Effect of addition elemental Sulfur as additive in the selective reduction process of limonite nickel ore with the presents of sodium sulfate

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Abstract. High temperatures in the smelting nickel ore increases the energy costs. The use of sulphur or sulphate as additives can optimize the reduction process at low temperatures through the formation of FeS compound. Biomass waste, which is palm shell charcoal, has potential as a reducing agent in the process of reducing laterite nickel ore because it has a fixed carbon value and a high heating value, besides that palm shell charcoal waste is more abundant as Indonesia’s palm oil industry develops. This research was carried out to investigate the effect of addition elemental sulphur as additives and palm shell charcoal as reducing agent in the selective reduction process of limonite nickel ore. This research used limonite ore with 1.38% Ni and 38.2% Fe content. The reduction of nickel ore was conducted at a reduction in temperature variations (950°C, 1050°C, 1150°C) with the presents of 10 wt.% additive sodium sulfate (Na₂SO₄) and addition 0%, 2.68% and 5% of elemental sulphur. The amount of reducing agent was stoichiometric variations (0.5, 1.0, 1.5). This research shows that the reduction process with 0% sulphur addition produced the most optimal grade and nickel recovery.

Keywords: palm shell charcoal, biomass, sulphur, selective reduction, sodium sulphate, limonite ore

1. Introduction
Nickel has many influences on industrial and commercial applications. It is use in the production of stainless steels, alloy steels, non-ferrous alloys and many other things [1]. In terms of nickel resources in the earth, more laterite nickel ore is found than nickel sulfide ore. Laterite nickel ore has the following susceptible composition of 10–40% Fe; 0.8–3.5% Ni; 1–2% Cr and 0.1–0.2% Co. It can be seen that about 60% - 70% of the nickel ore in the earth is laterite nickel ore [2].

Indonesia is one of the countries in the world that has sufficient laterite nickel ore reserves. Thus, it makes the refining process on laterite nickel ore is one of the interesting things to research. The use of energy on the refining process still one of the problem. The Blast Furnace (BF)
process is a comprehensive smelting technology in ferronickel production from lateritic nickel ore, but the high production costs are a consideration because the working temperature used only reaches at 1150°C [3]. The use of reducing agents that are not environmentally friendly also one of the problem in the refining process.

Selective reduction process, according to some research can reduce production costs because it can be reaches at low working temperatures [4]. Addition some additives which is sodium sulfate is needed to the process because it can be promoting the low-melting phase structure [5]. Reducing agents such as anthracite coal can be replaced with palm shell charcoal because it has a higher fixed carbon and heating value than other biomass reducing agent [6]. The use of elemental sulfur also could lower the reduction temperature process by low temperature-liquid phase formation. Therefore, it is necessary to study the effect addition elemental sulfur and palm shell charcoal as reducing agent in the selective reduction process.

2. Material and method

This research used nickel laterite ore from South East Sulawesi, Indonesia. The X-ray fluorescence (XRF) was performed to determine the nickel ore’s chemical compositions (Table 1). This study used palm shell charcoal as a reducing agent with a variety of stoichiometries, i.e. 0.5; 1.0; 1.5. The 10 wt. % of sodium sulfate (Na₂SO₄) and 0%, 2.68% and 5% of elemental sulfur was used as an additive. The additives, various amounts of palm shell charcoal, and 50 grams of limonite nickel ore were crushed into –100 mesh before mixing and agglomerating. The pelletizing process is conducted manually with diameters ranging from 10–15 mm. Then, it dried at 120°C for four hours to remove the moisture. The reduction process is carried out with various temperatures at 950°C; 1050°C; 1150°C for 60 minutes, then quenched using water and dried again at 120°C for four hours to remove the water content. After that, the reduced pellets were ground by using a shaker mill into the –200 mesh and continued with the wet magnetic separation process for separating concentrate (ferronickel) from tailing (impurities). The concentrate was tested by X-Ray Fluorescence (XRF) to observe the composition of nickel and iron. The X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) testings are carried out on reduced ore for studying the phase transformation and ferronickel particle growth, respectively.

| Element | Ni  | Fe  | SiO₂ | Al₂O₃ | CaO | MgO |
|---------|-----|-----|------|-------|-----|-----|
| wt.%    | 1.38| 38.2| 10.12| 5.30  | 0.13| 1.46|

3. Effect of temperature on reduction of laterite nickel ore

Figure 1a shows the nickel and iron grade resulting from the selective reduction process of nickel ore by using palm shell charcoal 0.5 stoichiometry with variations of reduction temperature which were 950°C, 1050°C, and 1150°C also without addition of elemental sulfur (0%S). The nickel grade increases with the increasing reduction of temperature from 950 °C to 1150 °C. The optimum nickel grade was found at a reduction temperature of 1150°C that contains 2.852% Ni. Similarly, the iron grade increases from temperature from 950 °C to 1050 °C. The highest grade of iron was found at a reduction temperature of 1050 °C that contains 82.654%.

