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To cite this article: I Setiawan et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 202 012019

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Low-Temperature Carbothermic Reduction of Indonesia Nickel Lateritic Ore with Sub-Bituminous Coal

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Abstract. In this work, the experiment was conducted to investigate the effect of temperature and sub-bituminous coal on upgrading nickel laterite ores by carbothermic reduction. The reduction was carried out in the muffle furnace at a temperature ranging of 800-1100 °C. The produced calcine from reduction step was grounded in vibrating mill, mixed with water and passed on a magnetic separator to separate nickel concentrates from the tailing. The experimental results showed that the concentrate with highest nickel grade was produced at temperature 1000 °C. The nickel grade on concentrate was 5.0 %, with the recovery of nickel was 80.6 %.

Keywords: laterite, carbothermic reduction, recovery, grade, concentrate

1. Introduction

Nickel laterite ore comprises 73% of the world’s nickel resources and will be the dominant source of nickel in the future. With the continuous depletion of high-grade nickel ores such as millerite and niccolite, nickel laterite ores have become the major source for the production of nickel metal. However, currently, only 42% of the world’s production of nickel comes from nickel laterite ore because the nickel content in the ore is low [1]. Nickel laterite ores are difficult to concentrate due to their low nickel content and isomorphic goethite or serpentine crystalline structure [2].

The presence of sulfur has a greater effect on the recovery achieved in weathered saprolite compared to fresh saprolite. The sulfur, in general, improves the recoveries of all the laterite species used in this study. Similar improvements in recoveries, however, area so achieved in the saprolite when reducing conditions are introduced prior to the dehydroxylation of the mineral phase [3]. Zhu et al [4] upgraded low-nickel content laterite ores using selective reduction with reduction agent is coal, followed by magnetic separation. These previous works investigated that coal-based reduction followed by magnetic separation is effective for the recovery of nickel and iron from nickel laterite ores. The reaction mechanism of the selective reduction of nickel laterite ore has also been characterized recently. A number of researchers suggested that the selectivity of reduction depends mainly on the reduction atmosphere and silica level; the presence of sulfur significantly promotes ferronickel particle growth to improve nickel enrichment in the metallic phases [1]. However, another researcher reported that the reduction with coal of ferrous minerals in the presence of Na$_2$SO$_4$ was not showed by the formation of fayalite or forsterite, whereas the decrease of iron metallization was exhibited to the formation of troilite (FeS) [5]. In their research, Jiang et al revealed a ferronickel
concentrate with a nickel grade about of 9.52% and a recovery of 84.04 % from high iron grade laterite ore using selective reduction and magnetic separation role, with the addition of 7% Na$_2$SO$_4$ at 1200°C for 50 min. Therefore, it is necessary to analyze the mechanisms of coal-based reduction of nickel laterite ore. In this study, the reduction roasting of low-grade nickel laterite ore was performed using coal-based reduction with sulfur addition and uses lignite as reducing agents. The effects of roasting reduction temperature on the growth of metallic particles were characterized. Moreover, the reduction mechanisms of nickel were investigated based on the properties of the crystal structure of the nickel laterite ore and the reduction route. The present study aims to provide a basis for the utilization of nickel laterite ores.

2. Experimental method

2.1. Material
A low-grade nickel laterite ores from Sulawesi island, Indonesia, was selected as the raw material for experiment. The chemical composition of the nickel laterite ores is presented in Table 1, which shows the nickel content in the nickel laterite ores is 1.71 %. Another material exists in the laterites ores are iron oxide, cobalt oxide, magnesium oxide, chrome oxide, manganese oxide, silicate, and alumina.

