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Author(s)	KHOEURN, Kimleang
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Long-term acid generation containing heavy metals from the tailings of a closed mine and its countermeasures

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

Kimleang KHOEURN



Division of Sustainable Resources Engineering
Graduate School of Engineering,
Hokkaido University, Japan
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ABSTRACT

Acid mine drainage (AMD) from abandoned mines is a well known problem all over the world. The AMD is mainly produced by the oxidation of pyrite and metal sulfides. A significant amounts of heavy metals (*e.g.*, Zinc (Zn), copper (Cu), iron (Fe), and others) are released and could affect the surrounding environment as well as human health when they are ingested through food, crop, and contaminated water. Numerous researches have been conducted to solve these problem by neutralizing the AMD (*e.g.*, calcium hydroxide (Ca(OH)_2), sodium hydroxide (NaOH), etc.). However, it remains unclear when the treatment would stop. To answer this question, leaching of heavy metals and acid generation from tailings dams were studied. In this dissertation, an in depth study of the mechanisms controlling the long-term leaching of heavy metals, such as Zn, Cu, and Fe from the tailings was conducted. First, the tailings dam was characterized and speciation of heavy metals was studied. Second, the column experiments were carried out at a different irrigation rate. Finally, chicken eggshell as a low-cost neutralizer for the AMD was applied. The dissertation contains 5 chapters.

Chapter 1 introduces the background of AMD from the tailings and gives the motivation, importance, and objectives of the study.

Chapter 2 addresses the mechanism of AMD generation in tailings from an abandoned mine site and predicts the evolution of Zn, Cu, and Fe concentrations. Batch leaching experiments and sequential extractions were conducted to investigate the leaching behavior of these contaminants from the tailings and to understand their solid-phase partitioning. Acid-base accounting and principal component analysis (PCA) were used to confirm factors affecting Zn, Cu, and Fe leaching and acid formation based on the leaching experiments. There were strong positive correlations between Zn, Fe, and electrical conductivity (EC) or sulfate ion (SO_4^{2-}), indicating that pyrite and sphalerite are the major minerals releasing Zn and Fe. This agreed with the PCA results. In the upper part of the tailings, the water-soluble and sulfide fractions of Zn, Cu, and Fe were almost flushed out, whereas they remained high deeper in the tailings. This implies that the tailings will likely continue to release these contaminants ($\text{Zn} > \text{Cu} > \text{Fe}$) for a long time unless remedial measures are taken.

After identifying the high content of heavy metals and ions in the deeper tailings samples, Chapter 3 addresses the understanding of long-term acid generation and leaching of Zn, Cu, and Fe. The unweathered tailings samples at depths of 1 to 3 m were collected from a tailings dam of a

closed mine. The mechanisms of long-term weathering of the tailings were assessed through leaching of heavy metals by three column experiments. Mineralogical and chemical constituents, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX), sequential extraction of the tailings, and chemical analysis of the leachates were carried out to determine the processes responsible for the leaching of Zn, Cu, Fe, and SO_4^{2-} . The contents of Zn, Cu, and Fe in the tailings were mainly associated with ion exchangeable and sulfide fractions. The pH values of the leachates from the columns were 3.0–3.7 throughout the column experiments over 84 weeks, and approximately 35-45% of Zn, 15-23% of Cu, 2.5-4% of Fe and 20-25% of S were leached out. Higher concentrations of Zn, Cu, Fe, and SO_4^{2-} at the beginning of the experiments were observed, which could be attributed to the dissolution of soluble sulfate minerals present in the tailings. This indicates that the formation and dissolution of secondary soluble sulfate minerals contributed to Zn and Cu leaching. After stabilizing the leaching concentrations of Zn, Cu, Fe, and SO_4^{2-} , they were still released from the tailings until the end of the experiments. This continuous leaching suggests the oxidation of pyrite and sulfide minerals. During these processes, ferrihydrite, goethite, lepidocrocite, and maghemite were formed and these minerals also acted as a sink for Zn and Cu by adsorption and/or co-precipitation. These results mean the significance of the long-term behavior of heavy metals released from mine tailings dams.

Chapter 4 focuses on the evaluation the effectiveness of the chicken eggshell for the neutralization of AMD and removal of the heavy metals. The eggshell were collected from kitchen wastes, and then washed, dried, grinded, and stored in air-dried containers before use. The batch adsorptions were conducted at different contact times, particle sizes, and dose of eggshell. The morphology of the eggshell before and after batch adsorption was analyzed by SEM-EDX. The results showed that pH reached 6.7 and the highest removal efficiency of Zn (60%) , Cu (98%), Fe (99%), and SO_4^{2-} (10%) were obtained at contact time of 24 h, particle size of 75-150 μm , and dose of 1 g/25 mL. The removal efficiency of heavy metals were in order $\text{Fe} > \text{Cu} > \text{Zn} > \text{Mn}$. The removal process of Cu and Fe was rapid and reached equilibrium at 24 h. This means that the removal of Cu and Fe is due to precipitation whereas that of Zn and Mn is due to adsorption. Based on the results, the chicken eggshells can be used for neutralization and removal of the heavy metals from the actual AMD.

Chapter 5 gives the overall conclusions of the research and suggestions for future study on the AMD as well as heavy metals from the tailings. The results could provide helpful information on the management of tailings dams after mine closure.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 Mine wastes

Mining activity has considerably increased due to notable population growth and worldwide demand for mineral resources. The waste generated by mineral extraction may be solid, tailings, or slurry, with the most common being tailings, waste rock, slag, and tail ends, although in certain circumstances, the vegetation and overburden may also be considered wastes (Pérez Cebada 2016). Mine wastes can be generally classified into two majors categories as shown in Figure 1.1.

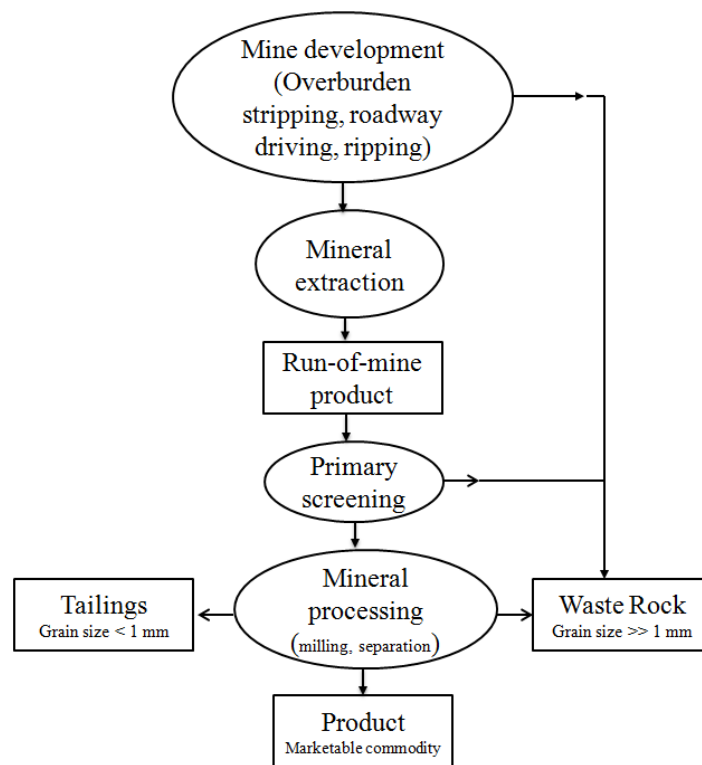


Figure 1. 1 A classification of mine wastes according to their origins within the mining and mineral processing cycle (Younger et al., 2002).

Beside genetic considerations, the fundamental distinction between waste rock and tailings is grain size, with most tailings being finer than 1 mm in diameter, and most waste rock being considerably coarser than 1 mm. Waste rock is moderately reactive if it is sulfidic, high permeability en masse, and generally tipped dry (Younger et al., 2002). As definition, the tailings are the mixture of crushed rock and processing fluids from mill, washeries or concentrators that remain after the extraction of economic metals, minerals, or coal from the mining resources (Hudson-Edwards et al., 2001; Younger and Wolkersdorfer, 2004; Lottermoser, 2007). In addition, as a function of their small size, these grains have a relatively large surface area to volume ratio,

which renders them kinetically prone to oxidation and likely ensuing release of incorporated contaminant element (i.e., sulfide oxidation and release of zinc (Zn), copper (Cu), iron (Fe), and manganese (Mn) (Gupta, 1999; Kossoff et al., 2011). This is the reason that tailings are the major source of environmental impact by mining industry.

1.2 Mineralogy and chemistry of tailings

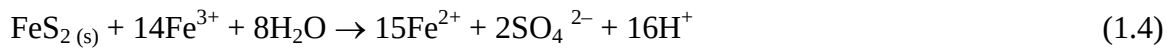
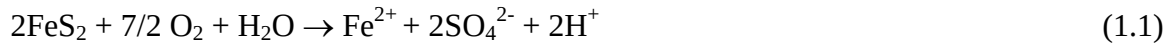
Mineralogy of tailings may be divided into three broad categories: the gangue fraction, residual uneconomic sulfide-oxide fraction, and secondary mineral fraction (Kossoff et al., 2014). In sulfide tailings remaining from precious metal extraction, the gangue fraction is dominated by quartz (SiO_2) and also can comprise K-feldspar (KAlSi_3O_8), sericite ($(\text{KAlSi}_3\text{O}_8)(\text{F},\text{OH}_2)$), and so on (Lottermoser and Ashley, 2005). Pyrite (FeS_2) is almost ubiquitous with the sulfide-oxide fraction, whereas sphalerite (ZnS), chalcopyrite (CuFeS_2), and galena (PbS) are also common (Keith and Vaughan, 2000; Kossoff et al., 2014). Fresh tailings grains are weathered in the field when exposed to oxic conditions, and secondary oxidized minerals formed (Kossoff et al., 2014). The particular secondary minerals may be formed depending on the interaction between source mineralogy and local condition, such as pH, climate and redox state. The representative one are goethite ($\alpha\text{-FeOOH}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), anglesite (PbSO_4), melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), and so on (Gleisner and Herbert, 2002).

The chemical composition of the tailings depends on the mineralogy of the ore body, the nature of the processing fluids used to extract the economic metals, the efficiency of the extraction process and the degree of weathering during storage in the impoundment (Seal et al., 2008; Kossoff et al., 2014). The presence of Si and Fe together with oxygen as well as major component (i.e., aluminium (Al), calcium (Ca), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), and sulfur (S)) is always found in the tailings (Kwong et al., 2003; Khorasanipour and Eslami, 2014; Adnani et al., 2016). Additionally, there are always metals and metaloids other than Fe present in the tailings. Arsenic (As), Cu, lead (Pb), and Zn are generally quantified and have high contents (i.e., David, 2003; Rabinowitz, 2005; Meck et al., 2006).

1.3 Formation of acid mine drainage (AMD)

Acid mine drainage (AMD) forms when sulfide minerals are exposed during mining, highway construction, and other large-scale excavations (Akcil and Koldas, 2006). Sulfides and sulfosalts are the reactive minerals, which are largely present in coal and metal mines (Chopard et al., 2017). The reactive mineral is exposed to an oxidant and water, either in oxic or anoxic systems,

AMD is formed. The processes leading to the AMD are numerous and complex and involve chemical, biological, and electrochemical reactions. The chemical oxidation of sulfides can follow a variety of pathways involving surface interactions with dissolved O₂, ferric iron (Fe³⁺), and microorganism (Blowes et al., 2014). Pyrite is relatively stable under both acidic and alkaline conditions but in the presence of O₂ and Fe³⁺, it is rapidly dissolved as illustrated by the following equations:



Equation (1.1) presents the oxidation reaction of pyrite by O₂ at near-neutral pH, and Equation (1.4) by Fe³⁺ at acidic pH under abiotic conditions. The rate of pyrite oxidation by Fe³⁺ is faster than by O₂ (Mylona et al., 2000). In addition, the Fe²⁺ generated in Equation (1.1) can be oxidized into Fe³⁺ and hydrolyzed, which leads to the overall pyrite oxidation reaction presented in Equation (1.4). The catalysis of AMD reactions by bacterial activities is well known. Thus, biological reactions and associated microorganisms have been increasingly studied in mine environments. Recently, Nordstrom et al. (2015) highlighted advances in the knowledge of microbial activity. For example, microbial activity can increase the oxidation rate of chalcopyrite by up to three orders of magnitude with respect to purely chemical weathering (Kwong et al., 2003), and can significantly enhance Zn dissolution in sphalerite (Natarajan 1992). Sulfate (SO₄²⁻) and metals, such as Fe, Cu, Pb, Ni, Mn, cadmium (Cd), and Al are also released into the water (Johnson and Hallberg, 2005; Akcil and Koldas, 2006; Udayabhanu and Prasad, 2010; Kefeni et al., 2017).

The primary factors that determine the rate of acid generation are: pH; temperature; oxygen content of the gas phase, if saturation is less than 100%; oxygen concentration in the water phase; degree of saturation with water; chemical activity of Fe³⁺; surface area of exposed metal sulfide; chemical activation energy required to initiate acid generation; and bacterial activities. Chemical, biological and physical factors are important for determining the rate of acid generation; physical factors, particularly waste rock dump permeability, are particularly important. Dumps with high permeability have high oxygen ingress, which contributes to higher chemical reaction rates,

hence, higher temperatures and increased oxygen ingress through convection (Akcil and Koldas, 2006).

In many environmental settings, the consequence of AMD is considered moderate to severe, mostly independent of pH and acidity. In other words, the environmental consequence is often considered at least moderate whether pH is 2 or 4 and whether acidity is 100,000 or 1,000 mg/L (Morin and Hutt, 1998).

In nature, acid-consuming minerals like carbonates and silicates typically exist together with acid-producing sulfide minerals, so the leachate pH is determined by the balance between acid producing potential (AP) and neutralization potential (NP) (White et al., 1999). Thus, AMD is formed when the neutralization potential ratio (NPR; NP/AP) is less than 1. If NPR is greater than 1, contaminated neutral drainage (CND) is generated instead of AMD, which sometimes contains more soluble heavy metals like Cu, Mn, nickel (Ni), and Zn as well as toxic metalloids such as selenium (Se), and As (U.S. EPA, 1994; Plante et al., 2014; Calugaru et al., 2016; Tabelin et al., 2017).

Static tests, which evaluate the balance between the acid-generating potential and acid-neutralizing potential for a given mine tailings, are characterized by a wide uncertainty zone in which it is difficult to accurately predict the AP (Cruz et al., 2001; Bouzahzah et al., 2014). Static tests are conducted at a given point in time, and do not account for the rate and evolution of the observed reactions rates (Adam et al., 1997). Subsequently, to better understand long-term AP, kinetic tests are performed to provide more information about the reaction rates of the acid-generating and acid-neutralizing minerals.

1.4 Acid mine drainage remediation

Acid mine drainage is considered to be a multifactor pollution since it affects the environment physically, chemically, biologically and ecologically. The impacts of AMD on human and the environment are attributed to its acidity and toxic metal concentrations and these negative impacts have been widely reported (Gray, 1997; Bell et al., 2001; Evangelou and Zhang, 2009; Simate and Ndlovu, 2014; Asif and Chen, 2016). Acid mine drainage impacts stream and river ecosystems by increasing acidity, depleting oxygen, releasing heavy metals such as Al and Fe. This affects photosynthesis aquatic plant visibility for animals continue indefinitely, causing an environmental damage long after the end of operation.

Knowing the formation of the AMD and its impact is the key factors to choose remediation methods. There are two primary strategies for AMD remediation: prevention and treatment. Preventing the formation or the migration of AMD from its source is generally considered to be a more preferable option. Prevention is a strategy to protect the formation of AMD completely and hence the AMD should not require the further treatment. One of the most commonly techniques used to prevent AMD is oxygen barrier. This method limits the availability of O₂ to sulfide-rich mine wastes by the use of dry covers and water covers. For the dry covers, the materials, such as soil, till, sewage sludge, kiln, clay, silt and cement can be used as single to multi-layered systems (Mylona et al., 2005; Igarashi et al., 2006; Borghetti Soares et al., 2009; Ahn et al., 2011; Gardner et al., 2012; Nason et al., 2014). Nevertheless, this strategy does not prevent the AMD formation entirely due to factors such as hydraulic conductivity and water saturation (Ragnvaldsson et al., 2014). Water covers are wisely used as an oxygen barrier due to the slow O₂ diffusion in water (Moncur et al., 2015). Unfortunately, this method is not applicable in arid and semi-arid regions where annual evaporation exceeds the precipitation (Lottermoser, 2005).

As in brief, the other prevention method, such as passivation/microencapsulation, biological source treatment (BST), backfilling, and co-disposal/blending (*i.e.*, limestone) have been reported (Skousen et al., 1998, Mylona et al., 2000; Diao et al., 2013; Villain et al., 2013; Alakangas et al., 2013). In recent years, industrial by-products and residues (*i.e.*, red gypsum, sugar foam, ashes from biomass combustion, green liquid dregs, fly ash, mesa lime, argon oxygen decarburization slag, cement kiln dust, and red mud bauxite) have become popular blending materials to inhibit the formation of AMD due to their high neutralization potentials (Yeheyis et al., 2009; Alakangas et al., 2013).

However, prevention strategy might not be feasible in many locations. In such a case, it is necessary to collect and treat it before discharging into water body. Various methods, such as desalination (sulfate removal) (GARD Guide, 2010; Madzivire et al., 2015), pH neutralization with alkaline substrates (*i.e.*, limestone, quicklime, hydrated lime, dolomite, and so on) (Steenari et al., 1999; Zinck, 2005; Madzivire et al., 2011, Macías et al., 2012, Alakangas et al., 2013; Madzivire et al., 2015), anaerobic constructed wetland, comprise of bedrock (limestone/gravel), soil, plants and an organic substrate (Vymazal, 2011; Sahinkaya et al., 2012; Mthembu et al., 2013; Allende et al., 2014; Zhang and Wang, 2014), sulfidogenic bioreactors (*i.e.*, animal manure, compost, saw dust, wood, cellulose waste, chips, and bark) (Newcombe and Brennan, 2010; Papirio et al., 2013; Sánchez-Andrea et al., 2014), adsorption (*i.e.*, dead biomass, clay, tree bark, tea leaves, natural zeolite, commercial chemical oxides and hydroxide, and eggshells) (Newcombe and Brennan, 2010;

Papirio et al., 2013; Sánchez-Andrea et al., 2014; Muliva et al., 2018), anoxic limestone drains (*i.e.*, limestone, clay) (Santomartino and Webb, 2007; Ouakibi et al., 2014) and permeable reactive barriers (*i.e.*, granular iron, zerovalent iron, limestone, quick lime, zeolite, sewage sludge, activated alumina, fly ash, ferric oxyhydroxides) (Blowes et al., 2000; Moraci and Calabro, 2010; Obiri-Nyarko et al., 2014). Figure 1.2 shows the summary of the AMD remediation methods that have been used.

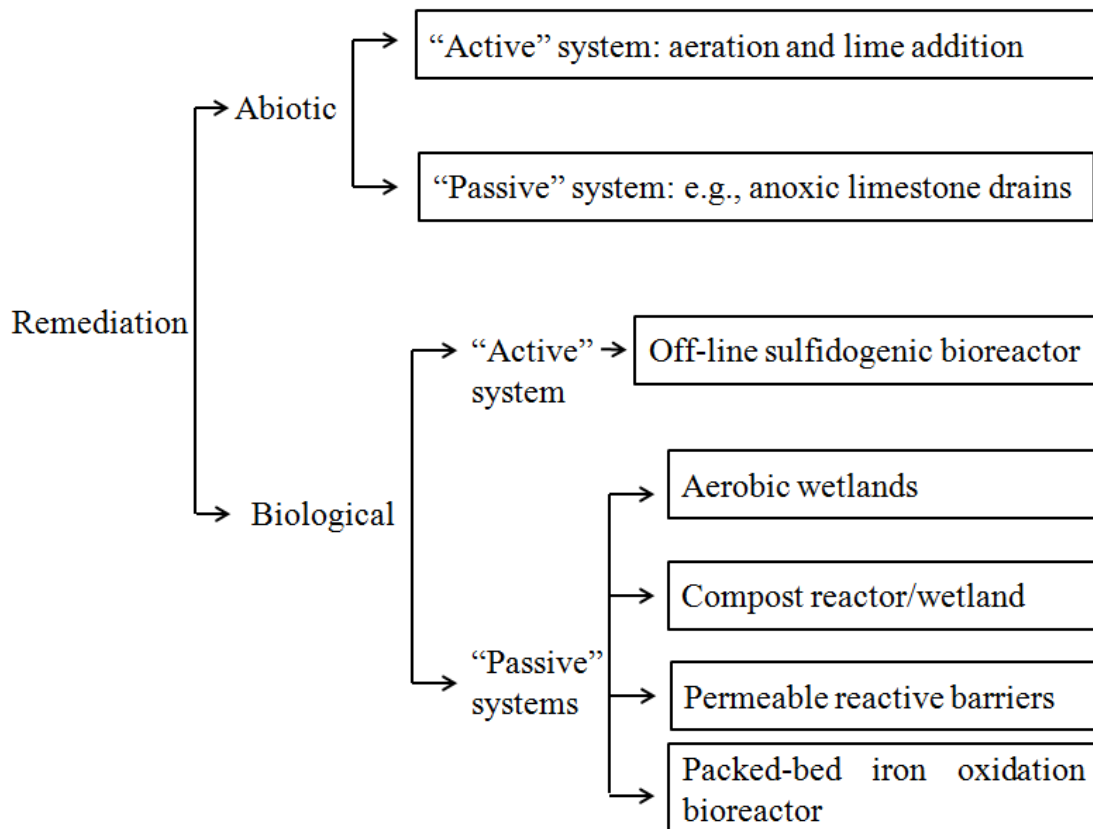


Figure 1. 2 Biological and abiotic strategies for remediating acid mine drainage waters (Johnson and Hallbert, 2005)

1.5 Statement of the problem and objectives of the study

Water pollution from acid generation containing heavy metals can continue to occur for a long period of time, even after mining closure (Benvenuti et al., 1997). Some authors believe that the oxidative dissolution of sulfides through sulfide oxidation is one of the most important factors that lead to environmental pollution in metal sulfide mine areas (Byerley and Scharer, 1992; Subrahmanyam and Forssberg, 1993; Salomons, 1995; Cruz et al., 2001; Liu et al., 2008).

A closed mine in Shimokawa, Hokkaido, has generated AMD for more than 40 years. Mine tailings were the major source of Zn, Cu, Fe, and SO_4^{2-} . When a significant release of these

hazardous metals is generated, they could affect the surrounding environment as well as human health when they are ingested through food crop and contaminated water. Therefore, in Japan, discharge from mine wastes has been treated before releasing into the nearby river. This is such a good practice for mine remediation, which is friendly to environment. However, the question is how long it would take to stop the treatment process. Thus, characterization of mine tailings and evaluation of leaching behaviors of heavy metals from the tailings would be a good answer to this question.

In previous works, numerous researches have been investigated on geochemical behaviors and acid generation from the tailings (Gleisner and Herbert, 2002; Hakkou et al., 2008; Blowes et al., 2014; Bouzahzah et al., 2014; Fadiran et al., 2014; Bogush and Lazareva, 2011; Chopard et al., 2017; Eugenia Nieva et al., 2018; Letina and Letshwenyo, 2018; Elghali et al., 2019); however, most of the studies were based on evaluation of a short-term behaviors of heavy metals leaching and the evaluation of their long-term behaviors, such as transformation of heavy metals, are still limited. Thus, a deep understanding of long-term behaviors of heavy metals in the tailings and treatment period should be required because different tailings would behave differently from one to another. A clearly understanding on a long-term acid generation and chemical form and leaching behaviors of heavy metals from the tailings could provide information on improvement of tailings management systems. By obtaining that information, a low-cost countermeasure is applied to evaluate its effectiveness of the remediation of mine tailings. Specifically, this study aims to achieve the following:

- a. To characterize the tailings dam (i.e., batch experiments)
- b. To evaluate long-term acid generation and heavy metals leaching from the unweathered tailings (e.g., column experiments), and
- c. To evaluate the effectiveness of eggshell for removal of metals and neutralization of AMD

1.6 Outline of dissertation

This dissertation consists of five chapters. The key contents of each chapter are outlined as follows:

Chapter 1 introduces type of mine waste, the background of the AMD and its countermeasures, statement of the problem, and objectives of the study.

