Recovery of Nickel from Selectively Reduced Laterite Ore by Sulphuric Acid Leaching

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The laterite ore with low nickel content deposits in Indonesia can be expected to be an alternative raw material of iron making due to its high iron content. One of the required processes is the separation of nickel and cobalt from the laterite ore by leaching it with H₂SO₄ at the atmospheric condition. The sample containing 50.88% iron, 0.03% cobalt and 0.30% nickel was selectively reduced with CO/CO₂ mixed gas to obtain metallic nickel and cobalt, as well as magnetite from hematite. Accordingly, in the leaching process metallic nickel and cobalt will be dissolved by controlling the iron dissolving. The effects of various parameters have been examined. These condition include leaching time, temperature (303–343 K), H₂SO₄ concentration (0.005–1.0) mol/l, as well as extraction rate of nickel.

The result of the analysis indicated that the influence of selective reduction could speed up the nickel extraction and obstructed the iron dissolution. The extraction rate of nickel was very high for small particle and slower for larger size. The optimal condition of the test was obtained at the leaching temperature of 343 K, 0.05 mol/l H₂SO₄ with a sample lower than 4.0 g/l. In 60 min after the test, about 93 mass% of nickel was extracted from the sample smaller than 44 µm. The nickel extraction would be higher by adding the leaching time. The rate of extraction was chemically controlled and the apparent activation energy was 42.2 kJ/mol. At the end of the leaching process, there was residual solid rich-magnetite and minimal nickel.

KEY WORDS: laterite ore; selective reduction; leaching; iron making.

1. Introduction

Laterite ore is one of the mineral resources containing several kinds of metal elements, such as nickel, cobalt, iron, silicon, aluminum and chromium. It is widely distributed in the equatorial region, such as Indonesia, and is mainly used as a nickel resource. However, the utilization is limited to only the laterite containing Ni more than two percent. While the Ni-less laterite ore has never been used effectively, in spite of its huge deposit, it sometimes has high content of iron of about 50 mass%. As Indonesia has no deposit of high-grade iron ore, the high-grade Fe laterite is quite attractive as a domestic iron resource. When the high-grade Fe laterite is used for iron and steel industries, the complicated chemical structure brings about some difficulties. The high amounts of nickel, cobalt and chromium contents result in the low quality of the iron product and the high content of aluminium oxide, so that the reduction and smelting process need large supply of energy. Therefore, an additional process is necessary to reduce the above components.

Some of the pyrometallurgical and hydrometallurgical methods have been reported to extract Ni and/or Co from laterite ore, such as leaching by sulphuric acid, hydrochloric leaching or nitric acid, sulphating process, and so on. One of the methods commercially applied is the direct pressure leaching using sulphuric acid (Moa Bay method) that is operated at the high temperature of 460–523 K. In the process, the nickel oxide in the laterite is dissolved into the pressurized sulphuric acid together with the ironhydrate. Since the main purpose of the method is the nickel extraction, no attention is paid to the iron recovery. Thus, the iron in the treated material has a difficult form to be recovered, making it difficult to apply the methods to the high-grade Fe laterite for its use as raw material in the iron making. Most of the works done in the past concerned the high pressure and high temperature process to extract the nickel and cobalt directly from ore without any pretreatments. These methods have never been paid attention to the extraction of iron. Therefore, the residual solids after the process have been treated as troublesome whereas the iron extraction is high.

This work is a part of the process development to utilize the Indonesian high-grade Fe laterite ore as an iron resource. Figure 1 shows the flow diagram of laterite processing. The purpose of the process is to separate the impurities of laterite ore by a combination process of selective reduction, leaching and magnetic separation. The selective reduction of the laterite ore by CO/CO₂ (30/70 vol%) mixed gas produced in metallic nickel and cobalt, together with
change of hematite to magnetite as reported by authors. The nickel will be extracted by leaching from selectively reduced laterite ore without insoluble iron, based on the difference affinity between metallic nickel and other metal oxides to acid. There will be a residue containing iron in the form of magnetite and other metal oxides. The residual solid after the extraction of nickel can be further treated by magnetic separation to recover the iron. Finally, the products of this process will be high iron content of magnetic concentrate that can be further processed as raw material for iron making. This paper describes the leaching process of laterite ore using sulphuric acid, including the effects of pretreatment of the laterite and leaching parameters on the nickel extraction under the atmospheric condition and lower temperature than 343 K.

