THE EFFECT OF SULFURIC ACID CONCENTRATION ON NICKEL RECOVERY FROM LATERITE ORE BY USING ATMOSPHERIC ACID LEACHING METHOD

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Abstract

The processing of laterite ore by pyrometallurgy requires high temperatures whereas the Atmospheric Acid Leaching (AAL) method can be performed below 100 ℃ although its nickel recovery is inconsistent. This research aims to determine the effect of sulfuric acid concentration on nickel recovery and to determine nickel recovery after extract purification by precipitation of non-nickel metals. AAL was performed with an operating temperature of 95 °C, an operating time of 5 hours, an ore-to-solvent ratio of 0.05 g/ml, a particle size of ± 200 mesh, and sulfuric acid concentration variation of 0.2–1 M. Iron precipitation was completed with a pH variation of 0.5–3.8 by the addition of ammonia. The result showed that the concentration of sulfuric acid increased nickel recovery. The nickel recovery reached 96.43% at a concentration of sulfuric acid of 1 M. Furthermore, after extract purification, nickel recovery reached 50.61%, which was achieved at an optimum pH of 3.2.

***Keywords**: atmospheric acid leaching, recovery, nickel laterite, sulfuric acid*

Introduction

Due to the development of electric vehicle battery industry, the global demand for nickel is increasing. Indonesia, which has 21 million tons of nickel reserves, has the opportunity to obtain advantages. The depletion of sulfide ore reserves provides laterite ore with the opportunity to meet further demand. Nowadays, with the development of the electric vehicle battery industry, the global demand for nickel is increasing. According to data from the Ministry of State-Owned Enterprises (2021), Indonesia's nickel reserves are 21 million tons of Ni, which is 23.72% of the world's nickel reserves. By this figure, Indonesia ranks first in the world's largest nickel reserves. On January 1, 2020, the government banned the export of raw nickel ore to be further processed to obtain added value.

Indonesia and other equatorial countries are rich in laterite nickel (Prasetyo, 2016). However, there is a serious problem with the processing of nickel ore, due to high energy consumption. In Indonesia, nickel processing through pyrometallurgy to process saprolite ore (Ni > 1.5%) has been carried out while hydrometallurgy to process limonite ore (Ni < 1.5%) is still new. The most common hydrometallurgy process in use today is High-Pressure Acid Leaching (HPAL). However, HPAL has drawbacks in terms of high capital cost and corrosion problems.

Until now, there have been several studies on the kinetics of laterite nickel ore processing using the Atmospheric Acid Leaching (AAL) process. The AAL process has many advantages over HPAL, including lower capital cost, relatively conventional equipment, and technology, lower costs of construction materials for equipment and maintenance, easier process control, and lower energy consumption. However, due to the inconsistency of nickel recovery and high acid consumption, the AAL process has not been well tested commercially. In addition, the main minerals of laterite ore in the form of goethite (α-FeOOH) are difficult to break at atmospheric pressure, resulting in a low level of leaching selectivity between nickel and iron. Rao et al. (2020) carried out ore pre-roasting to change the structure of goethite to hematite in order to increase the recovery of nickel.

Sulfuric acid has been widely applied in the nickel processing using hydrometallurgy. A research by Hidayat et al. (2021) using nickel ore with a 1.55% Ni content in 5 M and 6 M H_2SO_4 solvents where the ore to solvent ratio 20 g/200 ml resulted in a nickel recovery of 2.60%. A research by Febriana et al. (2018) using nickel ore with 1.42% Ni content in 1 M H_2SO_4 solvent where the ore to solvent ratio 2.5 g/100 ml resulted in a nickel recovery of 95.9%. Lastly, a research by Wanta et al. (2017) using nickel ore with a 2.93% Ni content in 0.1 M H_2SO_4 solvent resulted in 13% nickel recovery. From these researches, it can be concluded that the recovery has been inconsistent; therefore, it is necessary to investigate the effect of sulfuric acid concentration on nickel recovery. In addition, the content of other metals contained in the ore interferes the purity of the extract. One of the purification methods is precipitation other metals than nickel. The results of a research by Rao et al. (2020) showed that precipitation caused a decrease in iron concentration from 1660 µg/ml to 147 µg/ml and a decrease in nickel concentration from 1050 µg/ml to 1009 µg/ml. From this research, it can be concluded that precipitation reduces nickel recovery. Therefore, it is necessary to investigate the nickel recovery after precipitation.