It can be seen in Figure 1b, the recovery of nickel shows increasing with increasing temperature from 950°C to 1050°C. The optimum recovery nickel is found at a reduction temperature of 1050 °C, which is 75.05%. Nevertheless, iron recovery decreases with the increasing temperature from 1050 °C to 1150 °C. It is because at a reduction temperature of 1050 °C, which is above the eutectic temperature of Fe-FeS (988 °C), the FeO reacted with S to form FeS.
causes a decrease in the percentage of iron recovery. Nevertheless, at higher temperatures, the rate of iron reduction increases [7].

![Figure 1. Effect of temperature on stoichiometry 0.5 without addition elemental sulfur and addition of Na$_2$SO$_4$ by 10 wt.\%: a) grade, b) recovery of Ni and Fe](image)

From XRD analysis, as shown in Figure 2, the formation wuestite compounds (FeO) is dominated observed at a temperature of 950°C than ferronickel (FeNi) or FeS. At temperatures of 1050°C and 1150°C, most peaks are still dominated by magnesioferrite compounds (Fe$_2$MgO$_4$) and followed by the reformation of ferronickel compounds (FeNi) and FeS.

At 950°C, wuestite compounds still dominated and the formation of ferronickel and FeS has not been yet formed too much because it still forms as spinel compounds which were reduced from goethite also the reduction temperatures were still below the eutectic temperature of Fe-FeS (985°C) [6]. At 1050°C ferronickel compounds peaks high enough than other compounds. The decomposition of sodium sulfate generates Na$_2$S compounds, which react with FeO and SiO2 to form FeS and Na$_2$Si$_2$O$_5$ which prevent the metallization of Fe$^{2+}$ [8].

![Figure 2. Effect of variations temperature on phase change in 0.5 stoichiometry reducing agent using a selective reduction method with the addition of Na$_2$SO$_4$ by 10% weight of ore without addition elemental sulfur.](image)
From Optical Microscope (OM) results as shown in Figure 3, the white (bright) grains, which are ferronickel, becoming larger as an increase in temperature from 950°C to 1150°C and also indicates the increasing of FeNi content. At the temperature of 950°C the white (bright) grains are still scattered and quite small in size. Furthermore, after an increase in temperature to 1050°C the grains slowly began to fuse with another one. Then, white (bright) grains become larger at 1150°C. The higher reduction temperature can accelerate the growth of ferronickel grains as shown in Figure 4.

![Figure 3. OM results of selective reduction samples using palm shell charcoal at 0.5 stoichiometry with the addition of Na₂SO₄ by 10% weight of ore without addition elemental sulfur at temperature: a) 950°C, b) 1050°C, c) 1150°C.](image)

![Figure 4. Average size of ferronickel grains after reduction with temperatures 950°C, 1050°C and 1150°C](image)
4. Effect of the amount of reducing agent used based on stoichiometry

In this section, the effect of the reducing agent variations on stoichiometry calculations, which is 0.5; 1.0 and 1.5 of stoichiometry. The reducing agent used was palm shell charcoal without addition sulfur (0 %S). The reduction process was carried out at 1150˚C for 60 minutes. Figure 5 is shown in the form of a comparison graph between the nickel and iron grade also recovery with the variations of stoichiometry from the reducing agent.

**Figure 5.** Effect of amount reducing agent with variations stoichiometry without addition elemental sulfur and addition of Na₂SO₄ by 10 wt.% at temperatures 1150˚C: a) grade, b) recovery of Ni and Fe

Figure 5a shows the nickel grade is decreased along with the addition of 0.5 to 1 stoichiometry reducing agent. The optimum nickel grade is found at 0.5 stoichiometry of reducing agent, which is 2.852%. Otherwise, the iron grade increases with the addition of reducing agent. The highest iron grade is found in 1.5 of stoichiometry reducing agent, which is 83.559%. The effect of addition of reducing agent increased the activity of the metallization of iron, thus increasing the iron grade. Nevertheless, it lowers the nickel grade.

**Figure 6.** Effect of variations stoichiometry reducing agent using a selective reduction method with the addition of Na₂SO₄ by 10% weight of ore without addition elemental sulfur at temperatures 1150˚C.
Figure 5b shows the recovery of nickel is decreased along with the addition of 0.5 to 1 stoichiometry reducing agent. The optimum recovery is found at 0.5 stoichiometry of reducing agent, which is 73.51%. The recovery of iron also decreased along with the addition of 0.5 to 1 stoichiometry reducing agent. The highest iron recovery is found at 0.5 stoichiometry, which is 52.67%. Thus, an estimation of stoichiometry 0.5 is the most optimum ratio of carbon-based on XRF results in Figure 5a and Figure 5b.

