Phase Transformation of Limonite Nickel Ores with Na₂SO₄ Addition in Selective Reduction Process

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Abstract. This study aims to observe the transformations, both mineralogy and morphology of limonite nickel ore with coal as reducing agent and Na₂SO₄ as an additive in the selective reduction processes. A series of selective reduction processes were carried out at various temperatures in Carbolite muffle furnace for 1 hour. The range of reduction temperature was determined from Thermogravimetric-Derivative Thermal Analysis (TG-DTA). The mineralogy of raw and reduced ores was characterized by using XRD analysis. The morphology, particle size, and mapping were characterized by using SEM-EDS analysis. The results showed that goethite was the main component in the raw limonite nickel ore and it was decomposed by losing the crystalline water at 300 °C. The decompositions were continued to lizardite and trevorite at 600 °C and 800 °C respectively, then Fe and Fe-Ni were formed at 900 °C. Metallization continuously occurred by increasing reduction temperature up to 1100 °C. Moreover, the particle size and porosity of reduced ore were greater up to 2.5-times. The addition of Na₂SO₄ on the selective reduction processes decreased silica content; it also caused the formation of fayalite and FeS at 600 °C and 800 °C respectively. The intensity of fayalite and FeS decreased when the reduction temperature was more than 900 °C.

Keywords: Nickel, Limonite, Na₂SO₄, Reduction, Phase transformation

1. Introduction

Nickel ore is divided into two types, sulfide (high grade) and laterite (low grade). The world resources of laterite ore are up to 1.5 times higher than sulfide resources, but it does not reach a half of the total number of existing nickel resources used for world's nickel productions, sulfide ore dominates the raw material [1-4]. Utilizing the high-grade nickel ore is continued to rise, causing high-grade nickel resources to decrease, so the low-grade nickel resources get much attention and leads to be used as raw material, especially for nickel containing less than 2% wt. of Ni [5,6].

Indonesia is one of countries that has the highest laterite nickel ore resources in the world, that is about 12% [1]. In addition, another advantage of utilizing laterite nickel ore as raw material is location for mining; the laterite nickel ore can be mined by open-cut mining as it is located closer to the soil surface [4]. The first layer near the surface is limonite, then alunite, and saprolite [7]. Based on that condition, Indonesia has highly potential to develop nickel processing of limonite nickel ore through this research with the raw limonite nickel ore spread in several areas of Indonesia, especially in the east part of Indonesia.
Halmahera, North Maluku is one of the areas in Indonesia which has laterite nickel ore resources [8]. Limonite ore is one of laterite nickel types that has low Ni content (<1.50%) and high Fe content (> 40%)[9]. In Halmahera, it is not used for raw material of nickel ore processing. In this study, it is used to investigate the potency for ore processing nickel by using limonite ores.

Several studies about laterite nickel ore were carried out. Valix and Cheung [7] found that reducing conditions on dehydroxylation reaction have a significant influence on the transformation of mineral during the reduction. The phase was formed at 800 °C, and it was irreversible during cooling. For the reduction of saprolite after calcination at temperatures more than 700 °C, the forsterite was formed. In the reduction process with Na₂SO₄ addition at temperatures more than 800 °C has been performed by Guanghui Li [10]. Forsterite was formed and had not become inhibitor for further reduction process for the formation of FeS which can suppress the formation of metallic Fe. By this way, it could increase the Ni contain up to 9.48% [10]. On the other hand, nickel laterite from Indonesia has been studied by Subagia, et al. [11]. As much as 3.64% of Ni was obtained which is less than what resulted by Li in the selective reduction process with 20% addition of Na₂SO₄ [11]. Based on the research studied, it is known that selective reduction process with Na₂SO₄ addition is effective to increase nickel content due to the formation of FeS which can be physically separated by magnetic separation, which is related to the metallization process that leads transformation of metal and morphology. From those process, the product will be known from the composition of mixture in the reduction process at certain temperature, either as Fe-Ni, nickel matte or other products, but study which focuses on the phase transformation and its mechanism of reaction of limonite nickel ore from Indonesia by selective reduction process is still approximately, so it needs to identify the potency of limonite nickel ore from Indonesia, especially from Halmahera. The aims of this study are to examine the structural changes, both mineralogy and morphology of limonite ore in the selective reduction process by using coal as reducing agent and Na₂SO₄ as an additive.

