Study of Temperature and Holding Time of Second Stage in Two-stages Thermal Upgrading of Lateritic Nickel Ore

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Abstract. A two-stage thermal upgrading process with the addition of 10 wt.% sodium sulfate and sodium chloride followed by magnetic separation was conducted for treatment low-grade nickeliferous laterite ore to produce a ferronickel product. The aim of this experiment was to investigate the effect of reduction temperature and holding time in two-stage thermal upgrading process, which was carried out from 950°C to 1150°C for 30 to 90 minutes, into the grade and recovery of nickel also the morphology of ferronickel particle. A wet magnetic separation with 500 gauss magnet was conducted to produce ferronickel in concentrate. Increasing the reduction temperature of nickel laterite increased the nickel grade and recovery. The nickel grade and recovery also increased along with the longer holding time in the reduction process. Nevertheless, it decreased the iron recovery.

Keywords: Low-grade Nickel, Two-stage Thermal Upgrading, Ferronickel, Particle Growth, Sodium Sulfate, Sodium Chloride

1. Introduction

More than 65% of the nickel consumption is used to make stainless steel [1,2]. The demand ferronickel has been increased in the last few years due to the rapid development of stainless steel industries [3]. The continuous depletion of sulfide ore deposits forced the interest of the industry to focus on the utilization and start developing nickeliferous laterite deposits as one of the alternative raw material in nickel production [4].

Nickeliferous laterite ore was not desirable as a major source of nickel since the nickel concentration is lower than saprolitic nickel ore which is typically difficult to process by physical beneficiation methods [1]. It requires more energy intensive and complex processing to concentrate nickel from laterite ore [5]. Innovation development related to the process for increasing the nickel grade of lateritic ore was obtained by conducting a pre-treatment process of selective reduction roasting at the temperature below 1200°C using two-stage thermal upgrading mechanism and the addition of additives followed by magnetic separation [6]. A various operating condition such as temperature and holding time was performed to increase the growth of metal particle size which is favorable when magnetic separation is carried out.
The temperature influences metal enrichment on the nickel laterite ore. The high temperature increased the percentage of nickel grade in the ferronickel compound due to the wustite reduction rate simultaneously with the growth of ferronickel particles, increased to the formation dissolved nickel in taenite (γ-Fe-Ni) [7]. Longer holding time in the reduction process has a significant impact on nickel enrichment, especially at high temperature (700°C) [8,9]. In the reduction process, the percentage of nickel grade increases with the length of holding time [10].

In this study, the function of temperature and holding time in the reduction of low-grade nickel ore using 10 wt. % sodium sulfate (Na$_2$SO$_4$) and sodium chloride (NaCl) on promoting the growth of metallic ferronickel to increase the recovery and grade of nickel in the ferronickel concentrate was investigated clearly.

2. Experimental method

Nickel lateritic ore in this research is from Sulawesi, Indonesia. A 100 grams of raw materials were crushed into less than 147 µm and drying at 105°C for prior to the characterization analysis was performed. From X-Ray Fluorescence (XRF) analysis, the chemical composition of lateritic ore was 1.4 Ni - 50.5 Fe - 2.68 Cr - 16.5 Si - 4.86 Al - 1.81 Mg. The palm kernel shell was used as the reductant which contains 77% of fix carbon and 21% ash.

The drying process was conducted at 105°C into the as-received ore by using an oven for 24 h to remove the free water. The dried lateritic ore and reductant were crushed become less than 149 µm. The 50 grams of fine lateritic ore, 22 grams of reductant, and 10 wt. % of additives (Na$_2$SO$_4$ and NaCl) were thoroughly mixed for preparing pellets.

The pellets were dried at 100°C for 2 h, then it was charged into a crucible which made from graphite. The crucible was put in a muffle furnace at a certain temperature and holding time. The process consists of a pre-heating process (first stage) at an initial temperature of 500°C with holding time for 60 and 90 minutes. It was continued with the reduction process (second stage) at a final temperature of 950, 1050, and 1150°C with holding time for 30, 60, and 90 minutes.

After the reduction process, the reduced pellets were quenched in distilled water. The cooled-reduced pellets were ground to less than 74 µm using a vibrating mill before it was analyzed by using X-Ray Diffraction (XRD) to observe the transformation of mineral or phase compound after the reduction process. The magnetic separation was carried out to the finely reduced pellets by dissolved it in distilled water with 1:10 ratio and separated the concentrate and tailing using 500 gauss magnet. The iron and nickel content in concentrate and tailing was analyzed by using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES). A Scanning Electron Microscopy With Energy Dispersive X-Ray Spectroscopy (SEM-EDS) was performed to identify the chemical compound and to investigate its distribution after the magnetic separation process.

3. Results and discussion

3.1 Effect of Temperature on Selective Reduction Process

Figure 1 shows the result of the reduction and magnetic separation process of the lateritic pellets ore with the addition of 10 wt.% additives (Na$_2$SO$_4$ and NaCl). The reduction process of lateritic ore was conducted at 950 to 1150°C for 30 minutes. The preheating temperature was fixed at 500°C for 60 minutes. From figure 1, the Ni and Fe grades increased from 2.03% and 46.36% to 3.62% and 72.45% respectively, and the recovery of Ni and Fe also increased. The higher the temperature, the more troilite (FeS) was formed which increased the nickel grade. The reaction between Na$_2$SO$_3$ and olivine was also more considerable which increased the liberation of nickel and iron. In addition, nickel and iron oxide chlorination process was more considerable and led to higher grades and recoveries, both for iron and nickel [111].
Figure 1. Effect of temperature with the addition of 10 wt.% Na$_2$SO$_4$ and NaCl on (a) nickel and iron grades, (b) nickel and iron recoveries.

