Investigations on mineralogical characteristics of Indonesian nickel laterite ores during the roasting process

I Setiawan¹, E Febrina¹, R Subagja¹, S Harjanto² and F Firdiyono¹
¹Research Center For Metallurgy and Materials, Indonesian Institute of Sciences, Serpong, Tangsel, Indonesia enter of Minerals Processing and Corrosion Research
²Department of Metallurgical and Materials Engineering, Universitas Indonesia, Depok 16424, Indonesia

Email: iwan028@gmail.com

Abstract. Nickel is obtained from laterite ores by a metallurgical process to produce ferronickel. Nickel metal is present in a carrier mineral, a nickel magnesium silicate hydrate compound called garnierite. Garnierite is the common name of magnesium silicate hydrate minerals including chlorite, clay and serpentine. This study investigated the phase formed when the nickel ore is roasted from a temperature of 600°C to a temperature of 1000°C under atmospheric environmental. Microscopic analysis of roasted samples was analyzed by SEM-EDX and the dehydroxylation and recrystallization was studied using DTA-TGA. The endothermic peak was appear at 78.8°C, 293.7°C and 638.0°C, this corresponds to the release of free water and the release of crystalline water. While the exothermic peak occurs at 828.0°C. The exothermic temperatures associated with structural changes due to dihydroxylation of serpentine into a forsterite phase. Based on the XRD graph it is known that the sample of the roasting will produce the olivine and forsterite phases.

1. Introduction
The most important mineral carrying nickel from a laterite nickel ore is Garnierite. This mineral is a common name for a group of minerals which include nickel magnesium silicate minerals such as chlorite, clay and serpentine silicate. Garnierite has a fine grain structure, has a low crystallinity and consists of a mixture of several minerals. The constituent components of garnierite are usually Lizardite, Antigorite, Chrysotile and which have a nickel-rich structure namely serpentine [1], [2]. In the type of nickel sulfide ore, concentration can be done in traditional ways such as flotation and milling. Laterite ores can only be treated with minor upgrading by sieving. Apart from a lot of development process, laterite nickel ore can be processed well and economically by smelting while other techniques that are desired do not provide good results. Another problem is that nickel carrier minerals are finely dispersed in silicates and oxide ores. Although various investigations for the use of laterite ore in ferronickel and stainless steel smelting processes have been carried out, there are still many problems that need to be studied. The knowledge of nickel carrier minerals in laterite ores and their behavior at high temperatures is important for developing a pre-reduction process [3]. The nickel recovery process from laterite ores by pyrometallurgy has been intensively studied [4]. Rhamdhan [5] study on microstructure, phase characteristics and thermodynamic analysis and transformation during roasting of laterite nickel ore. Kim performs an increase in levels by looking at the effect of calcination from Indonesian laterite nickel ore before magnetic separation on various calcination and pulp density temperature variations. And the
optimum conditions for calcination temperature at 500°C for 1 hour at 0.5T magnetic field intensity will increase nickel grade from 1.5% to 2.9% with 48% recovery. Zhu et al. [6] performed elevated levels by selective reduction followed by magnetic separation. Reduction is carried out using coal (coal-base reduction) with calcium sulfate additive was carried on by Iwan [7] and with sodium sulphate by Li [8]. Bunjaku [9] studied the phenomenon that occurs when laterite nickel ore from Colombia is heated to 1300°C, so that it can provide information for reduction in order to increase levels. Nickel lateritic ore from Indonesia has been successfully reduced to produce ferronickel at low temperature reduction by Iwan [10]. However, the nature and mineralogy of the ore is very typical for each place, so to achieve optimum results a reduction process needs to study the character of the ore roasting. This study will study the behavior of laterite due to heating treatment and phase changes and morphology of laterite nickel ore when heated to 1000°C as a basis for reduction.

2. Methods and Materials
Nickel ore used in this experiment is laterite nickel ore from Sulawesi, Indonesia. Laterite or nickel oxide nickel ores are classified in the saprolitic category because they contain Ni and Fe in the range of 1.7% and 18.93%. One of the main characteristics of saprolitic ore is that it has a high content of MgO and SiO$_2$. The ore used for this study contained high levels of MgO and SiO$_2$, each at 13.4% and 24.64%, so that the ratio of MgO/SiO$_2$ was 0.54. Samples are made in the form of dry pellets in a pelletizer to produce pellet diameters ranging from 12 mm to 15 mm.

