Microencapsulation for Suppressing Acid Mine Drainage Formation: Applications in Mineral Processing and Metallurgical Operations

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Abstract

Acid mine drainage (AMD, and acidic leachate generated by the oxidation of sulfide minerals and enriched with toxic metal(loid)s, recognized as a persistent and widespread environmental threat to the mining industry. To suppress the AMD formation, microencapsulation techniques that limit the oxidation of AMD-forming minerals by creating surface protective coatings have been developed. Microencapsulation using aluminum (Al)-catecholate complexes created Al-oxyhydroxide coatings on the arsenopyrite surface, resulting in an approximately 70% reduction in arsenopyrite oxidation compared to the uncoated sample. In addition, the application of microencapsulation techniques has been proven effective in improving mineral processing and hydrometallurgical processes.

Keywords: Acid mine drainage, microencapsulation, sulfide passivation

Introduction

Mining and processing are essential activities for metal production, which is indispensable for sustaining modern living standards. However, these anthropogenic activities have resulted in the generation of large amounts of wastes, such as mine tailings. As a simple example, processing a copper (Cu) ore with a grade of 0.5% Cu, assuming 100% Cu recovery and a concentrate grade of 30%, would generate approximately 98.3 t of tailings per 100 t of ore processed. Since tailings generally have no economic value, they are disposed of in the tailings storage facilities (TSFs) located near mine sites. In TSFs, non-valuable sulfide minerals such as pyrite (FeS_2) and arsenopyrite (FeAsS) undergo oxidation upon exposure to oxygen and water, leading to the formation of acid mine drainage (AMD) – an acidic effluent enriched with toxic metal(loid) s. If not properly treated, AMD can cause severe environmental impacts on receiving water bodies.

The most widely used AMD treatment technique is chemical neutralization, in which AMD is mixed with alkaline materials (e.g., limestone ($CaCO_3$), quicklime (CaO), and slaked lime ($Ca(OH)_2$)) to increase the pH and induce the precipitation of metal ions (Johnson and Hallberg, 2005). This approach can be applied to a wide range of AMD conditions regardless of flow rate and water chemistry (Taylor *et al.*, 2005). However, AMD formation generally lasts for several decades to millennia, necessitating long-term treatment and resulting in high operational costs due to the continuous consumption of neutralizing agents and energy (Tabelin *et al.*, 2022). Furthermore, the generation of large volumes of sludge poses an additional challenge.

To overcome the above-mentioned drawbacks of chemical neutralization, microencapsulation (ME) techniques have been investigated to suppress AMD formation by passivating AMD-forming minerals. Microencapsulation is a technique that forms coatings to protect the core materials (e.g., particles or droplets) from environmental factors (e.g., light, moisture, temperature, and oxygen), extend shelf-life, and improve the release properties of core material (Jyothi *et al.*, 2012; Peanparkdee *et al.*, 2016). The first application of ME technique for suppressing AMD formation was reported by Evangelou (1995), who attempted to passivate pyrite using phosphate ions and hydrogen peroxide. Following ME treatment, the pyrite surface was coated with a ferric phosphate layer, effectively suppressing its oxidation.

The authors' research group has developed an advanced ME technique, termed carrier microencapsulation (CME), which utilizes metal–organic complexes to form metal oxyhydroxide coatings on the surfaces of AMD-forming minerals (Jha *et al.*, 2012; Li *et al.*, 2019, 2021; Park *et al.*, 2018a, 2018b, 2021; Satur *et al.*, 2007). A key advantage of this technique is its ability to selectively target electrochemically reactive minerals, particularly sulfide minerals, thereby reducing unnecessary reagent consumption in complex systems such as tailings. In this paper, CME technique for passivating pyrite and arsenopyrite to suppress AMD formation is introduced. Furthermore, its potential applications not only in supressing AMD formation but also in improving the efficiency of mineral processing and metallurgical operations are discussed.