Table 1. Chemical formulation of nickel laterite ore (mass fraction, %)

<table>
<thead>
<tr>
<th>Ni total</th>
<th>Fe$_2$O$_3$</th>
<th>Co$_2$O$_3$</th>
<th>MgO</th>
<th>Cr$_2$O$_3$</th>
<th>MnO$_2$</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>LOI</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.71</td>
<td>27.04</td>
<td>0.08</td>
<td>13.40</td>
<td>0.19</td>
<td>0.68</td>
<td>24.64</td>
<td>1.93</td>
<td>17.21</td>
<td>12.65</td>
</tr>
</tbody>
</table>

The sub-bituminous coal as reducing agents from Kalimantan province, Indonesia. The proximate analysis of the sub-bituminous coal is presented in Table 2. The coal is classified as a medium quality coal because of its medium fixed carbon content and low ash, volatile matter, and relatively low harmful element (S, P) content.

Table 2. Proximate analysis of sub-bituminous coal (mass fraction, %)

<table>
<thead>
<tr>
<th>Reducing agents</th>
<th>VM (%)</th>
<th>Ash (%)</th>
<th>Fixed Carbon (%)</th>
<th>S (%)</th>
<th>Moisture (%)</th>
<th>CV (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sub-bituminous</td>
<td>36.26</td>
<td>14.39</td>
<td>36.92</td>
<td>0.91</td>
<td>14.4</td>
<td>25.32</td>
</tr>
</tbody>
</table>

2.2. Carbothermic reduction and magnetic separation test
The experiment to increase a nickel content in concentrates were carried out according to the following steps i.e. pelletizing step, reduction roasting step of nickel laterite pellet and magnetic separation step. At pelletizing step, nickel laterite ores were first dried at 100 °C in the oven for 24 hours. The dried ores were mixed with a certainties amount of coal (13% weight), and they were grounded in the ball mill. The fine particle of mixed nickel laterite coal was pelletized in the pelletizer to produce nickel laterite pellets. The amount of sub-bituminous coal was added as reduction agent are 2 times (13% weight) of the stoichiometry calculations (~6.5% weight).

At the reduction step, 200 grams of laterite pellets samples were put in a ceramic crucible, and it was heated with a heating rate 10 °C/min, until certainty desired temperature was achieved, after that, the pellet samples were kept heated at a desired temperature for 1 hours in the furnace. Once the reduction experiments were finished, the samples were taken out of from the furnace and cooled to room temperature by water quenching. The quenched materials were mixed with water and passed to the wet magnetic separator to separate nickel concentrates from the tailing. The nickel and iron content
in the concentrates were analyzed with atomic Absorption spectrophotometers (AAS), their phases were analyzed with X-ray diffraction method (XRD 7000 Shimadzu), and to investigate the microstructures of reduced nickel laterite materials, those reduced nickel laterite pellets were analyzed by Scanning Electron Microscope (SEM JSM 6390A), in which the qualitative and mapping analysis were carried out by energy dispersive spectrometry (EDS) on an X-ray spectrometer combined with a SEM.

The Nickel and iron recovery in the concentrates were calculated by the following equations:

\[
\text{Ni Recovery} = \frac{\text{weight of Ni at concentrate}}{\text{weight of Ni at reduced pellet}} \times 100\% 
\]

(1)

\[
\text{Fe Recovery} = \frac{\text{weight of Fe at concentrate}}{\text{weight of Fe at reduced pellet}} \times 100\% 
\]

(2)

And the nickel and iron grade in the concentrate were calculated by the following equations:

\[
\text{Ni Grade} = \frac{\text{weight of Ni at concentrate}}{\text{weight of concentrate}} \times 100\% 
\]

(3)

\[
\text{Fe Grade} = \frac{\text{weight of Fe at concentrate}}{\text{weight of concentrate}} \times 100\% 
\]

(4)

3. Results

3.1. X-Ray Diffraction test result of nickel laterite ores

Figure 1 shows the X-ray diffraction pattern of nickel laterite ores. The crystalline phases of the raw nickel laterite ore mainly consisted of lizardite \([(\text{Mg,Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4]\), Talc \([\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]\), antigorite \([(\text{Mg,Al})_3(\text{Si,Al})_2\text{O}_5(\text{OH})_4]\), goethite \([\text{FeO.OH}]\), quartz \([\text{SiO}_2]\), and hematite \([\text{Fe}_2\text{O}_3]\).