The characteristics of the ore used were also further explored by conducting XRD testing. This test aims to find out the minerals contained in the ore. Based on the results of the X-ray Diffractometer (XRD) obtained, it is known that the ore is composed of group garnierite minerals, namely clinohrysoylte [(Mg,Ni)$_3$Si$_2$O$_5$(OH)$_4$], magnesium silicate hydroxide/ lizardite [Mg$_3$Si$_2$O$_5$(OH)$_4$], haematite [Fe$_2$O$_3$] mineral goethite [FeO(OH)], with hexagonal closed-packed oxygen crystal structure with Fe atoms in the octahedral interstition, and quartz mineral (SiO$_2$). XRD results show that the ore is dominated by magnesium silicate minerals. The results of the mineral mineralogy XRD testing are shown in Figure 1.

![Figure 1. Diffraction peak of nickel ore (T: Clinohrysoylte, A: Antigorite, L: Lizardite, Q: Quartz, G: Goethite, H: Haematite).](image-url)
Table 1. Minerals contained in laterite ores.

| Phase         | Formula                     |
|---------------|-----------------------------|
| Clinochrysotile | \( \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \) |
| Antigorite    | \((\text{Mg,Al})_3(\text{Si,Al})_2\text{O}_5(\text{OH})_4\) |
| Lizardite     | \((\text{Mg,Al})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8\) |
| Hematite      | \(\text{Fe}_2\text{O}_3\) |
| Goethite      | \(\text{FeOOH}\) |
| Quartz        | \(\text{SiO}_2\) |

The composition of ore material based on analysis using Shimadzu VF320 X-ray Fluorescence (XRF) is listed in Table 2.

Table 2. Chemical composition of ore (%).

| NiO          | Ni total | Fe\(_2\)O\(_3\) | CO\(_2\)O\(_3\) | MgO | Cr\(_2\)O\(_3\) | MnO\(_2\) | SiO\(_2\) | Al\(_2\)O\(_3\) | LOI | others |
|--------------|----------|----------------|----------------|-----|----------------|---------|----------|---------------|-----|---------|
| 2.17         | 1.71     | 27.04          | 0.08           | 13.40 | 0.19            | 0.68    | 24.64    | 1.93          | 17.21 | 12.65   |

In this experiment the heating treatment was carried out on the initial ore by roasting about 10-20 grams of pellet-shaped ore samples in a muffle furnace with a sample container that is crucible alumina, with a roasting range of 600, 700, 800, 900 and 1000°C with open atmosphere. The roasting detention was carried out for 1 hour at these temperatures and the samples were analyzed using XRD and SEM-EDX (Scanning Electron Dispersive X-ray Electron Microscopy). Thermal characterization of the ore using Shimadzu DTG-60H Thermo Gravimetry Analyzer (DTA/TGA) Differential Thermal Analyzer aims to determine the reactions that occur during roasting. Scanning Electron Microscopy (SEM) tools used are Jeol 6390A.

3. Result and Discussion

3.1. DTA-TG Analysis

Figure 2 is DTA / TG data from laterite nickel ore. In the picture there are 4 reactions that occur during the roasting process. There are endothermic reaction temperatures at 78.8°C, 293.7°C and 638.0°C, and exothermic temperatures at 828.7°C.

![DTA/TGA graphic of nickel ore.](image)
The endothermic reaction at 78.8°C is the beginning of free water evaporation. In this roasting, the temperature is held at a constant temperature so that the water evaporates all. Then the endothermic reaction then occurs at 293.7°C. At this stage there is a goethite dissociation reaction, namely goethite transformation into hematite with the following equation Error! Reference source not found.:  

$$2\alpha-\text{FeOOH} \rightarrow \alpha-\text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \tag{1}$$  

The water formed evaporates, characterized by a decrease in the sample mass so that a sample weight loss occurs on the TGA curve. Endothermic reaction at 638.0°C is a dehydroxylation reaction of hydroxy groups from serpentine minerals followed by exothermic reactions at 828.0°C which is a forsterite phase recrystallization. Based on the analysis using XRD it is known that the main minerals contained in the ore are serpentinic categories with the main lizardite minerals and contain little goethite. To obtain beneficiation from nickel, the structure of the lizardite and goethite must be damaged. Seen at a temperature of 659.4°C there is dehydroxylation of the lizardite according to the following reaction Error! Reference source not found.:  

$$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{MgSiO}_3 \rightarrow \text{Mg}_2\text{SiO}_4 + \text{H}_2\text{O} \tag{2}$$  

Based on Figure 2 it can be estimated that the weight loss due to water vapor evaporation from A to B is 15.4%, goethite crystal water loss is from B to C of 2.3% and the loss of crystal water to forsterite from C to D is 6.0%.

