On-site synthesis of schwertmannite and its application for arsenic immobilization at copper mines

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On-site Synthesis of Schwertmannite and Its Application for Arsenic Immobilization at Copper Mines

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

by

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September 2015
DECLARATION

I, SENGPA SITH HOUNGALOUNE, declare that the dissertation entitled “On-site synthesis of schwertmannite and its application for arsenic immobilization at copper mines”, submitted in partial fulfillment of the requirements for the degree of Doctorate in Engineering at the Hokkaido University, is my own original work and has not been previously submitted for any degree or diploma at any other university or other institute of higher learning. Any uses made within this dissertation of the works of other authors in any form are properly acknowledged at the point of their use. A full list of the references employed has been included.

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ABSTRACT

Arsenic (As), a very poisonous inorganic pollutant is a major toxicant at porphyry copper mines the principal source of copper production worldwide. It is important to find a suitable method to control or stabilize the toxic arsenic species that could be released from the large amounts of waste at copper mines. Among the current treatment processes for arsenic control at copper mine waste, retention of arsenic by schwertmannite (a ferric oxyhydroxy sulfate mineral, Fe₈O₈(OH)₈(SO₄)ₓ with x typically 1–1.75) has attracted much attention in recent years due to its strong binding affinity to toxic arsenic species. It may also be cost-effective as it may be possible to synthesize schwertmannite from solutions generated in heap leach operations at copper mines. Such leach solutions generally contain high concentrations of Fe³⁺ and SO₄²⁻, the components of schwertmannite. In this study, on-site synthesis of schwertmannite at porphyry copper mines by neutralization technique was proposed. First, synthesis of schwertmannite from the simulated copper heap leach solutions was investigated. The efficiency in arsenic removal by the synthesized schwertmannite and the stability of arsenic-sorbed schwertmannite were then evaluated, respectively. Finally, the applications of schwertmannite in As control of copper mine wastes were demonstrated.

In Chapter 1, the background and the objectives of the study were presented. The sources of arsenic contamination resulting from copper production were pointed out. The various approach for arsenic wastes control in mining and metallurgical operations was reviewed and schwertmannite was selected as an ideal technique applying for control the toxic arsenic species that could be presented from such large amounts of waste at copper mines. On-site synthesis of schwertmannite by neutralization of the copper heap leach solutions was subsequently proposed. The synthesis is expected to be performed by neutralizing the leach solutions to pH 3–4. The synthesized schwertmannite can be expected to find application in arsenic immobilization of copper mine waste in tailings and spent ore of either dump or heap leach piles.

Chapter 2 provided insight into the production of schwertmannite in porphyry copper mines by investigating the effect of co-existing metal ions (Cu²⁺ and Fe²⁺) and the reaction temperatures (25°C and 65°C) on the synthesis of schwertmannite by neutralization technique. It is shown that Cu²⁺ and Fe²⁺ play an important role for the schwertmannite synthesis at 65°C. However, Cu²⁺ and Fe²⁺ did not affect the synthesis at 25°C. It was observed that schwertmannite is formed at both 25°C and 65°C at all experimental conditions except for the solutions containing Fe²⁺ at 65°C, as goethite was generated at these conditions. It was found that goethite is formed by transformation of intermediated schwertmaninite during the synthesis at 65°C. However, Cu²⁺ has the ability to inhibit the transformation of schwertmannite to goethite in the presence of Fe²⁺. Although it is possible to synthesize schwertmaninite at both temperatures, their surface characteristics are different. The specific surface area of the schwertmannite synthesized at 65°C was much larger (147.4–176.9 m² g⁻¹) than the specific surface area of the schwertmannite synthesized at 25°C (14.1–21.4 m² g⁻¹), which this may affect their efficiency for arsenic removal.

In Chapter 3, arsenic sorption capacities by the synthesized schwertmannite were evaluated. The results indicate that As(V) in acidic solutions (pH 3-4) can be removed effectively by schwertmannite synthesized in the presence or absence of co-existing metal ions (Cu²⁺ and Fe²⁺) at 65°C with the maximum sorption capacity of 94-133 mg g⁻¹. A lower As(V) sorption capacity is observed in product containing goethite synthesized in the presence of Fe²⁺ at 65°C; here, the maximum As(V) sorption capacity is 58 mg g⁻¹. The maximum As(V) sorption capacities by
schwertmannite synthesized at 25°C are 17-23 mg g⁻¹, which are much lower than the maximum sorption capacities of the schwertmannite synthesized at 65°C. This should be taken into consideration for its application on mine sites.

In Chapter 4, the stability of As(V)-sorbed schwertmannite (Sch-As) under porphyry copper mining conditions was studied by investigating the effect of Cu²⁺, Fe²⁺, pH, and ageing time on the stability of Sch-As. The results indicated that Cu²⁺ has no significant effect on the stability of Sch-As and that the As(V) incorporated into schwertmannite can retard or significantly inhibit the Fe²⁺-catalyzed transformation of schwertmannite to goethite under acidic conditions (pH 3–4). The Sch-As aged at different pH ranges from 3 to 11 at 25°C exhibits no mineralogical phase changes even after ageing for 120-days; however the concentration of arsenic released from the solid phase appeared to be strongly pH-dependent also at ageing for 24 h. The release of As was almost negligible at pH 2 to 7, and a high release of As was observed at extremely acidic and alkaline conditions. This indicates that the release of As from Sch-As is controlled by environmental factors such as pH rather than time.

In Chapter 5, applications of the synthesized schwertmannite for arsenic immobilization in copper mine wastes were demonstrated. The study was divided into two models experiments. The first part was to demonstrate the application of schwertmannite for immobilization of arsenic in tailings resulting from copper flotation operations. The results indicated that high arsenic concentration was observed for the experiment without the addition of schwertmannite, which this may be due to the oxidation of arsenopyrite. The concentration of arsenic became significantly lower when schwertmannite was added; suggesting that schwertmannite synthesized from copper heap leach solutions may be suitable for arsenic immobilization in copper flotation tailings. The second part of this chapter was focused on the possibility in applying the synthesized schwertmannite for arsenic immobilization in mine waters containing the diluted concentration of arsenic. The high arsenic concentration is essential for long-term stability of schwertmannite. The synthesized schwertmannite was used as the sorbent-desorbent to remove the diluted arsenic concentration at low pH and strip it back in the high pH solution to generate higher arsenic concentration. The results indicated that the diluted concentration of As(V) in acidic solution can be sorbed efficiently by schwertmannite; and the arsenic can also strip back or release from the As(V)-sorbed schwertmannite at alkaline pH condition, suggesting that the synthesized schwertmannite may be suitable for arsenic treatment for the solution with diluted concentration of arsenic.

In Chapter 6, the summary and conclusions of the study were presented.
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Chapter I

GENERAL INTRODUCTION

1.1. STATEMENT OF THE PROBLEM AND OBJECTIVES OF THE STUDY

Porphyry copper deposits, the principal source of copper worldwide (Khorasanipour et al., 2011 and John et al., 2010) are relatively low-grade, epigenetic, intrusion-related deposits that are commonly mined by open-pit methods (Berger et al., 2008 and Khorasanipour et al., 2011). Extraction and beneficiation of copper ore produces large amounts of rock waste and mine tailings (Antelo et al., 2013 and Nordstrom, 2011). The waste may be divided into three major categories: (1) waste rock piles or dumps; (2) tailings ponds; and (3) spent ore piles where the leaching operation has ceased in the case of heap leach operations. These wastes may be exposed to the environment, presenting the potential for contaminant transport (Dold and Fontbote, 2001). Among the contaminants, arsenic (As) represents a specific concern because of its high toxicity at low concentrations, and some As-bearing minerals are highly soluble in a wide range of pH conditions (Coussy et al., 2012).

Arsenic is one of the most dangerous inorganic pollutants, causing environmental and health emergencies in several areas of the world (Ma and Bruckard, 2009). It is also a penalty element in many base metal concentrations (e.g. copper) that are destined for smelting to produce the relevant metallic products. Recently, the regulations for arsenic release to the environment have become more stringent with increasing public awareness of the toxicity of arsenic and better understanding of its impact on the environment (Long et al., 2012). Therefore, arsenic control is an important issue in mining and metallurgical operations at porphyry copper mines. It is important to find a suitable method to control or stabilize the toxic arsenic species that could be released from such large amounts of waste at copper mines. Stabilization of arsenic has been proposed with various approaches such as solidification/stabilization technique, arsenic disposal in the form of scorodite (FeAsO₄ · 2H₂O), immobilization by schwertmannite (Fe₈O₈(OH)₈(SO₄)ₓ with x typically 1–1.75), etc. Among the current treatment processes for arsenic control at copper mine waste, retention of As by schwertmannite has attracted much attention in recent years due to its strong binding affinity to toxic As species (Bigham et al., 1990, Bigham et al., 1996, Bigham et al., 1994, Fukushi et al., 2003 and Regenspurg and Peiffer, 2005). It can also be cost-effective as it is possible to synthesize schwertmannite from solutions generated in heap leach operations (i.e. raffinate). Such leach solutions generally contain high concentrations of Fe³⁺ and SO₄²⁻, the components of schwertmannite.

Schwertmannite can be synthesized by several techniques such as dialysis by adding ferric chloride/nitrate to sodium/potassium sulfate solutions at 60°C (Bigham et al., 1990); oxidation of FeSO₄ solutions by H₂O₂ (Regenspurg et al., 2004); and biooxidation of FeSO₄ solutions by Acidithiobacillus ferrooxidans (Liao et al., 2009). These techniques may not be suitable for schwertmannite generation at porphyry copper mines. For example, the dialysis technique requires a period of more than 30 days to be dialyzed against deionized water, which is a time-consuming and inefficient work for on-site synthesis of schwertmannite at copper mines. In this study, an appropriate method called neutralization technique for schwertmannite synthesis from copper heap leach solutions was proposed and its application for arsenic control of copper mine waste was investigated. The synthesis is expected to be performed by neutralization of leach solutions to pH 3–4. The synthesized schwertmannite can be expected to find application in arsenic immobilization of copper mine waste in tailings and spent ore of either dump or heap leach piles, as well as copper smelting plants.

The primary objective of this dissertation, therefore, is to investigate the applications of the proposed technique for schwertmannite production at porphyry copper mines and its efficiency in arsenic immobilization of copper mine waste. Particularly, this study aims to (1) exam the effects
1.2. ARSENIC CONTAMINATION

Arsenic (As) is a metalloid that can form inorganic and organic compounds (Choi et al., 2009). Inorganic As exists in several oxidation states: As(V), arsenate; As(III), arsenite; As(0), and As(-III), arsine (Shih and Lin, 2003). There is also As(-I) in Arsenopyrite (Kwong et al., 2007; Nesbitt et al., 1995) and As(+II) in realgar (Trentelman et al., 1996). Arsenate and arsenite are the most widespread forms of arsenic occur in the natural environment. The inorganic compounds can be methylated by microorganisms to form organic arsenic compounds. Generally, As(III) is the most toxic form of arsenic, followed by As(V), and to a lesser extent, methylated arsenic (Shih and Lin, 2003). As(III) is listed as 25-60 times more toxic than As(V) and has been reported to be more mobile in the environment (Moon et al., 2008). Arsenic toxicity, bioavailability, and mobility vary depending on type and source of As pollutant, environmental pH, oxidation–reduction potential, ligand exchange, the presence of iron oxides and other sulfur-containing compounds, as well as microbial activities (Coussy, et al., 2011; Shih and Lin, 2003).

Arsenic is an abundant element in the earth’s crust that is present in over 320 different minerals (Henke, 2009) and has an average terrestrial concentration of 5 ppm (Leetmaa, 2008). There are many countries in the world where high natural arsenic content in drinking water has caused public health problems, including India, Bangladesh, Mongolia, Argentina, Chile, China, and the United States of America (Kim et al., 2012). Worldwide, there are over 150 locations recognized as significant arsenic contamination sites as a result of ore deposit and mining (Gonzalez-Contreras et al., 2012). Chronic exposure to arsenic can cause serious human health problems including irritation of the stomach and intestines and, especially, an increase in the risk of developing lung, liver, kidney, and skin cancer (Kim et al., 2012, Moon et al., 2008).

Elevated arsenic concentrations found in copper mining environments are mainly due to the oxidation of As-bearing sulfide minerals such as arsenopyrite (FeAsS) and arsenian pyrite (Antelo et al., 2013 and Burton et al., 2009). Generally, As-bearing minerals are liberated and disposed as waste rock or tailings after mining and mineral processing due to the low economic value (Coussy et al., 2012). When disposed unprotected from the weather, the tailings react with atmospheric oxygen and meteoric water, leading to the release of sulfates, metals, and As in the drainage waters (Smedley and Kinniburgh, 2002). This is termed Acid Mine Drainage (AMD) when the pH is acidic and Contaminated Neutral Drainage (CND) when the pH remains circum-neutral (Coussy et al., 2012). For these reasons, As can occur in Acid-Mine Drainage (AMD) at hundreds of mg L⁻¹ and in acid-sulfate soil (ASS) groundwater at lower, mg L⁻¹, levels (Burton et al., 2009).

During copper pyrometallurgical operations, arsenic trioxide (As₂O₃) dust is produced in the smelting and roasting of sulfides concentrates (Gonzalez-Contreras et al., 2014). These processes usually operate at temperatures higher than 700°C, which leads to volatize arsenic. Arsenic is mobilized as arsenic oxide with the exhaust gases. Arsenic removal from flue gases is mostly achieved by arsenic trioxide collection in electrostatic precipitators or wet gas scrubbers (up to 30%wt. arsenic). Significant amounts of arsenic can also be recovered in the acid plant tail gas with sulfuric acid. In copper electrorefineries, arsenic is a major impurity and bleed streams are commonly recycled to concentrate arsenic in the electrolyte to 20 g L⁻¹ (Gonzalez-Contreras et al., 2014). Arsenic trioxides have a relatively high solubility in water and can therefore not be
stockpiled for long periods of time due to the danger of soluble arsenic release to the environment (Leetmaa, 2008).

Arsenic pollutions related to copper mining and smelting activities are profound in many countries (Choi et al., 2009). The leachability of As from the tailings of approximately 1000 abandoned metal mines has caused the serious contamination of soil, surface water, and groundwater surrounding the mining areas; and has been identified as one of most serious environmental problems in South Korea (Kim et al., 2012). Arsenic pollution presents a significant public concern including effects on workers, nearby residents, sediments, soils which resulted from improper management of copper smelting operation/wastes in Chile, China, and India (Luo et al., 2010; Shih and Lin, 2003).

Increasing environmental awareness is leading to stricter regulations in order to protect human health. The World Health Organization (WHO) recommended a maximum contaminant level (MCL) for arsenic in drinking water of 0.01 mg/L (Choi et al., 2009). The US Environmental Protection Agency (EPA) recently reduced its MCL from 0.05 to 0.01 mg/L and listed arsenic as a class A carcinogen with a LD50 (lethal dose) of approximately 1–4 mg/kg for an adult (Shih and Lin, 2003). Despite stricter legislations for drinking water, arsenic limit values for solid and liquid wastes have not decreased. Most countries follow the US-EPA recommendations and use the Toxicity Characteristic Leaching Procedure (TCLP) test (Gonzalez-Contreras et al., 2014). TCLP test is the most used procedure with the purpose to identify arsenic bearing waste. This test involves the evaluation of solid waste at a concentration of 50 g L\(^{-1}\) in a buffered acetic acid solution (pH 5) simulating landfill disposition. The dissolution of elements is measured after 20 hours of reaction. The arsenic limit concentration in the solution is 5 mg L\(^{-1}\) below which a material is classified as "non-hazardous". Arsenic limit concentration of the TCLP test is 500 times higher than the drinking water regulations.

1.3. MINERAL PROCESSING AND METALLURGICAL OPERATIONS AT PORPHYRY COPPER MINES

Porphyry copper deposits (PCDs) are the most important source of copper worldwide, accounting for more than 60% of the annual production of copper and they constitute about 65% of known copper ore resources (John et al., 2010). The PCDs are commonly categorized as multi-zone deposits (Figure 1-1), composed of a primary sulfide ore at depth, a secondary enrichment zone, and a naturally weathered (oxidized) zone above the water table where all of the copper has been oxidized (Bartlett, 1992; Osanloo et al., 2008). The PCDs are defined as large (greater than 100 million tons), low to medium-grade (0.3–2.0% copper) disseminated copper deposits, where the hypogene sulfides are primarily structurally controlled (John et al., 2010).

The mineral processing and metallurgical operations at porphyry copper mines are outline briefly in Figure 1-2. In the oxidized zones, the main copper minerals are malachite (\(\text{Cu}_2\text{CO}_3(\text{OH})_2\)), cuprite (\(\text{Cu}_2\text{O}\)), and azurite (\(\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2\)) (Bartlett, 1992). These oxide and carbonate minerals can be leached with dilute sulfuric acid, and copper ores mined from the oxidized zone are generally recovered by hydrometallurgical processes, including leaching (e.g. dump or heap leaching), solvent extraction, and electro-winning (SX/EW) (Peacey et al., 2004). The material remaining in either dump or heap leach piles when leaching ceases is called spent ore. Leach piles are reported to range in size from 6 m to over 30 m in height and may contain millions of tons of leached ore (EPA, n.d.). The spent ore becomes waste when active leaching ends. At present more than 20% of world copper production is from heap leach–SX/EW operations of oxide copper ores (Ochromowicz and Chmielewski, 2013).

Chalcocite (\(\text{Cu}_2\text{S}\)) and covellite (\(\text{CuS}\)) are common minerals in the secondary enrichment zone, and chalcopyrite (\(\text{CuFeS}_2\)) and bornite (\(\text{Cu}_5\text{FeS}_4\)) are common minerals in the primary sulfide ore zone (Bartlett, 1992). These copper sulfide minerals are mainly recovered by flotation as
concentrates (Osanloo et al., 2008). The fine-grained fraction of the waste generated during flotation is called tailings, which are discharged to the tailings impoundment structures (Lottermoser, 2003). Tailings commonly contain sulfide minerals, e.g. pyrite (FeS$_2$) and arsenopyrite (FeAsS), which weather when tailings are exposed to the air and oxygen (Antelo et al., 2013 and Burton et al., 2009). This can result in the liberation of arsenic and strong acid (i.e. AMD) from the tailings, which may pollute adjacent areas (Lottermoser, 2003). Once the copper sulfide mineral has been concentrated it can be converted into copper metal using pyrometallurgical processes, including smelting-converting and electrolytic refining (Ochromowicz and Chmielewski, 2013). Copper sulfide minerals from the secondary zone are also processed using bio-heap leaching combined with SX/EW at a number of locations worldwide (Neale et al., 2011; Watling, 2006).

![Figure 1-1: Copper porphyry ore deposit types showing primary, secondary enriched and oxide zones (Bartlett, 1992)](image-url)
Figure 1-2: Principal processes for extracting copper at porphyry deposit operation.
1.4. ARSENIC STABILIZATION TECHNIQUES IN THE MINING AND METALLURGICAL INDUSTRIES

Arsenic contamination of the environment and its risk management remains an important concern for the mining and metallurgical industries; thus the tailings containing As must be treated before its discharge into the environment to avoid environmental impacts on the surrounding ecosystems. In order to ensure a safe disposal environment for the final wastes, As must be stabilized. Stabilization of As has been studied extensively with various approaches, including solidification/stabilization (S/S), disposal in the form of scorodite, and removal with schwertmannite. The various approaches used in As stabilization are summarized as follows.

