature, the disproportionation reaction occurred to a greater extent by extending the leaching time from 5 to 30 days (Figure 5.16-B). A similar dependency of sulfur speciation on temperature was observed on day 30 of leaching. Specifically, 18% of total dissolved sulfur was detected as sulfate at 23 °C. The proportion of sulfate increased to 30% as temperature was increased to 50 °C, suggesting a higher proportion of thiosulfate disproportionated to sulfate and elemental sulfur. This result is consistent with the increasing total arsenic to total sulfur ratio observed (Figure 5.14-B).



🗆 Thiosulfate 🗆 Sulfate 🏛 Unidentified Sulfur 🔳 Sulfur Release 🗦 Thiosulfate 🗆 Unidentified Sulfur 🔳 Sulfur Release

Figure 5.16 Total sulfur dissolved and proportion of different sulfur species released from leaching of amorphous As₂S₃ at different T, pH 8.0 and DO 8.3 ppm: A) on day 5 of leaching; B) on 30 day of leaching.

5.7 Effect of bicarbonate/carbonate ions on arsenic release from As₂S₃

Arsenic sulfide minerals are usually found in mine rocks in association with carbonate minerals such as calcite. The dissolution of carbonate minerals generates carbonate and bicarbonate, which are common ions found in near neutral to alkaline mine water. The possible effect of carbonate/bicarbonate ions on the arsenic release from As₂S₃ was investigated in this study. Reactor leaching experiments were performed using sodium carbonate solution to control pH during leaching. For comparison, all leaching parameters were kept the same as the hydroxide system (pH control by sodium hydroxide): pH from 6.0 to 10.0, temperature from 23 to 50 °C, and DO concentration from 0.0 to 8.3 ppm. Due to the lack of equipment availability no speciation analyses of arsenic and sulfur were performed for the carbonate system.

Figure 5.17-A shows the dissolution behavior of amorphous As₂S₃ at different pH in the presence of carbonate/bicarbonate ions. Arsenic release increased with increasing pH in the presence of carbonate/bicarbonate ions. A complete dissolution was achieved on day 15 at pH 10.0. Over the

same leaching period of 15 days, the cumulative arsenic extraction in the presence of carbonate/bicarbonate was higher than in the hydroxide system, as shown in Figure 5.17-B. The magnitude of the difference was larger as pH was increased to 9 and above. The magnitude of the difference was calculated as the difference in the arsenic release percentage between the carbonate system and the hydroxide system divided by the percentage in the hydroxide system. At the same pH, the concentration of hydroxyl group should be the same, regardless of the presence or absence of carbonate/bicarbonate. Therefore, the contribution of hydroxyl group to arsenic release should be the same.



Figure 5.17 Effect of leaching pH on A) total arsenic released from amorphous As₂S₃ in the carbonate system, B) total arsenic released from amorphous As₂S₃ over a period of 15 days in the presence and absence of carbonate (DO 8.3 ppm and 23 °C). The magnitude of difference between the two systems was also plotted.

The enhanced extraction in the carbonate system was attributed to the formation of arsenic carbonate complexes on the As_2S_3 surface. The presence of carbonate and bicarbonate in solution has been reported to enhance the solubility of arsenic by producing thioarsenic and arsenic-carbonate complexes, such as $As(CO_3)_2$, $As(CO_3)(OH)_2^-$, $AsCO_3^+$, and $As(CO_3)_2(OH)_2^-$ (Henke, 2009; Kim et al., 2002). Kim et al. (2000) attempted to confirm the existence of these arsenic-

carbonate species by ion chromatography. Their results showed the emergence of unique peaks different from those of arsenite (III), arsenate (V), and carbonate, which were assigned to arsenic-carbonate complexes In order to explain the role of carbonate/bicarbonate ions, Eqs. (5-12) - (5-14) were proposed. The carbonate speciation diagram in Figure 5.18 shows that the fraction of carbonate (CO₃²⁻) increases with increasing pH. The larger magnitude of difference observed at higher pH may be attributed to the formation of larger amounts of arsenic-carbonate complexes.

$$2As_2S_3 + 4HCO_3^{-} + 6O_2 + 5H_2O = 4As(CO_3)(OH)_2^{-} + 3S_2O_3^{2-} + 6H^+$$
(5-12)

$$2As_2S_3 + 8HCO_3^{-} + 6O_2 + H_2O = 4As(CO_3)_2(OH)^{2-} + 3S_2O_3^{2-} + 6H^+$$
(5-13)

$$2As_2S_3 + 4CO_3^{2-} + 6O_2 + 5H_2O = 4As(CO_3)(OH)_2^{-} + 3S_2O_3^{2-} + 2H^+$$
(5-14)



Figure 5.18 Carbonate speciation in water as a function of pH.

Subsequent transformation of arsenic-carbonate complexes to the common arsenic oxyanions could also occur through the following reactions (Eqs. (5-15) and (5-16)) (Kim et al., 2000).

$$As(CO_3)(OH)_2 + H_2O = H_3AsO_3 + HCO_3$$
 (5-15)

$$As(CO_3)(OH)_2^{-} + H_2O = H_3AsO_3 + CO_3^{2-} + H^+$$
(5-16)

Figure 5.19-A shows the dissolution behavior of amorphous As_2S_3 at different concentrations of dissolved oxygen in the presence of carbonate/bicarbonate ions. Arsenic release increased with increasing DO in the presence of carbonate/bicarbonate ions. Figure 5.19-B demonstrates the comparison of the total arsenic dissolution on day 15 as a function of dissolved oxygen between hydroxide and carbonate systems. Higher arsenic extraction was observed in the presence of carbonate. The magnitude of the difference slightly increased at higher concentrations of dissolved oxygen, which agrees with the reactions proposed for the carbonate system (Eqs. (5-12), (5-13) and (5-14)). Dissolution of As_2S_3 in an anoxic environment and in the presence of bicarbonate ions was proposed as Eqs. (5-17)–(5-20) (Kim et al., 2000).

$$As_2S_3 + HCO_3^- \rightarrow As(CO_3)^+ + AsS_2^- + HS^-$$
(5-17)

$$As_2S_3 + 2HCO_3^- \rightarrow As(CO_3)_2^- + HAsS_2 + HS^-$$
(5-18)

$$As_2S_3 + HCO_3 + 2H_2O \rightarrow As(CO_3)(OH)_2 + HAsS_2 + HS^- + H^+$$
 (5-19)

$$HAsS_2 + H_2O \rightarrow HAsS_2(OH)^- + H^+$$
(5-20)

Figure 5.20-A shows the dissolution behavior of amorphous As_2S_3 at different leaching temperatures and in the presence of carbonate/bicarbonate ions. Arsenic release increased at elevated temperatures in and it was affected by the presence of carbonate/bicarbonate. Figure 5.20-

B shows that a higher percentage of arsenic was released from As_2S_3 to the aqueous phase in the presence of carbonate. The magnitude of the difference seemed to be more pronounced at higher temperatures. This may be explained by the formation of arsenic-carbonate complexes being more favorable at higher temperatures.



Figure 5.19 Effect of DO level on A) total arsenic released from amorphous As₂S₃ in the carbonate system, B) total arsenic released from amorphous As₂S₃ over a period of 15 days in the presence and absence of carbonate (pH 8 and 23 °C). The magnitude of difference between the two systems was also plotted.



Figure 5.20 Effect of temperature on A) total arsenic released from amorphous As₂S₃ in the carbonate system, B) total arsenic released from crystalline orpiment over a period of 15 days in the presence and absence of carbonate (pH 8 and DO 8.3 ppm). The magnitude of difference between the two systems was also plotted.

5.8 Conclusion

The behavior of arsenic and sulfur release from amorphous As_2S_3 was studied under the following conditions: pH from 6.0 - 10.0, dissolved oxygen concentration from 0.0 - 8.3 ppm, and temperature from 23 - 50 °C. The release rate of arsenic and sulfur increased with pH, DO concentration, and temperature. The presence of carbonate accelerated the rate of arsenic release. The speciation analysis shows that arsenic was first released into the aqueous phase as arsenite (V), which was subsequently oxidized to arsenate (V). The extent of oxidation depends on the solution conditions, as evidenced by increasing proportions of arsenate (V) when pH, DO concentration, and temperature were increased.

In terms of sulfur speciation, thiosulfate was first released as the predominant sulfur species and subsequently converted to sulfate, a thermodynamically more stable species. However, the conversion pathway was found to depend on the solution pH: (1) the disproportionation pathway that converts thiosulfate to sulfate and elemental sulfur at pH 8 and below. Elemental sulfur was precipitated out of the aqueous solution, which could explain the ratio of the total dissolved arsenic to the total dissolved sulfur being higher than the stoichiometric ratio of 1.6. The disproportion is more favored at lower pH, lower DO concentrations and higher temperatures; (2) the oxidation pathway that oxidizes thiosulfate to sulfate when pH was above 8, supported by the total dissolved arsenic to total dissolved sulfur ratio being at the stoichiometric value of 1.6.

Chapter 6: Amorphous As₂S₃ leaching kinetics and mechanism

6.1 Introduction

The dissolution behavior of amorphous As₂S₃ was explained in Chapter 5. It was shown that the leaching conditions including pH, dissolved oxygen concentration, and temperature significantly affected As₂S₃ dissolution. The aim of this chapter was to derive a kinetic equation that describes the rate of arsenic release from amorphous As₂S₃ as a function of pH, dissolved oxygen concentration, and temperature. The rate-limiting steps were then revealed by analysis of reaction orders and the activation energy. To interpret the leaching kinetics and support the proposed mechanism, the evolution of the solid surface properties during leaching, in particular, the formation of elemental sulfur on the solid surfaces, was investigated using SEM-EDX.

6.2 Derivation and interpretation of the kinetic equation

6.2.1 Derivation of the kinetic equation

Using the experimental results of the leaching tests reported in Chapter 5, a kinetic equation was derived by the method of non-linear least squares. This method minimizes the sum of the squares of the difference in arsenic release between an experimental value and a fitted value. The fitted values were obtained using the general model according to Eq. (4-5). The minimization of the sum was achieved by an iterative method, which requires initial values to be assigned to the model parameters. The choice of initial values is crucial, because inappropriate initial values can result in parameter estimates converging to a local minimum rather than the global minimum. The traditional shrinking core models (SCM) are widely used to describe sulfide mineral leaching.

Therefore, the initial values were determined using the SCM chemical reaction-controlled model as Eq. (6-1) (Levenspiel, 1999):

$$\frac{t}{\tau} = 1 - (1 - x)^{\frac{1}{3}} \tag{6-1}$$

In Eq. (6-1), x is the percentage of arsenic released from As_2S_3 , t is the leaching time, and the expression of τ is the same as Eq. (4-4), which includes the reaction order and the activation energy as the model parameters. Table 6.1 shows the initial values assigned to the model parameters derived from the shrinking core model (Eq. (6-1)). With the initial values assigned and by iteration, the set of optimal model parameters was obtained and also shown in Table 6.1, which gave the best fit to the experimental data.

The final kinetic equation derived, in the same format as the general model, is shown as Eq. (6-2). In this equation, the topological factor was 0.85, which is less than 1. Mathematically, this means that the leaching reaction would reach completion. The reaction orders with respect to $[H^+]$ and DO were – 0.28 and 0.51, and the activity energy was 45.6 kJ/mol. These parameters were further explained to uncover the possible rate-limiting steps that control arsenic release. For the convenience of showing the reaction orders and the activation energy, the kinetic equation was rearranged to a linear function, as shown in Eq. (6-3). The slope of this function is defined as the apparent rate constant k, which is a function of proton concentration, DO concentration, and temperature. The capability of this kinetic equation to describe the leaching experimental data was shown below for different pH, DO concentration, and temperature.