2. Experimental

2.1. Sample

Laterite ore from the deposit of Sebuku Island (Indonesia) was used as an original laterite sample. Prior to the leaching tests, the original sample was reduced with the CO/CO₂ (30/70 vol%) mixed gas at 973 K for 90 min. The previous investigation

revealed that the goethite in the original laterite ore becomes magnetite by the reduction treatment whereas the nickel and cobalt oxides are converted to the respective form of metallic. The chemical composition of the sample is listed in Table 1. Following to the reduction, the sample was then mechanically crushed into the size under 177 μm. The size distribution of the sample is listed in Table 2.

2.2. Sulphuric Acid Leaching

Sulphuric acid leaching was carried out in a glass vessel. For each run, 1.0 g of the laterite sample was fed into 500 cm³ of preheated sulphuric acid solution at 303, 323 or 347 K with stirring speed of 400 rpm for 1 h. During the experiment, 10 cm³ of the solution was periodically sucked up through a pipette, and then subjected to the elemental analysis by the Inductively Coupled Plasma (ICP) analysis method. The change of proton concentration in the sulphuric acid solution during leaching was continuously measured with pH meter. After the leaching test, the residual solid in the solution was filtered and subjected to the elemental analysis. In preparation of the analysis, 0.5 g of the residual solid, which was previously melted with 1.0 g of mixture of Na₂CO₃, B₂O₃ and NaNO₃ (the respective concentrations of 0.57, 0.38 and 0.05 mass%), was completely dissolved in a HCl aqueous solution (5.0 mol/l). Iron content in the solution was determined by the titration method using 0.1 mol/l K₂Cr₂O₇ solution. Nickel contents in the solution were measured by the ICP.

3. Results and Discussion

3.1. Effect of Reduction Treatment

At first, leaching was carried out to 1.0 g sample with 0.5 mol H₂SO₄/l of water at the temperature of 343 K for 60 min. In order to clarify the effect of reduction on nickel and iron dissolution, leaching of unreduced laterite ore was performed as preliminary test. Figure 2 shows the results of leaching experiments using unreduced and reduced laterite ore with time. It was seen that the reaction time had a positive influence on nickel and iron extraction for reduced laterite, but had not significant effect for unreduced ore, both in the nickel and iron extraction. Nickel extraction from unreduced laterite was only about 5.5 mass% from total nickel content in the ore after 5 min leaching time with constant rate extraction and the extraction rate was very small. Leaching of reduced ore, the extraction of nickel was faster and reached about half of the total nickel extracted only in 5 min with increasing leaching time, afterwards. The results are similar with the works by Clarkson et al. and Apostolidis et al. that the reduction of nickel form oxide brings into rapid leaching of nickel from iron ore.

The dissolving of iron also followed the same trend with
nickel during leaching of reduced ore. However, the initial rate was not as high as the nickel extraction. Furthermore, iron from the unreduced ore did not appear in the solution during the leaching condition, because of its availability in the form of goethite which was not converted into hematite. Chou et al.16) describes that iron in the goethite was converted into insoluble hematite during pressure leaching at high temperature. And, the high concentration of sulphuric acid may cause the dissolution amount of iron into the solution. Therefore, to avoid the dissolution of iron, leaching process should be conducted at the minimum concentration of sulphuric acid.

3.2. Effect of Leaching Temperature

In order to investigate the effect of leaching temperature, a series of experiments were carried out with the leaching temperature varied of 303, 323 and 343 K. Figure 3 shows the effect of leaching temperature on nickel extraction. The results showed that in the interval time of 5 min, the initial extraction reached about half from the total extraction, after 60 min, for all temperatures. Besides, the extraction rate increased with the increasing leaching time. The final extractions of nickel at 303 and 323 K reached the value of 45 and 63 mass%, respectively. The results suggest that the leaching temperature had an important role in the nickel extraction, where leaching at the temperature of 303 K did not give good condition for nickel to be leached. By heating up the solution to 323 K, the nickel extraction became higher and higher at 343 K.

