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Galvanic microencapsulation: a new technique to suppress pyrite oxidation
(ガルバニックマイクロエンキャプシュレーション:黄鉄鉱酸化抑制のための新しい方法)

Acid mine drainage (AMD) is one of the biggest environment concerns for centuries. This problem is generally caused by the exposure of sulfide minerals to oxygen and water. This process can occur naturally, however, mining industries are the major producer of such effluents. AMD is very acidic (less than pH 3) and contains high concentrations of hazardous heavy metals such as copper (Cu), lead (Pb), and zinc (Zn) as well as toxic metalloids like arsenic (As) and selenium (Se). The most widely used technique to mitigate the negative environmental impacts of AMD is via neutralization. In this technique, basic materials such as limestone are added to AMD to increase its pH and precipitate most of the heavy metal as metallic oxyhydroxides. Even though this technique is effective, AMD generation could continue for several decades or even centuries, so this approach is unsustainable. Microencapsulation is a promising and potentially more sustainable approach because it limits AMD production by suppressing pyrite oxidation directly through the formation of a passivating coating on the mineral. This study developed a new technique to prevent pyrite oxidation called “Galvanic microencapsulation”.

Chapter 1 gives a general introduction of acid mine drainage (AMD) formation and its mechanism as well as reviews AMD remediation, and prevention techniques. The statement of the problem and the objective of the study are highlighted to understand the key points and the structure of the entire research. The prevention techniques for prevent AMD are formation by controlling the migration of water, flooding and sealing of underground mine, alkaline amendment, alkaline recharge trenches, an aerobic and anaerobic wetland, limestone ponds, in-pit disposal, and encapsulation. Among these techniques microencapsulation to prevent pyrite from being oxidized by forming a protective coating on pyrite surface is recently gaining attention. The original microencapsulation techniques introduced by Evangelou (1995), used hydrogen peroxide (H_2O_2) to oxidize Fe^{2+} to Fe^{3+} for the formation of insoluble ferric phosphate on pyrite. Although this technique effectively suppressed pyrite oxidation, H_2O_2 was unable to selectively target pyrite in real, complex wastes leading to unnecessarily large consumption of expensive reagents. Moreover, handling and storage of H_2O_2 are both difficult especially in large scale applications. Carrier microencapsulation (CME) is, a microencapsulation technique that uses redox-sensitive metal(loid)-organic complexes to carry the coating material to the surface of pyrite where the complexes are adsorbed and decomposed, releasing the insoluble metal(loid) ion of the complex that is rapidly precipitated to form a protective coating on pyrite. Because pyrite dissolves via an electrochemical mechanism, the redox-sensitive metal (loid)-organic complexes have been shown to selectively target pyrite even in a complex system containing arsenopyrite and quartz.

Chapter 2 introduces a new encapsulation technique, called galvanic microencapsulation (GME). The

effects of GME on pyrite oxidation using zero-valent aluminum (ZVAL) or zero-valent iron (ZVI) at various dosages and under different conditions (leaching time and pH) were investigated. Pyrite oxidation was suppressed in the presence of ZVAL or ZVI. Galvanic interaction between pyrite and ZVAL in the first 3 days was negligible, which could be attributed to the Al-oxyhydroxide coating on ZVAL. After 7 days, however, ZVAL exhibited substantial suppressive effects on pyrite oxidation. In comparison, the suppressive effects of ZVI on pyrite oxidation was observed after just 1 day. Pyrite oxidation suppression mechanisms by GME during leaching were elucidated by electrochemical measurements. Cyclic voltammetry and chronoamperometry measurements showed that the suppressive effects of ZVAL and ZVI were predominantly due to galvanic interactions.

In Chapter 3, coating formation technique for prolonged suppressive effects of GME on pyrite oxidation using phosphate and ZVI was developed. In Chapter 2 galvanic interaction was observed, however, there are no coating formation on the pyrite surface. In the presence of phosphate, suppression of pyrite oxidation by ZVI was dramatically improved because of the combined effects of galvanic interactions and coating formation. The mechanism of protection could be explained as follows: ZVI oxidized on pyrite surface, released ferrous, and ferrous oxidized to ferric in the presence of oxygen. When phosphate was added, ferric phosphate was formed as a protective coating on pyrite surface.

In Chapter 4, GME was applied to improve the separation efficiency during mineral processing as well as suppress pyrite oxidation. GME treatment was carried out before flotation to change the surface of pyrite from hydrophobic to hydrophilic by phosphate coating. Iron phosphate coating in a ball mill grinding system was induced using steel ball as the electron donor and then followed by flotation treatment. The results showed improvement of flotation results and suppression of pyrite oxidation. Finally, Chapter 5 gives the general conclusions of this study.