Table 6.1 Kinetic model for amorphous As_2S_3 leaching: initial values for the model parameters derived using the SCM model and the optimal values derived for the general model using non-linear least squares method

Model parameter	Topological factor, φ	Reaction order with respect to H^+	Reaction order with respect to DO	Activation energy, E _a (kJ/mol)
Initial value	0.67	- 0.25	0.46	44.0
Optimal value	0.85	-0.28	0.51	45.6

$$\mathbf{x} = 1 - \left\{ 1 + 8.56 \times 10^{-6} \exp\left[\frac{45564}{8.314} \left(\frac{1}{296} - \frac{1}{T_{(K)}}\right)\right] (\mathrm{H}^+)^{-0.28}_{(\mathrm{M})} (\mathrm{DO})^{0.51}_{(\mathrm{ppm})} \mathbf{t}_{(\mathrm{days})} \right\}^{\frac{1}{1-0.85}}$$
(6-2)

1

$$\frac{1 - (1 - x)^{(1 - 0.85)}}{(1 - 0.85)} = 5.73 \times 10^{-5} \exp\left[\frac{E_a}{8.314} \left(\frac{1}{296} - \frac{1}{T}\right)\right] (H^+)^a (D0)^b.t$$
(6-3)

6.2.2 Reaction order with respect to H⁺ concentration

 As_2S_3 leaching experimental data obtained at different pH values were plotted together with the model fitted values derived from Eq. (6-3) at DO 8.3 ppm and 23 °C. Figure 6.1-A shows that the model is capable of describing the leaching data at different pH. The slope of each line represents the apparent rate constant k at a specific proton concentration. To show the reaction order with respect to the concentration of H⁺, the logarithm of the apparent rate constant was plotted versus the logarithm of the H⁺ concentration, as shown by Eq. (6-4).

$$\log k = -0.28 \log(H^{+}) + \log(5.73 \times 10^{-5} (D0)^{0.51})$$
(6-4)

Figure 6.1-B shows that a linear regression yielded a slope of -0.28, which represents the reaction order with respect to H⁺ concentration. The negative sign means that increasing proton concentration leads to a decrease in the apparent rate constant and therefore a decrease in the

arsenic release. Based on the electrochemical theory of sulfide leaching (Li et al., 1992), the value of 0.28 supports that the leaching process is a chemically-controlled rather than a diffusion-controlled reaction. A reaction order close to 1 is indicative of a diffusion-controlled reaction.



Figure 6.1 A) Application of the kinetic model to derive the apparent rate constant at different pH; B) Linear regression between the logarithm of the apparent rate constant and the logarithm of the H⁺ concentration, with the slope representing the reaction order with respect to proton concentration. (DO 8.3 ppm and 23 °C).

6.2.3 Reaction order with respect to dissolved oxygen concentration

Figure 6.2-A plotted the arsenic leaching experimental data at different DO concentration and the model fitted values obtained using Eq. (6-3) at pH 8 and 23 °C. The slope of a line represents the apparent rate constant at a specific DO concentration. The logarithm of these apparent rate constants was then plotted against the logarithm of the DO concentration, as shown by Eq. (6-5).

$$\log k = 0.51 \log(D0) + \log(5.7 \times 10^{-5} (H^{+})^{-0.28})$$
(6-5)

Figure 6.2-B shows that the linear regression gave a slope of 0.51, which represents the reaction order with respect to the dissolved oxygen concentration. The positive sign indicates that increasing dissolved oxygen concentration would increase arsenic release. Similar to the case of

proton concentration, a value of 0.51 consistently supports that arsenic leaching from amorphous As_2S_3 is a chemical reaction-controlled process.



Figure 6.2 A) Application of the kinetic model to derive the apparent rate constant at different DO concentration; B) Linear regression between the logarithm of the apparent rate constant and the logarithm of the DO concentration, with the slope representing the reaction order with respect to DO concentration. (pH 8 and 23 °C).

6.2.4 Activation energy

The general model was applied to describe the arsenic leaching at different temperatures (Figure 6.3-A). The slope of a line represents the apparent rate constant at a specific temperature. The natural logarithm of the apparent rate constant was plotted against the reciprocal of temperature, as shown by Eq. (6-6).

$$\ln k = \frac{E_a}{8.314} \left(\frac{1}{296} - \frac{1}{T} \right) + \ln \left(5.7 \times 10^{-5} (\text{H}^+)^{-0.28} (\text{DO})^{0.51} \right)$$
(6-6)

According to Arrhenius equation, a linear regression gives a slope of - Ea/R. Figure 6.3-B shows that the slope is - 5.48, with the corresponding activation energy (E_a) of 45.6 kJ/mol. The value of the activation energy has important information regarding the reaction mechanism. A lower activation energy (< 20 kJ/mol) typically indicates a diffusion-controlled reaction. A higher

activation energy is indicative of a chemically-controlled reaction (> 40 kJ/mol), which is more sensitive to the temperature change (Lasaga, 1992). An activation energy in between is typically associated with a reaction under a mixed rate control of reaction and diffusion processes. Consistent with the previous conclusions drawn based on the reaction orders, an activation energy of 45.6 kJ/mol supports that a surface chemical reaction was controlling the arsenic release from amorphous As_2S_3 . The oxidation and dissolution of many sulfide minerals have been shown to be surface reaction controlled under conditions encountered in nature (Berner and Holdren, 1977)..



Figure 6.3 A) Application of the kinetic model to derive the apparent rate constant at different temperatures; B) Arrhenius plot showing the logarithm of the apparent rate constant plotted against the reciprocal of temperature, with the slope representing -Ea/R. (pH 8 and DO 8.3 ppm).

6.3 Characterization of solid surface properties in amorphous As₂S₃ leaching

Based on the magnitude of the reactions orders and the activation energy, surface reaction was proposed to be the rate-limiting step in the arsenic release from amorphous As_2S_3 . To further support the proposed mechanism, the morphology and textural features of the reacted particle surfaces during leaching were examined by scanning electron microscopy. Such examination can provide valuable information on the reaction mechanism (Lengke, 2001). A rough and etched
surface is typically associated with a chemical reaction controlled process, whereas a smooth surface can be linked to a diffusion-controlled mechanism (Chen and Brantley, 1998).

The sulfur speciation analysis reported in Chapter 5 showed that thiosulfate was the initial sulfur species released from As_2S_3 surface. Thiosulfate was proposed to subsequently disproportionate to elemental sulfur and sulfate when pH was at 8 or below, resulting in the deviation of the ratio of the total dissolved arsenic to the total dissolved sulfur from the stoichiometric value of 1.6. To investigate the formation of elemental sulfur and its impact on the leaching kinetics, the surface elemental composition of the leaching residues was analyzed by EDX and XRD.

6.3.1 Changes in As₂S₃ surface morphology during leaching

To investigate the evolution of amorphous As_2S_3 surface morphology, the solid leaching residues were collected and characterized by scanning electron microscopy. The leaching conditions investigated were pH 9.0, DO 8.3 ppm, and 23 °C. Figure 6.4 shows the secondary electron images of the amorphous As_2S_3 sample prior to leaching and of the leaching residues corresponding to increasing levels of arsenic release.

By increasing the leaching time and correspondingly arsenic release, the morphology of the amorphous As₂S₃ surfaces changed significantly. Small holes and etch pits developed at the very beginning of leaching and the surface roughness gradually increased as leaching proceeded. Previous studies have found that textural features such as etch pits and cracks created as a result of solid-liquid leaching can reflect the dissolution mechanisms of minerals (Berner and Holdren,

1977; Brantley et al., 1986; Lengke, 2001). The roughness and a large number of etch pits observed on the surface of reacted As₂S₃ supported a chemical reaction mechanism.

Some fine spherical particles smaller than 2 μ m were observed on the surfaces of the leaching residues. These particles had a morphology and shape different from the bulk surfaces. They seemed to be detached from the spots where the etch pits were developed on the bulk surfaces. Fine particles were observed by researchers in the leaching of other sulfides. Douglas et al (1992) investigated the evolution of fine particles during realgar (AsS) leaching. They attributed the evolution of these particles to the transformation of realgar to pararealgar, which has the same chemical composition as realgar but a different crystalline form. Lengke and Tempel (2003) reported the formation of fine particles on the surfaces of the solid residue obtained from the oxidative leaching of amorphous AsS, the composition of which was not studied. Webster (1990) and Eary (1992) reported the formation of etch pits and segregated fine particles on the surface of As₂S₃. This could result in an increase in the available solid surface area, providing more high energy sites for leaching reagents to attack.



Figure 6.4 The secondary electron images of amorphous As_2S_3 leaching residues at varied leaching time corresponding to increasing arsenic release under the following conditions: pH 9.0, DO 8.3 ppm and 23 °C.

6.3.2 Formation of elemental sulfur supported by EDX and XRD analysis

Thiosulfate was proposed to be converted to sulfate via two pathways depending on the solution pH: oxidation and disproportionation. When pH was at 8 or below, thiosulfate disproportionated to elemental sulfur and sulfate, resulting in the deviation of the ratio of the total dissolved arsenic to the total dissolved sulfur from the stoichiometric value. To identify changes in the elemental composition of the solid surfaces and the formation of elemental sulfur, EDX elemental analyses were performed on the representative leaching residues. Two distinct leaching conditions were selected for the analyses: pH 9.0, DO 8.3 ppm and 23 °C; and pH 8.0, DO 8.3 ppm and 50 °C. These conditions were selected because a deviation from the theoretical value was at pH 8 and the most apparent at 50 °C, but absent at pH 9.

Figure 6.5 shows the spots on the unreacted amorphous As_2S_3 surfaces selected for the EDX analysis and the corresponding EDX spectrum obtained for spot 1. Using the EDX spectrum peak intensities, the average arsenic to sulfur ratio by weight of the selected spots was calculated to be 1.55, which is sufficiently close to the theoretical value of 1.6.



Figure 6.5 A) The spots selected for EDX analysis of the unreacted As₂S₃ sample surfaces; B) the EDX spectrum for spot 1 and the averaged arsenic to sulfur ratio.

Figure 6.6 shows the spots selected for the EDX analysis of the leached As₂S₃ collected at pH 9.0, DO 8.3 ppm and 23 °C and the corresponding EDX spectrum obtained for spot 1. Despite the changes in the surface morphology and the development of etch pits, the ratio of arsenic to sulfur remained close to the stoichiometric ratio. In addition, attempts were made to investigate the composition of the fine spherical particles detached from the bulk surfaces. As shown in Figure 6.7, these particles had arsenic to sulfur ratios very similar to the theoretical value, indicating that they have a similar chemical composition to the bulk.

Some uncertainties on these measurements should be noted. The general resolution of the EDX technique is $1-2 \mu m$ in depth. Because of the small sizes of these spherical particles, the possibility of measuring the surfaces beneath them should be considered. Nonetheless, these measurements were consistent with the analysis of the aqueous solution (Figure 5.7-B), which showed that the total dissolved arsenic to the total dissolved sulfur ratio remained close to the stoichiometric ratio during leaching. Therefore, a consistent conclusion could be drawn that there was no elemental sulfur formation at pH 9, i.e., thiosulfate was oxidized to sulfate via the oxidation pathway.



