Development of a Sustainable Process Based on Carrier-microencapsulation to Suppress the Formation of Arsenic-containing Acid Mine Drainage from Arsenopyrite

Ilhwan Park
Candidate for the Degree of Doctorate in Engineering
Supervisor: Professor Naoki Hiroyoshi
Division of Sustainable Resources Engineering

Introduction

Arsenopyrite (FeAsS), the most common primary arsenic (As)-bearing sulfide mineral in nature, plays an important role in the release of As into the environment. When exposed to atmospheric conditions either naturally or via anthropogenic activities like mining, mineral processing, metallurgy, and underground space developments, it is readily oxidized by oxygen (O$_2$) and/or ferric ion (Fe$^{3+}$) in the presence of water as illustrated by the following equations:

$$4\text{FeAsS(s)} + 11\text{O}_2$$\text{(aq)} + 6\text{H}_2\text{O} = 4\text{Fe}^{2+}$$\text{(aq)} + 4\text{H}_3\text{AsO}_3$$\text{(aq)} + 4\text{SO}_4^{2-}$$\text{(aq)} \quad (1-1)$$

$$\text{FeAsS}(s) + 11\text{Fe}^{3+}$$\text{(aq)} + 7\text{H}_2\text{O} = 12\text{Fe}^{2+}$$\text{(aq)} + \text{H}_3\text{AsO}_3$$\text{(aq)} + 4\text{SO}_4^{2-}$$\text{(aq)} + 11\text{H}^{+}$$\text{(aq)} \quad (1-2)$$

Arsenic is a strictly regulated substance because of its potential to cause numerous diseases like hyperpigmentation, keratosis, anemia, neuropathy, and several types of cancers even at minute amounts (Boddu et al., 2008; Mohan and Pittman, 2007). Moreover, the oxidation of arsenopyrite generates acid mine drainage (AMD), a serious environmental problem encountered by the mining and mineral processing industries throughout the world because of its extremely low pH (less than pH 3) and elevated concentrations of hazardous heavy metals (e.g., cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn)) (Johnson and Hallberg, 2005).

To mitigate these problems caused by arsenopyrite, this study investigated carrier-microencapsulation (CME), a process that suppresses arsenopyrite oxidation by forming surface protective coatings on the mineral. This technique uses a redox-sensitive organic compound to carry and deliver the coating material, usually an insoluble metal(loid) ion, preferentially to the surface of sulfide mineral where it is adsorbed and oxidatively decomposed. As a consequence of the complex decomposition, the relatively insoluble metal ion is freed, thus rapidly precipitating and forming a protective coating on the mineral surface. The primary advantage of this technique compared with other microencapsulation techniques is its ability to specifically target sulfide minerals even in complex systems because the oxidative decomposition of the complex occurs only on the surfaces of minerals that dissolve electrochemically like most of the sulfide minerals (Crundwell, 1988; Rimstidt and Vaughan, 2003).

The original CME study of Satur et al. (2007) used Ti-catecholate complex (i.e., [Ti(cat)$_3$]$_2^{2-}$) that could suppress the oxidation of pyrite by forming Ti-oxyhydroxide coating on it. However, the mechanisms involved in this process remain unclear due to the lack of understanding of how the Ti-catecholate complex is oxidatively decomposed. Moreover, the applicability of CME for arsenopyrite has not yet been studied. Thus, the objectives of this study are four-fold: (1) to elucidate the mechanisms involved in Ti-based CME in detail, (2) to apply Ti-based CME to arsenopyrite, (3) to improve the practicality of CME, and (4) to develop a sustainable process based on CME to prevent the formation of As-containing AMD from arsenopyrite.

Suppression of the Release of Arsenic from Arsenopyrite by Carrier-microencapsulation using Titanium-catecholate complex

Arsenopyrite oxidation causes the release of toxic arsenic into the environment as well as the acidification of receiving water. To limit these problems caused by arsenopyrite oxidation, CME using Ti-catecholate complex was studied.

Ti-catecholate complex, [Ti(cat)$_3$]$_2^{2-}$, was successfully synthesized by rapid neutralization of acidic Ti$^{4+}$ and catechol solution to pH > 5 and then used for treating arsenopyrite. Figure 1 shows the leaching results of arsenopyrite using deionized (DI) water, catechol only, and Ti-catecholate solution. The amount of As released from arsenopyrite was lower in Ti-catechol solution (CME) compared with the other two cases (Figure 1c). The pH was also higher in CME than those of control and catechol solution while Eh was the lowest (Figures 1a and 1b). These results suggest that the substantial decrease in As release from arsenopyrite could be attributed to passivation of the mineral itself by Ti-catecholate complex. The passivation of arsenopyrite was closely related to Ti$^{4+}$ precipitation that was apparent in the concentration decrease of dissolved Ti with time, which was not observed in Ti-catecholate solution without arsenopyrite (Figure 1d). Surface characterizations using scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and diffuse reflectance infrared Fourier transform
spectroscopy (DRIFTS) indicated that the surface of arsinepyrite was covered with Ti-oxyhydroxide.