Figure 6 shows the XRD analysis on the stoichiometry of 0.5, 1.0, 1.5 of palm shell charcoal, most of the peaks shows the formation of magnesioferrite compounds (Fe$_2$MgO$_4$) followed by the reformation of quartz also ferronickel (FeNi), and FeS. Figure 6 shows the highest peak on ferronickel is found in 0.5 stoichiometry of reducing agent. The ferronickel peak getting lower along with the addition of 0.5 to 1.5 stoichiometry reducing agent. The palm shell charcoal has a high silicate content [8]. Therefore, with the increasing stoichiometry reducing agent of the palm shell charcoal, the silicate content in the reduction process results also increases [9]. Silicate acts as an impurity in the reduction process which can inhibit the optimization of the reduction process.

Based on Figure 7, the results Optical Microscope (OM) show the images at 0.5; 0.5 and 1.5 of stoichiometry reductor. The white (bright) grains, which are ferronickel, becoming smaller as an increases in stoichiometry from 0.5 to 1 shown in figure 8, whereas dark ones indicate impurity. The increasing metallization of iron should be avoided in the selective reduction process due to the fact that it will reduce the nickel grade of ferronickel [3].

![Figure 7](image-url)
5. Effect of addition elemental sulfur on the reduction process of laterite nickel ore

Based on Figure 9, the highest nickel grade found in the 2.68% and nickel recovery in the 0%. However, during the addition of elemental sulfur from 2.68% to 5%, the dominant nickel and iron grade decreases. According to the study of Zhu et al. (2012) [2], addition of sulfur in large quantities will form a liquid phase that is very rich in sulfur (FeS-matte and NiS) so that it will reduce the levels of nickel and iron in the concentrate. Based on XRD analysis in Figure 10, the peak formation of ferronickel compounds is higher at 0% than 2.68% and 5% of sulfur. Most of the peaks shows the formation of magnesioferrite compounds (Fe$_2$MgO$_4$) followed by the reformation of quartz also ferronickel (FeNi), and FeS.

![Figure 8](image_url)

**Figure 8.** Average size of ferronickel grains after reduction with stoichiometry 0.5, 1 and 1.5

![Figure 9](image_url)

**Figure 9.** Effect of addition elemental sulfur with addition of Na$_2$SO$_4$ by 10 wt.% at temperatures 1150°C and 0.5 stoichiometry: a) grade, b) recovery of Ni and Fe.
Figure 10. Effect of variations sulfur using a selective reduction method with the addition of Na$_2$SO$_4$ by 10% weight of ore at temperatures 1150°C and 0.5 stoichiometry.

Figure 11. SEM results of selective reduction samples at temperatures 1150°C with the addition of Na$_2$SO$_4$ by 10% weight of ore with 0.5 stoichiometry and variations of sulphur: a) 2.68%, b) 5%.

Figure 12. SEM-EDAX results of selective reduction samples using palm shell charcoal 0.5 stoichiometry also the addition of Na$_2$SO$_4$ by 10% weight of ore at temperature 1150°C with variations of sulfur: a) 2.68%, b) 5%.
Figure 11 and Figure 12 show the SEM also EDAX analysis. It can be observed that white areas indicate the ferronickel compounds. Gray areas indicate iron sulfide (FeS) compounds, and dark areas indicate impurities (Na-Mg-Si-O), which can be silica, magnesium oxide, and others. The low melting phase can encourage the mass transfer of iron and nickel. Otherwise, sulfur appears toward the surface of the ferronickel alloy, which reduces the surface tension on the grains [10]. It reacted with iron to form FeS which could reduce the metallization of iron.

6. Conclusion
In this selective reduction process, the optimum reduction temperature was 1150°C at 0.5 stoichiometry without addition sulfur with a nickel grade and recovery was 2.852% and 73.51%, respectively. The iron and nickel grade increases with the increasing temperature. The compounds observed were dominated by magnesioferrite (Fe2MgO4), quartz (SiO2), ferronickel (FeNi), FeO and FeS. Ferronickel grain size increases along with a higher reduction of temperature. Increasing stoichiometry reducing agent of the palm shell charcoal, the silicate content in the reduction process results also increases. Silicate acts as an impurity in the reduction process which can inhibit the optimization of the process. Without addition elemental sulfur (0%), results a higher nickel recovery than addition 2.68% or 5% sulfur. More sulfur content addition will result in more sulfur content in the liquid phase.

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