Figure 6.6 A) The spots selected for EDX analysis of the leaching residues collected under the conditions of pH 9.0, DO 8.3 ppm and 23 °C; B) the EDX spectrum for spot 1 and the averaged arsenic to sulfur ratio.



Figure 6.7 Selection of the fine spherical particles labelled as "A" and the spots on the bulk surface labelled as "B" for EDX analysis of the leached As₂S₃ collected at pH 9.0, DO 8.3 ppm and 23 °C (image above). Their EDX spectra and the averaged As/S ratio were shown below.

In contrast, some fine particles with distinct morphology were observed from the secondary electron images of the leaching residue obtained at pH 8 and 50 °C, as shown in Figure 6.8. Figure 6.9 shows the elemental analysis of these particles in comparison with the bulk surfaces of the leaching residue. The results showed that the average arsenic to sulfur ratio of these particles was much lower than the stoichiometric value, supporting the formation of secondary phases enriched in elemental sulfur. These particles did not cover the surface of the amorphous As₂S₃, and therefore

should not act as a barrier to diffusion. This result agrees with the previous conclusion that the arsenic release from As_2S_3 is a chemical reaction-controlled process.

To further confirm the formation of elemental sulfur, XRD analysis was done on the leaching residues collected at pH 8.0, DO 8.3 ppm, and 50 °C. The XRD spectrum of the leaching residue in Figure 6.10 showed a broad peak, confirming the amorphous characteristic of the bulk leaching residue. More importantly, some new peaks were identified, which were matched with elemental sulfur peaks by the XRD Match software. Both EDX and XRD analysis provided consistent results that elemental sulfur was formed in leaching of amorphous at pH 8.0.



Figure 6.8 The secondary electron images of the leaching residue collected after about 80% of arsenic was leached at pH 8.0, DO 8.3 ppm and 50 °C.



Figure 6.9 Selection of the spots on the bulk surface labelled as "A" and the new fine particles labelled as "B" for EDX analysis of the leached As₂S₃ collected at pH 8.0, DO 8.3 ppm and 50 °C (image above). Their EDX spectra and the averaged As/S ratio were shown below.



Figure 6.10 XRD pattern of the solid residues collected from the amorphous As_2S_3 leaching at pH 8.0, DO 8.3 ppm and 50 °C.

6.3.3 Impact of elemental sulfur formation on As₂S₃ leaching

It has been shown by the existing studies that elemental sulfur can act as a barrier to diffusion when it is formed and accumulated on solid surfaces as a uniform and consistent layer, thereby inhibiting further oxidation of the solids (Corkhill and Vaughan, 2009; Cruz et al., 1997; Fernandez et al., 1996). In contrast, a non-uniform elemental sulfur layer is unlikely to act as a diffusion barrier and therefore has no effect on the solid oxidation rate (Mcguire et al., 2001; Mikhlin et al., 2006). The evidences collected in this study point that the latter is the case for amorphous As_2S_3 leaching.

To evaluate the influence of the elemental sulfur produced on the As_2S_3 dissolution behavior, a leaching test was conducted at pH 8.0, DO 8.3 ppm and 50 °C. The test was paused on day 10, which corresponded to about 65% arsenic release. The solid residue was collected and washed with CS₂ to remove any possible elemental sulfur formed. The washed residue was placed back into the leaching reactor for resumed leaching. The results on the arsenic release were then compared with the case under the same leaching conditions but without CS₂ washing.

Figure 6.11 shows an image of the elemental sulfur removed by CS_2 , confirming the generation of elemental sulfur during leaching. Figure 6.11 also compares the arsenic release in the two cases, with and without CS_2 washing. The leaching time at which the leaching test was paused for the sulfur removal by CS_2 is shown by a vertical dashed line in Figure 6.11. The results show that the elemental sulfur removal had no effect on the behavior of arsenic release from amorphous As_2S_3 , confirming that the elemental sulfur formed did not act as a diffusion barrier.



Figure 6.11 The effect of elemental sulfur removal by CS₂ on arsenic release behavior from amorphous As₂S₃, pH 8.0, DO 8.3 ppm and 50 °C.

6.4 Conclusion

A rate law was derived using the general model to describe the arsenic release rate as a function of the proton concentration, the dissolved oxygen concentration, and temperature. The reaction order with respect to the proton concentration was -0.28, suggesting that the arsenic release rate decreases with increasing proton concentration. The reaction order with respect to the dissolved oxygen concentration was 0.51, indicating that increasing the dissolved oxygen concentration accelerates the arsenic release. The activation energy was calculated to be 45.6 kJ/mol. The magnitude of both the reaction orders and the activation energy supports that the rate-limiting step in the arsenic release from amorphous As₂S₃ is the surface chemical reaction.

The SEM and EDX analyses of the solid residues showed that elemental sulfur was absent on the surfaces of the leaching residue collected at pH 9. In contrast, at pH 8, elemental sulfur was shown to form and segregate from the bulk surfaces of the leaching residue. The formation of elemental sulfur from thiosulfate disproportionation reduced the soluble sulfur concentration in the leachate. This can explain the deviation of the total dissolved arsenic to the total dissolved sulfur ratio from the stoichiometric value. The elemental sulfur produced did not act as a barrier to diffusion of reactants, as evidenced by the unresponsiveness of the leaching kinetics to the removal of elemental sulfur.

Chapter 7: Release behavior of arsenic and sulfur from crystalline orpiment

7.1 Introduction

Chapter 5 and Chapter 6 reported the arsenic and sulfur release behavior from poorly crystalline (amorphous) arsenic trisulfide (As_2S_3). The degree of crystallinity is considered to be a major factor influencing the behavior of arsenic and sulfur release. This chapter aims to investigate the effects of various parameters affecting the arsenic and sulfur release from crystalline orpiment. For comparison purposes, the experimental design and execution, the data collection and interpretation, and the reporting of research findings are structured in a similar way to the case of the amorphous arsenic trisulfide (As_2S_3).

Reactor leaching experiments were carried out to determine the effect of pH, dissolved oxygen concentration, and temperature on the release rates of arsenic and sulfur from crystalline orpiment. The speciation of arsenic and sulfur in different leaching conditions were analyzed to understand the possible reaction pathways explaining the orpiment dissolution. The possible effect of carbonate/bicarbonate ions on the arsenic release from crystalline orpiment was investigated by performing reactor leaching tests.

7.2 Leaching parameter control and test method reproducibility

7.2.1 Sample characterization

Figure 7.1 shows an image of the crystalline orpiment (As_2S_3) sample prior to leaching. A representative sub-sample was taken and characterized by X-ray diffraction. The Rietveld

refinement plot in Figure 7.2 shows that the mineral consists of orpiment (As_2S_3) and realgar (As_4S_4). The result of the quantitative phase analysis by Rietveld refinements is given in Table 7.1. The phase content represents the relative percentage of a crystalline phase normalized to 100%. The sample consists of 95% of orpiment and 5% of realgar.

The chemical composition of the crystalline orpiment sample was obtained by digesting the solid in aqua regia solution in a microwave digestion system, followed by analysis of the total arsenic and sulfur content by ICP-OES.

Table 7.2 shows the arsenic and sulfur content of the sample obtained as the average of the three replicated analyses. The relative standard deviation (RSD) was calculated by dividing the standard deviation by the average of the three replicates. In general, the RSD of the arsenic content was consistently low and therefore the analysis method was deemed precise and reliable. But the RSD of the sulfur content was occasionally high, and a re-calibration had to be performed. The re-calibration was done by adjusting the operating parameters of the ICP-OES, such as increasing the argon gas purging time and increasing the rinsing time after each reading. Trace metal contents in the sample were determined by four acid digestion method (HNO₃/HF/HClO₄/HCl), followed by analysis with ICP-OES. The results for trace metal contents are provided in Appendix A.

An SEM image of the sample prior to leaching is shown in Figure 7.3. The EDX elemental analysis was used to obtain the arsenic to sulfur weight ratio. Table 7.3 shows the arsenic to sulfur ratios (As/S) obtained by ICP and EDX analysis agrees with the theoretical value calculated from the atomic weight of arsenic and sulfur.



Figure 7.1 A sample of crystalline orpiment particles prior to leaching.

Mineral	Ideal formula	Phase content, %			
Orpiment	As_2S_3	95			
Realgar	As ₄ S ₄	5			
20		Realgar AsS			
18 -		Orpiment As ₂ S ₃			
stun 12 -					
O 10 -					
nsity 8 -					
- 9 Inte					
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5	10 15 20 25 30 35 40 45 50 5	5 60 65 70 75 80			
	Two Theta (Deg)				

Table 7.1 Qualitative analysis of orpiment by XRD

Figure 7.2 X-ray diffraction pattern of orpiment sample prior to leaching

Element	Symbol	Content analyzed, %	RSD, %
Arsenic	As	61.31	1.12
Sulfur	S	38.08	1.14

 Table 7.2 Chemical composition of the orpiment sample analyzed by ICP-OES. RSD represents relative standard deviation derived from three repeated measurements



Figure 7.3 An SEM image showing the morphology of the unreacted orpiment sample.

Table 7.3 The arsenic to sulfur ratio (by weight) obtained by ICP and EDX methods of the orpiment sample in comparison with the theoretical value

method	ICP	EDX	theoretical
Arsenic/Sulfur	1.54	1.64	1.56

7.2.2 Reproducibility of the leaching test method

Prior to performing the designed experiments to study the crystalline orpiment leaching behavior, the reproducibility of the leaching test method was evaluated by conducting three replicated leaching tests under the same leaching conditions: pH 8.0, dissolved oxygen 8.3 ppm, and 23 °C.

Figure 7.4 shows the average cumulative percentage of arsenic released from orpiment over time for the three replicates. For each leaching time interval, the standard deviation of the three replicates was first calculated, based on which the standard error was obtained by dividing the standard deviation by the square root of the number of repeats performed. The average standard error of all leaching time intervals was obtained to be 0.61%, which was used as the benchmark for assessing whether an observed difference in arsenic release is statistically significant. Only values higher than 0.61% were considered statistically significant.



Figure 7.4 The average percentage of arsenic released from orpiment leaching for the three replicates carried out under the following conditions: pH 8.0, DO 8.3 ppm, 23°C and without ORP control. The error bars represent the standard errors calculated from the three replicates.

7.2.3 Effect of ORP control during leaching on arsenic release

ORP is a key factor influencing sulfide leaching behavior. Attempts were made to control the ORP at a constant level of 250 mV during leaching by a dilute hydrogen peroxide. 250 mV is within the

typical range that could be encountered in a mine waste rock environment. A diluted hydrogen peroxide (3% by volume) solution was used in an attempt to prevent hydrogen peroxide from directly participating in the arsenic release reactions.

Figure 7.5 shows the effect of hydrogen peroxide addition on the arsenic release from crystalline orpiment. The arsenic release rate in the presence of hydrogen peroxide is much higher than the case without hydrogen peroxide addition. This result indicates that hydrogen peroxide added directly participated as an oxidant in the leaching reaction. Therefore, all the subsequent leaching experiments were conducted without ORP control to avoid any interference of an added oxidant to the arsenic release kinetics. Other parameters including pH, DO concentration and temperature were fully controlled. Figure 7.6 illustrates an example of pH control in the course of leaching, which shows that pH of a leaching solution could be maintained constant during leaching.



