Effect of sodium sulfate and sodium chloride in two-stage thermal upgrading of low-grade Nickel Lateritic Ore

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Abstract. Selective reduction process and magnetic separation of nickel lateritic ore were conducted through the two-stage thermal mechanism with the addition of sodium sulfate and sodium chloride as the additives agent. The first thermal process was pre-heating at the temperature of 500°C and holding for 90 minutes. Afterward, the reduction continued at the temperature of 1150°C for the same holding time. The mineralogical composition of the reduced samples was determined by XRD. The microstructure of reduced nickel laterite ore was also examined using SEM-EDS. The optimum composition of the additive was the combination of 10% Na2SO4 + 10% NaCl, which produced a concentrate with 5.52% and 85.89% for nickel grade and nickel recovery, respectively.

1. Introduction
Nickel is a precious metal in the infrastructure and technology field, especially in making industries of stainless steel, Ni-based alloy, alloy steels, electroplating, batteries, etc [1]. Nickel was used either in the form of metallic nickel or form of NPI/ferronickel with various of iron content [2]. The extraction process of nickel lateritic requires high intensive energy and usually, nickel is melted to produce low-grade ferronickel with the high amount of slag. Furthermore, this pyrometallurgy process is merely used for low-grade nickel lateritic ore containing nickel grade above 1.5%. Nevertheless, the grade of nickel lateritic ore around the world including Indonesia is about 1.45%. Therefore, this conventional process is ineffective [3]. Recently many researchers focus on the method of upgrading the effectivenes and efficiency of pyrometallurgy process to produce ferronickel by using selective reduction process followed by magnetic separation [4], [5]. Ferronickel is generally used in stainless steel making process so that the result of this process will be able to supply the market needs [6].

In the process of reduction, the addition of the optimum composition and selection of additive could generate the optimum recovery with low reduction temperature. It would be one of the efficient steps in the selective reduction of nickel lateritic ore [7].

In previous research, the sulfur compound had been used as the additive agent in selective reduction process, such as sodium sulfate (Na2SO4) [8],[9]. It resulted that the addition of sulfur compound in selective reduction process followed by magnetic separation process could be able to increase the nickel grade and recovery process [4],[10]. Another compound that can be used as the additive is chlorine salt [11],[12], such as sodium chloride (NaCl). Due to the characteristic of chloride

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which has low melting temperature and volatile properties, chloride compound generally used for extracting metal from its ore through chloridization and volatilization process [13].

The objective of recent work is to extracting nickel oxide of low-grade nickel ore from Desa Morombo, Konawe Utara District, Sulawesi Tenggara Province through selective reduction process followed by magnetic separation with the addition of the combination of sodium sulfate (Na$_2$SO$_4$) and sodium chloride (NaCl) as additive and palm kernel shell as the reductant.

2. Experimental

Raw materials in this research are low-grade nickel limonitic ore, palm kernel shell as reductant, sodium sulfate and sodium chloride as additives. The result of XRF analysis for nickel lateritic ore and proximate analysis of the reductant are listed in Table 1 and Table 2, respectively.

| Table 1. The Chemical composition of the nickel laterite ore (mass fraction, %) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Element        | Ni   | Fe   | Si   | Mg   | Al   | Ca   | Cr   | Mn   | Co   |
| Mass Fraction (%) | 1.4  | 50.5 | 16.5 | 1.81 | 4.86 | 0.177| 2.68 | 0.847| 0.0662 |

| Table 2. Proximate analysis of palm kernel shell (wt.%) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Reductant          | Volatile Matter | Ash  | Fixed Carbon | Moisture |
| Palm Kernel Shell | 22.57           | 21   | 77            | 0.43       |

The ore was dried in the oven at temperature 105°C for 24h to reduced the water content until less than 5 wt.%. Limonitic dried ore and the reductant were crushed and sieved to gain the particle less than 147 µm. Afterwards, the 50gr of ore, 5.5gr of reductant, and additives were mixed and pelletized with various composition of additives content, i.e. 15% Na$_2$SO$_4$ + 5% NaCl (code AB), 5% Na$_2$SO$_4$ + 15% NaCl (code AC), and 10% Na$_2$SO$_4$ + 10% NaCl (code L). The pellets were dried in the oven at the temperature of 100°C for 2h.

Two-stage thermal of selective reduction process was performed in this research. The first stage of reduction temperature was 500°C and the second stage temperature was 1150°C. Each stage was held for 90 minutes. After the selective reduction was done, the pellets were cooling rapidly in water. The pellets then were dried and crushed up to 74 µm.

The phase transformation was determined by XRD (X-ray Diffraction) to observe the transformation of mineral composition and phase which form after the selective reduction process. Samples were also examined by SEM-EDX (Scanning Electron Microscopy) to observe the microstructure of phase and its distribution. Afterward, the wet magnetic separation was conducted by dissolving the reduced ore into the water and separating the concentrate and tailing using 500 gauss magnet. The ratio of reduced ore and water in this magnetic separation process was 1:10.