Chapter 2 focuses on the characterization of the tailings, metals speciation in response to mobilization of metals, and the AMD prediction by a static test. Samples were collected from 4 boreholes of a tailings dam of Shimokawa (24 samples in total including tailings, soil covering, and lapilli tuff). The samples were provided for batch leaching tests and sequential extraction. The multivariate analysis was applied to add an interpretation of the obtained data.

Chapter 3 addresses the long-term leaching behaviors of the hazardous metals and acid generation from the tailings. Three columns were constructed with different irrigation rates. Spike test was introduced into columns 1 and 2 at week 37. After 84 weeks of the experiment, the tailings were separated into 5 segments, and then the batch leaching tests were applied. The comparison between concentration of Zn, Cu, and Fe in the effluents and fractions of sequential extraction were discussed. The effects Al and Si on pH changes and factors controlling pyrite oxidation were also discussed in this chapter. At the end of this chapter, the secondary minerals occurring inside the columns were identified.

Chapter 4 presents the effectiveness of the eggshell in AMD neutralization and removal of hazardous metals. The eggshell was collected from kitchen wastes, washed, dried, ground, sieved, and stored in airtight containers. Different contact time, particle sizes, and doses of eggshell were studied. The mechanism of the removal of hazardous metals was discussed at the end of the chapter.

Finally, general conclusions of the research were summarized based on the applied methodology and the achievement of research objectives. Suggestions for future research were also included in this chapter.

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CHAPTER 2

DISTRIBUTION OF ZINC, COPPER, AND IRON IN THE TAILINGS DAM OF AN ABANDONED MINE IN SHIMOKAWA, HOKKAIDO, JAPAN

2.1 Introduction

It has been estimated that more than 70% of the materials excavated during mining operations worldwide are wastes (Younger et al., 2002). Mine wastes can generally be classified into two major categories, waste rock and tailings. Tailings are produced when usable ore are separated from unusable materials, before smelting (Zhang et al., 2016).

Many closed mines are located in Hokkaido, Japan, most of which have been continuously generating AMD after their closure (Ito et al., 2010). The primary minerals in the tailings are quartz and pyrite, with secondary minerals such as goethite (Sasaki et al., 2002). The AMD is generated by the weathering of sulfide minerals like pyrite (Younger et al., 2002) when they are exposed to air and water, which has serious negative impacts on the surrounding soil, water resources, and ecosystem (Lee et al., 2005; Khan et al., 2008; Yadav, 2010). Some of the metals that dissolve out of the tailings are detrimental to human health when they are ingested through contaminated drinking water and food crops (Duruibe et al., 2007).

AMD generated from tailings dams and drifts at abandoned mine sites are treated before their re-introduction into the environment (Gazea et al., 1995; Gray, 1997). The most common and widely used AMD management approach is neutralization by an alkaline reagent (e.g., limestone, quicklime, or sodium hydroxide) to raise the pH and remove most of the metals through precipitation reactions (Matlock et al., 2002; Potgieter-Vermaak et al., 2006). During a short-term period, the neutralization is relatively cheap; however, if the treatment stretches for several decades or centuries, the combined costs of neutralization reagents, facilities, and sludge disposal become enormous (Ueda and Masuda, 2005). In addition, it is difficult to accurately predict when AMD generation will stop.

To select an appropriate remediation strategy, the properties of tailings, metal contents, and their spatial distribution should be clarified (Acosta et al., 2011). The distribution and chemical species of metals in a tailings dam differ, depending on the ore minerals, tailings properties, deposit time, and local climate (Duanmu et al., 2011). Several studies have shown changes in AMD generation rates (Morin and Hutt, 1998; Greenhill, 2000; Schafer, 2000; Hakkou et al., 2008; Lengke et al., 2010; Modabberi et al., 2013; Bouzahzah et al., 2014) and the leaching behaviors of

contaminants from mine sites over time (Lee et al., 2005; Bogush and Lazareva, 2011; Zhang et al., 2016; Wang et al., 2017). However, the factors and processes controlling AMD generation and distribution of potentially toxic elements in tailings dams are not fully understood. The aim of this chapter was to characterize the mineralogy and geochemistry of the tailings of a closed mine, to determine the release of acidity and contaminants, such as Zn, Cu, and Fe, from the tailings, and to predict changes in the chemistry of the AMD. The results of this chapter will be used to design more economical and sustainable mitigation approaches for closed mine sites.

2.2 Materials and methods

2.2.1 Study site

The study area (Figure 2.1) is a tailings dam of the Shimokawa mine, which is located about 60 km northeast of Asahikawa city in northern Hokkaido, Japan. The geology within the area of the mine consists of Tertiary strata, pre-Cretaceous black slates, basaltic rocks, and granitic rocks. The Shimokawa group, which is mainly composed of the Tertiary strata, consists of basaltic to andesitic lava flows and volcanoclastic rocks of the middle to late Miocene age (Sugawara, 1995). The mineralization occurs in the hanging-wall of a fault zone and is characterized by the coarse-grained nature, existence of spilitic facies with pillow structure, whitish coloration due to abundant carbonate veinlets, and the assemblage of the sulfide minerals (Ishio and Kubota, 1969).

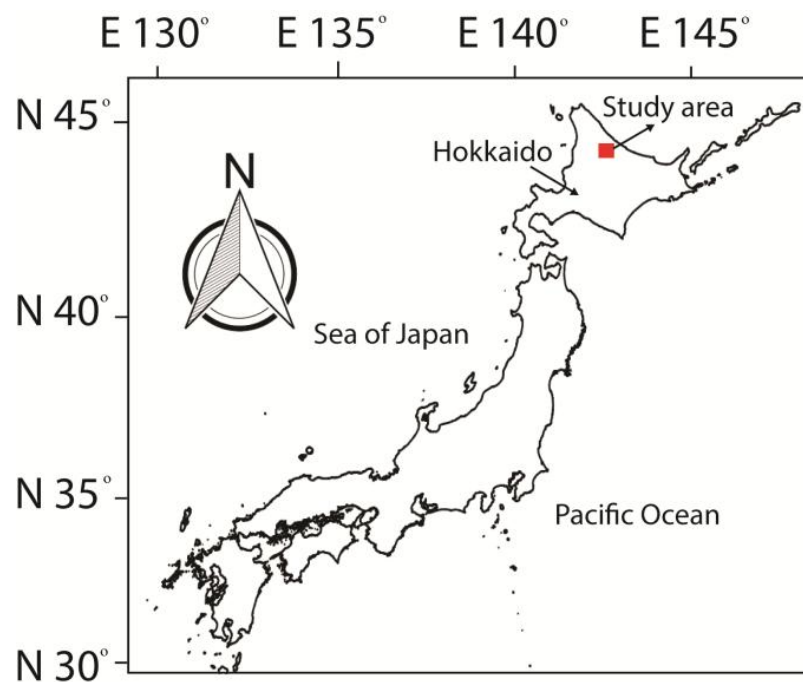


Figure 2. 1 Location of the Shimokawa mine

The ore deposit is considered syngenetic (Miyake, 1965). The major ore minerals were chalcopyrite, pyrite, pyrrhotite, and sphalerite. The vein minerals were quartz and chlorite (Sato, 1967). The ore body and iron sulfide dissemination zones were mined for gold (Au), silver (Ag), and Cu, cobalt (Co), Zn, and iron sulfides. Mining started in 1942 and stopped in 1987; the maximum amount of Cu (38,369 t) was produced in 1972. The tailings were deposited in tailings dams. AMD with high concentrations of Zn, Cu, and Fe has been generated at the site since the mine was closed. The bulk of the AMD from the tailings dams and drifts of the mine level has been treated by neutralization for the past 40 years. Representative AMD quality and volume treated in the mine site are shown in Table 2.1 The concentrations of Zn and Fe exceed the effluent standards in Japan, and the Cu concentrations almost exceeds the drinking water standard in Japan.

Table 2. 1 The quality of AMD in 2002 and 2010

Year	pH	Heavy metal concentrations			Treated quantity (m ³ /min)
		Zn (mg/L)	Cu (mg/L)	Fe (mg/L)	
2002	3.33	5.5	0.89	55.4	0.068
2010	3.52	8.6	0.62	71.4	0.041

2.2.2 Sampling, and chemical and mineralogical analyses

Figure 2.2 shows the plain view of the main tailings dam, which is divided into Dams 1, 2 and 3, and a cross-sectional view of one of the dams is shown in Fig. 2.3. These tailings dams are located along a river. The geology of the tailings dam consists of a talus cone, lapilli tuff, terrace deposit, covering soil, and bank (Fig. 2.3). Dam 1 (about 3.1 ha in area and 10 m deep) was selected in this research because the geology and construction procedures of the three dams were the same. In this site, the average rainfall is 969 mm/year with daily temperature ranging from −9.4 to 20.1 °C. Four boreholes were drilled in the tailings of Dam 1 as shown in Fig. 2.3 (B2, B3, B4, and B5). The depths of boreholes are 10 m for the boreholes B2 and B3, and 6 m for B4 and B5. Total 23 core samples were collected at different depths from B2 to B5. All samples were then dried at the room temperature before analysis.

The chemical composition and mineral constituents of the samples were determined using X-ray fluorescence spectrometry (XRF; XEPOS, Rigaku Corp., Japan) and X-ray diffraction spectrometry (XRD; MULTIFLEX, Rigaku Corp., Japan), respectively. Both analyses were done using pressed powders of samples (< 75 µm). Loss on ignition (LOI) was measured by heating 1 g of samples (< 2 mm) inside a furnace for 1 h at 750 °C after oven drying for 24 h at 110 °C.

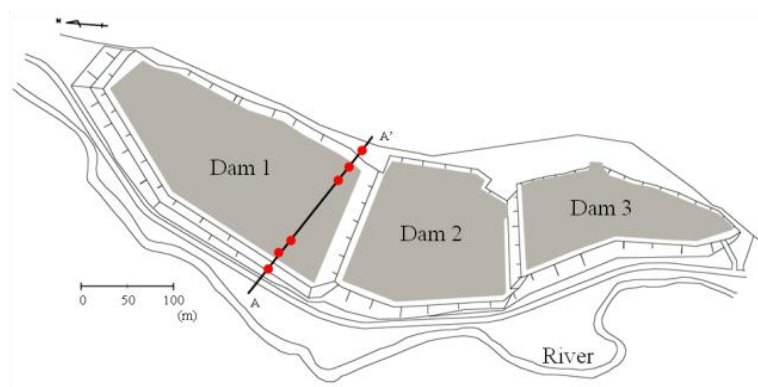


Figure 2. 2 Plain view of the tailings dams in the study site

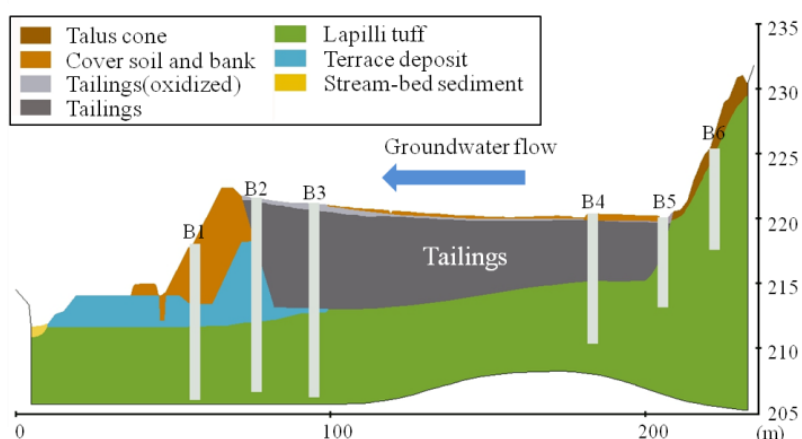


Figure 2. 3 Cross-sectional view of line A-A' in Fig. 2.2

Table 2. 2 Summary of sequential extraction procedure for heavy metals from tailings

Extraction step	Procedure	Preferentially dissolved minerals	References
1	1 g tailings, 50 mL deionized water, shaking for 1 h at room temperature (RT)	Water soluble fraction (e.g., gypsum)	Dold and Fontboté (2001)
2	1 M $C_2H_7NO_2$ at pH 7, shaking for 2 h at RT	Exchangeable fraction	Bogush and Lazareva (2011)
3	1 M $C_2H_7NO_2$ at pH 5, pH adjusted with acetic acid, shaking for 2 h at RT	Carbonate fraction (e.g., dolomite, calcite)	Dold and Fontboté (2001)
4	0.2 M $C_2H_8N_2O_4$ at pH 3, pH adjusted with oxalic acid, shaking for 1 h in darkness (using aluminum foil)	Poorly crystalline fraction (e.g., schwertmannite, amorphous ferrihydrite, manganese oxides)	Dold and Fontboté (2001)
5	0.2 M $C_2H_8N_2O_4$ at pH 3, pH adjusted with oxalic acid, heating in water bath at 80 °C for 2 h	Crystalline fraction (e.g., goethite, hematite, magnetite, jarosite, higher order ferrihydrite)	Dold and Fontboté (2001)
6	750 mg of $KClO_3$ and 15 mL 12 HCl, added 10 mL of 4 M HNO_3 , water bath at 90 °C for 20 min	Sulfide/organic fraction	Hall et al. (1996); Dold (2003)

2.2.3 Batch leaching experiments

Batch leaching experiments were carried out to investigate vertical profiles of Zn, Cu, and Fe concentrations leached from different layers. Samples less than 2 mm in diameter were provided for the experiments. Fifteen grams of samples were mixed with 150 mL of deionized water (18 M Ω -cm) in a 250 mL Erlenmeyer flask and the suspensions were mixed using a lateral-reciprocating shaker at a speed of 200 rpm for 6 h at room temperature. After shaking, pH, electrical conductivity (EC), temperature, and oxidation-reduction potential (Eh) of the suspensions were measured, followed by filtration of the leachates through 0.45 μ m Millex® filters (Merck Millipore, USA). All filtrates were preserved by acidification (pH < 2) prior to chemical analysis. The concentrations of Zn, Cu, and Fe, and other coexisting elements were analyzed using an inductively-coupled plasma atomic emission spectrometer (ICP-AES; ICPE-9000, Shimadzu Corp., Japan). The standard ICP-AES method has a margin of error of ca. 2–3%, and the detection limits of these elements by the standard ICP-AES range from 0.001 to 0.01 mg/L, depending on element.

2.2.4 Acid-base accounting (ABA)

The acid-neutralizing (NP) and acid-generating (AP) potentials of the tailings samples from borehole B3 were measured according to Lawrence and Wang (1997) and Wang et al. (2017). In this measurement, 2 g of pulverized tailings samples were poured into a 250 mL Erlenmeyer flask and approximately 90 mL of distilled water were added. Then, 1 mL of 1 M hydrochloric acid (HCl) was added to the suspension. After 2 h, another 1 mL of 1 M HCl was added. The suspension was allowed to react at room temperature for 24 h and titrated to pH 8.3 with 1 M sodium hydroxide (NaOH). Equation 1 was used to calculate NP (Lawrence and Wang, 1997; Wang et al., 2017). The AP was calculated using the content of sulfide sulfur (S_{sulfide} %; Eq. 2). The S_{sulfide} was determined by leaching experiments with hydrogen peroxide (H_2O_2) and calculated according to Equation 3 (Lengke et al., 2010). In the experiment, 1 g of samples was mixed with 100 mL of 15% H_2O_2 (pH = 7). The solution was kept at room temperature for 48 h and then heated to remove residual H_2O_2 . After cooling, the acidity of the suspension was determined by titration until pH 8.3 with 1 M NaOH. The difference between the values of NP and AP is the net acid-neutralizing potential (NNP = NP – AP). If the NNP value is between –20 and 20 kg $CaCO_3$ /t, the acid generation is uncertain; if the NNP value is below –20 kg $CaCO_3$ /t, acid generation is likely to occur; and if the NNP value is above 20 kg $CaCO_3$ /t, it is unlikely to generate any acid (Skousen et al., 2002; Lengke et al., 2010).

$$NP = \frac{50 \times (Xa - Yb)}{c} \quad (1)$$

where, NP (kg CaCO₃/t), X: volume of HCl (mL), Y: volume of NaOH (mL), *a*: normality of HCl (mol/L), *b*: normality of NaOH (mol/L), and *c*: mass of sample (g).

$$AP = 31.25 \times S_{sulfide} \quad (2)$$

$$S_{sulfide} = 1.6 \times V \quad (3)$$

where, AP (kg CaCO₃/t) and V: Volume of NaOH (mL)

2.2.5 Sequential extraction

Selective sequential chemical extractions are often used to determine the distribution of Zn, Cu, and Fe with different sorptive phases and their mobilization in soils and mine wastes (Dold and Fontboté, 2001). This method operationally partitions Zn, Cu, and Fe into six fractions: (1) water-soluble, (2) exchangeable, (3) carbonate, (4) poorly crystalline, (5) crystalline, and (6) sulfide/organic matter fraction (Table 2.2). The tailings samples from borehole B3 at different depths were used for sequential extraction and it was done in duplicate. One gram of samples was mixed with an extractant (Table 2.2) in a 50 mL centrifuge tube. The solid-liquid separation was achieved by centrifugation at 4,000 rpm for 45 min. The supernatant was then separated by a pipette and placed in a clean 50 mL volumetric flask. The residue was washed with 8 mL of deionized water before the next step was carried out. The mixture of the supernatant and washed water was provided for analysis of Zn, Cu, and Fe using ICP-AES. For the residue, the extractant was changed to proceed to the next fraction.

2.2.6 Statistical analysis using data of batch leaching experiments

The batch leaching experimental data were evaluated using principal component analysis (PCA) by OriginPro 2017 to understand the correlations between the different variables and to evaluate major components representing the leaching of Zn, Cu, and Fe from the tailings. The principal components were simplified by varimax rotation to increase the participation in the variables with higher contribution and reduce the participation in the other variables. Fourteen variables were used in the PCA.

2.3 Results and discussion

2.3.1 Characterization of core samples

The geology of B2 from the ground surface consists of oxidized tailings, tailings, terrace deposit, and lapilli tuff; that of B3 consists of oxidized tailings, tailings, and lapilli tuff; that of B4 consists of soil covering, tailings, and lapilli tuff; and that of B5 consists of tailings and lapilli tuff. The chemical compositions of samples from each borehole are listed in Table 2.3. Among all samples, the tailings, including oxidized tailings, contained greater levels of Zn (317–19,400 mg/kg), Cu (271–4,190 mg/kg), and Pb (18–48 mg/kg) than the lapilli tuff, covering soil, and terrace sediment samples. In the oxidized tailings, the contents of these elements (317–362 mg/kg for Zn, 271–464 mg/kg for Cu, and 25–34 mg/kg for Pb) were generally less than those of the deeper, unweathered tailings (3,800–19,400 mg/kg for Zn, 1,350–4,190 mg/kg for Cu, and 10–55 mg/kg for Pb). Similarly, the content of Fe_2O_3 was lower in the oxidized tailings samples (2.9–5.5 wt%) than in the deeper tailings samples (10–20 wt%). Sulfur (S) content was also less in the oxidized tailings (0.3–0.6 wt%) than in the deeper, unweathered tailings (2.5–5.5 wt%). These results indicate that Zn, Cu, Fe, and S had leached out of the weathered tailings in the top 0–0.4 m of the tailings during the past 40 years.

The XRD results (Table 2.4) showed that the major minerals in the tailings were quartz and albite while pyrite and sphalerite were detected as trace components. Nantokite and chlorite were also detected in the tailings samples. Iron-bearing minerals like goethite (FeOOH), schwertmannite, and ferrihydrite probably existed in the tailings but were not detected by XRD even though the Fe contents (3–20.6 wt%) were quite substantial. This may be due to their content being less than the detection limits or their amorphous form (Carlson and Schwertmann, 1981; Herbert, 1994). The soil, terrace deposit, and lapilli tuff contained quartz, albite, and anorthite, but no sulfide minerals were detected. The presence of pyrite in the tailings implies that weathering will continue to release acid water containing Zn, Cu, and Fe, although no Zn-, Cu-, or Fe-bearing minerals were detected.

2.3.2 Batch leaching experiments

Figures 2.4 to 2.6 illustrate the vertical distribution of pH, Eh, and concentrations of Zn, Cu, and Fe in batch leaching experiments, respectively, at boreholes B2, B3, B4, and B5. The geology of each borehole is described on the right side of each graph. The oxidized tailings are shown as light gray and the unweathered tailings as dark gray and the soil and bank are reddish-brown, the terrace deposit is blue, and lapilli tuff is green.

The pH values of the samples were 3.5–6 at B2, 4–7 at B3, 3–5 at B4, and 3–8 at B5. The higher pH values were found in the terrace deposit, lapilli tuff, and covering soil whereas the lower pH values were found in the tailings samples. These results showed that the tailings had an acidic pH, and were the main source of the acid water. The Eh was positive, irrespective of samples, ranging from 360–590 mV. These results were similar to those of Adnani et al. (2016).

The leached concentrations of Zn, Cu, and Fe were higher in the tailings samples (Zn ranging from 0.3 to 400 mg/L, Cu ranging from 0.2 to 300 mg/L, and Fe ranging from 0.5 to 50 mg/L) than in the other layers and in the order: $\text{Zn} > \text{Cu} > \text{Fe}$. The distribution of sulfate ion (SO_4^{2-}) was similar to those of Zn, Cu, and Fe. Focusing on only the tailings samples, the concentrations of Zn, Cu, Fe, and SO_4^{2-} were lower in the upper oxidized tailings. It appears that only the upper tailings have weathered; most parent sulfide minerals were transformed to secondary minerals, such as oxides, sulfates, and exchangeable fractions, and then flushed out, resulting in lower leaching concentrations. The leaching concentrations of Zn, Cu, Fe, and SO_4^{2-} in the deeper tailings remained higher (Fig. 2.6). However, the leaching concentrations of Zn, Cu, Fe, and SO_4^{2-} at the bottom part of the tailings were less than those in the middle part of the tailings. This means that Zn, Cu, Fe, and SO_4^{2-} were flushed out by greater groundwater flow near the weathered lapilli tuff, which has a higher hydraulic conductivity (10^{-5} m/s) than the tailings (10^{-7} m/s). Lead was not detected in the leachate of the batch leaching experiments although the tailings contained Pb.

The lower pH values in the batch leaching experiments likely resulted from pyrite oxidation, leading to higher Zn, Cu, Fe, and SO_4^{2-} concentrations (Figs. 4 and 6). Similar results were described by Todd et al. (2003). It was also found that the acid produced by pyrite oxidation enhanced the mobility of Zn, Cu, and Fe, dissolution of solids, and SO_4^{2-} (Dold and Fontboté, 2001; Devasahayam, 2007).