Figure 7.5 Comparison of arsenic release from crystalline orpiment between two systems: without ORP control and with ORP control by adding diluted hydrogen peroxide (3% by volume) solution. Other parameters: pH 10, DO 8.3 ppm, and 23 °C.



Figure 7.6 An example of pH control in the course of orpiment leaching. The leaching conditions were pH 8.0, DO 8.3 ppm and 23 °C.

7.3 Behavior of arsenic and sulfur release from crystalline orpiment at varying pH

7.3.1 Effect of pH on arsenic and sulfur release rate

• Arsenic release rate

To quantify the effect of pH on arsenic release from crystalline orpiment, a series of leaching experiments were conducted at different pH values between 6 and 10. The pH was maintained constant during leaching by adding sodium hydroxide solution. Figure 7.7-A shows the cumulative percentage of arsenic release from orpiment over time at different pH. The arsenic release rate was accelerated by increasing pH. After 60 days of leaching, 27% of the total arsenic was released at pH 6. As pH was increased by one pH unit from 6 to 7, the percentage of arsenic released increased by 11%. A stronger influence of pH was observed under more alkaline conditions. Over the same

leaching period, an increase of 25% in the arsenic release was observed when pH was increased from 9 to 10.



Figure 7.7 Effect of pH on A) total arsenic released from crystalline orpiment and B) the ratio of total dissolved As to total dissolved S released from orpiment at DO 8.3 ppm, and 23 °C. Dashed line represents the stoichiometric As/S ratio in As₂S₃.

The dependency of arsenic release on solution pH observed in this study agrees with other studies on orpiment and realgar dissolutions (Lengke and Tempel, 2002; Lengke et al., 2009; Suess and Planer-Friedrich, 2012a). Lengke and Tempel (2002) showed that leaching of natural orpiment was accelerated by increasing the basicity within the pH range of 6.8 to 8.2 in the presence of oxygen. Similar to the case of amorphous As_2S_3 , the arsenic release from orpiment can be explained by the adsorption of OH⁻ groups on the solid surfaces, rendering the surfaces more negatively charged. This induces bond polarization, which weakens the arsenic-sulfur bonds in the orpiment lattice, causing orpiment to dissolve. Introducing more OH⁻ groups into solution by increasing the solution pH would result in a higher rate of dissolution (Furrer et al., 1986).

In comparison, the dissolution rate of the crystalline orpiment was lower than that of the amorphous As_2S_3 (Figure 5.7-A). A linear dissolution behavior was observed with the amorphous

 As_2S_3 . An extrapolation of the kinetic model indicates that its dissolution would reach completion given sufficient leaching time. In contrast, the arsenic release rate of the crystalline orpiment plateaued after a certain period of leaching. The kinetic modelling indicates that its dissolution would not reach completion. The differences in the crystalline and amorphous lattice structures were considered as the possible reasons for these leaching behaviors, which are explained in Chapter 8.

Total dissolved arsenic to total dissolved sulfur ratio

The stoichiometry of a reaction reveals key information on the leaching mechanism and pathway. To investigate whether arsenic and sulfur were released in accordance with their stoichiometric ratio of 1.6 in the orpiment structure, the ratio of the total dissolved arsenic to the total dissolved sulfur was calculated from the ICP-OES results. Figure 7.7-B shows the total dissolved arsenic to the total dissolved sulfur ratio at different pH for orpiment dissolution in comparison with the stoichiometric value. Similar to the case of amorphous As₂S₃, the ratio was larger than the stoichiometric value when pH was 8 and below, and approximated to the stoichiometric value at pH 9 and above.

7.3.2 Arsenic and sulfur speciation at different pH

• Arsenic species

To determine the effect of pH on the speciation of the dissolved arsenic, leaching of crystalline orpiment was carried out by varying pH in the range from 6 to 10 at DO 8.3 ppm and 23 °C. Sampling of the leachate was done on day 5 and day 60 to assess the effect of leaching time on

arsenic and sulfur speciation. Figure 7.8-A shows the arsenic species released from the crystalline orpiment dissolution at increasing pH on day 5, along with the corresponding total arsenic released. The speciation analysis showed that at circumneutral pH arsenite (III) predominated in the leachates. After 5 days of leaching, arsenite (III) was the only species present at pH 6 and 7 and no arsenate (V) was formed in the aqueous phase. However, by increasing pH to 8 and above, both arsenite (III) and arsenate (V) were detected and the proportion of arsenate (V) increased with pH.

By extending the leaching time to 60 days, both arsenite (III) and arsenate (V) were detected, along with increases in the total dissolved arsenic, at all pH values tested. However, the proportion of arsenate (V) increased with increasing pH (Figure 7.8-B). 19% of the total dissolved arsenic was detected as arsenate (V) at pH 6 in comparison with 80% at pH 10.

The higher proportion of arsenate (V) observed could be attributed to a faster oxidation of arsenite (III) to arsenate (V) with increasing pH, which is consistent with the published results (Süß, 2011). The significant dependency of arsenic speciation on pH has been observed in the oxidation of orpiment, realgar, and arsenopyrite in a wide range of pH. (Lengke and Tempel, 2002, 2003, 2001; Suess and Planer-Friedrich, 2012b). Arsenite (III) was reported as the main species released from the orpiment oxidative dissolution at pH ranging from 6.8 to 8.2 (Lengke and Tempel, 2002). The dominancy of arsenate (V) was observed in the leaching of arsenopyrite and orpiment at more alkaline conditions (Suess and Planer-Friedrich, 2012a)



Figure 7.8 Total arsenic dissolved and proportion of different arsenic species released from crystalline orpiment dissolution at different pH, DO 8.3 ppm and 23 °C: A) on day 5 of leaching; B) on day 60 of leaching.

• Sulfur species

To investigate the effect of pH on sulfur speciation, the concentrations of different sulfur species, along with the total dissolved sulfur, were also analyzed in the same leachates used for analysis of the arsenic speciation. Figure 7.9-A shows the total dissolved sulfur and the proportion of different sulfur species at increasing pH on day 5 of leaching. The total dissolved sulfur increased with increasing pH, with more apparent increase at higher pH. Thiosulfate was observed as the main sulfur intermediate species at all pH values. Sulfate was detected in lower proportions. There were no discernable differences in sulfur speciation at different pH.

Figure 7.9-B shows the total dissolved sulfur and the predominant sulfur species on day 60. The total dissolved sulfur increased by extending the leaching time from 5 to 60 day. Similar to the results obtained on day 5, thiosulfate was still the main species on day 60, but its proportion decreased. Accordingly, the proportion of sulfate increased. Interestingly, different from day 5, there was a discernable difference in the sulfur speciation at different pH. The proportion of sulfate seemed to be the lowest at pH 8, below which it increased with decreasing pH and above which it

increased with increasing pH. The change in the sulfur speciation is attributed to thiosulfate being subsequently converted to sulfate via different pathways.



Figure 7.9 Total sulfur dissolved and proportion of different sulfur species released from crystalline orpiment dissolution at different pH, DO 8.3 ppm and 23 °C: A) on day 5 of leaching; B) on day 60 of leaching.

7.4 Proposed reaction pathways for crystalline orpiment dissolution

7.4.1 Primary arsenic and sulfur release reaction

Using the analytical data collected, we have shown the variations as a function of pH in the ratio of the total dissolved arsenic to the total dissolved sulfur and in the speciation of arsenic and sulfur. To explain these variations, we proposed a two-step process that involves primary reactions responsible for arsenic and sulfur release from orpiment and secondary reactions responsible for the subsequent transformation of dissolved arsenic and sulfur species.

The arsenic speciation analysis showed that although arsenite (III) was the predominant species, the proportion of arsenate (V) increased as leaching progressed for all tests. In the case of sulfur, thiosulfate was detected as the main sulfur species, but the proportion of sulfate became higher as leaching proceeded. In the proposed two-step process, arsenic is released as arsenite (III) and sulfur is released as thiosulfate via the primary reactions, shown as Eqs. (7-1) and (7-2).

$$2As_2S_3 + 6O_2 + 9H_2O = 4H_3AsO_3 + 3S_2O_3^{2-} + 6H^+$$
(7-1)

$$2As_2S_3 + 6O_2 + 9H_2O = 4H_2AsO_3^{-} + 3S_2O_3^{-2} + 10H^+$$
(7-2)

Eq. (7-1) was proposed to explain the release of arsenite (III) and thiosulfate from crystalline orpiment from pH 6 to 8, where H_3AsO_3 is the predominant arsenite (III) species based on the Pourbaix diagram (Figure 2.4). At pH 9 and 10, $H_2AsO_3^-$ becomes the predominant arsenite (III) species released as expressed by Eq. (7-2). Thiosulfate is commonly found as the initial sulfur species formed in the oxidative leaching of sulfides, such as orpiment, pyrite and arsenopyrite (Planer-Friedrich et al., 2009; Suess and Planer-Friedrich, 2012a; Zhang, 2004). Eqs. (7-1) and (7-2) show that protons are generated in the primary reactions, which explains the increased rates of leaching at higher pH.

7.4.2 Secondary arsenic oxidation and sulfur transformation reactions

• Arsenite (III) oxidation to arsenate (V)

It was shown that by increasing the leaching time, the proportion of arsenate (V) increased with a concomitant decrease in the proportion of arsenite (III). It was proposed that arsenite (III) undergoes oxidative transformation to the most thermodynamically stable oxidation state, arsenate (V). Eqs. (7-3), (7-4) and (7-5) were proposed to explain the oxidation of arsenite (III) to arsenate (V), which are the same as proposed by Yu et al. (2007). $H_2AsO_4^-$ is the stable arsenate (V) species

between pH 6 and 7, and HAsO4²⁻ is the stable arsenate (V) species between pH 7 and 10. Moreover, the proposed equations show that protons are generated in the reactions, indicating that the oxidation of arsenite (III) to arsenate (V) is faster with increasing pH. This is consistent with what was observed in the experiment that a higher proportion of arsenate (V) was present in the leachate at higher pH.

$$2H_3AsO_3 + O_2 \rightarrow 2H_2AsO_4 + 2H^+$$
(7-3)

$$2H_3AsO_3 + O_2 \rightarrow 2HAsO_4^{2-} + 4H^+$$
(7-4)

$$2H_2AsO_3^- + O_2 \rightarrow 2HAsO_4^{2-} + 2H^+$$
(7-5)

• Thiosulfate transformation

The sulfur speciation analysis indicated that thiosulfate is the initial sulfur intermediate resulting from the crystalline orpiment dissolution. Thiosulfate is thermodynamically unstable and would subsequently convert to different sulfur species. The observed increase in the proportion of sulfate by extending the leaching time indicated that thiosulfate was eventually transformed to sulfate in the aqueous phase. The experimental results also show that the ratio of the total dissolved arsenic to the total dissolved sulfur ratio deviated from the stoichiometric value at pH 8 and below. But such deviation was absent at pH 9 and above.

In light of the experimental observations in conjunction with the published results, it stands to reason that the transformation is not a one-step process and the actual pathways depend on the solution conditions. We proposed that thiosulfate transformation occurs via two different pathways: oxidation and disproportionation. The former is favored at pH higher than 8 and the latter is favored at pH 8 and below.

