

## 科学研究費助成事業 研究成果報告書

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研究課題名(和文) Micro-seeds-enhanced and smart-carrier assisted pyrite encapsulation to prevent the generation of acid mine drainage

研究課題名(英文) Micro-seeds-enhanced and smart-carrier assisted pyrite encapsulation to prevent the generation of acid mine drainage

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研究成果の概要(和文)：本研究では、酸性鉱山廃水の発生を防止するため、表面に被膜を形成して黄鉄鉱を不動態化する新しい方法として(1)マイクロシードを用いた方法と(2)スマートキャリアを用いた方法の2つを試験した。マイクロシードとしてヘマタイトやその他の酸化鉄(シュベルトマナイトなど)の微粒子を用いた方尾はpH3-6で効果的であった。黄鉄鉱や硫砒鉄鉱などの硫化鉱物の溶解反応は電気化学的反応なので、スマートキャリアとして酸化還元に敏感な金属-有機錯体を用いた方法を調べた。第2鉄イオン、第一鉄イオン、アルミニウム、チタンイオンのカテコール錯体は黄鉄鉱や硫砒鉄鉱の酸化抑制に用いることができた。

研究成果の概要(英文)：This research evaluated two new concepts to passivate pyrite and prevent acid mine drainage generation: (1) "micro-seeds" enhanced encapsulation, and (2) "smart-carrier" assisted encapsulation. Micro-seed enhanced encapsulation was more effective at pH 3-6 using hematite or other iron-oxide precursor minerals (e.g., schwertmannite) as micro-seeds. The coating formed under these conditions was uniform, thick and mechanically strong. As smart-carriers, organic molecules that form redox-sensitive metal-organic complexes could be used to specifically target sulfide minerals like pyrite and arsenopyrite because of the electrochemical nature of their dissolution. Our results showed that ferric-, ferrous-, aluminum- and titanium-catechol complexes could be used to suppress the oxidation of pyrite/arsenopyrite. We were also the first to report that metal oxides strongly influenced the fundamental half-cell reactions during pyrite oxidation.

研究分野：electrochemistry, environmental geochemistry

キーワード：pyrite oxidation pyrite encapsulation acid mine/rock drainage pyrite passivation

## 1. 研究開始当初の背景

Acid mine/rock drainage (AMD/ARD) is one of the oldest and most serious environmental problems encountered in many countries around the world. AMD/ARD refers to the very acidic and heavy-metals loaded leachate produced in abandoned mine sites [1], mining tailings [1], and tunnel construction waste rocks [2]. It pollutes river systems, soils and groundwater in affected areas, leading to the destruction of the surrounding ecosystem. Affected humans are also not spared, developing many diseases of the cardio-vascular organs (heavy metals), kidneys (cadmium and arsenic), nervous system (lead), bladder (arsenic), skin (arsenic) and bones (mercury). Although AMD/ARD is one of the most extensively studied environmental problems in the last few decades, scientifically sound and economically viable strategies for its mitigation are still elusive. To date, the most popular and common approach used in AMD/ARD management is through its neutralization using limestone, lime or other basic substances. It is effective, but only treats the “symptom” of the problem (AMD/ARD) and not the sources (pyrite/arsenopyrite). Thus, this approach requires the continuous treatment of the acidic leachate and disposal of hazardous sludges until all pyrites in the closed mine or tailings are oxidized. Unfortunately, pyrite oxidation is a relatively slow process and could continue for several decades or even centuries, so managing AMD/ARD this way for such a long time is both costly and unsustainable.

The less popular and rarely studied approach is to render the sources of AMD (*i.e.*, pyrite/arsenopyrite) un-reactive via chemical and/or biological treatments. Batch-reactor type experiments using substances like ferric phosphate [1], phospho-silicates [3], phospholipids [4] and iron-8 hydroxy-quinoline [5] to coat pyrite have shown that this passive-type treatment termed loosely as “pyrite encapsulation” is plausible. Unfortunately, these previous studies showed that such passive-type techniques suffer from two critical flaws: (1) the chemicals/reagents used to coat pyrite were very expensive and impractical for large scale applications, and (2) these chemicals do not specifically target pyrite grains in the wastes. To address the first serious issue, we are proposing the use of Fe-oxyhydroxides as coating material and the intensification of its precipitation on the pyrite surface. Dissolved Fe is produced during pyrite oxidation, so this material is not only cheap but also renders the coating “self-healing” and “self-sustaining”. To enhance the formation of Fe-oxyhydroxide coating on pyrite, we are introducing a new concept called “micro-seeds”-enhanced pyrite encapsulation. In this process,

“Micro-seeds” are introduced into the system that will attach to the pyrite surface and serve as building blocks of the coating. The process is analogous to building a solid wall with bricks and mortar – the “Micro-seeds” are the bricks and the precipitated Fe-oxyhydroxide is the mortar. For the second serious problem of passive techniques, we are proposing the development of a “Smart-carrier” material that will specifically target pyrite grains. Once the “carrier” comes close to pyrite, the coating material is released and coats the pyrite surface. Conceptual diagrams of our proposed methods are illustrated in Figures 1 and 2.