2. Experimental Method

Limonite nickel ore from Halmahera, North Maluku was dried by using an electric oven at 110 °C for 12 hours, then it was crushed, grounded and screened to get -100 mesh of particle size. The morphology and composition of limonite nickel ore were examined by using SEM-EDS analysis, and the mineralogy was examined by using XRD (X-Ray Diffraction) analysis. Sub-bituminous coal was used as reducing agent. It was prepared by crushing, grounding and screening with a 100 mesh of a sieve. Na₂SO₄ was used as an additive, the specification was chemical grade (P.A) for analysis.

The prepared limonite nickel ore, reducing agent, and Na₂SO₄ were uniformly mixed by physical blending before reduction process. The addition of reducing agent and additive was 10% wt. of limonite ore used respectively. TG-DTA (Thermogravimetry - Derivative Thermal Analysis) Setaram Setsys-1750 was performed to the prepared mixture from the previously step to determine the percentage of mass reduction and decomposition temperature. Selective reduction processes were carried out to the other part of the prepared mixture by using Carbolite muffle furnace in the graphite crucible. The crucible was put into the furnace when the furnace was turned on until reached the particular temperature and restrained for 1 hour. The range of temperature for selective reduction process was determined from decomposition temperature of TG-DTA. The reduced mixture was then characterized through XRD analysis to determine its phase transformation and SEM-EDS analysis to determine the morphology, particle size, and distribution of metal formed when it reached the ambient temperature. XRD analysis was performed with Shimadzu XRD 7000 and Match software used to interpret the phase formed. SEM-EDS analysis was performed with SEM-EDS JEOL 6390A.

3. Results and Discussion

3.1. Characterization of raw limonite nickel ore

The compositions of raw limonite nickel ore are listed in Table 1. The EDS result shows the main components of limonite nickel ore are Fe and O elements. It means that the minerals in the ore are
bound together with oxide as iron oxide which can confirm with XRD analysis for its phases. Fe is the main mineral in the ore followed by Si, Cu, Ni, Mg, Al, and Cr.

Figure 1 shows the phases of limonite ore used are lizardite ((Mg, Fe)_3Si_2O_5(OH)_4), goethite (FeO(OH)), hematite (Fe_2O_3), trevorite (NiFe_2O_4), quartz (SiO_2), and wustite (FeO), the diffraction pattern in accordance with Match result. Quartz shows having the highest intensity, followed by goethite and hematite in the few points. It indicates that the dominant component in the limonite ore used are silica and iron-based compound. This is agree with EDS result in Table 1. Goethite is the main component in the limonite ore [7], and shows a higher intensity at some point than the other elements, the sharp diffraction peak intensity of goethite at 20 at 21.25°, 36.5°, and 53°.

| Table 1. Composition of raw limonite nickel ore |
|-----------------------------------------------|
| **Element** | **Mass (%)** |
| O            | 10.9         |
| Fe           | 71.41        |
| Si           | 5.07         |
| Mg           | 2.24         |
| Ni           | 3.76         |
| Al           | 1.47         |
| Cr           | 1.13         |
| Cu           | 4.02         |

Figure 1. XRD analysis of limonite nickel ore

3.2 **TG-DTA Analysis**

The TG-DTA curve (Figure 2) shows that mass loss was started at 98 °C and 100 °C with 0.01% and 0.06% of mass loss respectively and represents the evaporation of water [12]. First endothermic peak occurred at 324 °C with 2.39% of mass loss; it represents the dehydroxylation of goethite to form hematite [13]. The low mass loss in TG indicates of poorly crystalline of goethite structure [13]. The first endothermic temperature was lower than 337 °C which was raw limonite nickel ore without reducing agent and additive performed [14], it means that reducing agent and additive addition makes reaction faster. The second endothermic peak occurred at 625 °C with no significant change of mass loss, 4.21%. Decomposition at temperature higher than 600°C represents the decomposition of lizardite [15]. The third endothermic peak at 902 °C with mass loss 7.39% and the last endothermic peak, accompanied by mass loss of 8.89%. Finally, an exothermic peak at 1236 °C represents recrystallisation. The mass loss between 625 °C and 902 °C have high gap of mass loss, it is more than twice from prior decomposition temperature that represents the high crystallinity phase occurred between that temperature. Therefore the decomposition at 800 °C is required to determine phase transformation between that temperatures. Based on the TG-DTA results, a series of selective
Reduction processes were performed at 300, 600, 800, 900, 1000, and 1100 °C, then XRD and SEM-EDS analysis were performed to analyse the decomposition occurred to the reduced ores between those range of temperature, both, phase and morphology transformation.

