Electrochemical Behavior of Nickel Laterite Ores Dissolution in Sulphuric Acid Solutions

Faizinal Abidin¹,², Abdul Hatta Gunawan Wibowo¹, Arya An Ambari¹, Sri Harjanto¹,*

¹Department of Metallurgical and Materials Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok 16424, Indonesia
²Center for Mineral Resources Development Technology, Agency for The Assessment and Application of Technology, 820 Building, Earth System Technology (Geostech), Puspiptek Area, South Tangerang 15314, Banten–Indonesia

*Corresponding Author E-mail: sri.harjanto@ui.ac.id

Abstract. Hydrometallurgical process of laterite nickel ore is carried out by leaching techniques at high temperatures. At atmospheric temperatures, the acquisition of nickel is low. Therefore, this study aims to characterize the electrochemical laterite nickel ore using a solution of sulfuric acid and hydrochloric acid at atmospheric temperature. Sulfuric and chloride acid solutions were used with solution concentrations of 1 M, 2 M, 4 M and 6 M. The study was carried out by sample and solution preparation, characterization by SEM-EDAX and Petrography method, and electrochemical characterization using the OCP, EIS method and LSV. The characterization results showed that the highest dissolution rate in both solutions was obtained at a concentration of 6 M solution. Increased concentrations of sulfuric acid reduced the value of OCP testing, while an increase in the concentration of hydrochloric acid increased the value of OCP. The EIS test results showed that the lowest R2 or Rct value in sulfuric acid solution was obtained at 2M concentration of 269.59 Ω while in hydrochloric acid solution it was obtained at a concentration of 6M of 523.07 Ω. The results of the second LP acid solution showed the formation of a passive layer at each concentration. The highest dissolution rate occurred at a concentration of 6M in each solution where the corrosion rate of sulfuric acid was 1.00 mm / year, while in hydrochloric acid it was 9.55 mm / year. Increasing the concentration of the two solutions led to the breakdown of the passive layer on the surface which can be seen from the Nyquist curve, the value of R2 is lower, the value of Q1 is higher and the value of N is lower, but in the sulfuric acid solution the formation of passive layers returns to increasing concentration starting from 4M. The three electrochemical tests show an increase in concentration to the optimum concentration increasing the dissolution rate and breaking the passive layer on the surface.

1. Introduction

The purpose of the dissolution process is separate valuable metals from impurities [1]. The dissolution process will produce two products, namely the first product which is not soluble or precipitated in the form of impurities that will be cleaned and discarded or processed by products and the second product is a solution containing valuable metals [1]. Solution selectivity is an important factor. The selectivity of the solvent to the ore is influenced by the concentration of the solution, temperature, and contact time [3].
Hydrochloric acid is widely used as a leach reactant for laterite minerals because it is considered easier than other reactants. In addition, there are several advantages, namely that it is more optimal to dissolve nickel metal compared to other solutions, has higher leachability for complex ores, regeneration of leaching agents, removal of impurities such as iron, cobalt and magnesium [4]. In a previous study by Ahmet Goveli in 2016, to dissolve nickel metal in laterite minerals was carried out with a number of variations including variations in solution concentration, dissolution time, and dissolution temperature. In laterite leaching, the most optimal solution concentration is HCl 4 M with a nickel yield that can be extracted at 97.69% of the initial content. The most optimal time variable for this leaching is 4 hours with a nickel yield that can be extracted at 24.60% of the initial content. Whereas the most optimal temperature variable for this leaching is 100°C with a nickel yield that can be extracted at 54.82% of the initial content [4]. Another study conducted by Jinhui Li et al. in 2018, dissolve valuable metals from laterite nickel ore with hydrochloric acid solution with varying concentrations of hydrochloric acid, leaching time and leaching temperature. The most optimal variation of hydrochloric acid concentration is 4 M HCl with a nickel leaching rate of 80.1%. For the most optimal leach temperature variation is at 90°C with a leaching rate reaching 88%. Whereas the most optimal time variation is 90 minutes or 1.5 hours with leaching rate reaching 86%. From these results that the variable concentration of solution, temperature, and time of leaching is directly proportional to the leaching rate of laterite nickel ore [5].

The most previous research topics on electrochemical studies were only carried out on sulfide ores such as pyrite (FeS) and chalcopyrite (CuFeS₂), studies have never been carried out on laterite nickel ores [6] [7] [8]. This research was conducted to study the behavior of laterite nickel ore when leaching with leachate solution with different concentrations. In this study, sulfuric acid and hydrochloric acid solutions were used as leachate solutions with different concentrations.