![Figure 1. XRD pattern of nickel laterite ore (T: Tale, A:Antigorite, L:Lizardite, Q:Quartz, G:Goethite, H:Hematite)](image-url)
3.2. Thermal properties of nickel laterites ores and carbothermic reduction with DTA-TG

In order to investigate the thermal properties of nickel laterites ores, a nickel laterites samples were analyzed by using Differential Thermal Analyzer (DTA). The result of DTA-TG analysis of nickel laterite ores is presented in Figure 2, which shows four steps of the weight loss process. First, the endothermic peak at 78.80 °C on the DTA curve, is attributed to the vaporization of free water. Second, an endothermic effect appears in 293.7 °C on the DTA curve, is attributed to the dehydroxylation of goethite and the desorption of crystalline water. Third, the endothermic peak center at 638.0 °C is caused by the dehydroxylation of lizardite or serpentine group minerals as clinochrysotile and antigorite. Finally, the exothermic peak at 828 °C does not have any associated mass loss resulting from there crystallization of forsterite.

![Figure 2. DTA-TG curves of the studied laterite ore (Heating rate 10 °C/min, atmosphere 20% CO₂)](image)

In order to characterize the thermal properties of nickel laterites ores reduced by coal, a nickel laterites samples were analyzed by using Differential thermal Analyzer (DTA) as shown in Figure 3. Thermal events that occur when nickel laterite reduced the use of coal can be predicted using a DTA-TG. Approximately 20 mg sample of laterite ore is mixed with 20% of coal is then heated in a chamber DTA-TG with a heating rate of 10°C/min into 20% CO₂ atmosphere. Based on the results shown in Figure 3, ore will undergo three endothermic reactions [6], namely;

1. At a temperature of 76.5 °C water began evaporation moisture / moisture
2. At a temperature of 344.9 °C FeO.H₂O goethite dehydroxylation reaction occurs;
3. At a temperature of 624.8 °C occurred dehydroxylation reaction carrier magnesium silicate mineral compound into magnesium silicate hydrate;

While the exothermic reaction will undergo two reactions [6], namely;

1. At a temperature of 305 °C which is the burning of coal;
2. At a temperature of 820.4 °C associated with the crystallization of magnesium silicate into forsterite 2MgO. SiO₂.

At a temperature of 624.8 °C nickel mineral carrier began to damage of structure so that a transition temperature that can be used for the benefit of the reduction to nickel and iron[7]. Due to the conditions of the transition will be water evaporation magnesium silicate hydrate crystals by way of release of the crystal lattice. At the time of the release of the structure will be open to possible contact
with surrounding conditions. The temperature of 820.4 °C is the crystallization of forsterite phase. At this temperature, phase is crystalline forsterite will be having a meeting and regular structure. In this condition everything was trapped in the crystal will be relatively inert to external influences. Similarly, if the element nickel or iron cannot be disassociated from this phase, it will be difficult to have suffered further treatment [8,9].

![Figure 3. DTG–DTA curves of the studied laterite ore with 13% coal. (heating rate 10°C/min, atmosphere 20% CO₂)](image)

3.3. The effect of temperature on nickel–iron grade in the nickel concentrates

In order to investigate the effect of reduction roasting temperatures to the nickel and iron content in the nickel concentrates, the nickel laterite pellets which containing 13 % sub-bituminous coal were roasted at temperatures 800, 900, 1000, and 1100 °C. The nickel and Iron grade which represents the nickel and iron content in the concentrate were determined by using AAS. Their results are presented in Figure 4. This figure shows that the nickel and iron grade in the concentrate increased when the reduction roasting temperatures were increased from 800 °C to 1100 °C. In the case of nickel recovery at concentrates, when the reduction roasting temperature was increased from 800 °C to 1000 °C, the nickel recovery increased, and it decreased when the reduction temperature was increased from 1000 °C to 1100 °C. The same tendencies are also found for iron recovery; it increased when the reduction temperature was increased from 800 °C to 1000 °C, and it decreased when the reduction temperature was increased from 1000 °C to 1100 °C. From this result, it is known that maximum recovery both for iron and nickel occurs at 1000 °C. The maximum grade percentages for Fe occur at 1000 °C and for Ni at 1100 °C. These results are in good agreement with the result of Zhu et al [1] which conducted an experiment for upgrading low nickel content laterite ores using selective reduction followed by magnetic separation. Their result of the experiment shows that the increase in temperature improved the degree of metallization of Ni and Fe. However, in the case of Fe recovery, when the reduction roasting temperature was increased from 1000 °C to 1100 °C, Fe recovery decreased due to the formation of fayalite is more dominant than the formation of metallic iron from wustite.
Figure 4. The effect of the reduction temperature on nickel beneficiation (a) and iron beneficiation (b).
(reduction with sub-bituminous coal 13% weight)