1.4.1. Solidification/stabilization technique

The solidification/stabilization (S/S) processes are generally used as pre-landfill waste treatment technologies that aim to reduce the mobility of As so as not to present an environmental hazard (Singh and Pant, 2006). The process involves mixing the waste, either in the form of sludge, liquid or solid, into a cementitious binder system (Sullivan et al., 2010). During stabilization, contaminants can be converted to forms which are much less mobile, soluble and toxic. Through solidification, the contaminants can be encapsulated within a monolithic solid with high structural integrity that exhibits long-term stability and minimal leaching (Moon et al., 2008).

S/S techniques are widely used for the treatment of hazardous wastes, beginning in the early 1970s. The S/S is one of the most common treatment processes for soil and waste, used to treat arsenic in 45 projects among 56 ongoing or completed Superfund projects in the US (Yoon et al., 2010; Choi et al., 2009). In Taiwan, a feasibility study was conducted on an abandoned copper smelter site in 1994 for potential remediation. The study indicated that the S/S treatment process would be the best practical technology to treat the arsenic waste (Shih and Lin, 2003). A cement based system was used to treat an industrial waste, originating from a metallurgical process in which copper is refined and containing large amounts of arsenic (42 wt%) (Dutré and Vandecasteele, 1995). In the optimized mix, 10 parts (by weight) of fly ash was mixed with 6 parts of Portland cement and 8 parts of lime (CaO). The concentrations of As leaching reduced from 5000 mg/l for the untreated waste to 5 mg/l after treatment. Choi et al. (2009) studied the cement based S/S of an abandoned mine tailings contaminated primarily with arsenic (up to 88mg/kg) and lead (up to 35 mg/kg). They observed that addition of more than 5% cement was found to be able to satisfy the Unconfined Compression Strength test (UCS) requirements; and the 7.5% addition of cement was optimal in reducing the leachabilities of arsenic and lead simultaneously to conservative levels.

S/S processes are recognized by the U.S. Environmental Protection Agency (EPA) as the Best Demonstrated Available Technology (BDAT) for the land disposal of most toxic elements. However, the cementitious binders used are often a major cost for this technique (Sullivan et al., 2010).

1.4.2. Arsenic disposal in form of scorodite

Over the past several decades, scorodite or a crystalline ferric arsenate dehydrate (FeAsO$_4$·2H$_2$O) has received considerable attention as potentially good carrier for the fixation of arsenic in the case of arsenic-rich and iron-deficient process solutions of the mining and metallurgical industries (Paktunc and Bruggeman, 2010, Bluteau et al., 2009). Scorodite has a high As removal capacity and a stoichiometric (Fe/As molar ratio =1) iron demand which would result in lower volumes of waste material per contained As (Bluteau et al., 2009). Moreover, scorodite is considered to have a low solubility, relatively high stability under acidic to neutral pH conditions.
(Shibata et al., 2012), and excellent dewatering characteristics (Majzlan et al., 2012); therefore, its precipitation from processing solutions has been investigated by numerous researchers.

Scorodite can be either produced by hydrothermal precipitation (Caetano et al., 2009) or by controlled precipitation under atmospheric pressure (Paktunc et al., 2008; Fujita et al., 2008). The temperatures higher than 125°C are required to produce well-crystallized precipitates with a lower molar Fe/As ratio, which allows for higher As content (Paktunc et al., 2008). However, the precipitation of scorodite without the need for autoclaves would be an attractive option from an economic point of view since hydrothermal operations require high capital and operational costs (Caetano et al., 2009). Thus, there have been attempts to obtain scorodite in more benign conditions. Synthesis of scorodite from solutions with Fe/As molar ratios of 1 under atmospheric conditions at 70°C was reported by Paktunc et al. (2008). The follow-up experiments pointed out that scorodite are able to form at temperatures as low as 40°C (Paktunc and Bruggeman, 2010). Demopoulos and co-workers have been vigorously studying this field (Shibata et al., 2012; Fujita et al., 2008). They proposed a synthetic scorodite approach at 95°C under atmospheric pressure conditions which can be summarized as: (1) oxidation of arsenic in effluents to As(V), (2) addition of Fe and MgO to adjust the pH, (3) addition of crystal seeds, and (4) 3–4 incremental increases of pH. Their ambient pressure precipitation process involves the two key techniques: 1) addition of scorodite seed to maintain a low supersaturation level of ferric arsenate; and 2) strict pH control for ferric arsenate solution by means of magnesium or calcium hydroxides. Besides, Fujita et al. (2008, 2009, 2012) indicated that the formation of scorodite can be obtained at 95°C by the controlled oxidation of arsenate-containing ferrous sulfate solutions. Moreover, Gonzalez-Contreras et al. (2012) indicated the possibility of precipitating biogenic scorodite or “bioscorodite” in batch systems at constant pH (1-1.2) and at a relatively low temperature of 70°C.

Recently, the atmospheric scorodite process became an industrial reality. Ecometales limited has designed and built the scorodite industrial plant with the capacity to abate up to 10,000 tons of arsenic and recover more than 25,000 tons of copper per year (Ecometales, 2012). DOWA Metals and Mining Co., Ltd. also demonstrated the industrial capability of a plant with 30 metric ton/month of arsenic capacity (the process has been named as DMSP®), proving that formation of crystallization of scorodite is industrially viable on commercial scale (Fujita et al., 2012). However, this technique is only suitable for treatment of high As concentration waste e.g., effluent from copper smelting plants.

1.4.3. Arsenic removal by schwertmannite

Among the current treatment processes, adsorption is considered to be the most promising technology for arsenic removal because it can be cost-effective, easier and safer to handle, and more versatile (Liao et al., 2011). Schwertmannite (ideally Fe₈O₈(OH)₆SO₄), a poorly crystalline iron oxyhydroxysulfate often precipitated from mine drainage discharges in iron- and sulfate-rich (~3,000 mg/L) acidic mine waters (pH=3.0-4.5) (Paikaray and Peiffer, 2012) and in acid-sulfate soils or from bioleaching environment (Liao et al., 2011). Schwertmannite has been found to be an efficient attenuator of arsenic in acid mine drainage (AMD) streams (Regenspurg and Peiffer, 2005; Fukushi et al., 2003) due to its high specific surface area (SSA ≥200 m²/g) and its positive surface charge in these acid systems as well as exchangeable SO₄²⁻ (Paikaray and Peiffer, 2012).

Schwertmannite is recognized as a metastable compound that is transformed to stable crystalline goethite via dissolution and re-precipitation. The transformation process may be delayed or accelerated depending on the pH of the surrounding environment and the presence of other ions in solution or in the mineral structure (Antelo et al., 2013). It has been found that arsenic partially exchanged with sulfate without significant structural disruption can stabilize schwertmannite and retard or significantly inhibit the transformation into goethite (Fukushi et al., 2003, Burton et al., 2010, Raghav et al., 2013 and Regenspurg and Peiffer, 2005).
Due to the abundance of arsenate species in AMD environments and the high retention capacity of schwertmannite at acidic pH, many authors have devoted their research on the retention of As(V). Fukushi et al., 2003 observed that the amount of leached As(V) in acid mine effluents was naturally attenuated to background level by incorporation into schwertmannite within few meters downstream, and the overall uptake is controlled by ligand exchange with surface or structural \( \text{SO}_4^{2-} \) and/or surface precipitation (Paikaray and Peiffer, 2012). As(V) incorporated into chemically synthetic schwertmannite has been shown to retard or significantly inhibit the transformation into goethite (Regenspurg and Peiffer, 2005; Fukushi et al., 2003). Also, increasing of \( \text{SO}_4^{2-} \) content significantly decreases the transformation rate into goethite (Regenspurg et al., 2004).

1.5. OUTLINE OF THE DISSERTATION

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

Chapter 1: introduces the background, statement of the problem and objectives of the study. The proposed technique for arsenic control at porphyry copper mines is described.

Chapter 2: presents the study on the synthesis of schwertmannite from copper heap leach solutions.

Chapter 3: describes the study on the arsenic removal by schwertmannite synthesized from copper heap leach solutions.

Chapter 4: details the study on the stability of As(V)-sorbed schwertmannite (Sch-As) under porphyry copper mine conditions.

Chapter 5: demonstrates the applications of the synthesized schwertmannite for arsenic immobilization in copper mine wastes and metallurgical plants.

Chapter 6: gives the summary and conclusion of the dissertation.
REFERENCES


Chapter II
SYNTHESIS OF SCHWERTMANNITE FROM COPPER
HEAP LEACH SOLUTIONS

2.1. INTRODUCTION

Schwertmannite, \( \text{Fe}_8\text{O}_8\text{(OH)}_8\cdot x\text{(SO}_4\text{)}_x \), with \( x \) typically 1–1.75, is a poorly crystalline Fe(III)-oxyhydroxysulfate mineral often formed in acidic iron- and sulfate-rich (1000–3000 mg L\(^{-1}\)) environments (Bigham and Nordstrom, 2000, Bigham et al., 1990 and Bigham et al., 1994). Several authors have reported the structure of schwertmannite as similar to that of akaganéite except that \( \text{SO}_4^{2-} \) instead of Cl occupies the parallel-extended square tunnels (Cornell and Schwertmann, 2003), with a unit cell of \( \text{FeO}_6 \) octahedra forming double chains and \( \text{SO}_4^{2-} \) ions present as both structural and adsorbed sulfate (Bigham et al., 1990 and Waychunas et al., 1995).

The occurrence of schwertmannite as an ochreous precipitate has been widely documented in acid-sulfate systems (Burton et al., 2008), including acid-mine drainage (AMD) streams (Acero et al., 2006 and Bigham et al., 1994), waters and sediments of mine-pit lakes (Regenspurg et al., 2004), acid-sulfate soils and associated waterways (Burton et al., 2006), as well as bioleaching environments (Liao et al., 2011), and in the layers covering wetlands treating AMD (Gagliano et al., 2004). Weathering of iron sulfide minerals leads to the formation of large amounts of secondary iron precipitates when \( \text{Fe}^{2+} \) is oxidized to \( \text{Fe}^{3+} \), in a process that may be mediated by bacterial activity following exposure of the minerals to the atmosphere (Antelo et al., 2012). The composition of these secondary iron precipitates is mainly determined by the composition of the aqueous phase, with pH and the \( \text{SO}_4^{2-} \) concentration as the main controlling variables (Jönnsson et al., 2005). Jarosite \( (\text{K,Na,H}_3\text{O[Fe}_3\text{(OH)}_6\text{(SO}_4\text{)}_2]) \) is formed at pH < 3 and at high \( \text{SO}_4^{2-} \) concentrations, ferrihydrite \( (\text{Fe}_2\text{O}_3\cdot 1.8 \text{H}_2\text{O}) \) and goethite \( (\alpha\text{-FeOOH}) \) are known to precipitate at neutral pH, and schwertmannite is commonly formed at pH 3.0–4.0 (Bigham and Nordstrom, 2000 and Bigham et al., 1996).

Schwertmannite is a metastable phase and over weeks or months (Liao et al., 2011) it readily undergoes phase transformation to more stable iron oxides such as goethite under some pH and oxidizing conditions (Antelo et al., 2012). However, it has been found that arsenic incorporated into schwertmannite retards or significantly inhibits the transformation into goethite (Fukushi et al., 2003 and Regenspurg and Peiffer, 2005). Extremely high arsenic concentrations in acid mine effluents have been reported to be naturally decreased to background levels by incorporation into schwertmannite (adsorption capacity up to 60 mg-As/g) within meters downstream of effluent outlets (Fukushi et al., 2003). The overall uptake of arsenic into schwertmannite is controlled by ligand exchanges with surface or structural \( \text{SO}_4^{2-} \) and/or surface precipitation (Carlson et al., 2002).

Recently, the regulations for arsenic release to the environment have become more stringent with increasing public awareness of the toxicity of arsenic and better understanding of its impact on the environment (Long et al., 2012). Therefore, arsenic control is an important issue in mining and metallurgical operations at porphyry copper mines. On-site synthesis of schwertmannite is of economic and environmental interest for As removal in porphyry copper mines. Generally, effluents of copper heap leaching are complex solutions, containing a range of constituents such as \( \text{Cu} \) (0.5–4.0 g L\(^{-1}\)), \( \text{Fe} \) (0.5–10 g L\(^{-1}\)), \( \text{S} \) (2.5–20 g L\(^{-1}\)), and others (Hernández et al., 2003, Jenkins et al., 1999 and John, 1999). The leach solutions contain high concentrations of \( \text{Fe}^{3+} \) and \( \text{SO}_4^{2-} \), the components of schwertmannite, suggesting that the solutions can be used for schwertmannite synthesis.
Although schwertmannite can be synthesized by several techniques such as dialysis by adding ferric chloride/nitrate to sodium/potassium sulfate solutions at 60°C (Bigham et al., 1990); oxidation of FeSO₄ solutions by H₂O₂ (Regenspurg et al., 2004); and biooxidation of FeSO₄ solutions by Acidithiobacillus ferrooxidans (Liao et al., 2009). These techniques may not be suitable for schwertmannite generation at porphyry copper mines. For example, the dialysis technique requires a period of more than 30 days for dialyze against deionized water, which is a time-consuming and inefficient work for real operation at copper mine sites. To overcome these obstacles, an appropriate technique for synthesis of schwertmannite from copper heap leach solutions is proposed. Schwertmannite synthesis is expected to be performed by neutralization of the copper heap leach solutions to pH 3–4.

Generally, the leach solutions contain significant concentrations of Cu²⁺ and Fe²⁺ as coexisting ions, and the effects of these ions on schwertmannite synthesis is not well known. Therefore, the main objective of this chapter is to investigate the effects of coexisting Cu²⁺ and Fe²⁺ on schwertmannite synthesis by neutralization of Fe₂(SO₄)₃ solutions; as well as the effect of reaction temperatures (25°C and 65°C) on the properties of the schwertmannite products formed by the neutralization technique.

2.2. MATERIALS AND METHODS

2.2.1. Solution preparation

Solutions containing known concentrations of H₂SO₄, Na₂CO₃, Fe³⁺, Fe²⁺, and Cu²⁺ were prepared by dissolving reagent-grade H₂SO₄, Na₂CO₃, FeSO₄·7H₂O, Fe₂(SO₄)₃·nH₂O, and CuSO₄·5H₂O (Wako Pure Chemical Industries, Ltd., Japan) in distilled/ion-exchanged water. The results for the solid-phase analyses are presented on a dry weight basis, unless noted otherwise.

2.2.2. Schwertmannite synthesis

Solutions containing known concentrations of H₂SO₄, Na₂CO₃, Fe³⁺, Fe²⁺, and Cu²⁺ were prepared by dissolving reagent-grade H₂SO₄, Na₂CO₃, FeSO₄·7H₂O, Fe₂(SO₄)₃·nH₂O, and CuSO₄·5H₂O (Wako Pure Chemical Industries, Ltd., Japan) in distilled/ion-exchanged water. The results for the solid-phase analyses are presented on a dry weight basis, unless noted otherwise.

2.2.3. Effect of Cu²⁺ and Fe²⁺ on schwertmannite synthesis

Using these solutions, syntheses were carried out following the experimental procedures detailed in Section 2.2.2.
2.2.4. Effect of Cu\(^{2+}\) and Fe\(^{2+}\) on the transformation of schwertmannite to goethite

The synthesized schwertmannite prepared with the procedure in Section 2.2.2, was suspended in solutions containing Cu\(^{2+}\) and Fe\(^{2+}\) to investigate the phase transformation of schwertmannite to other solid phases such as goethite. Solution containing predetermined amounts of FeSO\(_4\)·7H\(_2\)O, CuSO\(_4\)·5H\(_2\)O and Na\(_2\)SO\(_4\) was added to a 500-mL beaker and heated to 65 °C, and the pH was adjusted by addition of 10 mM H\(_2\)SO\(_4\) and 4.5 g of synthesized schwertmannite was subsequently introduced into the solution. A small amount (several milliliters) of suspension was removed from the beaker at 5, 15, 30, 45, and 60 min, and filtered immediately through a filter membrane (pore size, 0.2 μm). The filtrate was subsequently subjected to pH, redox potential, and Fe concentration measurements. After 60 min the suspended solid in the beaker was harvested by filtering through a 5A filter paper. The recovered solid, after being dried overnight in a vacuum dryer, was ground in an agate mortar, and subjected to XRD analysis.

2.2.5. Effect of reaction temperature on schwertmannite synthesis

To investigate the effect of reaction temperature on the synthesis of schwertmannite, syntheses were carried out as follows: 500 mL of solution containing 10 mM H\(_2\)SO\(_4\) and 50 mM Fe\(^{3+}\) with or without Cu\(^{2+}\) and Fe\(^{2+}\) was prepared and added into a beaker under magnetic stirring at 350 rpm and at 25 or 65°C. After discontinuing the magnetic stirring 1 M Na\(_2\)CO\(_3\) was titrated to the solution to adjust the final pH to 3.0–4.0 (titration rate, 1500 µL/min). The resulting suspension was left to settle, and the supernatant was subsequently replaced with deionised water. This rinsing procedure was repeated 5 times to remove soluble ions. The precipitate in the beaker was then filtered, dried at 40°C in a vacuum oven for 24 hours, and subjected to X-ray diffraction (XRD) analysis. To identify the composition of the synthesized products, 0.1 g of dried precipitates were dissolved in 100 mL of 0.1 M HCl and the Fe and S contents were determined with inductively coupled plasma atomic emission spectroscopy (ICP-AES). The dried precipitates were also subjected to specific surface area analysis by multiple-point BET (Brunauer-Emmett-Teller).

2.2.6. Analytical methods

A pH-meter and combined electrode with temperature compensation was used to measure the pH and was calibrated regularly with standard buffer solutions of pH 1.68, 4.01, and 6.86. The redox potential was measured using an ORP combined electrode consisting of Pt and Ag/AgCl reference electrodes. The measured values of the redox potential were converted to the values against a standard hydrogen electrode (SHE). The concentrations of iron, copper, and sulfur in the aqueous phase were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Seiko instruments SPS7800. In the ICP-AES analyses, calibration with sets of standards was performed and the regression coefficients exceeded 0.999; and dilutions from 1:10 to 1:1000 were used to ensure that the concentrations of the elements in the samples were within the concentration range of the standards, the error was estimated to be below 5%.

Solid samples were ground to a homogeneous powder in a mortar and subsequently analyzed by X-ray diffraction (XRD) using a JEOL JDX-3500 powder diffractometer with CuKα radiation (40 kV and 40 mA) to identify the minerals present in the samples. The specimens were step scanned from 10° to 70° 2θ with continuous scans at a rate of 1/2° 2θ/min. Peak maxima were read from the diffractogram and minerals were identified by comparison with a schwertmannite standard from an XRD pattern identical to that of the schwertmannite described by Bigham et al. (1990). The specific surface area was measured by multiple-point BET using a NOVA 1000e surface area analyzer and N\(_2\) as the adsorbate. Before the measurements, samples were heated at 120°C for 1 hour in glass tubes (to eliminate moisture completely) and then weighed.
2.3. RESULTS AND DISCUSSION

2.3.1. Characterization of schwertmannite

The XRD analysis was used to identify the formation of schwertmannite. Figure 2-1 shows the XRD pattern of a sample synthesized from 50 mM Fe$^{3+}$ solution (without Cu$^{2+}$ and Fe$^{2+}$). The result confirms that schwertmannite is the only mineral detectable in the synthesized product. As mentioned above schwertmannite is described by the formulation Fe$_8$O$_8$(OH)$_{4.98}$(SO$_4$)$_{1.51}$, with $x$ ranging between 1 and 1.75. The amount of Fe and S measured after complete dissolution of synthesized product in 0.1 M HCl were 8.6 ± 0.3 mmol g$^{-1}$ and 1.62 ± 0.06 mmol g$^{-1}$, respectively. The molar Fe/S ratio, determined from the Fe and S molar proportions, is 5.3 ± 0.35 which agrees with the molar values suggested previously for schwertmannite (molar Fe/S ratio = 4.5–8.0, Bigham et al., 1990 and Bigham et al., 1994). On this basis, the synthesized schwertmannite composition can be represented as Fe$_8$O$_8$(OH)$_{4.98}$(SO$_4$)$_{1.51}$. This composition is very close to the average value reported in Bigham et al. (1996), Jönsson et al. (2005), and Paikaray et al. (2011).