This research was conducted to determine the effect of sulfuric acid concentration as a solvent on the recovery of nickel and to determine the recovery of nickel after purification of extracts by precipitation of non-nickel metals. The results of this study are expected to provide another view on the processing of laterite nickel ore, especially with the AAL method.

Research Methods

Tools and materials

The materials used were nickel laterite ore obtained from PT. Antam Pomalaa, Southeast Sulawesi, 98% technical sulfuric acid, 25% technical ammonia, aquades, and standard solutions of nickel and iron for Atomic Absorption Spectrophotometry (AAS) calibration. The equipments used were ball mill, sieve shaker, porcelain crucible, furnace, analytical digital scale, a set of lab scale AAL equipment, and AAS SavantAA.

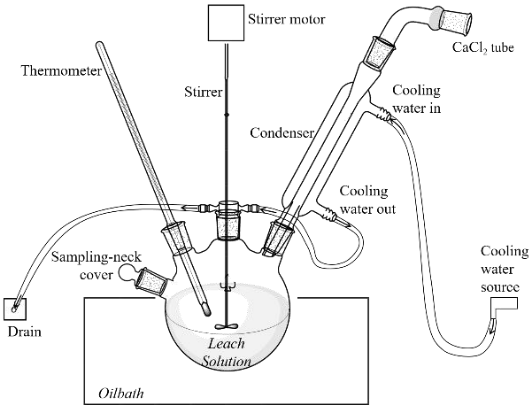

Figure 1. Schematic of atmospheric acid leaching equipment

Preparation of nickel ore

The preparation of raw materials began with drying the nickel ore. Then, the ore was ground using a ball mill and sieved. The particles processed to the AAL stage were 60 to 230 µm in size. The ground ore was then analyzed for its metal composition using the X-Ray Fluorescence (XRF) Portable Thermo Scientific Niton type XL3t 500 Analyzers instrument at the Indonesian Institute of Sciences. Then, the pre-roasting of the ore was done at a temperature of 400 °C for 1 hour using a furnace.

Atmospheric acid leaching process

The AAL process was conducted at the Unit Process Laboratory of the Chemical Engineering Department, State Polytechnic of Bandung. This process was completed in a set of lab scale AAL equipment consisting of a four-necked flask which was heated using an oil bath and was equipped with a thermometer, stirrer, condenser, and a sampling point as presented in Figure 1. The AAL process is carried out at a temperature of 95 ºC (Safitri et al., 2021). Stirring is done at a speed of 100 rpm (Agacayak & Zedef, 2012). The slurry ratio is 0.05 g ore/ml solvent (Fathoni & Mubarok, 2015). The concentration of sulfuric acid in each run were 0.2 M, 0.4 M, 0.6 M, 0.8 M, and 1 M. The AAL process was carried out for 5 hours. In the first 2 hours, samples were taken every 30 minutes and the next 3 hours samples were taken every 1 hour. Each sampling took as much as 2 × 5 ml.

Atomic absorption spectrophotometry analysis

Ni content in samples were analyzed using AAS-Ni cathode lamp with a wavelength of 352.4 nm. Each sample was filtered using Whatman No. 42 then diluted 100 times in order to meet the working range of 0.70–28.0 ppm.

Precipitation process

Furthermore, non-nickel metal precipitation was done by adjusting the pH. Ammonia 5% was added to the leach solution until the pH value matched the variation, namely 0.5; 0.8; 1.1; 1.4; 1.7; 2.0; 2.3; 2.6; 2.9; 3.2; 3.5; and 3.8. Sampling was carried out on each end result of variations in pH. The samples were analyzed for nickel and iron content using AAS. Each sample was filtered using Whatman No. 42. To analyze the iron content, an Fe cathode lamp with a wavelength of 372 nm was used. The sample was diluted 100 times in order to meet the working range of 20–80 ppm.

Results and Discussion

Pre-treatment of nickel ore

Laterite ore, which was a clod, was dried in direct sunlight. The weight of the ore was reduced by 25% from the original 2 kg to 1.5 kg. The dry ore was easier to grind with a ball mill. The results were sieved to obtain ore size of 63–250 microns or equivalent to 230–60 mesh. The smaller the particle size, the larger the surface area of the particles in contact with the solvent and the more nickel can be extracted. The appearance of each fraction is presented in Figure 2.