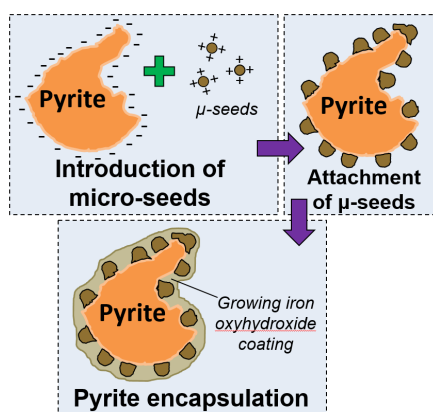


Figure 1. Schematic diagram of “micro-seed” enhanced encapsulation

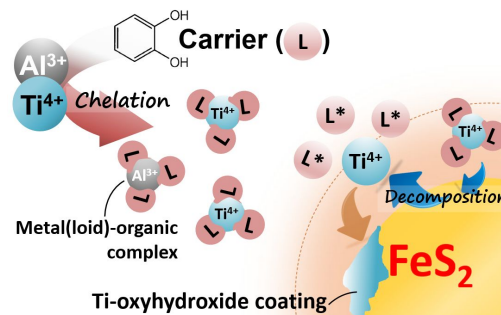


Figure 2. Schematic diagram of “Smart-carrier” assisted encapsulation

## 2. 研究の目的

We based the concept of “micro-seeds”-enhanced pyrite encapsulation on several well-known surface properties of pyrite as well as our extensive experiences on adsorption. In the pH range of ca. 2-10, pyrite has a negatively charged surface, so we thought that if we introduce fine particles with net positively charged surfaces to the pyrite-water system, they will easily attach to the pyrite surface via electrostatic attraction reducing the effective surface area of pyrite undergoing oxidation (Figure 1). If this happens, the partial barrier created by the “micro-seeds” will substantially reduce the diffusion rate of dissolved Fe from the pyrite surface to the bulk solution and at the same time increase its solute activity. These conditions at slightly alkaline pH

values are favorable for the precipitation of Fe-oxyhydroxides on or near the surface of pyrite. Moreover, these “micro-seeds” could speed-up the formation of the coating by acting as nucleation sites of Fe-oxyhydroxide precipitation.

In the second concept, we call it a “Smart-carrier” because we envision that it would have the ability to specifically target the pyrite surface. How can we do such a thing? The dissolution of pyrite is electrochemical in nature. This means that for this mineral to dissolve, electrons must be transported from distinct anodic and cathodic sites on the pyrite surface. Because this kind of dissolution is unique to certain sulfide minerals like pyrite and arsenopyrite, it is possible to target pyrite in real tailings containing mostly aluminum-silicate minerals (Figure 2).

### 3 . 研究の方法

#### (1) “Micro-seed” enhanced encapsulation

This concept was evaluated using two types of experiment: static and dynamic. In the static-type experiments, a suspension of hematite (<40 μm) were introduced into a single-crystal quartz crystal vessel containing freshly cleaved pyrite. Periodically, photomicrographs of the surface of pyrite were observed using a high resolution light microscopy. After the predetermined time, pyrite crystals were taken out, washed thoroughly with ultrapure water, and analyzed by high-resolution light microscope and scanning electron microscope with energy dispersive X-ray spectroscopy. Another set of experiments were conducted to evaluate the effects of “micro-seeds” attachment on the formation of oxyhydroxide layer. This was done by pretreating freshly cleaved pyrite particles in hematite suspension for 24 h and inducing pyrite oxidation via exposure of the crystals for 36 days to slightly alkaline-oxidizing conditions. After the treatment, pyrite grains were analyzed by a high-resolution light microscope and scanning electron microscope with energy dispersive X-ray spectroscopy.