3. Results and Discussions

Figure 1 shows the iron and nickel grade and recovery of the concentrate in this selective reduction process with various additives.
Figure 1. Effect of various additive on (a) grade of nickel and iron, (b) recovery of nickel and iron in concentrate at the reduction temperature of 1150°C

The nickel grade of sample AC is 3.61%. The grade is increased up to 5.53% in sample L and decrease to 5.41% in sample AB. The recovery of iron has the opposite tendency with the nickel grade. When the nickel grade is getting higher, the recovery of iron is decreased. The recovery of iron in sample AC is 45.09% and decreasing to 30.31% in sample L, but it was increased to 41.28% in sample AB.

Figure 2 shows that the observed phase in each additive composition is kamacite (FeNi), wustite (FeO), magnetite, troilite (FeS), silica, fayalite, and nepheline. The less addition of sodium sulfate in sample AC than sample AB resulted in a small amount of FeS which was found in reduced ore, as shown in Figure 2. The intensity of FeS in sample L is higher than in sample AC due to more addition of sodium sulfate composition in sample AC. The appearance of FeS caused to lower iron recovery due to its non-magnetic characterization. In the magnetic separation process, the magnet will bind magnetic mineral and bring it to concentrate. FeS which has no magnetic characterization will not get into concentrate [8].

The addition of sodium chloride promotes in decreasing iron recovery due to the segregation process. Sodium chloride in pellets reacted with water vapor in it through pyrohydrolysis process to form hydrochloride acid. It reacted with metal oxide to form metal chloride. Nickel chloride and iron chloride absorbed on the surface of the carbon particle, then reduced by hydrogen and carbon monoxide. It produces segregated chloride [12]. The segregation rate of iron chloride is lower than nickel chloride. Therefore, most of the iron chloride is volatilizing before it segregated so that the iron recovery decreased. The excess addition of sodium chloride would result in more intensive of
chloridization process, thus the volatilizing of nickel chloride happened and it will decrease the recovery of nickel.

Figure 3. SEM Mapping of Optical Micrograf of Sample L at reduction temperature of 1150°C

Figure 4. SEM Mapping of Sample L powder at the reduction temperature of 1150°C

The appearance of new FeO peak at the 2θ angle of 42° in sample L indicates that the appearance of FeO is multiplying in the reduced ore. The excess of sodium chloride will bind more FeO to form iron chloride, meanwhile in the excess addition of sodium sulfate will bind more FeO to form FeS. The value of FeO in sample AB and AC are measy and its peak cannot be observed. The increasing of FeS in sample AB is due to the more sulfur in the additive. Silica and wustite are in sample L. It could be caused by obstruction of the reaction which happened to both because of a particular mechanism. This mechanism somehow happened because of the balance composition.
between sodium sulfate and sodium chloride which added as the additive in sample L. The presence of both phases would be an advantage in the result of magnetic separation process because both of these phases will not get into the concentrate, so the nickel grade in concentrate will increase.

Figure 3 and Figure 4 show that iron can be separated away from the gangue element such as sodium, silicon, magnesium, and aluminum. Iron has its own mapping pattern and concentrated with nickel element to form ferronickel. Iron with sulfur element enfold ferronickel and becoming troilite. Meanwhile, it can be seen a few irons concentrated with silicone and oxygen forming fayalite. Some of the oxygen element concentrated with silicon to form silica and some of them concentrated with iron to form iron oxide. Sodium seems to be concentrated with silicone, magnesium, and aluminum to form a nepheline phase.

Figure 5 shows the average of ferronickel particle size is 61.75µm. At the temperature of 1100°C, the reaction of NaO-MgO-SiO₂ forms nepheline (Na₂Mg₂Si₂O₇). The low melting point of nepheline created liquidus phase at 1100°C, thus promoted the growth of ferronickel particle size [10].

4. Conclusions
The phases which formed in the reduced ore with the addition of sodium sulfate and sodium chloride at the reduction temperature of 1150°C for 90 minutes are kamacite (FeNi), wustite (FeO), troilite (FeS), fayalite (Fe₂SiO₄), and nepheline (Na₂Mg₂Si₂O₇). The sulphidation, chloridization, and segregation process will occur because of the addition of sodium sulfate and sodium chloride. It will increase nickel grade and recovery. Furthermore, sulfur in sodium sulfate will generate the grain growth of kamacite particle through the forming of Fe-FeS system. Nepheline phase that occurs in the low temperature can also facilitate the grain growth. The optimum percentage composition of the combination of the additive is 10% Na₂SO₄ + 10% NaCl which generates nickel grade of 5.52% and nickel recovery of 85.89%.

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