![Figure 2-1: XRD pattern for sample synthesized from 50 mM Fe$^{3+}$ solution without Cu$^{2+}$ and Fe$^{2+}$. The numbers in the figure indicate the d-spacings (Å) for schwertmannite reported by Bigham et al. (1990).](image)

2.3.2. Effect of Cu$^{2+}$ on the synthesis

Numerous facilities have been designed and operated to extract copper from leach solutions of various compositions. It has been reported that the pregnant leach solutions (PLS) generated by heap or dump leaching typically contain 0.5–4 g L$^{-1}$ of copper (Ochromowicz and Chmielewski, 2013), and that the raffinate from SX-EW plants contain 0.01–1.5 g L$^{-1}$ of copper (Jenkins et al., 1999). This suggests a range of copper concentrations in PLS and raffinate in heap leach-SX-EW operation of about 0.1–100 mM.

Considering the above, the effect of 1, 10, and 100 mM Cu$^{2+}$ on the synthesis of schwertmannite was investigated. Figure 2-2(a) shows XRD patterns of the products synthesized from 50 mM Fe$^{3+}$ solutions containing various concentrations of Cu$^{2+}$. As suggested by Figure 2-2(a), schwertmannite appears as the dominant phase formed with all products synthesized in the presence of Cu$^{2+}$. The XRD patterns suggest that there is no formation of new or other phases among the products synthesized with Cu$^{2+}$ ≤ 10 mM. Traces of brochantite (Cu$_4$(SO$_4$)$_2$(OH)$_6$) could be inferred for samples synthesized at high concentration of Cu$^{2+}$ (100 mM), but also here, schwertmannite is the major mineral detected. This indicates that addition of Cu$^{2+}$ alone has no significant effect on the schwertmannite synthesis.
Figure 2-2: XRD patterns for samples synthesized from 50 mM Fe$^{3+}$ solution containing: (a) various concentrations of Cu$^{2+}$, (b) various concentrations of Fe$^{2+}$, and (c) 100 mM Fe$^{2+}$ and various concentrations of Cu$^{2+}$. Schwertmannite is denoted as “sh”, brochantite as “br”, and goethite as “G”.
2.3.3. Effect of Fe\(^{2+}\) on the synthesis

It has been reported that the initial concentration of Fe\(^{2+}\) played an important role in determining the type of iron hydroxysulfate precipitates in the acidic sulfate-rich environments (Bai et al., 2012). The effect of 1, 10, and 100 mM Fe\(^{2+}\) on the synthesis of schwertmannite was investigated in the present study.

The XRD patterns of the products synthesized from 50 mM Fe\(^{3+}\) solutions containing various Fe\(^{2+}\) concentrations are shown in Figure 2-2(b). The results indicate that schwertmannite remains the dominant mineral for product synthesized with 1 mM Fe\(^{2+}\). Some goethite (αFeOOH) peaks appear with 10 mM Fe\(^{2+}\), and the goethite contribution continues to increase with Fe\(^{2+}\) concentration. At the initial Fe\(^{2+}\) concentration of 100 mM, goethite is the main mineral phase formed, indicating that Fe\(^{2+}\) has a significant effect on the synthesis of schwertmannite.

Two goethite formation processes in the presence of Fe\(^{2+}\) need to be considered. One coprecipitation with schwertmannite or direct formation of goethite from solution; and the other is the transformation of intermediate schwertmannite to goethite during the synthesis process.

Goethite (FeOOH) contains Fe\(^{3+}\) and it is not formed directly from Fe\(^{2+}\). When Fe\(^{2+}\) is oxidized to Fe\(^{3+}\), however, goethite is precipitated from solutions. Numerous studies on goethite precipitation discussed the oxidation of Fe\(^{2+}\) compounds precipitated by mixing sodium hydroxide and Fe\(^{2+}\) salts. The parameter playing the major role in promoting goethite precipitation is \(R = \text{[Fe}^{2+}\]/[OH\(^-\)]\), the concentration ratio of the reactants. Goethite is preferentially formed with a large excess of OH\(^-\) ions, e.g. \(R \leq 0.2\), or with a large excess of Fe\(^{3+}\) ions, e.g. \(R \geq 2.5\) (Gilbert et al., 2008). It had been also reported that goethite is an alteration product of schwertmannite at pH exceeding 4.5 (Antelo et al., 2012 and Bigham et al., 1994). Additionally, it has been reported that goethite is commonly obtained at intermediate temperatures, between 25 and 45 °C (Gilbert et al., 2008).

The experiments in the present study were carried out at pH ≤ 3.5 and at 65 °C. The Fe\(^{2+}/\text{OH}^-\) ratio, R, is also outside the above mentioned range suitable for goethite precipitation (R < 0.2 and R > 2.5): Here the R value is calculated to be around 1 for the experiments using 100 mM Fe\(^{2+}\), by assuming that addition of 1 mol Na\(_2\)CO\(_3\) is equivalent to 2 mol of OH\(^-\). Therefore, goethite would not be likely to form directly under the conditions of synthesis in the present study and it may be assumed that goethite is formed by transformation of intermediate schwertmannite. To clarify this model, experiments of the transformation of schwertmannite to goethite were carried out and are discussed in detail in Section 2.3.5.

2.3.4. Effect of the coexistence of Cu\(^{2+}\) and Fe\(^{2+}\) on the synthesis

In general, both Cu\(^{2+}\) and Fe\(^{2+}\) are present in copper heap leach liquids. Therefore, it is important to examine the behavior of schwertmannite synthesis in the presence of both Cu\(^{2+}\) and Fe\(^{2+}\). As mentioned above, Fe\(^{2+}\) influences the synthesis of schwertmannite, especially at high concentrations (here 100 mM) of Fe\(^{2+}\) and, experiments were carried out with 50 mM Fe\(^{3+}\) solution containing 100 mM Fe\(^{2+}\) and 0–100 mM Cu\(^{2+}\). The XRD results with the synthesized products (Figure 2-2(c)) demonstrate that goethite is the dominant phase formed in the presence of 100 mM Fe\(^{3+}\) and the absence of Cu\(^{2+}\). Some goethite peaks become absent and some schwertmannite is detected for the product synthesized with the addition of 10 mM Cu\(^{2+}\). Schwertmannite becomes the prominent mineral with no goethite phase detected in the synthesized product in the presence of 100 mM Cu\(^{2+}\), similar to the results of the original synthesized schwertmannite (without Cu\(^{3+}\) and Fe\(^{2+}\)) in the present study. This indicates that Cu\(^{3+}\) has the ability to inhibit goethite formation in the presence of Fe\(^{2+}\); further details are discussed in Section 2.3.5.
2.3.5. Effect of Cu$^{2+}$ and Fe$^{2+}$ on the transformation of schwertmannite to goethite and the mechanism of the transformation

To investigate the effects of Cu$^{2+}$ and Fe$^{2+}$ on the transformation of schwertmannite to goethite, the synthesized schwertmannite was suspended in 4 different types of solutions as follows:

(i) 200 mM Na$_2$SO$_4$ + 10 mM H$_2$SO$_4$
(ii) 100 mM CuSO$_4$·5H$_2$O + 10 mM H$_2$SO$_4$ + 100 mM Na$_2$SO$_4$
(iii) 100 mM FeSO$_4$·7H$_2$O + 10 mM H$_2$SO$_4$ + 100 mM Na$_2$SO$_4$
(iv) 100 mM CuSO$_4$·5H$_2$O + 10 mM H$_2$SO$_4$ + 100 mM FeSO$_4$·7H$_2$O

The total SO$_4^{2-}$ concentrations are the same in all four solutions by the addition of Na$_2$SO$_4$ to solutions (i), (ii), and (iii). Therefore, when comparing the results of the experiments using these solutions, the effect of the SO$_4^{2-}$ concentration on the transformation can be disregarded.

The XRD patterns of the recovered solids after suspension of the synthesized schwertmannite for 60 min in the various solutions are shown in Figure 2-3. The results show schwertmannite peaks and there is no formation of other phases in the solid suspended in solution (i) with 0 mM Cu$^{2+}$ and 0 mM Fe$^{2+}$. This indicates that the schwertmannite here is stable and that no solid phase transformation occurs in a solution that does not contain Cu$^{2+}$ or Fe$^{2+}$. In solution (ii) containing 100 mM Cu$^{2+}$, schwertmannite remained as the dominant phase in the recovered solid. When schwertmannite was suspended in solution (iii), containing 100 mM Fe$^{2+}$, goethite peaks are clearly observed in the XRD pattern of the recovered solid, indicating that Fe$^{2+}$ affects the phase transformation of schwertmannite to goethite. When schwertmannite was suspended in solution (iv) containing both Cu$^{2+}$ and Fe$^{2+}$, there is no goethite peaks detected in the XRD pattern of the recovered solid phase, strongly indicating that Cu$^{2+}$ inhibits Fe$^{2+}$-catalyzed the phase transformation of schwertmannite to goethite.

Figure 2-3: X-ray diffractograms of the solids suspended in solutions containing various concentrations of Fe$^{2+}$ and Cu$^{2+}$ for 60 min. Diffractograms of the synthesized schwertmannite is also shown for comparison. Schwertmannite is denoted as “sh” and goethite as “G”.

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During the experiments, the dissolved Fe concentration, redox potential, and pH of the filtrates were measured. As shown in Figure 2-4, for the experiments carried out without Fe\(^{2+}\) (solutions (i) and (ii) above), approximately 0.1 mM of dissolved Fe was detected shortly after adding the synthesized schwertmannite into the solution. For the experiments carried out with solutions containing Fe\(^{2+}\) (solutions (iii) and (iv) above), the dissolved Fe concentrations are slightly higher than the initial concentration of 100 mM for the duration of the experiment. These results indicate that a small amount of Fe\(^{3+}\) was extracted from the suspended schwertmannite.

Figure 2-5 shows the redox potentials of the filtrates, and in all solutions it increased within 5 min after schwertmannite was added. This may be ascribed to a decomposition of Fe\(^{3+}\), an oxidizing chemical species, from the suspended schwertmannite. The redox potential is 0.38–0.48 V vs. SHE for the experiments with Fe\(^{2+}\), for solutions (iii) and (iv), much lower than in the experiments without the addition of Fe\(^{2+}\) (0.58–0.73 V vs. SHE, solutions (i) and (ii)), which may be ascribed to the high concentration of Fe\(^{2+}\), a reducing chemical species, present in solutions (iii) and (iv) during the period of the experiments.

**Figure 2-4:** Dissolved Fe concentrations of filtrate recovered from schwertmannite suspensions containing various Cu\(^{2+}\) and Fe\(^{2+}\) concentrations.

**Figure 2-5:** Redox potentials (E) of schwertmannite suspensions containing various Cu\(^{2+}\) and Fe\(^{2+}\) concentrations.
As shown in Figure 2-6, the pH of the suspensions shows behaviors strongly depending on the experimental conditions. The pH value remains stable (3.5 to 3.6) throughout the experimental period for the suspension without \( \text{Cu}^{2+} \) and \( \text{Fe}^{2+} \) (solution (i) above). The pH value of the solution ((ii) above) containing 100 mM \( \text{Cu}^{2+} \) decreases from 3.6 to 3.1 within a few minutes of the addition of schwertmannite to the solution, and then becomes constant. The rapid pH decline after the addition of schwertmannite may be explained by assuming that proton–copper ion exchange occurs at the surface of the schwertmannite, as may be described by the following reaction:

\[
2 \text{H}^{+}\text{ad} + \text{Cu}^{2+} \rightarrow 2 \text{H}^{+} + \text{Cu}^{2+}\text{ad} \tag{2-1}
\]

where \( \text{H}^{+}\text{ad} \) and \( \text{Cu}^{2+}\text{ad} \) represent the proton and copper ions adsorbed on the surface of the schwertmannite. Assuming this reaction, the \( \text{Cu}^{2+} \) adsorbed amount per 1 g schwertmannite is calculated to be approximately 25 μmol.

With the solution ((iii) above) containing 100 mM \( \text{Fe}^{2+} \), the pH value is about 3.6 before adding schwertmannite and then decreases continuously till the end of the experiment to reach around 3.0 after 60 min. As shown in Figure 2-3 the schwertmannite here has transformed to goethite, something that may be ascribed to the presence of the \( \text{Fe}^{2+} \). The overall reaction of the phase transformation can be expressed as (Knorr and Blodau, 2007):

\[
\text{Fe}_8\text{O}_8(\text{OH})_8(\text{SO}_4)_x + 2x \text{H}_2\text{O} \rightarrow 8 \text{FeOOH} + x \text{SO}_4^{2-} + 2x \text{H}^+ \tag{2-2}
\]

Here protons are generated when schwertmannite is transformed to goethite and the lowering in the pH value after the addition of schwertmannite may be ascribed to the proton generation by reaction (2-2).

The pH decrease during the period of the experiment was also observed even when schwertmannite does not transform to goethite (Figure 2-6). When using a solution ((iv) above) containing both \( \text{Cu}^{2+} \) and \( \text{Fe}^{2+} \), transformation of schwertmannite to goethite was not observed by the XRD analysis, but the pH value decreases from 3.0 to 2.6 after 60 min. To clarify the reason for the pH decline, pH changes were investigated for the solution containing 100 mM \( \text{Cu}^{2+} \) and \( \text{Fe}^{2+} \) (solution (iv) above), without schwertmannite. It was found that the pH value is decreased similar to the decrease in the experiment conducted with the addition of schwertmannite at 60 min, indicating that the decreases in pH is not due to the presence of schwertmannite, and a small amount of precipitate was observed at the end of this experiment. From these results, it may be assumed that oxidation of \( \text{Fe}^{2+} \) by \( \text{Cu}^{2+} \) and oxidation of \( \text{Cu}^{2+} \) by \( \text{O}_2 \) have occurred (Cher and Davidson, 1955 and Zhang et al., 2000), and that the precipitation of ferric components such as \( \text{Fe(OH)}_3 \) are generated with the solution containing both \( \text{Cu}^{2+} \) and \( \text{Fe}^{2+} \) (solution (iv) above). These reactions are expressed as follows:

\[
4 \text{Cu}^{2+} + 4 \text{Fe}^{2+} \rightarrow 4 \text{Cu}^+ + 4 \text{Fe}^{3+} \tag{2-3}
\]
\[
4 \text{Cu}^+ + 4 \text{H}^+ + \text{O}_2 \rightarrow 4 \text{Cu}^{2+} + 2 \text{H}_2\text{O} \tag{2-4}
\]
\[
4 \text{Fe}^{3+} + 12 \text{H}_2\text{O} \rightarrow 4 \text{Fe(OH)}_3 + 12 \text{H}^+ \tag{2-5}
\]

with the overall reaction summarized as:

\[
4 \text{Fe}^{2+} + \text{O}_2 + 10 \text{H}_2\text{O} \rightarrow 4 \text{Fe(OH)}_3 + 8 \text{H}^+ \tag{2-6}
\]

Therefore, the decline in the pH value may be due to the protons (\( \text{H}^+ \)) released in the reaction in Equation (2-6).
As mentioned previously, Fe\(^{2+}\) causes a phase transformation from schwertmannite to goethite. Further, Cu\(^{2+}\) inhibits the phase transformation occurring in the presence of Fe\(^{2+}\). These results correspond well with the effect of Cu\(^{2+}\) and Fe\(^{3+}\) on the synthesis of schwertmannite from Fe\(_2\)(SO\(_4\))\(_3\) solution as described in Section 2.3.3 and 2.3.4. Consequently, it is considered that the “intermediated schwertmannite model” as assumed earlier in this study provides a plausible explanation for the results presented here.

Schwertmannite is a metastable compound that is transformed to stable crystalline goethite via dissolution and re-precipitation. The transformation is a relatively slow process requiring years or decades in acidic and oxic environments (Acero et al., 2006, Jönsson et al., 2005 and Regenspurg et al., 2004). This transformation process is generally accelerated in higher pH environments, but requires more than 100 days under near-neutral, oxic conditions (Knorr and Blodau, 2007 and Regenspurg et al., 2004). Kumpulainen et al. (2008) reported a one-year duration for complete transformation of schwertmannite to goethite at pH 8. Schwertmann and Carlson (2005) observed complete transformation of schwertmannite to goethite in deionized water at pH 7.2 after 100 days. Incomplete transformation at pH 6 after 543 days of aging was reported by Jönsson et al. (2005), and others have reported transformation of schwertmannite to accelerate under weakly acidic or near-neutral, anoxic conditions in the presence of Fe\(^{2+}\) (Burton et al., 2007 and Burton et al., 2008).

Burton et al. (2008) investigated factors affecting the transformation rate of schwertmannite to goethite in a chloride solution at 25 °C. Here, the transformation rate is increased in the presence of Fe\(^{2+}\) and at pH > 5; and complete conversion of schwertmannite to goethite occurred within only 3–5 h at pH > 6 and Fe\(^{2+}\) ≥ 5 mmol L\(^{-1}\).

Such Fe\(^{2+}\) -catalyzed transformation of iron minerals also occurs for other minerals than schwertmannite. Yee et al. (2006), and Hansel et al. (2005) reported that the transformation of ferrihydrite to goethite phase is catalyzed by Fe\(^{2+}\), and used isotopes to confirm that electron transfer between Fe\(^{2+}\) adsorbed from the solution phase and structural Fe\(^{3+}\) in the ferrihydrite lattice during the transformation process. Referring to these studies, Burton et al. (2008) proposed a model of the Fe\(^{2+}\) -catalyzed transformation of schwertmannite to goethite as suggested in Figure 2-7(a).

![Figure 2-6: pH values of filtrates recovered from schwertmannite suspensions containing various Cu\(^{2+}\) and Fe\(^{2+}\) concentrations.](image-url)
In this model, the phase transformation involves the adsorption of Fe\(^{2+}\) to the schwertmannite surface. Schwertmannite has a point of zero charge (PZC) of 7.2 (Jönsson et al., 2005), and its surface is positively charged in the acidic region, Fe\(^{2+}\) also with a positive charge, is absorbed with difficulty on the schwertmannite surface. Under higher pH conditions, the schwertmannite surface becomes negatively charged, enabling Fe\(^{2+}\) to adsorb on the surface of schwertmannite by electrostatic attraction, so increasing the amount of adsorption. An electron transfer subsequently occurs between the adsorbed Fe\(^{2+}\) (acting as an electron donor) and the structural Fe\(^{3+}\) at the mineral–water interface via overlapping d-orbitals (Williams and Scherer, 2004). The transferred electron must remain sufficiently localized on a single Fe atom within the schwertmannite surface for a shift in valency to occur (Burton et al., 2008). The surface layer of schwertmannite is destabilized due to the presence of this nascent structural Fe\(^{2+}\), causing a reductive dissolution and the release of the adsorbed Fe\(^{3+}\), structural Fe\(^{2+}\), SO\(_4^{2-}\), and OH\(^-\). Finally, the desorbed Fe\(^{3+}\) rapidly hydrolyzes and precipitates as a thermodynamically more stable phase mainly as goethite (Hansel et al., 2005). The released Fe\(^{2+}\) is available to readсорb to the schwertmannite surface, thereby continuing the overall transformation process. In this way, relatively small amounts of Fe\(^{2+}\) can catalyze the transformation of large amounts of schwertmannite to goethite (Burton et al., 2008).

![Figure 2-7: Scheme summarizing the transformation of intermediated schwertmannite to goethite](image)

The experimental conditions of the present study (sulfate solution, 65 °C, pH 3–4) are different from those of previous studies, for instance Burton et al. (2008) (chloride solution, 25 °C, pH > 5). Therefore, it is difficult to subject the results of the present study to a quantitative description by the above model, however qualitatively the processes involved are similar.

