



Title	Development of a Sustainable Process Based on Carrier-microencapsulation to Suppress the Formation of Arsenic-containing Acid Mine Drainage from Arsenopyrite [an abstract of dissertation and a summary of dissertation review]
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学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Development of a Sustainable Process Based on Carrier-microencapsulation to Suppress the Formation of Arsenic-containing Acid Mine Drainage from Arsenopyrite
(硫砒鉄鉱からのヒ素を含む酸性鉱山廃水の発生を抑制する持続的なキャリアマイクロエンキャプシュレーション法の開発)

Acid mine drainage (AMD), an acidic leachate contaminated with toxic and hazardous heavy metals, is formed by the oxidation of sulfide minerals in tailing dams of metal and coal mines when exposed to air and water, and it is one of the most serious environmental problems associated with mining industries. When arsenopyrite (FeAsS), the primary arsenic (As)-bearing sulfide mineral in mineralized zones, is contained in the tailings, its oxidation together with pyrite (FeS_2) generates As-containing AMD. Arsenic is a highly toxic and strictly regulated element known to increase the risks of developing numerous diseases like hyperpigmentation, keratosis, anemia, neuropathy, and several types of cancers even at minute amounts. Because of this, the development of methods to suppress arsenopyrite oxidation is important. Carrier-microencapsulation (CME) has been proposed as a new technique to suppress AMD formation by forming a protective coating on sulfide minerals using metal-catecholate complexes. In this study, the applicability of CME to arsenopyrite was investigated to suppress the formation of As-containing AMD.

Chapter 1 describes the statement of the problem, objectives of this study, background and a literature review of the formation of AMD and its control.

In Chapter 2, the effects of CME using Ti-catecholate complex (Ti-based CME) on arsenopyrite oxidation were investigated by leaching and electrochemical experiments. The results of leaching experiments showed that the release of As from arsenopyrite was substantially suppressed by Ti-based CME, and SEM-EDX and DRIFT analyses of CME-treated residue indicated that arsenopyrite was covered with a Ti-oxyhydroxide coating. The results of cyclic voltammetry and SEM-EDX analysis of a platinum electrode in Ti-catecholate complex solution showed that $[\text{Ti}(\text{cat})_3]^{2-}$ was oxidized to form an intermediate phase at 680 mV vs. SHE via partial oxidation of either one or two of the catechol molecules with distorted Ti-O bonds. This was then followed by the chemical decomposition of the intermediate finally releasing Ti^{4+} that is precipitated as Ti-oxyhydroxide coating. Chronoamperometric measurements using an arsenopyrite electrode treated with Ti-catecholate complex confirmed that the coating formed by Ti-catecholate complex suppressed both anodic and cathodic half-cell reactions of arsenopyrite oxidation.

In Chapter 3, the kinetic aspects of Ti-based CME for suppressing arsenopyrite oxidation were investigated. Ti-based CME could successfully suppress arsenopyrite oxidation by forming a surface protective coating, but it required at least 14 days of treatment to generate a coating thick enough to be effective under ambient conditions. To improve the kinetics of Ti-based CME, elevated tem-

perature and the addition of chemical promoters like Cu^{2+} or $\text{Cu}^{2+} - \text{NH}_3$ complex were examined. As temperature increased, the decomposition rate of Ti-catecholate complex became faster, resulting in the suppression of arsenopyrite oxidation achieved early. The results of Ti-catecholate complex decomposition fitted well with a pseudo first-order kinetic model. The rate constants of complex decompositions at 30, 50, and 70°C were estimated at around 0.009, 0.021, and 0.051 h^{-1} , respectively, and its activation energy was calculated to be 37.4 kJ/mol. As another option to accelerate the decomposition of Ti-catecholate complex under ambient conditions, the effects of Cu^{2+} addition on Ti-based CME treatment for arsenopyrite were investigated. Instead of dissolved oxygen, Cu^{2+} and $\text{Cu}^{2+} - \text{NH}_3$ complex acted as an oxidant and enhanced the decomposition of Ti-catechol complex, causing faster precipitation of Ti^{4+} and stronger suppressive effects on arsenopyrite oxidation.

In Chapter 4, Al^{3+} -catechol complex was evaluated as a candidate of the metal-organic complex used for CME to suppress arsenopyrite oxidation. Al(III) ion and catechol formed three complex species depending on the pH: (1) $[\text{Al}(\text{cat})]^+$ between 4.7 and 5.5, (2) $[\text{Al}(\text{cat})_2]^-$ between 5.5 and 8.5, and (3) $[\text{Al}(\text{cat})_3]^{3-}$ between 8.5 and 14.0. Electrochemical study confirmed that the decomposition of Al-catecholate complexes occurs sequentially: $[\text{Al}(\text{cat})_3]^{3-} \rightarrow [\text{Al}(\text{cat})_2]^- \rightarrow [\text{Al}(\text{cat})]^+$

Al^{3+} . Leaching experiments and surface characterizations of the residue by SEM-EDX, DRIFT, and XPS showed that in the presence of Al-catecholate complexes, arsenopyrite was covered with an Al-oxyhydroxide coating and As release from arsenopyrite was suppressed. The decomposition rate of Al-catecholate complex was faster than that of Ti-catecholate complex, and the suppression of As release from arsenopyrite was substantial with Al-based CME. The electrical charge of Al^{3+} is smaller than that of Ti^{4+} , and thus this may cause the weaker bond and faster decomposition rate with Al-catecholate complex than Ti-catecholate complex. Among the three Al-catecholate complexes, $[\text{Al}(\text{cat})]^+$ suppressed As release most effectively because it had the fastest complex decomposition/coating formation rate. Chronoamperometric measurements of arsenopyrite electrode treated with $[\text{Al}(\text{cat})]^+$ indicated that both anodic and cathodic half-cell reactions of arsenopyrite oxidation were suppressed by the surface protective coating formed on it. Long-term stability of CME-treated arsenopyrite was evaluated using weathering cell tests for ca. two months and the results showed that arsenopyrite oxidation was successfully suppressed by treating it with Al-based CME.

Chapter 5 summarized the most important findings of this dissertation and proposed a possible application of CME to simultaneously suppress the release of arsenic from arsenopyrite and the formation of AMD.