Leaching of limonitic nickel from Sorowako with sulfuric acid at atmospheric pressure

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Abstract. Indonesia has the largest nickel laterite reserves in the world that it plays an important role in fulfilling the demand for stainless steel, nickel-based alloys, and the issue of using electric cars in the future. Currently, low-grade nickel laterite ore has not been maximally processed into value-added products domestically. The extraction process that is widely applied in the industry for low-grade laterite nickel ore through the hydrometallurgical route, which is the leaching method at atmospheric pressure in a sulphuric acid solution. The characterization of nickel ore from Sorowako has been studied that included water content analysis, sieve analysis, XRF analysis, XRD analysis, and leaching in sulphuric acid solution with agitation method at various leaching times. The results showed that the nickel ore sample from Sorowako had a water content of 5.51% with a dominant size fraction of -4 +14 mesh. XRD and XRF analysis results have shown that the chemical compositions of laterite nickel from Sorowako were Limonitic type of goethite (FeOOH) and quartz (SiO2) with the content of Ni, Co, Mg, and Fe of 1.5%, 0.02%, 0.05%, and 23.82%, respectively. The highest percentages of nickel and iron extract that were obtained at the 12 hour leaching time were 90.01% and 97.11%, respectively.

1. Introduction
Nickel is a non-ferrous metal that is widely needed in various applications. Nickel has corrosion resistance, strength, ductility, and high thermal and electrical conductivity, making it possible to be used for various purposes. The primary use of nickel is as a raw material for the manufacture of stainless steel, base metal in nickel-based alloys, superalloys, batteries, and metal alloy components used in high-temperature applications[7]. The increasing demand for nickel in the world is due to the increasing demand for stainless steel and nickel-based alloys and the issue of using electric cars in the future[5].

The primary source of nickel and cobalt comes from nickel ore with two types of deposits, namely sulfides and oxides. Production of nickel in the world is mostly from sulfide ore although the large reserves of nickel ore are oxide ores [1]. Broadly speaking, there are 2 types of oxide ore or laterite nickel, namely saprolite ore with 1-3% Ni content which has high nickel content, and Limonitic ore with 0.8-1.5% Ni content which has low nickel content [2]. Apart from containing nickel, Limonitic nickel ore also contains cobalt.

Indonesia is known as one of the countries that has the largest nickel laterite ore reserves in the world. About 12% of the world’s nickel reserves are reported to be in Indonesia in the form of nickel laterite ore [3]. Laterite nickel ore deposits are abundant in eastern Indonesia, namely on the island of Sulawesi,
Maluku island, parts of the islands around Papua, Halmahera Island, and small islands around it such as Gag and Gebe Islands.

The processing technology for laterite nickel ore varies, from processing via pyrometallurgical, hydrometallurgical, or a combination of both. Currently, low-grade nickel laterite ore has not been maximally processed into value-added products domestically [4]. The extraction process that is widely applied in the industry for low-grade laterite nickel ore is through the hydrometallurgical route. Currently, the hydrometallurgical plant to process nickel laterite has not been implemented in Indonesia.

Leaching low-grade nickel laterite ore by agitation method at atmospheric pressure in sulfuric acid solution is an alternative nickel extraction process using the hydrometallurgical pathway which is widely researched and is urgent to develop due to reduced reserves of high grade nickel ore. This research studied the leaching of laterite nickel ore from Sorowako with sulfuric acid leaching with various concentrations of sulfuric acid at various leaching times. This study also studied the characteristics of laterite nickel ore from Sorowako used in research with XRD and XRF analysis.

2. Materials and methods
Limonitic nickel ore samples used in the experiment were obtained from Sorowako, South Sulawesi, namely from PT. Vale, Indonesia. The experiment was started with the preparation, characterization, and leaching of limonitic nickel ore at atmospheric pressure in a solution of sulphuric acid.

2.1. Preparation and characterization of laterite nickel ore samples
Limonite ore sample preparation includes homogenization, sampling, drying, grinding, and sieving the sample. In the first stage, the Limonite ore sample was homogenized by stirring the entire sample then coning and quartering sampling was carried out to obtain a representative sample for the leaching experiment. Prior to the grinding and sieving process, the ore is dried for 24 hours at a temperature of 120°C to remove the free moisture contained in the ore. Furthermore, the samples of dried ore were re-sampled using a splitter to obtain approximately 2 kilograms of samples for ore characterization purposes. For the leaching experiment, the sample used was a size fraction of -65 + 100 mesh. Sample preparation is done by grinding using a mortar (mortar and pestle), then sieving using a sieving machine (sieving machine) with a sieve size of -65 + 100 mesh. After obtaining ore with a size fraction of -65 + 100 mesh, coning and quartering sampling were carried out for the leaching process. Characterization carried out on ore samples that will be used in the experiment include:

2.1.1. Determination of the water content of limonitic Ore samples. Analysis of surface moisture content in Limonite ore samples was carried out by calculating the sample weight loss before and after drying. Limonite nickel ore samples were dried in an oven for 24 hours at a temperature of 120°C.