Table 2. 3 Chemical composition of samples of different geological formations

Borehole/depth (m)	Sample type	SiO ₂ (wt%)	TiO ₂ (wt%)	Al ₂ O ₃ (wt%)	Fe ₂ O ₃ (wt%)	MnO (wt%)	MgO (wt%)	CaO (wt%)	Na ₂ O (wt%)	K ₂ O (wt%)	P ₂ O ₅ (wt%)	S (wt%)	Zn (mg/kg)	Cu (mg/kg)	Pb (mg/kg)	LOI (wt%)
Borehole B2																
0.1-0.3	Oxidized tailings	59.4	0.46	14.4	2.92	0.12	0.55	1.57	0.82	2.68	0.10	0.32	317	464	34	5.77
2.5-2.7	Tailings	58.7	0.84	16.3	10.1	0.10	3.06	2.19	1.56	1.99	0.16	2.89	4,550	3,270	31	6.71
5.5-5.7	Tailings terrace sediment	55.5	1.04	17.2	8.10	0.15	2.62	3.02	2.42	2.34	0.11	0.95	1,670	607	22	2.97
7.8-8.0	Terrace deposit	65.3	0.53	19.7	4.65	0.13	0.82	1.18	1.5	2.29	0.16	0.33	177	49	22	7.78
9.8-10	Lapilli tuff (weathering)	52.0	0.79	15.3	7.81	0.09	1.18	3.61	2.8	0.97	0.07	0.06	162	32	19	2.46
Borehole B3																
0.2-0.4	Oxidized tailings	62.5	0.51	10.3	5.49	0.09	0.76	1.45	1.07	2.34	0.11	0.66	362	271	25	4.03
2.0-2.2	Tailings	59.5	0.61	12.2	14.2	0.13	4.22	3.99	2.05	1.02	0.16	5.32	8,520	3,190	32	6.33
3.0-3.2	Tailings	51.3	0.65	11.9	19.2	0.13	5.72	3.85	2.04	0.81	0.16	4.95	6,910	2,860	30	6.42
5.0-5.2	Tailings	50.0	0.65	11.1	19.4	0.09	5.49	3.13	1.34	0.82	0.15	4.94	7,580	2,250	22	6.5
7.0-7.2	Tailings	49.5	0.58	9.00	20	0.07	4.95	1.73	0.69	0.81	0.12	5.39	19,400	2,510	25	6.12
8.0-8.2	Tailings	71.9	0.42	8.8	19.8	0.10	3.29	3.41	1.22	0.72	0.10	3.45	6,280	1,990	10	4.22
9.0-9.2	Lapilli tuff	70.7	0.57	14.6	18.9	0.07	4.33	4.57	3.03	0.37	0.08	0.05	85	15	16	2.35
Borehole B4																
0.1-0.3	Soil covering	63.6	0.48	20.1	5.16	0.06	0.45	0.56	1.2	2.75	0.02	0.67	94	160	25	5.86
0.5-0.7	Tailings	61.2	1.04	11.7	5.47	0.12	1.07	2.02	0.67	2.01	0.15	3.76	3,800	4,190	48	6.85
1.0-1.2	Tailings	49.0	0.56	11.9	17.8	0.17	4.73	2.79	0.74	1.05	0.16	4.59	6,380	1,350	47	5.83
2.5-2.7	Tailings	45.8	0.52	12.6	20.6	0.15	5.08	3.37	1.13	0.91	0.16	5.49	6,720	2,170	47	6.8
4.0-4.2	Tailings	44.2	0.59	13.7	20.5	0.15	6.52	3.47	1.29	0.86	0.18	4.57	4,870	3,470	48	3.44
5.5-5.7	Lapilli tuff	46.4	0.65	16.5	19.1	0.1	6.44	4.04	2.77	1.19	0.08	0.74	165	58	20	4.47
Borehole B5																
0.6-0.8	Tailings	54.5	0.69	13.3	14.2	0.10	4.02	1.27	0.49	1.06	0.12	2.47	2,860	1,650	19	7.33
1.8-2.0	Tailings	49.7	0.61	12.6	17.6	0.10	3.96	2.34	1.01	1.10	0.18	4.8	5,390	1,760	38	7.56
3.3-3.5	Tailings	46.9	0.54	13.2	20.1	0.10	5.29	3.78	1.48	1.03	0.20	4.22	5,440	1,940	55	5.93
4.0-4.2	Lapilli tuff weathering	55.7	0.69	14.4	18.5	0.10	5.45	4.14	2.16	1.06	0.07	0.10	73	13	18	3.23
6.0-6.2	Lapilli tuff weathering	73.4	0.52	14.1	5.27	0.10	6.45	4.31	2.81	2.76	0.67	0.10	67	11	17	3.39

※Detection limits of major elements are 0.01 - 0.1 wt% whereas those of minor elements are 1 mg/kg.

Table 2. 4 Mineral constituents of samples of different geological formations

Borehole/Depth (m)	Type of sample	Mineralogical composition
Borehole B2		
0.1-0.3	Oxidized tailings	Quartz, albite, chlorite
2.5-2.7	Tailings	Quartz, albite, chlorite, pyrite
5.5-5.7	Tailings terrace sediment	Quartz, albite, clinocllore
7.8-8.0	Terrace deposit	Quartz, albite, chlorite
9.8-10	Lapilli tuff (weathering)	Quartz, anorthite
Borehole B3		
0.2-0.4	Oxidized tailings	Quartz, anorthite, jianshuiite
2.0-2.2	Tailings	Quartz, albite, clinocllore, ferroactinolite, pyrite
3.0-3.2	Tailings	Quartz, albite, chlorite, pyrite
5.0-5.2	Tailings	Quartz, anorthite, chlorite
7.0-7.2	Tailings	Quartz, anorthite, chamosite, nantokite, pyrite
8.0-8.2	Tailings	Quartz, albite, chlorite
9.0-9.2	Lapilli tuff	Quartz, anorthite
Borehole B4		
0.1-0.3	Soil covering	Quartz, anorthite, halloysite
0.5-0.7	Tailings	Quartz, anorthite, chlorite, pyrite
1.0-1.2	Tailings	Quartz, clinocllore, pyrite, nantokite
2.5-2.7	Tailings	Quartz, chlorite, magnesioriebeckite, pyrite
4.0-4.2	Tailings	Quartz, albite, chlorite, pyrite
5.5-5.7	Lapilli tuff	Quartz, albite, anorthite, chlorite, sanidine
Borehole B5		
0.6-0.8	Tailings	Quartz, albite, clinocllore, ferroactinolite, pyrite
1.8-2.0	Tailings	Quartz, chlorite, sphalerite, pyrite
3.3-3.5	Tailings	Quartz, albite, clinocllore, ferroactinolite, pyrite
4.0-4.2	Lapilli tuff weathering	Quartz, albite, anorthite
6.0-6.2	Lapilli tuff weathering	Quartz, anorthite

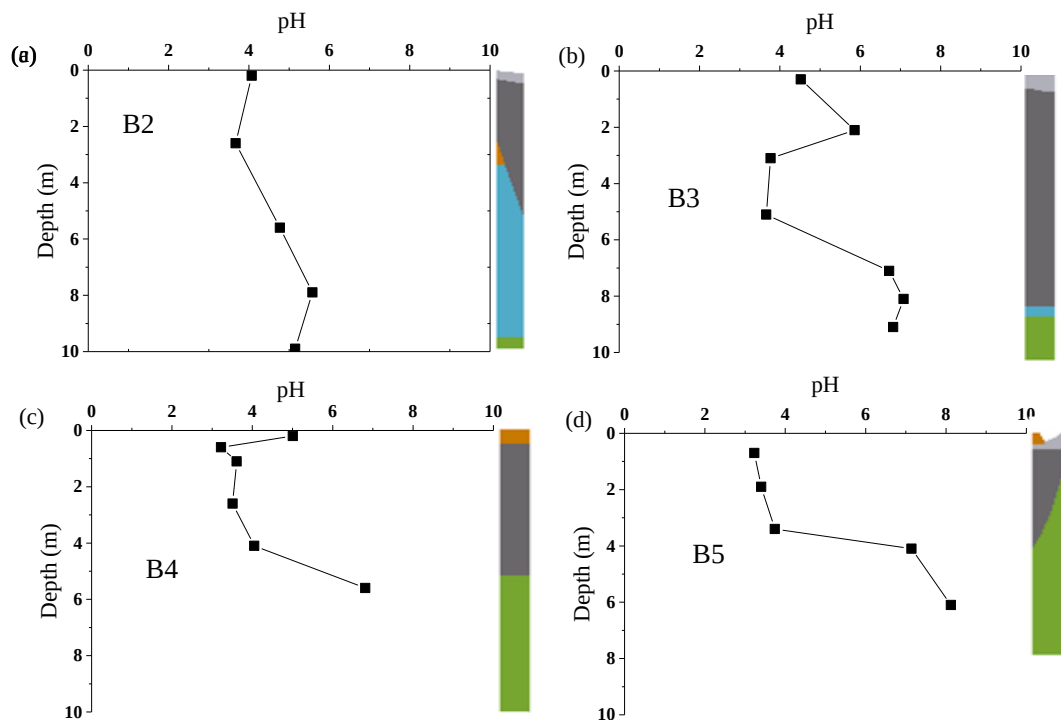


Figure 2.4 Vertical profiles of pH at B2 (a), B3 (b), B4 (c), and at B5 (d) in batch leaching experiments

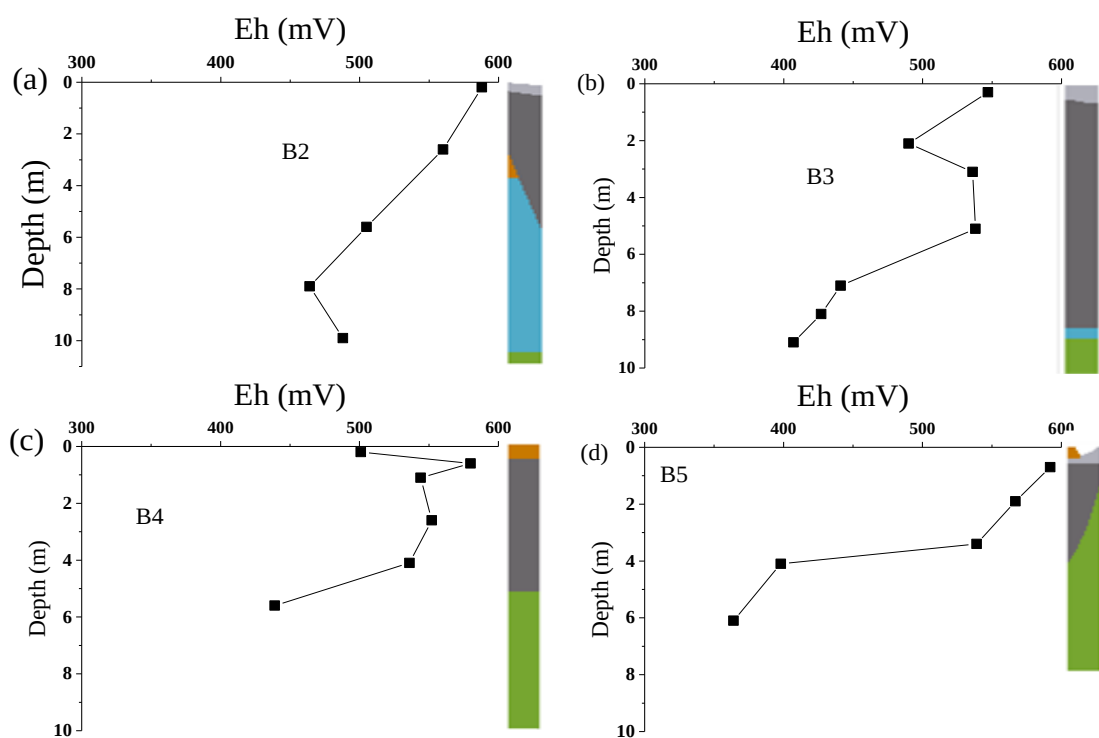


Figure 2.5 Vertical profiles of Eh at B2 (a), B3 (b), B4 (c), and at B5 (d) in batch leaching experiments

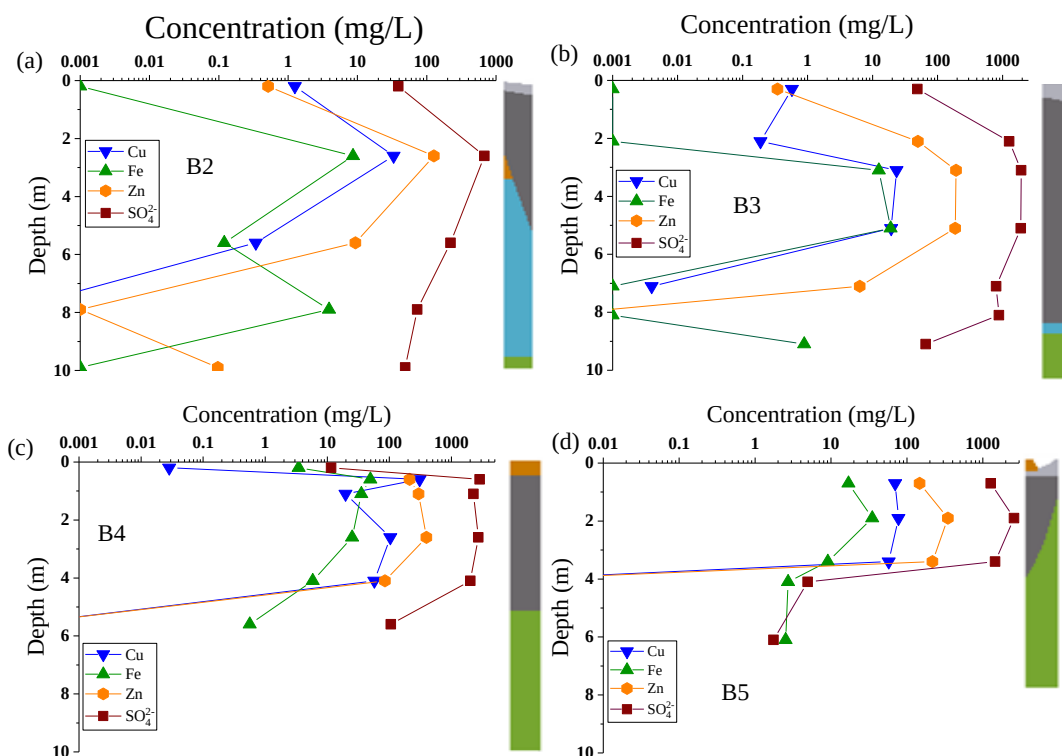


Figure 2. 6 Vertical profiles of Zn, Cu, Fe, and SO_4^{2-} concentrations at B2 (a), B3 (b), B4 (c), and B5 (d) in batch leaching experiments

2.3.3 Acid-base accounting (ABA)

Table 2.5 summarizes the results of the modified ABA static tests of the tailings samples from borehole B3. All tailings samples had low NP values, ranging from -8.75 to 18.75 kg CaCO_3/t , whereas the AP values were between 20 and 70 kg CaCO_3/t , which corresponds to negative NNP values, ranging from -73.7 to -23.7 kg CaCO_3/t . The NNP values clearly indicate that the tailings are acid-generating, which is consistent with the XRD results showing the existence of pyrite and the low pH values of the leaching experiments.

Table 2. 5 Acid-base accounting of the tailings samples from borehole B3

Depth (m)	kg CaCO_3/t		
	AP	NP	NNP
0.2-0.4	20.0	-3.80	-23.7
2-2.2	60.0	-2.50	-62.5
3-3.2	65.0	-8.80	-73.7
5-5.2	70.0	18.80	-51.3
7-7.2	62.5	6.24	-56.3
8-8.2	55.0	5.93	-49.1

2.3.4 Solid-phase partitioning of Zn, Cu, and Fe

Results of the sequential extraction of tailings samples from borehole B3 are shown in Figs. 2.7 (a), (b), and (c) for Zn, Cu, and Fe, respectively. The water-soluble fractions of Zn and Cu were greater in the middle part of the tailings, and lower at the surface and bottom of the tailings (Figs. 2.7(a), and (b)). The water-soluble fraction of Fe was negligible irrespective with depth (Fig. 2.7(c)). These results reflect that the water-soluble fractions of these elements were almost flushed out from the oxidized tailings and the bottom of the tailings. The amounts of Zn, Cu, and Fe in the water-soluble fraction were likely related to the degree of oxidation.

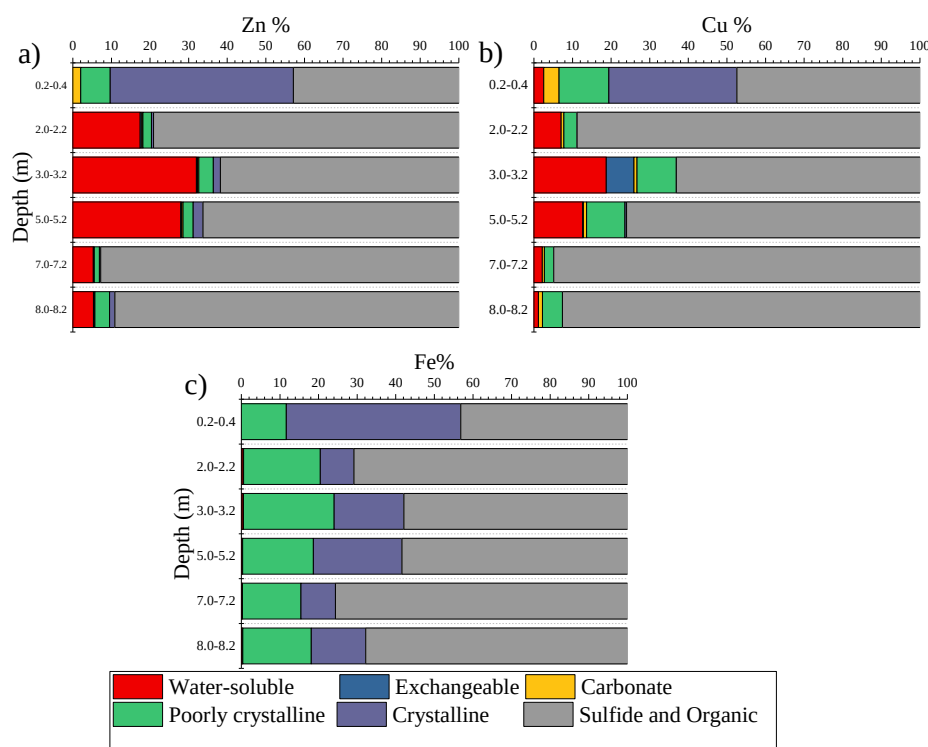


Figure 2. 7 Results of sequential extraction of Zn, Cu, and Fe in the tailings samples from borehole B3: Zn (a), Cu (b), and Fe (c)

The NH_4 -acetate extractant is used to determine the exchangeable elements at pH 4 to 5, and calcite is also dissolved by this extractant (Dold and Fontboté 2001). The exchangeable and carbonate fractions are separated by using the same extractant (NH_4 -acetate) at pH 7 and 5, respectively (Bogush and Lazareva, 2011). The exchangeable fractions of Fe was negligible in all of the tailings samples while those of Zn and Cu were <0.3 and 7%, respectively. The Fe carbonate fraction was negligible in the tailings whereas those of Zn and Cu in the surface tailings were 2 and 4%, respectively, much higher than deeper in the tailings. This can be explained by the addition of calcium carbonate as a neutralizer in the shallower part of the tailings dams. It is inferred that AMD was prevented for a while by the addition of the neutralizer when the tailings were being deposited.

The application of 0.2 M HN_4 -oxalate at pH 3 extracted secondary ferric phases, such as schwertmannite and jarosite. The Fe content of this poorly crystalline fraction ranged from 12 to 23%, was less found at the surface of the tailings. On the other hand, the levels of Zn and Cu associated with this fraction were higher in the oxidized tailings (8% for Zn and 13% for Cu) than in the deeper tailings (1.4–4% for Zn and 2–10% for Cu). These results suggest that the secondary Fe-bearing minerals formed at the surface of the tailings co-precipitate or adsorb Zn and Cu.

Crystalline Zn, Cu, and Fe were relatively abundant in the oxidized tailings (47% for Zn, 33% for Cu, and 45% for Fe) and decreased with depth (0.3–2.5% for Zn, 0.04–0.4% for Cu, and 9–22% for Fe). The high contents of these elements suggest that ferrihydrite or goethite likely precipitated in the upper part of the tailings, and that Zn and Cu may be absorbed or incorporated into the structure of the Fe(III) oxyhydroxide minerals. Crystalline and poorly crystalline Fe compounds in the weathered tailings can act as a sink of trace elements (Cu, Pb, Se, and Zn) through adsorption, substitution, or co-precipitation (McGregor and Blowes, 2002; Khorasanipour et al., 2011). Thus, these elements in crystalline and poorly crystalline phases are considered stable; however, these elements can be slowly released over time (Fadiran et al., 2014).

The highest amounts of Zn, Cu, and Fe occurred in the sulfide fraction and generally increased with depth. Sulfur content was also depleted in the surface tailings (Table 2.3). This indicates that the weathering of sulfide minerals has generally proceeded from the surface during the past 40 years.

Zinc, Cu, and Fe contained in sulfides are transformed into water-soluble/exchangeable fractions by oxidation, and then into crystalline and poorly crystalline mineral forms; thus, the tailings are likely to continue to release Zn, Cu, and Fe. The upper tailings have been oxidized because of the abundance of oxygen and water, and the soluble Zn, Cu, and Fe have been almost leached out from these tailings. However, the deeper tailings have not yet been oxidized because of the lower concentrations of electron donor. The contaminants in the middle parts of the tailings could be mobilized when they contact air and water.

2.3.5 Statistical analysis of obtained data

Multivariate statistical analysis and PCA were used to reduce the number of variables to confirm the most representative variables and to support the interpretation of the geochemical data from the tailings samples. PCA has been used for multivariate analysis of contaminant leaching from soil (Li et al., 2015) and to predict the geochemical hazards of coal mine tailings (Park et al.,

2017). Table 2.6 lists the correlation coefficients of the results of the leaching experiments. Strong positive correlations (correlation coefficient > 0.8) were found for Fe-SO₄²⁻, Zn-SO₄²⁻, EC-SO₄²⁻, Ca-EC, K-Na, and pH-Eh. The strong positive correlations of Fe-SO₄²⁻, Zn-SO₄²⁻, and EC-SO₄²⁻ reflect the fact that pyrite and sphalerite are likely the major minerals releasing Fe and Zn from the tailings. As expected, a negative correlation was observed between Fe-pH and SO₄²⁻-pH (i.e., correlation coefficient < -0.6) (Table 2.6), so a lower pH (higher acidity) was related to higher concentrations of Fe and SO₄²⁻.

Table 2.7 shows the PCA results of the leaching experiments. The first three components accounted for 79% of the total variation. The loadings of the first component were larger for Zn, Cu, Fe, SO₄²⁻, pH, EC, and Eh, which accounted for 46% of the total variance. This simply reflects the fact that the sulfide minerals (e.g. pyrite, sphalerite, and chalcopyrite) produce Zn, Cu, Fe, and SO₄²⁻. These minerals also contribute to the contamination from the tailings. The loadings of the second component, which was 19%, were attributed to K, Na, and Si, reflecting the fact that minerals like feldspar influenced K, Na, and Si leaching concentrations. However, the third component accounted for 14% of total variance, which was dominated by Ca. This likely reflects the addition of a neutralizer during tailings deposition, as pointed out by the sequential extraction results.

Figure 2.8 shows a dendrogram of cluster analysis of leaching experiments of the tailings samples. This figure clearly reveals two clusters: (1) the middle part of the tailings, which produce acidic water containing Zn, Cu, and Fe; and (2) the tailings near the lapilli tuff, immediately below the weathered tailings, which produce a higher pH.

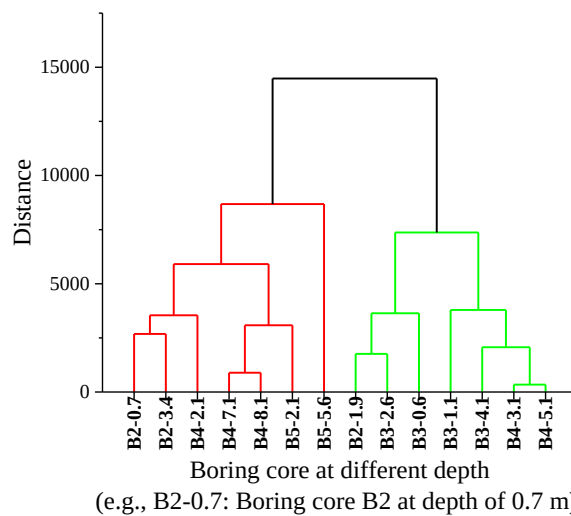


Figure 2. 8 Dendrogram of results of leaching experiments of the tailings samples

Table 2. 6 Correlation coefficients of analyzed items (Significant correlations are marked in bold)

Variables	Al	Ca	Cd	Cu	Fe	K	Na	Zn	Si	Cl ⁻	SO ₄ ²⁻	pH	EC	Eh
Al	1.000													
Ca	-0.120	1.000												
Cd	0.564	-0.041	1.000											
Cu	0.752	0.249	0.417	1.000										
Fe	0.657	0.431	0.572	0.755	1.000									
K	-0.370	-0.145	-0.213	-0.352	-0.172	1.000								
Na	-0.435	0.032	-0.430	-0.376	-0.292	0.827	1.000							
Zn	0.310	0.494	0.560	0.413	0.772	-0.227	-0.227	1.000						
Si	-0.182	0.161	0.063	-0.090	0.169	0.745	0.414	0.132	1.000					
Cl ⁻	-0.148	0.299	0.046	0.058	0.163	-0.281	-0.042	0.624	-0.088	1.000				
SO ₄ ²⁻	0.376	0.780	0.395	0.639	0.831	-0.189	-0.173	0.814	0.275	0.393	1.000			
pH	-0.544	-0.161	-0.588	-0.497	-0.679	0.062	0.057	-0.740	-0.185	-0.372	-0.590	1.000		
EC	0.236	0.840	0.305	0.507	0.746	-0.126	-0.094	0.786	0.346	0.420	0.983	-0.523	1.000	
Eh	0.688	0.069	0.671	0.559	0.679	-0.091	-0.092	0.677	0.125	0.260	0.554	-0.970	0.468	1.000

Table 2. 7 Results of the principal component analysis of leaching experiments

Parameters	PC1	PC2	PC3
Al	0.252	-0.320	0.288
Ca	0.193	0.292	-0.425
Cd	0.257	-0.169	0.264
Cu	0.294	-0.170	0.064
Fe	0.360	0.016	0.080
K	-0.130	0.452	0.402
Na	-0.137	0.450	0.205
Zn	0.346	0.113	-0.109
Si	0.041	0.466	0.286
Cl ⁻	0.155	0.116	-0.351
SO ₄ ²⁻	0.354	0.186	-0.164
pH	-0.320	-0.046	-0.249
EC	0.325	0.259	-0.213
Eh	0.319	-0.028	0.319
Eigenvalues	6.422	2.688	1.949
Percentage of variance (%)	46	19	14
Cumulative (%)	46	65	79

2.4 Conclusion

The tailings dams of the Shimokawa mine were characterized by leaching experiments, ABA, and sequential extraction. Pyrite was the main factor controlling AMD formation and mobilization of Zn, Cu, Fe, and SO₄²⁻ in the tailings. The NNP values of the tailings were less than -20 kg CaCO₃/t, indicating that the tailings still have acid-generating potential. Although the tailings were disposed of 40 years ago, the tailings will likely continue to produce AMD containing Zn, Cu, and Fe for a long period of time unless remedial measures are taken. The weathered tailings was observed at the depth of 0.4 m after being disposed to the environment for 40 years.

