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Galvanic microencapsulation: A novel technique to passivate pyrite and prevent acid mine drainage formation

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The results are significant because galvanic microencapsulation could target pyrite and prevent acid mine drainage (AMD) formation. It could be applied to existing mineral processing plants using a ball mill. Finally, new ways to passivate pyrite using AMD and galvanic interaction were discovered.

This research proposes "galvanic microencapsulation" as a novel technique to passivate pyrite and prevent acid mine drainage formation. The most important achievements of this study are as follows: (1) galvanic interaction was more extensive under acidic conditions, (2) zero-valent iron was better than zero-valent aluminium in suppressing pyrite oxidation, (3) addition of phosphate in pyrite and zero-valent iron system produced iron-phosphate coatings on pyrite that limited its oxidation, (4) phosphate-enhanced galvanic microencapsulation was successfully applied in a ball mill using grinding balls as source of dissolved Fe, (5) galvanic microencapsulation could be used to improve coal and pyrite separation during flotation, (6) ferric phosphate coatings on pyrite could be formed even under very acidic pH (1-3) even without zero-valent iron, and (7) a potentially new process was discovered to create iron phosphate coatings on pyrite using acid mine drainage rich in ferrous ions.

Geochemistry; Environment; Electrochemistry

Acid mine drainage　Pyrite　Passivation　galvanic effects

Japan is an old mining country and has more than 5,000 abandoned or closed mines that are continuously generating very acidic leachates containing toxic elements called acid mine/rock drainage (AMD/ARD). This problem is being addressed by both the national government and private mining firms. For example, JX Nippon Mining & Metals Corporation is operating twelve treatment facilities in their closed mines [1]. The treatment method most commonly used is chemical neutralization whereby limestone, lime or other basic substances are mixed with AMD/ARD to raise its pH and precipitate most of the heavy metals. It is effective, but only treats the "symptom" of the problem (AMD/ARD) and not the "cause" (sulfide minerals), so it requires the continuous treatment of acidic leachate and disposal of hazardous neutralization sludge until all sulfides in the closed mine or tailings are oxidized. Unfortunately, pyrite oxidation is a relatively slow process that could persist for several decades or even centuries [2], so managing tailings dams and AMD/ARD this way for such a long time is both costly and unsustainable.

The dissolution of pyrite, the most widespread sulfide mineral in nature and the main cause of AMD/ARD, proceeds via an electrochemical mechanism [3], which could be taken advantage of to prevent its oxidation [4]. However, the passivation of pyrite has two main problems when applied to real tailings: (1) the chemicals/reagents used to coat pyrite are very expensive and impractical for large-scale applications, and (2) these chemicals do not selectively target pyrite grains in the tailings. One way to selectively target pyrite in a complex system is via galvanic interaction, a phenomenon that occurs when two conductive or semi-conductive materials having different rest potentials come in close contact with each other. In this process, the material having a lower rest potential becomes the anode and is dissolved while the other material with higher rest potential becomes the cathode and is galvanically protected [5]. Using this concept, we developed a novel technique to suppress pyrite oxidation called "galvanic microencapsulation" (GME). In this technique, there are two reactions that would potentially suppress pyrite oxidation (Fig. 1): (1) sacrificial effect of the anode, and (2) coating formation using the oxidation products from the anode. GME, in theory, will be selective because pyrite oxidation is an electrochemical process and GME involves electron transfer between anodic and cathodic sites.
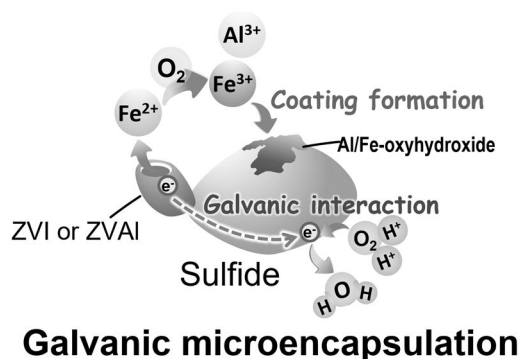

Galvanic microencapsulation

Figure 1. A schematic diagram of the supression mechanisms of "galvanic microencapsulation". Note that ZVI and ZVAl stand for zero-valent iron and zero-valent aluminum, respectively.