2.1.2. Sieve analysis. The sample that was used for the sieve analysis was the sample that had been dried in an oven for 24 hours at a temperature of 120°C using 4, 14, 28, 48, 65, 100, 200, and 325 mesh sieves. Sieve analysis was performed to determine the size distribution of the Limonite ore sample. Sieve analysis was carried out twice.

2.1.3 Determination of the chemical composition of ore by xrd and xrf analysis. The chemical composition of Limonite ore samples was analyzed using XRF (X-Ray Fluorescence Spectrophotometer) and X-Ray Diffraction (XRD) [8]. This XRF analysis aims to identify and determine the number of elements contained in the ore sample. Meanwhile, to determine the presence of the dominant compound in the sample, an XRD test was carried out. Prior to analysis, the ore sample was ground using a mortar and then sieved to obtain a fraction of -65 + 100 mesh. Furthermore, the ore with a size fraction of -65 + 100 mesh is subjected to a sampling process for later XRD and XRF analysis.
2.2. Limonitic nickel ore leaching

Limonitic nickel ore leaching is carried out using a reactor at a solid-liquid ratio condition of 350/1000 (g/mL) at 95°C [10] at 400 rpm for 24 hours using an IKA RCT Basic magnetic stirrer equipped with a temperature sensor so that the process temperature can be kept constant. The reactor used is a glass reactor with a two-liter capacity equipped with a five-neck reactor cover and a condenser to condense the moisture formed during the leaching process so that the volume of the solution can be kept constant. To determine the concentration of dissolved metals, an analysis was carried out using AAS. The metal weight from the AAS reading is then calculated using the following equation:

\[
\text{Metal mass (mg)} = \text{concentration (ppm)} \times \text{dilution factor} \times \text{solution volume}
\]  

(1)

To calculate the percent of metal extraction, the following equation is used:

\[
\text{Metal extract (%) } = \frac{\text{dissolved metal mass}}{\text{mass of metal in the sample}} \times 100
\]

(2)

3. Results and discussion

3.1. Characteristic of limonitic nickel ore

The average moisture content of as received Limonitic ore was 5.51%. Based on the results of the sieve analysis, it is known that the Limonitic ore samples obtained from PT Vale Sorowako are dominated by a size fraction of -4 + 14 mesh and a fraction of minus 325 mesh size. The samples obtained are already of fine size so that only grinding is carried out using a mortar to obtain a fraction of -65 + 100 mesh that is used in the leaching experiment. The results of the sieve analysis are shown in Table 1.

Table 1. Analysis results of Limonite ore sample sieve

| Size Fraction | Accumulated Weight I (gr) | % Accumulated I | Accumulated Weight II (gr) | % Accumulated II | % Accumulated Average |
|---------------|---------------------------|-----------------|-----------------------------|-----------------|-----------------------|
| (+4)#         | 33.5                      | 8.3333          | 35.2                        | 8.7978          | 8.5656                |
| (-4 +14)#     | 127                       | 31.5920         | 123.2                       | 30.7923         | 31.1922               |
| (-14 +28)#    | 53.7                      | 13.3582         | 50.7                        | 12.6718         | 13.0150               |
| (-28 +48)#    | 40.5                      | 10.0746         | 39.5                        | 9.8725          | 9.9736                |
| (-48 +65)#    | 12.5                      | 3.1095          | 12.1                        | 3.0242          | 3.0668                |
| (-65 +100)#   | 28.3                      | 7.0398          | 31.3                        | 7.8230          | 7.4314                |
| (-100 +200)#  | 29.7                      | 7.3881          | 30.1                        | 7.5231          | 7.4556                |
| (-200 +325)#  | 22.2                      | 5.5224          | 21.6                        | 5.3987          | 5.4605                |
| (-325)#       | 54.6                      | 13.5821         | 56.4                        | 14.0965         | 13.8393               |
| Total         | 402                       | 100             | 400.1                       | 100             | 100                   |

The results of XRD analysis showed that the dominant minerals contained in the Limonitic nickel ore samples obtained from Sorowako were goethite (FeOOH) and quartz (SiO₂) minerals[9]. In this study, a leaching experiment was carried out in a concentrated sulfuric acid solution to dissolve Ni and Co in goethite (FeOOH) crystal lattice. The XRF analysis results show that the laterite nickel ore sample obtained is of the Limonitic type with the composition, as shown in Table 2.
Figure 1. X-Ray Diffraction Spectrum of Limonite ore sample.