The leaching concentrations, total contents, and sulfide fractions of Zn, Cu, and Fe were higher in the samples in the deeper part of the tailings than in the oxidized tailings, lapilli tuff, covering soil, and terrace deposit. The Zn, Cu, and Fe in the tailings were mainly bound to the sulfide and water-soluble fractions. However, weathering transformed these elements from sulfide to exchangeable/water-soluble and poorly crystalline and crystalline forms. In addition, some of Zn and Cu may be adsorbed onto or incorporated into the Fe(III) oxyhydroxide minerals.

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CHAPTER 3

LONG-TERM ACID GENERATION AND HEAVY METAL LEACHING FROM THE TAILINGS: COLUMN STUDY UNDER NATURAL CONDITION

3.1 Introduction

The minerals that represent economically valued ores are chemically stable under in situ geological conditions (Paul et al., 2002). However, these solid phases become unstable when they are excavated and exposed to the atmosphere. Mining and milling processes (i.e., crushing, grinding, washing, etc.) generate four major categories of wastes and wastewater, i.e., (i) mine waste (low-grade ore, overburden, and barren rocks), (ii) tailings, (iii) dump heap leach and (iv) acid mine drainage (AMD). These wastes are disposed to the surrounding land and water body in more or less an environmentally acceptable manner (Shu et al., 2001; Paul et al., 2002; Schuwirth et al., 2007; Zhang et al., 2016).

Large quantities of tailings have been disposed to the environment by past and present-day mining and processing activities. Mine tailings have potential to release significant quantities of metals to water and soils (Moncur et al., 2009; Modabberi et al., 2013) because tailings contain significant amounts of pyrite (FeS_2) and other metal-bearing sulfides, oxide, and silicate minerals, as well as processing compounds (Lindsay et al., 2015).

Acid mine drainage is primarily released during the weathering of pyrite in a solution containing dissolved oxygen. The AMD with metal ions represents significant environmental hazards to freshwater resources. In addition, weathering and oxidation of sulfide minerals contained in the tailings, especially in unsaturated layers, can produce acidic water laden with high concentrations of heavy metals (e.g., Olyphant et al., 1991; Benzaazoua et al., 2003; Khorasanipour et al., 2011; Cheong et al., 2012; Goumih et al., 2013). Moreover, the variation in drainage quality from tailings impoundments is mainly a function of grain-size distribution and compositional variations (e.g., iron-sulfide and carbonate-mineral contents) within individual mine-rock lithologies, local climatic conditions, and presence of the microorganism (Ardau et al., 2009).

Precipitation of the widespread secondary solid phases like evaporative and secondary phases is another important consequence of weathering and oxidation of tailings (Flohr et al., 1995; Nordstrom, 2011; Carbone et al., 2013). Some of these secondary phases like efflorescent salts are often very soluble and represent only a temporary host for a variety of metals (Frau, 2000; Jambor

et al., 2002; Buckby et al., 2003; Hammarstrom et al., 2005), while others such as ochreous precipitates represent a more stable sink of heavy metals and reduce metal mobility through adsorption or co-precipitation.

Although climate conditions provide fundamental control of many reactions, such as weathering intensity, secondary mineral formation, and mobility of hazardous metals from tailings (Olyphant et al., 1991; Dold, 1999; Dold and Fontboté, 2001; Dold, 2003; Redwan and Rammlmair, 2012), the mobility of metals from tailings may be different depending on the type of tailings. Numerous researches have been conducted on the behavior of the metals from tailings, e.g., sulfide-rich tailings, and non-sulfide tailings, both in situ and laboratory observation (Smuda et al, 2007; Yeheyis et al., 2009; Goumih et al., 2013; Root et al., 2015; Kandji et al., 2017; Wang et al., 2017). Laboratory experiments are also required prior to the disposal of mine wastes. This is because rates of acid-producing and acid-neutralizing mineral dissolution in the laboratory are sufficiently similar to those in the field to apply the laboratory results to predictive models of full-scale waste piles (Jurjovec et al., 2002; Benzaazoua et al., 2003; Álvarez-Valero et al., 2009; Kandji et al., 2017).

A closed mine site in Hokkaido has generated AMD for more than 40 years. Mine tailings were the major source of Cu, Zn, Fe, and SO_4^{2-} (Khoeurn et al., 2018). Thus, the AMD has been treated with calcium hydroxide ($\text{Ca}(\text{OH})_2$) before the effluents are discharged into the nearby river. However, the treatment period remains unclear and leaching behavior of hazardous metals in the dam is not well understood. Understanding how physical, geochemical, mineralogical, and biological processes control mobility, bioavailability, and toxicity of hazardous metals is important in minimizing environmental impacts on ecosystems including humans and other biotas. Unfortunately, little information is known about the transformation of minerals and mobility of related metals in the tailings. The aim of this chapter is to investigate the changes in mineralogy and geochemistry of the tailings, to evaluate long-term leaching behaviors of hazardous metals like Cu and Zn from the tailings due to weathering processes with different irrigated rainfalls, and to identify releasing fractions of the metals. The results will help to improve remediation and management system after mine closure. At the same time, such information is fundamental in the advanced understanding of metal cycling in the environment.

3.2 Materials and methods

3.2.1 Collection and characterization of the tailings samples

The details of sample collection were described in Chapter 2. But in this study the tailings samples at the depth of 1-3 meters of each bohale were combined because the samples were not weathered and contained higher amounts of Cu, Zn, and Fe. The tailings samples were then air-dried, crushed using a mortar, and sieved through a 2 mm aperture screen. A particle size of less than 2 mm was chosen for the experiments. The samples were then stored in air-tight containers to minimize exposure to moisture.

For chemical and mineralogical analyses, the samples were finely ground ($< 75 \mu\text{m}$). The chemical composition of the tailings was analyzed by using an X-ray fluorescence spectrometer (XRF) (Spectro Xepos, Rigaku Corporation, Japan) while the mineralogical composition was analyzed by using X-ray diffractometer (XRD) (MultiFlex, Rigaku Corporation, Japan). The tailings samples were also observed by a high magnification optical microscope (VHX-1000, Keyence Corporation, Japan) and then analyzed by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) (SSX-550, Shimadzu Corporation, Japan).

3.2.2 Sequential extraction

Several different sequential extraction methods were used to evaluate the mobility of Cu, Zn, and Fe for contaminated soils, sediments, and mine wastes by a variety of authors (Tessier et al., 1979; Dang et al., 2002; Marumo et al., 2003; Anju and Banerjee, 2010). The sequential extraction procedure used in this study was based on Marumo et al. (2003) for the determination of the leachability of hazardous metals from soils and sediments. Marumo et al. (2003) developed their method by revising the procedure of Tessier et al. (1979) and Clevenger (1990). This method was applied to the tailings sample (Clevenger, 1990; Dang et al., 2002; Anju and Banerjee, 2010). The details of the sequential extraction procedure used in this study were summarized in Table 3.1. For the procedure, 1 g of the $< 2 \text{ mm}$ tailings sample was used. The residue of each extraction step was washed with 10 - 15 mL of deionized water, and the supernatant and washing water were then combined and diluted to 50 mL for analysis.

Table 3. 1 Details of sequential extraction procedure

Steps	Extractant	pH	Liquid to solid ratio (mL/g)	Temperature (°C)	Duration (h)	Mixing speed (rpm)	Extracted phase
1	1 M MgCl ₂	7	20/1	25	1	200	Exchangeable
2	1 M CH ₃ COONa	5	20/1	25	5	200	Carbonates
3	0.04 M NH ₂ OH.HCl in 25% acetic acid	5	20/1	50	5	200	Fe-Mn oxides
4	0.04 M NH ₂ OH.HCl in 25% acetic acid; 30% H ₂ O ₂ ; 0.02 M HNO ₃	5	36/1	85	5	200	Sulfide/organics mater
5			Calculated				Residual

3.2.3 Laboratory column experiments

Column set up

A column experiment is a kind of kinetic test that is commonly used to evaluate the long-term geochemical behavior of mine wastes and soils. The experiment attempts to mimic natural weathering of mine wastes in a laboratory scale. Thus, the experiment can provide information on sulfide oxidation rates and weathering characteristics of wastes (Benzaazoua et al., 2003), and is used to provide an indication of the change in the quality of the drainage. A schematic diagram and details of the column dimensions are shown in Fig. 3.1. Three columns (cases 1, 2, and 3) were constructed and placed at room temperature. The columns are made of polyvinyl chloride (PVC) tubes mounted on the top of a steel stand accommodating three columns. The columns have a height of 300 mm and an inner diameter of 52 mm. Moreover, covers with small holes were also designed to simulate rainfall and protect the column from outside contaminants and dust. The columns were packed with 438 g of the tailings to a thickness of 15 cm for a bulk density of 1.374 g/cm³ and porosity equal to 45%.

Irrigation and sample collection

Distilled water (100, 200 and 400 cm³) was introduced into the columns (cases 1, 2, and 3, respectively) once a week and allowed to flow down by gravity. Details of the case of the column study were summarized in Table 3.2. Addition of distilled water started simultaneously for all columns until 84 weeks. After 2 days, the effluents were first collected for cases 2 and 3 while that of case 1 was first collected after the second rainfall introduction, meaning the second week of the experiment. Afterward, the effluents were collected 2 days after the irrigation. Spike tests with 1000 mg-Cu/L and 1000 mg-Zn/L were also conducted once in columns of cases 1 and 2 at week 37.

The pH, Eh, EC and temperature were measured immediately after the collection of effluents. After that, the effluents were then filtered through a 0.45 μm Millex[®] filter and stored at room temperature prior to chemical analyses. The room temperature during the experimental period (March 2016–October 2017) was 20 ± 3 °C. The leaching of Cu, Zn, and Fe was not significantly affected by the variation of temperature.

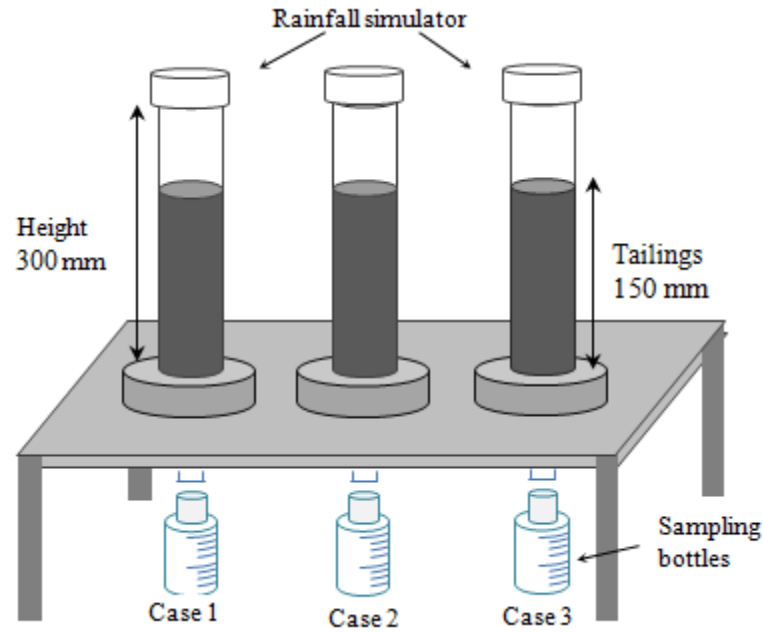


Figure 3. 1 Schematic diagram of the columns used

Table 3. 2 List of column experimental conditions

Case	Infiltration rate (cm ³ /week)	Thickness of the tailings (mm)	Bulk density (g/cm ³)	Tailings mass (g)	Porosity (%)	Spike tests
1	100	150	1.374	437	45	Yes
2	200	150	1.374	437	45	Yes
3	400	150	1.374	437	45	No

3.2.4 Post-experiment characterization

After 84 weeks, the experiments were stopped because the leaching concentrations appeared to reach steady state. The tailings samples of each case were divided into sections 30 mm thick and air-dried for a few weeks. Chemical and mineralogical composition analyses and sequential extraction were conducted for the sectioned tailings using the same procedure mentioned earlier. Batch leaching tests were conducted to characterize the vertical profiles of leaching concentrations of Cu, Zn, and Fe. Fifteen grams of samples were mixed with 150 mL of deionized water (18

MΩ-cm) in a 250 mL Erlenmeyer flask and the suspensions were mixed using a lateral-reciprocating shaker at a speed of 200 rpm for 6 h at room temperature. After shaking, pH, Eh, EC, and temperature of the suspensions were measured, followed by filtration of the leachates with 0.45 μm Millex® filters (Merck Millipore, USA). All filtrates were preserved by adding HCl (pH < 2) prior to chemical analysis.

3.2.5 Chemical analysis

The concentrations of Cu, Zn, Fe, and coexisting ions in effluents and leachates were measured by ICP-AES (ICPE-9000, Shimadzu Corporation, Japan), which was linearly calibrated from 0 to 10 mg/L with custom multi-element standard solution IV (1000 mg/L: Ag, Al, Ca, Cu, Fe, K, Mg, Mn, Na, and Zn) before running samples to be analyzed. Diluted solutions were also prepared using deionized water (18 MΩ-cm). Some samples were diluted several times if needed. The accuracy and precision of the analysis were tested through triplicate analyses of selected samples. The results of the analyses using the standard method of ICP-AES had a margin of error of ca. 2–3%, and the detection limits of these metals ranged from 0.001 to 0.01 mg/L, depending on element. Moreover, sulfur in the effluents and leachates was predominantly in the form of SO_4^{2-} based on the results of anion chromatograph (ICS-90, Dionex Corporation, USA), so for faster and easier determination of SO_4^{2-} , ICP-AES was used. All chemicals used in the preparation and analysis were reagent grade.

3.2.6 Geochemical Modeling

To aid interpretation of the data, saturation indices (*SI*) of important minerals (i.e., oxyhydroxides, oxides, carbonates, and sulfates) that could potentially affect mobilities of metals were calculated using an equilibrium geochemical modeling software called PHREEQC (version 3.2.0-9820) (Parkhurst and Appelo, 1999) using the MINTEQ.V4.DAT database. This program is one of the most extensively used geochemical models.

3.3 Results

3.3.1 Characterization of tailings samples of the pre- and post-column experiments

The chemical compositions and mineralogical properties of the tailings samples of pre- and post-column experiments are shown in Table 3.3 and Fig. 3.2, respectively. Prior to the experiment, the original tailings contained 43.3wt% of SiO_2 and 9.08wt% of Al_2O_3 . The Si and Al indicate the presence of silicates and alumino-silicates in the gangue minerals. The tailings also contained

1.3wt% of CaO, 0.1wt% of MnO, and 3.8wt% of MgO. It was highly enriched in Cu of 3,730 mg/kg and Zn of 17,500 mg/kg, respectively. The high contents of S and Fe₂O₃ were also found in the tailings of 11.2wt% and 26.9wt%, respectively. The tailings had a similar composition to other tailings reported elsewhere, in that they had higher amounts of Cu, Zn, Fe, and S (e.g., Gleisner and Herbert, 2002; Zhang et al., 2016; Christou et al., 2017).

After finishing column experiments, the contents of Cu, Zn, and S in the tailings were depleted, but Fe₂O₃ were similar for all cases (Table 3.3). The contents of Cu, Zn, and S were lower in the top tailings than those in the deeper tailings. Overall, the total contents of Cu, Zn, and S in case 1 was higher than those of cases 2 and 3 (case1 > case 2 > case 3) (Table 3.3). These differences may be due to the influence of the irrigation rate.

The mineralogy of the pre- and post-experiment is depicted in Fig. 3.2. The pre-experiment tailings were composed predominantly of quartz, chlorite, gypsum, anorthite, and pyrite while the post-experiment tailings similarly contained quartz, clinocllore, anorthite, and pyrite. Gypsum, however, was not detected in the post-experiment tailings. Although high contents of Cu and Zn in both the pre- and post-experiment tailings were observed, Cu and Zn-bearing minerals such as chalcopryrite and sphalerite were not detected by XRD. Carbonate minerals like calcite were not detected by XRD.

SEM-EDX investigation was performed for both pre- and post-experiment tailings samples (Figs. 3.3–3.6). Samples from different depths were not shown here because the results were not dependent on depth. The SEM-EDX observation of the pre-experiment tailings showed the presence of silicate (SiO₂), S, Fe, Cu, and Zn (Fig. 3.3). However, it can be seen from the elemental mapping images that Cu, Zn, and Fe were presented in some areas of the tailings (a fine grain of Cu, Zn, and Fe; a large spot with high intensities of S and Si). These elements were also found in some parts of the post-experiment tailings samples of all cases (Figs. 3.4-3.6). These results indicated that residual Cu, Zn, and Fe, and precipitated Fe still existed in the columns. The Si was likely related to quartz and chlorite/clinochlore while S was related to sulfide and sulfate minerals. This means that Cu, Zn, and Fe are likely associated with the impurity of pyrite/iron oxyhydroxide/ferrihydrite, respectively, because pyrite was frequently observed in all samples.

Table 3. 3 Mineralogical composition of the tailings before and after column experiments

Depth (cm)	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	S	Cu	Zn	Pb
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	mg/kg	mg/kg	mg/kg
Pre-tailings	43.30	0.41	9.08	26.85	0.10	3.77	1.32	< 0.1	0.61	0.13	11.24	3,730	17,480	48.7
Post-tailings: Case 1														
0-3	43.39	0.42	8.63	24.41	0.07	3.56	0.81	< 0.1	0.60	0.24	8.20	2,720	5,280	48
3-6	41.03	0.44	8.58	24.71	0.08	3.52	0.81	< 0.1	0.60	0.23	8.92	2,930	7,860	56
6-9	49.98	0.47	10.77	28.88	0.08	4.70	0.98	< 0.1	0.72	0.38	11.31	3,300	7,870	45
9-12	40.65	0.41	8.61	24.29	0.08	3.46	0.90	< 0.1	0.57	0.21	9.00	3,930	10,770	61
12-15	41.53	0.41	8.98	23.56	0.07	3.69	0.84	< 0.1	0.59	0.24	8.90	3,160	7,980	48
Post-tailings: Case 2														
0-3	41.29	0.43	8.76	25.54	0.08	3.53	0.73	< 0.1	0.60	0.25	8.50	2,880	4,920	48
3-6	41.05	0.38	8.67	23.39	0.07	3.57	0.69	< 0.1	0.54	0.24	9.06	2,590	4,660	49
6-9	42.34	0.38	9.59	22.78	0.07	3.90	0.76	< 0.1	0.56	0.26	8.68	3,150	7,020	50
9-12	42.92	0.40	9.62	22.95	0.08	3.90	0.84	< 0.1	0.59	0.19	8.23	3,680	8,950	58
12-15	50.83	0.48	10.96	28.08	0.09	4.70	1.07	< 0.1	0.72	0.30	10.53	4,070	11,390	69
Post-tailings: Case 3														
0-3	45.25	0.43	9.28	25.45	0.08	3.72	0.74	0.36	0.62	0.22	6.78	2,540	3,370	53
3-6	42.53	0.39	8.60	23.61	0.07	3.60	0.71	0.15	0.56	0.23	8.33	2,380	4,040	46
6-9	44.78	0.41	9.08	21.75	0.07	3.86	0.80	< 0.1	0.57	0.23	8.30	2,990	7,370	39
9-12	44.88	0.42	9.45	22.58	0.08	3.90	0.87	< 0.1	0.58	0.23	7.63	3,630	9,200	58
12-15	59.73	0.33	12.43	18.67	0.06	5.62	0.73	< 0.1	0.49	0.25	9.85	2,420	6,990	35

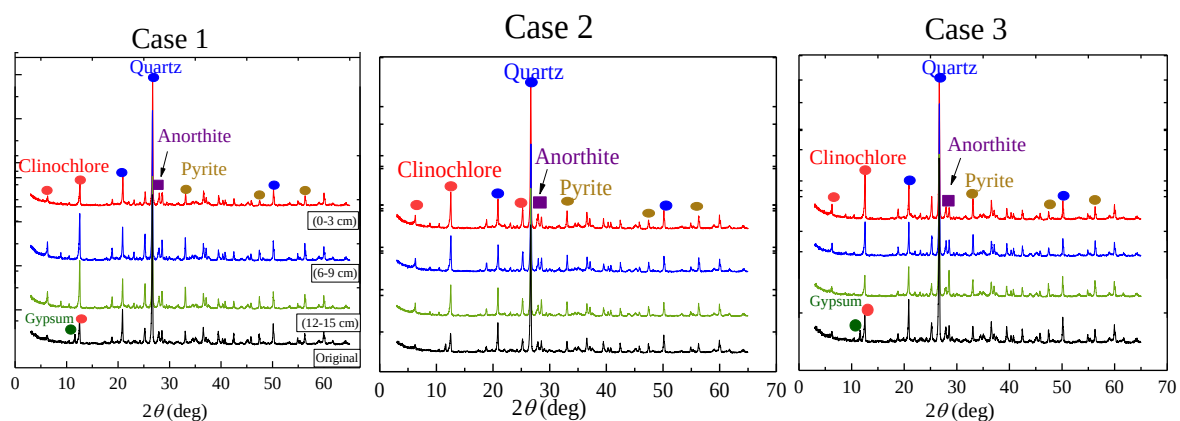


Figure 3.2 Results of mineralogical characterization by XRD of the tailings before experiment (black) and after experiment (red: upper tailings; blue: deeper tailings; green: bottom tailings)

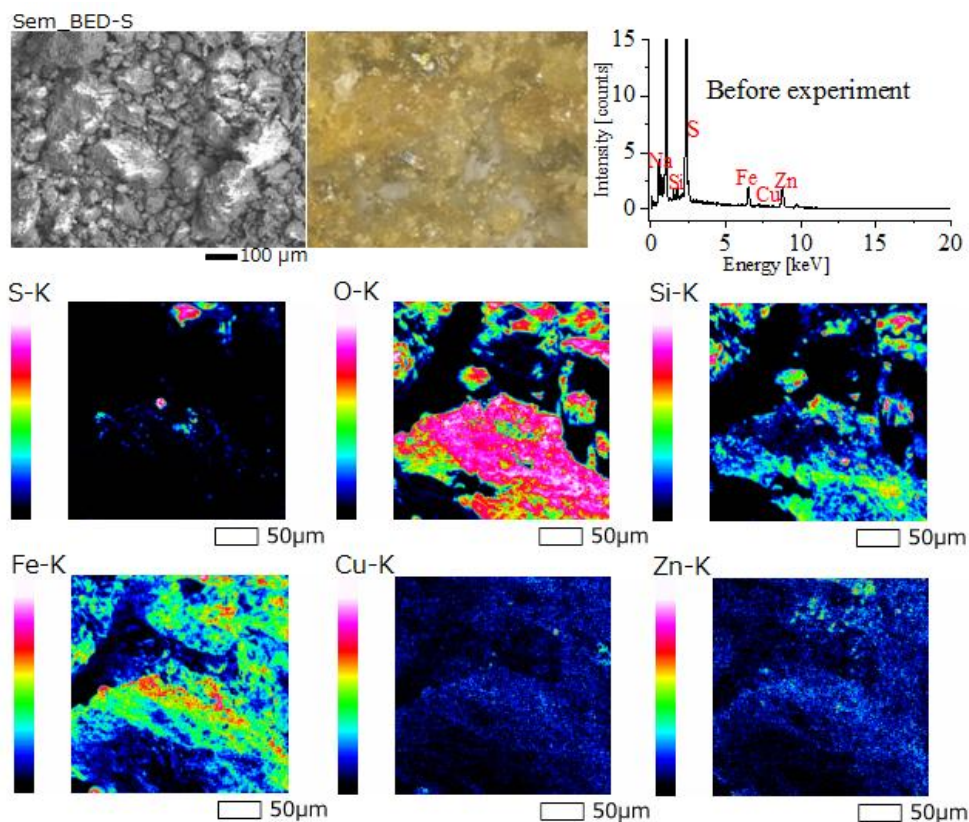


Figure 3. 3 SEM photomicrographs, optical photomicrograph, and corresponding elemental maps of S, O, Si, Fe, Cu and Zn in the pre-experiment tailings sample

