Effects of reduction time on carbothermic reduction of lateritic nickel ore using palm kernel shell as green reducing agent

Dwipuji Rahayu¹, Ahmad Maksum¹, ² and Johny Wahyuadi Soedarsono¹, ³

¹Center of Minerals Processing and Corrosion Research, Department of Metallurgical and Materials Engineering, Universitas Indonesia, Depok 16424, Indonesia
²Department of Mechanical Engineering, Politeknik Negeri Jakarta, Depok 16425, Indonesia
Email: jwsono@metal.ui.ac.id

Abstract. Lateritic nickel ore is one of the biggest mineral resources in Indonesia. This ore has a huge potential, i.e., economic value for processing and purification, however requires high energy in the separating of mineral and gangue minerals, in addition the production cost is also high. Therefore, to resolve the problems, a pre-reduction stage called carbothermic reduction process is carried out. Carbothermic reduction process is usually used for saprolite-type lateritic nickel ore which needs a reductor for the reduction reaction to produce pure nickel. Common reductors used are coal and cokes. In this study, a development on carbothermic reduction of saprolite, type of lateritic nickel ore using biomass reductor palm kernel shell, is proposed. The lateritic nickel ore is obtained from East Halmahera and the palm kernel shells are obtained from the waste of palm oil plantation at Palangkaraya, Central Kalimantan. The purpose of this study is to find out the effect of reduction time variation on carbothermic reduction result of lateritic nickel ore with constant temperature and mass ratio value. Reduction time variation used in this study was 1, 2, 3, and 4 hours. All samples were tested at 800°C with the mass ratio of 1:4 (lateritic nickel ore : palm kernel shell) which were put into a crucible and then the carbothermic reduction process was done in a melting furnace. Peak formed on the XRD pattern showed that the process was able to reduce hematite or magnetite to wustite within one hour. XRF and recovery calculation results showed that the reduction time of one hour is the optimum time because nickel oxide (NiO) content was the highest i.e. 2.68% compared to other time variation.

1. Introduction
Nickel lateritic ore deposits are commonly found in tropical regions such as Indonesia, particularly in Pomalaa (Southeast Sulawesi) and Halmahera (North Maluku). Lateritic nickel is divided into two types of ore i.e., saprolite and limonite. The major mineral constituents of the limonite layer are geothite [FeO(OH)] and hematite (Fe₂O₃), while the saprolite layer is composed by serpentine minerals [(Ni,Mg)SiO₃.nH₂O] [1]. Most of the lateritic nickel ore deposits in Indonesia have not been optimally processed due to several difficulties in the processing of lateritic nickel ore. One of the problems is the high energy usage in the mineral separation process or gangue minerals at recovery
process [2]. Nowadays, pyrometallurgy process is still used for saprolite nickel ore because saprolite is generally more heterogeneous in terms of its chemical composition and mineralogy. However, this process requires high amount energy and produce air pollution due to the use of coal and cokes as reducing agent.

Considering the environmental problems generated from the pyrometallurgical process, a new technology innovation has been developed to reduce nickel ore by using biomass energy or waste from natural resources. Utilization of waste has begun developing further as a major alternative to replace coal as the reductor of nickel ore [3–5]. Biomass can be converted to fuel as reductor through pyrolysis and gasification processes. The process of pyrolysis and gasification will produce reducing gases such as carbon monoxide (CO), hydrogen (H$_2$), carbon dioxide (CO$_2$), methane (CH$_4$), and other hydrocarbons gas. Gas produced in the form of CO and H$_2$ served as the reducing agents [6]. Palm kernel shell is studied to be a reductor of low grade iron ore because its C, H, O element contents; low ash content; high calorific value and high amount of fixed carbon [7]. In addition, this research will study the effect of reduction time variation on carbothermic reduction of saprolite lateritic nickel ore using palm kernel shell as a reductor.

2. Materials and method

2.1. Materials

The lateritic nickel ore used in this study is initially characterized by XRD testing. Figure 1 presents the results of XRD testing of lateritic nickel ore.

![Figure 1. XRD pattern of initial lateritic nickel ore.](image)

Proximate and ultimate analysis tests, as shown in table 1, have been done on the palm kernel shell is used as the reductor in this research.