Eqs (7-6a-d) show the series of reactions that are involved in the oxidation pathway to oxidize thiosulfate to sulfate, as proposed by other researchers (Lengke and Tempel, 2001; Xu and Schoonen, 1995). Thiosulfate undergoes a series of oxidation reactions to polythionates ($S_nO_6^{2-}$) and finally to sulfate, the thermodynamically most stable species. Even though the formation of a series of intermediate sulfur species has been reported, we encountered analytical difficulties to detect them. Sulfate was the only species that could be determined in the aqueous phase. This oxidation pathway can be used to explain the ratio of the total dissolved arsenic to the total dissolved sulfur observed at pH above 8. The ratio approximated to the stoichiometric value of 1.6 at pH 9 and 10 (Figure 7.7-B), suggesting that all dissolved arsenic and sulfur remained in the aqueous phase. That is to say that no solid phase, such as elemental sulfur, was produced.

$$4S_2O_3^{2-} + O_2 + 2H^+ \rightarrow S_4O_6^{2-} + H_2O$$
(7-6a)

$$S_4O_6^{2-} + S_2O_3^{2-} \rightarrow S_5O_6^{2-} + SO_3^{2-}$$
 (7-6b)

$$S_5O_6^{2-} + S_2O_3^{2-} \rightarrow S_6O_6^{2-} + SO_3^{2-}$$
 (7-6b)

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-}$$
 (7-6b)

The disproportionation pathway is favored at pH 8 and below. Eq. (7-7) represents the disproportionation pathway, as proposed by Basu and Schreiber (2013). It is apparent that decreasing pH or increasing proton concentration will drive the reaction in the forward direction, producing elemental sulfur. This pathway supports the total dissolved arsenic to the total dissolved

sulfur ratios observed. At pH 8 and below, the ratio was observed to deviate from the stoichiometric value of 1.6. The level of deviation was larger with decreasing pH, which can be explained by more elemental sulfur being produced and leaving the aqueous solution.

$$S_2O_3^{2-} + H^+ = HSO_3^{-} + S^0$$
 (7-7)

7.5 The role of dissolved oxygen in the dissolution of crystalline orpiment

7.5.1 Effect of DO on arsenic and sulfur release rate

Dissolved oxygen (DO) is the oxidant in the primary reactions proposed to explain the release of arsenic and sulfur from crystalline orpiment (Eqs. (7-1) and (7-2)). This means that varying the DO concentration in the leaching system would affect the rate of orpiment dissolution. In order to determine the effect of DO, leaching experiments were conducted at different DO levels from 0 to 8.3 ppm, with pH and temperature kept constant at 8 and 23 °C, respectively.

• Arsenic release rate

Figure 7.10-A shows the results obtained from the leaching experiments at different levels of DO. It was observed that the arsenic release rate from orpiment was dependent on DO concentration. By increasing the DO concentration from 2.0 ppm to 8.3 ppm, the dissolution of orpiment increased from 15% to 22% for 10 days of leaching. By extending the leaching time to 60 days, 38% and 53% of the total arsenic was detected in the leachate at 2.0 ppm and 8.3 ppm of dissolved oxygen, respectively. These experimental results are in agreement with those reported in the previous studies on orpiment and realgar dissolution, which showed a positive dependency of

arsenic release on the concentration of dissolved oxygen (Lengke and Tempel; 2003, 2001). On the other hand, the system in which oxygen was removed also showed the release of arsenic. Studies have reported that arsenic can be dissolved from orpiment in anoxic conditions, such as in tailings and groundwater (Floroiu et al., 2004; Kim et al., 2000).

The arsenic release was faster from amorphous As_2S_3 (Figure 5.11-A) than from crystalline orpiment at different dissolved oxygen concentrations. A linear kinetics was observed with the amorphous As_2S_3 , whereas the dissolution rate decreased with time in the case of the crystalline orpiment. This was attributed to the differences in their leaching mechanisms. The former is controlled by a chemical reaction mechanism (Chapter 6). The latter is a mixed-controlled reaction, where the diffusion of the dissolved oxygen through a surface product layer partially controls the reaction rate (see Chapter 8).



Figure 7.10 Effect of DO on A) total arsenic released from crystalline orpiment and B) the ratio of total dissolved As to total dissolved S released from orpiment at pH 8, and 23 °C. Dashed line represents the stoichiometric As/S ratio in As₂S₃.

• Total arsenic to total dissolved sulfur ratio

Figure 7.10-B shows the total dissolved arsenic to the total dissolved sulfur ratio at different DO concentration. The ratios at all DO concentrations tested were higher than the stochiometric value, which can be described as incongruent leaching. This result is not surprising because all tests were carried out at pH 8. A lower concentration of dissolved oxygen resulted in the ratio being further away from the theoretical value, indicating that a higher proportion of the dissolved sulfur was converted to elemental sulfur.

The above experimental observations are consistent with the reaction pathways proposed for the thiosulfate conversion. As can be seen from Eqs. (7-6a-d), higher concentrations of dissolved oxygen favor the oxidation pathway, resulting in the total dissolved arsenic to the total dissolved sulfur ratio approximating to the theoretical value. Namely, a lower DO concentration favors the disproportionation pathway (Eq. (7-7)), leading to a higher proportion of elemental sulfur being produced.

7.5.2 Arsenic and sulfur speciation at different DO

• Arsenic species

Different concentrations of dissolved oxygen were used to investigate the effect of DO on arsenic and sulfur speciation in the dissolution of crystalline orpiment. Liquid samples were collected on day 5 and day 60 to analyze the concentrations of different arsenic and sulfur species in the leachates. Figure 7.11-A shows the total dissolved arsenic and the predominant arsenic species expressed as percentages of the total dissolved arsenic at different DO levels on day 5. It was observed that 100% of the total dissolved arsenic was present in the aqueous phase as arsenite (III) at all DO levels except at 8.3 ppm, at which a small percentage of arsenate (V) was detected. By extending the leaching time to 60 days, arsenate (V) were detected at all DO levels. At higher DO levels, the proportion of arsenate (V) was larger. This can easily be explained by Eqs. (7-3), (7-4) and (7-5), which show that the oxidation of arsenite (III) to arsenate (V) is accelerated by increasing DO concentration.

In the absence of oxygen, it is expected that arsenite (III) is the only species present in the aqueous phase regardless of the leaching time. Floroiu et al. (2004) proposed that in anoxic systems arsenic was released as arsenite (III) oxyanions in the form of H_3AsO_3 and $H_2As_3S_6$, as shown in Eqs. (7-8) and (7-9). However, a small proportion of arsenate (V) was detected on day 60, which could possibly be caused by the residual DO in the liquid that could not be completely removed and/or the introduction of oxygen in the sample preparation and analysis.

$$As_2S_3 + 6H_2O = 2H_3AsO_3 + 3HS^- + 3H^+$$
(7-8)

$$2As_2S_3 + 3H_2O \to H_3AsO_3 + H_2As_3S_6^- + H^+$$
(7-9)



Figure 7.11 Total arsenic dissolved and proportion of different arsenic species released from crystalline orpiment dissolution at different levels of DO, pH 8, and 23 °C: A) on day 5 of leaching; B) on day 60 of leaching.

• Sulfur species

Figure 7.12-A shows the total sulfur released and the predominant sulfur species on day 5 at different DO levels. It was observed that at all DO concentrations, thiosulfate was the predominant species and only a small proportion of sulfate was present in the solution at the highest DO concentration tested. Figure 7.12-B shows the concentration of the sulfur species in the leaching solutions after 60 days of leaching. Comparison of the results on day 5 and day 60 showed that by extending the leaching time, the proportion of sulfate as a percentage of the total dissolved sulfur decreased. Accordingly, the proportion of sulfate increased, which means that the extent of oxidation to sulfate of thiosulfate and other possible sulfur intermediates increased with time.

Furthermore, on day 60 the proportion of sulfate was higher at a higher concentration of dissolved oxygen. This is because dissolved oxygen acted as the oxidant and oxidized more sulfur intermediates to sulfate via the oxidation pathway (Eqs. (7-6a-d)). That is to say that the disproportion pathway is less favored at higher DO concentrations. For the oxygen removed test, a very small amount of sulfate was also detected in the solution. This could be caused by the

introduction of a small amount of DO in the sample dilution and IC analysis process, both performed in an environment open to the atmosphere.



Figure 7.12 Total sulfur dissolved and proportion of different sulfur species released from crystalline orpiment dissolution at different levels of DO, pH 8, and 23 °C: A) on day 5 of leaching; B) on day 60 of leaching.

7.6 Arsenic and sulfur release from crystalline orpiment at varying temperature

7.6.1 Effect of temperature on arsenic release rate

• Arsenic release rate

The effect of temperature on the arsenic release from orpiment was studied in a series of leaching experiments carried out at 23, 30, 40, and 50 °C. Figure 7.13-A demonstrates the total dissolved arsenic released from orpiment versus leaching time at varying temperatures. Increasing the leaching temperature resulted in higher concentrations of arsenic released from orpiment for the same period of leaching. For example, 22% of arsenic entered the aqueous phase after 10 days of leaching at 23 °C in comparison with 49% at 50 °C. Further extending the leaching time caused more arsenic to enter the leaching solution. At 50 °C the arsenic release reached a maximum level

of 60% after 30 days of leaching. In contrast, at 23 °C the maximum achievable arsenic release was 47%, which was achieved in a much longer leaching time (50 days).

The leaching experimental results showed that the arsenic release from amorphous As_2S_3 was faster than that of crystalline orpiment at different temperatures. In the amorphous system a near complete dissolution was observed at 50 °C after 25 days (Figure 5.14-A). However, the leaching rate of the crystalline orpiment decreased with time and eventually plateaued. Similarly, the difference can be attributed to two different leaching mechanisms at play (see Chapter 8).

• Total dissolved arsenic to total dissolved sulfur ratio

Figure 7.13-B shows the total dissolved arsenic to the total dissolved sulfur ratio for orpiment dissolution versus time at different leaching temperatures. This ratio was always higher than the theoretical value of 1.6 in orpiment. Increasing the leaching temperature resulted in an increase in the ratio, suggesting a higher proportion of sulfur loss as elemental sulfur. This result could be explained by the greater disproportionation of thiosulfate to elemental sulfur at higher temperatures according to Eq. (7-7). The elemental sulfur formed precipitated out of the aqueous phase, leading to a decrease in the ratio of total sulfur to total arsenic in the aqueous phase. The formation of elemental sulfur in orpiment leaching has been reported to occur at elevated temperatures by Long (2000), who showed that by increasing the leaching temperature to as high as 190 °C, 50% of the total sulfur could still be present as elemental sulfur.



Figure 7.13 Effect of temperature on A) total arsenic released from crystalline orpiment and B) the ratio of total dissolved As to total dissolved S released from orpiment at pH 8, and DO 8.3 ppm. Dashed line represents the stoichiometric As/S ratio in As₂S₃.

7.6.2 Arsenic and sulfur speciation at different temperatures

• Arsenic species

Figure 7.14-A shows the total dissolved arsenic and the predominant arsenic species in the leaching solutions resulting from orpiment dissolution on day 5 at different temperatures. It was observed that at all temperatures arsenite (III) was the major arsenic species in the system, but a higher proportion of arsenate (V) was detected at higher temperatures. This result indicates that the oxidation of arsenite (III) to arsenate (V), as shown by Eqs. (7-3), (7-4) and (7-5), is temperature sensitive. The oxidation rate was accelerated by elevating the temperature. Moreover, at the same temperature, the proportion of arsenate (V) in the system increased by extending the leaching time from 5 to 30 days (Figure 7.14-B).