Table 2. XRF analysis results of Limonite nickel ore samples at a size fraction of -65 + 100 mesh

| Compounds | Content (%) | Elements | Content (%) |
|-----------|-------------|----------|-------------|
| SiO₂      | 3.19        | Si       | 1.491       |
| Al₂O₃     | 6.51        | Al       | 1.723       |
| Fe₂O₃•T   | 68.12       | Fe       | 23.823      |
| MnO       | 0.42        | Mn       | 0.325       |
| MgO       | 0.086       | Mg       | 0.052       |
| CaO       | <0.001      | Ca       | <0.001      |
| Na₂O      | 0.19        | Na       | 0.070       |
| K₂O       | <0.001      | K        | <0.0004     |
| TiO₂      | 0.077       | Ti       | 0.046       |
| P₂O₅      | 0.017       | P        | 0.004       |
| V₂O₅      | 0.050       | V        | 0.014       |
| Cr₂O₃     | 4.56        | Cr       | 1.560       |
| Co₂O₃     | 0.054       | Co       | 0.019       |
| CuO       | 0.011       | Cu       | 0.009       |
| NiO       | 1.87        | Ni       | 1.470       |
| ZnO       | 0.039       | Zn       | 0.031       |
| LOI       | 14.73       | LOI      | 14.730      |

3.2. Results of the limonite nickel ore leaching experiment
A 24-hour leach trial was carried out to determine the best trial leach time. The experiment was carried out at a solid/liquid ratio (g/mL) of 350/1000 using a sample with a limonite ore particle size distribution of -65 + 100 mesh. The leaching experiment was carried out at a temperature of 95°C with a sulfuric acid concentration of 4.5 M (2x stoichiometry) and a constant stirring speed of 400 rpm. The percentages of nickel and iron extraction are presented in Table 3 and the composition of the dissolved metals in PLS is presented in Table 4.
Table 3. Percent of nickel and iron extraction as a function of time

| Time | % Extraction |
|------|--------------|
| Minute | Hours | Ni   | Fe    |
| 0     | 0      | 0    | 0     |
| 30    | 0.5    | 71.06| 73.24 |
| 60    | 1      | 80.46| 81.16 |
| 120   | 2      | 87.35| 85.56 |
| 240   | 4      | 89.86| 93.57 |
| 480   | 8      | 88.28| 87.57 |
| 720   | 12     | 90.01| 97.11 |
| 1440  | 24     | 87.35| 99.38 |

Table 4. The dissolved metals composition in PLS

| Metallic ions | Concentration (ppm) |
|---------------|---------------------|
| Ni            | 4468                |
| Co            | 116                 |
| Fe            | 120143              |
| Mg            | 555                 |
| Mn            | 716                 |
| Al            | 4787                |
| Cr            | 2228                |
| Zn            | 65.55               |
| Cu            | 22.60               |

Figure 2. Percent profile of nickel and iron extraction as a function of leaching time
The leaching experiment was conducted to determine the best leaching time for nickel extraction from limonite nickel ore. Experiments were carried out at 4.5M sulfuric acid concentration [11], temperature 95°C, S/L 350/1000 (g/ml), stirring speed 400 rpm, with a size fraction of -65 + 100 mesh for 24 hours. The percent profiles of nickel and iron extraction as a function of time are presented in Figure 2. It is seen that the percent nickel and iron extraction increases sharply up to 4 hours of leaching time. The highest nickel extraction percentage was obtained at 90.01% at the 12-hour leaching time, where the percentage of iron extraction was also quite high, reaching 97.11%.

Based on the percent nickel and iron extraction profile above, the best leaching time with a high percent nickel extraction and a lower percent iron extraction is at 4 hours leaching with nickel and iron extraction percent respectively 89.86% and 93.57% . The composition of the dissolved metals in 12 liters of PLS solution is Ni of 4.468 ppm, Fe of 120.143 ppm, Co of 116 ppm, Mg of 555 ppm, Mn of 716 ppm, Al of 4787 ppm, Cr of 2.228 ppm, Zn of 65.55, and Cu of 22.60 ppm. The PLS composition data above shows that iron is the main impurity with the highest concentration of 120 g/L, so for the next refining stage, iron precipitation must be carried out gradually[6].

4. Conclusion
The results showed that the nickel ore sample from Sorowako had a water content of 5.51% with a dominant size fraction of -4 +14 mesh. XRD and XRF analysis results have shown that the chemical compositions of laterite nickel from Sorowako were Limonitic type of goethite (FeOOH) and quartz (SiO₂) with the content of Ni, Co, Mg, and Fe of 1.5%, 0.02%, 0.05%, and 23.82%, respectively. The highest percentages of nickel and iron extract that were obtained at the 12 hour leaching time were 90.01% and 97.11%, respectively.

Acknowledgement
Thanks to PT. Vale Indonesia which has provided nickel ore samples for this research, TekMIRA testing laboratory, Chemical engineering laboratory ITB for characterization so that this research can be carried out smoothly. Thanks also to the ITB Hidro dan Elektrometalurgi Laboratory who assisted in the preparation and characterization ore samples and leaching experiment.

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