![Figure 2. TG-DTA analysis of limonite nickel ore, reducing agent and additive mixture](image)

### 3.3 Phase Transformation of Reduced Ore

Phase transformation of reduced limonite nickel ore with a reducing agent and Na₂SO₄ additive at various temperature is shown in Figure 3. It indicates that hematite and goethite were observed at XRD pattern at 300 °C, whereas lizardite, quartz, wustite and trevorite were not observed. The sharp diffraction peak intensity of goethite was at 2θ at 21.25° and 41.25°, while hematite was at 23°, 33°, 54.5°, 41°, 45°, and 71°. At this temperature, the structure must be destroyed, as well goethite starts to lose most of the crystalline water to form hematite and lizardite and start to lose of crystalline water, but the transformation is not entirely completed [3] [16]. It caused XRD pattern of the sample treated at 300 °C is amorphous. Dehydroxylation of goethite and lizardite occurred such as reaction (1) and reaction (2), it can be confirmed with free energy diagrams, Figure 4., which shows that reaction (1) and reaction (2) have the lowest standard free energy at about 100 °C, and 300 °C respectively.

\[
\begin{align*}
2\text{FeO(OH)} & \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \quad (1) \\
(\text{Mg,Fe})_2\text{Si}_2\text{O}_5(\text{OH})_4 & \rightarrow (\text{Mg,Fe})_2\text{SiO}_4 + (\text{Mg,Fe})\text{SiO}_3 + 2\text{H}_2\text{O} \quad (2)
\end{align*}
\]

For reduction temperature at 600 °C, the crystal with high intensity was observed. Hematite was reduced to magnetite with the presence of CO(g). Sharp diffraction peak intensity of magnetite at 2θ was at 30.25°, 35.3°, 58°, and 62.5°. Nickel mineral could not be liberated in the limonite ore, after the structure of trevorite damage was at 300 °C, it was incorporated with the hematite forming trevorite [13], as in reaction (6). Lizardite was continued to decompose to form MgSiO₃ and Mg₂SiO₄, as Lu Jie, et al. result [15]. Na₂SO₄ presence cause Fe liberates from Mg at lizardite [10-15], causing the formation of fayalite (Fe₂SiO₄), as in reaction (7). The sharp diffraction peak intensity of fayalite at 2θ was at 35.3° and 37.25°. Reaction (9) is the intermediate reaction that was reacted in further reduction temperature. From Figure 4, reaction (9) has the lowest free energy values at 800 °C.

\[
\begin{align*}
\text{C} + \text{O}_2 & \rightarrow \text{CO}_2 \quad (3) \\
\text{CO}_2 + \text{C} & \rightarrow 2\text{CO} \quad (4) \\
3\text{Fe}_2\text{O}_3 + \text{CO}(g) & \rightarrow 2\text{Fe}_3\text{O}_4 + \text{CO}_2(g) \quad (5)
\end{align*}
\]
Fe$_2$O$_3$ + NiO $\rightarrow$ NiFe$_2$O$_4$ \hfill (6) \\
(Mg,Fe)$_2$SiO$_4$ $\rightarrow$ Mg$_2$SiO$_4$ + Fe$_2$SiO$_4$ \hfill (7) \\
(Mg,Fe)SiO$_2$ $\rightarrow$ MgSiO$_3$ + FeSiO$_3$ \hfill (8) \\
FeSiO$_3$ + Na$_2$SO$_4$ + CO$_{(g)}$ $\rightarrow$ FeO + Na$_2$SiO$_3$ + SO$_{2(g)}$ + CO$_{2(g)}$ \hfill (9)

Na$_2$SO$_4$ attached quartz to form sodium metasilicate, so the presence of Na$_2$SO$_4$ at reduction process can decrease silica content, then the intensity of silica decreases. According to the standard free energy diagrams (Figure 4), Na$_2$SO$_4$ reacts spontaneously with quartz at 500 ºC and more spontaneously with the increasing temperature.