Figure 7.14 Total arsenic dissolved and proportion of different arsenic species released from crystalline orpiment dissolution at different temperatures, pH 8, and DO 8.3 ppm: A) on day 5 of leaching; B) on day 30 of leaching.

• Sulfur species

Figure 7.15-A shows the total dissolved sulfur and the sulfur species released from orpiment on day 5 at different temperatures. Among the sulfur species detected in the solution, thiosulfate was the predominant one at all temperatures. However, by increasing the leaching temperature, the proportion of sulfate increased. After 5 days of leaching, 16% of the total dissolved sulfur was detected as sulfate at 50 °C as opposed to only 7% at 23 °C. For the same temperature, extending the leaching time from 5 to 30 days resulted in higher proportions of sulfate (Figure 7.15-B).

Sulfate was thought to be generated from the thiosulfate disproportionation reaction (Eq. (7-7)), which was accelerated by increasing the leaching temperature. This statement is supported by the previous analyses of the ratio of the total dissolved arsenic to the total dissolved sulfur. Those analyses showed that the ratio deviated from the stoichiometric value to a greater extent at higher temperatures, implying that the disproportionation pathway was favored at higher temperatures.



Figure 7.15 Total sulfur dissolved and proportion of different sulfur species released from crystalline orpiment dissolution at different temperatures, pH 8, and DO 8.3 ppm: A) on day 5 of leaching; B) on day 30 of leaching.

7.7 Effect of bicarbonate/carbonate ions on arsenic release from crystalline orpiment

Similar to amorphous As_2S_3 , the possible effect of carbonate/bicarbonate ions on the arsenic release behavior from crystalline orpiment was investigated. Reactor leaching experiments were conducted using sodium carbonate solution to control pH during the experiments. Other parameters were varied as follows: pH from 6.0 to 10.0, DO centration from 0.0 to 8.3 ppm, and temperature from 23 to 50 °C.

• pH variation

Figure 7.16-A shows the dissolution behavior of crystalline orpiment at different pH values and in the presence of carbonate/bicarbonate ions. The results showed a similar response of arsenic release to pH in the presence of carbonate/bicarbonate ions. Figure 7.16-B compares the cumulative arsenic extraction obtained at the end of leaching as a function of pH between the carbonate and the hydroxide system. For both systems, arsenic release was accelerated by increasing pH in both systems, a higher arsenic extraction was observed in the presence of
carbonate. The magnitude of the difference was the most pronounced at pH 10. The magnitude of difference was calculated as the difference in the arsenic release between the carbonate and the hydroxide system, divided by the arsenic release in the hydroxide system.



Figure 7.16 Effect of leaching pH on A) total arsenic released from crystalline orpiment in the carbonate system, B) total arsenic released from crystalline orpiment over a period of 60 days in the presence and absence of carbonate (DO 8.3 ppm and 23 °C). The magnitude of difference between the two systems was also plotted.

The enhanced extraction in the carbonate system is attributed to the formation of arsenic carbonate complexes. In order to explain the role of carbonate/bicarbonate ions, Eqs. (7-10) - (7-12) were proposed.

$$2As_2S_3 + 4HCO_3 + 6O_2 + 5H_2O = 4As(CO_3)(OH)_2 + 3S_2O_3^2 + 6H^+$$
(7-10)

$$2As_2S_3 + 8HCO_3^{-} + 6O_2 + H_2O = 4As(CO_3)_2(OH)^{2-} + 3S_2O_3^{2-} + 6H^+$$
(7-11)

$$2As_2S_3 + 4CO_3^{2-} + 6O_2 + 5H_2O = 4As(CO_3)(OH)_2^{-} + 3S_2O_3^{2-} + 2H^+$$
(7-12)

Subsequent transformation of the arsenic-carbonate complexes to the common arsenic oxyanions could occur through the following reactions (Eqs. (7-13) and (7-14)) (Kim et al., 2000).

$$As(CO_3)(OH)_2^{-} + H_2O = H_3AsO_3 + HCO_3^{-}$$
(7-13)

$$As(CO_3)(OH)_2 + H_2O = H_3AsO_3 + CO_3^{2-} + H^+$$
(7-14)

• DO concentration

Figure 7.17-A shows the dissolution behavior of crystalline orpiment at different concentrations of dissolved oxygen in the presence of carbonate/bicarbonate ions. The arsenic release increased with increasing DO in the presence of carbonate/bicarbonate ions. Figure 7.17-B shows the comparison between the total arsenic dissolution at the end of leaching as a function of dissolved oxygen between the hydroxide and carbonate systems. For both systems, the orpiment dissolution was enhanced by increasing DO. Different from the results of the pH experiments, the magnitude of difference between the two systems was almost indiscernible. Dissolution of orpiment in an anoxic environment and in the presence of bicarbonate ions was proposed as Eqs. (7-15)-(7-18) (Kim et al., 2000).

$$As_2S_3 + HCO_3^- \rightarrow As(CO_3)^+ + AsS_2^- + HS^-$$
(7-15)

$$As_2S_3 + 2HCO_3^{-} \rightarrow As(CO_3)_2^{-} + HAsS_2 + HS^{-}$$
(7-16)

$$As_2S_3 + HCO_3^- + 2H_2O \rightarrow As(CO_3)(OH)_2^- + HAsS_2 + HS^- + H^+$$
 (7-17)

$$HAsS_2 + H_2O \rightarrow HAsS_2(OH)^2 + H^+$$
(7-18)



Figure 7.17 Effect of DO level on A) total arsenic released from crystalline orpiment in the carbonate system, B) total arsenic released from crystalline orpiment over a period of 60 days in the presence and absence of carbonate (pH 8 and 23 °C). The magnitude of difference between the two systems was also plotted.

• Temperature variation

Figure 7.18-A shows the dissolution behavior of crystalline orpiment at different leaching temperatures in the presence of carbonate/bicarbonate ions. The arsenic release increased with temperature. Figure 7.18-B shows that a higher percentage of arsenic was released from orpiment to the aqueous phase in the presence of carbonate than that of the hydroxide system. The magnitude of the difference seemed to be more pronounced at higher temperatures. This may be explained by the formation of arsenic-carbonate complexes being more favorable at higher temperatures.



Figure 7.18 Effect of temperature on A) total arsenic released from crystalline orpiment in the carbonate system, B) total arsenic released from crystalline orpiment over a period of 30 days in the presence and absence of carbonate (pH 8 and DO 8.3 ppm). The magnitude of difference between the two systems was also plotted.

7.8 Conclusion

To understand the degree of crystallinity on the dissolution of arsenic trisulfide, crystalline orpiment was used as the mineral sample to investigate the release behavior of arsenic and sulfur under different leaching conditions. These conditions include pH from 6.0 to 10.0, temperature from 23 to 50 °C, and the dissolved oxygen concentration from 0.0 to 8.3 ppm. The experimental results show that similar to the case of amorphous As_2S_3 , the release of arsenic and sulfur from crystalline orpiment increased with pH, DO concentration, and temperature. But the release rate for crystalline orpiment was in general lower than that of the amorphous form. The presence of carbonate/bicarbonate was shown to accelerate the dissolution, especially at more alkaline pH and higher temperatures.

The ratio of the total dissolved arsenic to the total dissolved sulfur was higher than the stoichiometric value in the orpiment when pH was set at pH 8 and below. Such discrepancy was not observed at pH 9 and above. Similar to the case of amorphous As_2S_3 , the deviation from the

stoichiometric value was attributed to the formation and precipitation of elemental sulfur. The analysis of arsenic and sulfur speciation showed the predominance of arsenite (III) and thiosulfate as the initial arsenic and sulfur species. These species were proposed to be released from orpiment leaching via the primary reactions. Subsequently, via the secondary reactions, arsenite (III) was oxidized to arsenate (V); thiosulfate underwent two possible conversion pathways depending on pH. The oxidation pathway involves the oxidation of thiosulfate to sulfate; the disproportionation pathway generates elemental sulfur and sulfate.

Chapter 8: Crystalline orpiment leaching kinetics and mechanism

8.1 Introduction

Results reported in Chapter 7 show that the orpiment dissolution was significantly affected by pH, dissolved oxygen concentration and temperature. In this Chapter, the leaching experimental results were used to derive a kinetic equation that quantifies the rate of arsenic release from orpiment as a function of pH, DO concentration and temperature. The analysis of the reaction orders and the activation energy uncovered the rate-determining step in orpiment dissolution. The proposed leaching mechanism was substantiated with examination of the surface morphology and elemental composition of the solid residues collected from the leaching experiments. Particularly, the generation of elemental sulfur and its impact on the leaching rate were experimentally confirmed. Finally, the experimental results for amorphous and crystalline arsenic trisulfide were compared to demonstrate the effect of the degree of crystallinity on the arsenic and sulfur release behavior.

8.2 Derivation and interpretation of the kinetic equation

8.2.1 Derivation of the kinetic equation

The experimental results obtained from the leaching tests reported in Chapter 7 were used to derive a kinetic equation. The method of non-linear least squares was used to minimize the sum of squares of the difference between the experimental values and the fitted values obtained from the equation. Similar to what was described in Section 6.2.1, the minimization was done by adjusting the model parameters, including the reaction orders with respect to H^+ and DO, the activation energy, and

the topological φ . The initial values were determined by using the shrinking core model (SCM) for pore diffusion control as expressed by Eq. (8-1) (Ekmekyapar et al., 2012; Levenspiel, 1999).

$$\frac{t}{\tau} = 1 - 2(1 - x)^{\frac{1}{3}} + (1 - x)^{\frac{2}{3}}$$
(8-1)

Where x is the fraction of total arsenic released from crystalline orpiment and t is the leaching time in days. τ is the timescale of the reaction, which is a function of proton and DO concentrations and the activation energy, as described in Eq. (4-4). Table 8.1 shows the initial values obtained from the SCM model. Using the initial values and by iteration, a set of optimal model parameters was calculated and shown in Table 8.1.

Table 8.1 The kinetic model for crystalline orpiment leaching: initial values for the model parameters derived using the SCM model and the optimal values derived for the general model using non-linear least squares method

Model parameter	Reaction order with respect to H ⁺	Reaction order with respect to DO	Activation energy, E _a (kJ/mol)
Initial value	- 0.29	0.64	29.6
Optimal value	- 0.35	0.67	35.0

The kinetic model with the set of optimal model parameters is shown as Eq. (8-2). In this equation, the topological factor, φ , was 3.73. A value larger than 1 means that the leaching reaction would not reach completion. The reaction orders with respect to H⁺ and DO were – 0.35 and 0.67, and the activation energy was 35 kJ/mol. These parameters were further explained to uncover the possible rate-limiting step that controls arsenic release. To show the reaction order with respect to each parameter, Eq. (8-2) was rearranged to Eq. (8-3). The coefficient of the right-hand side of Eq.