Microencapsulation for the Suppression of AMD Formation

In CME, various metal ions (e.g., Ti^{4+}, Si^{4+}, Fe^{3+}, and Al^{3+}) complexed with organic ligand – pyrocatechol (1,2-dihydroxylbenzene, $C_6H_4(OH)_2$) – forming metal-organic complexes $[Me(cat)_n]^{m-2n}$; where Me: metal ion, cat: catechol, m: valency of metal ion (3 for Fe^{3+} and Al^{3+}; 4 for Ti^{4+} and Si^{4+}), n: the number of catechol molecules complexed) have been examined to suppress the oxidation of pyrite and arsenopyrite (Jha *et al.*, 2012; Li *et al.*, 2019, 2021; Park *et al.*, 2018a, 2018b, 2021; Satur *et al.*, 2007). Among them, this paper introduces CME using aluminum (Al)-catecholate complexes to passivate arsenopyrite. Figure 1 shows the working principle of CME on how Al-catecholate complexes passivate sulfide minerals.

As can be seen, Al-catecholate complexes are electrochemically sensitive, and thus they are oxidatively decomposed on the surface of semiconducting minerals like arsenopyrite (Eqs. 1–3):

$$[Al(cat)_3]^{3-} \rightarrow [Al(cat)_2]^{-} + Q + 2e^{-} \qquad (1)$$
$$[Al(cat)_2]^{-} \rightarrow [Al(cat)]^{+} + Q + 2e^{-} \qquad (2)$$
$$[Al(cat)]^{+} \rightarrow Al^{3+} + Q + 2e^{-} \qquad (3)$$

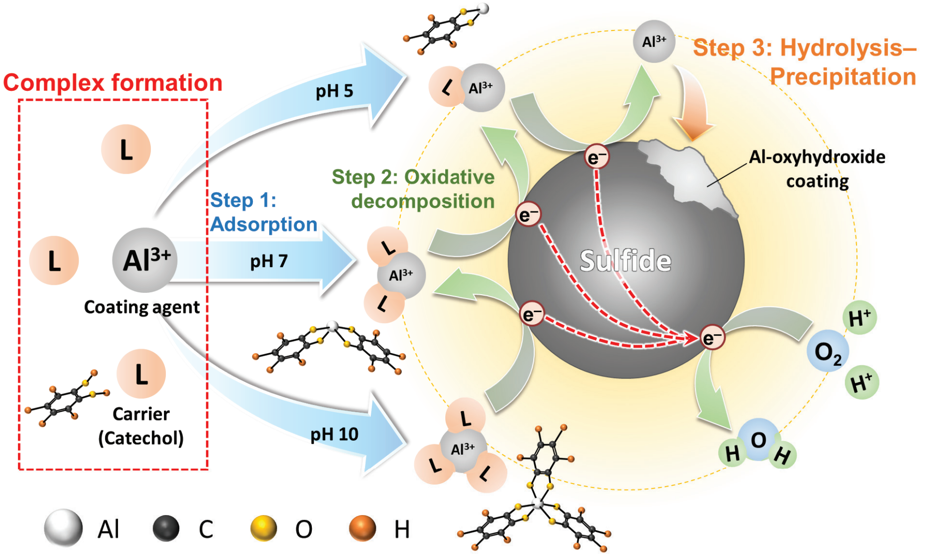

Figure 1 A schematic illustration of CME technique for sulfide passivation. Reproduced with permission from Park et al., 2018b.

where Q denotes 1,2-benzoquinone ($C_6H_4O_2$) – an oxidation product of catechol. As a result, Al^{3+} is released from the complex and precipitated as Al-oxyhydroxide under appropriate pH conditions (i.e., pH 5–8) (Eq. 4).

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+ \quad (4)$$

Through the complex decomposition followed by metal precipitation reactions, sulfide minerals are passivated by Al-oxyhydroxide coatings.

