Valuable Metals Precipitation of Low Grade Nickel Ore Leachate Using Sodium Hydroxide

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Abstract. Nickel metal is widely used in various industries. Nickel sources come from nickel sulfide ores and nickel oxide ores (laterite). Nickel content in laterite ore is 1.5-2.5 % (weight basis), lower than the nickel content in sulfide ores. Indonesia is one of the major nickel producers with laterite nickel ore reserves of 1576 million tons or 15 % of total world reserves. The distribution of laterite nickel in Indonesia is found in several regions such as Maluku, Sulawesi and Papua. However, the low grade nickel processing in Indonesia has not been well established. Thus research on valuable metals extraction from ow grade nickel ore has put some interest to some researchers. In this study, precipitation of valuable metals from low grade nickel leachate was conducted using sodium hydroxide as the precipitation reagent. Nickel ore used in this experiment was obtained from Pomalaa, Southeast Sulawesi. After leaching at optimum condition resulting of about 75 % recovery of nickel using HCl (1 M at 90 °C and stirring for 1 hour), the leachate was then added sodium hydroxide to varied pH of 8, 10, and 12. Along with the pH conditioning, temperature was kept to the value of 55 °C, 70 °C, and 85 °C. The optimum nickel recovery of 83.97 % is obtained at pH 12 and temperature of 85 °C. The residual metals concentration in the solution after precipitation was analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES).

1. Introduction
Nickel is a transition metal that is needed by various industrial fields. Nickel is often used as steel coatings, copper coatings, battery sources, and the automotive industry [1]. Based on research, as much as 66.2 % of Nickel metal consumption is dominated by the stainless steel industry [2]. Nickel on the earth is in the form of oxides and sulfides. Sulfide nickel has a higher Nickel content than Nickel Oxide (laterite Nickel), so the processing process is easier. Though nickel deposits in the soil are dominated by laterite nickel. Ore in the form of sulfide (Ni, Fe)S₂ there is only about 27 % of the total nickel ore in the world.

Indonesia is one of the countries with significant nickel resources, the resources of laterite ore in Indonesia reached 3.5 billion tons, equivalent to 52.2 million tons of Ni metal spread in Maluku,
Sulawesi and Papua [3]. Most nickel ore reserves in Indonesia are from laterite nickel. The processed nickel laterite profile comes from zone limonite (Ni 0.8 % -1.5 %) and low grade saprolite zone (1.5 % - 1.8 %). In general, nickel ore processing is carried out with two processes, namely hydrometallurgy and pyro metallurgy (smelting). The pyro metallurgical process of nickel processing in the limonite and saprolite zones requires high energy, so the costs incurred are also high. The hydrometallurgical process can be chosen as an alternative to processing low grade nickel ore <1.5 %. So far, many hydrometallurgical processes with a leaching process use high pressure HPAL / PAL with the main NiS products which are also costly and high energy. The Caron process is also one of the hydrometallurgical methods where the main product is NiO. The process of leaching in current atmospheric conditions has attracted many researchers. The leaching process in atmospheric conditions are a direct leaching of laterite nickel ore using organic and inorganic acids. Leaching using inorganic acids in atmospheric conditions has been carried out [4] and Leaching with organic acids [5], [6], [7], [8], [9], [10].

For nickel-rich leaching solutions, they are selectively deposited using the hydroxide precipitation, sulfuric precipitation, and hybrid precipitation methods [11]. The advantages of the Hydrochloric Acid leaching method include the reactant materials used are easily available, relatively inexpensive, and easy to do [6]. The optimum conditions for nickel laterite extraction were obtained at a temperature of 100 °C and a concentration of 5.5 M [12].

The leaching process is carried out to extract nickel components in nickel ore. But not only nickel components are taken when doing leaching. Leaching solutions contain several metal ions such as Fe³⁺, Fe²⁺, Al³⁺, Cr³⁺, Ni²⁺, Co³⁺, Mn²⁺, and Mg²⁺. The solution obtained from leaching chloride was precipitated using NaOH. Precipitation can be carried out in the pH range 7.5 - 9.0 and at temperatures between 25 - 75 °C [13].

In this study the influence of temperature and pH on the deposition process of low grade nickel ore leaching solutions using NaOH will be observed. The choice of NaOH settling because it is a hygroscopic compound in which NaOH has the ability to absorb moisture from the environment.