![Figure 1. Schematic testing of electrochemical characterization](image)

2. Materials and Methods

Laterite nickel ore were obtained from the island of Sulawesi. Scanning Electron Microscopy (Inspect F50) and Energy Dispersive X-Ray Analysis (AMETEK) as well as petrographic tests are carried out to characterize the chemical composition of the samples and types of laterite nickel ore, petrographic test was performed by Nikon Eclipse Ci-POL Polarization Microscope equipped DS-Ri2 Nikon Camera and integrated with NIS-Elements software is used to identification and measure content of mineralogy. The ore sample tested for SEM-EDAX is the same sample for the petrographic test, the results of the two tests to determine and assure the type of nickel ores used in this study.

The solution used for testing is sulfuric acid solution (H₂SO₄) concentration of 96% (Merck, EMSURE®). The solution is diluted using distilled water to reduce its concentration. The solution used to dissolve the sample was divided into concentrations 1 M, 2 M, 4 M and 6 M. Laterite nickel ore was then prepared into a working electrode for further testing. Polishing machine (METASERV, Universal Polisher) is used to prepare the surface of the sample before electrochemical studies are conducted. Silver chloride electrode (Ag / AgCl) is used as a reference electrode and platinum metal is used as an auxiliary electrode. Copper wire is used as a connecting electrochemical cell. Samples of laterite nickel ore were prepared for the electrochemical characterization process. Large samples are cut into small
The samples that have been cut are each mounted using a resin that is added with a hardener in a ratio of 15: 1. The sample surface was prepared by polishing with # 500, # 1000, and # 1500 and the surface exposed to the solution was only 1 cm$^2$ in size. Potentiostat-galvanostat (Metrohm Autolab, PGSTAT302N) integrated with Metrohm NOVA Autolab software was used to perform the electrochemical measurement, open circuit potential (OCP) was always measured until the electrode potential stabilized to a chance in the electrode potential of no more than 0.1 mv.min$^{-1}$. After steady OCP was observed electrochemical impedance spectroscopy (EIS) experiments were performed at OCP using an AC perturbation of ± 5 mV in the frequency range 10 kHz – 10 mHz. The electrochemical characterization test scheme is shown in Figure 1.

3. Result and Discussion

Based on the petrographic test results, laterite nickel ore samples used are peridotite rocks with harzburgite types undergoing serpentinization with typical “mesh” and “sea and island” textures. Peridotite rocks based on laterite nickel ore profiles are found in the bedrock and bottom saprolite layers.

| Table 1. Mineralogy of Laterite Nickel Ores |
|-------------------------------------------|
| Mineralogy                  | Percentage (%) |
| Primary                     |                |
| Olivine                     | 40             |
| Enstatite                   | 20             |
| Picotite                    | 3              |
| Secondary                   |                |
| Serpentine                  | 30             |
| Goethite                    | 3              |
| Iddingsite                  | 3              |
| Smectite                    | 1              |

The main minerals contained in the sample are olivine ((Mg$^{2+}$, Fe$^{2+}$)$_2$SiO$_4$), pyroxene variation of enstatite (Mg$_2$Si$_2$O$_6$) with augite thin lamella ((Ca, Na)(Mg, Fe, Al)(Si, Al)$_2$O$_6$), and picotite ((Fe, Mg)(Al, Cr)$_2$O$_4$), while the secondary minerals contained in the sample are serpentine – antigorite variations (Mg$_6$(Si$_2$O$_5$)(OH)$_4$), iddingsite (MgO·Fe$_2$O$_3$·3SiO$_2$·4H$_2$O), goethite (Fe$^{3+}$O(OH)$_3$), smectite, talc (Mg$_{2}$Si$_{4}$O$_{10}$(OH)$_{2}$), and magnetite (Fe$_3$O$_4$). The secondary mineral that predominates is serpentine – antigorite variation that is spread on the rock matrix with a sea texture and is present with either goethite or magnetite. No samples were found for the primary ore mineral nickel. The results of mineral identification in laterite nickel ore samples can be seen in Table 1.

| Table 2. Elements detected by EDAX scanning. |
|--------------------------------------------|
| Element | Wt%  | At%  |
| C       | 4.92 | 9.10 |
| O       | 28.69| 41.03|
| Mg      | 19.56| 18.71|
| Al      | 1.64 | 1.35 |
| Si      | 24.54| 20.19|
| Ca      | 6.36 | 3.53 |
| Ti      | 3.17 | 1.49 |
| Fe      | 9.69 | 4.01 |
| Ni      | 1.43 | 0.59 |

The SEM-EDAX test results show the presence of nickel content in laterite nickel ore. The nickel contained in laterite nickel ore is concentrated in certain parts. The microstructure and elements contained are shown in Figure 2. The chemical composition of the sample is shown in Table 2. The electrochemical study of the dissolution of laterite nickel ore produces graph data in the form of Nyquist
plot, open circuit potential, and polarization curves for each different solution concentration used in the test.