Based on these findings, a detailed mechanism of Ti-based CME was proposed as illustrated in Figure 2. Ti(IV) tris-catecholate complex is adsorbed on the surface of arsinepyrite where it is partially decomposed and forms an intermediate coating. This intermediate is further decomposed and releases “free” Ti⁴⁺ that is precipitated and forms Ti-oxyhydroxide coating protecting arsinepyrite against further oxidation.

Figure 1. Leaching of arsinepyrite in DI water (control), catechol only, and Ti-catechol complex (CME): evolution of (a) pH and (b) Eh, and changes in the concentrations of (c) As and (d) Ti with time.

Figure 2. The schematic diagram of a proposed mechanism of Ti-based CME.

Improvements in the Kinetics of Titanium-based Carrier-microencapsulation

Although Ti-based CME could suppress arsinepyrite oxidation by forming a surface protective layer on its surface, it requires long-term treatment at least 14 days to create coatings thick enough to be effective, which makes Ti-based CME impractical. To overcome this limitation, the effects of temperature and chemical additives on the kinetics of Ti-based CME were investigated.

Figure 3 shows the leaching results of arsinepyrite using Ti-catechol solution at various temperatures. The suppressive effects of arsinepyrite oxidation was achieved early at higher temperature (Figure 3a), which is most likely attributed to the faster complex decomposition/coating formation as shown in Figure 3b.

As another option, the utilization of Cu²⁺ in Ti-based CME was investigated because Cu²⁺ may have an ability to accelerate the complex decomposition by changing the surface property of sulfide minerals (Chandraprabha et al., 2005; Guongming and Hongen, 1989). As shown in Figure 4, the release of As from arsinepyrite was suppressed in the presence of Cu²⁺ while the precipitation of Ti⁴⁺ was promoted. At the same time, Cu²⁺ was also precipitated and SEM-EDX analysis of arsinepyrite treated with Cu²⁺ confirmed that on the surface of arsinepyrite, there were particulates mainly composed of Cu and S with low signals of Fe and As, which indicated the adsorption of Cu²⁺ on the surface of arsinepyrite as CuS-like compound.

Figure 3. Leaching of arsinepyrite in Ti-catechol solution under various temperature: changes in the concentration of (a) As and (b) Ti with time.

Figure 4. Leaching of arsinepyrite in Ti-catechol solution with and without Cu²⁺: changes in the concentration of (a) As and (b) Ti & Cu with time.

When copper sulfides (e.g., chalcocite (Cu₂S) and covellite (CuS)) and arsinepyrite are in contact, a galvanic cell would be formed, where copper sulfide with a lower rest potential acts as an anode and is preferentially dissolved while the arsinepyrite with a higher rest potential
behanes like a cathode and is galvanically protected (Allison et al., 1972). According to Walker et al. (2006), anodic half-cell reaction of arsenopyrite oxidation is the rate-determining step. The anode property of arsenopyrite was changed in the presence of Cu\(^{2+}\) due to the formation of CuS-like compounds on arsenopyrite surface, and thereby the rate of Ti-catecholate complex decomposition was most likely accelerated (Figure 4b).

**A New Complex-based Carrier-microencapsulation: The Decomposition Mechanism of Aluminum-catecholate Complexes, and Its Application to Suppress Arsenopyrite Oxidation**

The high stability of [Ti(cat)]\(^3^-\) could be considered as a main reason why its decomposition kinetics was slow, which delayed the formation of Ti-oxyhydroxide coating. Although the coating formation by Ti-based CME could be accelerated by either increasing temperature or utilizing chemical additives, these approaches have less practicality. To accelerate coating formation and improve the practicality of CME, thus, a new metal-catecholate complex that is easily synthesized and more readily decomposed is required as an alternative.

Al-catecholate complexes are promising candidates because according to Xu (2013), the cross-linking strength between metal and catechol weakens as oxidation state of the metal atom decreases. In other words, Al\(^{3+}\)-catecholate complexes are theoretically easier to decompose oxidatively compared with Ti\(^{4+}\)-catecholate complex, which could accelerate coating formation. Moreover, Al is ubiquitous in nature, which makes it a good candidate material for the complex synthesis.