Dynamic experiments were done by batch-reactor tests. Prior to the batch-reactor experiments, the pyrite sample was washed to remove any oxidized layer formed during sample preparation. This involves ultrasonic cleaning and desliming in ethanol, washing with 1 M HNO<sub>3</sub>, rinsing with deionized water, and dewatering with acetone under vacuum. For the batch-reactor experiments, 1 g of washed pyrite was mixed with 10 ml of deionized water or α-Fe<sub>2</sub>O<sub>3</sub> suspensions (2 and 200 mg/l) in 50 ml Erlenmeyer flasks. The suspensions were shaken in a constant temperature water bath (30°C) at 80 rpm from 1 to 7 days. Some of the experiments

were done in triplicates to ascertain that the differences and trends observed were statistically significant. After the predetermined mixing time, the pH and oxidation-reduction potential (ORP) of suspensions were measured, and the leachates were collected by filtration through 0.22 μm syringe-type membrane filters (Sartorius AG, Germany). The concentrations of dissolved Fe and S in the leachates were measured using an inductively coupled plasma atomic emission spectrometer (ICP-AES). On the other hand, the solid fraction (i.e., oxidized pyrite) were collected, washed carefully with deionized water, and then dried in a vacuum drying oven at 40°C. After drying, the solid fraction was crushed manually to <50 μm and then analyzed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to determine the bonding properties of the chemical phases formed after pyrite oxidation with and without hematite.

Electrochemical studies (cyclic voltammetry and chronoamperometry) were also done to understand whether the presence of hematite on the surface of pyrite has substantial effects on the anodic and cathodic half-cell reactions during pyrite oxidation.

#### (2) “Smart-carrier” assisted encapsulation

The concept of “smart-carrier” enhanced encapsulation was elucidated using electrochemical studies and batch-reactor type experiments. Two important criteria of potential carrier are that they form stable metal-complexes and these complexes could be decomposed oxidatively. There are several organic molecules that exhibit these important properties, two of the most commonly found in nature are catechol and salicylate. In this research, we only used catechol for its potential as smart-carrier, but evaluated several metal-catechol complexes of Ti<sup>4+</sup>, Al<sup>3+</sup> and Fe<sup>3+</sup>. To understand the electrochemical decomposition of these metal-catechol complexes, cyclic voltammetry and chronoamperometry were conducted on platinum and pyrite surface.

The batch-reactor experiments were done using pyrite and arsenopyrite by varying conditions like pH, metal-carrier ratio and leaching time. Suppression of the oxidation of pyrite and arsenopyrite were monitored using dissolved S and As, which were measured by ICP-AES. The treated sulfide minerals were also analyzed by DRIFTS and SEM-EDX composition of the coating formed.

### 4 . 研究成果

#### (1) “Micro-seeds” enhanced encapsulation

Our results on this part of the project showed that the interactions between micro-seeds and pyrite is strongly dependent on their surface charges relative to each other. For example, hematite that

is positively charged at  $\text{pH} < 7$  were attracted to the negatively charged surface of pyrite [6]. However, the attachment of these minerals were not entirely due to the surface charge because alumina, which is also positively charged under these conditions barely attached onto the pyrite surface [6]. In addition, we found that minerals attached on the surface of pyrite strongly affected the net oxidation of the mineral, which also had a negative impact on coating formation [6]. More detailed investigation on the effects of hematite and alumina using electrochemical techniques suggests that they played important roles in both the anodic and cathodic half-cell reactions of pyrite oxidation (Figure 4) [7].

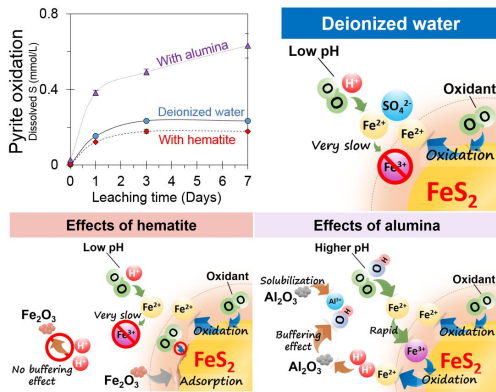


Figure 3. Effects of hematite and alumina on pyrite oxidation [6]

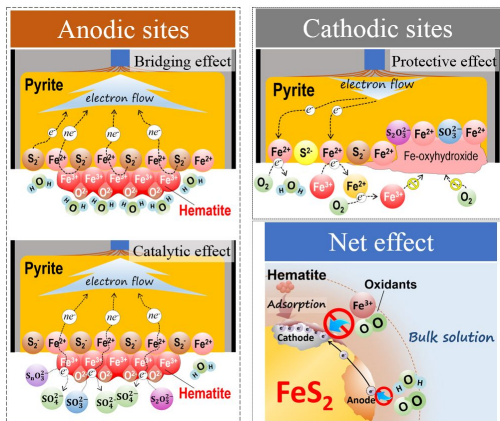


Figure 4. Effects of hematite and alumina on the anodic and cathodic half-cell reactions of pyrite oxidation [7].