**Figure 2.** Surface microstructure of lateritic nickel ore from SEM observations from 10,000 magnifications (left) and concentrated elements at the EDAX scan point (right).

Figure 3 shows a graph of OCP with respect to time of testing at different concentrations. At a concentration of 1 molar, the curve fluctuates up to 50 seconds. Then the curve is sloping with a tendency to rise until 140 seconds. At 0-15 seconds, there is a potential increase from 0.124 to 0.129 V vs Ag/AgCl. At a concentration of 2M, the curve decreased without a change in slope up to 300 seconds from a potential of 1.328 - 0.1 V vs Ag/AgCl. Stability is achieved at a potential of 0.1 V vs Ag/AgCl at 300 seconds. At 4M concentration, the curve increases regularly until 300 seconds from a potential of 0.075 to 0.08 V vs Ag/AgCl. At a concentration of 6M, the curve has decreased until 300 seconds from a potential of 0.094 to 0.083 V vs Ag/AgCl. Stability is achieved at 300 seconds at a potential of 0.083 V vs Ag/AgCl. The effect of the concentration of the solution on OCP from laterite nickel ore is shown in Figure 4. OCP decreases when adding concentrations from 1M to 4M. After that, the OCP did not experience a significant change from 4M to 6M concentrations.

**Figure 3.** OCP Graph of laterite nickel ore at room temperature.

Testing with the LSV method produces the linear polarization curve shown in Figure 5. Electrochemical polarization parameter data from the LSV graph is shown in Table 3. The corrosion rate of the dissolution of the sample from each solution concentration is also shown in Figure 6. The EIS test results have been fitted using the equivalent electrical circuit shown in Figure 7. From the results of the fittings, the EIS test parameter data is shown in Table 4. Resistance of R1 solution is related to testing the high frequency range of 10,000 Hz. The charge transfer resistance R2 at the film layer is
related to testing the intermediate frequency range 100-1 Hz with the constant phase element CPE1/Q1 as the charge capacitance at the film layer.

![Graph](image)

**Figure 4.** Effect of sulphuric acid concentration on laterite ore OCP

The nickel that is deposited in lateritic nickel comes from olivine and orthopyroxene in ultramafic rocks which are the source of nickel, then it is sentinized and undergoes lateritization due to interacting with sea water or during alteration. Olivine undergoes hydration and turns into amorphous silica, serpentine, and limonite. Nickel accumulates in serpentine through cation exchange, especially with Mg$^{2+}$ ions, when the olivine reaction becomes smectite, goethite, serpentine, and talc. The nickel accumulation process is further characterized by the formation of nickel-enriched filo-silicate minerals such as kerolite (Ni-talc), neupoite (Ni-serpentine), and pimelite (Ni-smectite) [9]. Nickel concentration can also be associated with goethite through the adsorption process [10].

**Table 3.** Electrochemical polarization parameters of laterite nickel ore dissolution in H$_2$SO$_4$ solution at room temperature.

| Concentration (M) | jcorr (µA/cm$^2$) | Ecorr (mV) | Corrosion Rate (mm/year) |
|-------------------|-------------------|------------|--------------------------|
| 1                 | 9,74              | 47,67      | 0,113                    |
| 2                 | 12,03             | 103,04     | 0,140                    |
| 4                 | 10,37             | 29,78      | 0,120                    |
| 6                 | 86,24             | -52,34     | 1,002                    |

![Graph](image)

**Figure 5.** Linear polarization curves of LSV test results at sulphuric acid solutions
From the EDAX test results, it can be concluded that laterite nickel ore samples contain elements of oxygen, magnesium, silica, titanium, iron, and nickel. Previously it was found that the minerals making up of laterite nickel ore were dominated by olivine primary minerals and serpentine secondary minerals. The detected nickel element can be found in serpentine as a substitute ion for Mg$^{2+}$. The content of the element most contained in the sample was oxygen with a content of 28.69 wt% while the nickel content contained as much as 1.43 wt%.

