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The effect of iron content on the reduction of nickel laterite by direct reduction method

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Abstract. Reduction and the compounds formed when the reduced laterite nickel has been investigated. Nickel laterite with average grain size below 0.149 mm mixed with 13% (weight percent) of coal as reductant then reduced in muffle furnace with temperature from 700 °C to 1000 °C. Type of laterite is used which has high iron (saprolite) and low iron content (limonite). Reaction time varied 30, 60 and 90 minutes. The reduction of nickel during reduction is determined by an analysis of metallization values. Metallization analysis used bromine methanol method, while the compound analysis was formed using x-ray Diffractometer. Based on the metallization test, it is known that the laterite nickel ore containing high iron will produce a higher nickel reduction than the laterite nickel ore containing low iron. This corresponds to the oxide phases formed. The higher iron contain on the ore tend to produce the fayalite mixture and slightly forsterite, while at low iron content will form a forsterite. Forsterite tends to inhibit reduction of nickel.

1. Introduction

Nickel consists of two types of common ores, sulfides and laterite ores. Laterite nickel ore, which comprises 73% of the world's proven nickel reserves is the dominant source of nickel. However, only 42% of the world's production of nickel comes from laterite nickel ore [1], [2]. Ferronickel processing from laterite ores requires high energy costs, especially when laterite ores with low nickel content are processed. Because energy is mostly used to melt ore and produces only a little nickel metal and a large amount of slag. In addition, areas where large deposits of laterite ore are located do not have access to cheap electricity sources. Unlike sulfide ores, nickel in laterite is finely dispersed in ore and cannot be increased by fine grinding or other physical methods [3].

There are three main processes of commercial processes: rotary kiln electric furnaces (RKEF) and rotary kiln magnetic separators, Caron process, and high pressure acid leaching (HPAL). In general, laterite ore types are suitable for certain process, such as crystals for leaching high pressure acids or saprolite for RKEF. A significant problem is the presence of MgO and SiO₂ contents which will affect reductibility level on temperature used in the process. Reduction results from laterite will produce forsterite (Mg₂SiO₄), fayalite (FeSiO₃), and enstatite (MgSiO₃) simultaneously. This intermediate phase is very irregular and thus has high chemical reactivity. Kawahara [4] and Hallet [5] have found that nickel oxides will be bound in pyroxene and are particularly strong in the olivine phase, and consequently the reduction of nickel oxide becomes much more difficult. Stevens, et. al. [6] and Hayashi [7,16] concluded the role of forsterite structure formation in saprolite at high temperatures, inhibiting the reduction of nickel and cobalt. Several investigations of the reduction of nickel oxide or laterite nickel ore have been carried out and are related to the effects of phases on the reduction and formation of nickel metal particles. For example, Krasuk et al. [9] studied the reduction of nickel oxide with CO,



Utigard et al. [10] studied the nickel oxide reduction kinetics using hydrogen, and James et al. [11] using X-ray diffraction to study the reduction of nickel oxide by hydrogen. Reduction of laterite nickel ore by gases containing H₂ and CO in horizontal tube furnaces and in laboratory-scale reactors was studied by Utigard [10]. Valix et al. [12] study the effect of sulfur on laterite ores during temperature reduction. Li et al. [13] completed a simulation study of pre-reduction and calcination of nickel laterite ore with coke to determine the effect of temperature, time, atmosphere and CaO content on nickel reduction rates. Enriching metallic nickel from laterite nickel ore using the process of separating thermal carbon magnetic reduction with activated carbon powder as a reductant was investigated by Xu et al [14]. Other additives have been added in order to study the effect on the reduction of nickel metal which in principle suppresses the growth of the inert phase forsterite by adding chemicals such as CaSO₄ [14,15], Sulfur [12], silica [4] and CaO [13]. There several main factors influenced the reductibility of nickel from ore. These parameter are minerology of ore, composition of reductor, temperature, reduction time, aditif and the composition of slag. There are two general type slag as by product forsterite and fayalite. The type of slag produced will affected the success of reduction. This study has investigated the effect of iron content due to type of slag produced. The reduction level of ore with the difference iron contained was determined by reducing it with coal followed by analysis using bromine-methanol for determination of the degree of metallization. So that the reduction properties of laterite types can be known.

2. Methodology

The research was carried out at first by grinding the saprolite and limonite ore from Sulawesi Island into powder form. After that, sieving with a size of > 100 mesh, to get a uniform powder size. Then the powder is dried at a temperature of 100 °C. After drying the laterite powder, initial characterization to obtain the chemical content of laterite by XRF and thermal characterization using TG/DTA. There are three composition of samples: limonite, saprolite, and mixed of them. The mixed samples are made by mixing saprolite with limonite with a ratio of 1: 1 (% by weight). The chemical composition listed in table 1.