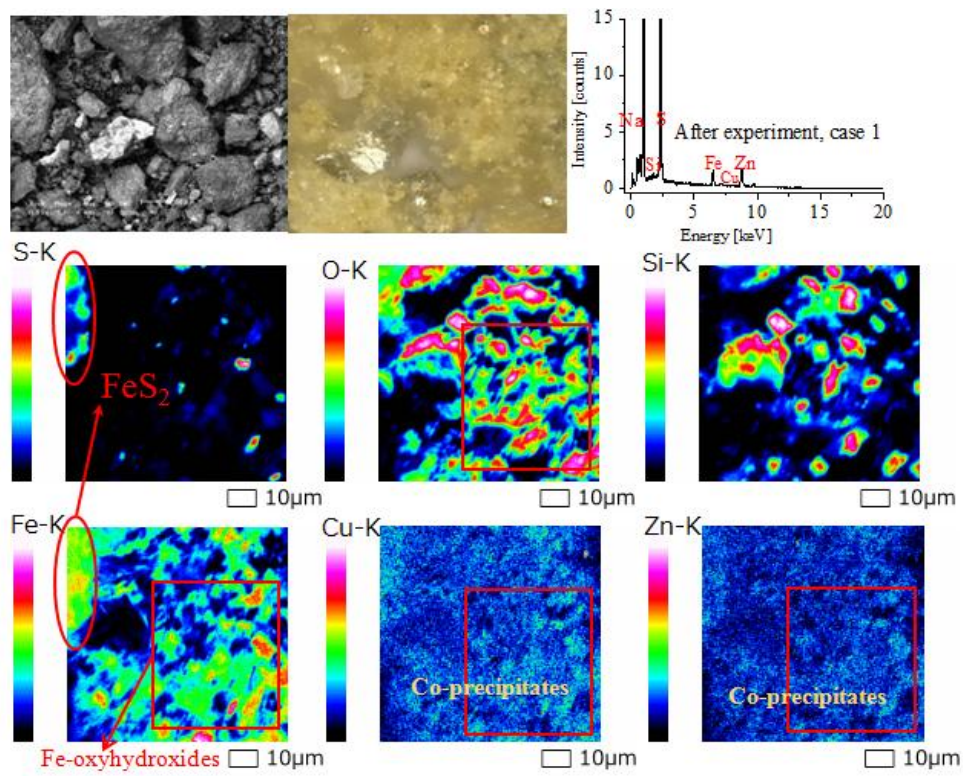


Figure 3. 4 SEM photomicrographs, optical photomicrograph, and corresponding elemental maps of S, O, Si, Fe, Cu and Zn in the post-experiment tailings sample (Case 1)

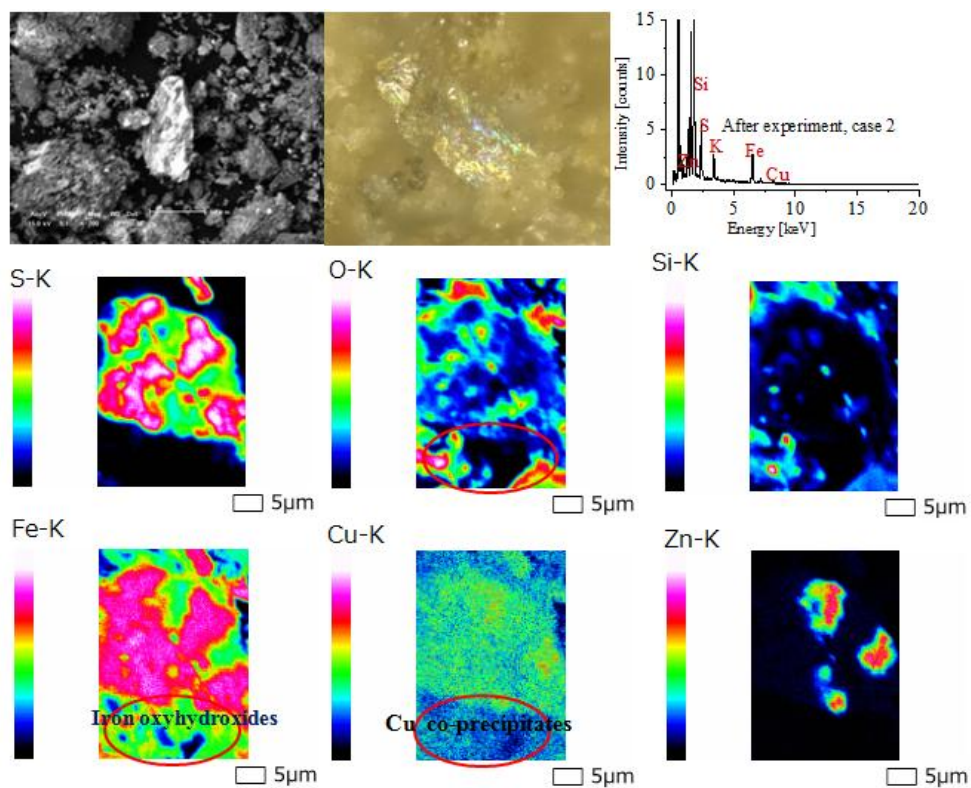


Figure 3. 5 SEM photomicrographs, optical photomicrograph, and corresponding elemental maps of S, O, Si, Fe, Cu and Zn in the post-experiment tailings sample (Case 2)

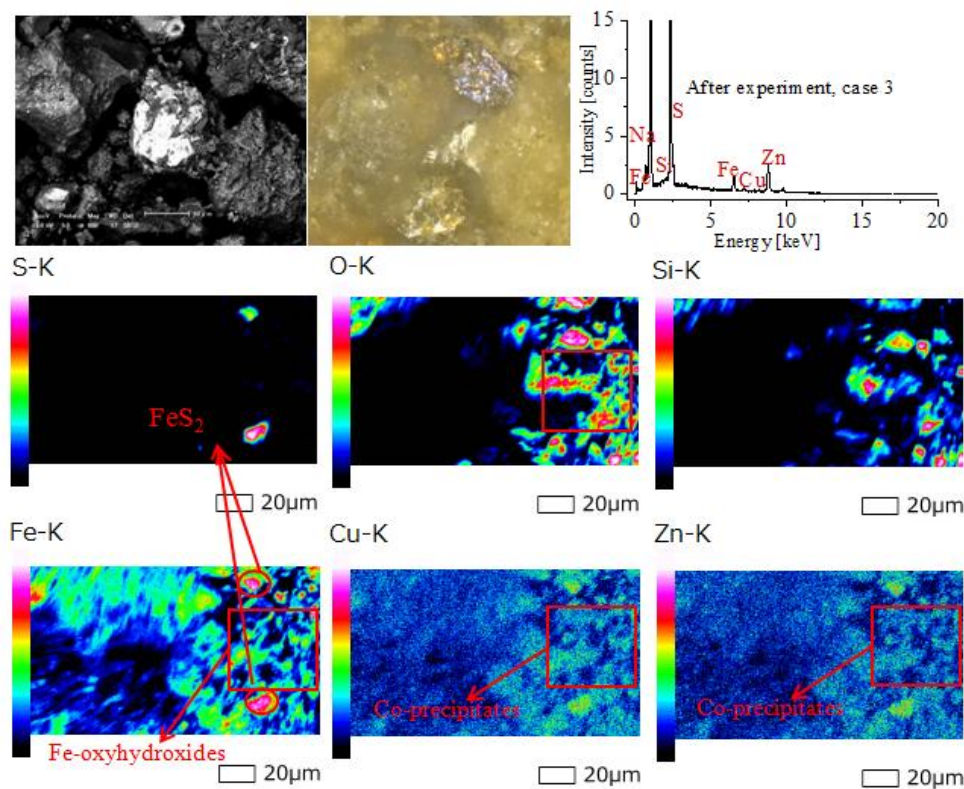


Figure 3. 6 Photomicrographs, optical photomicrograph, and corresponding elemental maps of S, O, Si, Fe, Cu and Zn in the post-experiment tailings sample (Case 3)

3.3.2 Column experiments

The evolution of Cu, Zn, Fe, and major ions (Ca , Mg , K , SO_4^{2-}), as well as parameters involved in the oxidation-neutralization processes (pH , Eh , EC , Al , Mn , and Si) in the effluent of the columns, was observed. Figures 3.7, 3.8, and 3.9 represent the evolution of the measured data versus time. The plotted values corresponded to the concentration released without considering the recovered volume of effluent or the mass of the solid sample.

pH, Eh, and EC of leachates

The changes in pH , Eh , and EC values of the effluents from the column experiments are illustrated in Figs. 3.7(a)-(c), respectively. The pH values in cases 1 (2.7–3.3, mean 3.1), 2 (2.5–3.4, mean 3.4), and 3 (2.7–3.7, mean 3.5) were observed. These pH values were in acidic condition throughout the experiments (84 weeks). At the beginning of the experiments, the pH values were lower in all cases and followed the order of case 3 > case 2 > case 1, and then they slightly increased and followed the order of case 3 $\approx$ case 2 > case 1 (Fig. 3.7 (a)). The oxic conditions were observed throughout the experiments (Fig. 3.7(c)). The Eh values in all three cases were variable (500-800 mV), but remained under oxidizing conditions throughout the duration of the experiments.

This condition is favorable to the oxidation of residual sulfide minerals. The EC values of the effluents, which represent major ions present in the solution, were also monitored throughout the duration of the experiments. Figure 3.7(b) illustrates the evolution of EC in cases 1, 2, and 3. The highest EC values were found in the first leachate in all cases (28, 30, and 16 mS/cm for cases 1, 2, and 3, respectively) and decreased gradually as time elapsed. This implies that easily dissolved chemical species were released promptly after the addition of distilled water. The EC values were in the order of case 1 > case 2 > case 3. Lower pH values corresponded to higher EC values.

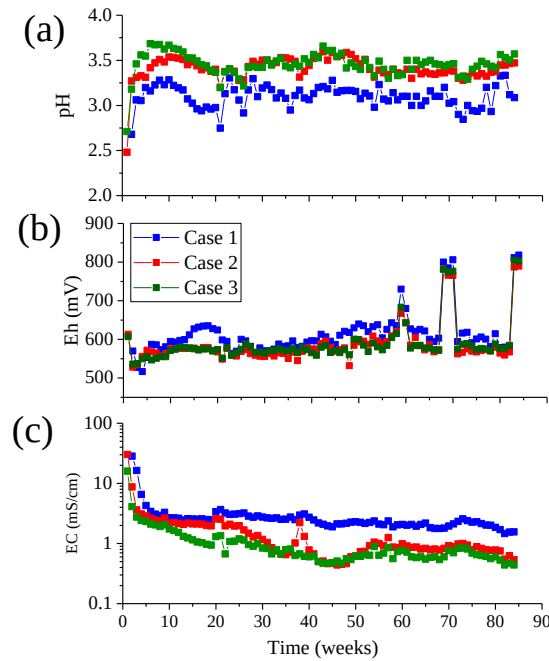


Figure 3. 7 Changes in pH (a), Eh (b), and EC (c) with time for column effluents

Leaching concentrations of Cu, Zn, Fe, and major ions

The leaching concentrations of Cu, Zn, and Fe in the effluents were higher at the beginning of the experiment, and then decreased dramatically within 10 weeks (Fig. 3.8). After that, the concentration fluctuated in lower concentration ranges. The leaching concentration ranges of Cu, Zn, and Fe were 0.1-1,950 mg/L, 4-22,100 mg/L, and 22-5,440 mg/L, respectively.

The changes in the concentrations of SO_4^{2-} , Al, Ca, K, Mg, Mn, and Si are illustrated in Figs. 3.8 and 3.9. As a general trend, the higher concentrations of these elements were observed at the beginning of the experiments and then decreased and approached almost constant concentrations as time elapsed except for Ca. The Ca concentrations in cases 1 and 2 were similar for the first few weeks of the experiment, and almost constant from the beginning to week 20. As time elapsed, the

concentration of Ca gradually decreased. The Ca concentration in case 3 was almost constant during the first few weeks and then gradually decreased throughout the experiment (Fig. 3.9 (a)).

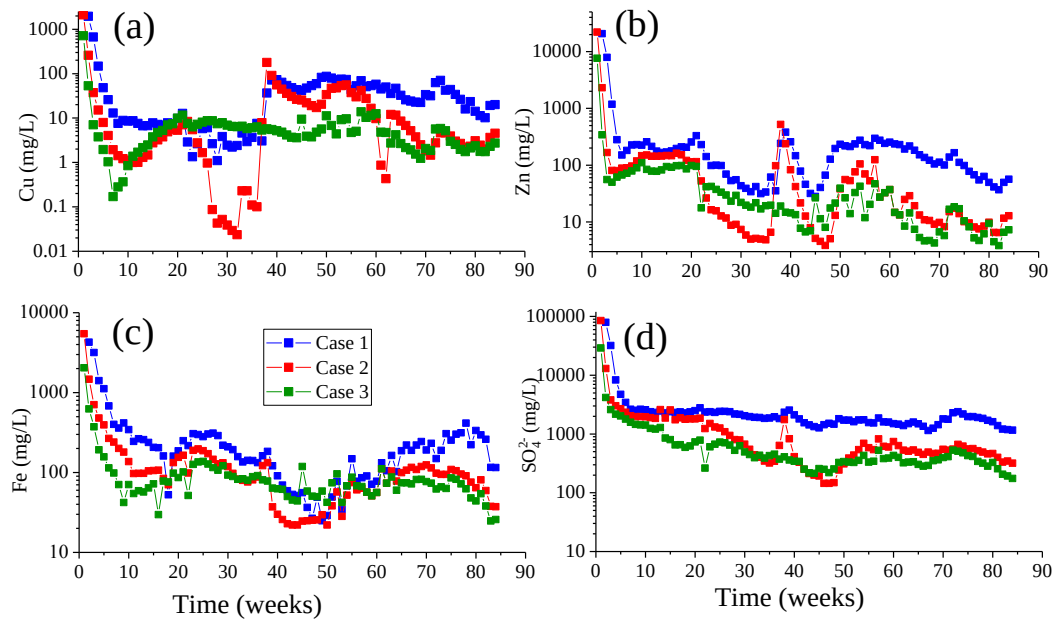


Figure 3. 8 Changes in concentrations of (a) Cu, (b) Zn, (c) Fe, and (d) SO_4^{2-} with time for column effluents

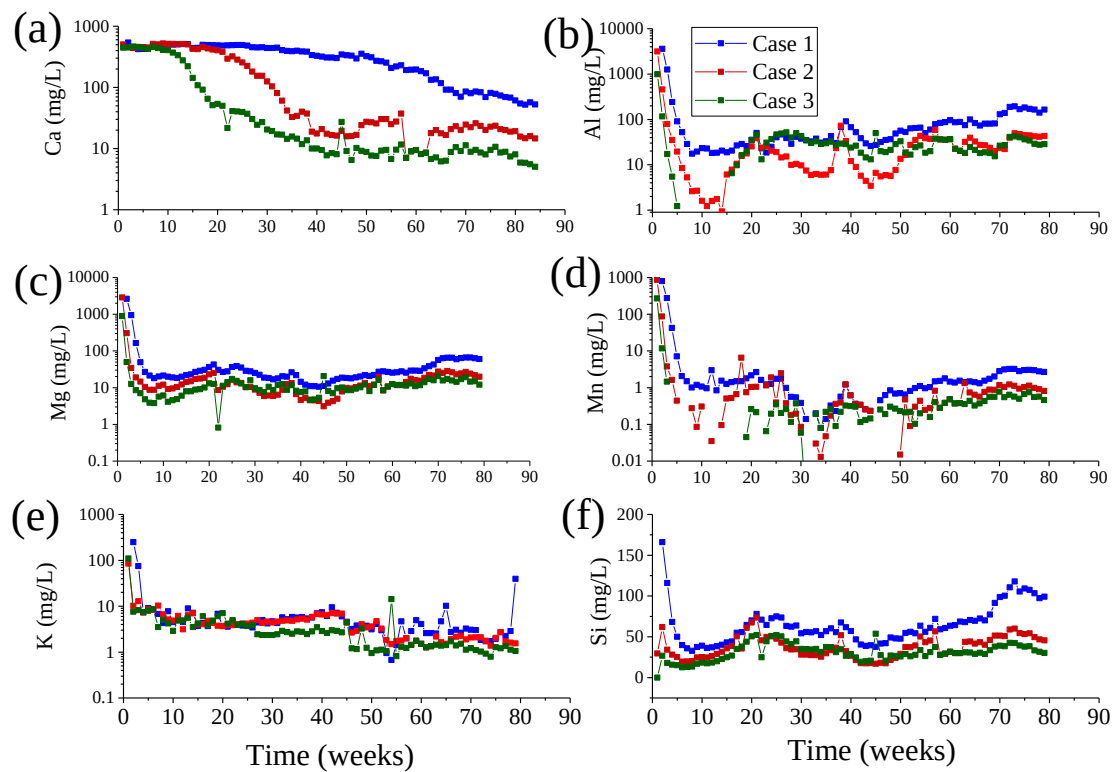


Figure 3. 9 Changes in concentrations of (a) Ca, (b) Al, (c) Mg, (d) Mn, (e) K, and (f) Si with time for column effluents

3.3.3 Sequential extraction of the pre- and post-experiment tailings

The speciation of hazardous metals by sequential extraction could provide detailed information about the origin, chemical forms, biological and physico-chemical availability, mobilization, and transport of metals. Each of the fractions extracted represents a different form and different mechanism of availability (Tiemmer et al., 1979; Clevenger 1990; Dang et al., 2002; Anju and Banerjee 2010). The results of the sequential extraction of Cu, Zn, and Fe of pre- and post-experiment tailings are presented in Fig. 3.10. The sequential extraction scheme is designed to target the fractions as listed in Table 3.1.

Prior to the experiment, Cu and Zn fractions were dominated by ion exchangeable of 470 and 4,270 mg/kg, sulfide fractions of 460 and 1,350 mg/kg, and the residual fraction of 460 and 420 mg/kg, respectively. The large amount of Fe was mainly associated with the residual fraction of 30,800 mg/kg. Additionally, the Fe fraction associated with ion exchangeable, oxide, and sulfide fractions were 1,440, 19,100 and 11,700 mg/kg, respectively.

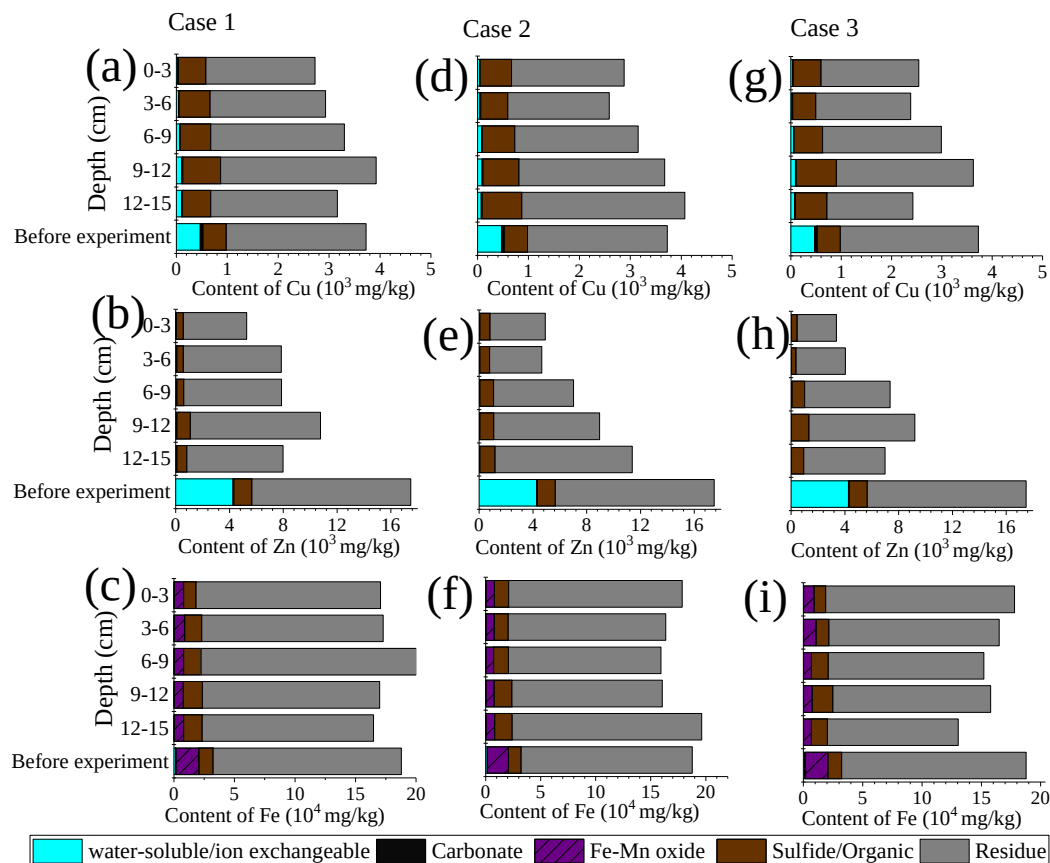


Figure 3. 10 Sequential extraction of the pre- and post-experiment tailings in Case 1: (a) Cu, (b) Zn, and (c) Fe; Case 2: (d) Cu, (e) Zn, and (f) Fe ; and Case 3: (g) Cu, (h) Zn, and (i) Fe

In the post-experiment tailings, their exchangeable fractions (Case 1: Cu: 30-109 mg/kg, Zn: 20-50 mg/kg, and Fe: 90-190 mg/kg; Case 2: Cu: 40-90 mg/kg, Zn: 20-34 mg/kg, Fe: 80-110 mg/kg; Case 3: Cu: 20-92 mg/kg, Zn: 8-40 mg/kg, Fe: 80-120 mg/kg) were lower than the original. The sulfide fractions of Cu and Fe in the post-experiment tailings were almost the same as those in the pre-experiment tailings. However, the sulfide fraction of Zn in the post-experiment tailings was less than that in the pre-experiment tailings (Figs. 3.10 (b), (e), and (h)).

Overall, most of Cu, Zn, and Fe fractions in the original tailings were dominated by ion exchangeable, sulfide, and residual fractions while those in the post-experiment tailings were dominated by sulfide and residual fractions.

3.3.4 Vertical profiles of Cu, Zn, Fe, and SO_4^{2-} leaching after column experiments

Figure 3.11 shows the vertical profiles of Cu, Zn, Fe, and SO_4^{2-} leaching concentrations after column experiments. The lower pH values and leaching concentrations were found at the top tailings, and in overall the leaching concentration followed the order of case 1 > case 2 > case 3. However, the fact that the higher concentrations of Cu, Zn, Fe, and SO_4^{2-} were found in the deeper tailings sample agreed with the results of the field observation by Khoeurn et al. (2018). These results indicate that the exchangeable phase was almost flashed out from the top tailings (Fig. 3.11). This result might be a good indicative factor to reveal that oxidation prevails from the top tailings and less oxidation in the deeper tailings. The SO_4^{2-} concentrations were not significantly different with depth.