Galvanic interaction is a well-known phenomenon in corrosion science and the mineral processing of sulfide ores, but this is the first study that proposed its use to target and passivate pyrite. In this research project, we selected two metals common in waste streams as anodes – zero-valent iron (ZVI) and zero-valent aluminum (ZVAl) because their dissolved metal ions (*i.e.*, Al^{3+} and Fe^{3+}) could be precipitated as oxyhydroxides under certain conditions (Fig. 1). Specifically, the objectives of this research project are as follows:

(1) Evaluate the effects of pH, metal dosage and treatment time on the suppression of pyrite oxidation.
(2) Understand the suppression mechanisms involved in GME.
(3) Characterize the coating formed on pyrite and evaluate its electrochemical properties.
(4) Elucidate the possible application of GME in mineral processing and coal cleaning.

Galvanic interactions between pyrite and ZVI or ZVAl were elucidated using electrochemical techniques like cyclic voltammetry (CV) and chronoamperometry. For these experiments, the pyrite electrode was prepared by cutting a cuboid out of a large single-crystal pyrite sample obtained from Cerro de Pasco mine, Peru. The pyrite sample was connected to copper wires using silver conducting paste and then fixed inside a plastic tube using Technovit® non-conducting resin (Heraeus Kulzer GmbH, Germany). Pyrite in the electrode was exposed using Si-carbide papers of increasing grit numbers (#200→#600→#1000→#1500) followed by polishing with 5 and 1 μm Al_2O_3 pastes on a smooth glass plate. Finally, the electrode was

ultrasonically cleaned for 5 minutes to remove residual Al_2O_3 particles and then washed thoroughly with deionized (DI) water. For the electrochemical measurements, a conventional three-electrode setup was used connected to a computer-controlled electrochemical measurement unit (SI 1280B, Solartron Instruments, UK). In this type of cell setup, pyrite was the working electrode, platinum plate was the counter electrode and Ag/AgCl in saturated KCl was the reference electrode. The supporting electrolyte in all experiments was 0.1 M Na_2SO_4 maintained at 25°C by a thermostat water recirculation system [3].

The effects of pH, metal dosage and treatment time were evaluated using batch-reactor experiments. Prior to these experiments, pyrite was washed to remove fine particles and any oxidation products formed during sample preparation and storage [6]. The batch-reactor experiments were done by mixing washed pyrite and 10 ml of prepared solution or metal suspension up to 21 days in a thermostat water bath shaker (25°C) at 120 rpm. Some of the experiments were done in triplicates to ascertain that the differences and trends observed were statistically significant. After the predetermined mixing time, samples are taken out of the shaker, the pH and redox potential of suspensions were measured, and the leachates collected by filtration through 0.2 μm membrane filters. Meanwhile, the solid residues were washed thoroughly with DI water and dried in a vacuum drying oven at 40°C for 24 h. The chemical composition of leachates was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (ICPE-9820, Shimadzu Corporation, Japan) while the dried residues were observed under a high-resolution 3D digital microscope (VHX-1000, Keyence Corporation, Japan) and scanning electron microscope with energy dispersive X-ray spectroscopy (Superscan SSX-550, Shimadzu Corporation, Japan). Selected samples were also analyzed by diffused reflectance infrared Fourier transform (DRIFT) spectroscopy (FT/IR-6200HFV with DR PRO410-M attachment, Jasco Analytical Instruments, Japan).

To evaluate the possible application of GME in mineral processing, GME treatment was conducted in a ball mill pot with a diameter of 8 cm for 3 h using 100 g of pyrite samples and steel ball grinding media (diameter 0.6 cm). One gram of GME-treated pyrite from the ball mill was then leached in 10 ml DI water for 7 days. After the predetermined leaching period, the leachates were collected and analyzed. The residues were also collected, washed thoroughly with DI water, dried in a vacuum drying oven and analyzed by SEM-EDX.

Coal flotation experiments were carried out using a mixture of Kushiro coal (16 g; 100–150 μm) pyrite (3 g; 100–150 μm; with and without GME treatment) and quartz (1 g; 100–150 μm). Flotation tests (impeller speed of 1000 rpm and aeration rate of 0.75 L/min) were carried out in an Agitair-type batch flotation cell (FT-1000, Heiko, Japan) with 400 ml of suspension containing 20 g of the coal-pyrite-quartz mixture. The suspension was first agitated for 3 minutes followed by the addition of 15 μl of methyl isobutyl carbinol (MIBC) as frother. Agitation was continued for an additional 3 minutes prior to the introduction of air for flotation. Froth products were recovered for 3 minutes without a collector, after which, 2 μl of kerosene (collector) and 15 μl of MIBC were added, agitated for 3 minutes and frother products were collected for 3 minutes after the introduction of air. The latter procedure was repeated with 3, 5 and 5 μl of additional kerosene (cumulative kerosene volume was 2, 5, 10 and 15 μl). The froth products were collected separately from each flotation stage and the ash value of the froth and tailing products were determined according to the Japanese Industrial Standards (JIS) (M8812).

