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学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Mechanism of redox potential dependent chalcopyrite dissolution in acidic ferric chloride solutions
(酸性塩化第二鉄溶液中での酸化還元電位に依存する黄銅鉱溶解のメカニズム)

Chalcopyrite (CuFeS_2) is the most abundant mineral in copper ore bodies, accounting for more than seventy percent of the world copper reserves. However, with increasing the consumption of copper worldwide, high-grade ores are depleting. To guarantee the sustainable supply of copper, nowadays, low-grade ores are explored, mined, and concentrated with high amounts of impurities that are toxic such as arsenic. The concentrate of chalcopyrite together with arsenic as impurities are then processed for copper metal extraction. The conventional method to extract copper from chalcopyrite concentrate is pyro-metallurgy. However, the pyro-metallurgical process is facing the problem of high running cost and environmental issues related to the release of arsenic through stack emission.

Thus, hydrometallurgy is considered as a promising alternative approach to extract copper from low-grade chalcopyrite concentrate, owing to its low cost and safe removal and handling of arsenic that concomitantly dissolved in aqueous solution. Leaching is the first step of hydrometallurgy, where the metal ions are released (leached) into the solution from the solid particles (minerals). The biggest challenge of copper hydrometallurgy is to overcome the extremely slow leaching rate of chalcopyrite. To propose a good method to improve the chalcopyrite leaching rate, it is important to understand the chalcopyrite leaching mechanism. Therefore, this study aims to clarify the mechanism of chalcopyrite leaching in acidic chloride solution through an understanding of redox potential dependence of chalcopyrite leaching and the effect of chloride ions.

Chapter 1 gave the general introduction including background, statement of the problem, and a literature review on chalcopyrite leaching.

Chapter 2 investigated the effects of temperature and solution composition on the redox potential dependence of chalcopyrite leaching. The leaching experiments were carried out in acidic ferric chloride solutions using a specially designed batch leaching experimental setup that accurately determined and monitored the redox potential changes with time. Assuming that chalcopyrite oxidation with Fe(III) occurred stoichiometrically, the concentration ratio of Fe(III) to Fe(II) and the relationship between leaching rate versus redox potential were then determined from the redox potential data.

A peak behavior was observed in the copper extraction rate versus the redox potential plot. The leaching rate increased with increasing redox potential reaching a (local) maximum (i.e., the peak rate) at a certain redox potential (i.e., the peak redox potential) followed by the gradual decrease in leaching rate at higher redox potentials.

The effects of temperature and solution composition (Cu(II) , Fe(III) , and Cl^- concentrations) on the peak rate and peak redox potential were investigated. The results showed that the peak rate increased with increasing temperature, and decreased with increasing HCl and Fe(III) concentrations but was not strongly affected by the concentration of Cu(II) . In comparison, the peak redox potential was less dependent on the temperature and the concentrations of HCl and Fe(III) . Although Cu(II) concentration was not crucial in the peak rate, it was a major factor affecting the peak redox potential, that is, the peak redox potential increased with increasing the cupric ion concentration. Based on these results, an empirical equation for the relationship between the peak redox potential and Cu(II) concentration was derived.

Chapter 3 investigated the effects of solution composition on the anodic polarization curve of chalcopyrite. Anodic polarization experiments were carried out using a conventional three-electrode system, with chalcopyrite as a working electrode, at 298 K under the nitrogen atmosphere.

The results indicated that in the absence of Cu(II) and/or Fe(II) , the current density increased monotonically with increasing applied redox potential. Only in the presence of both Cu(II) and Fe(II) in solution, the peak behavior

was observed in anodic polarization curve, which was similar to the peak leaching rate, reported in leaching experiments. At low redox potential region (lower than 0.50 V), the current density in the presence of Cu(II) and Fe(II) was much higher than that in the absence of these ions. This result indicated that the coexistence of Cu(II) and Fe(II) promoted the dissolution of chalcopyrite at low redox potentials.

The effects of chloride ions on the anodic dissolution of chalcopyrite in the presence of both Cu(II) and Fe(II) were investigated. In the solutions containing 0.1 M HCl, 0.05 M Cu(II), 0.05 M Fe(II), and various concentration of NaCl, current density increased with increasing NaCl concentration. It indicated that chloride ions were promoters for the dissolution of chalcopyrite. From the thermodynamic point of view, when both Cu(II) and Fe(II) present in solution, they react to form Cu(I). From the result of Geochemist's Workbench® with MINTEQA2 database, Cu(I) formed cuprous chloride complexes with chloride ions and thus, became more stable at high chloride concentration. It suggested that Cu(I) might play an important role in the chalcopyrite leaching.

The effects of Cu(I) on the anodic dissolution of chalcopyrite were examined using a solution containing 0.1 M HCl with 0.001 M CuCl. The result showed that Cu(I) promoted the chalcopyrite dissolution rate at low redox potentials and the peak behavior appeared on the anodic polarization curve even with only Cu(I) present in solution. Considering the promotion effect of Cu(I), the effects of coexistence Cu(II) and Fe(II), as well as chloride ions could be explained as follows. The high leaching rate achieved at low redox potential in the presence of both Cu(II) and Fe(II) was due to the formation of promoter Cu(I). The stability of Cu(I) at high chloride ions concentration resulted in a faster chalcopyrite leaching rate at higher chloride ions concentration.

In Chapter 4, the electrochemical impedance spectroscopy (EIS) was conducted to understand different processes happening at the electrode surface. The measurements were done at varied applied potentials on the chalcopyrite electrode in an electrolyte containing 0.05 M Cu(II) and 0.05 M Fe(II) in 0.1 M HCl at 298 K under the nitrogen atmosphere. The results of EIS measurements were plotted in complex plane plots and fitted using equivalent circuits.

At redox potentials lower than 0.45 V, the impedance data were plotted on a straight line of 45 degrees in the complex plane plots and fitted using an equivalent circuit composed of solution resistant (R_s) and constant phase element (CPE) in series. The results suggested that chalcopyrite dissolution at the low redox potential was controlled by a diffusion process.

At redox potentials higher than 0.45 V, the impedance data were plotted on a compressed semi-circle (at high frequencies) connected with a straight line (at low frequencies). The data were fitted with an equivalent circuit containing a parallel circuit of R and CPE, which corresponds to a product layer formed on the surface of the chalcopyrite electrode. With increasing redox potential, the value of R in the parallel circuit increased, suggesting that the product layer grew on chalcopyrite surface and the layer thickness increased with increasing redox potential. This passivation layer hindered the further dissolution of chalcopyrite, resulted in a slow reaction kinetics and leading to a decrease in current density at high redox potential.

In Chapter 5, based on the experimental results in previous chapters, a reaction model assuming the formation of an intermediate Cu_2S at low redox potentials were proposed for chalcopyrite leaching in acidic chloride solutions. The intermediate Cu_2S is easier to dissolve than chalcopyrite, thus enhanced the copper extraction rate at low redox potentials. The formation reaction of intermediate Cu_2S involved three steps. Firstly, chalcopyrite reacted with H^+ in solution to release Cu(II), Fe(II), and H_2S into the solution. Then Cu(II) and Fe(II) reacted to form Cu(I). Finally, Cu(I) reacted with H_2S to form Cu_2S precipitated on the chalcopyrite surface. The intermediate Cu_2S was oxidatively decomposed to release Cu(II) and form elemental sulfur. Once elemental sulfur was formed, it acted as a passivation layer suppressing further chalcopyrite dissolution. Using the reaction model, the experimental results observed in the previous chapters were discussed.

Chapter 6 gave the summary, implications, and conclusion of the dissertation.