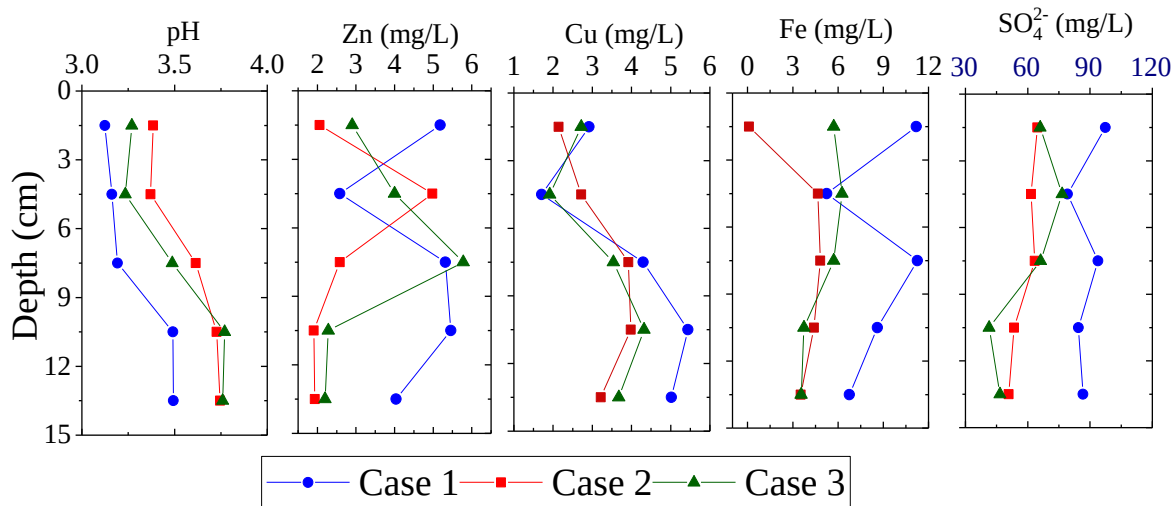


Figure 3.11 Vertical profiles of pH, and Zn, Cu, Fe, and SO_4^{2-} concentrations of post-experiment tailings by batch leaching tests

3.3.5 Spike tests of cases 1 and 2

The changes in Cu and Zn concentrations after spike tests for cases 1 and 2 are shown in Fig. 3.12. After adding the 1000 mg-Cu-Zn/L solution into columns at week 37, the peak concentrations of Cu and Zn appeared at week 39 in cases 1 while their peaks were observed at week 38 in case 2. This means that the leaching concentrations suddenly increased to their highest peaks (case 1: 70 mg/L of Cu; 380 mg/L of Zn at week 39 and case 2: 180 mg/L of Cu; 500 mg/L of Zn at week 38) were observed. Then, the concentration of Zn decreased almost equal to the baseline concentration (case 1: 35 mg/L of Zn and case 2: 6 mg/L of Zn) before the spike tests, at week 45. Unlike the behavior of Zn, Cu concentration slowly decreased but was far higher than the baseline concentration (case 1: 3 mg/L of Cu and case 2: 7 mg/L of Cu) before the spike test. The recovery ratios of Cu were 38.9 and 48.3 % in cases 1 and 2, respectively, while those of Zn were 87.3 and 95.8 % in cases 1 and 2, respectively, by considering their baseline concentrations. The results revealed that Zn is more mobilized than Cu and the retardation of Cu was observed. This might be because Cu likely adsorbed onto Fe-oxyhydroxide or replaced the Zn from ZnS in the tailings.

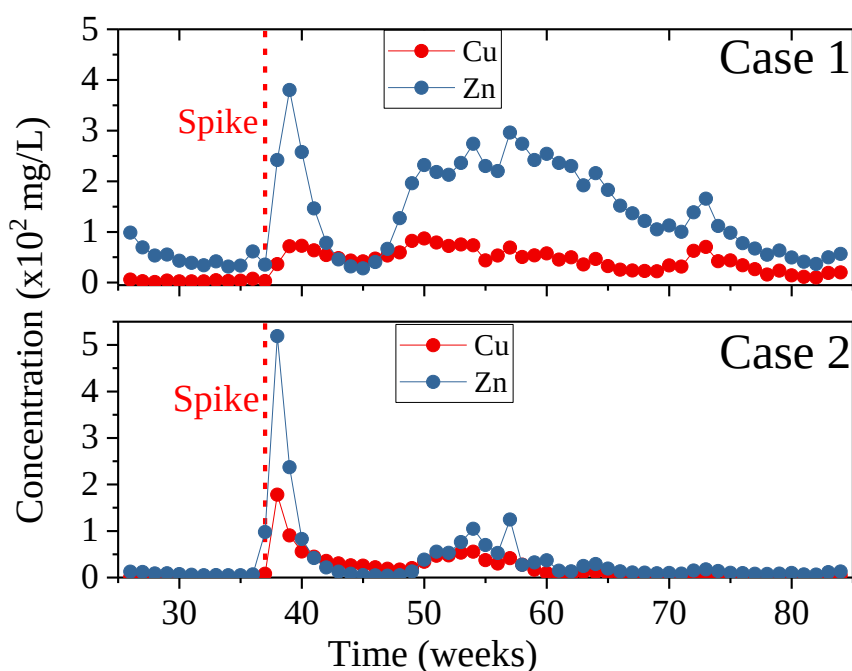


Figure 3. 12 Changes in concentrations of Cu and Zn for cases 1 and 2 during spike tests

3.3.6 Geochemical calculations of effluents from column experiments

The results of *SI* calculations for the effluents from all cases throughout the experiments are presented in Fig. 3.13. The calculated *SI*s of chalcantite, melanterite, goslarite, and kaolinite were strongly negative for all cases, implying dissolution (Fig. 3.13; Left). Those of cupricferite, goethite, lepidocrocite, maghemite, and K-jarosite were strongly positive, implying precipitated (Fig. 3.13;

Right). Unlikely, SI values of ferrihydrite were distributed around zero, implying dissolution/precipitation equilibrium during the experiment, whereas that of gypsum was almost zero (almost saturated) at the beginning of the experiments for all cases and then decreased to less than zero with time (Fig. 3.13; Left). SI values of $AlOH\text{SO}_4$ and SiO_2 (am-gel) were around zero throughout the experiment, implying almost saturated (Fig. 3.13; Left).

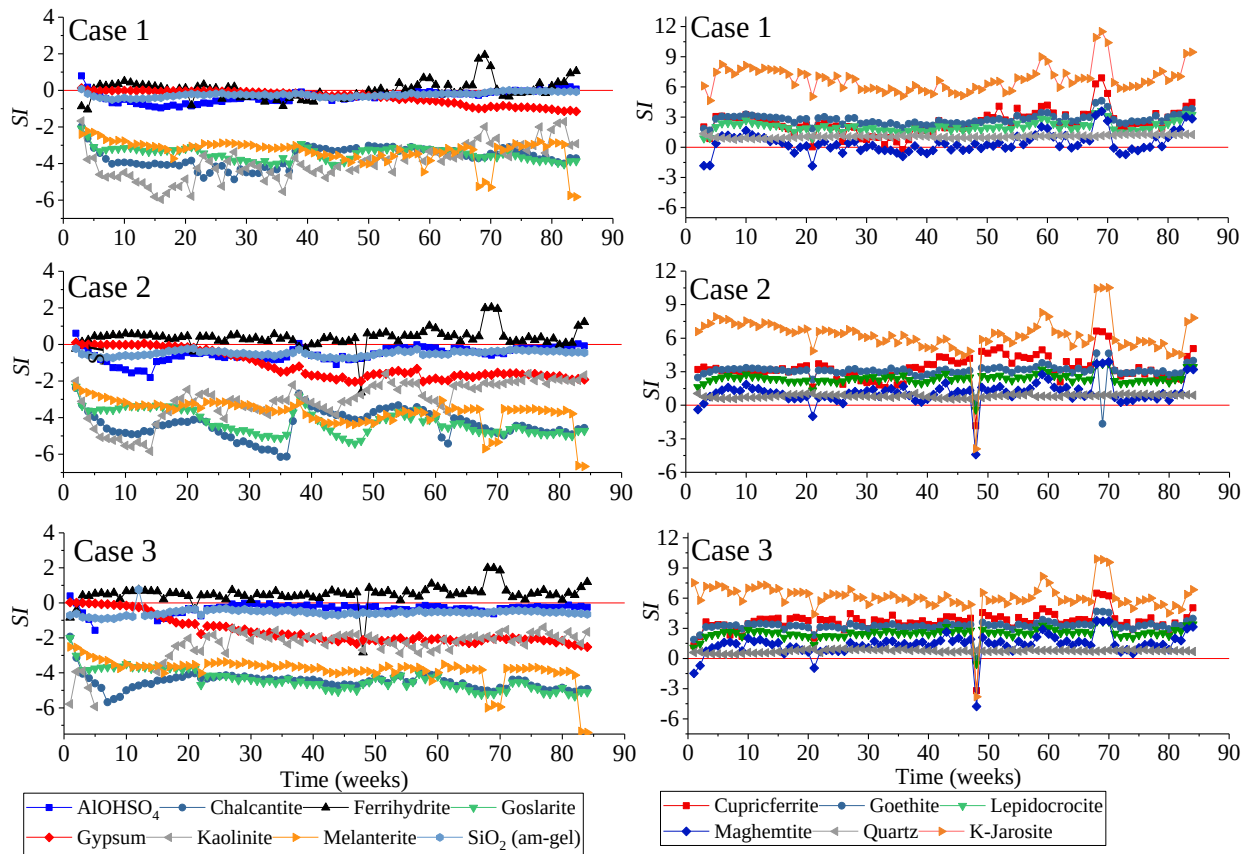


Figure 3.13 Saturation indices (SI) of effluents from column experiments (Left: $SIs \leq 0$; Right: $SIs > 0$)

3.4 Discussion

3.4.1 Effects of infiltration rate on the mobility of heavy metals and their leaching behaviors

In case 1 (the lowest infiltration rate), the first effluent sample of 66 mL was collected at the second week, whereas the effluent samples of 78 mL and 280 mL of cases 2 and 3 were collected at the first week, respectively. These results indicate that variations of the infiltration rate directly influenced the water residence time in the columns. Table 3.4 shows the water balance in all columns until 84 weeks of the experiment. The highest percentage of recovery was obtained in case 3 at 97.6%, followed by case 2 at 96% and case 1 at 93%. The differences between the volume of water added and collected are attributed to evaporation and residual water inside the columns.

Overall, the pH value were in order pH in Case 3 > Case 2 > Case 1 while the Eh and EC values were in order Case 1 > Case 2 > Case 3. Similar behaviors to EC were also observed for Cu, Zn, Fe, and ion concentrations (Figs. 3.7-3.9). These results reveal that the infiltration rate plays a role as a dilution factor in these column experiments and also promotes mineral precipitation faster (high intensity of Fe, O, S, and Si by SEM in Figs. 3.5 and 3.6). This is also supported by a reddish-brown color at the top tailings, which occurred more in case 3 followed by cases 2 and 1 after finishing the experiment (Fig. 3.16 (b)). The results of bulk chemical compositions showed that the highest depletion of Cu, Fe, Zn, and S were observed with the highest infiltration rate (Table 3.3).

Table 3. 4 Water balances in the columns throughout the experiments (84 weeks)

Cases	Total volume of influent (mL)	Total volume of effluent (mL)	Total volume retained and lost (mL)
1	8,400	7,785	615
2	16,800	16,167	633
3	33,600	32,804	796

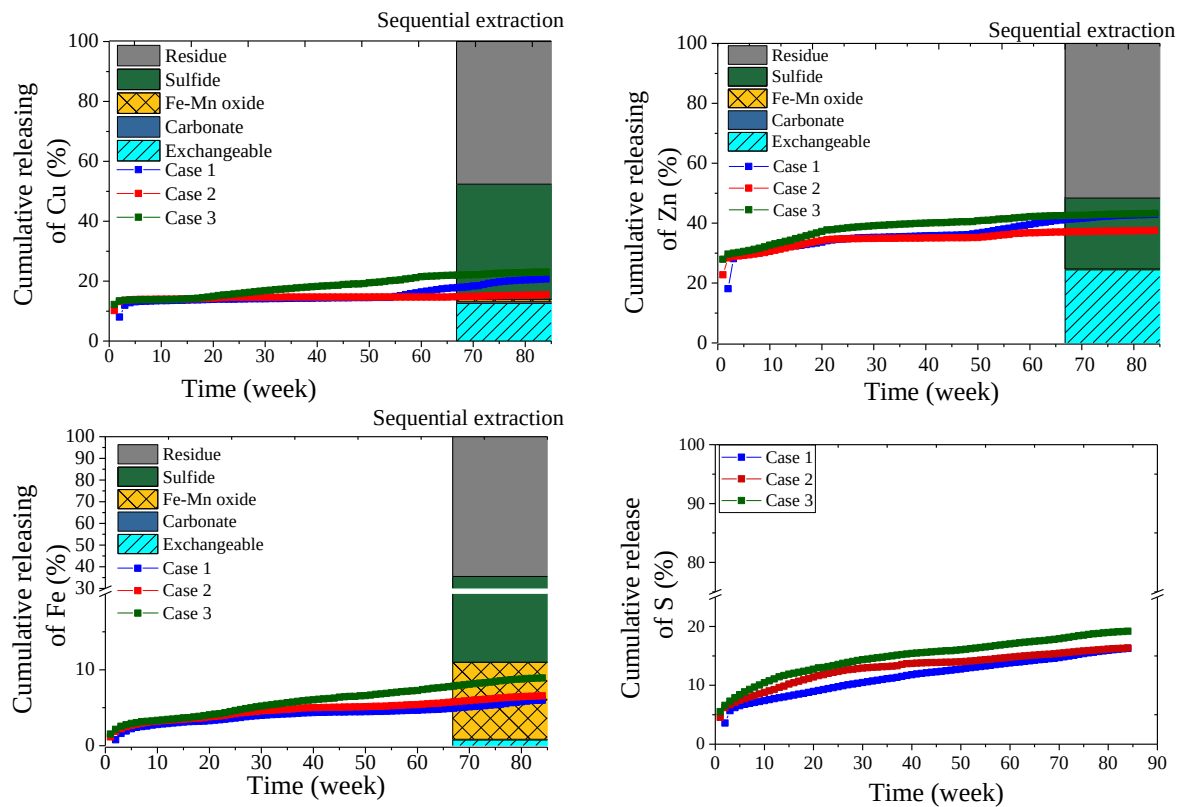


Figure 3. 14 Cumulative releasing of Cu, Zn, Fe, and S from the tailings of column experiments with time and sequential extraction

3.4.2 Leaching concentration changes compared with fractions of metals by sequential extraction

Results from column experiments revealed that there were two patterns of leaching concentration of potentially hazardous metals and ions. The first pattern is likely to be the dissolution of pre-existing soluble salts (i.e., gypsum), present in the sample prior to sample collection or oxidation products formed during sample storage. This is expected to influence chemistry of the effluent during the first few weeks of the experiment. The rapid dissolution of the soluble salts and hydrolysis of dissolved ions like Al^{3+} , Mg^{2+} , and Mn^{2+} were reported to occur during the onset of the wet season especially in the initial flushing event (Keith et al., 2001; Romero et al., 2007; Khorasanipour et al., 2011). The second pattern is a slow oxidation process of the remaining sulfide minerals due to the weathering process, which well agrees with Younger et al. (2002). The results of chemical, mineralogical, and geochemical calculations suggest that the effluent patterns in Figs. 3.8 and 3.9 were governed not only by oxidation of sulfide minerals, but also by the formation and dissolution of secondary phases and the sorption and co-precipitation of Cu and Zn to these phases.

Figures 3.14 (a)-(c) show the comparison between the cumulative release of Cu, Zn, and Fe from columns and fractions of Cu, Zn, and Fe by sequential extraction. The cumulative release of S is also shown in Fig. 3.14 (d). From week 1 to 5 of column experiments, the cumulative releases of Cu, Zn, and Fe likely corresponded to ion exchangeable fraction. After week 5 of the experiments, the total leached amounts of Cu and Zn are considered to be from the sulfide fraction of the sequential extraction, whereas that of Fe is likely from Fe-Mn oxides fraction and sulfide fraction. The sequential extraction results revealed that the hazardous metals in most mobile fraction (i.e., ion-exchangeable, carbonates, Mn-Fe oxides, and sulfides/organic matter) were the primary sources in the tailings. The ion exchangeable fraction is the most labile bonded to the tailings, and therefore, the most dangerous and bio-available for the environment. It consists of exchangeable fraction and soluble fraction in water under slightly acidic conditions. In Fe-Mn oxides fraction, the metals are adsorbed or co-precipitated and are unstable under reduced conditions. In sulfide/organics fraction, the metals are complexed and sorbed. Under oxidizing conditions, this fraction can be degraded to result in the release of soluble metals (Dang et al., 2002; Dold and Fonboté 2003). It can be assumed from this result that Cu, Zn, and Fe may continue to leach out into the environment for a longer period of time by changing the fraction of dominant sources. In addition, the sample taken from the Shimokawa tailings contained higher contents of hazardous metals and S than those of the other tailings samples studied by many authors (Jurjovec et al., 2002; Ardaş et al., 2009; Goumih et

al., 2013; Zhang et al., 2016; Kandji et al., 2017). This means that long-term leaching behavior of hazardous metals should be taken into account.

The cumulative releasing trends of Cu, Zn, Fe, and S from all columns during the experiment were nearly linear except for the first week of the experiment (previously stated that it was due to soluble salts). The cumulative release was in order $Zn > Cu > S > Fe$. This implies that Zn is leached from the tailings at a higher rate than that of Cu. This result agreed with that of the spike tests (Fig. 3.12), which showed that Zn leaching was faster than Cu leaching.

3.4.3 Prediction of the release of heavy metals from sulfide fraction

It is understood that the continuous release of heavy metals was from the sulfide fraction contained in the tailings. The amount of the sulfide fraction of heavy metals and their weekly release are known. Thus, the release period of heavy metals can be calculated by the following formula and the parameter used are shown in Table 3.5.

$$\frac{\text{Content of sulfide fraction} - \text{Sum of leached content (w6-84)}}{C \times \text{volume}} = \text{Release period (weeks)} \quad (\text{Eq. 3.1})$$

Table 3. 5 The parameters used to predict the release period of Cu and Zn from sulfide fraction in Case 3

Parameters	Case 3	
	Cu	Zn
Remaining sulfide fraction (mg/kg)	1077	1907
Mass of the tailings (mg)	438	438
Volume (L)	389	389
Weekly release (mg/L)	2.5	8
Prediction-release period	485	268

※ The multiplication of sulfide fraction (mg/kg) and mass tailings (mg) gives the total contents of sulfide fraction in (mg). That of concentration (mg/L) and volume (L) gives concentration in (mg).

The results suggests that it would take approximately 485 and 268 weeks to release Cu and Zn from the tailings of column case 3, respectively, after finishing the experiment.. By following the Eq. 3.1, the prediction can be applied to the actual tailing dam under the actual rainfall (300 mm/y). However, if the water flow rate in slow, it is considered that the residence time becomes longer in which the leaching concentration is likely increased. Thus, the release period might be shorter than the prediction.

3.4.4 Effects of Al and Si concentrations on pH changes in the effluents

Figures 3.15 (a)-(c) show concentrations of Al and Si in the effluents as a function of pH and the comparison between oxidation-neutralization curves for all cases, respectively. In case 1 (Fig. 15 (a)), the pH value was lower than those of cases 2 and 3, resulting in higher Al and Si concentrations in case 1 than those in cases 2 and 3 (Fig. 3.15(b), (c)). The Al and Si concentrations were negatively correlated with pH. This indicates that the oxidation of sulfide minerals resulted in the release of acid into the effluents of the tailings whereas gangue minerals such as alumino-silicate minerals incorporated in the tailings neutralized the acid. Their dissolution typically leads to a distinct sequence of pH buffering plateaus (Jurjovec et al., 2002). Gangue minerals contributing to acid-neutralization in the Shimokawa tailings are predominantly alumino-silicates. Consequent dissolution of alumino-silicate minerals within the sulfide oxidation zone also contributes to Al dissolution (Blowes et al., 1991; Jurjovec et al., 2002; Gunsinger et al., 2006).

Figure 3.15 (d) shows the oxidation-neutralization curves between cumulative molar concentrations of Al and Si and that of SO_4^{2-} based on the results of column experiments. The curves compared the evolution of the products of sulfide oxidation (dissolved S as sulfates in the experiments) with those of acid neutralization (Al and Si, which might be from alumino-silicate like anorthite). The curves of all cases show two phases separated by an inflection point: a lower slope value in the early 15 weeks of the experiments followed by a steeper slope for the rest of the duration of the experiment. The steeper slope toward the neutralization products means that alumino-silicate (anorthite) and chlorite likely neutralize the AMD in the tailings. Although silicate dissolution rates increase under highly acidic conditions, corresponding pH buffering is generally minimal due to the relatively high rates of acid production (Jambor et al., 2002; Jurjovec et al., 2002; Salmon and Malmström, 2006). In addition, the neutralizing capacity of some alumino-silicate is controversial since the Al released can generate acidity after hydrolysis and precipitate as hydroxides (Kwong and Ferguson, 1997; Lappako and White, 2000).

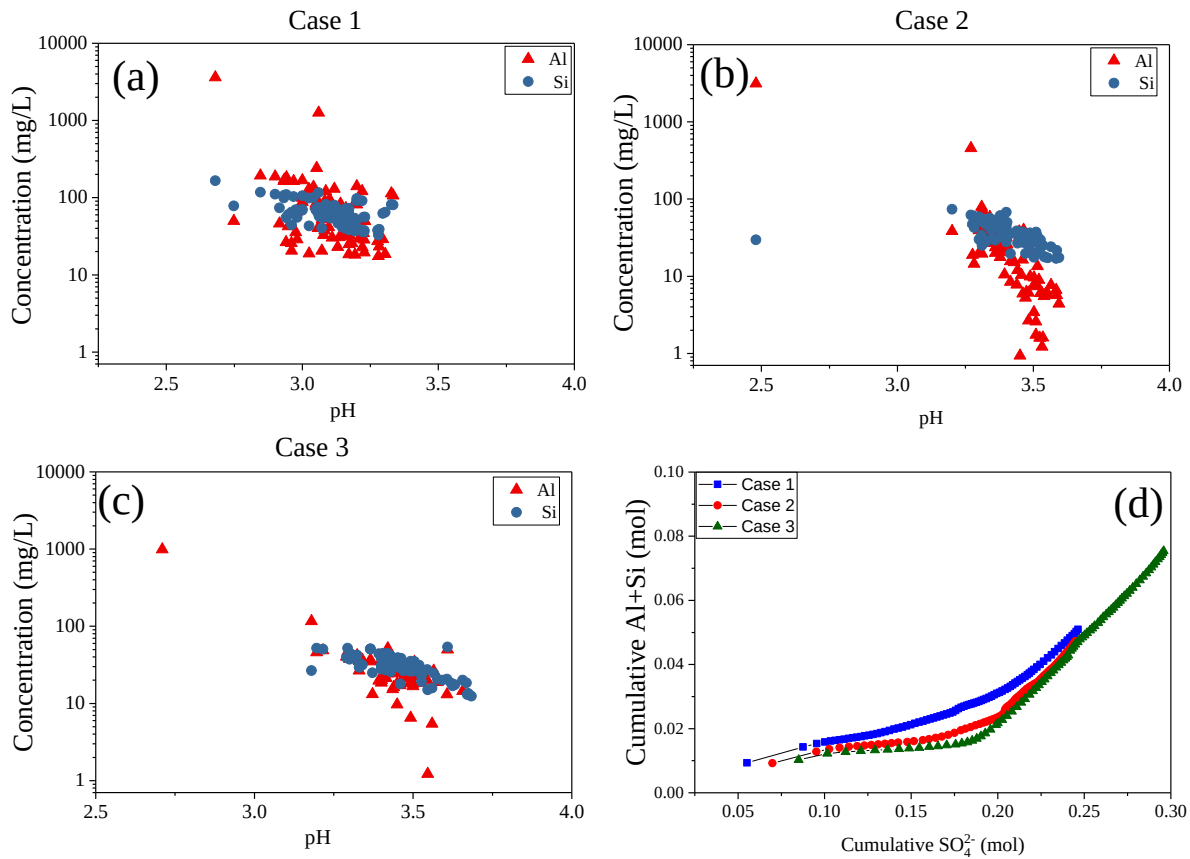


Figure 3. 15 Concentrations of Al and Si versus pH from column experiments ((a), (b), and (c)); comparison between the oxidation-neutralization curves

3.4.5 Factors affecting pyrite oxidation

In the column experiments, oxidation of pyrite occurs by contacting with atmospheric O_2 , dissolved O_2 (DO), water, and/or microorganism (Silverman, 1967). Theoretically, oxidation of 1 mole of pyrite consumes 3.5 moles of DO in order to produce 1 mole of Fe^{2+} and 2 moles of SO_4^{2-} . The calculation of DO consumed and Fe^{2+} and SO_4^{2-} produced after 6 weeks of experiments are shown in Table 3.6 by considering DO in the infiltrated distilled water at each week. At 20 °C, the distilled water contained about 8.84 mgO_2/L (Langmuir, 1997). The amount of DO consumed was far lower than those of Fe^{2+} and SO_4^{2-} produced, which means that oxidation of pyrite was not only affected by DO but also other factors, such as atmospheric O_2 and/or ferric iron (Fe^{3+}). At atmospheric exposure, pyrite oxidation begins within minutes, commencing with oxidation of S^{2-} species and producing SO_4^{2-} while iron-sulfate was produced within a few minutes (Chandra and Gerson, 2010). Sulfate is the main oxidation product of prolonged atmospheric exposure (Chandra and Gerson, 2010) and Todd et al. (2003) identified this to be largely presented as Fe -sulfate ($\text{Fe}_2(\text{SO}_4)_3$). The $\text{Fe}_2(\text{SO}_4)_3$ easily dissolves into Fe^{3+} and SO_4^{2-} when it contacts with water. The

ferric iron (Fe^{3+}) is more aggressive and effective than O_2 for pyrite oxidation (Moses et al., 1987; Chandra and Gerson, 2010). Hence, there is markedly less direct oxidation potential in the deeper tailings of the column when compared with sub-aerial tailings (surface tailings).