Figure 2(a) shows the changes in dissolved Al concentration after CME treatment of arsenopyrite using 5 mM Al^{3+} in the form of mono-, bis-, and tris-catecholate complexes, which predominantly form at pH 5, 7, and 10, respectively. The amounts of Al^{3+} precipitated after CME treatment were 83 mg/L for $[Al(cat)]^+$, 53 mg/L for $[Al(cat)_2]^-$, and 10 mg/L for $[Al(cat)_3]^{3-}$. This trend indicates that increasing catecholate coordination number decreases Al precipitation due to the enhanced stability and solubility of higher-order Al-catecholate complexes. The concentrations of Fe, As, and S released from arsenopyrite during CME treatment increased in the order $[Al(cat)]^+ < [Al(cat)_2]^- < [Al(cat)_3]^{3-}$ (data not shown), indicating that a strong correlation between the amount of Al precipitated and the suppression of arsenopyrite oxidation. These results suggest that among the three complex species, $[Al(cat)]^+$ is the most effective one in suppressing the arsenopyrite oxidation.

In addition to the complex species, the complex concentration also showed a significant effect on arsenopyrite oxidation; specifically, the release of S from arsenopyrite decreased from ≈90 mg/L with no complex to <10 mg/L with 15 mM $[Al(cat)]^+$, due to the greater amount of coating formed at higher complex concentrations (date not shown).

Figure 2(b) shows the XPS Al 2p spectra of untreated and CME-treated arsenopyrite using $[Al(cat)]^+$. The Al 2p spectrum of untreated arsenopyrite showed no discernible peak, whereas three distinct peaks corresponding to boehmite (γ-AlO(OH)) at 73.9 eV, gibbsite (γ-$Al(OH)_3$) at 74.3 eV, and bayerite (γ-$Al(OH)_3$) at 74.8 eV were observed for the CME-treated arsenopyrite. These results indicate that Al-based CME forms Al-oxyhydroxide coatings on the arsenopyrite surface.

The effect of CME treatment on suppressing arsenopyrite oxidation was evaluated by a weathering cell test. The procedure for the weathering cell test followed that described by Bouzahzah *et al.* (2014). Two samples were tested: (i) arsenopyrite leached in deionized (DI) water for 7 days (control), and (ii) arsenopyrite treated with 15 mM $[Al(cat)]^+$ for 7 days. As shown in Fig. 2(c), both samples continued to oxidize, releasing sulfur species into the leachate; however, the extents of dissolved S release differed significantly between the two. After 6 weeks of the weathering cell tests, the cumulative S concentration reached ≈700 mg/L for the control and ≈200 mg/L for the CME-treated sample; that is, CME treatment suppressed arsenopyrite oxidation by approximately 70%.

Application of Microencapsulation in Mineral Processing and Metallurgical Operations

As confirmed in the previous section, the ME technique is effective in suppressing the oxidation of AMD-forming minerals. Although the ME technique can be applied to wastes generated after mineral processing and metallurgical operations, its optimum application would be prior to ore processing, aiming to separation and extraction efficiencies while simultaneously suppressing AMD formation. In the subsequent sub-sections, the application of the ME technique to coal cleaning and gold hydrometallurgy is presented.

Microencapsulation for Coal Cleaning

Pyrite is a common gangue mineral associated with coal and is removed by gravity concentration technique like jigging due to the different specific gravities of pyrite (≈5 g/cm^3) and coal (1.1–1.5 g/cm^3). The appropriate particle size for coal cleaning by the conventional jig is > 10 mm, so its efficiency dramatically decreased when processing 1 mm size fraction (Phengsaart *et al.*, 2023).

To improve the separation efficiency of fine particles, the authors developed the hybrid