2.2. Experiment

The lateritic nickel ore sample which has been prepared to form fine powder (#270) and mixed with palm kernel shell was inserted into crucible in a melting furnace. The process of lateritic nickel ore
reduction was done in variation of increasing reduction time, respectively 1, 2, 3, and 4 hours. When the carbothermic reduction occured, only the reduction time variables were changed, while the temperature and mass ratio was set at a fixed value; 800°C with a mass ratio of 1 : 4 (lateritic nickel ore : palm kernel shell). Carbothermic reduction process took place in the melting furnace.

Table 1. Proximate and Ultimate Analysis of palm kernel shells.

| Parameter                  | Content (% adb) |
|----------------------------|-----------------|
| **Proximate Analysis**     |                 |
| Moisture in air dried sample | 3.70            |
| Ash                        | 2.09            |
| Volatile Matter            | 74.04           |
| Fixed Carbon               | 20.17           |
| **Ultimate Analysis**      |                 |
| Carbon                     | 49.90           |
| Hydrogen                   | 6.00            |
| Nitrogen                   | 0.28            |
| Oxygen                     | 41.66           |

After the carbothermic reduction process, XRD and XRF tests are performed to analyze possible formed phase and to find out the amount of compounds like oxides or other elements contained in the reduced lateritic nickel ore.

3. Result and discussion

Figure 2 shows the XRD test result comparison of samples after carbothermic reduction at all reduction time variation. It could be seen that during the process of carbothermic reduction with reduction time variation, there was no significant change in the phase formed; the only difference was the amount of the peak number of certain phase that increased or decreased.

![Figure 2](image-url)
In the initial sample of lateritic nickel ore shown in figure 1, there are peaks that identified as lizardite, kaolinite, geothite and quartz phases. After one hour of reduction, the result showed the formation of quartz (SiO₂), wustite (FeO), forsterite (Mg₂SiO₄), and Ni-olivine (Ni₂SiO₄). Peak phases present in the initial sample such as lizardite, geothite and kaolinite phases is no longer formed because it has been dehydroxylated to form new phases described in equation (3.1) to (3.8). The dehydroxylated goethite phase formed the hematite phase (Fe₂O₃), then the hematite was reduced entirely as it reacted with the reductor to form magnetite (Fe₃O₄) which would be reduced to wustite (FeO) [8].

In equation (3.4), the dehydroxylated lizardite phase formed ferrous forsterite phase [(Mg₂Fe₃)₂SiO₄] at the temperature of 700°C and clinoenstatite phase (MgSiO₃). As the reduction temperature increased to 800°C, the ferrous forsterite turned into forsterite [9]. The absence of clinoenstatite phase possibly because it has reacted with MgO to form forsterite phase, increasing the forsterite phase amount after one hour reduction time.

Additionally, there was also an identified Ni-olivine phase shown in equation (3.8). The phase was formed by dehydroxylation of serpentine (Ni,Fe,Mg)₂SiO₅(OH)₅ during the reduction process which formed the olivine phase (Mg₂Fe₂Ni)₂SiO₄ [10]. The nickel cations might be substituted into magnesium cations (because of similar atomic radius, 0.068 and 0.065 nm) and replaced the magnesium sites presented in the olivine crystals, causing the formation of Ni-olivine. However, Ni-olivine was a phase that was difficult to reduce because the elements present in olivine such as Ni, Mg and Fe were covered by other non-reactive minerals that prevents further reduction of both nickel and iron oxide.

\[
2\alpha - FeO(OH) \rightarrow \alpha Fe₂O₃ + H₂O \quad (3.1)
\]
\[
3Fe₂O₃ + CO \rightarrow 2Fe₃O₄ + CO₂ \quad (3.2)
\]
\[
Fe₃O₄ + CO \rightarrow 3FeO + CO₂ \quad (3.3)
\]
\[
[(Mg,Fe)]₃Si₂O₅(OH)₄ \rightarrow [(Mg,Fe)]₂SiO₄ + MgSiO₃ + H₂O \quad (3.4)
\]
\[
[(Mg,Fe)]₂SiO₄ \rightarrow Mg₂SiO₄ \quad (3.5)
\]
\[
MgSiO₃ + MgO \rightarrow Mg₂SiO₄ \quad (3.6)
\]
\[
Al₂Si₂O₅(OH)₄ \rightarrow Al₂Si₂O₅ + H₂O \quad (3.7)
\]
\[
(Ni,Fe,Mg)₂Si₂O₅(OH)₅ \rightarrow 2(Ni,Fe,Mg)₂SiO₄ + 4H₂O + SiO₂ \quad (3.8)
\]

Meanwhile, the quartz phase remained after one hour of reduction process. Quartz phase was not able to be reduced at the temperature of 800°C because quartz required temperature above 1000°C to change phase.