SiO$_2$ + Na$_2$SO$_4$ + CO $\rightarrow$ Na$_2$SiO$_3$ + SO$_2$ + CO$_2$ \hfill (10)

Figure 3. XRD analysis of reduced ores at 300º - 1100ºC

At the XRD pattern of the reduction temperature of 800 ºC, fayalite shows higher intensity than the previous one. Trevorite partially was decomposed into NiO and magnetite. The sharp diffraction peak intensity of NiO at 20 at 37º, 43º and 63º. Instead, MgSiO$_3$ and Mg$_2$SiO$_3$ were not observed at peak with reduction temperature above 600 ºC [10]. It changes because limonite nickel ore has small Mg
content [9] so the peak was not apparent. FeS started to form at 800 °C, reaction (12). The sharp diffraction peak intensity of FeS at 2θ of 44°.

\[
1.5\text{NiFe}_2\text{O}_4 + \frac{1}{2} \text{C} \rightarrow 1.5\text{NiO} + \text{Fe}_3\text{O}_4 + \frac{1}{2} \text{CO}
\]

(11)

\[
\text{FeO} + \text{SO}_2 + \text{CO} \rightarrow \text{FeS} + \text{CO}_2
\]

(12)

Magnetite was reduced to form FeO at 900 °C, then with trevorite form (Fe,Ni)O.Fe$_2$O$_3$ [13] and led kamacite (Fe, Ni) phase and Fe$_3$O$_4$. It is appropriate with the XRD pattern that FeO and (Fe,Ni) were observed. The sharp diffraction peak intensity of FeO at 2θ was at 42°, 60.8°, and 73°, while Fe-Ni was at 44.5°. FeO partially reduced to Fe and also reacted with SO$_2$ to form FeS. Between 800° – 900°C, fayalite has highest intensity. It is appropriate with DTA curve that shows the increasing in heat flow. Instead, intensity of NiO decreased because partially incorporated to form kamacite.

\[
\text{NiFe}_2\text{O}_4 + \text{Fe}_3\text{O}_4 \rightarrow (\text{Fe,Ni})\text{O}.\text{Fe}_2\text{O}_3 + \text{Fe}_2\text{O}_3
\]

(13)

\[
2\text{Fe}_2\text{O}_3 + 2\text{CO} \rightarrow 4\text{FeO} + \text{CO}_2
\]

(14)

\[
\text{Fe}_3\text{O}_4 + \text{CO} \rightarrow 3\text{FeO} + \text{CO}_2
\]

(15)

\[
\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2
\]

(16)

\[
\text{FeO} + \text{SO}_2 + \text{CO} \rightarrow \text{FeS} + \text{CO}_2
\]

(17)

For reduction temperature at 1000°C, intensity of kamacite phase was higher than previous, instead trevorite and magnetite decrease. Fayalite and FeS decreased with reduction temperature more than 800°C, for further reduction temperature trevorite and goethite totally reduced and intensity kamacite was higher than previous.

XRD pattern shows the decomposition, either physical or chemical that is previously shown in the TG-DTA curve. Temperature affects the metallization process whereas additive Na$_2$SO$_4$ affects the Fe and silica content. Moreover, it increases the reaction rate. Na$_2$SO$_4$ addition provides beneficial for increasing selectivity of Ni by formation of fayalite and FeS that can be separated by magnetic separation.

![Figure 4](image)

**Figure 4.** Free energy diagram in various temperature. Data calculated by HSC Chemistry 6

If we compare between TG-DTA curve and XRD pattern, it can determine the phase transformation of limonite nickel ore at reduction temperature up to 1100 °C with Na$_2$SO$_4$ addition and coal as reducing agent. At 324 °C, endothermic reaction occurred that caused the loss of crystalline water that restructuring limonite nickel ore. At 625 °C, endothermic reaction causes decomposition lizardite to form fayalite. At 902 °C FeO is formed as a result of reduction of magnetite.
and Fe-Ni was formed at a temperature 900 °C. At 1019 °C, goethite completely reduced into magnetite and at 1236 °C recrystallization of Fe-Ni occurred.