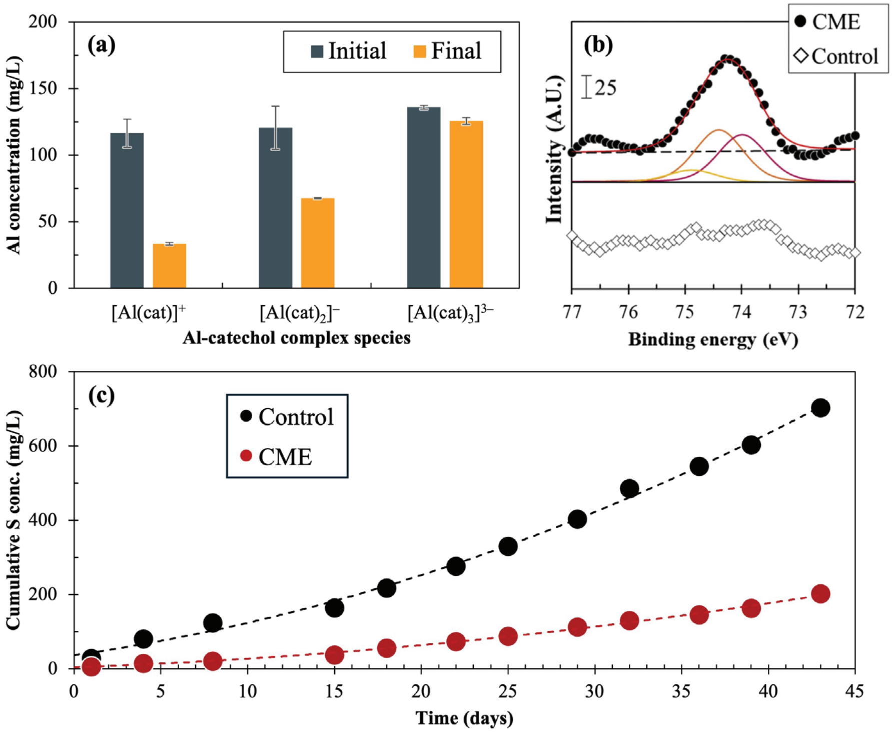

Figure 2 (a) Changes in dissolved Al concentration before and after CME treatment, (b) XPS Al 2p spectra of untreated and CME-treated arsenopyrite, and (c) weathering cell test results of control and CME-treated arsenopyrite. Reproduced with permission from Park et al., 2018b, 2020.

jig, which combines the principles of jigging and flotation (i.e., jigging while introducing air) (Hori *et al.*, 2009). In order for hybrid jig to work, air bubbles should be selectively attached to coal particles. However, the selective bubble attachment is impossible due to the fact that both coal and pyrite are inherently hydrophobic. To overcome this problem, ME treatment was applied to selectively render pyrite hydrophilic, while coal particles remain hydrophobic to be able to attach air bubbles (Phengsaart *et al.*, 2023). Pyrite and coal were each treated with a solution containing 1 mM ferrous (Fe^{2+}) and phosphate (PO_4^{3-}) ions at pH 3 for 1 h. Ferrous ions are selectively oxidized to ferric ions on the pyrite surface, after which ferric ions react with phosphate ions to precipitate as ferric phosphate.

The XPS analysis of untreated and ME-treated pyrite and coal showed that the peaks of Fe(III–PO_4 and P(V–O were observed only in the spectrum of ME-treated pyrite. Figure 3 shows the distribution of coal and pyrite (particle size: −1.4+1.0 mm) in each layer after conventional jig, hybrid jig and hybrid jig with ME treatment. The conventional jig result at the separation time of 0.5 min (Fig. 3(a-1)) showed that pyrite content in the middle layer was ≈11%. Although pyrite content in the middle layer decreased to 4.2% by extending the separation time to 5 min, the sulfur content of the product exceeded the criterion for low-sulfur coal (Fig. 3(b-1)). In the case of hybrid jig, the result was worse compared to the conventional jig due to non-selective bubble attachment (Figs. 3(a-2) and 3(b-2)). When ME treatment was applied, however, the efficiency of hybrid jig separation was improved (Figs. 3(a-3) and 3(b-3)); that is, pyrite content in the middle layer was 1% and 0% at the separation time of 0.5 min and 5 min, respectively, indicating low-sulfur coal could be produced by ME treatment followed by hybrid jig separation and the separation time can be shortened.

