The effect of pre-treatments to the nickel limonite leaching using dissolved gaseous SO$_2$-air

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Abstract. Nickel limonite leaching has been subjected to a number of studies, one of the method is by using dissolved gaseous SO$_2$-air. The selectivity of nickel over iron extracted from leaching using dissolved gaseous SO$_2$-air is advantageous, however the nickel that can be recovered is limited. This paper studies pre-treatments that is applied to the nickel ore prior leaching in order to increase the recovery of dissolved nickel from nickel limonite ore. There two pre-treatments that were carried out in this research, roasting and alkali-roasting using Na$_2$CO$_3$. The extraction was carried out for 180 min with pH 2, 3, 4, and 5 and temperature 30, 55, and 80 °C. It is found that the highest yield is achieved at pH 2 and 80 °C with nickel recovery of 61.39%. At pH 2, for alkali-roasting pre-treatment, the nickel yield raised from 28.17% to 100% and for roasting pre-treatment the nickel yield increased from 20.42% to 61.39%. However, at pH 2, the nickel to iron selectivity decreased from 96272 to 534 for roasting pre-treatment and from 1.8 to 1 for alkali-roasting pre-treatment.

1. Introduction

Nickel is a type of the metal that has various uses and application in industry. There are two types of nickel ore, nickel sulphide and nickel laterite. The latter is more abundant, as 70% of nickel ores in the world is categorized as nickel laterite. Currently, 60% of nickel used in industry is originated from nickel sulphide. The limited supply of nickel sulphide forces metallurgy industry to begin using nickel laterite as raw material. Based on the depth zone, nickel laterite is categorized into nickel limonite (low nickel content, <1.5% w/w) and nickel saprolite. Nickel limonite ore reserves in Indonesia reached 464 million wet metric tons while nickel saprolite ore reserves were only about 361.3 million wet metric tons. The common methods to extract nickel from nickel laterite ore is by using hydrometallurgy route, for example high pressure acid leaching (HPAL). This method extracted nickel by using sulphuric acid as leaching agent at 250 °C and 50 bar. Therefore, HPAL is not economical as it required high investment and operating cost.

Another method that has been developed to extract nickel laterite is by using dissolved gaseous SO$_2$-air. This method is known to provide a high nickel to iron selectivity [1], as well as rapid reaction rates at low temperatures and mild pressure [2]. Some factors that affect extraction results using SO$_2$ are the concentrations of solvent and operating temperature [3]. The higher the operating temperature as well as the more concentrated of solvent used, the more nickel is obtained. Previous research by the authors has obtained decent nickel selectivity but the nickel recovery is still low [4]. It is found that the good condition was obtained at pH 3, temperature of 80 °C, and 180 min leaching time, with nickel leaching efficiency of 21% from original nickel content. The selectivity nickel towards iron, defined by the extracted nickel (%) divided by extracted iron (%), has been found up to 2743 [4].

Pre-treatment is required prior to extraction to increase the nickel recovery rate. Of many pre-treatments that are available in the literatures, roasting and alkali-roasting are shown to increase the recovery of nickel. The presence of heating before extraction can increase the porosity of the nickel laterite ore and will expose the main mineral, goethite, thus accelerating the interaction between the reducing gas and the nickel species during the leaching process [5]. The pre-treatment of alkali-

roasting is done by adding Na_2CO_3 into limonite nickel ore. This alkali-roasting pre-treatment aims to get rid of Cr and Al from nickel ore.

This study is a further development of work of the authors to determine the effect of pre-treatment on the nickel recovery from limonite nickel ore extraction and to understand which of the pre-treatments give the highest nickel recovery.

2. Methodology

This study used nickel laterite ores originated from PT Bhumi Karya Utama located in South East Sulawesi, Indonesia. The composition of the ores is shown in Table 1. The nickel content in the ore is 1.33 %, with Fe content of 15.53 %. The schematic experimental setup is shown in figure 1. The experiments were conducted in three steps: pre-treatment, extraction, and analysis. There are two types of pre-treatment, roasting and alkali-roasting. Roasting pre-treatment was carried out by preparing limonite nickel ore into corundum crucibles then roasted at 650 °C in 46100 muffle furnace for 1 hour.