2. Materials and Methods

2.1. Materials

The raw materials used are nickel ore and hydrochloric acid solutions. A 750 ml solution of 0.1 M hydrochloric acid was prepared and then put into a three neck flask equipped with a stirrer, thermometer and reverse cooler. Uniform nickel ore (-200 mesh particle diameter) weighs 150 grams. Furthermore, nickel ore is put into a three-neck flask. An acid solution containing nickel ore is heated to 90 °C. The leaching process is carried out for 4 hours. The results of leaching are then filtered using filter paper to separate solids and liquids. The filtered sample will then be analyzed using the AAS Inductively Coupled Plasma (ICP) [6]. Table 1 is the result of analysis using ICP-AAS low grade nickel ore leaching solution using hydrochloric acid.

The other raw materials used were NaOH obtained from PT Merck and aquades obtained from the Laboratory of Energy Conservation and Pollution Prevention (KEPP), Faculty of Engineering UGM Yogyakarta.

| Table 1. ICP-AAS Analysis Results for Laterite Ore Nickel Leaching Solution |
|---------------------------------|-----------------|
| Component | Concentration (ppm) |
|----------------|-----------------|
| Fe | 4588.69 |
| Al | 587.09 |
| Si | 546.02 |
| Ni | 160.77 |

The results of the analysis of the initial leaching solution were used as a comparison to the precipitation results. The metals were analyzed by ICP AAS as many as 4 metals, namely Fe, Al, Si, and Ni. The metal was chosen because the percentage of concentration was the highest. Table 1 shows
that Fe is the main metal composing leaching solution which is equal to 4588.69 ppm and Ni metal obtained is 160.77 ppm.

2.2. Methods
Leaching results that have been analyzed, then placed in a beaker. 15 % NaOH solution is prepared. Precipitation is done using a shaker. The extract solution (leaching) of 100 ml was put into Erlenmeyer then 15 % NaOH was added to pH 8. Erlenmeyer was then put into a shaker. Shakers are set at 55 °C and turned on for 1 hour. The results of the sediment are then filtered using filter paper and oven at 90 °C.

The filtered liquid is then analyzed using an Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The experiment was repeated under depositional conditions pH 10 and 12 and temperatures of 70 °C and 85 °C.

3. Results and Discussions
The deposition process is carried out by adding 15 % NaOH to the desired pH. The variations in pH used are 8, 10, and 12. The temperature used is 55 °C, 70 °C, and 85 °C. Deposition results show that the higher the pH, the more sediment formed darkens. At pH 12, the color of the precipitate formed tends to be close to black because more oxidized metal [14].

![Figure 1 Precipitate at pH 8, pH 10, pH 12, of (a) before Filtering and (b) after Filtering](image)

The solution resulting from leaching chloride is precipitated using NaOH, for the metal deposits formed are hydroxides with solubility values as shown in Table 2. The following are the reactions that occur in the deposition of hydrochloric acid leaching solutions with NaOH [14]:

\[
\text{NiCl}_2 + 2 \text{NaOH} \rightarrow \text{Ni(OH)}_2 + 2 \text{NaCl} \quad (1) \\
\text{FeCl}_3 + 3 \text{NaOH} \rightarrow \text{Fe(OH)}_3 + 3 \text{NaCl} \quad (2) \\
\text{AlCl}_3 + 3 \text{NaOH} \rightarrow \text{Al(OH)}_3 + 3 \text{NaCl} \quad (3)
\]

| Compound    | Ksp     |
|-------------|---------|
| Ni(OH)_2    | \(1.6 \times 10^{-16}\) |
| Fe(OH)_3    | \(6.0 \times 10^{-38}\) |
| Al(OH)_3    | \(5.0 \times 10^{-34}\) |

The greater the Ksp value, the more soluble the compound will be, making it more difficult to settle. Based on table 2, the compounds Fe(OH)_3, Al(OH)_3, will precipitate because they have relatively small Ksp values compared to other compounds with relatively close values. Precipitation is carried out in a range of pH 7.5-9.0 and at temperatures between 25 - 75 °C [13].