As shown in Figure 5, three types of complex species were formed depending on the pH: (1) [Al(cat)]\(^+\) between 4.7 and 5.5, (2) [Al(cat)_2]\(^+\) between 5.5 and 8.5, and (3) [Al(cat)_3]\(^3^-\) between 8.5 and 14. To investigate the effects of each complex species on arsenopyrite oxidation, three types of Al-catecholate solutions were prepared at pH 5, 7, and 10, and then used for leaching experiments (Figure 6). Substantial changes in pH and Eh in arsenopyrite suspensions were apparent after 7 days of leaching, regardless of the complex species used (Figures 6a and 6b). The concentrations of dissolved Fe, As, and S released from arsenopyrite were lower in the presence of [Al(cat)]\(^+\) compared with those of [Al(cat)_2]\(^+\) and [Al(cat)_3]\(^3^-\) (Figure 6c). Dissolved S concentration, an indicator of the extent of sulfide oxidation (Bonnissel-Gissinger et al., 1998), was 13 mg/L in [Al(cat)]\(^+\), which was around four- and nine-fold lower than those in [Al(cat)_2]\(^+\) and [Al(cat)_3]\(^3^-\), respectively. These results also coincided well with the order of decline in dissolved Al: [Al(cat)]\(^+\) > [Al(cat)_2]\(^+\) > [Al(cat)_3]\(^3^-\) (Figure 6d). This indicates that Al-catecholate complex becomes more difficult to decompose as the number of ligands coordinated with Al\(^{3+}\) increases.

![Figure 5](image1.png)  
**Figure 5.** Characterization of Al-catecholate complexes: speciation diagram of (a) Al\(^{3+}\) only ([Al\(^{3+}\)]: 1 mM) and (b) Al\(^{3+}\)-catechol system ([Al\(^{3+}\)]: 1 mM, [H\(_2\)Cat\(^-\)]: 3 mM) (Nurchi et al., 2009), (c) solubility of Al\(^{3+}\) with pH in the absence and presence of catechol, and (d) UV-vis spectra of catechol only and Al-catecholate solution at pH 5, 7, and 10.

![Figure 6](image2.png)  
**Figure 6.** Effects of Al-catecholate complexes on the oxidation of arsenopyrite: evolution of (a) pH and (b) Eh, and changes in (c) dissolved Fe, As and S concentrations, (d) dissolved Al concentration. Note: [Al\(^{3+}\)] = 5 mM; [H\(_2\)Cat\(^-\)] = 15 mM; [Cl\(^-\)]\(_{tot}\) = 15 mM; leaching time = 7 days; pH = 5, 7 and 10 for [Al(cat)]\(^+\), [Al(cat)_2]\(^+\) and [Al(cat)_3]\(^3^-\), respectively.

After CME treatment of arsenopyrite using [Al(cat)]\(^+\), the residue was analyzed by X-ray photoelectron spectroscopy (XPS) to characterize the nature of coating formed on it. As shown in Figure 7, XPS spectrum (Al 2p) of the control has no distinct peak while the spectrum of CME-treated arsenopyrite shows a broad peak centered at around 75 eV. Deconvolution of this peak using a Gaussian-Lorentzian function indicates that it has two Al 2p transitions at 74.6 and 75.3 eV, respectively. According to
Kloprogge et al. (2006), the former is associated with bayerite (γ-Al(OH)₃) and the latter is most likely its amorphous phase. XPS spectrum (O 1s) of CME-treated arsenopyrite shows two O 1s transitions at 532.1 and 533.1 eV, respectively, most likely attributed to the hydroxyl groups in the crystal structure of bayerite (i.e., Al–O–H) and adsorbed water on the surface (H–O–H) (Kloprogge et al., 2006). In contrast, XPS spectrum (O 1s) of the control shows an additional peak of O(–II), indicating that arsenopyrite oxidation has proceeded to much greater extent compared with CME-treated arsenopyrite (Nesbitt et al., 1995).

Based on these findings, a detailed mechanism of Al-based CME was proposed as illustrated in Figure 8. Al-catecholate complexes are adsorbed on arsenopyrite surface where it is sequentially decomposed and releases “free” Al³⁺ that is precipitated and forms Al-oxyhydroxide coating.

**Figure 7.** XPS spectra of arsenopyrite treated with control and CME for (a) Al 2p and (b) O 1s.

**Figure 8.** The schematic diagram of a proposed mechanism of Al-based CME.

**General Conclusions**

This dissertation aims at developing a sustainable process based on CME to suppress the formation of As-containing AMD from arsenopyrite. Taking all of these findings into consideration, a more sustainable process that would prevent As-containing AMD from mine wastes was proposed as illustrated in Figure 9. After mining and mineral processing, the mine wastes containing problematic minerals like pyrite and arsenopyrite are treated with metal-catecholate complexes. Afterwards, the suspension goes to thickener to separate solid and liquid. In the case of solids, it is disposed of into the tailings dam where AMD will not be generated due to the formation of surface protective coatings on sulfide minerals. In the case of liquid, it contains organic compounds, which can be regenerated by electrolysis. After CME treatment, thus, wastewater undergoes regeneration process and afterward it would be reused for the treatment, which makes this process more cost-effective and sustainable.

**Figure 9.** The proposed process based on CME for treating mine wastes.

**References**