From the OCP test data, fluctuations can be expected from the formation and separation of corrosion products formed on the metal surface. However, the corrosion products that are formed need to be characterized again [6]. A steady increase in potential indicates the formation of a corrosion product where a passive layer might have formed on the surface of the sample [7] [8]. A gentle curve shows a stable corrosion-free potential where corrosion occurs throughout the sample surface. When viewed in the Ni-O-H pourbaix diagram, the OCP value is in the nickel dissolution area, which is above -0.288 vs Ag/AgCl. When compared with the pourbaix diagram, the OCP value of each solution concentration is in the dissolving region. OCP value is potential when the sample begins to react or undergo dissolution. Increasing the concentration results in a decrease in the potential OCP of the sample, indicating that laterite nickel ore is dissolved faster with increasing concentration.

![Figure 6. Graph of the relationship between corrosion rate and solution concentration.](image)

![Figure 7. Nyquist Plot of Laterite Nickel Ores at Sulphuric Acid](image)
### Table 4. Element values of EIS test results.

| Element | Parameter | Solution |
|---------|-----------|----------|
| R1      | R (Ohm)   | 144.01   | 2122.3  | 10.1    | 0.175   |
| Q1      | Y₀ (Mho/Ohm⁻¹) | 9.11×10⁻⁵ | 3.49×10⁻⁵ | 1.48×10⁻³ | 4.44×10⁻⁴ |
| N       |           | 0.406    | 0.853   | 0.131   | 0.508   |
| R2      | R (Ohm)   | 1780.09  | 269.59  | 1.10×10⁻¹ | 403.49  |

Passivation areas on the polarization graph are shown by a potential increase but current that tends to remain or decrease. The highest anodic reaction is shown at the highest current point occurring in the active region or linear curve. However, at the dissolution of 2M concentration, pseudo-passive behavior is shown which is shown on a linear curve with a steep slope in the potential range of 0.2 V to 0.92 V. This behavior can be associated with partial passive layer loss due to certain ions [10]. In the Ni-OH Pourbaix diagram, the dissolution of Ni does not occur when the potential is below -0.738 V vs Ag/AgCl and the hydrogen evolution reaction occurs at a potential of -0.288 V vs Ag/AgCl at pH below 8. Of the four concentrations, it can be said that the curve the reduction in the graph shows the hydrogen evolution reaction. The evolution of hydrogen causes a lack of protons on the surface of the sample, causing inhibition at concentrations of 1 M, 2 M and 6 M. While at 4 M concentration, inhibition does not occur that can be seen from the reduction curve that does not experience significant potential changes at the lowest potential up to potential of -0.5 V vs Ag/AgCl [9]. Corrosion rate did not change significantly when the concentration of the solution increased to 4 M. The rate increased rapidly when the concentration of the solution was increased from 4 M to 6 M. This shows that corrosive dissolution occurred in the 6 M solution. Dissolution of nickel ore at room temperature did not increase significantly when the concentration increases, but the increase in dissolution is more influenced by an increase in temperature [11].

The formation of a semicircular curve in the Nyquist diagram is related to the charge transfer resistance where the magnitude of the charge transfer resistance is related to the diameter of the formed curve [12]. At the dissolution of 1 M and 4 M concentrations, two curves are formed at high frequency and at low frequency. These two curves can show the existence of double layers and layers of corrosion products on the surface [13]. The formation of a semicircular curve at high frequency can also indicate the formation of the main dissolving product of laterite nickel ore on the surface due to the immersion of the ore at the beginning of dissolution [10].

From the N value in the table it can be explained that the dissolution of the sample at a solution concentration of 1 M and 6 M has an N value close to the warburg impedance (N = 0.5) where the surface layer of the film pivots. In a solution with a concentration of 4 M, the value of the parameter N approaches the value of 0. A decrease in the value of N indicates a more severe attack on the exposed surface. The decrease in the value of Q₁ capacitance with increasing concentration also indicates the formation of a film layer. Formation of the film layer is the cause of decreased capacitance [10].

### 4. Conclusions

The samples tested were serpentinized harzburgite peridotite rocks. This type of rock has the main mineral content of olivine ((Mg²⁺, Fe²⁺)₂SiO₄) and pyroxene variation enstatite (Mg₂Si₂O₆). From SEM and EDAX results also confirmed the main minerals contained in the sample where the dominant elements detected were O, Si, and Mg. The results of all electrochemical characterization showed that the surface of laterite nickel ore formed a passive layer that experienced destruction when the concentration of the solution rise to optimum concentration which are 4 M for sulphuric acid, then an increase in the rate of dissolution...
exceeding optimum concentration caused the re-formation of the previously destroyed passive layer. Ore samples used in dissolving with different concentrations are recommended using the same sample. This is because the use of different samples can affect the test where each sample can have a different surface texture.

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