The transformation of schwertmannite to goethite in this study occurred faster (within 1 h) and at lower pH values (3–4) than reported by Burton et al. (2008). This may be due to the higher Fe\(^{2+}\) concentration (100 mM) and high temperature (65 °C), which could accelerate the
transformation rate. It has been reported by Jönsson et al. (2005) that the transformation rate of schwertmannite to goethite is slower at lower temperatures. In addition, Yee et al. (2006) found that the transformation rate of schwertmannite to goethite is slower at lower temperatures. In addition, Yee et al. (2006) found that in the presence of Fe$^{2+}$, the transformation of poorly ordered ferrihydrite into crystalline goethite is significantly faster at 60°C than at 21°C. This indicates that the transformation rate is dependent on temperature. In addition to higher Fe$^{2+}$ concentration and temperature, the presence of a high concentration of SO$_4^{2-}$ in the present study may also cause the Fe$^{2+}$-catalyzed transformation of schwertmannite to goethite at the lower pH observed here, because SO$_4^{2-}$ is a component of schwertmannite and SO$_4^{2-}$ would act as a charge determining ion for this mineral. If this is the case, high concentrations of SO$_4^{2-}$ cause a shift of the PZC to lower pH values, resulting in the adsorption of Fe$^{2+}$ at lower pH with the Fe$^{2+}$-catalyzed transformation of schwertmannite.

The present study confirms that Cu$^{2+}$ inhibits the transformation of schwertmannite to goethite, a transformation that is catalyzed by Fe$^{2+}$; assuming the model in Figure 2-7(a) to hold, the transformation may be described as: (1) adsorption of Fe$^{2+}$ and Cu$^{2+}$ onto the schwertmannite surface; (2) reductive dissolution of schwertmannite by the absorbed Fe$^{2+}$, a process that may involve two steps: both Fe$^{2+}$ and Cu$^{2+}$ are positively charged and these ions may affect the electrostatic attraction to the schwertmannite surface, the Cu$^{2+}$ would prevent the adsorption of Fe$^{2+}$ onto the surface. Further, Cu$^{2+}$ functions as an oxidizing agent (electron acceptor), whereas Fe$^{2+}$ is a reducing agent (electron donor). When Fe$^{2+}$ supplies electrons to schwertmannite, some of these electrons are consumed by the Cu$^{2+}$, and the reductive dissolution rate of schwertmannite can be expected to decrease. This discussion is summarized in Figure 2-7 (b1 and b2). However, further investigation is required to establish the details of these phenomena.

**2.3.6. Effect of reaction temperature on schwertmannite synthesis**

The synthesis was conducted at 25°C and 65°C to investigate the effect of reaction temperature on the schwertmannite synthesis. Generally, both Cu$^{2+}$ and Fe$^{2+}$ are present in copper heap leach solutions, and it is also important to examine the behavior of schwertmannite synthesis in the presence of both Cu$^{2+}$ and Fe$^{2+}$.

**2.3.6.1. Mineralogy of the synthesized products**

The XRD analysis was used to identify the formation of schwertmannite. The XRD patterns of a sample synthesized from 50 mM Fe$^{3+}$ solution with or without Cu$^{2+}$ and Fe$^{2+}$ at 65°C are shown in Figure 2-8(a). The results confirm that schwertmannite appears as the dominant phase of the product synthesized without Cu$^{2+}$ and Fe$^{2+}$. Traces of brochantite (Cu$_4$(SO$_4$)(OH)$_6$) could be inferred for samples synthesized with 100 mM Cu$^{2+}$, and also here, schwertmannite is the major mineral component detected. Goethite ($\alpha$FeOOH) appears as the main mineral phase formed for samples synthesized at the initial Fe$^{2+}$ concentration of 100 mM. Schwertmannite becomes the prominent mineral with no goethite phase in the synthesized product in the presence of 100 mM Cu$^{2+}$ and 100 mM Fe$^{2+}$. Figure 2-8 (b) shows the XRD patterns of the samples synthesized at 25°C. As suggested by Figure 2-8 (b), schwertmannite appears as the main mineral phase for all products synthesized with or without addition of Cu$^{2+}$ and Fe$^{2+}$.

The mineralogy of the products synthesized at 65°C suggests that addition of Cu$^{2+}$ alone has no significant effect on the schwertmannite synthesis, and that Fe$^{2+}$ has a strong effect on the synthesis. However, Cu$^{2+}$ has the ability to inhibit goethite formation in the presence of Fe$^{2+}$. The results for the products synthesized at 25°C imply that the presence of Cu$^{2+}$ and Fe$^{2+}$ do not affect the schwertmannite synthesis. In conclusion, schwertmannite can be synthesized at both 25°C and 65°C from all solutions except for solutions containing Fe$^{2+}$ at 65°C, as goethite is generated at this condition.
Figure 2-8: XRD patterns for samples synthesized from 50 mM Fe$^{3+}$ solution in the absence or presence of Cu$^{2+}$ or Fe$^{2+}$ at (a) 65°C and (b) 25°C. Schwertmannite is denoted as “sh”, brochantite as “br”, and goethite as “G”.
As mentioned previously that there are two possibilities for goethite formation processes in the presence of Fe$^{2+}$. One is co-precipitation with schwertmannite or direct formation of goethite from solution; and the other is the transformation of intermediate schwertmannite to goethite during the synthesis process. The results (Section 2.3.5) has suggested that goethite would not be likely to form directly from the solutions; and it was also confirmed that Fe$^{3+}$-catalyzed the transformation of schwertmannite to goethite under pH 3-4 at 65°C within 1 h, suggesting that goethite is formed by transformation of intermediate schwertmannite during the synthesis at 65°C.

The effect of Fe$^{2+}$ on the transformation of schwertmannite to goethite at 25°C was also investigated under same experimental conditions as performed at 65°C. The XRD data (Figure 2-9) confirm negligible degrees of schwertmannite transformation, even suspended with 100 mM Fe$^{2+}$. This suggests that the transformation rate may be dependent on temperature, and Jönsson et al. (2005) reported that the transformation rate of schwertmannite to goethite is slower at lower temperatures. Yee et al. (2006) also found that Fe$^{3+}$-catalyzed transformation of poorly ordered ferrihydrite into crystalline goethite is significantly faster at 60°C than at 21°C.

![Figure 2-9: XRD patterns for schwertmannite suspended in solutions containing various Fe(II) concentrations at 25°C, at pH 3-4 for 1 h. Schwertmannite is denoted as "Sh" and goethite as "G".](image)

Although the results showed the possibility for schwertmannite synthesis at both temperatures, the properties of the products synthesized at 25°C and 65°C may be different. Therefore, the characteristics of all synthesized products were investigated and are discussed in the following section.
2.3.6.2. Elemental and surface analyses of the synthesized products

The elemental compositions of the products synthesized with or without Cu$^{2+}$ and Fe$^{2+}$ at 25°C and 65°C are shown in Table 2-1. The results show that the molar Fe/S ratios, determined from the Fe and S molar proportions, were 4.9-6.4 and 5.5-5.7 for the schwertmannite products synthesized at 25°C and 65°C, respectively. These values agree well with the molar Fe/S ratios reported previously for natural and synthesized schwertmannite (Table 2-2).

There was a relatively high molar Fe/S ratio of 13.8 of the goethite product synthesized with the solution containing Fe$^{2+}$ at 65°C. Generally, goethite does not contain sulfate, however the solutions used for the synthesis in the present study contain high concentrations of sulfate. Goethite may adsorb $\text{SO}_4^{2-}$, especially at low pH (pH 3-4) where the net surface charge of goethite is positive (Juang and Wu, 2002). Here the total quantity of $\text{SO}_4^{2-}$, associated with goethite is small compared to schwertmannite products (Table 2-1).

Table 2-1: Elemental composition and the molar ratios of products synthesized at 25°C and 65°C

<table>
<thead>
<tr>
<th>Samples</th>
<th>Elemental composition (mmol g$^{-1}$)</th>
<th>Fe/S</th>
<th>Chemical formulation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu$^{2+}$ (mM)</td>
<td>Fe$^{2+}$ (mM)</td>
<td>Fe</td>
</tr>
<tr>
<td>65°C</td>
<td>0</td>
<td>0</td>
<td>9.11</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>10.23</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0</td>
<td>7.37</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>7.25</td>
</tr>
<tr>
<td>25°C</td>
<td>0</td>
<td>0</td>
<td>8.31</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>8.83</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0</td>
<td>8.06</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>8.47</td>
</tr>
</tbody>
</table>

Figure 2-10: Specific surface area of the products synthesized with or without Fe$^{2+}$ and Cu$^{2+}$ at 25°C and 65°C.
The specific surface area of the products synthesized with or without Fe$^{2+}$ and Cu$^{2+}$ at 25°C and 65°C is shown in Figure 2-10. Here, the specific surface area of the schwertmannite synthesized at 65°C is much larger (147.4–176.9 m$^2$ g$^{-1}$) than the specific surface area of the schwertmannite synthesized at 25°C (14.1–21.4 m$^2$ g$^{-1}$). This may imply that the temperature of the synthesis has a significant effect on surface characteristic of the products.

The specific surface areas of schwertmannite product synthesized at 65°C are similar to those obtained by the dialysis technique at 60°C (Table 2-2). The specific surface areas of schwertmannite product synthesized at 25°C are similar to those obtained by oxidative or biosynthesis techniques carried out at room temperature. The large difference in surface area of these schwertmannite specimens may be related to the particles morphology. As suggested by several studies that particles formed by the dialysis technique are long needle-shaped crystals (hedge-hog like schwertmannite); and the oxidative synthesis method generated spheroids with a diameter of 250-500 nm (Bigham et al., 1990; Paikaray et al., 2011; Regenspurg et al., 2004; Vithana et al., 2014).

The specific surface area of goethite product (168.4 m$^2$ g$^{-1}$) synthesized in the presence of Fe$^{2+}$ at 65°C agrees well with the specific surface area of natural goethite formed by acid mine drainage (100-200 m$^2$ g$^{-1}$, Murad and Rojik, 2004).
<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>References</th>
<th>Fe/S mole ratio</th>
<th>Chemical formulation</th>
<th>BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biosynthesis</td>
<td>Paikaray et al. (2011)</td>
<td>5.3</td>
<td>Fe₈O₈(OH)₄.₉⁸(SO₄)₁.₅₁</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>Lioa et al. (2009)</td>
<td>4.3-4.5</td>
<td>-</td>
<td>3.4-23.4</td>
</tr>
<tr>
<td></td>
<td>Antelo et al. (2013)</td>
<td>8.15</td>
<td>Fe₈O₈(OH)₃.₉₄(SO₄)¹.₀₃</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fukushi et al. (2003)</td>
<td>5.3</td>
<td>Fe₈O₈(OH)₄.₉⁸(SO₄)₁.₅₁</td>
<td>154</td>
</tr>
<tr>
<td></td>
<td>Regenspurg et al. (2004)</td>
<td>-</td>
<td>-</td>
<td>175-220</td>
</tr>
<tr>
<td></td>
<td>Paikaray et al. (2011)</td>
<td>6.4</td>
<td>Fe₈O₈(OH)₂.₅₀(SO₄)₁.₂₅</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>Vithana et al. (2014)</td>
<td>4.3</td>
<td>Fe₈O₈(OH)₁.₃(SO₄)₁.₈₅</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Paikaray and Peiffer (2012)</td>
<td>6.3</td>
<td>Fe₈O₈(OH)₃.₉₄(SO₄)₁.₀₃</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td>Regenspurg et al. (2004)</td>
<td>-</td>
<td>-</td>
<td>4-14</td>
</tr>
<tr>
<td></td>
<td>Burton et al. (2010)</td>
<td>5.0</td>
<td>Fe₈O₈(OH)₁.₈(SO₄)₁.₆</td>
<td>4-14</td>
</tr>
<tr>
<td></td>
<td>Paikaray et al. (2011)</td>
<td>4.7</td>
<td>Fe₈O₈(OH)₁.₆₀(SO₄)₁.₇₀</td>
<td>5.3</td>
</tr>
<tr>
<td></td>
<td>Jonsson et al. (2005)</td>
<td>5.4</td>
<td>Fe₈O₈(OH)₂.₀₂(SO₄)₁.₄⁹</td>
<td>42.9</td>
</tr>
<tr>
<td>Natural</td>
<td>Regenspurg et al. (2004)</td>
<td>-</td>
<td>-</td>
<td>72</td>
</tr>
<tr>
<td>Neutralization</td>
<td>This study (25°C)</td>
<td>4.9-6.4</td>
<td>Fe₈O₈(OH)₁.₇₄.₅₅(SO₄)₁.₂₅.₁.₆₃</td>
<td>14.1-21.4</td>
</tr>
<tr>
<td></td>
<td>This study (65°C)</td>
<td>5.5-5.7</td>
<td>Fe₈O₈(OH)₁.₁₀.₅₂(SO₄)₁.₄₀.₁.₄₅</td>
<td>147.4-176.9</td>
</tr>
</tbody>
</table>
2.4. CONCLUSION

This chapter provides insight into the production of schwertmannite in porphyry copper mines by investigating the effect of co-existing metal ions (Cu$^{2+}$ and Fe$^{2+}$) and the reaction temperatures (25°C and 65°C) on the synthesis of schwertmannite by neutralization technique. It is shown that Cu$^{2+}$ and Fe$^{2+}$ play an important role for the schwertmannite synthesis at 65°C. However, Cu$^{2+}$ and Fe$^{2+}$ did not affect the synthesis at 25°C. It was observed that schwertmannite is formed at both 25°C and 65°C at all experimental conditions except for the solution containing 100 mM Fe$^{2+}$ at 65°C, as goethite was generated at this condition. To clarify the intermediated schwertmannite transformation model, experiments on the transformation of schwertmannite to goethite were conducted. It was shown that complete transformation occurred in only 1 h, at pH 3–4, and at 65°C in the presence of 100 mM Fe$^{2+}$, suggesting that goethite is formed by transformation of intermediated schwertmannite during the synthesis at 65°C. Cu$^{2+}$ has the ability to inhibit the transformation of schwertmannite to goethite in the presence of Fe$^{2+}$. On the other hand, Fe$^{2+}$-catalyzed the transformation of schwertmannite to goethite did not occur at 25°C, suggesting that the transformation rate may be dependent on reaction temperature. Although it is possible to synthesize schwertmannite at both temperatures, their surface characteristics are different. The specific surface area of the schwertmannite synthesized at 65°C was much larger (147.4–176.9 m$^2$ g$^{-1}$) than the specific surface area of the schwertmannite synthesized at 25°C (14.1–21.4 m$^2$ g$^{-1}$), which this may affect on their capacity for arsenic removal. Therefore, arsenic sorption capacities by these synthesized products were evaluated and are discussed in detail in the next Chapter.
REFERENCES


Chapter III

ARSENIC REMOVAL BY SCHWERTMANNITE SYNTHESIZED FROM COPPER HEAP LEACH SOLUTIONS

3.1. INTRODUCTION

Elevated arsenic concentrations usually found in copper mine waste are mainly due to the oxidation of As-bearing sulfide minerals such as arsenopyrite (FeAsS) and arsenian pyrite (Antelo et al., 2013 and Burton et al., 2009). Generally, As-bearing minerals are liberated and disposed as waste rock or tailings after mining and mineral processing due to the low economic value (Coussy et al., 2012). When disposed unprotected from the weather, the tailings react with atmospheric oxygen and meteoric water, leading to the release of sulfates, metals, and arsenic in the drainage waters (Smedley and Kinniburgh, 2002). For these reasons, arsenic can occur in Acid-Mine Drainage (AMD) at hundreds of mg L⁻¹ and in acid-sulfate soil (ASS) groundwater at lower, mg L⁻¹, levels (Burton et al., 2009).

Recently, the regulations for As release to the environment have become more stringent with increasing public awareness of the toxicity of As and better understanding of its impact on the environment (Long et al., 2012). Therefore, As control is an important issue in mining and metallurgical operations at porphyry copper mines. It is important to find a suitable method to control the toxic arsenic species that could be released from such large amounts of waste at copper mines. Stabilization of arsenic by schwertmannite has been proposed here due to the strong binding affinity of schwertmannite to toxic arsenic species. It can also be cost-effective as it is possible to synthesize schwertmannite from the effluent or raffinate of copper heap leach solutions as demonstrated in Chapter 2.

Although it is possible to synthesize schwertmannite from the effluent or raffinate of copper heap leach solutions at various conditions (i.e., in the presence or absence of co-existing metal ions, at different reaction temperatures), their characteristics are different which may affect on their capacity for arsenic removal. Therefore, arsenic sorption capacities by those products synthesized as described in Chapter 2 are evaluated and discussed in detail in this Chapter.

3.2. MATERIALS AND METHODS

3.2.1. As(V) sorption kinetics

In a 200-mL flask, 100 mL of solution containing 1.5 mM of Na₃HAsO₄·7H₂O (As (V)) was mixed with 100 mg of dried schwertmannite product as described in Section 2.2.2 (Chapter 2). After the pH of the schwertmannite suspension was adjusted to 3-4 by dropwise addition of NaOH or H₂SO₄, the flask was shaken in a water bath at 25°C at 120 rpm. At a preset time, the suspension was sampled with a syringe and this sample was filtered through a 0.2-μm filter membrane. The supernatant was analyzed for arsenic and pH. The amount of sorbed arsenic was calculated from the differences between the initial (added) amount and final (remaining) amount of As in the solutions.

3.2.2. As(V) sorption isotherms

Arsenic sorption experiments were conducted in a 200-mL flask with 100 mg of dried synthesized products (as described in Section 2.2.2, 2.2.3, and 2.2.5 of Chapter 2) and 100 mL of the solutions containing known concentrations of Na₃HAsO₄·7H₂O (As (V)) at the initial pH 3.0–
4.0. The flask was shaken for 24 h in a water bath at 25°C at 120 rpm. After 24 h, the solution was filtrated through a membrane filter (pore size, 0.2 μm) and analyzed for arsenic by ICP-AES. The amount of sorbed arsenic was calculated from the differences between the initial (added) amount and final (remaining) amount of As in the solutions.

Among the empirical models, the Langmuir model and the Freundlich model are used to describe the adsorption isotherms (Mamindy-Pajany et al., 2011). These representations allow calculating thermodynamic values induced by the adsorption process. The Langmuir model assumes a monolayer sorption mechanism with homogeneous sorption energies, and Freundlich model is an empirical model demonstrating multilayer sorption sites and heterogeneous sorption energies (Weber and DiGiano, 1996). Arsenate adsorption was modeled with the Langmuir adsorption isotherm using the following equation (Liao et al., 2011):

$$q = \frac{q_m K_L C}{1 + K_L C} \tag{3-1}$$

where q (mg g⁻¹) is the amount of adsorbed As(V), C (mg L⁻¹) is the equilibrium solute (As) concentration, qₘ (mg g⁻¹) is the maximum adsorption capacity, and Kₐ is the equilibrium constant for the overall adsorption process.

The Freundlich relationship modeled the arsenic adsorption by evaluating log q versus log C according to the following equation (Liao et al., 2011):

$$q = K_F C^{1/n} \tag{3-2}$$

where Kᵢ is the Freundlich constant, and n represents the degree of nonlinearity in the relationship between q and C.

