ATMOSPHERIC LEACHING OF NICKEL FROM LOW-GRADE INDONESIAN SAPROLITE ORES BY BIOGENIC CITRIC ACID

アウトゥティ, ウィディ

https://doi.org/10.15017/1543960

出版情報：九州大学, 2015, 博士（工学）, 課程博士
バージョン：

（様式２）

氏　　名　：　　　ウィディ　アストゥティ

論 文 名　：　　　Atmospheric Leaching of Nickel from Low-grade Indonesian Saprolite Ores by Biogenic Citric Acid
（生合成クエン酸を用いたインドネシア低品位サポロライト鉱石の常圧ニッケルリーチングに関する研究）

区　　分　：　　　甲

論　文　内　容　の　要　旨

Nickel laterite ores are abundant in Indonesia. Many studies have focused on discovering effective, profitable, inexpensive, and environmentally friendly methods for extracting nickel from these resources. Methods suitable for low grade ores are of particular interest. For laterite processing, leaching by organic acids and fungal bioleaching at atmospheric pressure are emerging technologies. Some studies have investigated the application of these techniques to Indonesian saprolite ores, but the leaching mechanisms are not well understood. In this research, the leaching mechanism with citric acid and biogenic citric acid was investigated with two low-grade Indonesian saprolite ores from different regions of the country. The low-grade Indonesian saprolite ores used in the study were obtained from Sulawesi (ore SS) and Halmahera (ore SH). These ores were used to study the influence of mineralogical composition on the nickel leaching. The comprehensive investigations conducted in this research include a comparison of citric acid with other leaching reagents, optimization of citric acid leaching, and kinetic modeling of the citric acid leaching process. In addition, biogenic citric acid is produced, and the effectiveness of this acid for nickel recovery is investigated.

This thesis contains six chapters. Chapter 1 presents the background and objectives of this study, an overview of the chemical leaching and bioleaching of laterite ores, citric acid production, and kinetics of the laterite leaching process. Previous studies of relevance are also discussed in this chapter.

In Chapter 2, nickel extraction is investigated with citric acid and other leaching reagents, including inorganic acids (sulfuric, nitric, and hydrochloric acids) and other organic acids (lactic and oxalic acids). The leaching performance and mineral dissolution behavior for the two ores (SS and SH) with the different leaching reagents are evaluated. X-ray diffraction (XRD), thermogravimetric-differential thermal analysis, and scanning electron microscopy/energy-dispersive X-ray spectroscopy results for the chemical and mineral compositions of the raw ores are presented. These results showed the SS ore had lizardite (serpentine group mineral), goethite, and clinochlore (chlorite group mineral) as major minerals, while the SH ore contained talc and goethite as predominant minerals. These differences affected the leaching results and metal dissolution behavior. Citric acid and sulfuric acid were more effective than the other acids tested for nickel extraction from both ores. Citric acid was very effective for dissolving nickel from lizardite, but did not recover nickel from goethite. By contrast, the inorganic acids (sulfuric, nitric, and hydrochloric) could extract nickel from goethite and lizardite. The nickel recoveries achieved with sulfuric acid were higher than those achieved with the other inorganic acids. Using citric acid, the nickel recovery from SS was higher than that from SH. By contrast, with the inorganic acids and lactic acids, the nickel recoveries from SS and SH were similar. Oxalic acid was the least effective reagent for nickel extraction because of nickel oxalate precipitation after nickel dissolution. In addition, the effect of sulfuric acid–citric acid mixtures on the nickel dissolution rate was investigated to confirm the individual influences of citric acid and sulfuric acid on the leaching behavior of each sample. The results showed that an increase in the proportion of sulfuric acid in the mixture affected the dissolution rate of nickel leached from SH much more than it affected nickel leaching from SS.

In Chapter 3, the nickel dissolution mechanism and optimum conditions for nickel extraction using citric acid are evaluated. The effects of leaching temperature, citric acid concentration, pulp density, and ore

particle size on leaching are investigated for the two saprolite ores. The maximum nickel recovery was achieved under the following leaching conditions: citric acid concentration 1 M, leaching temperature 40 °C, leaching time 15 days, ore particle size 212–355 μm, shaking speed 200 rpm, and pulp density 20 % w/v. The maximum nickel recovery from SS (96 %) was higher than that from SH (73 %) under the same leaching conditions. The dissolution behaviors of the raw saprolite ores and leaching residues were studied using XRD. The mineral contents of the ores greatly affected the leaching performance and mineral dissolution behavior. The results suggested that all dissolved nickel originated from lizardite, which were more easily leached than goethite, talc, and clinochlore. The lizardite content of SH was lower than that of SS, and therefore, nickel recovery from SH was lower than that from SS. In terms of the kinetics of nickel extraction, although the rate of nickel extraction for SS was faster than that for SH, the kinetics for leaching from the two ores was similar. Nickel leaching from SS and SH followed the shrinking-core model (SCM) and was controlled by diffusion through the solid product layer.

In Chapter 4, kinetics modeling of leaching of the ores by citric acid at atmospheric pressure is presented in more detail. The experimental data were well explained by the SCM, with the rate of reaction controlled by diffusion through the solid product layer. The apparent activation energy for the dissolution of nickel was around 12 kJ/mol. Based on the SCM, an empirical kinetic model for leaching of nickel from the Indonesian saprolite ore is proposed. This mathematical model is consistent with the observed experimental results.

In Chapter 5, the production of biogenic citric acid from corn starch and corn cobs using *Aspergillus niger* is described. Application of this biogenic citric acid to nickel leaching from Indonesian saprolite ores is also presented. The citric acid concentration was determined using ultraviolet-visible spectrophotometry, and high performance liquid chromatography was used to identify the products in the culture filtrate. The concentration of citric acid (0.05 M) was produced from 50 g/L corn starch after 5 days incubation at 30 °C with 3 % (volume fraction) methanol as an additive. This gave a citric acid yield of 230.4 g per kilogram of dry corn starch. Optimization of nickel leaching with the biogenic citric acid was attempted by varying several leaching parameters. The maximum nickel recovery (38–39 %) from SS and SH was achieved with a leaching temperature of 40 °C, 5 % of pulp density, <75 μm ore particle size, and 200 rpm shaker speed. The maximum nickel recovery from SS was reached quicker (3 days) than that from SH (7 days). The metal and mineral dissolution behaviors of the raw saprolite ores and leaching residues were studied using XRD. The results suggested that most nickel in the leaching solution originated from lizardite. This result was consistent with that obtained using citric acid. Compared with citric acid, biogenic citric acid was more effective for nickel leaching. Nickel extraction using biogenic citric acid from the fermentation of corn starch and corn cobs with *A. niger* will be a profitable method for processing of low-grade Indonesian saprolite ores.

Chapter 6 summarizes the conclusions of this study and recommendations for further study.