3.3. Effect of Acid Concentration

A number of experiments was conducted varying the H₂SO₄ concentration from 0.005 to 1.0 mol/l, while maintaining the temperature at 343 K and 1.0 g sample/l. The results of leaching for 15 and 45 min were plotted in Fig. 4. In general, acid concentrations gave positive effect to the nickel extraction. The most obvious feature of the figure was that under given conditions, nickel was leached faster at the acid concentration ranging from 0.005 to 0.05 mol/l. By increasing the acid concentration to 1.0 mol/l, the rate of nickel extraction became slower, both after 15 and 45 min leaching. The features indicated that nickel was most attractive to be dissolved at low acid concentration less than 0.1 mol/l.

The leaching of nickel metal in atmospheric acid solution can be defined as an electrochemical process. This process can be simplified as an analog of short-circuited cell. In this process, anodic metal oxidation releases electrons as consumption for cathodic reduction reaction. Thus, the dissolution process of metallic nickel during leaching should be assumed according to the reaction (1) and reaction (2) for the reduction reaction:

\[ \text{Ni} \rightarrow \text{Ni}^{2+} + 2e^- \] ..............................(1)
\[ 2H^+ + 2e^- \rightarrow H_2 \]..............................(2)

The exchange current density of reaction (2) is probably high in high acid concentration of solution. Thus, in the desired range acidity of solution, the reaction rate increases with acid concentration.

It should be noted that acid concentration of lower than 0.05 mol/l resulted in low of iron dissolution both after 15 and 45 min. However, the rate increased drastically by increasing the acid concentration to 1.0 mol/l and leaching time. The rates of iron dissolution were more sensitive in the high acid concentration than that of nickel. This phenomenon indicated that the high acid concentration led to iron-sulphate formation as described by Chou. Hirasawa et al.17) clarified that if the reaction between iron and sulphuric acid occurs, the iron sulphate was not re-transformed into hematite during leaching at low temperature. Therefore, in this experimental condition, the iron should be remained in the solid residue in the form of magnetite.

Figure 5 shows the X-ray patterns of samples after leaching. The appearance of magnetite peaks indicated that the iron remained in the solid residue as magnetite without any transformation to hematite. As expected that the nickel should be completely extracted with a minimum dissolution of iron, the acidity of solution should be set by H₂SO₄ concentration of lower than 0.05 mol/l.

3.4. Effect of Sample Feed

The effect of sample feed on the nickel and iron extraction was studied with experiments at constant temperature of 343 K and 0.05 mol H₂SO₄/l and by varying the samples feed of 1.0, 4.0, 5.0 and 10.0 g/l. The results were plotted in
Fig. 6 that shows the correlation between nickel extractions with time. Comparing the experimental results shown in this figure, it was seen that the sample feed below 4.0 g/l did not have significant effect on nickel leaching. From the data plot for sample feed of 10.0 g/l, the extraction rate decreased drastically to be half of the extraction rate for sample feed of 4.0 g/l or lower. This low value of nickel extraction could be seen after 5 min leaching and, at the end of experiment, the nickel extraction received only about 40 mass%. The concentrations of nickel in the solution are similar at the sample feed of 10.0 and 5.0 g/l while the contents decreased gradually at 4.0 and 1.0 g/l feed samples. It explained that low in sample feed results in the low nickel content. The quantity of nickel in the solution was proportional to that of nickel in the sample. In fact, the lowest of the sample feed resulted in the highest rate of extraction. Moreover, the concentration of \([H^+]/H_1\) in the solution, which was calculated based on the pH measured during leaching, showed the same result as the nickel concentration. Figure 7 shows that \([H^+]/H_1\) concentration drops in few minutes after starting, then decreased gradually and essentially remained constant thereafter in all cases. The \([H^+]/H_1\) concentration for 10.0 g/l was closed to that of 5.0 g/l, which clearly explains that at 5.0 g/l of sample feed or higher may cause the solution in passive condition. The same result also shown for leaching using large and narrow particle size range of 44–63 and 106–150 μm. The rates of nickel extraction increased gradually, and even the smaller particle gives higher extraction.