Table 1. Chemical composition of sampel limonite, saprolite and mix saprolite-limonite 1:1 (%w/w).

Ore	Ni Total	Fe Total	MgO	SiO ₂	Al ₂ O ₃	LOI
Limonite	1.31	47.5	2.35	8.27	5.32	10.4
Saprolite	1.71	18.9	13.0	15.7	0.53	17.2
Mix 1 : 1	1.51	31.2	4.32	11.3	4.20	14.2

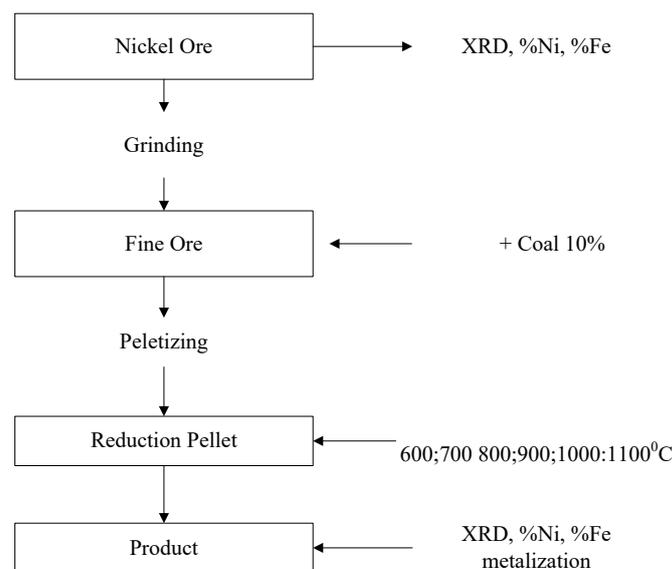


Figure 1. Flowchart of Reduction.

The weight of metal nickel is obtained by dipping the reduced sample in bromine-methanol solution to calculate "% reduced metal" or can also be called "metallization degree" using the equation [8].

$$\% \text{ metallization} = \frac{\text{weight of reduced nickel}}{\text{weight of nickel total}} \times 100\% \quad (1)$$

3. Result and Discussion

3.1. Thermal Characteristic

Figure 2 is DTA/TG data from laterite nickel ore. The picture shows the endothermic reaction temperature at 75, 290, and 638 °C, and exothermic temperature at 830 °C.

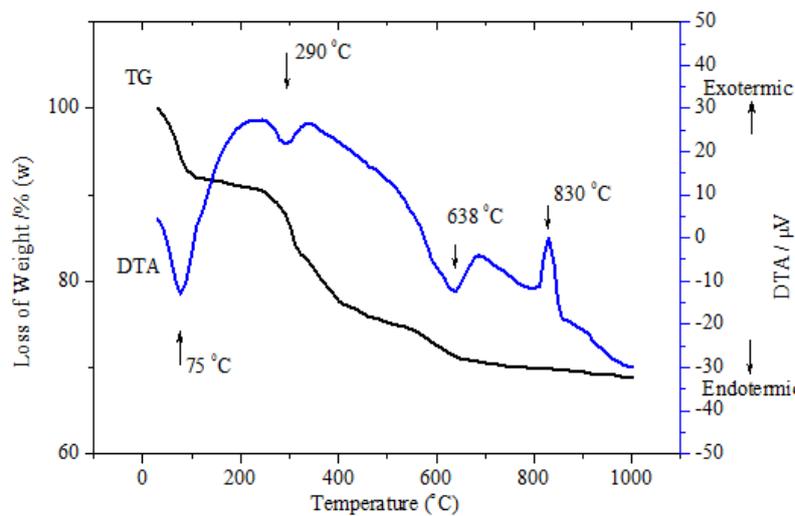
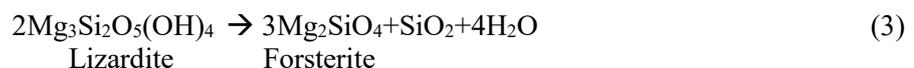


Figure 2. Graph of DTA / TGA of laterite ore (heating conditions : 20 °C /minute, CO2 50mL/s).

The endothermic reaction at 75°C is the beginning of free water evaporation. In this heating, the temperature is held at a fixed temperature so that the all water evaporates. Then the endothermic reaction then occurs at 290°C. At this temperature there will be free water evaporation and from goethite with the following equation.