(1) Galvanic interactions of pyrite with zero-valent iron or zero-valent aluminum

Among the three factors evaluated in this research project, the pH was found to be the most important factor for GME. Suppression of pyrite oxidation was better at pH < 4 regardless of the metal used as the anode. In the case of ZVI, for example, concentrations of dissolved S, an indicator of the extent of pyrite oxidation, were significantly lower at pH < 4 compared with those at higher pH values (Fig. 2). The importance of pH could be explained by the crucial role of H^+ in the cathodic reaction during galvanic interactions (Fig. 1) and the less likely formation of passivating oxyhydroxide films on ZVI and ZVAl under acidic conditions.

Between the two metals, ZVI was better than ZVAl because the formation of a passivating
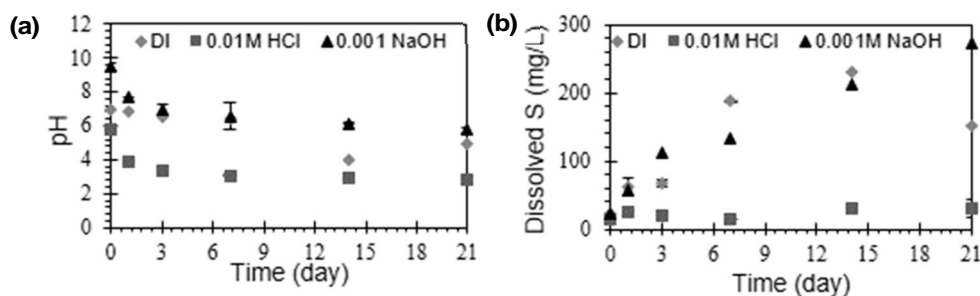

Figure 2. Evolution of leachate chemistry in deionized (DI water), 0.01M HCl, and 0.001M NaOH: (a) pH change with time, and (b) dissolved S concentration change with time [5].

oxyhydroxide/oxide film on the former was sluggish than the latter. This means that galvanic interactions were more extensive between pyrite and ZVI as explained in Fig. 3a. Moreover, adsorption of ZVI onto pyrite suppressed the cathodic half-cell reaction of pyrite oxidation (Fig. 3b). Both metals limited the oxidation of pyrite, but their suppressive effects were only temporary because coating formation on pyrite was negligible [5].
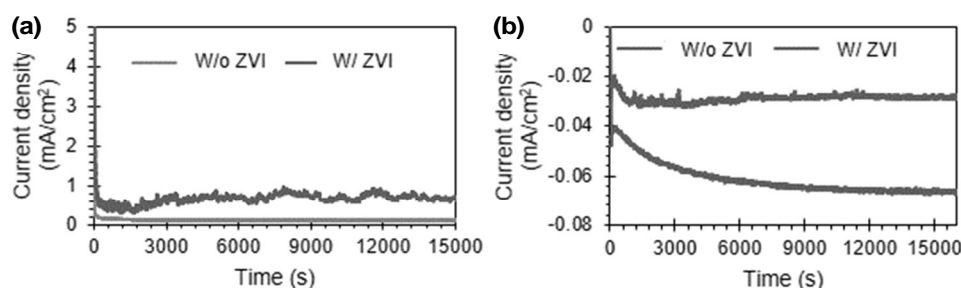

Figure 3. Chronoamperometry measurements of pyrite with and without ZVI: (a) anodic polarization curves with time of pyrite with and without attached with ZVI, and (b) cathodic polarization curves with time of pyrite with and without attached with ZVI. [5].