The reduction of nickel laterite at the temperature of 1150°C resulted in highest nickel grade and recovery rather than at temperatures of 950 and 1050°C, which was 3.62% and 77.15%, respectively. The grade and recovery of Ni and Fe increased as the temperature further increased from 950 to 1150°C. It was agreed with Li et al. (2012) that increasing temperature from 800 to 1200°C in the selective reduction process with the presence of additives increased the nickel grade, iron grade, nickel and iron recovery [12]. In addition, the increase in nickel grade and recovery due to the increasing metallization of iron and nickel, more FeO and NiO are reduced to Fe and Ni metals [10]. Increasing temperatures also increase the aggregate activation of ferronickel, molecular movement of reactive gases. Increasing CO/CO$_2$ ratio in systems affecting Fe and Ni particle growth and reaction rate that have a direct impact on increasing nickel and iron [13,14].

3.2 Effect of Holding Time on Selective Reduction Process
The results of the reduction and magnetic separation reduced laterite pellet at reducing time from 30 to 90 minutes is shown in figure 2. The preheating temperature was fixed at 500°C for 90 minutes and the second stage temperature at 1150°C.

Figure 2. Effect of holding time with the addition of 10 wt.% Na$_2$SO$_4$ and NaCl on (a) nickel and iron grades, (b) nickel and iron recoveries.

The results showed that prolonged reducing periods favorable for the Ni and Fe grades. From Figure 2 (a), the Ni and Fe grades of the magnetic separation increase from 3.57% and 88.51% to 4.31% and 89.34%, respectively. The longer holding time in the reduction process resulted in the increasing concentration of reducing gas which increased the reduction of iron and nickel oxide, thus it affected the increasing of nickel and iron grades in concentrate [8]. An increasing in nickel grade from 3.69% to 4.31% at a holding time of 60 to 90 minutes could be attributed to the decreasing recovery of Fe in concentrate from 60.05% to 48.89%. The Ni and Fe recoveries initially increased to a maximum value and then decreased after 60 minutes. It could explain that with increasing the length of holding time, more FeS were formed and went into tailing when the magnetic separation process carried out. From
the experimental results with the variation of holding time at the reduction process (second stage), it was found that sample with 90 minutes of reducing time was optimal due to the highest grade of nickel and the lowest of iron recovery.

3.3 The Phase Transformation of Lateritic Nickel Ore during the Reduction Process

As shown in Figure 3, the XRD patterns of the reduced pellet at 950°C that SiO$_2$, NaCl, FeS, FeNi, fayalite, and nepheline (Na$_2$Mg$_2$Si$_2$O$_7$) were found. The formed nepheline indicated that iron and nickel liberation occurred from the lizardite. Fayalite was a by-product of the reaction due to the high iron content. Trevorite (NiFe$_2$O$_4$) reduction resulted in the formation of FeNi at temperature of 950°C. The trevorite phase reduced to NiO and Fe$_3$O$_4$ at temperature of 900°C [15]. Magnetite was found at all temperatures. Based on the thermodynamic analysis, the magnetite reduction reaction with the solid carbon has a more negative free energy compared with the reduction of CO gas. However, at the temperature from 950 to 1150°C, the available solids carbon has been reduced due to boudouard reaction, thus the magnetite reduction was inhibited. At a temperature of 1050°C, the intensity of NaCl and SiO$_2$ was decreased because both of them were reacted to form HCl and Na$_2$SiO$_3$. The FeS as the result of a reaction between FeO with Na$_2$S and NiS was also observed at this temperature, as expressed in equation (1) and (2).

$$\text{Na}_2\text{S} + \text{FeO} + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{FeS} \quad \Delta G^0 = -24,821 \text{ Kcal} \quad (1)$$

$$\text{NiS} + \text{FeO} + \text{CO} \rightarrow \text{FeS} + \text{Ni} + \text{CO}_2 \quad \Delta G^0 = -6,628 \text{ Kcal} \quad (2)$$

![Figure 3. The XRD patterns of reduced lateritic pellets at 950, 1050 and 1150°C temperatures for 30 minutes with 10 wt.% of additives (Na$_2$SO$_4$ and NaCl).](image)

Figure 4 shows the microstructures of a sample with temperature of 1050°C by using SEM-EDS. Figure 4 shows the size of the ferronickel grains observed at the temperature of 1050°C, which was 28.5 μm. This phenomenon was due to a grain growth mechanism from the formation of the Fe-FeS liquid phase eutectic system at temperature of 998°C. Nevertheless, the morphological analysis of grain size on ferronickel for the temperature of 950°C was not conducted due to the very small size and it was unfavorable when the magnetic separation was carried out.
4. Conclusion
Increasing the reduction temperature improved the grade and recovery of nickel due to the maximum nickel liberation from the lizardite phase. The longer holding time increased the grade and recovery of nickel but decreased the iron recovery at the concentrate due to the increasing amount of FeS, which decreased the recovery of iron. The growth of FeNi particles increased with the higher reduction temperature.

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