The water formed evaporates, marked by a decrease in the sample mass so that there is a decrease in the curve on the graph. The endothermic reaction at 638°C is a dehydroxylation reaction of hydroxy groups from serpentine minerals followed by an exothermic reaction at 820°C which is a forsterite phase recrystallization. According to Brindley [18], the water loss reaction in this dehydroxylation event is because the migration of protons from H⁺ ions joins OH⁻ ions to form H₂O molecules, and magnesium and silicon ion ions migrate in opposite directions to keep the charge neutral. At a temperature of 638°C, the structure of the lizardite and goethite is damaged so that at this temperature it is a good time to process nickel because the structure of the lizardite is open to outside influences. If the final product is forsterite and silica, the overall chemical equation can be written as follows:



At a temperature of 820 °C there is a crystallization reaction from the formed forsterite. This is according to what has been explained in detail by Ball that serpentine will undergo several stages of reaction when heated (evaporation of free water), dehydroxylation (evaporation of crystal water) and crystallization of forsterite at temperature about 800°C.

3.2. Effect of the amount of coal on metallization

The degree of reduction of laterite samples at various temperatures and the time of the reduction process of saprolite ore and limonite samples shown on figure 3. Figure 3 is the relationship between the reduction temperature of saprolite samples at various variations of reduction time. There is the influence of the amount of reducing agent on metallization of nickel at a reduction temperature at fixed temperature 900 °C. Based on figure 3 known that the optimum amount of coal is 13%(w/w). Metallization, sometimes referred as a “% reduction level” or “% reducibility”, is defined as the weight of a the total weight metal as element in the sample, metal element in a sample which is in a state of element or oxidation number "zero", compared to the total of element weight.

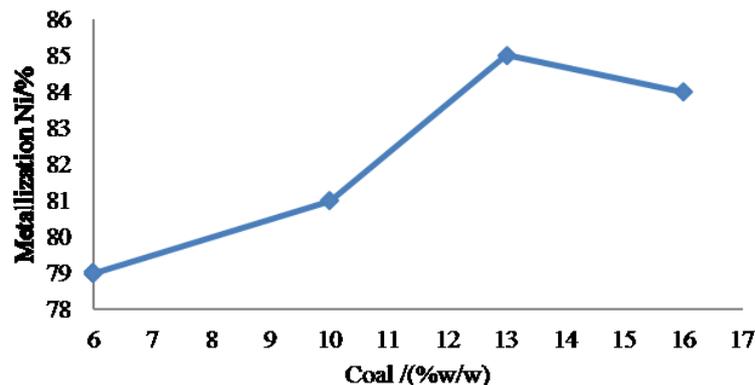


Figure 3. Relationship between the amount of coal and nickel metallization (%) at a reduction temperature of 900°C.

3.3. Comparison of metallization of limonite, saprolite and mix

For saprolite ore (ore mixed with coal 13%) the amount of reduced nickel metal increases after reduction is carried out for more than 30 minutes. From the temperature of 700°C, the nickel reduced was significant increase. But after 700°C, the degree of reduction will rise slowly. For limonite ores with a rise in temperature will increase the degree of reduction but slightly different from saprolite, the increase in the degree of reduction of each temperature change is higher. The highest degree of metallization is 85% from 900°C to 1000°C for 60 minutes reduction time. The degree of metallization does not seem to increase significantly with the increase in temperature even though it is higher than 1000°C. The metallization degree of saprolite is lower than limonite at the same temperature, this is related to the ratio of SiO₂ to MgO.

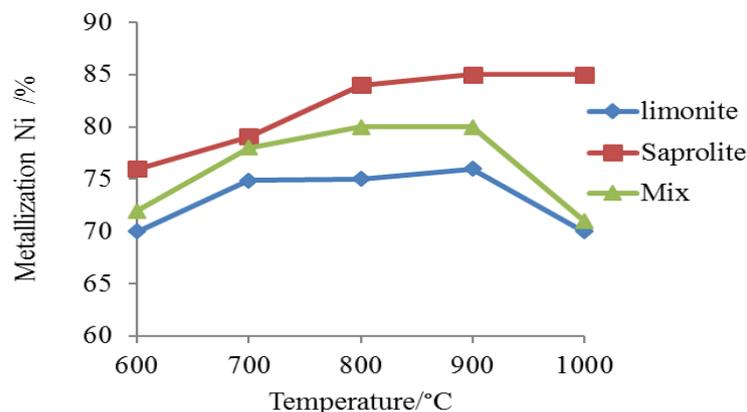


Figure 4 Relationship between the reduction temperature of saprolite samples (13%) and limonite with% reduced nickel (metallization) at various reduction times.