3.2.3. Effect of pH on As(V) sorption

To determination the effect of pH on As(V) sorption capacity, 100 mg of dried schwertmannite product as described in Section 2.2.2 (Chapter 2) was added to a 200-mL flask containing 100 mL of solution consisting of 1.5 mM of initial As (V) (Na₂HAsO₄·7H₂O). The solution pH was adjusted to desired values ranging from 3 to 12 by dropwise addition of NaOH or H₂SO₄. All flasks were shaken in a water bath at 25°C at 120 rpm. After shaking for 24 h, aliquots of the samples in the flasks were withdrawn, filtrated, and analyzed for arsenic and pH. The amount of sorbed arsenic was calculated from the differences between the initial (added) amount and final (remaining) amount of As in the solutions.

3.2.4. Analytical methods

A pH-meter and combined electrode with temperature compensation was used to measure the pH and was calibrated regularly with standard buffer solutions of pH 1.68, 4.01, and 6.86. The redox potential was measured using an ORP combined electrode consisting of Pt and Ag/AgCl reference electrodes. The measured values of the redox potential were converted to the values against a standard hydrogen electrode (SHE). The concentrations of iron, copper, and sulfur in the aqueous phase were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Seiko instruments SPS7800.
3.3. RESULTS AND DISCUSSION

3.3.1. As(V) sorption kinetics

There have been extensive studies of As(V) sorption on schwertmannite and sorption was suggested to occur through a combination of surface complexation with active hydroxyl groups, exchange with both surface-adsorbed and structural $\text{SO}_4^{2-}$ sites, and electrostatic interactions (Antelo et al., 2012, Burton et al., 2009, Carlson et al., 2002 and Fukushi et al., 2003). The kinetic of As(V) removal by schwertmannite synthesized without $\text{Cu}^{2+}$ and $\text{Fe}^{2+}$ at 65°C is shown in Figure 3-1. The results indicate that the removal of As(V) by schwertmannite is considerably fast during the initial period of sorption. For example, after sorption for 1 and 3 h, the removal efficiency of As(V) is 54.3% and 71.9%, respectively, while removal efficiency of 82.9% and 88.8% is obtained after adsorption for 7 and 14 h, respectively. After 24 h, ~91% of the maximum sorption takes place, thus 24 h is adequate for As(V) to reach sorption equilibrium on schwertmannite. The data here is consistent with Carlson et al. (2002) who found that As(V) sorption equilibration was achieved within 24 h. Therefore, all the isotherm studies (Section 3.3.2) were conducted for 24 h to allow maximum As(V) sorption.

![Figure 3-1: Kinetics of As(V) removal by schwertmannite synthesized without $\text{Cu}^{2+}$ and $\text{Fe}^{2+}$ at 65°C. Experimental conditions: pH 3-4, schwertmannite = 1.0 g L$^{-1}$, initial As(V) = 1.5 mM, at 25°C, and 120 rpm.](image)

3.3.2. As(V) sorption isotherms

3.3.2.1. As(V) sorption by the solids synthesized with various concentrations of co-existing metal ions.

The As(V) sorption data for the products synthesized with various $\text{Cu}^{2+}$ and $\text{Fe}^{2+}$ concentrations at 65°C (as described in Section 2.2.2 and 2.2.3 of Chapter 2) are demonstrated in Figure 3-2. The equilibrium sorption data were fitted using Langmuir and Freundlich adsorption models, and the thermodynamic parameters calculated for both models are listed in Table 3-1. The Langmuir model fitted the experimental data better (higher correlation coefficient, $R^2$) than the Freundlich model, also for the goethite synthesized in the high Fe$^{2+}$ concentration. Asta et al. (2009) and Mamindy-Pajany et al. (2011) reported that the arsenate sorption isotherm for goethite is well described by the Langmuir model. For schwertmannite synthesized in the absence of $\text{Cu}^{2+}$ and $\text{Fe}^{2+}$, the maximum As(V) sorption capacity is calculated to be approximately 114 mg g$^{-1}$. 

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Figure 3-2: Adsorption isotherms of As(V) onto products synthesized at 65°C in the presence of: (a) various Cu²⁺ concentrations, (b) various Fe²⁺ concentrations, and (c) various mixtures of Cu²⁺ and Fe²⁺ in the initial solution. Experimental conditions: pH = 3–4, adsorbent = 1.0 g L⁻¹, equilibrium time: 24 h.
Figure 3-2(a) shows As(V) sorption data for the synthesized products in the presence of various concentrations of Cu$^{2+}$. It shows that the As(V) sorption capacity of these synthesized products are consistent with the sorption capacity of product synthesized in the absence of Cu$^{2+}$ and Fe$^{2+}$. Calculated from the Langmuir equation, the maximum As(V) sorption capacity was found to be approximately 94, 133, and 120 mg g$^{-1}$ for the products synthesized with 1, 10, and 100 mM Cu$^{2+}$, respectively.

Sorption data for As(V) on synthesized products in the presence of various Fe$^{2+}$ concentrations are shown Figure 3-2(b). The results demonstrate that the As(V) sorption capacity of the synthesized product decreases with increasing Fe$^{2+}$ concentration. The maximum sorption capacities were estimated from graphs based on the data, and the results show that synthesized product in the presence of 1 mM Fe$^{2+}$ has the maximum sorption capacity ($q_{\text{max}} = 149$ mg g$^{-1}$), approximately five times that of product synthesized with 100 mM Fe$^{2+}$ ($q_{\text{max}} = 58$ mg g$^{-1}$). This is due to the dominant formation of goethite at the higher Fe$^{2+}$ concentration. In other studies of As(V) sorption by goethite, Lehmann et al. (2005) investigated the As(V) sorption onto natural goethite at pH 3 and found that the maximum capacity absorbed is approximately 45 mg g$^{-1}$, which is very similar to the finding reported by Matis et al. (1997). At pH 1.6-4, the sorption capacities ranged from 12 mg g$^{-1}$ to 15 mg g$^{-1}$ on synthesized goethite according to Asta et al. (2009) and Dixit and Hering (2003).

Figure 3-2(c) shows the As(V) sorption data on the synthesized products in the presence of both Cu$^{2+}$ and Fe$^{2+}$. The results show that the As(V) sorption capacity onto these synthesized products are consistent with the sorption capacity onto synthesized schwertmannite without the addition of Cu$^{2+}$ and Fe$^{2+}$, but are higher than the sorption capacity on synthesized product at the high Fe$^{2+}$ concentration (100 mM). Calculated from the Langmuir equation, the maximum As(V) sorption capacity is approximately 115-128 mg g$^{-1}$ for products synthesized with addition of both Cu$^{2+}$ and Fe$^{2+}$. This result implies that the presence of Cu$^{2+}$ in copper heap leach liquid may assist to synthesize schwertmannite with high As sorption capacity also in the presence of Fe$^{2+}$ which acts as a catalyst to transform schwertmannite to goethite.

Table 3-1: Freundlich and Langmuir parameters obtained from the modeling of arsenate adsorption isotherms on synthesized products in the presence of various amounts of Cu$^{2+}$ and Fe$^{2+}$. Experimental conditions: synthesized product 1.0 g L$^{-1}$, pH 3-4, 120 rpm, and equilibrium time 24 hrs.

<table>
<thead>
<tr>
<th>Fe$^{2+}$ (mM)</th>
<th>Cu$^{2+}$ (mM)</th>
<th>Freundlich model</th>
<th>Langmuir model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$R^2$</td>
<td>$K_F$</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.98</td>
<td>79.6</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0.46</td>
<td>89.8</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>0.99</td>
<td>86.0</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>0.94</td>
<td>78.8</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0.73</td>
<td>25.4</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0.91</td>
<td>26.5</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0.95</td>
<td>26.3</td>
</tr>
<tr>
<td>100</td>
<td>10</td>
<td>0.98</td>
<td>51.4</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>0.99</td>
<td>71.2</td>
</tr>
</tbody>
</table>
The As(V) sorption capacities on schwertmannite obtained in this study were compared with results obtained with natural and synthesized schwertmannite (Table 3-2). The results here show that the maximum As(V) sorption capacity calculated is between 94-133 mg g⁻¹ at pH 3.0-4.0. This exceeds the sorption capacities of 33 mg g⁻¹ (at pH 7.0) and 60 mg g⁻¹ (at pH 3.4) reported by Dou et al. (2013) and Fukushi et al. (2003), respectively. The data here are consistent with Antelo et al. (2012) who found that schwertmannite adsorbed 123.5 mg g⁻¹ at pH 4.5. However, the sorption capacity observed here is lower than some other values reported in the literature. Burton et al. (2009) found a maximum arsenate sorption capacity of 200 mg g⁻¹ at pH 3.0; and Carlson et al. (2002) observed maximum sorption of 175 mg g⁻¹ at pH 3.0. The difference in As(V) sorption capacity with these samples may be due to differences in synthesizing methods and schwertmannite concentrations in the sorption experiments (Liao et al., 2011). For instance, the schwertmannite concentrations used in the sorption studies by Burton et al. (2009) was over ten times greater than that reported by Antelo et al. (2012) and this study. Furthermore, the sulfate content of the schwertmannite preparations can be attributed to the As(V) sorption capacities (Antelo et al., 2012). As indicated by Fernandez-Martinez et al. (2010), a relatively low sulfate content is indicative of the presence of only inner-sphere sulfate complexes. With higher sulfate content both inner- and outer-sphere complexes are present in the structure. The outer-sphere complexes play a more active role in the anion exchange mechanism than the inner-sphere complexes, which have higher energy stabilities and are less reactive (Antelo et al., 2012).

3.3.2.2. As(V) sorption isotherms by the solids synthesized at different reaction temperatures.

The As(V) sorption data for the products synthesized in the absence or presence of Cu²⁺ and Fe²⁺ at different reaction temperature are plotted in Figure 3-3, and the thermodynamic parameters calculated for Langmuir adsorption model are listed in Table 3-3. The results show that the maximum As(V) sorption capacities of the schwertmannite synthesized at 65°C was much higher (114-128 mg g⁻¹) than the maximum sorption capacities of the schwertmannite synthesized at 25°C (17-23 mg g⁻¹). As detailed in Chapter 2, the temperature of the synthesis has a significant effect on the surface characteristics of schwertmannite products, and this may be a cause of the differences in As(V) sorption capacities. The maximum As(V) sorption capacity is approximately 58 mg g⁻¹ for goethite product synthesized from the solutions containing Fe²⁺ at 65°C, similar to the maximum As(V) sorption capacity of goethite reported previously by Lehmann et al. (2005) and Matis et al. (1997).

Although schwertmannite can be synthesized at both reaction temperature (25°C and 65°C), however their efficiency for arsenic removal are very different. This should be taken into consideration for its application on mine site.
Table 3-2: Summary of experimental conditions and As(V) removal capacities of schwertmannite obtained in this study and in earlier work.

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Solid concentration (g L(^{-1}))</th>
<th>Initial As(V) (mmol L(^{-1}))</th>
<th>Sorption time (h)</th>
<th>pH</th>
<th>As(V) removed (mg g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carlson et al. (2002)</td>
<td>Bigham et al. (1990)</td>
<td>-</td>
<td>10</td>
<td>24</td>
<td>3.0</td>
</tr>
<tr>
<td>Carlson et al. (2002)</td>
<td>Natural</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.4</td>
</tr>
<tr>
<td>Fukushi et al. (2002)</td>
<td>-</td>
<td>-</td>
<td>10(^{-4})–1</td>
<td>24</td>
<td>3.2–3.4</td>
</tr>
<tr>
<td>Fukushi et al. (2003)</td>
<td>Natural</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3.4</td>
</tr>
<tr>
<td>Burton et al. (2009)</td>
<td>Regenspurg et al. (2004)</td>
<td>13.0</td>
<td>4.8–60</td>
<td>60</td>
<td>3.0</td>
</tr>
<tr>
<td>Antelo et al. (2012)</td>
<td>Bigham et al. (1996)</td>
<td>1.0</td>
<td>0.5–4.0</td>
<td>72</td>
<td>4.5</td>
</tr>
<tr>
<td>Antelo et al. (2012)</td>
<td>Bigham et al. (1996)</td>
<td>1.0</td>
<td>0.5–4.0</td>
<td>72</td>
<td>7.0</td>
</tr>
<tr>
<td>Antelo et al. (2012)</td>
<td>Bigham et al. (1996)</td>
<td>1.0</td>
<td>0.5–4.0</td>
<td>72</td>
<td>8.0</td>
</tr>
<tr>
<td>Antelo et al. (2012)</td>
<td>Bigham et al. (1996)</td>
<td>1.0</td>
<td>0.5–4.0</td>
<td>72</td>
<td>9.0</td>
</tr>
<tr>
<td>Dou et al. (2013)</td>
<td>Cornell and Schwertmann (2003)</td>
<td>0.5</td>
<td>0.02–0.27</td>
<td>24</td>
<td>7.0</td>
</tr>
<tr>
<td>This study</td>
<td>Neutralization</td>
<td>1.0</td>
<td>0.5–3.0</td>
<td>24</td>
<td>3.0–4.0</td>
</tr>
</tbody>
</table>
Figure 3-3: Sorption isotherms of As(V) onto products synthesized in the absence or presence of Cu$^{2+}$ and Fe$^{2+}$ at (a) 65°C and (b) 25°C. Experimental conditions: pH = 3-4, adsorbent = 1.0 g L$^{-1}$, equilibrium time: 24 hrs.

Table 3-3: Langmuir parameters obtained from the modeling of arsenate sorption isotherms on synthesized products in the absence or presence of Cu$^{2+}$ and Fe$^{2+}$ at 25°C and 65°C. Experimental conditions: synthesized product 1.0 g L$^{-1}$, pH 3-4, 120 rpm, and equilibrium time 24 hrs.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cu$^{2+}$ (mM)</th>
<th>Fe$^{2+}$ (mM)</th>
<th>R$^2$</th>
<th>$q_m$ (mg g$^{-1}$)</th>
<th>K$_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>65°C</td>
<td>0</td>
<td>0</td>
<td>0.99</td>
<td>114</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>0.90</td>
<td>58</td>
<td>0.10</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0</td>
<td>0.90</td>
<td>120</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>0.98</td>
<td>128</td>
<td>0.39</td>
</tr>
<tr>
<td>25°C</td>
<td>0</td>
<td>0</td>
<td>0.99</td>
<td>17</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>100</td>
<td>0.94</td>
<td>23</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>0</td>
<td>0.98</td>
<td>14</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>100</td>
<td>0.99</td>
<td>21</td>
<td>0.8</td>
</tr>
</tbody>
</table>
3.3.4. Effect of pH on As(V) sorption

Removal of As(V) in solution with initial pH ranging from 3 to 12 through sorption onto schwertmannite synthesized at 65°C without co-existing metal ions is shown in Figure 3-4. The results indicate that As(V) sorption capacity on schwertmannite decrease with increase of pH value. The maximum As(V) sorption capacity is observed at around pH 3-4 in which the removal percentage was approximately 90%. The minimum As(V) sorption capacity occurs at around pH 11-12 in which the removal percentage was less than 10%. The As(V) sorption curve obtained here are similar to those observed in the previous studies. For example, Antelo et al. (2012) and Burton et al. (2009) reported that the sorption of As(V) to schwertmannite was strongly pH-dependent. As(V) sorption was greater at low pH and decreased at higher pH.

This can be explained by considering aqueous As(V) speciation and the surface charge of schwertmannite. The aqueous speciation of As(V) comprises H₃AsO₄⁰, H₂AsO₄⁻, HAsO₄²⁻, and AsO₄³⁻ (Burton et al., 2009 and Smedley and Kinniburgh, 2002). Aqueous As(V) is predominantly present as H₂AsO₄⁻ at low pH (below about pH 6.9) and as HAsO₄²⁻ at higher pH (H₃AsO₄⁰ and AsO₄³⁻ may be present in extremely acidic and alkaline conditions, respectively). These As(V) species are expected to sorb strongly at low pH because at low pH, schwertmannite has a very large positive charge (PZC = 7.2, Jönsson et al., 2005). These factors facilitate relatively effective sorption of As(V) to schwertmannite at low pH.

![Figure 3-4: Effect of solution pH on As(V) sorption on schwertmannite synthesized at 65°C without co-existing metal ions. Experimental conditions: adsorbent = 1.0 g L⁻¹, initial As(V) = 1.5 mM, equilibrium time: 24 hrs.](image)

3.4. CONCLUSION

The arsenic removal efficiency in aqueous solutions by schwertmannite synthesized from copper heap leach solutions was investigated. The results indicate that As(V) in acidic solutions (pH 3-4) can be removed effectively by schwertmannite synthesized in the presence or absence of co-existing metal ions (Cu²⁺ and Fe²⁺) at 65°C with the maximum sorption capacity of 94-133 mg g⁻¹. A lower As(V) sorption capacity is observed in product containing goethite synthesized in the presence of Fe²⁺ at 65°C; here, the maximum As(V) sorption capacity is 58 mg g⁻¹. The maximum As(V) sorption capacities by schwertmannite synthesized at 25°C are 17-23 mg g⁻¹, which are much lower than the maximum sorption capacities of the schwertmannite synthesized at 65°C. Although schwertmannite can be synthesized at both reaction temperature (25°C and 65°C), however their efficiency for arsenic removal are very different. This should be taken into consideration for its application on mine site.
REFERENCES


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Chapter IV

STABILITY OF As(V)-SORBED SCHWERTMANNITE (SCH-As) UNDER PORPHYRY COPPER MINE CONDITIONS

4.1. INTRODUCTION

Extraction and beneficiation of copper ore from porphyry deposits produces large amounts of rock waste and mine tailings (Antelo et al., 2013 and Nordstrom, 2011). The waste may be divided into three major categories: (1) waste rock piles or dumps; (2) tailings ponds; and (3) spent ore piles where the leaching operation has ceased in the case of heap leach operations. These wastes may be exposed to the environment, presenting the potential for contaminant transport (Dold and Fontbote, 2001). Among the contaminants, arsenic (As) represents a specific concern because of its high toxicity at low concentrations, and some As-bearing minerals are highly soluble in a wide range of pH conditions (Coussy et al., 2012). It is important to find a suitable method to control the toxic arsenic species that could be released from such large amounts of waste at copper mines.

Retention of arsenic by schwertmannite has been proposed here due to the strong biding affinity of schwertmannite to toxic arsenic species. It can also be cost-effective as it is possible to synthesize schwertmannite from the effluent or raffinate of copper heap leach solutions with high efficiency enabling As(V) removal as demonstrated in Chapter 2 and 3.

Schwertmannite can be expected to find application in As immobilization of copper mine waste in tailings and spent ore of either dump or heap leach piles. The particulars of the copper mine tailings may be very varied, for example they may contain significant amounts of iron ions due to oxidation of the rejected pyrite (FeS₂) and other sulfide minerals (Davidson et al., 2008 and Lottermoser, 2003), and some amount of copper ions could also be present in the tailings as 100% copper recovery is not possible in the extraction processes. Further, copper mine waste may present a wide range of pH-values, particularly in tailing ponds. This makes it of interest to evaluate the stability of As(V)-sorbed schwertmannite in copper mine tailing conditions. This chapter investigates the effect of Cu²⁺, Fe²⁺, pH, and ageing time on the stability of As(V)-sorbed schwertmannite.

4.2. MATERIALS AND METHODS

4.2.1. Solution preparation

Solutions containing known concentrations of H₂SO₄, Na₂CO₃, Fe³⁺, Fe²⁺, Cu²⁺, and As(V) were prepared by dissolving reagent-grade H₂SO₄, Na₂CO₃, FeSO₄·7H₂O, Fe₂(SO₄)₃·nH₂O, CuSO₄·5H₂O, and Na₂HAsO₄·7H₂O (Wako Pure Chemical Industries, Ltd., Japan) in distilled/ion-exchanged water.