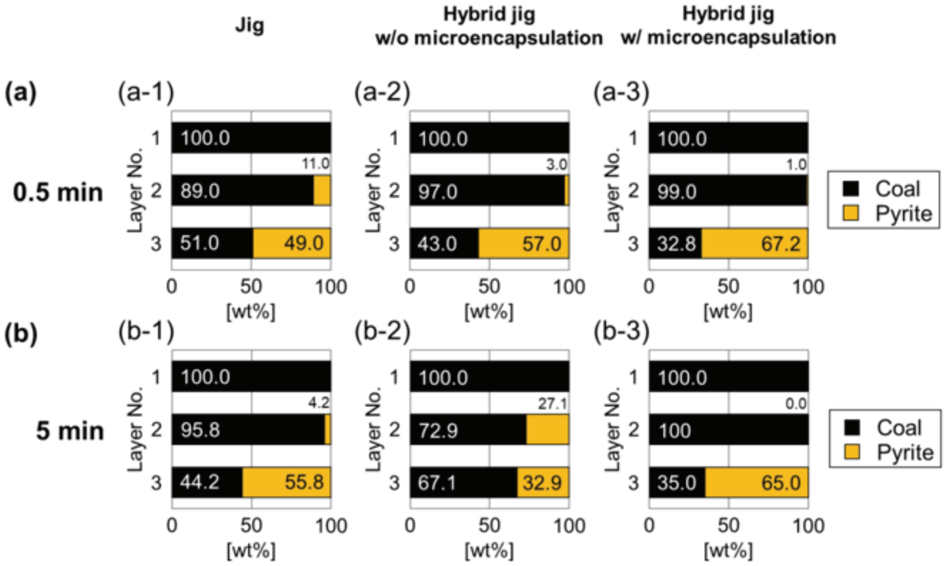

Figure 3 *Distribution of coal and pyrite in each layer after jig separation for 0.5 min (a-1) and 5 min (b-1), hybrid jig separation for 0.5 min (a-2) and 5 min (b-2), and hybrid jig separation with ME treatment for 0.5 min (a-3) and 5 min (b-3) (Phengsaart et al., 2023).*

Microencapsulation for Gold Hydrometallurgy

The conventional method to extract gold from ores is the cyanidation process. Although cyanide is inexpensive and highly effective for gold extraction, its use in gold processing has been increasingly challenged by environmental organizations and governments due to its toxicity (Bocse, 2021). Because of this drawback of cyanide, many studies have been conducted to find alternative lixiviants to cyanide, the candidates of which are thiourea, thiocyanate, halogen-based, and thiosulfate solvents (Mhandu *et al.*, 2023). Among them, thiosulfate is considered the most promising lixiviant due to its high selectivity, fast leaching rate, low toxicity, and low corrosivity. However, the applicability of thiosulfate medium is challenging when processing arsenopyritic gold ores because of unwanted thiosulfate decomposition occurring on the arsenopyrite surface (Mhandu *et al.*, 2023). To solve this problem, the applicability of the ME treatment using ferrous and phosphate prior to thiosulfate leaching of gold was investigated. As can be seen in Fig. 4, when processing with untreated arsenopyrite, only 16% of gold was extracted, whereas it was improved to 72% by employing the ME treatment. This proved that $FePO_4$ coating formed on the arsenopyrite surface reduced thiosulfate decomposition, thus improving gold extraction efficiency.

Conclusions

The ME technique was demonstrated to be effective in suppressing the oxidation of AMD-forming minerals by forming protective coatings on their surfaces. In

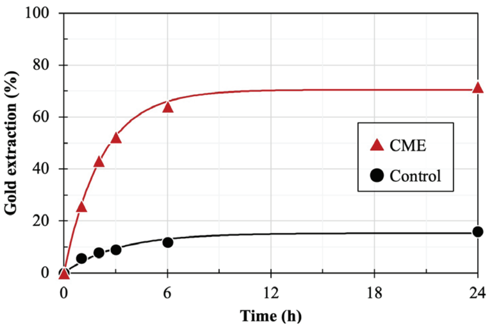

Figure 4 *Gold extraction by thiosulfate in the presence of untreated and ME-treated arsenopyrite.*

addition to its environmental benefits, ME was shown to enhance separation efficiency in coal cleaning and improve gold extraction in hydrometallurgical processes. These findings highlight the potential of ME as a versatile pre-treatment strategy that not only mitigates environmental risks but also enhances the efficiency of mineral processing and metallurgical operations.

Acknowledgements

This research was funded by the Japan Society for the Promotion of Science (JSPS) grant-in-Aid for Early-career Scientists (JP24K17639).

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