3.4. X-Ray diffraction of reduced pellet
To determine the phases that form the calcine is cooled quickly with water, dried and then using magnetic separation performed manually and analyzed using XRD well to concentrate, tailings and ore early (Figure 5). The main compounds in the initial sample, namely; lizardite, goethite, and quartz, concentrates consisting of forsterite, quartz and taenite (FeNi), while in the tailings is dominated by quartz, forsterite and hematite.

Figure 5. XRD graph sample concentrates, tailings and laterite (T = 1000 °C) (Q; quartz, F: forsterite, T; taenite, G: goethite, H: hematite, L; lizardite)

The main types of minerals contained in the ore are lizardite a compound of magnesium silicate hydrate. Another mineral contained quartz and goethite. After reduction and then separated magnetically, the concentrate contained tainite (FeNi) and forsterite phase that still brought when using magnetic separation. Goethite in ore will be transformed into hematite and will be integral as tailings.
3.5. Morphology of reduced pellets
To determine the morphology of the sample surface elemental mapping analysis using SEM-EDX of calcine after magnetic separation.

Figure 6. Elemental mapping of tailing

Figure 6 is a mapping of samples of concentrate. Based on these images, there are two groups of elements of nickel metal and iron came together to form a ferronickel, and a collection consisting of the elements Mg, Si and O which may compound forsterite or olivine mixed with fayalite. The size of a nickel metal look is still below 10 µm.
Figure 7. Elemental mapping of concentrate

Figure 7 shows an image of the tailings sample mapping; nickel metal found only a small point in the sense of a lower concentration of nickel concentrate. Set of elements consisting of elements Fe and oxygen with the possibility of iron oxide, and the other is a collection of Mg, Si and O form forsterite. The reduction reaction of nickel oxide with carbon in a reaction carbothermic can be estimated as follows:

\[
\text{NiO} + \text{C} \rightarrow \text{Ni} + \text{CO} \quad (5)
\]

\[
2\text{NiO} + \text{C} \rightarrow 2\text{Ni} + \text{CO}_2 \quad (6)
\]

The existence of CO and CO\(_2\) is an equilibrium reaction following the Boudouard and equilibrium CO at atmospheric pressure. Both CO and CO\(_2\) are at a position of equilibrium when the reduction is run under 1000 °C. But at temperatures above 1000 °C in the C-CO-CO\(_2\) almost all in a state of CO so that the reduction reaction of nickel follow the following equations of reaction.

\[
\text{NiO} + \text{CO} \rightarrow \text{Ni} + \text{CO}_2 \quad (7)
\]

\[
\text{CO}_2 + \text{C} \rightarrow 2\text{CO} \quad (8)
\]

\[
\text{NiO} + \text{C} \rightarrow \text{CO} \quad (9)
\]

When plotted standard energy from reactions with a temperature above then it will look like in Figure 7.
It appears that at standard atmospheric pressure state nickel oxide will readily reduce. A temperature of 430 °C is the minimum temperature reduction to metallic nickel.

4. Conclusion
The rise in temperature increases the degree of reduction of Fe and Ni metal. In specific circumstances, the reducibility of Ni decreases due to the formation of forsterite which protects the nickel ions from further reduction. At the low-temperature reduction (<1000 °C) carbothermic reduction with sub-bituminous coal as reductant produce an increasing grade of ore from 1.7% to 5%.

5. References