4.2.2. Sample preparation

Schwertmannite was prepared using the procedure described in section 2.2.2 (Chapter 2). The schwertmannite loaded with As(V) was prepared by adding 0.1 g of dried schwertmannite to 200-mL flasks containing 100 mL of 1.5 mM As(V)solution. This suspension was adjusted to pH 3–4 by drop-wise addition of HCl and shaken for 24 h in a water bath at 25°C at 120 rpm. The solid phase was separated by filtration, oven dried at 40°C and stored at room temperature. In the following, pure schwertmannite and schwertmannite loaded with As(V) will be denoted as Sch and Sch-As, respectively.
Both dried Sch and Sch-As products were next subjected to X-ray diffractometry (XRD). The composition of Sch and Sch-As was determined after digestion of the dried solids in 1 M HCl (1 g L\(^{-1}\)) and the Fe and S contents were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results for the solid-phase analyses are presented on a dry weight basis, unless noted otherwise.

4.2.3. Effect of Cu\(^{2+}\) on Sch-As stability

The prepared Sch-As samples were suspended in solution containing various concentrations of Cu\(^{2+}\). Experiments were carried out as follows: 0.1 g of dry Sch-As and predetermined amounts of CuSO\(_4\)·5H\(_2\)O and Na\(_2\)SO\(_4\) powers were added to 100-mL of preheated (65°C) distilled water in a glass bottle. Here, the total SO\(_4^{2-}\) concentrations were set to be the same in all solutions by the addition of Na\(_2\)SO\(_4\). Therefore, when comparing the results of the experiments, the effect of the SO\(_4^{2-}\) concentration on the stability of the Sch-As can be disregarded. The suspensions were adjusted to pH 3–4 by drop-wise addition of HCl or NaOH and stirred at 350 rpm at 65°C. After a 24 h reaction period, the solid phase was separated by centrifugation at 3500 rpm for 5 min and the supernatant was subjected to arsenic analysis. The recovered solid was subjected to XRD analysis after drying overnight in a vacuum dryer at 40°C.

4.2.4. Effect of Fe\(^{2+}\) on Sch-As stability

For the determination of Fe\(^{2+}\) effects, 0.1 g of dry Sch-As and predetermined amounts of FeSO\(_4\)·7H\(_2\)O and Na\(_2\)SO\(_4\) were added to 100 mL of preheated (65°C) distilled water in a glass bottle. Here, the total SO\(_4^{2-}\) concentrations were set to be the same in all solutions by the addition of Na\(_2\)SO\(_4\). Therefore, when comparing the results of the experiments, the effect of the SO\(_4^{2-}\) concentration on the stability can be disregarded. The suspensions were adjusted to pH 3–4 by drop-wise addition of HCl or NaOH and stirred at 350 rpm at 65°C under a nitrogen atmosphere. After 24 h, the solid phase in the flask was separated by centrifugation at 3500 rpm for 5 min, the supernatant was subjected to arsenic analysis, and after drying overnight in a vacuum dryer at 40°C, the recovered solid was subjected to XRD analysis.

4.2.5. Effect of pH on Sch-As stability

To investigate the effect of pH on Sch-As stability, 0.1 g of dried Sch-As was added to 100 mL of distilled water in a 200-mL flask. The initial pH was adjusted to pH ranges between 1 and 12 with NaOH or HCl prior to addition of the Sch-As. The flask was subsequently shaken in a water bath at 25°C at 120 rpm for 24 h. Then the final pH was measured and the suspended solid was harvested by centrifugation at 3500 rpm for 5 min. The supernatant was subjected to arsenic and sulfur analysis. The recovered solid was subjected to XRD analysis after drying overnight in a vacuum dryer at 40°C.

4.2.6. Effect of time on Sch-As stability

Experiments were carried out for 120 days with 0.1 g of Sch or Sch-As in 100 mL deionized water in 200-mL flasks. The experiments were performed at various pH conditions. The initial pH was adjusted to pH ranges between 3.5 and 12 with NaOH or HCl prior to the addition of the Sch and Sch-As. The flasks were shaken reciprocally in a water bath at 25°C at 120 rpm under normal atmospheric conditions. At a preset ageing time, the suspension was sampled with a syringe and this sample was filtrated through a 0.2-μm membrane. The supernatant was analyzed for sulfur, arsenic, and pH. After 120 days, the suspended solid was harvested by centrifugation at 3500 rpm for 5 min. The recovered solid was subjected to XRD analysis after drying overnight at 40°C.
4.2.7. Analytical methods

The aqueous phase was analyzed for iron, sulfur, arsenic, and pH. The concentrations of arsenic, iron, and sulfur were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Seiko Instruments SPS7800. In the ICP-AES analyses, calibration with sets of standards was performed and the regression coefficients exceeded 0.999; dilutions from 1:10 to 1:1000 were used to ensure that the concentrations of the elements in the samples were within the concentration range of the standards, the error was estimated to be below 5%. A pH-meter and combined electrode with temperature compensation was used to measure the pH and was calibrated regularly with standard buffer solutions of pH 1.68, 4.01, and 6.86. The solid phase was ground to a homogeneous powder in a mortar and subsequently analyzed by X-ray diffraction (XRD) using a RIGAKU powder diffractometer with CuKα radiation (40 kV and 30 mA) to identify the minerals present in the samples. Peak maxima were read from the diffractogram and minerals were identified by comparison with a schwertmannite standard from an XRD pattern identical to that of the schwertmannite described by Blgham et al. (1990).

4.3. RESULTS AND DISCUSSION

4.3.1. Characterization of Sch and Sch-As

The XRD patterns (Figure 4-1) confirm that schwertmannite is the only mineral detectable in both the Sch and Sch-As samples. The elemental composition of Sch and Sch-As are shown in Table 4-1. The molar Fe/S ratio, determined from the Fe and S molar proportions, is 5.3 and 8.2 for Sch and Sch-As, respectively. The Sch-As contained As/Fe at a ratio of 0.16. Based on the Fe, S, and As contents, the average stoichiometry of the Sch and Sch-As products can be represented as $\text{Fe}_8\text{O}_8(\text{OH})_{4.98}(\text{SO}_4)_{1.51}$ and $\text{Fe}_8\text{O}_8(\text{OH})_{4.98}(\text{SO}_4)_{0.93}(\text{AsO}_4)_{1.28}$, respectively. The chemical formula shows that Sch represents a product with intermediate sulfate content. Low (1.02–1.30) and high (1.60–2.05) values of the relative sulfate content have previously been reported for other synthesized schwertmannites (Antelo et al., 2013, Burton et al., 2010, Burton et al., 2009, Burton et al., 2008, Liao et al., 2011 and Paikaray and Peiffer, 2012). The lower sulfate content is related to the number of inner-sphere sulfate complexes in the schwertmannite structure, with the higher relative sulfate content related to the contribution of outer-sphere complexes (Antelo et al., 2013 and Fernandez-Martinez et al., 2010). Here, it may be assumed that the sulfate is present both as inner- and outer-sphere complexes in the Sch sample in the present study. The lower relative sulfate content for Sch-As is related to the exchange of sulfate for arsenic during the As(V) sorption. Such sorption has been suggested to occur through a combination of surface complexation with active hydroxyl groups, exchanges of both surface-adsorbed and structural $\text{SO}_4^{2-}$ (Antelo et al., 2012, Carlson et al., 2002 and Fukushi et al., 2003). It has been reported that As(V) can replace sulfate up to half of the total sulfate in schwertmannite at pH 3.0–3.4 (Antelo et al., 2013, Burton et al., 2009 and Fukushi et al., 2003). Mass balance calculations demonstrated that the Sch-As contains ~100 mg As(V) per g Sch (As(V) loading ~10 wt%) in the present study.
Figure 4-1: XRD patterns for (a) Sch and (b) Sch-As samples. Schwertmannite peaks are denoted as “Sh”.

Table 4-1: Elemental composition and the molar ratios of Sch and Sch-As.

<table>
<thead>
<tr>
<th></th>
<th>Fe (mmol g⁻¹)</th>
<th>S (mmol g⁻¹)</th>
<th>As (mmol g⁻¹)</th>
<th>Fe/S</th>
<th>As/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sch</td>
<td>8.59</td>
<td>1.62</td>
<td>0.00</td>
<td>5.3</td>
<td>0.00</td>
</tr>
<tr>
<td>Sch-As</td>
<td>8.48</td>
<td>1.03</td>
<td>1.35</td>
<td>8.2</td>
<td>0.16</td>
</tr>
</tbody>
</table>

4.3.2. Effect of Cu²⁺ on Sch-As stability

Copper is one of the major constituents of mine waste/tailings resulting from porphyry copper mines and it is often found in areas affected by AMD outflows (Antelo et al., 2013 and Branson and Ammons, 2004). The presence of copper ions in aquatic systems has the potential to affect the stability of Sch-As, and to establish details of this the effect of 1, 10, 50, and 100 mM Cu²⁺ on the stability of Sch-As was investigated in the present study. The experiments were carried out at 65 °C in order to accelerate the transformation.

Figure 4-2(a) shows XRD patterns of recovered solids after suspension of Sch-As in solutions containing various concentrations of Cu²⁺. The results show schwertmannite peaks and there is no indication of other phases for any of the samples suspended in these solutions with Cu²⁺. This indicates that the Sch-As here is stable and that no solid phase transformation has occurred. The concentration of As released from the Sch-As solid suspended in the solutions containing various concentrations of Cu²⁺ was also measured. As suggested by Figure 4-3(a), only a small fraction of released As (<2% of total solid phase As) was detected in any of these experiments carried out with or without Cu²⁺. This indicates that Cu²⁺ has no significant effect on the stability of Sch-As. Several authors have investigated the effect of Cu²⁺ on the stability of schwertmannite under acidic conditions. Antelo et al. (2013) reported that the presence of copper ions increases the stability of schwertmannite at pH 3 and 5.
Figure 4-2: XRD patterns for Sch-As samples suspended in solutions containing various concentrations of (a) Cu$^{2+}$ and (b) Fe$^{2+}$ for 24 h at pH 3–4 and 65°C. Schwertmannite peaks are denoted as “Sh”.
4.3.3. Effect of Fe\(^{2+}\) on Sch-As stability

The effect of Fe\(^{2+}\) on the stability of schwertmannite has been reported by several researchers. Burton et al. (2008) found that the transformation of schwertmannite to goethite is accelerated in the presence of Fe\(^{3+}\); and that complete conversion occurred in only 3–5 h at pH > 6 and Fe\(^{2+}\) \(\geq\) 5 mmol L\(^{-1}\). Our results in chapter 2 indicated that transformation of schwertmannite to goethite occurred within 1 h in the presence of Fe\(^{2+}\) at lower pH conditions (pH 3–4). To elucidate this further, the effect of 1, 10, 50, and 100 mM Fe\(^{2+}\) on the stability of Sch-As was investigated in the present study. The experiments were conducted at 65°C to accelerate the transformation.

The results show that schwertmannite appears as the dominant phase for all Sch-As products suspended in solutions containing various concentrations of Fe\(^{2+}\) (Figure 4-2(b)), suggesting that no solid phase transformation occurs in the presence of Fe\(^{2+}\). Small fractions of released arsenic (<2% of the total solid phase As) were detected in all experiments carried out in the presence or absence of Fe\(^{2+}\) (Figure 4-3(b)). This indicates that the As(V) incorporated into schwertmannite may retard or significantly inhibit the Fe\(^{2+}\)-catalyzed transformation of schwertmannite to goethite. It has also been reported that the presence of As(V) stabilizes schwertmannite and inhibits or significantly retards Fe(II)-catalyzed transformation to goethite (Burton et al., 2010 and Raghav et al., 2013).

Figure 4-3: Amount of released As for Sch-As samples suspended in solution containing various concentrations of (a) Cu\(^{2+}\) and (b) Fe\(^{2+}\) for 24 h at pH 3–4 and 65°C.
4.3.4. Effect of pH on Sch-As stability

The stability of As(V)-incorporated schwertmannite have been extensively studied under acidic conditions (Acero et al., 2006, Antelo et al., 2013, Burton et al., 2013, Burton et al., 2010, Burton and Johnston, 2012, Fukushi et al., 2003, Dou et al., 2013 and Regenspurg and Peiffer, 2005), therefore the current understanding on the stability of As(V)-incorporated schwertmannite is limited to a narrow range of pH conditions. This makes it important to investigate As(V)-incorporated schwertmannite stability over a wider range of pHs, as the pH of copper mine waste varies over a wide range (Nordstrom, 2011). To improve understanding of this the effect of pH on the stability of Sch-As was investigated in the present study.

As indicated by reaction (Equation 2-2, Chapter 2), it may be expected that the transformation of schwertmannite to goethite releases significant proportions of SO$_4^{2-}$ back to the aqueous phase (Paikaray and Peiffer, 2010). Figure 4-4(a) shows the amount of SO$_4^{2-}$ released from Sch-As after suspension in solutions with different pH values (final pH). The lowest concentration of SO$_4^{2-}$ release was observed at pH 2.5–4.0, and the release rate increased both at lower and higher pHs.

The higher release of SO$_4^{2-}$ at pH less than about pH 2 may be due to dissolution of Sch-As. Mineral dissolution reactions tend to be most rapid under extremely acidic pH (Smedley and Kinniburgh, 2002). The increase in SO$_4^{2-}$ release at higher pH (above about pH 4) may due to desorption of SO$_4^{2-}$ from the structure of Sch-As, as it has been reported by Stumm and Morgan (1996) that the surface of Fe-oxyhydroxides become less positively charged as solution pH increases, and that SO$_4^{2-}$ retention therefore is less likely. The direct exchange of OH$^-$ for SO$_4^{2-}$ ions is a possible reason for desorption of SO$_4^{2-}$ at higher pH conditions (Burton et al., 2010, Jönsson et al., 2005, Rose and Elliot, 2000 and Paikaray and Peiffer, 2012). As previously mentioned, SO$_4^{2-}$ is associated with schwertmannite both through bonding in the internal structure and adsorption on the surface that may make up 35% of the total SO$_4^{2-}$ content (Paikaray and Peiffer, 2010). For the Sch-As suspended in solutions with a pH above pH 2 and below pH 7, the SO$_4^{2-}$ release is most likely to be due to desorption of loosely bound surface SO$_4^{2-}$ from sites with relatively weak electrostatic attraction (Jönsson et al., 2005 and Paikaray and Peiffer, 2010).

The release of SO$_4^{2-}$ at pH above pH 7 indicates a contribution of SO$_4^{2-}$ release form both the internal structure and the surface of Sch-As. Here, transformation of schwertmannite to goethite is expected to occur at pH above 7. However, the XRD results (Figure 4-5) show that schwertmannite appears as the dominant phase and there is no formation of any new phase at any of the pH-values (final pH), indicating that no transformation of schwertmannite to goethite occurred. The loss of schwertmannite-bound SO$_4^{2-}$ without simultaneous mineralogical changes has also been reported as a result of pH-dependent SO$_4^{2-}$ desorption (Burton et al., 2010 and Jönsson et al., 2005).
Figure 4-4: Amount of (a) SO$_4^{2-}$ and (b) As released from Sch-As samples suspended at different pH at 25°C for 24 h. The dashed lines correspond to the total amounts of (a) sulfate and (b) arsenic in the initial Sch-As.
Figure 4-5: XRD patterns for Sch-As products aged at different pH for 24 h, plotted with the original pattern (initial Sch-As). Schwertmannite peaks are denoted as “Sh”.

The amount of As released from the Sch-As after suspension in solutions with different pH values (final pH) was also measured. The results show that the release of As was strongly pH-dependent (Figure 4-4(b)). At extremely acidic conditions (below about pH 2), a high release of As was observed, which may be due to the dissolution of Sch-As. It has been reported that iron oxides dissolve under strongly acidic conditions and minor elements including As will also tend to be released during this dissolution (Smedley and Kinniburgh, 2002). The release of As was almost negligible from above about pH 2 to neutral pH conditions and increased at alkaline conditions (above pH 7). This can be explained by considering aqueous As(V) speciation and the surface charge of schwertmannite. The aqueous speciation of As(V) comprises $\text{H}_3\text{AsO}_4^0$, $\text{H}_2\text{AsO}_4^-$, $\text{HAsO}_4^{2-}$, and $\text{AsO}_4^{3-}$ (Burton et al., 2009 and Smedley and Kinniburgh, 2002). Aqueous As(V) is predominantly present as $\text{H}_2\text{AsO}_4^-$ at low pH (below about pH 6.9) and as $\text{HAsO}_4^{2-}$ at higher pH ($\text{H}_3\text{AsO}_4^0$ and $\text{AsO}_4^{3-}$ may be present in extremely acidic and alkaline conditions, respectively). These As(V) species are expected to desorb at high pH because at high pH, schwertmannite has a very large negative charge (PZC = 7.2, Jönsson et al., 2005). These factors facilitate significant desorption of As(V) at high pH.

It has been extensively reported that within durations of a few months schwertmannite transforms to more stable iron oxides at various pH conditions (Antelo et al., 2013, Knorr and Blodau, 2007, Paikaray and Peiffer, 2012, Regenspurg et al., 2004 and Schwertmann and Carlson, 2005). Here, Schwertmann and Carlson (2005) observed the complete transformation of schwertmannite to goethite in deionized water at pH 7.2 after 100 days. Paikaray and Peiffer (2012) reported the transformation of schwertmannite to goethite after a 120-day ageing period at pH 7 and 8. Antelo et al. (2013) found that conversion of schwertmannite to goethite was almost complete within 94 days even at pH 3. These results suggest that pH is an important factor affecting the long-term stability of schwertmannite, therefore long-term stability of Sch-As at various pH conditions were carried out and will be discussed in detail in Section 4.3.5.
4.3.5. Effect of time on Sch-As stability

For the determination of time effects, experiments were carried out with Sch or Sch-As samples at different pH-values at 25 °C for 120 days. The $SO_4^{2-}$ release from the Sch and Sch-As structure to the solution at 120-day is shown in Figure 4-6. The results show a clear pH dependence of the released $SO_4^{2-}$. The released $SO_4^{2-}$ after 120 days increased with increasing pH. At pH 3, the amount of $SO_4^{2-}$ released from solid phase $SO_4^{2-}$ was 46.6% for Sch and 24.3% for Sch-As. At pH 11, the amount of released $SO_4^{2-}$ increased to 99.1% for Sch and 90.4% for Sch-As. The released $SO_4^{2-}$ observed here might be due to the transformation of schwertmannite to goethite according to Equation 2-2 (Chapter 2). If this is the case, the result in Figure 4-6 indicates that the transformation is more significant at higher pHs.

![Figure 4-6: Release of $SO_4^{2-}$ from Sch (black) and Sch-As (white) after suspension in solutions with different pH for 120 days. The total amounts of sulfate in the initial Sch (dashed line) and Sch-As (dotted line) are shown for comparison. The indicated pH values are the final pH after 120-day of ageing.](image)

Figure 4-7 shows the XRD patterns of (a) Sch and (b) Sch-As products after 120 days of ageing at different final pH-values. The results indicate that schwertmannite remains the dominant mineral with the appearance of few characteristic goethite peaks for the Sch sample aged at pH 3 and pH 4 (Figure 4-7(a)). Some goethite peaks appear at pH 6, and the goethite contribution continues to increase with the pH value. At pH 11, goethite peaks are clearly observed in the XRD patterns, indicating that the transformation rate is strongly pH-dependent for Sch. Schwertmannite appears as the dominant phase without formation of other phases for the Sch-As products aged 120 days at all pH-values (Figure 4-7(b)), indicating that Sch-As products here may be stable and that no solid transformation occurs. As(V) incorporated into schwertmannite may retard or significantly inhibit the transformation into more stable iron oxides (Fukushi et al., 2003, Burton et al., 2010, Burton et al., 2009, Raghav et al., 2013 and Regenspurg and Peiffer, 2005).
Figure 4-7: XRD patterns for (a) Sch and (b) Sch-As aged at different pH for 120 days, plotted with the original pattern (initial Sch and initial Sch-As). Schwertmannite peaks are denoted as “Sh”, goethite peaks are denoted as “G”; and the indicated pH values are the final pH after 120-day of ageing.