3.2. Structure analysis by XRD

Diffraction analysis using X-rays is done to identify the phases formed before and after roasting treatment. The main mineral contained in laterite is garnierite and is a mixture of lizardite $$[(\text{Mg,Al,Ni})_6(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8])$$, clinochrysotile $$[(\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$$ and antigorite $$[(\text{Mg,Al,Ni})_3(\text{Si,Al})_2\text{O}_5(\text{OH})_4]$$, after heating are forsterite $$[\text{Mg}_2\text{SiO}_4]$$, Quartz $$[\text{SiO}_2]$$, Olivine $$[(\text{Fe}_{0.24}\text{Mg}_{1.76}\text{O}_4\text{Si})]$$.

![Figure 3. Diffraction patterns from ore samples to roasting 1000°C (F:Forsterite, Q:Quartz, Ov:Olivine, L: Lizardite, G:Goethite, Py:Pyroxene, M:Magnetite).](image-url)
Table 3. The main minerals formed at some roasting temperature.

| Raw          | 600°C | 700°C | 800°C | 900°C | 1000°C |
|--------------|-------|-------|-------|-------|--------|
| lizardite    | lizardite | quartz | quartz | quartz | quartz |
| quartz       | quartz | forsterite | forsterite | forsterite | forsterite |
| goethite     | forsterite | olivine | olivine | olivine | olivine |
| pyroxene     | pyroxene | pyroxene | pyroxene | magnetite | magnetite |

Based on XRD analysis in Figure 3, the minerals formed after roasting are forsterite, olivine and trevorite which are oxidation products from minerals. Garnierite group (clinochrysotile, antigorite, lizardite) transforms into forsterite and olivine.

Garnierite, Goethite $\rightarrow$ Forsterite + Olivine + Magnetite + H₂O (3)

Based on Figure 3 and Table 3, it can be seen that the formation of forsterite has occurred at a temperature of 700°C, and according to the DTA-TG around a temperature of 659.4°C, which at this temperature occurs dehydroxylation of crystalline water from the lizardite. At that time the structure of the lizardite became open so that the nickel and iron metals in the ore body lizardite were easy to reduce. But if heated further, the fast exothermic reaction will occur at the crystallization temperature of forsterite. At this stage nickel and iron metal will be difficult to reduce further because the phase formed will trap iron and nickel metal into it so that the reduction process will be hampered [3,9].

3.3. Analysis by SEM-EDX

Analysis of element distribution in the surface of the sample before and after roasting was investigated using an elemental mapping analysis using the SEM-EDX tool where the gradation of colors from points from black to red indicates the possibility of finding elements in red indicating more elements in the place. Figure 4 is a microstructure image of the initial laterite before roasting. From the picture, the main elements such as Mg, Si, O, Fe and Ni are spread evenly. Fe and Ni metals do not appear to be grouped so that they indicate Ni and Fe metals are present in the mineral structure of garnierite. Chemical composition analysis, with the same test conditions being made, was carried out on the surface of the initial sample found that the peak intensity of Fe and Ni metal was higher than the results of chemical composition analysis on the roasting samples as shown in Figure 5, this is likely because after partially roasting nickel and iron trapped in forsterite crystals so that the chemical composition of nickel and iron on the surface of the sample will decrease.
Figure 4. Element mapping analysis from SEM-EDX on the surface of raw laterite samples.

Figure 5. Chemical composition of the sample surface in the sample before roasting.
Figure 6. Analysis of elemental mapping from SEM-EDX on the surface of laterite samples after roasting 1000°C.

Figure 7. Chemical composition of the sample surface in the sample after roasting 1000°C.
Even in Figures 6 and 7 the Ni element is not detected in the surface of the sample being tested which indicates that at that temperature the nickel and iron metals are inside the forsterite.

4. Conclusion
The main mineral type of nickel metal carrier is the serpentine group with the Lizardite mineral type. Based on the analysis using the DTA-TG that the endothermic peak occurs at a temperature of 78.8°C, 293.7°C and 638.0°C and this is related to the evaporation of water vapor and the release of crystalline water from goethite and the release of serpentinic mineral crystals to form the forsterite phase. Forsterite crystallization temperature occurs at a temperature of 828.0°C.

At a roasting temperature of 700.0°C, there has been a reaction of dehydroxylation of laterite nickel to forsterite, at which temperature the mineral undergoes a structural change and at that time the time is right to reduce nickel and iron in it before the forsterite crystallization reaction will cause nickel and iron to be inert against outside influences.

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