Table 1. Nickel limonite sample composition from PT Bhumi Karya Utama (in wt%)

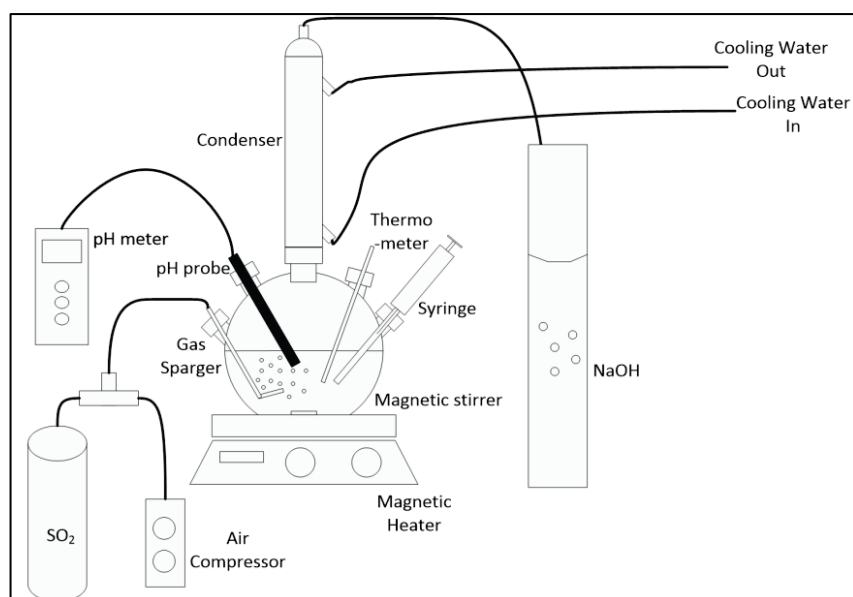| Ni (%)	Co (%)	Fe (%)	SiO_2 (%)	CaO (%)	MgO (%)	MnO (%)	Cr_2O_3 (%)	Al_2O_3 (%)	P_2O_5 (%)	TiO_2 (%)	SO_3 (%)
1.33	0.03	15.53	43.19	0.55	19.49	0.23	0.99	2.07	0.02	0.02	<0.01

Figure 1. Schematic experimental setup [4]

Alkali roasting pre-treatment was carried out by preparing a mixture of nickel limonite and Na_2CO_3 in corundum crucibles with Na_2CO_3 60% w/w. The mixture is then heated at 940 °C for 2 hours. It was then extracted using water at 95 °C for 30 minutes. The extraction results are then filtered using a filter paper and a Buchner funnel. The residue (unfiltered solids) will be processed at the later stage. The experimental procedure is similar to previous work [4]. The extraction process began by adding 1000 mL deionized water into the reactor and setting the temperature at 30, 55, or 80 °C. Then, 8 gram of pre-treated nickel limonite ore were fed into the reactor. Samples, 10 mL each, were withdrawn from the reactor at specified time range and then filtered using a syringe filter. Its metal content was then

analyzed by AAS (atomic absorption spectrometer) analysis. At the end of the extraction (180 minutes), the residue was separated from the solution using a Buchner funnel. The dried residue was then analyzed by using XRD (X-ray diffraction) and TGA-DSC (thermogravimetric analysis – differential scanning calorimetry). The nickel to iron selectivity was calculated using equation 1.

$$nickel\ selectivity = \frac{\left(\frac{nickel}{iron}\right) in\ solution}{\left(\frac{nickel}{iron}\right) in\ ores} \tag{1}$$
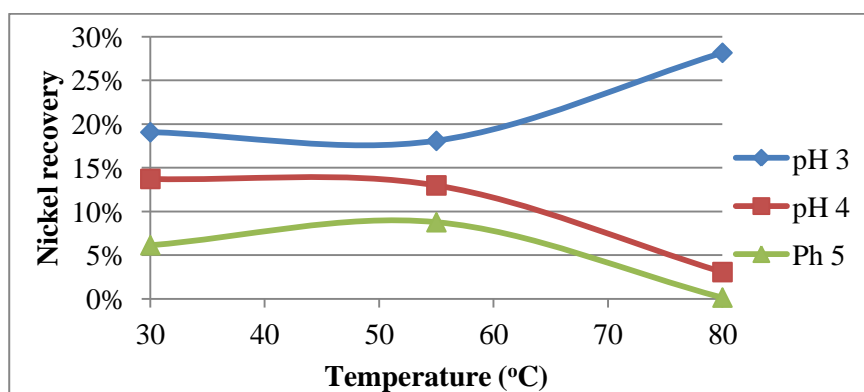
3. Results and Discussions

Figure 2. Nickel recovery at various pH and temperature.