As suggested by Figure 4-8(a), a fraction of the arsenic was released from the Sch-As solid phase throughout the 120-day ageing period at all pH-values. After the maximum release of As from the Sch-As solid at all pH-values, the amount of As measured in the aqueous phase was subsequently dropped as the ageing period increased. These gradual declines in released As may represent a re-sorption of arsenic onto Sch-As solid phases. As shown in Figure 4-8(b), all pH-values were gradually decreased throughout the ageing period, enabling the anionic As(V) species to re-sorp onto Sch-As at lower pH because at lower pH, schwertmannite processes more positively charged sorption sites.
Re-sorption of As(V) may have caused blocking of the crystal growth of new minerals as reported for other anions such as As(III) (Paikaray and Peiffer, 2012), SO$_4^{2-}$ (Davidson et al., 2008), and for trace metals (Lin et al., 2003 and Sun et al., 1996). Paige et al. (1996) demonstrated that 1 mol% As(V) restricted the transformation of ferrihydrite to goethite due to surface adsorption and inhibition of growth of a new mineral. It was also found that the incorporation of As can prevent the crystal growth of schwertmannite (Maillot et al., 2013, Vithana et al., 2014 and Waychunas et al., 1995). This may be the reason why no solid transformation occurred for the Sch-As aged for 120 days at any pH-value. However, further investigation is required to establish details of these phenomena.

Figure 4-8: (a) Release of arsenic and (b) pH values after ageing for different times at different pH within 120-day of Sch-As stability experiments. Note the two y-axis in Figure 4-8(a) and the indicated pH values are the final pH after 120-day of ageing.
The data plotted in Figure 4-8 (a and b) is re-plotted as pH versus the amount of released arsenic (Figure 4-9) in an attempt to describe the effect of pH on the release of arsenic from Sch-As solid phases during the 120-day ageing period. As suggested by Figure 4-9, Sch-As products released a very low amount of arsenic into the solution with pH less than about 7; and the release were significant at higher pH throughout the ageing period. This indicates that the As release from Sch-As was mainly controlled by outside environmental factors such as pH rather than time. The curve in Figure 4-9 could be well fitted by Equation 4-1, as exhibiting a regression coefficient ($R^2$) of 0.8361.

$$Y = 0.031 \exp^{0.6975X}$$  \hspace{1cm} (4-1)

where $X$ is the pH value of the solution, and $Y$ (mg L$^{-1}$) is the amount of arsenic release from the Sch-As solid phases during the ageing experiments. At a given pH value, the amount of released arsenic can be calculated according to Equation 4-1, which could be useful to predict the immobilization of arsenic by schwertmannite under various pH conditions at copper mine waste systems.

**Figure 4-9**: Relationship between pH-values and amount of released arsenic during the 120-day of Sch-As stability experiments. Note the total amount of arsenic in the initial Sch-As is $\sim$100 mg L$^{-1}$.

### 4.3.6. Environmental implications

At porphyry copper mines, copper sulfide minerals are mainly recovered by flotation as concentrates that can be converted into copper metal using pyrometallurgical processes, including smelting–converting and electrolytic refining (Ochromowicz and Chmielewski, 2013). The fine-grained fraction of the waste generated during flotation is called tailings, which are discharged to the tailings impoundment structures (Lottermoser, 2003). Tailings commonly contain sulfide minerals, e.g. pyrite (FeS$_2$) and arsenopyrite (FeAsS), which weather when tailings are exposed to the air and oxygen (Antelo et al., 2013 and Burton et al., 2009). This can result in the liberation of arsenic and strong acid (i.e. AMD) from the tailings, which may pollute adjacent areas (Lottermoser, 2003).

Copper oxide ores are generally recovered by hydrometallurgical processes, including leaching (e.g. dump or heap leaching), solvent extraction, and electro-winning (SX/EW) (Peacey et al., 2004). The material remaining in either dump or heap leach piles when leaching ceases is
called spent ore. Leach piles are reported to range in size from 6 m to over 30 m in height and may contain millions of tons of leached ore (EPA, n.d.). The spent ore becomes waste when active leaching ends.

Elevated arsenic concentrations are usually found in copper mine waste (Lottermoser, 2003). Tailings and spent ore of either dump or heap leach piles constitute over 60% of the total waste at copper mines (EPA, n.d.). It is important to find a suitable method to control the toxic arsenic species that could be released from such large amounts of waste at copper mines. Among the current treatment processes for arsenic control at copper mine waste, immobilization of arsenic by schwertmannite may be considered the most promising technology and it can be cost-effective as it is possible to synthesize schwertmannite from solutions generated in heap leach operations (i.e. raffinate). It is necessary to investigate the stability of arsenic-incorporated schwertmannite (Sch-As) under copper mine waste conditions. The present study has investigated the effect of Cu\(^{2+}\), Fe\(^{2+}\), pH, and ageing time on the stability of Sch-As. The results indicate that Cu\(^{2+}\) and Fe\(^{3+}\) have no significant effect on the stability of Sch-As; and that arsenic immobilization by schwertmannite takes place only at pH from 2 to 7. Based on the results of this study, schwertmannite may be practical for arsenic immobilization of copper mine waste as indicated in Figure 4-10.

An arsenic treatment process of tailings is expected to be carried out during the active mining. First, schwertmannite is synthesized from dump or heap leach solution (raffinate). The synthesized schwertmannite (slurry) is then pumped out and mixed with the flotation tailing slurries before discharge to tailings ponds. Generally, the pH values here range from 7.5 to 11.5 in most flotation operations (Branson and Ammons, 2004), with high pH values in tailing ponds (alkaline) at the initial stage. However, the pH values generally decrease to acidic pH with time due to the oxidation of the sulfide minerals present in the tailings. Heavy metals and arsenic are usually dissolved from the original minerals in AMD generation. The dissolved arsenic is expected to be sorbed by the schwertmannite in the tailings pond during the pH decline; and at this stage the toxic arsenic is considered to become stabilized by schwertmannite.

The AMD water in tailings ponds is commonly treated by addition of chemical-neutralizing agents such as lime. However, since the arsenic incorporated with schwertmannite may potentially be released back into the mine tailings water due to desorption of arsenic at high pH (i.e. pH > 7), treatment of AMD water needs to be carried out separately (additionally). The AMD from tailings ponds can then be pumped out and treated in other ponds or tanks where the chemical-neutralizing agent is added to raise the pH.

As mentioned previously, the spent ore of either dump or heap leach piles becomes waste when active leaching ends, and arsenic immobilization by schwertmannite is expected to have to be carried out during the post-closure stages of dump or heap leach operations. The spent ores may contain a residual of lixiviant (H\(_2\)SO\(_4\)) and associated metal ions (iron), which are the main components of schwertmannite. A neutralizer (Na\(_2\)CO\(_3\)) can be sprayed on the dump or heap piles; and schwertmannite is expected to be formed during the neutralization. The arsenic released within the piles may be subsequently immobilized by the precipitated schwertmannite.

Control of arsenic contamination in copper mine waste treatment are expected to be performed following the methods mentioned above. However, further study must be carried out to substantiate details of these treatment processes.
Figure 4-10: Flowsheet of the proposed treatment process for arsenic immobilization by schwertmannite at porphyry copper mines.
4.4. CONCLUSION

This study provides insight into the stability of As(V)-sorbed schwertmannite (Sch-As) under porphyry copper mining conditions by investigating the effect of Cu$^{2+}$, Fe$^{2+}$, pH, and ageing time on the stability of Sch-As. The results indicate that Cu$^{2+}$ has no significant effect on the stability of Sch-As and that the As(V) incorporated into schwertmannite can retard or significantly inhibit the Fe$^{2+}$-catalyzed transformation of schwertmannite to goethite under acidic conditions (pH 3–4). The Sch-As aged at different pH ranges from 3 to 11 at 25°C exhibits no mineralogical phase changes even after ageing for 120-days; however the concentration of arsenic released from the solid phase appeared to be strongly pH-dependent also at ageing for 24 h. The release of As was almost negligible at pH 2 to 7, and a high release of As was observed at extremely acidic and alkaline conditions. This indicates that the release of As from Sch-As is controlled by the outside environmental factors such as pH, Cu$^{2+}$, and Fe$^{2+}$ rather than time. Control of arsenic contamination in copper mine waste treatment are expected to be performed following the methods mentioned in this Chapter. However, further study should be carried out to substantiate details of these treatment processes.
REFERENCES


Chapter 5

APPLICATION OF SCHWERTMANNITE FOR ARSENIC IMMOBILIZATION IN COPPER MINE TAILINGS AND METALLURGICAL PLANTS

5.1. INTRODUCTION

At porphyry copper mines, copper minerals are mainly recovered by flotation as concentrates that can be converted into copper metal using pyrometallurgical processes, including smelting–converting and electrolytic refining (Ochromowicz and Chmielewski, 2013). The fine-grained fraction of the waste resulting from copper flotation operations is called tailings and it constitutes about 50% of the total waste at copper mines (Stjernman Forsberg, 2008). Flotation tailings commonly contain residual arsenic bearing sulfides, arsenopyrite (FeAsS) and arsenian pyrite (Antelo et al., 2013; Burton et al., 2009). When disposed unprotected from the weather, the tailings react with atmospheric oxygen and meteoric water, leading to the release of metals, arsenic, and strong acid in the drainage water, which may pollute surrounding areas (Smedley and Kinniburgh, 2002; Stjernman Forsberg, 2008). Therefore, arsenic may be presented in tailings generated by flotation operations.

In copper ores, arsenic is often contained within tennantite (Cu$_{12}$As$_4$S$_{13}$) or enargite (Cu$_3$AsS$_4$). These copper–arsenic minerals contain 51.6% and 48.4% copper respectively, and they float similar to other copper sulfide minerals, incorporated in the concentrate (Long et al., 2012). During copper pyrometallurgical operations, arsenic trioxide dust is generated in the smelting and roasting of sulfide concentrates (Gonzalez-Contreras et al., 2014). These processes usually operate at temperatures higher than 700°C, which volatize arsenic. Arsenic is mobilized as arsenic oxide with the exhaust gases, and arsenic removal from flue gases is mostly achieved as arsenic trioxide (As$_2$O$_3$) collected in electrostatic precipitators or wet gas scrubbers (up to 30%wt. arsenic). These forms of arsenic are soluble in water and can therefore not be stockpiled for long periods of time due to the danger of soluble arsenic release into the environment (Leetmaa, 2008). Arsenic stabilization by formation of iron-arsenic co-precipitates, scorodite (FeAsO$_4$) is a common arsenic elimination method employed in smelting industry worldwide (Shibata et al., 2012).

Based on the results detailed in Chapter 4, the flowsheet of the treatment processes for arsenic immobilization by schwertmannite at copper mines was proposed. The arsenic treatment process of the tailings is proposed to be carried out by mixing schwertmannite synthesized from the leach solutions (raffinate) with the flotation tailing slurries before discharge to tailings ponds. The arsenic dissolved from related minerals (e.g. arsenopyrite) can be expected to be sorbed by the schwertmannite in the tailings pond and the toxic arsenic will be stabilized by the schwertmannite. However, further study must be carried out to demonstrate and evaluate details of these treatment processes; and immobilization of arsenic in flotation tailings by the synthesized schwertmannite is investigated in this Chapter. In addition, the use of schwertmannite for arsenic immobilization in mine waters containing the diluted concentration of arsenic is also proposed here.

5.2. MATERIALS AND METHODS

Solutions containing known concentrations of H$_2$SO$_4$, Na$_2$CO$_3$, Fe$^{3+}$, and As(V) were prepared by dissolving reagent-grade H$_2$SO$_4$, Na$_2$CO$_3$, Fe$_2$(SO$_4$)$_3$·nH$_2$O, and Na$_2$HAsO$_4$·7H$_2$O (Wako Pure Chemical Industries, Ltd., Japan) in distilled/ion-exchanged water. The results for the solid-phase analyses are presented on a dry weight basis, unless noted otherwise. Schwertmannite sample was prepared using the procedure described in section 2.2.2 (Chapter 2).
5.2.1. Arsenic immobilization in copper floatation tailings

5.2.1.1. Preparation of flotation tailing slurries

Tailings resulting from copper floatation operations commonly contain pyrite and arsenopyrite, which are the main source of arsenic contaminations. Therefore, the simulated flotation tailing slurry containing arsenopyrite and pyrite was prepared in this study. Arsenopyrite sample was taken from Toroku mine, Miyazaki, Japan; and pyrite sample was taken from Mina Cerro Pasco, Peru. The sample was ground with a ball mill; and subjected to the mineralogical and particle size analysis. The flotation tailing slurry was then prepared by mixing 0.1 g of arsenopyrite, 0.1 g of pyrite, and 10 mL of 10 mM Ca(OH)$_2$ solution.

5.2.1.2. Arsenic stabilization in flotation tailings by synthesized schwertmannite

The immobilization experiments were carried out by adding various amount of the synthesized schwertmannite (0–0.15 g) to the prepared flotation tailing slurries (10 mL) in the flasks. The flasks were shaken for a week in a water bath at 25°C at 120 rpm. After a week, the concentration of arsenic in the aqueous phase of each flask was measured by ICP-AES. The initial and final pHs of the slurries were also measured.

5.2.2. The use of schwertmannite as medium for arsenic sorption-desorption

Arsenic sorption experiment was conducted in a plastic centrifuge tube with 50 mg of dried schwertmannite product and 50 mL of the solution containing 0.15 mM As (V) at the initial pH 3.0–4.0. The plastic tube was shaken horizontally for 24 h in a water bath at 25°C at 120 rpm. After 24 h, the suspension in the tube was centrifuged for 30 min at 3500 rpm to separate solid and liquid phases. The supernatant was subjected to ICP-AES for arsenic analysis. The amount of sorbed arsenic was calculated from the differences between the initial (added) amount and final (remaining) amount of arsenic in the solutions. On the other hand, the remained residue was suspended with 5 mL of the solution (volumic sorption-desorption stripping ratio, 10:1) at the initial pH 12-13 in the same plastic tube to investigate for the arsenic desorption efficiency. The plastic tube was then shaken again in a water bath at 25°C at 120 rpm for 24 h. After 24 h, the suspended solid was separated by centrifugation and the supernatant was analyzed for arsenic. The remained solid in the plastic tube was subjected to the arsenic sorption-desorption experiments again using the same procedure as mentioned above. The sorption-desorption experiments were repeated 4 times, and the recovered solid after the 4th cycles of desorption was subjected to XRD analysis.

The effects of the volumic sorption-desoprtion stripping ratio of 5:1, 10:1, and 100:1 prepared by adjusting the solution of desoption to 10, 5, 0.5 mL, respectively were investigated. The experiments were carried out following the same procedures detailed as above.

5.2.3. Analytical methods

The concentrations of arsenic were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Seiko Instruments SPS7800. The solid phase was ground to a homogeneous powder in a mortar and subsequently analyzed by X-ray diffraction (XRD) using a RIGAKU powder diffractometer with CuKα radiation (40 kV and 30 mA) to identify the minerals present in the samples.
5.3. RESULTS AND DISCUSSION

5.3.1. Arsenic immobilization in copper floatation tailings

5.3.1.1. Characterization of arsenopyrite and pyrite

The XRD pattern of the arsenopyrite sample is shown in Figure 5-1; and the result indicates that most peaks are attributed to arsenopyrite, and quartz was detected as impurity. For the pyrite sample, the XRD result (Figure 5-2) shows that most peaks are attributed to pyrite, and trace phases of quartz were detected as impurity. The ground arsenopyrite sample has particle size less than 75 μm and \(d_{80} = 50 \, \mu m\) (Figure 5-3) and the particle size of the ground pyrite powder is also less than 75 μm, which these are the average particle size commonly found at flotation operations.

![XRD pattern for arsenopyrite sample. Arsenopyrite peaks are denoted as “A” and quartz peaks are denoted as “Q”.

![XRD pattern for pyrite sample. Pyrite peaks are denoted as “Py” and quartz peaks are denoted as “Q”.

Figure 5-1: XRD pattern for arsenopyrite sample. Arsenopyrite peaks are denoted as “A” and quartz peaks are denoted as “Q”.

Figure 5-2: XRD pattern for pyrite sample. Pyrite peaks are denoted as “Py” and quartz peaks are denoted as “Q”.

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5.3.1.2. Arsenic immobilization in flotation tailings

Generally, the pH values range from 7.5 to 11.5 in most flotation operations (Branson and Ammons, 2004). The pH value of the prepared flotation tailing slurries in the present study was about 9.5 at the initial stage, and it was decreased to acidic pH after shaking for a week at 25°C. Figure 5-4 shows the final pH of flotation tailing slurries after shaking with the addition of various amount of the synthesized schwertmannite at 25°C for a week. The results show that the final pH was about 3 to 4 for all experimental conditions. The decrease of pH may be due to the oxidation of arsenopyrite and pyrite presented in the tailings. It is well documented that arsenopyrite and pyrite minerals undergo weathering process when tailings are exposed to the air and oxygen (Antelo et al., 2013; Burton et al., 2009; Corkhill and Vaughan, 2009; Davidson et al., 2008; Lottermoser, 2003; Yu et al., 2007).

![Figure 5-3: Particle size distribution of the arsenopyrite sample.](image)

![Figure 5-4: The final pH of flotation tailing slurries after shaking for a week at 25°C with the addition of various amount of the synthesized schwertmannite.](image)
Stoichiometric chemical reactions are commonly used to describe the oxidation mechanisms of pyrite. The pyrite oxidation is primarily accomplished by the indirect oxidation. The indirect oxidation of pyrite involves the chemical oxidation of pyrite by oxygen and ferric iron ($\text{Fe}^{3+}$), which occurs in three interconnected steps. The following chemical equations show the generally accepted sequence for such indirect oxidation of pyrite (Lottermoser, 2003):

$$\text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 2 \text{H}^+ \quad (5-1)$$

$$\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \quad (5-2)$$

$$\text{FeS}_2 + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ \quad (5-3)$$

In the initial step (Reaction 5-1), pyrite is oxidized by oxygen to produce dissolved ferrous iron ($\text{Fe}^{2+}$), sulfate and hydrogen ions. The release of hydrogen ions with the sulfate anions results in an acidic solution. The second step (Reaction 5-2) represents the oxidation of $\text{Fe}^{2+}$ to $\text{Fe}^{3+}$ by oxygen and occurs at a low pH. In the third step (Reaction 5-3), pyrite is oxidized with the help of $\text{Fe}^{3+}$ generated in Reaction 5-2. Thus, $\text{Fe}^{3+}$ acts as the oxidizing agent of pyrite.

The overall equation describing the oxidation of arsenopyrite can be expressed as follows (Corkhill and Vaughan, 2009; Walker et al., 2006):

$$4 \text{FeAsS} + 11 \text{O}_2 + 6 \text{H}_2\text{O} \rightarrow 4 \text{FeSO}_4 + 4 \text{H}_3\text{AsO}_3 \quad (5-4)$$

Arsenopyrite may also react with ferric ion, generating ferrous sulfate and arsenic acid (Iglesias and Carranza, 1994):

$$\text{FeAsS} + 11 \text{Fe}^{3+} + 7 \text{H}_2\text{O} \rightarrow 12 \text{Fe}^{2+} + \text{H}_3\text{AsO}_3 + 11\text{H}^+ + \text{SO}_4^{2-} \quad (5-5)$$

The ferrous iron is then oxidized to ferric iron ready for further leaching of the sulfide minerals (Ubaldini et al., 1997). As can be seen that oxidation of arsenopyrite can result in the liberation of arsenic as As(III) and strong acid. The As(III) can be further oxidized to As(V) as HAsO$_4^{2-}$ and H$_2$AsO$_4$ (Walker et al., 2006); and its mechanism can be represented as (Ubaldini et al., 1997):

$$2 \text{FeAsS} + 7 \text{O}_2 + \text{H}_2\text{SO}_4 + 2 \text{H}_2\text{O} \rightarrow \text{Fe}_2\text{(SO}_4)\text{O}_3 + 2 \text{H}_3\text{AsO}_4 \quad (5-6)$$

$$2 \text{FeAsS} + \text{Fe}_2\text{(SO}_4)\text{O}_3 + 6 \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow 4 \text{FeSO}_4 + \text{H}_2\text{SO}_4 + 2 \text{H}_3\text{AsO}_4 \quad (5-7)$$

Therefore, it can be concluded that the decrease of pH observed in the present study is due to the oxidation of arsenopyrite and pyrite presented in the flotation tailings.