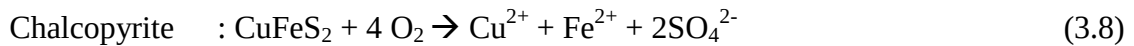
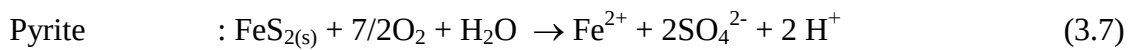
Another support of oxidation occurring in the tailings is the pre- and post- experiment S masses, which showed that considerable amounts of S were leached (Table 3.3). Sulfur was lost from all three columns in proportion to the irrigation rate. The overall decline in S during the course of the experiment is indicative of an ongoing process of oxidation. The concentrations of Zn, Cu, Fe, and SO_4^{2-} still remained higher in the deeper tailings, which could support the continuous oxidation reduced with depth (Fig. 3.11).

Table 3. 6 Mass balance of amount of consumed dissolved oxygen and produced Fe and SO_4^{2-} by pyrite oxidation

Cases	Dissolved oxygen (mole)	Iron (Fe^{2+}) (mole)	Sulfate (SO_4^{2-}) (mole)
1	$0.3 \times 10^{-4} \pm 0.015 \times 10^{-4}$	$2.7 \times 10^{-4} \pm 1.72 \times 10^{-4}$	$15.4 \times 10^{-4} \pm 2.8 \times 10^{-4}$
2	$0.55 \times 10^{-4} \pm 0.03 \times 10^{-4}$	$2.6 \times 10^{-4} \pm 1.1 \times 10^{-4}$	$9.7 \times 10^{-4} \pm 3 \times 10^{-4}$
3	$1.1 \times 10^{-4} \pm 0.06 \times 10^{-4}$	$4.4 \times 10^{-4} \pm 1.2 \times 10^{-4}$	$13.9 \times 10^{-4} \pm 3.3 \times 10^{-4}$

3.4.6 Formation and dissolution of secondary minerals in the tailings during the column experiments

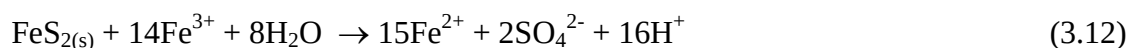
Figure 3.16 (a) shows the relationship between a sum of molar concentrations of Ca, Mg, Cu, Mg, Zn, and Fe in the effluents and that of SO_4^{2-} . A green straight line in this figure shows the theoretical relationship by assuming stoichiometric dissolution of soluble salts (Eq. (3.2)-(3.5)), which might occur during sampling, transportation or air-dried under room temperature. A red straight line shows the theoretical relationship by assuming stoichiometric dissolution of gypsum, pyrite, sphalerite, and chalcocopyrite (Eq. (3.6)-(3.9)).



The first 5 weeks of the experiments, the plots were likely on the theoretical line of soluble salts. These results agreed with the first pattern of leaching, soluble salt dissolution. From week 6 to 30 of the experiments, the plots were likely on the theoretical line of dissolution of gypsum, and oxidation of chalcopyrite, sphalerite, and pyrite, which means that slower oxidation process controlled the leaching concentrations of Zn, Cu, Fe, and SO_4^{2-} in the effluents. As time elapsed, the sum of the actual molar concentrations was lower than the theoretical line. Thus, at least two phenomena could explain this difference. The first is the precipitation of secondary minerals like iron-oxyhydroxide/ferrihydrite. The second is co-precipitation or adsorption of Cu and Zn onto the surface of these secondary minerals. This is because the iron (III)-precipitates were clearly observed by the reddish-brown color of the tailings at the top of the column (Fig. 3.16(b)). The depth of redish brown of the tailings was about 1.2 cm from the top and about 9 cm around the wall of the tailings (Case 3). In addition, the calculation of saturation indices by PHREEQC also clarified that secondary minerals, such as ferrihydrite, goethite, maghemite, lepidocrocite, and cupricferite were precipitated in the system (Fig. 3.13). Another possible evidence for precipitation of secondary phases is that the SEM-EDS observations of samples after the experiment revealed the presence of iron-oxyhydroxide.

An Eh-pH diagram illustrating the speciation of Fe was also created with the measured pH and Eh values during the column experiments (Fig. 3.17). All of the plots in all cases are localized around the boundary of Fe^{2+} , FeOH^{2+} , and hematite. Hematite crystals can be formed as a secondary mineral by weathering processes in soil, and along with other iron oxides or oxyhydroxides such as goethite (Hammarstrom et al., 2005).

Ferrous iron (Fe^{2+}) might be oxidized to ferric iron (Fe^{3+}) (Eq. 3.10). At neutral or higher pH level, Fe^{3+} can precipitate (Eq. 3.11). But, at very low pH level, it can remain in solution and act as the electron acceptor in pyrite oxidation (Eq. 3.12) (Singer and Stumm, 1970).



The cycle of reactions (3.10)-(3.12) is likely to occur during the column experiments. The iron precipitates can act as a sink of trace elements (Cu, Pb, Se, and Zn) through adsorption and/or co-precipitation (Khorasanipour et al., 2011; McGregor and Blowes, 2002). This may contribute to the decrease in Cu, Zn, and Fe concentrations in the effluents.

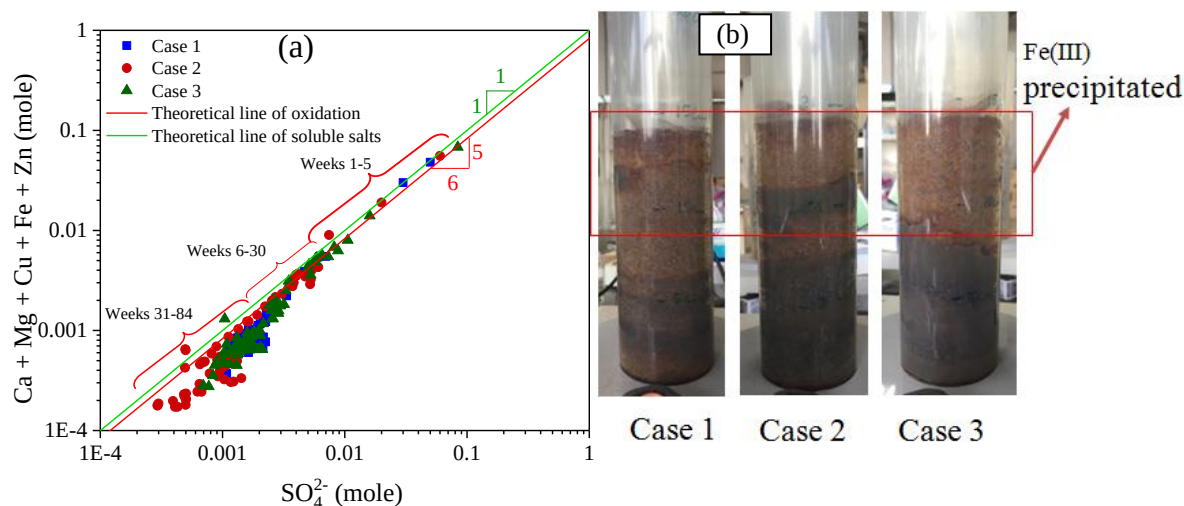


Figure 3. 16 (a) Relationship between observed concentrations in effluents from the columns and theoretical stoichiometry by considering pyrite, chalcopyrite, and sphalerite oxidation and gypsum dissolution (red line), and dissolution of soluble salts (green line) and (b) image of columns cases 1, 2, and 3

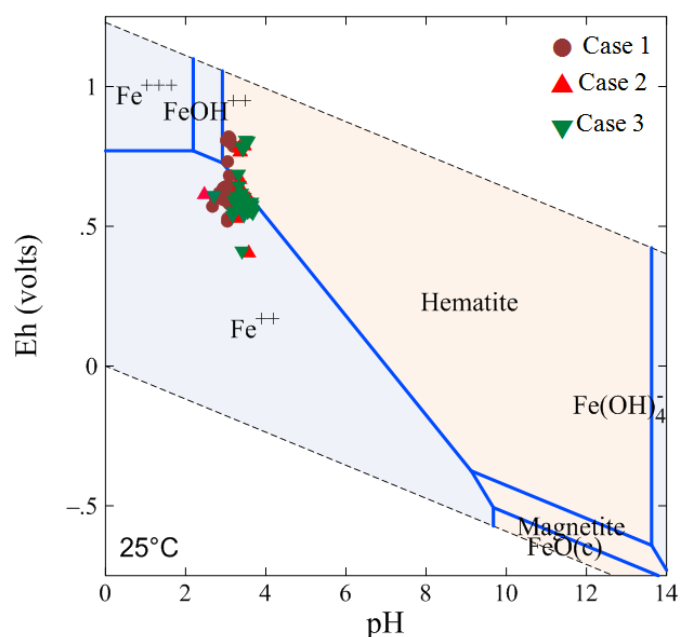


Figure 3. 17 Eh-pH predominance diagram of Fe at $T = 25^\circ\text{C}$, $P = 1.013$ bars, activity = 10^{-9} , $a[\text{H}_2\text{O}] = 1$. The plots represent Eh and pH values of effluents from the columns in all cases.

3.5 Conclusion

Chemical characterization of effluents from the tailings of a closed mine site was performed to understand the leaching behaviors of hazardous metals (i.e., Cu, Zn, and Fe) from the tailings and to compare with the results of the sequential extraction. The findings are the following:

- 1) Pyrite oxidation likely occurred by the exposure to atmospheric O₂ and contact with DO and Fe³⁺, which resulted in acidic pH in the effluents. Such an acidic pH could dissolve hazardous metals, such as Cu and Zn as well as alumino-silicate into the effluents. The dissolution of alumino-silicate could neutralize the pH for a longer period of the experiments.
- 2) The main release mechanisms of Zn, Cu, and Fe were considered into three phases. At the first and second phases, they were released by the easy dissolution of more labile species (ion exchangeable and sulfates) and oxidation of the remaining sulfide minerals (sulfide fraction) in the tailings. At the third phase, their release mechanisms were still controlled by oxidation of the remaining sulfide minerals but some of Fe was precipitated (Fe-Mn oxide fraction), such as iron oxyhydroxides/ferrihydrite, maghemite, lepidocrocite, and goethite. These minerals could act as a sink for Zn and Cu by co-precipitation or adsorption. These results were well agreed with the field observation in previous chapter.
- 3) The releasing rate of hazardous metals was in order Zn > Cu > Fe and significant amounts of Cu, Zn, Fe, and S existed in the columns at the end of the experiments. This suggests that residual minerals continue to produce acidic water and hazardous metals.
- 4) The highest irrigated rainfall resulted in diluting the concentrations of hazardous metals in the effluents as well as pH values and promoted faster precipitation of secondary minerals. Based on these results, the irrigation rate is one of the important parameters that should be considered when designing a remediation system.
- 5) The weathered tailings was observed at the depth of 1.2 cm after 84 weeks of experiments, which almost well agreed with the field observation (Chapter 2).

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CHAPTER 4

NEUTRALIZATION OF THE ACID MINE DRAINAGE FROM THE TAILINGS BY USING CHICKEN EGGSHELL

4.1 Introduction

The various methods used to treat AMD can be classified as active or passive systems based on their requirements for chemical addition, infrastructure, maintenance and monitoring (Younger et al., 2002). A variety of passive treatment systems such as aerobic wetlands, anaerobic or compost wetlands (Peiravi et al., 2017), vertical flow wetlands, AMD treatment ponds, bioreactors and permeable reactive barriers (Johnson and Hallberg, 2005; Wang and Ren, 2014) are available to treat AMD. However, the requirement of relatively large land area, high installation cost and system failure (poor design, winter conditions or due to accumulation of metal hydroxides) are the major disadvantages associated with these treatment systems. Active treatment methods of acid mine drainage water typically involve alkali addition in order to raise the pH to between 6.5 and 8.5, oxidation, and sedimentation (Younger et al., 2002).

Numerous methods such as adsorption (Hong et al., 2014; Masindi et al., 2015), lime neutralization and precipitation (Coulton et al., 2003), ion-exchange (Khan, 2014), electrochemistry (Chartrand and Bunce, 2003) and bioremediation (Rakotonimaro et al., 2017) are used for AMD treatment. Amongst these, limestone/lime neutralization has been used as adsorbent to remove heavy metals (*i.e.*, Cu, Fe, Zn, and As) from aqueous solution as well as actual wastewater (Miller et al., 2013; Sdiri et al., 2012; Labastida et al., 2013). Recently, adsorption technology employing naturally-derived materials has received increasing attention (Bulut and Tez, 2007), as an effective, efficient and economical method for sequestration of heavy metals from aqueous solution (Gupta and Nayak, 2012). In addition, adsorption has been universally accepted by the world environmentalists for the disposal of hazardous and toxic inorganic as well as organic pollutants present in various effluents.

Literature reports indicate that activated carbon (Goher et al., 2015), chitosan (Bassi et al., 2000), banana and orange peels (Annadural et al., 2003), sugar cane bagasse (Joseph et al., 2009), sawdust (Yu et al., 2001) and rice husks (Hegazi, 2013) among others, have the potential to sequester metal ions from polluted water. The use of eggshell (ES) as an adsorbent has been recently paid attention by numerous authors (*i.e.*, Oke et al., 2008; Yeddou and Bensmaili 2007; Angelis et al., 2017; Abdel-Khalek et al., 2017; Muliwa et al., 2018; Li et al., 2018; Flores-Cano et al., 2013). However, only few of these researches used ES as an absorbent for actual AMD.

Acid mine drainage from the Shimokawa tailings is highly acidic ($\text{pH} < 3$), has high concentrations of dissolved toxic metals, such as Cu, Zn, Fe, Cd, Mn and other major ions. The toxic characteristics of AMD can permanently damage surrounding ecosystems unless remediation is taken. Thus, suitable management and treatment methods to remediate affected water bodies are required. Although the AMD from Shimokawa tailings has been treated with $\text{Ca}(\text{OH})_2$, the low-cost absorbent for such AMD should be required to be searched. Consequently, to ameliorate the AMD problem, innovative, efficient and low-cost treatment methods should be studied.

The eggshell was selected in this study for three reasons. The first reason is its availability. Unlike scallop, which is available only in the coastal area, the eggshell was available all over the world. The second reason is to reduce waste to the environment. Recently, increased egg production and processing has resulted in increased eggshell waste (Muliva et al., 2018). The disposal of eggshell waste is an environmental burden worldwide, and especially in countries where the egg product industry is well developed (Hassan and Aigbodion, 2015). According to Windhorst et al. (2013), approximately 124,800 tons of eggshell waste was produced globally in the year 2010 as a result of industrial egg processing. Furthermore, statistics by the Food and Agricultural Organization (FAO) indicates that the global egg production is likely to hit 86.8 million tons by 2030 (FAO, 2014). The increase in egg production, therefore, means large quantities of eggshell will be produced and disposed of as waste. Thus, it is necessary to find alternative ways to transform eggshell into a valuable item for overcoming environmental challenges. The last reason is it contains highly in CaCO_3 , which can be used as neutralizer or adsorbent.

The aim of this chapter is to evaluate the ES on remediation of the real AMD from the Shimokawa mine tailings. The dose of ES and contact time were changed to identify the optimum.

4.2 Materials and methods

4.2.1 Eggshell preparation and characterization

The ES used in this experiment was collected from kitchen wastes, Japan. The ES samples were then washed several times with distilled water to remove impurities and dirt. The ES was then dried in oven at $40\text{ }^\circ\text{C}$ for 5 days. The dried ES was ground by a mortar and pestle and finally sieved to obtain the desired particle size (75, 150, 250, 500, and $500 - 1000\text{ }\mu\text{m}$). The prepared ES was stored in an air-tight container for future use. The ES powder was analyzed for chemical composition, morphology, and functional group by XRF, SEM-EDX (SSX-550, Shimadzu

corporation, Japan), and DRIFTS (FT/IR-6200HFV with DR PR0410-M attachment, Jasco, Japan), respectively.

4.2.2 Mine water preparation and chemical analysis

Acid mine drainage were prepared by batch leaching of the tailings sample at solid to liquid ratio of 1:10. Ten grams of the tailings were mixed with 150 mL of deionized water (DI) at a speed of 200 rpm at room temperature. After shaking for 24 hours, the pH, EC, and temperature of the leachates were immediately measured, followed by filtration of the leachates through 0.45 μm Millex® filters (Merck Millipore, USA), and then proceeded to the batch adsorption experiments as described in section 4.2.3. The concentrations of heavy metals in the filtrate were determined using ICP-AES. The concentration of Fe^{2+} was determined by using the UV-Spectrometry. The characteristics of the AMD is shown in Table 4. 1.

Table 4. 1 Characteristic of the AMD from the tailings

Parameters	Value
Al	68.4
Ca	324
Mg	75
Mn	19.5
Cd	0.688
Cu	52.4
Zn	515
Fe	218
Fe^{2+}	206
SO_4^{2+}	3,100
pH	3.0
ORP	369

※ All elements are in mg/L except for pH and ORP (mV)

4.2.3 Batch experiments

In order to investigate the effect of the particle size of ES on pH and removal efficiency of heavy metals, 1 g of ES at different particle size (75-1000 μm) and 25 mL of the AMD were mixed in a polypropylene conical tube and then shaken horizontally on a mechanical shaker at a speed of 200 rpm at room temperature for 24 h. The effect of ES dose on the removal efficiency of heavy metals was evaluated by the same procedure at the dose ranging from 0.2 to 2 g. The effect of contact time (5 min - 30 h) on the removal of heavy metals was explored by mixing 25 mL of AMD and 1 g of ES of 150 μm particle size. Then samples were shaken at speed of 200 rpm at room temperature for 24 h.

The removal efficiency, R (%) was calculated based on the difference between the initial and final concentrations as follows:

$$R\% = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (4.1)$$

where, C_i and C_f are the initial and final concentrations (mg/L) in the raw and treated AMD, respectively.

The amount of sorption of heavy metals is the concentration of the metals on ES and can be calculated based on the balance principle:

$$q = \frac{(C_i - C_f) \times V}{m} \quad (4.2)$$

where, q represents the amount of metal uptake per unit mass of the sorbent (mg/g), V is the volume of the solution (L), m is the mass of ES (g).

4.2.4 Sorption isotherm model

Sorption isotherm is a relationship between amount of sorption (mass of solute adsorbed per unit mass of adsorbent) and the equilibrium concentration of the solute remaining in the solution. Although there are many sorption isotherm models, Langmuir and Freundlich models are commonly used for sorption isotherms. Thus, the data from adsorption experiments were fitted with Freundlich and Langmuir isotherms, which were calculated using Eq. (4.3) and (4.4), respectively.

$$q = K_f \times C^{1/n} \quad (4.3)$$

$$q = \frac{q_{\max} \times K \times C}{1 + K \times C} \quad (4.4)$$

where, K_f and n in Eq. (4.3) are empirical constants and K_L and $q_{\max}$ in Eq. (4.4) correspond to the affinity of the adsorbent for the solute of interest (i.e., Cu, Zn, Cd, and Fe) and the maximum sorption capacity of the solid (mg/g), respectively.

The Freundlich isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data (Oke et al., 2008). It can be written in a linear form as follow:

$$\log q = \log K_f + \left(\frac{1}{n} \right) \log C \quad (4.5)$$

Plotting $\log q$ vs $\log C$ gives a straight line. The slope is the value of $1/n$ and the intercept is equal to $\log K_f$.

The Langmuir isotherm is based on three assumptions: sorption cannot proceed beyond monolayer coverage, all surface sites are equivalent and can accommodate at most one sorbed atom; and the ability of a molecule to sorb at a given site is independent of the occupation of neighboring sites (Oke et al., 2008). Rearranging Eq. (4.4) can linearise as follow:

$$\frac{C}{q} = \frac{1}{K_L} C + \frac{1}{K_L \times q_{\max}} \quad (4.6)$$

Plotting C/q vs C gives a straight line, where $1/K_L$ is the slope and $1/K_L q_{\max}$ is the intercept.

4.3 Results and discussion

4.3.1 Characterization of the eggshell

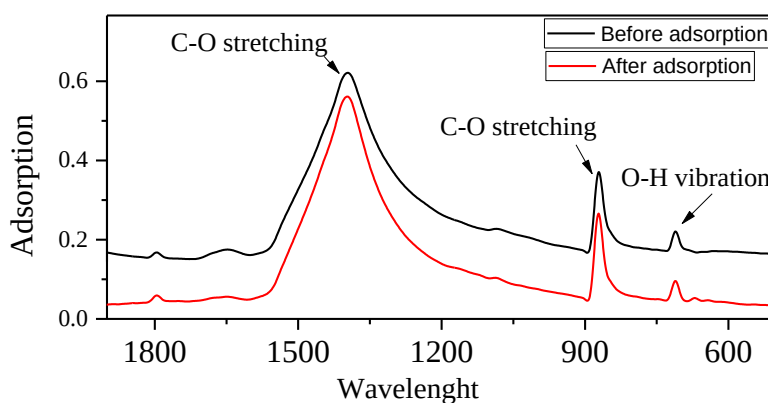
The pH of the eggshell when contacted with deionized water was strong alkaline (pH 10.04). This strong alkali can neutralize AMD.

The XRF results before batch adsorption experiments, in Table 4.2, revealed that the raw ES consisted mainly of CaO (57wt%), which might be CaCO_3 in reality. It decreased after batch adsorption experiments (54wt.%), meaning the dissolution of CaCO_3 in AMD. The increase in weight of Fe_2O_3 and contents of S, Cu, Cd, and Zn after batch adsorption experiments indicated that these elements were precipitated or sorbed onto ES. The similar results were reported by numerous authors (*i.e.*, Yeddou et al., 2007; Zheng et al., 2007; Ahmad et al., 2012; Flores-Cano et al., 2013; Elabbas et al., 2016; Muliwa et al., 2018). The main component of the ES is CaCO_3 , which can be used as a complexing, binding or ion exchange agent for metal ions in wastewater. The CaCO_3 of the ES can neutralize the AMD and then precipitate and adsorb metals onto the ES surface.

Figure 4.1 shows FT-IR spectra recorded in the range of 500 to 2,000 cm^{-1} . A band at 860 and 1,400 cm^{-1} in the ES before and after batch adsorption experiments was ascribed to C-O stretches that confirmed the presence of CaO and CaCO_3 . There is no difference between the ES before and after batch adsorption. This likely means that heavy metals precipitation (amorphous) or adsorb onto the ES might be lower than the detection limits of the machine.

Table 4. 2 Chemical composition of the ES before and after batch adsorption

Composition of ES	Before	After
MgO (wt%)	1.33	1.00
Al ₂ O ₃ (wt%)	0.27	1.00
CaO (wt%)	57.4	54.0
MnO (wt%)	4.42	9.40
Fe ₂ O ₃ (wt%)	0.01	1.00
S (wt%)	0.70	1.20
Cu (mg/kg)	3.10	1,190
Cd (mg/kg)	<0.70	10.0
Zn (mg/kg)	<0.50	4,320

**Figure 4. 1** Functional group of ES before and after experiments

The morphological image and elemental maps of the ES before and after batch adsorption are shown in Fig. 4.2 and 4.3, respectively. The SEM micrograph of ES before batch adsorption illustrates that particles of ES are in irregular shapes and sizes. In addition, the elemental maps showed that the presence of Ca, C, O, Mg, and Na in the original ES sample confirmed CaCO₃ in the form of calcite as the main component in ES (Fig. 4.2). After the ES reacted with the AMD, the SEM micrograph image illustrated that surface of the ES likely appeared to be coated with cracked surface. This might be resulted from oxidation, sorption, and precipitation of contaminants onto its surface. Moreover, elemental maps revealed the presence of new elements, such as Fe, Cu, Zn, Cd, and Mn on the surface of the ES (Fig. 4.3). This confirmed that these elements were removed by the ES.