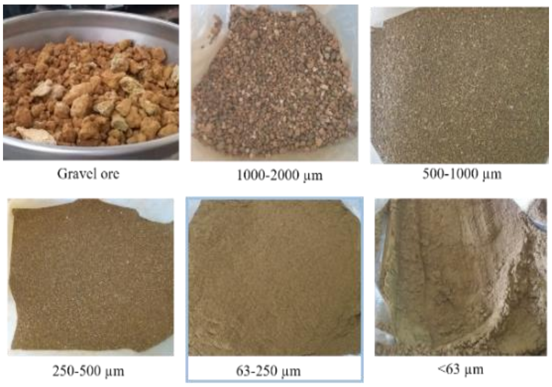

Figure 2. Visual appearance of ore fraction

Characteristics of nickel ore

The XRF test results of nickel ore in this research was compared to the research by Safitri et al. (2021). It is presented in Table 1.

Table 1. The XRF test results of nickel ore

Elements	Unit	This Research	Safitri et al. (2021)
Ni	(%)	1.895	1.47
Mo	(%)	0.002	
Zn	(%)	0.045	0.031
Co	(%)	0.082	0.019
Fe	(%)	29.93	23.823
Mn	(%)	0.336	0.325
Cr	(%)	0.941	1.56
Ti	(%)	0.038	
Cd	(%)	0.099	
Ag	(%)	0.096	
Pd	(%)	0.052	
Mg	(%)		0.052
Si	(%)		1.491
Al	(%)		1.723
Ca	(%)	0.054	<0.001
Cu	(%)		0.009
Bal	(%)	66.441	

Source: Safitri et al. (2021)

Balance (Bal) shows the amount of metal content that cannot be detected by the instrument, namely magnesium, aluminum, silicate, and the others. Each element has a different level of reactivity. Reactivity indicates the ease of reaction of an element with other compounds. Figure 3 shows the level of reactivity of several elements.

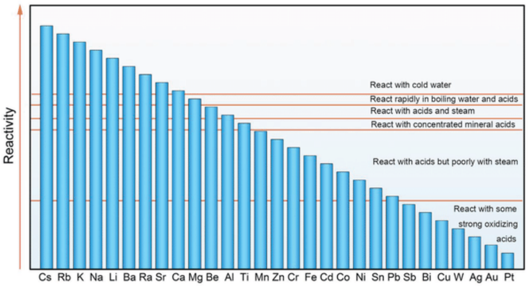

Figure 3. The level of reactivity of several Elements (Liu et al., 2019)

XRF results show that the dominant element in laterite ore is iron. Based on Figure 3, the level of reactivity of iron is higher than nickel. This causes sulfuric acid to react more easily with iron than nickel. Therefore, after the AAL process, the iron needs to be separated from the nickel by precipitation. Other elements to consider are manganese, chromium, and magnesium. Manganese content in ore is 0.336% and chromium content in ore is 0.941%. Both elements have higher reactivities to acids than nickel. Magnesium content in Indonesian laterite ore is 0.052% (Safitri et al., 2021). This value causes the presence of magnesium to be insignificant even though it has a high acid reactivity compared to nickel.

Pre-roasting of nickel ore

The weight of the ore was reduced by 15% from 589.8715 g to 501.6549 g. Pre-roasting turned goethite into hematite. The change reaction of goethite (FeOOH) to hematite (Fe_2O_3) is shown in Equation 1. This structural change formed nano-voids which increased the specific surface area of the ore. Thus, the contact between the ore and the acid solution during leaching is enable to be increased (Landers & Gilkes, 2009; Rao et al., 2020).

$$2FeOOH_{(s)} \rightleftharpoons Fe_2O_{3(s)} + H_2O_{(g)} \qquad (1)$$

Effects of sulfuric acid concentration on the recovery of nickel

The graph of nickel recovery for each variation is presented in Figure 4. The visual appearance of the final leach solution after 5 hours or 300 minutes at each variation is presented in Figure 5.