As mentioned above that the oxidation of arsenopyrite can result in liberation of arsenic either as As(III) or As(V). The different oxidation states of arsenic presented in the tailing slurries could significantly affect the immobilization of arsenic by schwertmannite. It has been reported that the sorption behavior of As(III) and As(V) by schwertmannite are totally different (Burton et al., 2009). Under acidic condition (i.e. pH 3-4), schwertmannite has a higher sorption capacity for As(V) compared to As(III). Therefore, it is important to know the oxidation states of arsenic resulting from arsenopyrite oxidation in the flotation tailing slurries.
To investigate the concentrations of As(III) and As(V), the experiments were carried out as follows: the flotation tailing slurries prepared by mixing 0.1 g of arsenopyrite and 10 mL of 10 mM Ca(OH)₂ solution with or without 0.1 g of pyrite were shaken in the flasks for 24 h at 25°C and at 120 rpm. After 24 h, the concentration of As(III) and As(V) in the aqueous phase was then measured by ICP-AES. The results (Figure 5-5) show that As(III) is predominant with the trace amount of As(V) for the experiment conducted without pyrite. On the other hand, As(V) became dominant with some portion of As(III) for the experiment conducted in the presence of pyrite. The results here suggest that pyrite can facilitate the oxidation of As(III) to As(V). It has been reported that pyrite was found as a catalyst of As(III) oxidation by Fe(III) (Mandl and Vyškovský, 1994).

![Figure 5-5](image)

**Figure 5-5**: The concentrations of As(III) and As(V) in flotation tailing slurries after shaking for 24 h at 25°C with or without pyrite.

The amount of arsenic released from arsenopyrite in flotation tailing slurries with pyrite after shaking for a week at 25°C with the addition of various amount of the synthesized schwertmannite was also measured. The results (Figure 5-6) indicate that high arsenic concentration (2.3 mM) was observed for the experiment without the addition of schwertmannite. On the other hand, the concentration of arsenic became lower when schwertmannite was added. The arsenic concentration decreased with increasing amount of schwertmannite; and less than about 0.4 mM of arsenic was observed with the addition of 0.15 g schwertmannite, indicating that the arsenic released from arsenopyrite is sorbed by the added schwertmannite. However, as can be seen that not the entire released amount of arsenic was sorbed by the added schwertmannite, which this may be due to the different oxidation states of arsenic presented in the tailing slurries.

![Figure 5-6](image)

**Figure 5-6**: The amount of arsenic released from arsenopyrite in flotation tailing slurries with pyrite after shaking for a week at 25°C with the addition of various amount of the synthesized schwertmannite.

It has been reported that the sorption of As(III) and As(V) to schwertmannite was strongly pH-dependent (Antelo et al., 2012; Burton et al., 2009). Sorption is most significant at lower pH for As(V) and at higher pH for As(III). This can be explained by considering aqueous As(V) speciation and the surface charge of schwertmannite. The aqueous speciation of As(V) comprises H₃AsO₄⁺, H₂AsO₄⁻, HAsO₄²⁻, and AsO₄³⁻, with pKₐ¹ = 2.3, pKₐ² = 6.8, and pKₐ³ = 11.6 (Burton et al., 2009; Smedley and Kinniburgh, 2002). Aqueous As(V) is predominantly present as H₂AsO₄⁻ at low pH (below about pH 6.8) and as HAsO₄²⁻ at higher pH (H₃AsO₄⁺ and AsO₄³⁻ may be present in extremely acidic and alkaline conditions, respectively). These As(V) species are expected to sorb strongly at low pH because at low pH, schwertmannite has a large positive charge.
(PZC = 7.2, Jönsson et al., 2005). These factors facilitate relatively effective sorption of As(V) to schwertmannite at low pH.

On the other hand, the aqueous speciation of As(III) comprises H$_3$AsO$_3$\(^0\), H$_2$AsO$_3$, HAsO$_3^{2-}$, and AsO$_3^{3-}$, with \( pK_{a1} = 9.2 \) and \( pK_{a2} = 12.7 \) (Burton et al., 2009; Smedley and Kinniburgh, 2002). At pH less than pH 9.2, the uncharged arsenic species H$_3$AsO$_3$\(^0\) will predominate. The high \( pK_a \) values for As(III) reflect a strong tendency for protons to outcompete positively charged specific sorption sites for the AsO$_3^{3-}$ moiety at low pH. This results in relatively minor sorption for As(III) to schwertmannite at low pH and greater sorption at higher pH.

![Figure 5-6: Total arsenic concentration in flotation tailing slurries after shaking for a week at 25°C with the addition of various amount of the synthesized schwertmannite.](image)

As shown in Figure 5-4, the final pH of tailing slurries was about pH 3 to 4 for all experimental conditions. The As(V) presented in tailing slurries are expected to be sorbed effectively by schwertmannite under pH 3-4. On the other hand, incompletely oxidized-As(III) portion presented in the system may sorb poorly by the added schwertmannite under pH 3-4. Thus some amounts of the released arsenic are still remained in the tailing slurries even with the addition of schwertmannite up to 0.15 g. However, the completed-oxidation of As(III) to As(V) may be occurred at tailings pond respect to weathering time. The results in this study suggested that schwertmannite synthesized from copper heap leach solutions may be suitable for arsenic immobilization in copper flotation tailings.
5.3.2. The use of schwertmannite as medium for arsenic adsorption-desorption

This part demonstrates the possibility in applying the synthesized schwertmannite for arsenic immobilization in mine waters containing the diluted concentration of arsenic. The high arsenic concentration is essential for long-term stability of schwertmannite. The synthesized schwertmannite was used as the sorbent-desorbent to remove the diluted arsenic concentration at low pH and strip it back in the high pH solution to generate higher arsenic concentration.

The volumic sorption-desorption stripping ratio of 10:1 was used, and the arsenic concentration after desorption process was expected to be 10 times higher (112.5 mg L$^{-1}$) than the initial concentration of arsenic (11.25 mg L$^{-1}$) in sorption process. The results (Figure 5-7) show that As(V) sorption capacity by schwertmannite at pH 3-4 is about 11.2 mg L$^{-1}$ (over 99% of the total aqueous phase As), and the amount of arsenic released from the As(V)-sorbed schwertmannite after desorption process at pH 12-13 is about 74.9 mg L$^{-1}$ (about 66.7% of the total solid phase As) in the first experimental cycle. The spent schwertmannite from the first experimental cycle was then re-used again in the next sorption-desorption processes several times. The As(V) sorption capacities remain high (over 96% of the total aqueous phase As) even the spent schwertmannite was recycled back in the sorption-desorption processes repeatedly up to 4 times. The concentrations of arsenic in desorption experiments are over 70 mg L$^{-1}$ (>64% of the total solid phase As) for all 4 cycles.

The remained solid after the 4th cycle of desorption was subjected to XRD analysis to examine the possibly phase transformation of schwertmannite. The results (Figure 5-8) show schwertmannite peaks and there is no formation of other phases detected, indicating that the spent schwertmannite here is stable and that no solid phase transformation occurs.

![Figure 5-7](image_url): The As(V) sorption-desorption by schwertmannite repeatedly 4 cycles. Experimental conditions: initial As(V) concentration for sorption = 11.25 mg L$^{-1}$, sorption pH = 3-4, desorption pH = 12-13, volumic sorption-desorption stripping ratio = 10:1, reaction temperature = 25°C, equilibrium time = 24 h.

![Figure 5-8](image_url): XRD analysis results showing schwertmannite peaks with no formation of other phases.
5.3.2.1. Effect of volumic sorption-desorption stripping ratio

The initial As(V) concentration of 11.25 mg L\(^{-1}\) for sorption experiments and various volumic sorption-desorption stripping ratio (5:1, 10:1, and 100:1) were used for arsenic sorption-desorption by schwertmannite, which are repeatedly 4 cycles. Figure 5-9 shows the effects of different volumic sorption-desorption stripping ratio (5:1, 10:1, and 100:1) on the As(V) sorption-desorption by schwertmannite. The results indicate that As(V) sorption capacities are between 10.75-11.23 mg L\(^{-1}\) (>95% of the total aqueous phase As) for all experimental conditions during the whole 4 cycles of sorption-desorption processes. The amounts of arsenic released from the As(V)-sorbed schwertmannite in desorption process are 36.8-40.2 mg L\(^{-1}\) (>65% of the total solid phase As), 72-85 mg L\(^{-1}\) (>64% of the total solid phase As), and 101-108 mg L\(^{-1}\) (<10% of the total solid phase As) for the experiments conducted with volumic sorption-desorption stripping ratio of 5:1, 10:1, and 100:1, respectively. The desorption became less effective at high stripping ratio (i.e. 100:1), indicating that the volumic sorption-desorption stripping ratio has a significant effect on the desorption of arsenic from the As(V)-sorbed schwertmannite. At high volumic sorption-desorption stripping ratio (i.e. 100:1), the solid (~50 mg) to liquid (~0.5 mL) ratio is very high which this may causes the poorly desorption capacity at high stripping ratio.

The remained solids after the 4th cycles of desorption of each experimental conditions were subjected to XRD analysis to examine the possibly phase transformation of the spent schwertmannite. The results (Figure 5-10) show schwertmannite peaks and there is no formation of other phases detected for all experiments conducted using various volumic sorption-desorption stripping ratio, indicating that the spent schwertmannite here is stable and that no solid phase transformation occurs.

Figure 5-8: XRD patterns for (a) initial schwertmannite and (b) the spent schwertmannite after the sorption-desorption for 4 cycles repeatedly using the initial As(V) concentration for sorption: 11.25 mg L\(^{-1}\) and volumic sorption-desorption stripping ratio of 10:1. Schwertmannite peaks are denoted as “Sh”.

![XRD patterns](image-url)
Figure 5-9: Effect of volumic sorption-desorption stripping ratio, (a) 5:1, (b) 10:1, and (c) 100:1, on the As(V) sorption-desorption by schwertmannite that are repeatedly 4 cycles. Experimental conditions: initial As(V) concentration for sorption = 11.25 mg L⁻¹, sorption pH = 3-4, desorption pH = 12-13, reaction temperature = 25°C, equilibrium time = 24 h.
Figure 5-10: XRD patterns for the spent schwertmannite after the sorption-desorption repeatedly 4 cycles using the initial As(V) concentration for sorption: 11.25 mg L\(^{-1}\) and various volumic sorption-desorption stripping ratio (5:1, 10:1, and 100:1). Schwertmannite peaks are denoted as “Sh”.

Initial Schwertmannite

Stripping ratio: 5:1

Stripping ratio: 10:1

Stripping ratio: 100:1
5.4. CONCLUSION

This chapter demonstrates the applications of the synthesized schwertmannite for arsenic control at copper mines, which it was divided into two models experiments. The first part is to demonstrate the application of schwertmannite for immobilization of arsenic in tailings of copper flotation operations. The immobilization experiments were carried out by adding various amount of the synthesized schwertmannite to the simulated flotation tailing slurries in the flasks that were shaken for a week in a water bath at 25°C at 120 rpm. The results indicated that high arsenic concentration in solutions was observed for the experiment without the addition of schwertmannite due to the oxidation of arsenopyrite. The concentration of arsenic became significantly lower when schwertmannite was added; suggesting that schwertmannite synthesized from copper heap leach solutions may be suitable for arsenic immobilization in copper flotation tailings.

The second part of this chapter was focused on the possibility in applying the synthesized schwertmannite for arsenic immobilization in mine waters containing the diluted concentration of arsenic. The high arsenic concentration is essential for long-term stability of schwertmannite. The synthesized schwertmannite was used as the sorbent-desorbent to remove the diluted arsenic concentration at low pH and strip it back in the high pH solution to generate higher arsenic concentration. The results indicated that the diluted concentration of As(V) in acidic solution can be sorbed efficiently by schwertmannite; and the arsenic can also strip back or release from the As(V)-sorbed schwertmannite at alkaline pH condition, suggesting that the synthesized schwertmannite may be suitable for arsenic treatment for the solution with diluted concentration of arsenic. However, the pilot scales for both model experiments are still needed before these techniques can be approved for real applications at mine sites.
REFERENCES


Chapter 6

GENERAL CONCLUSION

Arsenic (As), a very poisonous inorganic pollutant is a major toxicant at porphyry copper mines the principal source of copper production worldwide. The regulations for arsenic release to the environment have become more stringent in recent years, and arsenic control is therefore an important issue in mining and metallurgical operations at copper mines. Among the current treatment processes for arsenic control at copper mine waste, retention of arsenic by schwertmannite (Fe$_x$O$_y$(OH)$_{z-2x}$(SO$_4$)$_x$ with x typically 1–1.75) has attracted much attention in recent years due to its strong binding affinity to toxic arsenic species. It can also be cost-effective as it is possible to synthesize schwertmannite from solutions generated in heap leach operations. Such leach solutions generally contain high concentrations of Fe$^{3+}$ and SO$_4^{2-}$, the components of schwertmannite. In this study, an appropriate method called neutralization technique for on-site synthesis of schwertmannite was proposed. Synthesis of schwertmannite from the simulated copper heap leach solutions was investigated. The efficiency of arsenic removal by the synthesized schwertmannite and the stability of arsenic-sorbed schwertmannite were evaluated, respectively. The applications of schwertmannite in As control of copper mine waste were then demonstrated.

This dissertation is composed of six chapters that detailed the different model experiments and the outcomes of the investigations. In Chapter 1, the background and the objectives of the study were presented. The sources of arsenic contamination resulting from copper production were pointed out. The various approach for arsenic wastes control in mining and metallurgical operations was reviewed and schwertmannite was selected as an ideal technique applying for control the toxic arsenic species that could be presented from such large amounts of waste at copper mines. On-site synthesis of schwertmannite by neutralization of the copper heap leach solutions was subsequently proposed. The synthesis is expected to be performed by neutralizing the leach solutions to pH 3–4. The synthesized schwertmannite can be expected to find application in arsenic immobilization of copper mine waste in tailings and spent ore of either dump or heap leach piles, as well as copper smelting plants.

Chapter 2 provided insight into the production of schwertmannite in porphyry copper mines by investigating the effect of co-existing metal ions (Cu$^{2+}$ and Fe$^{2+}$) and the reaction temperatures (25$^\circ$C and 65$^\circ$C) on the synthesis of schwertmannite by neutralization technique. It is shown that Cu$^{2+}$ and Fe$^{2+}$ play an important role for the schwertmannite synthesis at 65$^\circ$C. However, Cu$^{2+}$ and Fe$^{2+}$ did not affect the synthesis at 25$^\circ$C. It was observed that schwertmannite is formed at both 25$^\circ$C and 65$^\circ$C at all experimental conditions except for the solutions containing Fe$^{3+}$ at 65$^\circ$C, as goethite was generated at these conditions. It was found that goethite is formed by transformation of intermediated schwertmannite during the synthesis at 65$^\circ$C. However, Cu$^{2+}$ has the ability to inhibit the transformation of schwertmannite to goethite in the presence of Fe$^{3+}$. Although it is possible to synthesize schwertmannite at both temperatures, their surface characteristics are different. The specific surface area of the schwertmannite synthesized at 65$^\circ$C was much larger (147.4–176.9 m$^2$ g$^{-1}$) than the specific surface area of the schwertmannite synthesized at 25$^\circ$C (14.1–21.4 m$^2$ g$^{-1}$), which may affect their efficiency for arsenic removal.

Therefore, arsenic sorption capacities by these synthesized products were evaluated and discussed in detail in Chapter 3. The results indicate that As(V) in acidic solutions (pH 3-4) can be removed effectively by schwertmannite synthesized in the presence or absence of co-existing metal ions (Cu$^{2+}$ and Fe$^{2+}$) at 65$^\circ$C with the maximum sorption capacity of 94-133 mg g$^{-1}$. A lower As(V) sorption capacity is observed in product containing goethite synthesized in the presence of Fe$^{3+}$ at 65$^\circ$C; here, the maximum As(V) sorption capacity is 58 mg g$^{-1}$. The maximum As(V) sorption capacities by schwertmannite synthesized at 25$^\circ$C are 17-23 mg g$^{-1}$, which are much lower than the
maximum sorption capacities of the schwertmannite synthesized at 65°C. This should be taken into consideration for its application on mine sites.

In Chapter 4, the stability of As(V)-sorbed schwertmannite (Sch-As) under porphyry copper mining conditions was studied by investigating the effect of Cu²⁺, Fe²⁺, pH, and ageing time on the stability of Sch-As. The results indicated that Cu²⁺ has no significant effect on the stability of Sch-As and that the As(V) incorporated into schwertmannite can retard or significantly inhibit the Fe²⁺-catalyzed transformation of schwertmannite to goethite under acidic conditions (pH 3–4). The Sch-As aged at different pH ranges from 3 to 11 at 25°C exhibits no mineralogical phase changes even after ageing for 120-days; however the concentration of arsenic released from the solid phase appeared to be strongly pH-dependent also at ageing for 24 h. The release of As was almost negligible at pH 2 to 7, and a high release of As was observed at extremely acidic and alkaline conditions. This indicates that the release of As from Sch-As is controlled by the outside environmental factors such as pH, Cu²⁺, and Fe²⁺ rather than time. Control of arsenic contamination in copper mine waste treatment are expected to be performed following the methods mentioned in this Chapter. However, further study should be carried out to substantiate details of these treatment processes.

Chapter 5 demonstrated the applications of the synthesized schwertmannite for arsenic immobilization in copper mine wastes and metallurgical plants. The study was divided into two models experiments. The first part was to demonstrate the application of schwertmannite for immobilization of arsenic in tailings resulting from copper flotation operations. The results indicated that high arsenic concentration in solutions was observed for the experiment without the addition of schwertmannite due to the oxidation of arsenopyrite. The concentration of arsenic became significantly lower when schwertmannite was added; suggesting that schwertmannite synthesized from copper heap leach solutions may be suitable for arsenic immobilization in copper flotation tailings. The second part of this chapter was focused on the possibility in applying the synthesized schwertmannite for arsenic immobilization in mine waters containing the diluted concentration of arsenic. The high arsenic concentration is essential for long-term stability of schwertmannite. The synthesized schwertmannite was used as the sorbent-desorbent to remove the diluted arsenic concentration at low pH and strip it back in the high pH solution to generate higher arsenic concentration. The results indicated that the diluted concentration of As(V) in acidic solution can be sorbed efficiently by schwertmannite; and the arsenic can also strip back or release from the As(V)-sorbed schwertmannite at alkaline pH condition, suggesting that the synthesized schwertmannite may be suitable for arsenic treatment for the solution with diluted concentration of arsenic. However, the pilot scales for both model experiments are still needed before these techniques can be approved for real applications at mine sites.
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- SENGPASITH -
LIST OF RESEARCH ACCOMPLISHMENTS

I. Papers in Peer-Reviewed Journals (Related to the PhD Dissertation)


II. Papers in Peer-Reviewed Journals (Others)


III. Papers in Conference Proceedings (Related to the PhD Dissertation)


IV. Papers in Conference Proceedings (Others)