Another important finding of this part was that it is possible to passivate pyrite with a uniform and mechanically strong coating when precursor minerals like ferric arsenate and schwertmannite are used instead of the more crystalline iron-oxides (e.g., hematite) (Figure 5) [8]. Finally, another approach to passivate pyrite was discovered through this project; that is, we found that it is possible to passivate pyrite using galvanic interaction [9, 10]. However, more research is needed to understand how the less crystalline iron-oxyhydroxides/arsenates coated pyrite and under which conditions would

galvanic interaction have the best passivating effects.

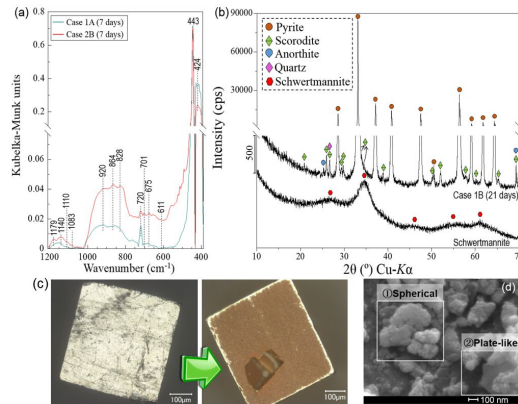


Figure 5. (a) DRIFTS spectra of pyrite with the reddish coating, (b) XRD pattern of pyrite with coating, (c) photomicrographs of a pyrite crystal with coating, and (d) FE-SEM photomicrograph of the coating material [8].

## (2) “Smart-carrier” assisted encapsulation

Our result in this part of the project showed that the electrochemical nature of pyrite/arsenopyrite oxidation could be used to specifically target these minerals in a complex system. Among the metal-organic complexes, we found that the best one is Titanium (Ti)-catechol because Ti-oxide (anatase) formed on the pyrite surface was evenly distributed, mechanically strong and very stable under both acidic and alkaline conditions ( $\text{pH} 2 - 10$ ) (Figure 6) [11]. One disadvantage of using Ti ion is the difficulty of its extraction from its ores by organic ligands. We solved this problem by developing a new synthesis method wherein very acidic sulfate  $\text{Ti}^{4+}$  solutions are used as starting condition for Ti-catechol complex synthesis. The ores of Ti are easily dissolved under very acidic conditions ( $\text{pH} < 1$ ), so this made the use of this particular metal-organic complex economically plausible.

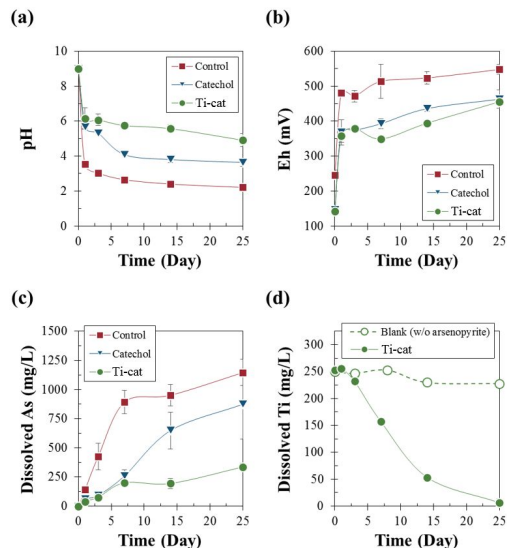


Figure 6. (a) pH as a function of treatment time, (b) Eh as a function of treatment time, (c) As as a function of treatment time, and (d) Ti as a function of treatment time [11].

Aluminum-catechol and iron-catechol complexes also showed some promising results. For example, ferric-catechol could be used at around pH 8 (Figure 7) [12]. However, more detailed studies are being done with regards aluminum- and iron-catechol complexes because they form three kinds of complexes that have differing stabilities and electrochemical properties.

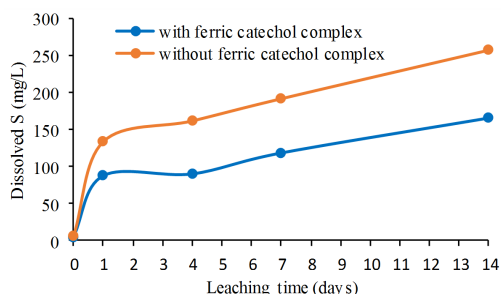


Figure 7. Effects of ferric-catechol complex on pyrite dissolution [12]

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## 5. 主な発表論文等

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〔図書〕(計 件)

〔産業財産権〕

出願状況(計 件)

名称:

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名称:

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番号:

出願年月日:

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〔その他〕

ホームページ等

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