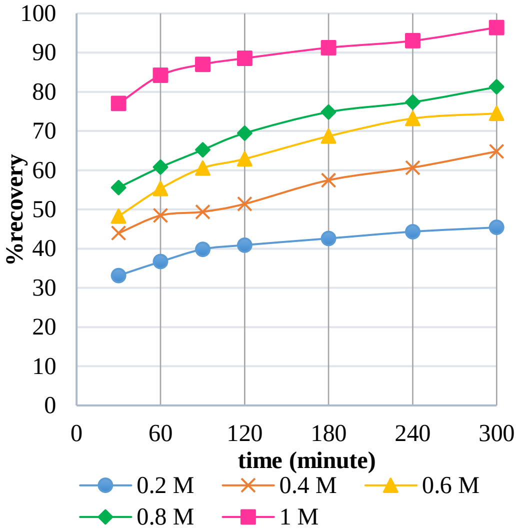

Figure 4. Nickel recovery for various sulfuric acid concentrations

Figure 4 shows that the higher the concentration of sulfuric acid used, the higher the recovery of nickel. The acid concentration is directly proportional to the recovery of nickel up to the maximum nickel recovery of 96.43%. However, if the sulfuric acid concentration exceeds 1 M, the nickel recovery will actually decrease. This has been demonstrated in a research conducted by Li et al., (2017). It is explained that at the use of sulfuric acid above 5.6 M, nickel recovery decreases. At concentrations of sulfuric acid above 5.6 M, the nickel sulfate produced is not completely soluble in water. $NiSO_4(H_2O)$ becomes a precipitate that forms on the surface of the ore. This causes the contact surface area to decrease which makes the reaction rate decreases.

Solvent: H_2SO_4 0.2 M	Solvent: H_2SO_4 0.4 M	Solvent: H_2SO_4 0.6 M	Solvent: H_2SO_4 0.8 M	Solvent: H_2SO_4 1 M

Figure 5. The visual appearance of final leach solution

Acid not only extracts nickel but also other metals which are dominated by iron (Fe). Based on Figure 5, the leach solution with the higher recovery of nickel is more greenish because it contains more Ni^{2+} compounds, while in the leach solution with the lower recovery of nickel, the color of the solution is brown because the solution contains more Fe^{3+}. The recovery of nickel reached 96.43% at the use of 1 M sulfuric acid after the AAL process lasted for 300 minutes.

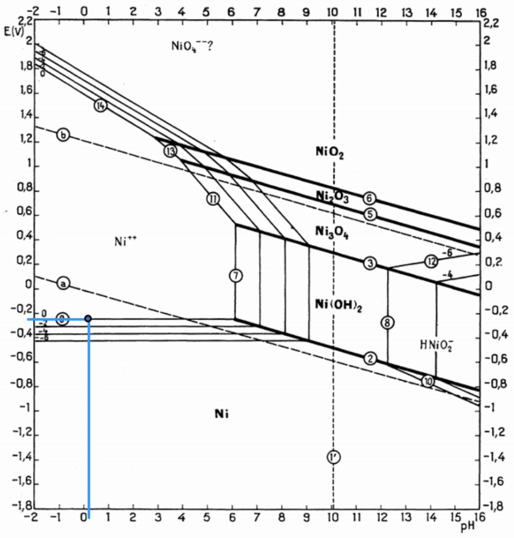

Figure 6. Pourbaix diagram for nickel
Source: Anderson et al. (2012)

Figure 6 shows Pourbaix diagram for nickel on the Nickel-H_2O system at 25 °C. Based on Figure 6, it can be seen that the change of Ni to Ni^{2+} occurs on the line which is influenced by the potential value. The potential value of $Ni^{2+} + 2e^- \rightleftharpoons Ni$ is -0.27 V and the AAL process takes place at pH 0.2. In the Pourbaix diagram, this point is in the corrosion zone which makes Ni reacts with acid. The AAL process was carried out at a temperature of 95°C; therefore, the reaction speed increased.

Precipitation of non-nickel metal

The non-nickel metal precipitation stage was performed to minimize the concentration of impurities (non-nickel metal) and to enable the process of the next stage to be carried out efficiently. Non-nickel metal precipitation was done in leach solution which produced the optimal recovery of nickel, namely the use of 1 M sulfuric acid. The results of precipitation at various pH values are shown in Figure 7.

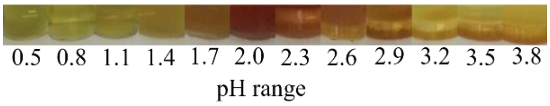

Figure 7. The Results of Precipitation

Based on Figure 7, it can be seen that at a higher pH, more precipitates are formed. It is because the reaction between iron and other metals with ammonia causes metal precipitation. The reaction between iron and ammonia is shown in equation 2 as follows.

$$Fe_2(SO_4)_{3(aq)} + 6NH_4OH_{(aq)} \rightarrow 3(NH_4)_2SO_{4(aq)} + 2Fe(OH)_{3(s)} \qquad (2)$$

The precipitate of $Fe(OH)_3$ formed was rust brown as shown in Figure 7. The concentration of nickel and iron in the liquid after metal precipitation at various pH variations is shown in Figure 8 as follows.