The phases formed in the reduction time variation of 2 to 4 hour were similar to the one-hour reduction time such as quartz, wustite, forsterite, and Ni-olivine. At the reduction time of 4 hours, the number of wustite peak, forsterite and Ni-olivine phase peak were the highest compared to other reduction times. Forsterite formation caused Ni to be stable or inert at the reduction of saprolite nickel ore and the role of sulfur was very important to limit the formation of the forsterite phase here [11]. In addition, the formation of forsterite allowed the closure of the oxide to grain and to inhibit the development of further reduction of nickel and iron. Due to the increasing number of forsterite phases, wustite became difficult to reduce to Fe metallic on the variation of reduction time. This was probably because of the longer reduction time used, the amount of carbon used to reduce was decreasing.

Based on the XRF test results, as carbothermic reduction time increased, the element or compound content in the sample did not change significantly or remains constant. After 1 hour of carbothermic reduction process, the NiO content increased from 2.662% to 2.68%.
The result showed that decreasing percentage of NiO after 2, 3 and 4 hours during experiment. This condition was reported by Zhu et al.[18] in his research which states that as the reduction time increases, the nickel content obtained will increase until it reaches the optimum point. If the reduction time exceeds the optimum point, it will result in a decreasing of nickel content which corresponds to the increasing Fe content in the lateritic nickel sample. In addition, a decrease in nickel content might occur because the reductor used was decreasing due to an increase in CO$_2$ gas concentration which caused the gas-solid reaction limit to be filled by CO$_2$ gas and might inhibit the progress of the reduction reaction [12].

The carbothermic reduction process using the palm kernel shell as reductor results then studied further to find out how much % recovery of Ni in concentrate at each time variation, as shown in figure 3.

| Sample          | NiO (%) | Fe$_2$O$_3$ (%) |
|-----------------|---------|-----------------|
| Initial Sample  | 2.662   | 15.82           |
| 1 hour Roasting | 2.680   | 15.90           |
| 2 hours Roasting| 2.392   | 15.51           |
| 3 hours Roasting| 2.417   | 15.63           |
| 4 hours Roasting| 2.518   | 16.33           |

Figure 3 showed that the highest recovery percentage of nickel is obtained after 1 hour reduction time. Therefore, 1 hour of reduction with 74.7% recovery, which is the highest % recovery of Ni among other reduction time variations, was already able to reduce the nickel. So, it did not require a longer reduction time than 1 hour to reduce the lateritic nickel ore used in this study.

In this study, the palm kernel shell has been able to reduce hematite or magnetite to wustite. However, wustite required more CO gas to be reduced to Fe metallic. This was possible because the reducing gas has not reached the maximum value to be able to reduce the wustite. Therefore, the resulting reduction result in this study was limited to form wustite. In addition, there was no identification of the NiO peak phase in the sample characterization results using XRD. This was because NiO in lateritic nickel ore is a type of mineral complex (silicate-bearing) that has a tendency to bind to form Ni-olivine making it more difficult to reduce.

4. Conclusion
The study on effects of reduction time on carbothermic reduction of lateritic nickel ore using palm kernel shell as green reducing agent yields results that can be concluded as follows:

a. Palm kernel shell can be used as reductor as an alternative replacements of coal or coke with the fixed carbon amount of 20.17%.

b. The XRD test results revealed that in the reduced lateritic nickel ore at reduction time variation of 1 hour, 2 hours, 3 hours, and 4 hours, NiO reduction process to Ni didn’t occur because the ore classified as complex minerals type (silicate-bearing), so Ni is difficult to reduce. However, 1 hour reduction time can reduce hematite or magnetite to wustite.

c. XRF test results revealed that in the variation reduction time of 1 hour there was an increasing of nickel oxide composition (NiO) from 2.662% to 2.68%.

d. The highest % recovery of Ni in laterite nickel ore was 74.7%, obtained at 1 hour reduction time. Thus, 1 hour reduction time is enough to reduce laterite nickel ore with palm kernel shell as reductor without requiring longer reduction time.

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