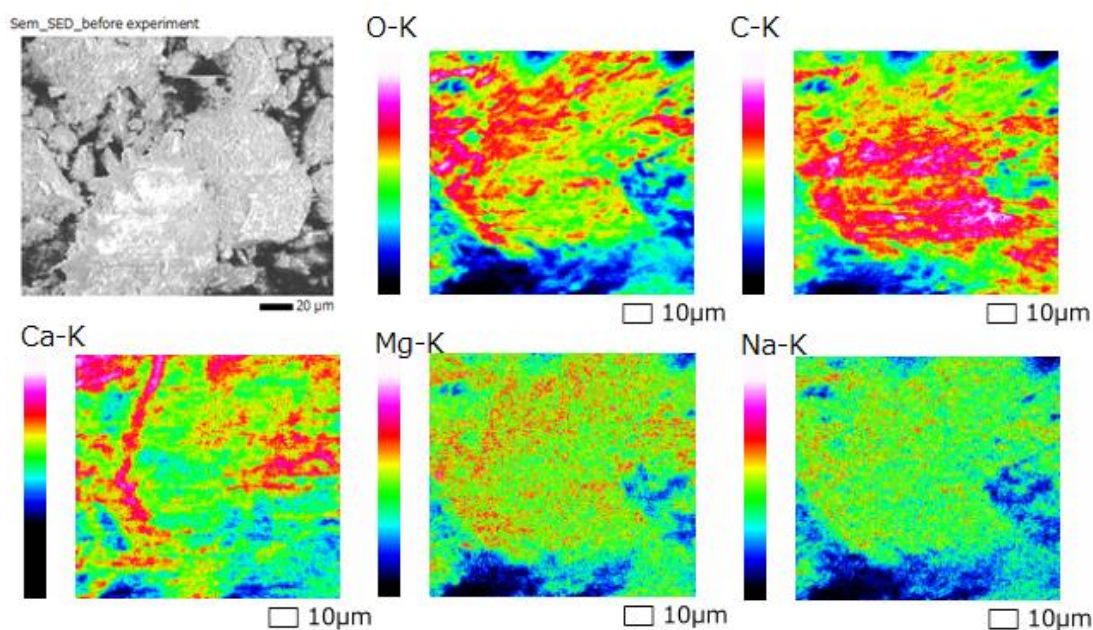


Figure 4. 2 Elemental mapping of the eggshell before batch adsorption

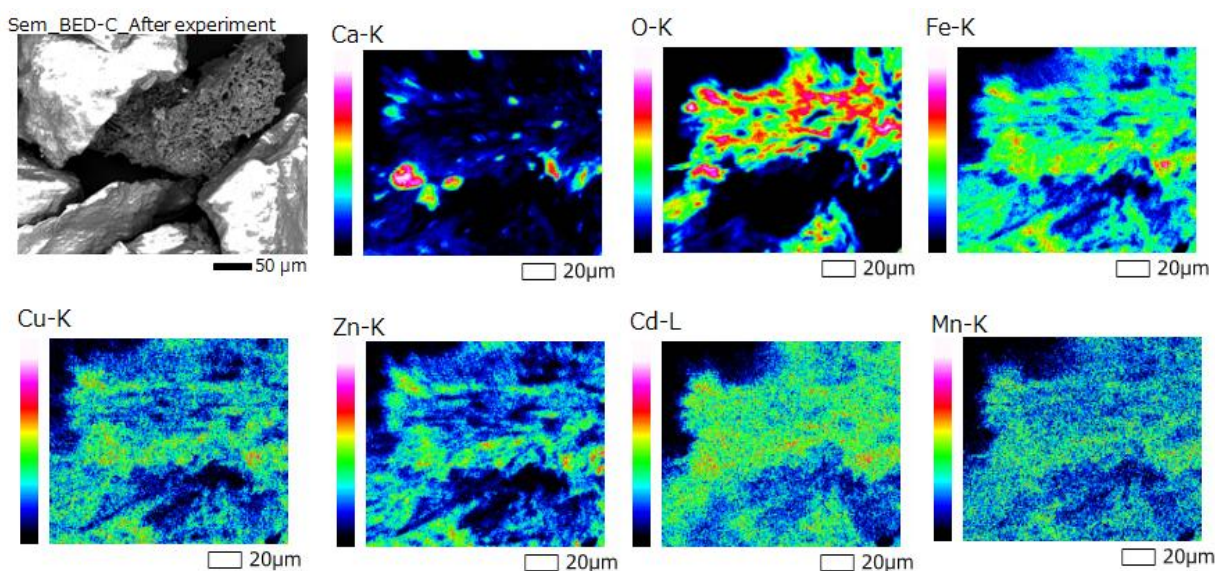


Figure 4. 3 Elemental mapping of eggshell after batch adsorption

4.3.2 Effect of ES particle size on removal efficiency

The particle size of an adsorbent is one of the factors that affect the efficiency of the removal process. Figures 4. 4 (a) and (b) show the effect of the particle size of ES on pH values and the removal efficiency of heavy metals (Zn, Cu, Fe, Cd, and Mn) from the AMD, respectively. The results showed that the pH value and the removal efficiency of heavy metals decreased with increase in particle size. At a fixed ES dose of 1 g, the pH value of the treated water decreased from 6.75 to 6.4, when the particle size range varied between 75 µm to < 1000 µm. The removal

efficiency of the Zn, Cu, Fe, Cd, and Mn decreased from 60 to 40%, 99.98 to 97%, 100 to 98%, 60 to 20%, and 20 to 10%, respectively, in the same order. Notably, for smaller particle size range, there was CO₂ gas accumulating as a result of reaction between CaCO₃ of ES and the acid in water. Smaller ES particle size exhibits large physical surface area, leading to increased dissolution of CaCO₃ in the ES. As a result, acid neutralization and metal precipitation increase and the overall treatment efficiency is enhanced. Moreover, smaller particles are known to exhibit faster reaction, which might play an important role in the sorption and neutralization process (Muliwa et al., 2018).

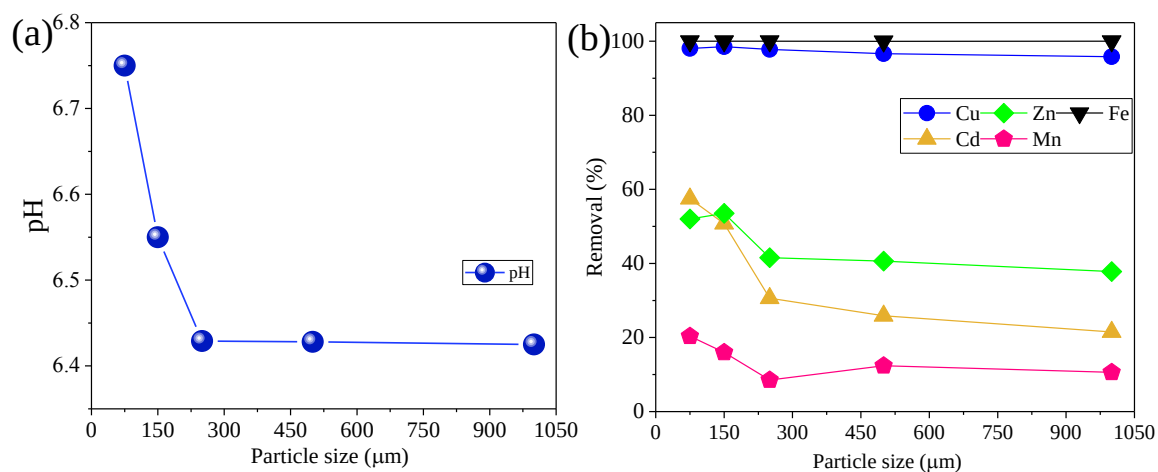


Figure 4. 4 Effect of particle size of ES on (a) pH and (b) removal efficiency of the hazardous metals

4.3.3 Effect of ES mass on removal efficiency of hazardous metals

Solid-liquid ratio is another important variable because it relates to the number of active sites and consequently affects the overall efficiency of the treatment system. Figure 4.5 shows the pH value and removal efficiency of heavy metals with changes in ES mass. The pH value increased from 3 to 6.8 when the ES mass increased from 0.1 to 2 g. Similar to pH change, the removal efficiency of Zn, Cu, Fe, Cd, and Mn increased from 15 to 60%, 30 to 98%, 40 to 99.99%, 10 to 90%, and 5 to 30%, respectively. The high removal of Cu and Fe was attributed to both precipitation and adsorption (as supported by SEM-EDX). Miller et al. (2007) reported that Fe was removed predominantly as their respective hydroxide. Zinc and Cd might be attributed to adsorption onto surface of Fe-oxyhydroxide and ES because the their removal efficiency was likely increased after Cu and Fe were completely removed. However, Mn was partially removed. Emmanuela and Rao (2008) and Edwards et al. (2009) observed that it is difficult to remove Mn, especially in the

presence of high concentrations of other ions. The removal followed the order: $\text{Fe} \geq \text{Cu} > \text{Cd} > \text{Zn} > \text{Mn}$, which corresponded to the electronegativity of the respective ions.

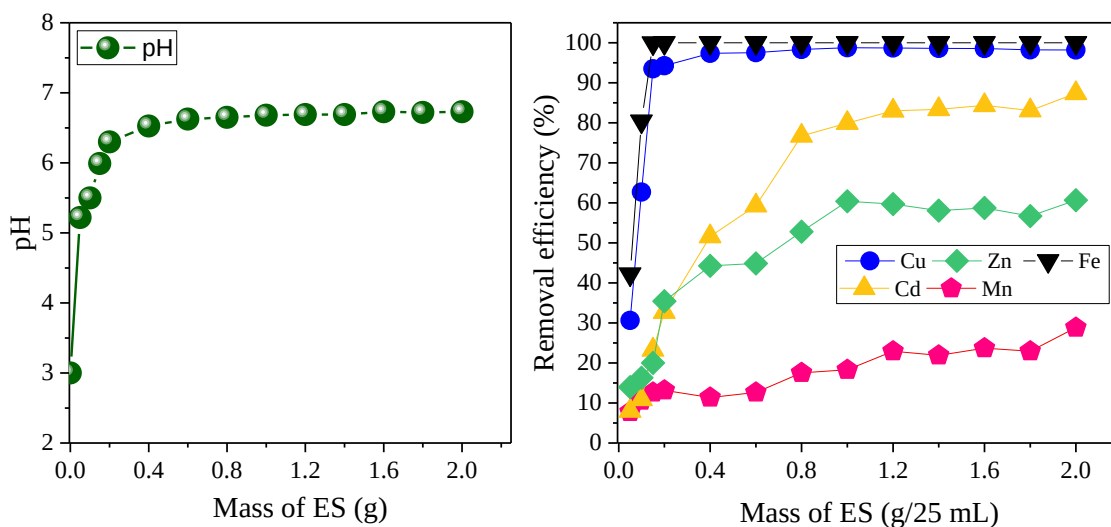


Figure 4. 5 Effect of ES mass on (a) pH and (b) removal efficiency of the heavy metals

4.3.4 Effect of contact time on removal efficiency

Figure 4.6 shows the changes in pH and removal efficiency of heavy metals with time. The pH value increased rapidly from 3 to 5.7 for just 5 min of the experiment and then slightly increased to the almost equilibrium (6.5) at the contact time of 2 h. Iron and Cu were removed rapidly, and 30 and 40 min mixing, respectively, was required to achieve complete removal. The results revealed that Fe and Cu were co-precipitated. Moreover, the faster removal of Cu might be attributed to the lower initial concentration compare to that of Fe.

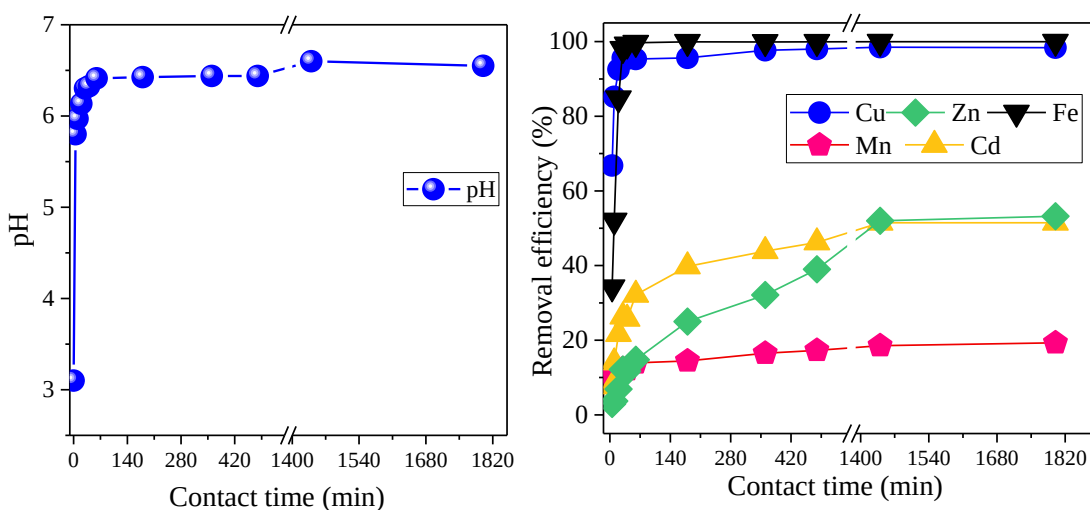


Figure 4. 6 Effect of contact time on (a) pH and (b) removal efficiency of the heavy metals

On the contrary, the sorption of Zn, Cd, and Mn was a slow process and only 47, 50, and 20% removal, respectively, was achieved throughout the experiments. Based on these figures, the rate of Zn and Cd removal was improved after Fe and Cu were completely removed, indicating that Fe precipitates played a role in adsorbing Zn and Cd.

4.3.5 Mechanism of sorption process

Figure 4.7 shows the concentration of Fe and pH with time when the AMD from the tailings is reacted with ES. It was noted that 30 min was needed for raising the pH from 3.0 to 6.0 and for complete removal of Fe. The pH change had 3 stages. During stage 1 the pH increased rapidly from 3.0 to 6.4 when free acid was neutralised. During stage 2 the pH remained constant at 6.4 while Fe^{2+} was being oxidised to Fe^{3+} . During stage 3 the pH increased from 6.4 to 6.6 when the final traces of Fe^{2+} were oxidized and when CO_2 was stripped from solution. Maree et al. (2004) demonstrated that the rate of Fe oxidation was also catalysed by suspended solids when CaCO_3 was used for neutralisation.

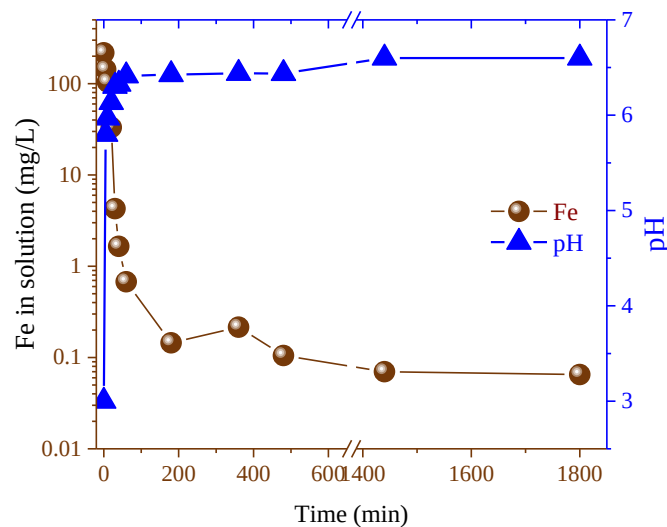


Figure 4. 7 Concentration of Fe and pH changes during the reaction of ES with AMD

Precipitation is a process that involves the formation of precipitates when a solid is formed during chemical reaction. The ES is a kind of low-cost material, which is easily dissolved by acid solution. In this study, the pH of the AMD was 3.0, in which dissolution of the ES likely occurs to provide CO_3^{2-} and Ca^{2+} in solution. These ions are well-known as acid neutralizer and the hydrolysis of CO_3^{2-} in water gives OH^- . The AMD contained 94% of Fe^{2+} . The OH^- enabled the formation of $\text{Fe}(\text{OH})_2$, which was oxidized easily into water insoluble ferrihydrite even just under the air (Li et al., 2018). Thus, the concentration of Fe^{2+} decreased rapidly and became almost

undetectable in 40 min, with color of precipitate changed rapidly from white to yellow. From the results, the main mechanism of metal removal was precipitation. The precipitation mechanism may become important also for the of Zn, Cu, Cd, and Mn. Furthermore, FTIR analysis indicates that the carbonyl (C-O) groups present in the ES are responsible for complexation with metal ions. Following are the reaction likely occurred during the experiments:



4.4 Conclusion

The sorption experiment were conducted as a function of ES doses, ES particle size, and contact time. The pH values increased rapidly at the beginning of batch tests due to the fast dissolution of ES in the acidic condition of the AMD and after two hour progressed, the pH increased at a lower rate until the establishment of the steady state. As a result of adequately mixture of 1 g of ES and 25 mL of the AMD for 24 h, significant concentration decreases were achieved, such as Zn (60.0%), Cu (99.0%), Fe (99.99%), Cd (80%), and Mn (20.0%).

The sorption process was rapid and reached equilibrium within 30 min of Fe, 40 min of Cu, and 24 h of Zn, Cd, and Mn. The mechanism of removal of Zn, Cu, Fe, Cd, and Mn was complex, Fe was mainly precipitated which provided the adsorption surface for Zn, Cu, Cd, and Mn. Zinc, Cd, and Mn also likely adsorbed onto the ES.

Since the material is abundant, low-cost, biodegradable, and has valuable applications in chemistry and chemical technology, further detailed studies on this material may propel its classification as an excellent material in these areas of research.

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CHAPTER 5

GENERAL CONCLUSION AND SUGGESTION FOR FURTHER RESEARCH

5.1 General conclusions

Based on the results from this study, the objectives were achieved by several laboratory experiments, such as batch leaching, acid-bas accounting (ABA), column experiments, and sequential extraction. This dissertation is comprised of 5 chapters in which each methodology and outcome are detailed. Chapter 1 presents the background, importance and objectives of the study. Mine wastes are primary categorized into two: waste rock and tailings. The tailings is a by-products after extraction of valuable minerals and it is slurry originating from the processing of ores and contains abundant amounts of metals, metalloids, sulfates, other salts and minerals, thus posing great pollution risks to the environment. It is well known that the tailings is a main source of heavy metals (*i.e.*, Cu, Zn, Fe) and acid mine drainage (AMD). The AMD containing heavy metals affects the environment physically, chemically, biologically, and ecologically. Numerous researches on AMD remediation have been conducted in both prevention and treatment strategies to solve this problem. However, in order to select appropriate methods for AMD remediation, site characterization (*i.e.*, climate, type of waste, time of disposal), behaviors of AMD and leaching of hazardous metals should be well understood. In addition, research regarding the leaching of hazardous metals from this kind of tailings is lacking in literature and appropriate answer to the question how long it would take to treat the AMD from the tailings still remains unclear. Thus, the factors as well as mechanisms important in the release of heavy metals from this kind of tailings were understood. These factors and mechanisms will be used to predict the period of the acid generation and the release of heavy metals and introduction of an low-cost countermeasure for AMD.

In chapter 2, the tailings was characterized by batch leaching experiment and ABA. Speciation of heavy metals (*i.e.*, Cu, Zn, Fe) was also identified. The tailings samples corresponded to acid generation because the value of NNP was $< -20 \text{ kgCaCO}_3/\text{t}$. The high concentrations of Cu, Zn, and Fe were observed in the deeper tailings than that of the top tailings (weathered tailings). The tailings was under weathered for about 40 years and the weathered tailings was found at the deep of 0.4 m. Within this weathered tailings, the water-soluble fraction of Zn, Cu, and Fe were almost flushed out, whereas their poorly crystalline and crystalline fractions were formed, indicating that the secondary minerals likely form as Fe-oxyhydroxides. Zinc, Cu, and Fe in the weathered tailings were mainly bounded to the poorly crystalline, crystalline, and sulfide fraction

while those of the deeper tailings were bounded to water soluble and sulfide fraction. This means that the tailings will likely to continue to produce AMD containing Cu, Zn, and Fe for a long period of time unless remedial measures are taken.

After identifying the high content of hazardous metals in the deeper tailings, their long-term leaching behaviors were studied by using three columns at different irrigation rates. The pH was acidic and did not significantly fluctuate throughout the duration of the column experiments. The highest irrigated rainfall played an important role in diluting the concentrations of heavy metals in the leachates as well as pH values and promoted faster precipitation of secondary minerals. The cyclic wetting and drying can result in dramatic seasonal variation in acidity and heavy metals loads, especially after first flushing. The concentrations of Zn, Cu, and Fe were higher in the deeper tailings inside the column, which suggests that other minerals may restrict its solubility. The main release mechanisms for Zn, Cu, and Fe seem to be easy dissolution of more labile species (ion exchangeable and sulfates) and oxidation of the remaining sulfide minerals in the tailings. The oxidation of pyrite to sulfate releases dissolved ferrous iron and acidity into the water. The ferrous iron precipitates as iron oxyhydroxides/ferrihydrite, maghemite, lepidrocrocite, and goethite. These minerals could act as a sink for Zn and Cu to co-precipitation or adsorption. The fraction controlling mobilization of Zn, Cu, and Fe was likely to be the ion exchangeable and sulfide fractions, and Zn was mobilized faster than Cu in the effluents from the tailings. The releasing rate of these elements was in order $\text{Zn} > \text{Cu} > \text{Fe}$. On the other hand, significant amounts of pyrite and sulfide fraction of Zn, Cu, and Fe remained at the end of the experiments. This suggests that pyrite and other sulfide minerals continue to be oxidized, producing acidic water containing Zn and Cu for some time. The weathered tailings after 84 weeks of the experiments was observed at the depth of 1.2 cm from the top and 9 cm around the wall of the tailings, which well almost agreed with weathered tailings at the field observation. The column experiments can mimic the actual situation of the actual tailings.

In Chapter 4, the effects of ES doses, ES particle size, and contact time on AMD neutralization and metal removal were evaluated. The pH values increased rapidly at the beginning of the batch adsorption tests due to the fast dissolution of ES in the acidic condition of the AMD, and after two hours the dissolution progressed at a lower rate until the establishment of steady state. As a result of adequately mixture of 1 g of ES and 25 mL of the AMD for 24 h, significant removal of Zn (60.0%), Cu (99.0%), Fe (99.99%), Cd (80%), and Mn (20.0%) was achieved. The sorption process was rapid and reached equilibrium within 30 min of Fe, 40 min of Cu, and 24 h of Zn, Cd, and Mn. The mechanism of removal of Fe, Cu, Zn, Cd, and Mn was complex. Iron was mainly precipitated, which provided the surface for Cu, Zn, Cd, and Mn adsorption. Zinc, Cd, and Mn were

also likely to be adsorbed onto the ES. The rapid recovery of pH values and decreases in the concentrations of heavy metals after performing batch tests in the study revealed the applicability and removal efficiency of ES as a low-cost material for remediation of abandoned mining sites. Moreover, it could contribute to the environmentally friendly disposal of AMD. Since the material is abundant, low-cost, biodegradable, and has valuable applications in chemistry and chemical technology, further detailed studies on this material may propel its classification as an excellent material in these areas of research.

5.2 Suggestions for future research

At circumneutral pH, the oxidation rate of sulfide minerals is chemically controlled and usually very slow. However, at low pH, the oxidation rate is microbiologically controlled and can be accelerated by iron- and/or sulfur-oxidizing microbes by up to six orders of magnitude. In this research, it is still doubtful that the mechanism of pyrite oxidation may be involved not only by exposure to atmospheric O₂ and dissolved O₂ but also by microorganism at the site. Therefore, microorganisms involved in sulfide oxidation should be identified and this may lead to a more understanding of factors in response to leaching and mineral precipitation in the actual tailings.

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