The precipitated sample is then filtered by the sediment. The precipitate formed is oven at 90 °C then weighed to determine the mass formed. The filtrate obtained was analyzed using ICP-AES to find out the remaining metal which was not taken into sediment. In figure 2, 3, 4 and 5, it can be seen that the
ppm concentrations of Fe, Al, Si, and Ni are left in the leaching solution. ICP AAS analysis is easy to do, but this analysis is very sensitive to impurities.

![Graphs showing concentration vs temperature for Fe, Si, Al, and Ni](image)

Figure 2. Graphic of the pH and Temperature Functions on Filtrate for (a) Fe Concentrations, (b) Al Concentration, (c) Ni Concentrations and (d) Si Concentrations.

Figure 2 (a) shows the relationship between the concentration of Fe in the filtrate solution and the temperature at various pH. For all pH, the amount of Fe metal at 70 °C is higher than the amount of Fe metal at 55 °C. At 85 °C the amount of Fe in the filtrate decreases. That is, the amount of Fe metal that settles at 70b °C decreases then rise again at 85 °C. This is because at a temperature of 70-75 °C, the precipitate formed switches from the form of hydroxide to oxide [13]. At pH 8 and 10, the amount of Fe metal remaining is almost the same. Whereas at pH 12, the remaining Fe metal is smaller, the higher the pH Fe the more it settles. Figure 2 (b) that the concentration of Al metal is left in the filtrate solution. The graph shows the higher the temperature, the less metal is drawn. Al solubility increases with increasing temperature.

Ni metal in filtrate solution can be seen from figure 2 (c). The graph shows that at pH 8 and pH 10 the concentration is almost the same at all temperatures. The Ni metal concentration of 70 °C at pH 12 increased from 55 °C, then returned to a temperature of 85 °C. This happens because at a temperature of 70 °C it is the transition temperature where Ni(OH)2 changes to NiO. The higher the temperature, the higher the solubility of Ni(OH)2, so that the less deposited Ni. Conversely, the higher
the temperature, the smaller the solubility of NiO. So that NiO deposits are more stable [16]. Figure (d) shows that the higher the temperature of Si concentration in the filtrate solution decreases because the solubility decreases, so many Si metals are deposited.

The percentage of the results Fe, Al, Ni, and Si metals is calculated by comparing the concentration of the extract solution before and after deposited with 15 % NaOH. The results of Fe metal at pH 8, 10, and 12 are fairly low in the range of 0.10 - 0.50 %. Fe metal tends to settle at low pH, which is a pH range of 2.5-4.5. As for Al metal, the higher the temperature, the smaller the collection. The highest percentage of Al collection was obtained at pH 12 at 55 °C which was equal to 67.91 %. The results of Al metal collection are quite high because Al(OH)₃ is easier to settle at high pH.

![Graphs of Figure 3](image)

**Figure 3. Graphic Percentage Metal Recovery of (a) Fe, (b) Al, (c) Ni and (d) Si**

Nickel is the main product you want to get. Nickel in the pH range 8-12 with alkaline atmosphere can be precipitated in the form of Ni(OH)₂ and NiO. The higher the pH, the more precipitate formed. The effect of temperature can be seen that the higher the temperature, the deposition of Ni(OH)₂ decreases because Ksp increases (solubility increases), to a point Ni(OH)₂ changes to NiO. At pH 12 and a temperature of 70 °C it is the transitional point of Ni deposit formation. The maximum Ni collection results obtained at pH 12 temperature 85 °C which is equal to 83.97 %. The result of Si metal collection decreases with decreasing temperature.
The sediment mass is obtained after drying for 2 hours. The sediment mass at 70 °C increases from the mass of the sediment at 55 °C. However, at a temperature of 85 °C the sediment mass formed decreases. Whereas based on ICP AAS analysis the results of leaching filtrate showed that Fe, Al, Ni metal deposits decreased at 70 °C. This is because the metals analyzed are only Fe, Al, Ni, and Si. It is possible for other metals such as Mn, Mg, Cu, Co, etc. to settle more easily at 70 °C, so that the analysis of the total mass of the precipitate formed increases. Table 3 shows that the higher the pH, the more precipitate formed.

4. Conclusion

From the results of the experiment it can be proven that NaOH is proven to be used to deposit Ni metal with optimum conditions obtained at pH 12 and 85 °C with recovery as much as 83.97 % and Temperature 70 °C as the transition temperature of Ni(OH)₂ to NiO so that at this point Ni recovery is the smallest.