3.1. Roasting pre-treatment

Figure 2 shows the nickel recovery at various pH and temperature. In addition to the nickel recovery, the nickel selectivity to iron from limonite nickel extraction is also evaluated. Table 2 shows nickel recovery for roasting pre-treatment and extraction for 180 minutes. Iron recovery from extraction with roasting pre-treatment is much lower compared to nickel recovery. This is due to the use of dissolved gaseous SO_2-air in the extraction process which has higher selectivity rate for nickel than iron [1]. Thus, the use of dissolved gaseous SO_2-air for limonite nickel extraction is considered suitable as the iron in the nickel is not extracted and no further iron separation is needed. At pH 2, the nickel recovery is 61.39%, much higher compared to other process condition; however, iron also starts to dissolve significantly, with a recovery of 3.5% and leads to a selectivity of 17.5.

3.2. Alkali roasting pre-treatment with Na_2CO_3

In alkali-roasting pre-treatment using Na_2CO_3, a TGA-DSC analysis is needed to determine the temperature at which the reaction between nickel limonite and Na_2CO_3 (mass ratio 0.6:1) occur, the result is shown in Figure 3. There are three temperature ranges at mass changes occurs: 30°C to 160°C, 200°C to 330°C, and 730°C to 940°C.

    This result was then compared to the work of Astuti *et al* which analyze saprolitic ore using DSC [6]. The largest mass changes (10.3%) occurred when the temperature range 730°C to 940°C. First, mass change was occured at temperatures of 30°C to 160°C followed by endothermic peaks on DSC results, this mass change is caused by the evaporation of water absorbed in nickel ore. Subsequent mass changes was caused by the presence of de-hydroxylation of goethite. This is indicated by the temperature of the mass changes that are in the vicinity of goethite de-hydroxylation temperature [6]. Usually goethite-hematite transformation occurs at temperature 385°C for goethite which has high crystalline structure, whereas goethite with low crystallinity and fine grains will undergo transformation at lower temperature [7]. The reaction between Na_2CO_3 and nickel limonite begins

with the decomposition of Na_2CO_3 to Na_2O and then reacts again with chromium(III) oxide (Cr_2O_3), alumina (Al_2O_3), silica (Si_2O_3) and iron(III) oxide (Fe_2O_3). This reaction starts to occur at 850°C.

Table 2. Nickel and iron recovery at various pH and temperature.

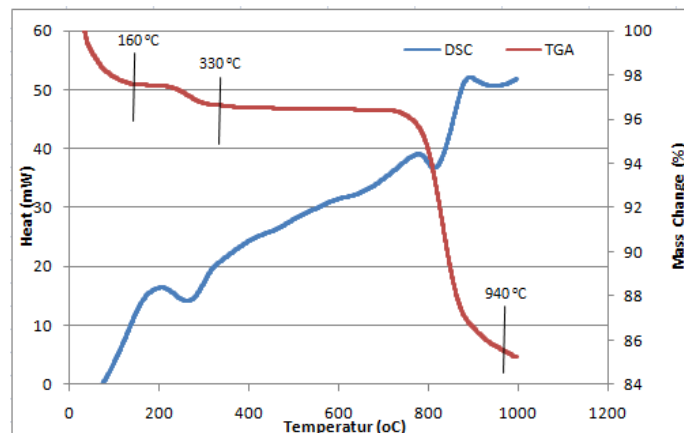| pH	Temperature (°C)	Nickel recovery	Iron recovery	Selectivity
2	80	61.39%	3.5%	17.5
3	30	19.08%	0.4203 %	45.4
3	55	18.09%	0.0003 %	61821.9
3	80	28.7%	0.0003 %	96272.6
4	30	13.73%	0.0003 %	46930.9
4	55	12.99%	0.0003 %	44398.3
4	80	3.07%	0.0003 %	10237.5
5	30	6.14%	0.0003 %	20993.8
5	55	8.78%	0.0003 %	30010.8
5	80	0.16%	0.0003 %	534

Figure 3. TGA result for Na_2CO_3 and nickel limonite mixture.

Table 3. Nickel and iron recovery from extraction with alkali roasting pre-treatment.

pH	Temperature (°C)	Nickel recovery	Iron recovery	Selectivity
2	80	100%	100%	1
3	30	20.42%	11.1%	1.8
3	55	3.95%	0.0158%	250.2
3	80	5.71%	0.0130%	438.7

The data distribution of iron recovery, nickel recovery, and selectivity levels can be seen in Table 3. Nickel recovery profile for roasting and alkali roasting pre-treatment is similar. However, the

recovery obtained in alkali roasting pre-treatment is smaller than roasting pre-treatment (20.42% compared to 28.7%). When the extraction is done in pH 2, nickel recovery reach 100%, but the iron that dissolves with nickel is also quite high, reaching 100%. Therefore, this condition cannot be used further due to significant decreased in nickel selectivity compared to extraction at pH 3.