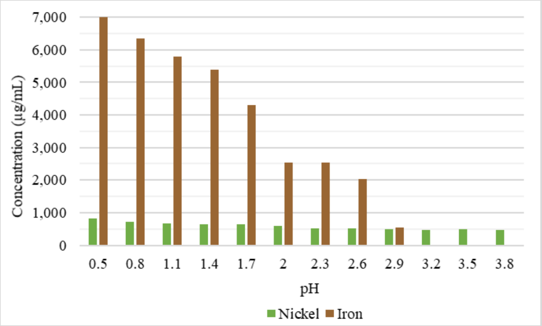

Figure 8. Concentration of residual nickel and iron after precipitation

Figure 8 shows that there was an increase in iron precipitation in the pH range of 0.8 to 2. Some of the nickel also precipitated, after which the rate of iron precipitation decreasing from pH 2. At a pH of 0.5–2.9, it can be seen that there was remaining iron content unprecipitated. At pH 3.2, all the iron had precipitated while the nickel concentration was reduced from 914 µg/ml to 480 µg/ml. It was the optimum pH for the non-nickel metal precipitation process using ammonia from a metal-sulphate solution.

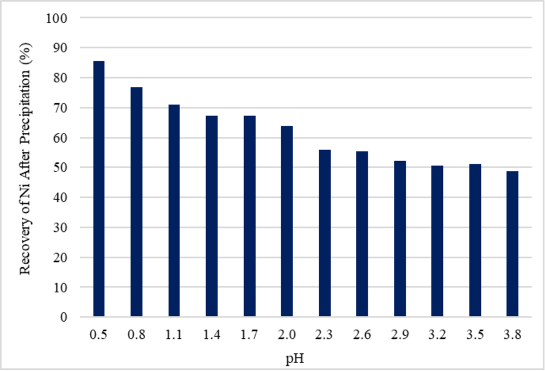

Figure 9. Recovery of nickel after precipitation

Figure 9 shows the recovery of nickel obtained after the precipitation process at various pH levels. Based on Figure 9, it can be seen that the recovery of nickel after precipitation at the optimum pH of 3.2 was 54.70%. The research conducted by Rao et al. (2020) showed the similar trends, namely the optimum precipitation of iron occurred at pH 3,0. Comparison of nickel and iron concentrations before and after precipitation in this research and the research conducted by Rao et al., (2020) is shown in Table 2.

Table 2. The comparison of nickel and iron concentrations before and after precipitation

	This study		**Rao et al (2020)**	
	Ni	**Fe**	**Ni**	**Fe**
Concentration in *leach solution* (µg/mL)	914	9875	1050	1660
Concentration of Fe/concentration of Ni	10.81		1.58	
Concentration in liquid after precipitation (µg/mL)	480	0	1009	147
Decrease of concentration	434	9875	41	1513
Decrease of Fe concentration/decrease of Ni concentration	23		36	

Source: Rao et al. (2020)

In this research, the difference between nickel and iron concentrations in the leach solution was very far, 8961 µg/mL (Fe/Ni ratio = 10.81), whereas in the research by Rao et al., (2020), the difference was not far, 610 µg/mL (Fe/Ni ratio = 1.58). In this research, the purity of nickel was improved because iron can be completely precipitated after precipitation. However, there was also a decrease in nickel concentration from 914 µg/mL to 480 µg/mL. The concentration of iron in the leach solution in the research by Rao et al. (2020) was not as great as in this research; therefore, the decrease in nickel concentration was not as much as in this research.

Furthermore, the nickel processing process can be continued with the solvent extraction method to separate nickel from other metal impurities (Al, Mn, Co, etc.) and then proceed with solution concentration and electrowinning to obtain solid nickel metal.

Conclusion

Based on the results of the research that has been conducted, it can be concluded that the concentration of sulfuric acid increases the recovery of nickel, and the recovery of nickel reaches 96.43% at 1 M sulfuric acid concentration. The nickel recovery after iron precipitation was 50.61%, which was achieved at an optimum pH of 3.2. Furthermore, as a follow-up, it suggests that the XRF test is better if the instrument is enabled to analyze more complete metal contents such as silicates, aluminum and magnesium. In addition, it is necessary to conduct further research regarding the process of acid solvent wastewater used for the AAL process. In industrial scale calculations, heating the solution to 95 °C within 5 hours with an ore to solvent ratio of 0.05 µg/ml is still relatively expensive. Additionally, conducting further research regarding the recovery of nickel which was co-precipitated during the non-nickel metal precipitation process using ammonia is needed.

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