3.4 Morphology Transformation of Reduced Ore

Figure 5 shows the microstructure transformation of the reduced ores at 300 °C – 1100 °C. It can be seen that particle size was growing. The particle size of limonite ore is greater as the temperature reduction increases. This is also happening in the porosity. It can be seen in Figure 5 (a), and (b) that it still looks homogeneous, but in Figure 5 (c) it can be seen their separation because of the decomposition process at temperatures up to 900 °C, Figure 5 (d) and (e). In Figure 4 (f) and (g), aggregation occurred, so the size of metal particles formed is larger and better in porosity. Limonite ore size before reduced is about 27.41 μm and was continued to grow in line with increasing reduction temperature up to 60 μm at 1000 °C and 70.73 μm at 1100 °C. This is appropriate with the XRD analysis that showed an increasing intensity of metal formation in line with increasing the reduction temperature, it must be indicating the larger particle size.

Figure 5. SEM-EDS images of limonite nickel ore (a), and reduced ore for 1 hour of limonite nickel ore (b) at 300 °C, (c) at 600 °C, (d) at 800 °C, (e) at 900 °C, (f) at 1000 °C, (g) at 1100 °C

Figure 6 shows the mapping of SEM-EDS analysis of the reduced ore at 1000 °C for 1 hour. The elemental mapping illustrates the distribution of several elements, such as O (Figure 6 (b)), Fe (Figure 6 (c)), Ni (Figure 6 (d)), Si (Figure 6 (e)) and S (Figure 6 (f)). The distribution of element is indicated by the color indicator (left side) on the morphology of SEM analysis that refers to Figure 6 (a). The color indicator also shows the qualitative analysis. From the pictures it can be seen that the Fe has the highest concentration followed by O, Si, S, and Ni, it can be confirmed from EDS which shows the semi-quantitative analysis in Table 2. In mapping, Fe and S elements have similarities, but S distribution is not as high as Fe distribution, it shows that FeS formed is not in large amount. Mapping Fe and Si also have similarities. It indicates that fayalite has larger quantities than FeS, according to the XRD patterns, fayalite observed at some point even with weak intensity. It is also observed that Fe and O have the same distribution, which indicates the presence of iron oxides such as goethite and magnetite. Distribution of Fe and Ni in mapping also have similarities with the smaller amount of Ni indicating the Fe-Ni distributions.
Table 2. Composition of reduced ore at 1000 ºC based on EDS result

| Element | Mass (%) | Element | Mass (%) |
|---------|----------|---------|----------|
| O       | 6.31     | Fe      | 74.94    |
| Mg      | 0.56     | Ni      | 4.49     |
| Al      | 1.97     | Cu      | 3.25     |
| Si      | 3.43     | Zn      | 1.27     |
| S       | 1.11     | Cr      | 2.67     |

Figure 6. Images of (a) reduced ore at 1000 ºC, (b) mapping for O atom, (c) mapping for Fe atom, (d) mapping for Ni atom, (e) mapping for Si atom, (f) mapping for S atom

4. Conclusion
Phase transformation occurred to the reduced ore in the selective reduction temperature processes at 300 - 1100 ºC for 1 hour. Four endothermic peaks were observed at TG-DTA that indicated the decomposition of goethite, lizardite, and trevorite, respectively. Moreover, one exothermic peak indicated recrystallization of Fe-Ni. The presence of Na$_2$SO$_4$ in the selective reduction process led the fayalite formation at 600 ºC, and FeS formation at 800 ºC, also decreased silica content with the Na$_2$SiO$_3$ formation. A higher reduction process at a temperature more than 900 ºC gave an advantage for Fe and Fe-Ni formation. Otherwise, fayalite and FeS formation decreased. Phase transformation affected microstructure change, so the size and porosity also transformed. The size and porosity of the limonite ore particles were greater up to twice at 1000 ºC and 2.5 times at 1100 ºC with uniform distribution.

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