3.3. Comparison of the roasting and alkali roasting pre-treatment
Figure 4 shows the nickel recovery with and without pre-treatment at pH 3 and 80°C. Nickel recovery increases with time of extraction.
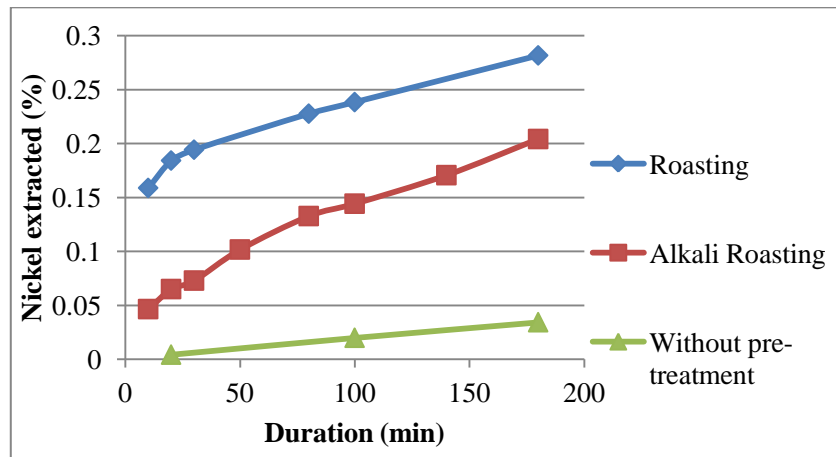

Figure 4. Result of nickel recovery from nickel limonite extraction with and without pre-treatment.
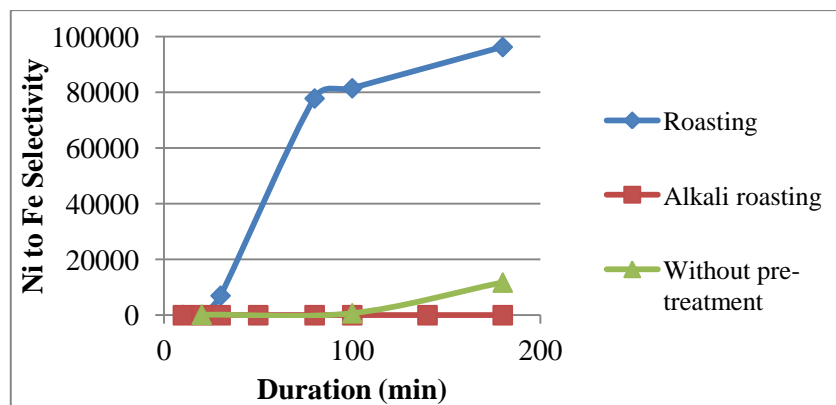

Figure 5. Nickel to iron selectivity with and without pre-treatment.

In addition, the curve also shows that pre-treatment is proven to increase nickel gain from 3.5% to 20.4% for alkali-roasting pre-treatment, and 28.2% for pre-treatment roasting. Figure 5 shows the selectivity of nickel to iron with and without pre-treatments. In general, selectivity for limonite nickel ore with pre-treatments increased with increasing extraction duration while selectivity for alkali-roasting pre-treatment tended to be constant. Roasting pre-treatment has the highest selectivity level of about 96272.6. Therefore, it can be concluded that the most suitable method of pre-treatment for limonite nickel extraction using SO_2-air is roasting at 650°C.

4. Conclusions

In this paper, the effect of pre-treatments to leaching of limonite ore using dissolved SO2-air was carried out. The roasting pre-treatment has shown better leaching recovery compared to the Na_2CO_3 roasting. The highest nickel recovery was obtained at pH condition of 2 at 80 °C using roasting pre-treatment, with nickel recovery of 61.39%. However, the selectivity of nickel over iron is 17.5, implying that many iron still dissolves in the leaching solution. The best process condition with highest nickel selectivity towards iron is at pH 3 and temperature of 80 °C, with nickel recovery of 28.7% and selectivity of 96000. Alkali roasting pre-treatment has shown nickel recovery to 100% at pH 2 and temperature of 80° C process condition, but with trade-off of the dissolution of all iron to the leaching solution.

Acknowledgment

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