(2) Galvanic microencapsulation using zero-valent iron and phosphate

The results of leaching experiments and electrochemical measurements suggest that pyrite oxidation was suppressed mainly via galvanic interactions. Although rapid, this suppressive effect was only temporary because a passivating coating on pyrite was not formed. To prolong the suppression of pyrite oxidation by GME, phosphate was introduced to enhance the formation of iron phosphate coatings. Iron phosphates have higher stabilities under acidic condition than the iron oxyhydroxides, which means that suppression of pyrite oxidation could be improved under acidic conditions because both galvanic interactions and coating formation could occur. Fig. 4a shows lower concentrations of dissolved S when both ZVI and phosphate were present, and iron phosphate coatings were formed on pyrite as illustrated in Fig. 4b. This means that combining ZVI and phosphate improved the suppression of pyrite oxidation because both galvanic interactions and coating formation occurred.
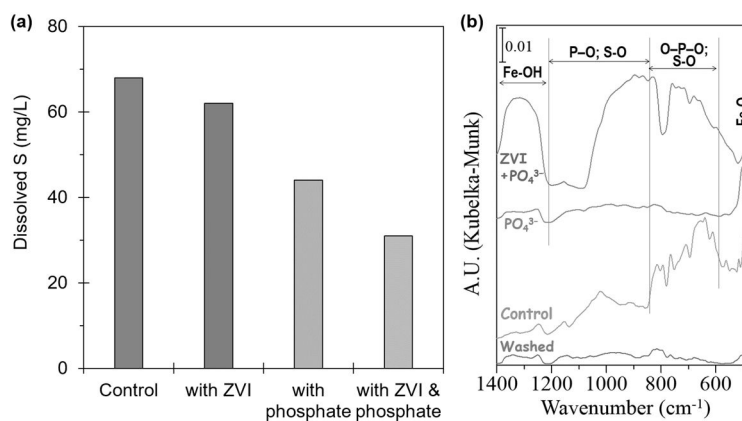

Figure 3. (a) Concentration of dissolved S after pyrite treatment for 7 days in DI water (control), ZVI suspension, phosphate solution and ZVI + phosphate mixture, and (b) diffuse reflectance infrared Fourier transform (DRIFT) spectra of pyrite before treatment (washed) and after 7 days in various solutions/suspensions.

(3) Application of galvanic microencapsulation to mineral processing

GME treatment in a ball mill was conducted under various conditions and the products were leached in DI water up to 7 days to evaluate the suppression of pyrite oxidation by GME. The leaching results showed that dissolved S and Fe concentrations were lower with phosphate and air induction (Fig. 4). SEM-EDX observations of the leaching residues indicate that the surface of pyrite was coated with a Fe-P-O containing phases, which means that GME could be applied in a ball mill with steel ball media as source of dissolved Fe so long as there is enough oxygen supply to convert Fe^{2+} to Fe^{3+} (e.g., intermittent air induction).

Using untreated and GME-treated pyrite, coal flotation was conducted, and the results showed that ash recovery was lower after GME treatment of pyrite (Fig. 5). This could be attributed to the more hydrophilic nature of GME-treated pyrite because of the presence of iron phosphates that are inherently hydrophilic. These results imply that GME treatment of pyrite using a ball mill improved not only the separation efficiency of coal and pyrite during flotation but also suppressed pyrite oxidation.
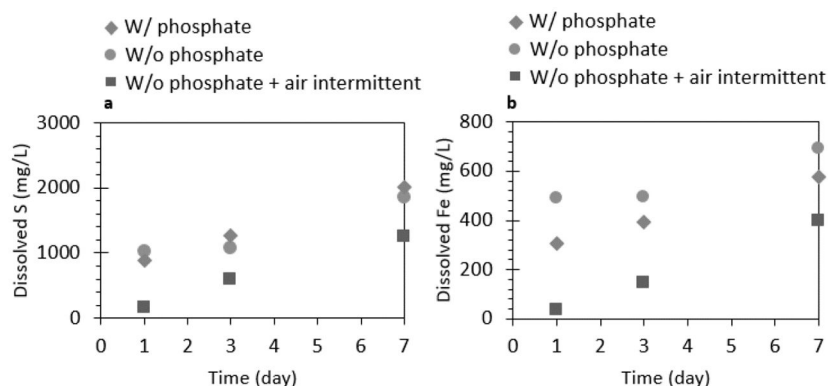
Figure 4. Changes with time of (a) dissolved S, and (b) dissolved Fe in the leaching experiments after GME in a ball mill under various conditions.
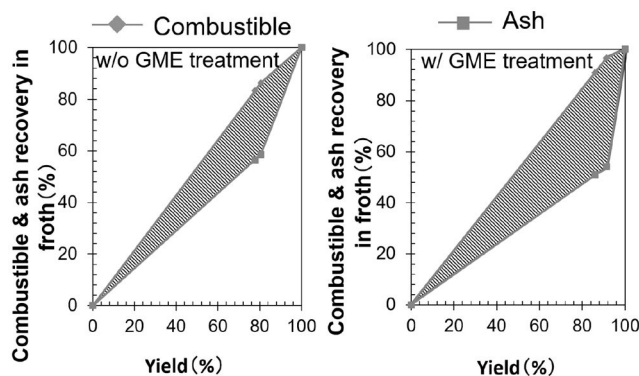

Figure 5. Combustible and ash recovery of coal (a) without treatment, and (b) with GME treatment.

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