Olivine which has a chemical structure of $2\text{MgO}\cdot\text{SiO}_2$. Based on the above results it is very clear that nickel reduction is very dependent on the type of minerals contained in the ore. Based on its iron content, limonitic ores have a much higher iron content. It is known that nickel oxide ore contains relatively high magnesium and silica. This will inhibit the reduction of nickel at high temperatures. This phenomenon is related to the formation of olivine, which is an iron-magnesium-silicate. The atomic radius of the Ni^{2+} atom is very close to the radius of Mg^{2+} (0.068 and 0.065 nm) so that the Ni atom can exchange places with the Mg. Limonite ores have relatively low levels of MgO and SiO_2 so formation of olivine is less significant. When reduced at high temperatures the interference of the formation of olivine can be ignored so that the amount of reduced nickel will be relatively proportional to the increase in temperature.

Phase analysis and diffraction on figure 5 is an XRD graph of the saprolite sample as initial ore and after reduction at several temperatures. All reductions were carried out within 60 minutes using coal in a closed muffle furnace.

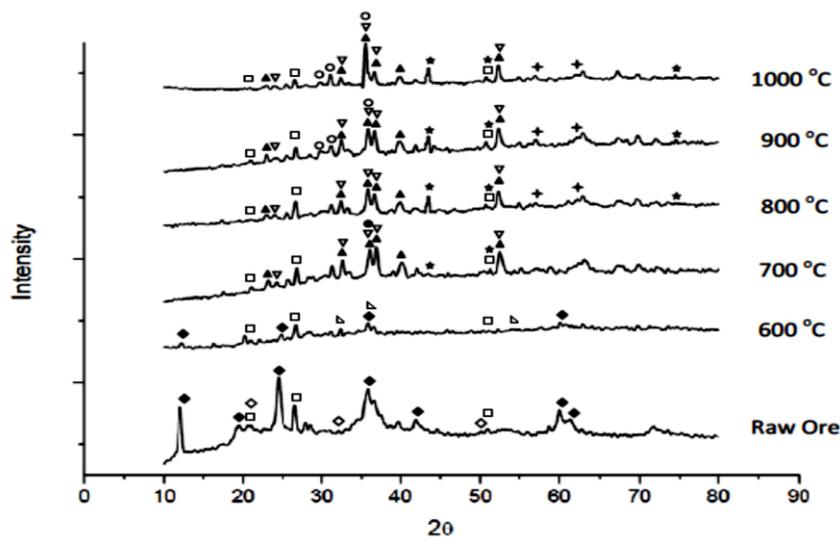
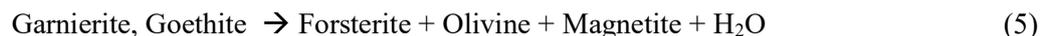


Figure 5 Diffraction pattern of *Saprolite* before and after reduced (\square silika, \blacklozenge Lizardite, \blacklozenge Goethite, \blacktriangle Olivine, \star Taenite, ∇ Forsterite, \blackplus Magnetite, \circ Pyroxene, \blacktriangle Hematite.

The main mineral contained of saprolite mineral there are lizardite, quartz and goethite. Lizardite contains 3 main peak there are 2θ 12.04; 24.30 and 35.87 (ICDD No. 09-0444). The silica peak appear on 2θ : 26.64; 20.86 and 50.13. (ICDD No. 79-1910). Peaks of *goethite* appears with the low intensity on 2θ : 21.24; 33.28 and 33.62 (ICDD No. 17-539) from goethite to hematite.



Further reduction of the hydroxyl group Garnierite group serpentine (clinochrysotile, antigorite, lizardite) transforms into forsterite and olivine $(\text{Mg,Fe})_2\text{SiO}_4$.



Ferronickel metal in the form of taenite (ICDD no. 47-1417) with 3 strongest peaks, that 2θ are 43.5; 50.7 dan 74.5 appears on 700°C The main mineral that appears at high temperatures is magnesium silicate in the form of forsterite and olivine. Figure 6 is an XRD graph of the limonite sample as initial ore and after reduction at several temperatures. All reductions were carried out within 60 minutes using coal in a closed muffle furnace.