(8-3) stands for the apparent rate constant, which is a function of proton concentration, dissolved oxygen concentration and temperature.

$$\mathbf{x} = 1 - \left\{ 1 + 4.68 \times 10^{-5} \exp\left[\frac{34999}{8.314} \left(\frac{1}{296} - \frac{1}{T_{(K)}}\right)\right] (\mathrm{H}^+)^{-0.35}_{(\mathrm{M})} (\mathrm{D0})^{0.67}_{(\mathrm{ppm})} \mathbf{t}_{(\mathrm{days})} \right\}^{\left(\frac{1}{1-3.73}\right)}$$
(8-2)

$$\frac{1 - (1 - x)^{(1 - 3.73)}}{(1 - 3.73)} = 1.71 \times 10^{-5} \exp\left[\frac{E_a}{8.314} \left(\frac{1}{296} - \frac{1}{T}\right)\right] (H^+)^a (D0)^b.t$$
(8-3)

8.2.2 Reaction order with respect to H⁺ concentration

The experimental results for orpiment dissolution obtained at different pH levels at DO 8.3 ppm and 23 °C were plotted together with the model fitted values derived from Eq. (8-3). The linear lines in Figure 8.1-A shows that the model could describe the leaching results at all pH values except pH 10 (explained later in the Chapter). The experimental results at pH 10 was excluded in the calculation of the reaction order with respect to H⁺ concentration. The slope of the linear lines stands for the apparent rate constant at each pH. The reaction order with respect to the concentration of H⁺ is derived by plotting the logarithm of the apparent rate constant versus the logarithm of the proton concentration, as shown by Eq. (8-4).

$$\log k = -0.35 \log(H^+) + \log(1.71 \times 10^{-5} (DO)^{0.67})$$
(8-4)

Figure 8.1-B shows that plotting Eq. (8-4) gave a linear line with a slope of -0.35, which represents the reaction order with respect to proton concentration. The negative value means that increasing the proton concentration would result in a decrease in the apparent rate constant and thus a decrease

in arsenic release from orpiment. The value of 0.35 supports that the surface reaction between OH⁻ and arsenic-sulfur bonds is one of the rate-limiting steps.



Figure 8.1 A) Application of the kinetic model to derive the apparent rate constant at different pH; B) Linear regression between the logarithm of the apparent rate constant and the logarithm of the H⁺ concentration, with the slope representing the reaction order with respect to proton concentration. (DO 8.3 ppm and 23 °C).

8.2.3 Reaction order with respect to dissolved oxygen concentration

Figure 8.2-A plotted the results from the leaching experiments conducted at different DO levels at pH 8.0 and 23 °C against the model fitted values derived by Eq. (8-3). The apparent rate constant at each DO level was calculated as the slope of the linear line. To obtain the reaction order with respect to the DO concentration, the logarithm of the apparent rate constant was plotted against the logarithm of the DO concentration, as shown by Eq. (8-5).

$$\log k = 0.67 \log(DO) + \log(1.71 \times 10^{-5} (H^+)^{-0.35})$$
(8-5)

A slope of 0.67 was given by the linear regression of the plotted data in Figure 8.2-B, which represents the reaction order with respect to the dissolved oxygen concentration. The positive sign of the slope supported the positive dependency of the arsenic release on the dissolved oxygen

concentration. A value of 0.67 supports that the arsenic leaching rate was controlled by the diffusion of oxygen through a product layer formed on the orpiment surface.



Figure 8.2 A) Application of the kinetic model to derive the apparent rate constant at different DO concentration; B) Linear regression between the logarithm of the apparent rate constant and the logarithm of the DO concentration, with the slope representing the reaction order with respect to DO concentration. (pH 8 and 23 °C).

8.2.4 Activation energy

Figure 8.3-A plotted the experimental results for the orpiment dissolution obtained at different temperatures together with the model fitted values derived from Eq. (8-3). The apparent rate constant for each temperature was calculated as the slope of the corresponding line. The natural logarithm of the apparent rate constant was plotted versus 1/T (Kelvin) as shown by Eq. (8-6) in Figure 8.3-B.

$$\ln k = \frac{E_a}{8.314} \left(\frac{1}{296} - \frac{1}{T} \right) + \ln \left(1.71 \times 10^{-5} (\text{H}^+)^{-0.35} (\text{DO})^{0.67} \right)$$
(8-6)

The linear regression in Figure 8.3-B gave a slope of - Ea/R, which is - 4.21. An activation energy (E_a) of 35 kJ/mol was calculated. The value of the activation energy has important information regarding the reaction mechanism. Low activations energies (< 20 kJ/mol) are usually assigned to

diffusion-controlled reactions, whereas a high activation energy (> 40 kJ/mol) is an indication of a reaction-controlled mechanism (Feng et al., 2015; Lasaga, 1992). A value in the range of 20 to 40 kg/mol is for a reaction under a mixed rate control of reaction and diffusion processes. The magnitude of the activation energy obtained here falls in the range for a mixed-control reaction mechanism.



Figure 8.3 A) Application of the kinetic model to derive the apparent rate constant at different temperatures; B) Arrhenius plot showing the logarithm of the apparent rate constant plotted against the reciprocal of temperature, with the slope representing -Ea/R. (pH 8 and DO 8.3 ppm).

Based on the values of the reaction orders with respect to H^+ and DO concentrations and the activation energy obtained, we proposed a mixed-control reaction mechanism to explain arsenic release from crystalline orpiment. Specifically, the rate limiting steps were considered to be the surface chemical reaction between OH^- and orpiment and the diffusion of oxygen through a product layer formed on the solid surfaces. In order to support the proposed mechanism, the surfaces of the solid residues collected from the leaching experiments were analyzed to explore whether a product layer was formed during leaching.

8.3 Characterization of solid surface properties in crystalline orpiment leaching

8.3.1 Changes in orpiment surface morphology during leaching

The morphological changes of the orpiment surfaces resulting from leaching were investigated by characterizing the leaching residues using scanning electron microscopy. Figure 8.4 shows the evolution of the crystalline orpiment surface during dissolution at pH 8.0, DO 8.3 ppm and 50 °C. The figure shows that as the leaching progressed, the morphology of the orpiment surface changed compared with the unreacted sample. Cracks were developed and small nodules were formed on the surfaces during leaching. The solid surfaces became rougher, which was attributed to the chemical attack of the solid surfaces by OH⁻ groups present in the solution. This is consistent with the magnitude of the reaction order with respect to the proton concentration, which supports that the surface reaction between OH⁻ and arsenic-sulfur bonds is one of the rate-limiting steps.

By increasing the leaching time, the number of the fine nodules adhering to the solid surfaces increased. The morphology of these particles was completely different from the spherical particles observed on the surfaces of the amorphous As_2S_3 leaching residues (Figure 6.7). The latter seemed to segregate from the solid surfaces as a result of etch pits formation and had a similar chemical composition to the bulk. In contrast, the particles on the surfaces of the crystalline orpiment leaching residues were not spherical and did not segregate from the solid surfaces. This may be among the factors that differentiate the dissolution behavior of crystalline orpiment from amorphous arsenic trisulfide.



Figure 8.4 The secondary electron images of crystalline orpiment leaching residues at varied leaching time corresponding to increasing arsenic release under the following conditions: pH 8.0, DO 8.3 ppm and 50 °C.

8.3.2 Analysis of surface elemental composition

To investigate the composition of the fine nodules formed and explore the possible formation of a product layer on the solid surfaces, the elemental composition of the leaching residue surfaces was analyzed using SEM/EDX and XRD. Two distinct leaching conditions were selected for the analyses: pH 8.0, DO 8.3 ppm and 50 °C and pH 10.0, DO 8.3 ppm and 23 °C.

• SEM/EDX analysis

Figure 8.5 shows an SEM image of the unreacted orpiment with the spots selected for EDX analysis. The EDX spectrum showed the presence of arsenic and sulfur as the major elements on the surface. Using the EDX spectrum peak intensities, the average arsenic to sulfur ratio was calculated to be 1.64 which is sufficiently close to the theoretical value of 1.6.

Figure 8.6 shows the EDX elemental analysis of the bulk surface and the fine nodules formed on the leaching residue collected at pH 8, DO 8.3 ppm and 50 °C. The average arsenic to sulfur ratio on the bulk surface was lower than the stoichiometric value of 1.6, suggesting an arsenic-deficient surface. The average arsenic to sulfur ratio of the fine nodules was much lower than the stoichiometric value, suggesting the formation of secondary phases enriched in sulfur. It seems that the arsenic-deficient layer and the sulfur-enriched nodules covered the surfaces of the reacted orpiment and therefore could act as barriers to diffusion of the dissolved oxygen. This result agrees with the experimental observation that the arsenic release eventually plateaued after a certain period of leaching.

We proposed mechanisms by which the arsenic-deficient layer and the elemental sulfur form on the solid surfaces. Crystalline orpiment lattice consists of weaker arsenic-arsenic (As-As) and arsenic-sulfur (As-S) bonds and stronger sulfur-sulfur (S-S) bonds (Gibbs et al., 2010). XPS analysis shows that sulfur is present on the unreacted orpiment surfaces as monosulfide (S^{2-}) and disulfide (S_2^{2-}) (Corkhill et al., 2006; Knipe and Fleet, 1997). The easier breaking of As-As and As-S bonds leads to a faster dissolution of arsenic at early stages, resulting in an arsenic-deficient surface layer (Douglass et al., 1992; Lengke, 2001). Concurrently, a sequential oxidation of sulfur from disulfide to polysulfide to elemental sulfur by dissolved oxygen could explain the formation of elemental sulfur on the surfaces. This elemental sulfur is apparently different from the elemental sulfur formed from the disproportionation of thiosulfate, which did not act as a diffusion barrier.

Figure 8.7 shows an SEM image of the solid residue collected at pH 10.0, DO 8.3 ppm and 23 °C and the spots selected for the EDX analysis of arsenic to sulfur ratio. The leaching results obtained at this pH could not be fit by Eq. (8-3), which may indicate a change in the reaction mechanism when pH was increased to 10. The SEM image shows that there were cracks and corroded spots developed on the solid surfaces, but no fine particles or new phases could be observed on the surfaces.

The EDX spectrum in Figure 8.7 shows that the arsenic to sulfur ratio was 1.59, the same as the stoichiometric ratio in orpiment, indicating the absence of an arsenic-deficient sulfur-enriched layer on the surfaces. Due to the low chemical stability of elemental sulfur at pH 10 and above, the sequential oxidation of sulfur on the solid surfaces may mainly produce thiosulfate instead of elemental sulfur (Kleinjan et al., 2005). This result implies that the leaching process is no longer controlled by diffusion of dissolved oxygen through the sulfur-enriched layer, which agrees with the linear leaching kinetics observed at this pH.



Figure 8.5 A) The spots selected for EDX analysis of the unreacted orpiment sample surfaces; B) the EDX spectrum at spot 1 and the average of arsenic to sulfur ratios.



Figure 8.6 A) Selection of the spots for EDX analysis and the spectrum at spot 1 of the crystalline orpiment leaching residue collected at pH 8.0, DO 8.3 ppm and 50 °C: A) the bulk surface; B) the fine particles adhering to the surfaces.



Figure 8.7 A) The spots selected for EDX analysis of the leaching residues collected under the conditions of pH 10.0, DO 8.3 ppm and 23 °C; B) the EDX spectrum at spot 1 and the average of the arsenic to sulfur ratios.

• XRD analysis

To further support the presence of elemental sulfur, XRD analysis was done on the leaching residue collected at pH 8.0, DO 8.3 ppm and 50 °C. Figure 8.8 shows the XRD spectrum for the solid residue. The spectrum showed similar peaks for orpiment and some new peaks, which were detected as elemental sulfur by the XRD Match software.



Figure 8.8 XRD pattern of the solid residue collected from crystalline orpiment leaching at pH 8.0, DO 8.3 ppm and 50 °C.