Table 3 shows chemical compositions of several residues after leaching using laterite sample under 44 μm. The samples residue contain about 52% of iron and 0.01% of nickel. The present of cobalt in the original ore was mostly dissolved during leaching, therefore its content was not detect-
ed at the residue due to the very low concentration. The contents of alumina, chromium and silica has been little change at the residues. It indicated that a part of these elements were dissolved during leaching process however their dissolution rate were seem very low.

### 3.6. Kinetics of Nickel Extraction

In order to study the kinetics of nickel extraction, a widespread shrinking core model was applied to analyze the experimental data. Under the conditions used in this work the rate of reaction was examined by the following parameter:\(^{18}\):

1. Chemical reaction at the surface:
   \[ 1 - (1-X)^{1/3} = a k_r f \] ..........................(3)

2. Internal diffusion through the porous layer:
   \[ 1 - 3(1-X)^{2/3} + 2(1-X) = \beta k_d f \] ..................(4)

3. Mixed step of chemical reaction and internal diffusion:
   \[ t/F = \gamma(3F - 2F^2) + \delta \] ...........................(5)

where, \( F = 1 - (1-X)^{1/3} \), \( k_r \): rate constant for chemical reaction (cm/min), \( k_d \): rate constant for diffusion (cm/min), \( t \): time (min), \( X \): fraction of nickel extraction (–), \( \alpha, \beta, \gamma, \delta \): constants at fixed condition (–).

To determined the most controlling mechanism during the nickel extraction, the experimental data presented in Fig. 8, the rates controlling are examined by plotting the left-hand side of Eqs. (3) and (4) versus time, and then relation between \( t/F \) versus \( 3F - 2F^2 \) for Eq. (5). The results are given in Fig. 9. From the value of regression coefficients \( R^2 \), the best fitting was obtained for Eq. (3) at particle size range of 44–63 \( \mu m \), suggesting a chemical reaction-controlled. The second fitting was the particle size range of 106–150 \( \mu m \), however, plot for wide range of particle size (0–44 and 0–177 \( \mu m \)) did not give a good fitting. The various of particle size with wide range resulted in different trends of extraction rate. Although the plots of first order reaction \( \ln(1-X) \) versus time was also examined, the fitting was worsted comparing with that of chemical reaction control plots as shown in Fig. 9. To determine the kinetic of nickel extraction by a shrinking core model, the particle size should be narrow down to get a homogenous particle. Here, the kinetic study was evaluated for the experimental data using particle size 44–63 \( \mu m \) at 303, 323 and 343 K. The plots of the left-hand side of Eq. (3) versus time is given in Fig. 10. The data plotted in the figure was fairly well. There was a reasonable correlation between the current nickel extraction data and Eq. (3), suggested that the most probable rate controlling reaction was the cathodic reaction in Eq. (2). From the slopes of the figure, the rate constants were obtained and the logarithmic values of \( k \) were plotted against reciprocal temperature. Figure 11 shows the Arrhenius plot for nickel extraction. The plots are straightly change with the reciprocal temperature, indicated that the temperature had a sharp effect on the nickel extraction.

From the temperature dependency as shown in Fig. 11, the apparent activation energy was obtained and given by the following equation:

\[ \ln k_r = 2.31 - 42.2x10^3/RT \] ..........................(6)
where, \( T \) is temperature (K) and \( R \) is gas constant, 8.314 J/mol.

Concerning with the purpose of this study, the residual solid was analyzed for the elemental composition using ICP. The nickel content measured from the residue was less than 0.02 mass% and the content of cobalt was undetected.

4. Conclusion

In order to utilize laterite ore for iron making, the leaching process was investigated by mean of \( H_2SO_4 \) to recover nickel selectively. Selective reduction of nickel oxide to metallic nickel led to the rapid leaching with minimum iron dissolution. The optimal process was obtained under the following conditions of 0.05 mol/l \( H_2SO_4 \) and 4.0 g/l of sample at 343 K.

The leaching rate of nickel was chemically controlled by the cathodic reaction of the solid surface. For the rate controlling process, the obtained activation energy was about 42.2 kJ/mol.

The residual solid containing less nickel and cobalt can be further processed as raw material for iron making by magnetic separation to recover the magnetite.

REFERENCES