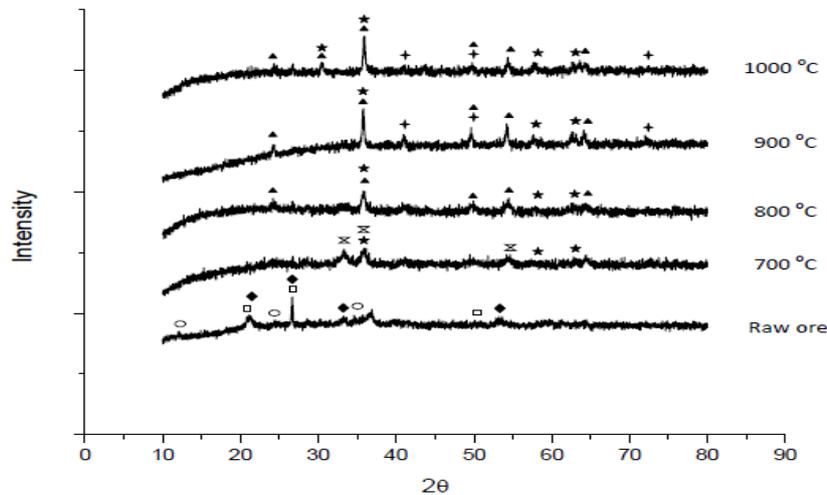


Figure 6. Diffraction pattern of *limonite* ore from 700 °C to 1000 °C before and after reduced (▲Fayalite, ■Silica, ◆Goethite, ●Antigorite, ★Magnetite, †Taenite, ✕Hematite).

The main mineral that appears after reduction at a temperature of 1000 °C is magnetite (ICDD No. 84-308) dan *fayalite* (ICDD No. 76-0852) marked of appearance of 2θ on 21.2; 33.3; 33.6 for *magnetite*, and 35.9; 31.7; 51.5 for *fayalite*. FeNi substance as *taenite* (ICDD No. 47-1417) first appears on 900 °C.

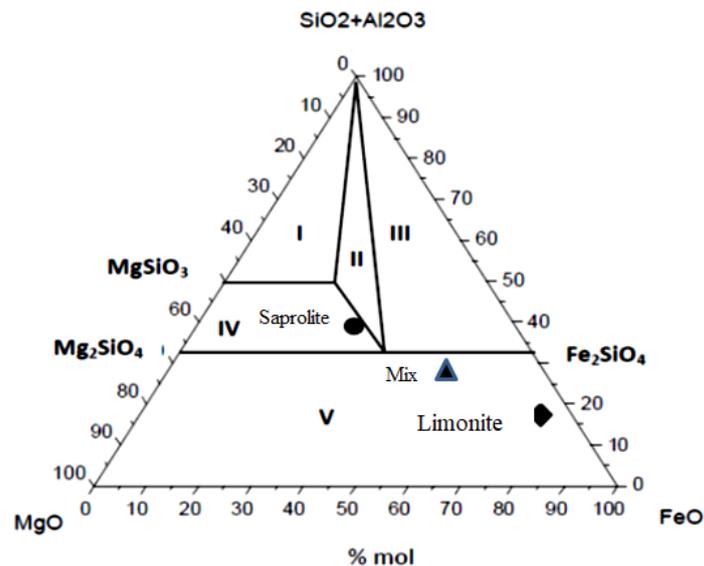


Figure 7. Composition of *saprofite* and *limonite* and mix, on SiO₂-MgO-FeO system phase diagram.

Figure 6 is the ternary diagram of silica, magnesia dan iron oxide. These three types of ore have a significant difference from the chemical composition of the main constituent elements, there are composition main element such as iron, magnesium, silicon and aluminum oxide. To further explore the reductibility of these ores, the composition as % mol of each of these oxides was calculated and plotted on a ternary diagram of FeO-SiO₂-MgO from Kawahara and this diagram is shown in Figure 7. Based on Figure 7 from Kawahara, There are 5 parts in the graph that can be grouped as below;

- Part I, each containing pyroxene and SiO₂,

- Part II, *pyroxene*, SiO₂ and *olivine*
- Part III, *olivine*, SiO₂
- Part IV, *olivine*, *pyroxene*
- Part V, magnesio *Wustite* and *olivine*.

Saprolite samples used in this study will be in part IV which in this composition contain *olivine* and *pyroxene*. NiO will be difficult to reduce in these phases, but if NiO is present in magnesioferrite or fayalite phases then NiO is easily reduced as well as on part V. The chemical composition of *limonite* oxides is in part V which contains a little magnesium silicate so that nickel in the *limonite* sample is easier to reduce.

4. Conclusion

Increased iron content in laterite nickel ore samples will increase the reducibility of nickel metal. The goethite mineral in the ore functions as a fayalite or magnesioferrite forming which does not trap nickel when the reduction is carried out as well as *forsterite*.

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