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## 学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 Li Xinlong

## 学 位 論 文 題 名

Effects of Ferric Ions on Carrier-microencapsulation for Suppressing Pyrite Oxidation  
(黄鉄鉱酸化抑制のためのキャリアマイクロエンカプセレーションに及ぼす第二鉄イオンの影響)

Pyrite is a common sulfide mineral in nature and it is separated from valuable minerals and disposed to tailing dams in coal and metal mines. When pyrite is exposed to air and water, it is oxidized to form sulfuric acid, which causes acid mine drainage (AMD), a serious environmental problem in mining industry. Neutralization techniques have been commonly used to treat AMD, but they are unsustainable because AMD formation could be continued even after closure of mine. It is important to develop a sustainable method to suppress pyrite oxidation in tailings dam and prevent AMD formation. Carrier-microencapsulation (CME) has been proposed as a promising method to prevent the formation of AMD by forming a protective coating on pyrite surface. Using model experiments, the previous studies demonstrated that CME using titanium-, silicon- or aluminum-catecholate complexes effectively suppressed pyrite oxidation by forming metal-oxyhydroxide coating on pyrite surface. Considering the actual operation of CME, it is needed to understand the effects of co-existing metal ions. A common co-existing metal ion associated with pyrite is ferric ion, because it is a product of pyrite oxidation process. In this study, the effects of coexisting ferric ions on CME for suppressing pyrite oxidation was investigated.

Chapter 1 described the statement of the problem, objectives of this study, and conducted a literature review of pyrite oxidation, formation of AMD and its control.

In chapter 2, the thermodynamic and redox properties of ferric-catecholate complex was compared to aluminum- and titanium-catecholate complexes. Mono-, bis- and tris-catecholate complexes were formed in the solution containing ferric ions and catechol as same as aluminum-catechol system, while only tris-catecholate complexes was formed in solution containing titanium ions and catechol. The results of linear sweep voltammetry (LSV) indicated that ferric-catecholate complexes was decomposed sequentially: tris-catecholate complex was decomposed to bis-catecholate complex, and bis-catecholate complex was decomposed to mono-catecholate complex, then finally mono-catecholate complex was decomposed to release ferric ions. The sequential decomposition also occurred for aluminum-catecholate complexes while decomposition of titanium-catecholate complex was one-step reaction: tris-catecholate complex was directly decomposed to release titanium ions. Among three complexes, ferric -catecholate complex was decomposed at lowest redox potential and decomposition rate was fastest. The coating formed with ferric-catecholate by polarization strongly suppressed the dissolved oxygen reduction on platinum electrode.

In chapter 3, the effects of ferric-catecholate complexes on pyrite oxidation were investigated. Microscope observation confirmed that coating was formed on pyrite treated with mono- and bis-catecholate complexes. Results of SEM-EDX and ATR-FTIR indicate that the coating is mainly com-

posed of iron oxyhydroxide phases. The results of leaching experiments showed that pyrite oxidation was suppressed by ferric-catecholate complexes via two mechanisms: (1) electron donating effects of the complexes, and (2) formation of a protective coating on pyrite.

In chapter 4, the details of coating formation with ferric-catecholate complexes and the effect of the coating on pyrite oxidation were investigated by conducting a series of electrochemical studies. The results of theoretical calculation showed that the sequential decomposition of ferric-catecholate complexes on pyrite occurred at different electrode potentials corresponded to the different HOMO energy levels of the tris-, bis-, and mono-catecholate complexes of ferric ions. Chronoamperometry and EIS using a rotating disk platinum (Pt) electrode indicated that a passive coating was formed when oxidative decomposition of ferric-catecholate complexes occurred. When longer decomposition time and higher anodic potentials were applied, defects in the coat decreased, resulting in the formation of a more resistant coating. A comparison of the chronoamperometry results of coated and uncoated pyrite electrodes suggests that the coating formed with ferric-catecholate complex suppressed both anodic and cathodic half-cell reactions of pyrite oxidation by limiting the diffusion of reactants and products between pyrite and bulk solution phase.

In chapter 5, electrochemical properties of ferric-complexes with catechol derivatives, which are catechol substituted with electron donating groups (EDGs) and electron withdrawing group (EWGs) as potential carrier for CME was evaluated. Results of LSV indicated that the oxidation potential of ferric-complexes decreased with EDGs but increased with EWGs. Chronoamperometry and EIS showed the coating formation was enhanced with presence of EDGs while suppressed with EWGs. Results of leaching experiments suggested that ferric-complexes with EDGs suppressed pyrite oxidation by forming protective coating on pyrite surface while no suppressive effect was achieved by the complexes with EWGs.

Chapter 6 evaluated the effects of ferric-catecholate complexes on Ti-based CME. UV-Vis spectra indicated that both ferric- and titanium-catecholate complex were formed in solutions. The results of LSV, chronoamperometry and EIS indicated that ferric- and titanium-catecholate may be oxidatively decomposed at similar potential to form a Fe-Ti-oxyhydroxide due to the co-precipitation of titanium and ferric ions. Shaking flask experiments showed that with ferric-catecholate complexes, decomposition of titanium-catecholate complex to release titanium ions was enhanced.

Chapter 7 summarized the most essential findings of this dissertation.