8.3.3 Impact of elemental sulfur formation on orpiment leaching

To evaluate whether the elemental sulfur produced could passivate the solid surfaces, CS_2 washing was used to remove the elemental sulfur from the solid surface. A leaching test was conducted at pH 8.0, DO 8.3 ppm and 50 °C. The test was paused on day 19, which corresponded to about 55% arsenic release. The solid residue was collected and washed with CS_2 to remove any possible elemental sulfur formed. The washed residue was placed back into the leaching reactor for resumed leaching. The results on the arsenic release were then compared with the case under the same leaching condition but without CS_2 washing.

Figure 8.9 compares the arsenic release in the two cases: with and without CS_2 washing. The leaching time at which the leaching test was paused for the sulfur removal by CS_2 is shown by a vertical dashed line. The results showed that CS_2 washing slightly enhanced the arsenic release from orpiment, which support the role of elemental sulfur as a passivating layer on the surfaces of the reacted orpiment. However, the small level of increase implies that the elemental sulfur was only partially responsible for the slowed arsenic release from orpiment. Given the presence of arsenic deficient surface layer observed by the SEM-EDX analysis, a combination of elemental sulfur and polysulfide passivation was concluded to be responsible for the slowed-down arsenic release from the crystalline orpiment.



Figure 8.9 The effect of elemental sulfur removal by CS₂ on arsenic release behavior from crystalline orpiment, pH 8.0, DO 8.3 ppm and 50 °C.

8.4 Comparison of the dissolution behavior between amorphous and crystalline orpiment

• The unit structures of crystalline and amorphous As₂S₃

Both amorphous and crystalline forms of arsenic trisulfide have the same formula as As_2S_3 (Gouda, 2012), but different possible unit structures. Figure 8.10 shows the differences in the unit structures of crystalline and amorphous As_2S_3 and the interactions between As_2S_3 unit cell and OH⁻ groups in an aqueous solution. The crystalline orpiment has a ruffled layered sheet structure of trigonal pyramidal As_2S_3 . These sheets are connected together in the lattice. The structure includes chains of [As-S₃] units with strong covalent arsenic and sulfur bonds. These units are connected by bridging bonds in a perfect crystalline structure (Day, 2006). Lucovsky and Galeener (1980) reported a unit cell consisting of eight arsenic atoms and twelve sulfur atoms. All arsenic atoms are arranged into the inter-layer space behind the sulfur atoms. Therefore, the interaction of

crystalline orpiment with an alkaline solution is determined by the interaction of the S atoms (slightly negative charged) with the H atoms in the OH⁻ groups (positively charged).

In contrast, the amorphous form consists of a cross-linked structure, which has no medium or longrange order in its atomic structure (Gouda, 2012). Because of the fragmental structure of amorphous As_2S_3 , hydroxide ions can react with both arsenic and sulfur atoms. The topology of the amorphous unit makes the arsenic atoms more exposed to a leaching reagent. Mamedov and Mikhailov (1997) mentioned that the hydroxide ions can interact efficiently with the arsenic atoms in the $AsS_{3/2}$ fragments in amorphous As_2S_3 .



Figure 8.10 The unit structures of crystalline and amorphous As_2S_3 and their interactions with OH^- groups in an aqueous solution (Mamedov and Mikhailov, 1997).

• Difference in the dissolution behavior of crystalline and amorphous As₂S₃

Due to the differences in their structures, crystalline orpiment is reported to be more stable than the amorphous As_2S_3 (Eary, 1992; Hu et al., 2019). Lengke (2001) discussed that the oxidation of orpiment involves breaking bonds in the orpiment crystal structure, whereas the oxidation of amorphous As_2S_3 does not involve crystallographic framework destruction, which can cause a faster oxidation of amorphous As_2S_3 .

The leaching experimental results reported in Chapter 5 and Chapter 7 show that the arsenic release from amorphous As_2S_3 was always faster than that of crystalline orpiment. A linear kinetic behavior was observed in the amorphous system. The kinetic modelling shows that a complete dissolution of As_2S_3 can be achieved under all experimental conditions tested. Both the kinetic modelling and the solid surface characterization support that surface chemical reaction is the ratelimiting step that controls the arsenic release from amorphous As_2S_3 . In contrast, the kinetics of the crystalline orpiment dissolution was shown to be determined by a mixed-control mechanism. The kinetic modelling shows that a complete dissolution cannot be achieved in the case of crystalline orpiment. The plateaued dissolution was attributed to the formation of an arsenicdeficient layer and elemental sulfur, which act as diffusion barriers to the dissolved oxygen.

8.5 Conclusion

A rate law was derived to relate the arsenic release rate from orpiment to the proton concentration, the dissolved oxygen concentration and temperature. Note that this rate law could not describe the leaching data collected at pH 10. The reaction order with respect to the proton concentration was -0.35, suggesting that increasing pH increases the arsenic release rate. The reaction order with respect to the dissolved oxygen concentration was 0.67, indicating a positive dependency of arsenic release on the dissolved oxygen concentration. The activation energy was calculated to be 35 kJ/mol. The magnitude of the reaction orders and the activation energy support a mixed-control

reaction mechanism, in which the surface chemical reaction and the diffusion of dissolved oxygen through a product layer control the arsenic release rate.

The SEM image shows that the solid surfaces became rough during leaching and that fine particles formed on the surfaces of the leaching residue collected at pH 8. The EDX analysis of the leaching residue shows that the bulk surfaces of the leaching residue resembled an arsenic-deficient phase and the fine particles were enriched in elemental sulfur. The presence of elemental sulfur on the surfaces of the leaching residue was also proved by the XRD analysis. Both the arsenic-deficient layer and the elemental sulfur could act as a barrier to diffusion of the dissolved oxygen, thereby slowing down the arsenic release. This was proved by an enhanced leaching following the removal of elemental sulfur from the solid surfaces by CS_2 washing. At pH 10, a diffusion barrier, either in the form of an arsenic-deficient phase or elemental sulfur, was absent on the solid surfaces, which agrees with the linear leaching kinetics observed.

Chapter 9: Conclusions and recommendations

A thorough understanding of the geochemical interactions of arsenic minerals with the surrounding environment is essential to predict arsenic release from mine wastes. This prediction is imperative to minimize the occurrence of arsenic in aquatic systems, to assess the risk of arsenic contamination, and to design and implement remediation measures.

The overall objective of this research was to gain a fundamental understanding of the arsenic and sulfur release from amorphous As_2S_3 and crystalline orpiment. This research investigated the behavior of arsenic and sulfur release from amorphous As_2S_3 (Objective I), determined the rate law and the mechanism of arsenic release from amorphous As_2S_3 (Objective II), and assessed the effect of the degree of crystallinity on the dissolution of arsenic trisulfide (Objective III).

9.1 Conclusions

• Objective I

The release rate of arsenic and sulfur from amorphous As_2S_3 increases with pH, DO concentration, and temperature. Arsenic is first released from As_2S_3 as arsenite (III) via the primary reactions. Arsenite (III) is subsequently oxidized to arsenate (V), the rate of which increases with pH, DO concentration, and temperature. Thiosulfate is first released from As_2S_3 as the predominant sulfur species. Thiosulfate subsequently disproportionates to sulfate and elemental sulfur at pH 8 and below. At pH 9 and above, thiosulfate is directly oxidized to sulfate without elemental sulfur formation. • Objective II

The kinetic equation derived supports that the rate-limiting step in the arsenic release from amorphous As_2S_3 is the surface chemical reaction. The solid residue characterization confirmed that elemental sulfur formed at pH 8 but was absent at pH 9. The elemental sulfur produced did not act as a barrier to diffusion of reactants, which further proves that the surface chemical reaction is the step that limits arsenic release.

Objective III

The release rate of arsenic and sulfur from crystalline orpiment is always slower than that of amorphous As_2S_3 . The rate law derived supports a mixed-control reaction mechanism, in which the surface chemical reaction and the diffusion of dissolved oxygen through a product layer control the arsenic release rate. Characterization of the surface properties shows that the product layer is an arsenic-deficient phase enriched in elemental sulfur.

9.2 Contributions to knowledge

• The effect of such factors as pH, dissolved oxygen concentration, and temperature was investigated in the ranges that are more relevant to the actual mine waste environments. The importance of each factor was incorporated into the kinetic equations derived. The kinetic modelling provides a tool for predicting arsenic release as a function of a series of of key factors. This knowledge will assist industry and regulators in developing practical mitigation strategies by manipulating those key factors.

- Arsenic and sulfur speciation were studied at different pH, dissolved oxygen concentration, and temperature. Although thermodynamics can predict possible reactions and predominant species at equilibrium, the actual species present in the system are often determined by kinetics. The knowledge on kinetically stable arsenic and sulfur intermediates is essential to assessing their mobility and toxicity.
- The surface properties of amorphous As₂S₃ and crystalline orpiment before and after leaching were investigated using SEM-EDX technique to explore the possible formation of non-stoichiometric intermediates, elemental sulfur, and arsenic-deficient polysulfide. This information has not been reported in the literature for the leaching of amorphous As₂S₃ and crystalline orpiment in neutral to alkaline leaching conditions.
- This research will provide guidance on developing concrete measures for controlling arsenic release at the source, with a focus on reducing the oxygen content and adjusting pH of a waste rock pile. Such measures may be implemented by placing a cover on top of a waste rock pile, mixing pH-changing chemical agents with rock particles, and designing a better waste rock pile.

9.3 Recommendations

• The presence of other ions in the aqueous phase, such as Ag⁺, and the coexistence of other sulfide minerals in the solid phase, such as arsenopyrite and pyrite, may influence the dissolution behavior of orpiment. It is recommended that further studies be carried out in the presence of other minerals in more complex aqueous solutions.

- There is insufficient research on the role of microbes on the dissolution of orpiment. It is suggested that further bioleaching studies be carried out to understand the catalytic or inhibitory effect of microorganisms on arsenic release from orpiment.
- The EDX technique used in this study has a general resolution of $1-2 \mu m$ in depth. It is recommended that more accurate surface analysis such as XPS be used to determine the oxidation states of sulfur at near surface regions of the solid residues and to support the formation of polysulfides.
- Arsenic trisulfide is a preferable precipitate in arsenic removal from metallurgical waste streams owing to its high arsenic content, but its long-term stability in the environment is questionable. This study shows that crystalline orpiment is more stable than the amorphous As₂S₃. It is recommended that the possibility of arsenic removal in or transformation to crystalline orpiment be studied.

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Appendix

Element	Unit	Quantity	Element	Unit	Quantity
Sb	ppm	1245	Sc	ppm	<1
Ag	ppm	6	Sr	ppm	<1
Ba	ppm	<10	Th	ppm	<20
Be	ppm	< 0.5	Tl	ppm	10
Bi	ppm	<2	U	ppm	<10
Cd	ppm	< 0.5	V	ppm	<1
Co	ppm	<1	W	ppm	<10
Cr	ppm	2	Zn	ppm	5
Cu	ppm	23	F	ppm	<20
Ga	ppm	<10	Al	%	0.01
La	ppm	<10	Ca	%	< 0.01
Mn	ppm	<5	Fe	%	0.02
Мо	ppm	10	K	%	< 0.01
Ni	ppm	<1	Mg	%	< 0.01
Р	ppm	<10	Na	%	< 0.01
Pb	ppm	9	Ti	%	< 0.01

Table A.1 Chemical composition of trace elements in crystalline orpiment structure