References

[1] M. Vlachou, J. Hahladakis, and E. Gidarakos, “Effect of Various Parameters in Removing Cr and Ni from Model Wastewater by using Electrocoagulation,” vol. 15, no. 4, pp. 494–503,2013.
[2] Z. H. U. De-qing, C. U. I. Yu, S. Harupoda, K. Vining, and P. A. N. Jian, “Mineralogy and crystal chemistry of a low grade nickel laterite ore,” vol. 22, 2012.
[3] P. Prasetyo, “Sumber Daya Mineral di Indonesia Khususnya Biji Nikel Laterit dan Masalah Pengolahannya Sehubungan dengan UU MINERBA 2009,” no. November, pp. 1–10, 2016.
[4] D. B. and H. T. B. M. P. W Astuti, N M Prilitasari, Y Iskandar, “Leaching behavior of lanthanum, nickel and iron from spent catalyst using inorganic acids Leaching behavior of lanthanum, nickel and iron from spent catalyst using inorganic acids,” pp. 0–7, 2018.
[5] W. Astuti, T. Hirajima, K. Sasaki, and N. Okibe, “Comparison of effectiveness of citric acid and other acids in leaching of low- grade Indonesian saprolitic ores Comparison of effectiveness of citric acid and other acids in leaching of low-grade Indonesian saprolitic ores,” Miner. Eng., vol. 85, no. January, pp. 1–16, 2016.
[6] H. Sekar et al., “Pelindian Nikel dari Bijih Limonit Low-Grade Pomalaa Menggunakan Pelarut Asam Asetat,” no. April, pp. 1–7, 2018.
[7] B. Journal, S. Sahu, N. C. Kavuri, and M. Kundu, “Dissolution Kinetics of Nickel Laterite Ore using Different Secondary Metabolic Acids,” vol. 28, no. 02, pp. 251–258, 2011.
[8] K. C. Wanta, H. T. B. M. Petrus, and I. Perdana, “Uji Validitas Model Shrinking Core terhadap Pengaruh Konsentrasi Asam Sitrat dalam Proses Leaching Nikel Laterit,” vol. 11, no. 1, pp. 30–35, 2017.
[9] L. Li et al., “Recovery of metals from spent lithium-ion batteries with organic acids as leaching reagents and environmental assessment,” vol. 233, pp. 180–189, 2013.
[10] R. G. Medonald and B. I. Whittington, “Atmospheric acid leaching of nickel laterites review. Part II. Chloride and bio-technologies,” vol. 91, pp. 56–69, 2008.
[11] F. Mohammadreza, N. Mohammad, and S. S. Ziaeddin, “Nickel extraction from low grade laterite by agitation leaching at atmospheric pressure International Journal of Mining Science and Technology Nickel extraction from low grade laterite by agitation leaching at atmospheric pressure,” Int. J. Min. Sci. Technol., vol. 24, no. 4, pp. 543–548, 2019.
[12] T. S. Magnetik, “Pengaruh Konsentrasi Nikel pada Proses Leaching Mineral Geothite terhadap

| pH  | 50 °C | 70 °C | 85 °C |
|-----|-------|-------|-------|
| 8   | 0.1435| 0.1983| 0.3417|
| 10  | 0.1931| 0.4622| 0.4341|
| 12  | 0.3445| 0.4979| 0.4216|
[11] Susceptibilitas Magnetik,” pp. 1–5, 2011.

[13] Mubarok & Lieberto, “Precipitation of Nickel Hydroxide from Simulated and Atmospheric-leach Precipitation of Nickel Hydroxide from Simulated and Atmospheric-Leach Solution of Nickel Laterite Ore,” Procedia Earth Planet. Sci., vol. 6, no. December 2013, pp. 457–464, 2015.

[14] Y. Chang, X. Zhai, B. Li, and Y. Fu, “Hydrometallurgy Removal of iron from acidic leach liquor of lateritic nickel ore by goethite precipitate ☆,” Hydrometallurgy, vol. 101, no. 1–2, pp. 84–87, 2010.

[15] E. Care, “CRC Handbook of Chemistry and Physics.”

[16] D. A. Palmer, P. Bénézeth, and D. J. Wesolowski, “Solubility of Nickel Oxide and Hydroxide in Water,” pp. 264–269, 1980.