The role of sodium-based additives on reduction process of nickel lateritic ore

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Abstract. In this present work, the selective reduction of nickel laterite was conducted by using 5 to 15 wt. % of sodium carbonate, sodium chloride and sodium sulfate as additives. The 5% wt. of palm shell charcoal was used as the reductant. The selective reduction process for nickel laterite was carried out at 1150°C for 60 minutes followed by wet magnetic separation using 500 Gausses permanent magnet. The characterization of reduced ore was performed by using X-ray Diffraction, optical microscope and Scanning Electron Microscope with Energy Dispersive X-ray Spectroscopy, while the chemical composition of concentrate or ferronickel was identified by X-ray Fluorescence. The results showed that the increase of nickel grade and recovery of nickel laterite was significantly more affected by the addition of sodium sulfate rather than sodium carbonate and sodium chloride. The ferronickel particle was agglomerated and growth with the increasing of reduction temperature and doses of additives, thus it provided favorable conditions for the separation of ferronickel from impurities in the magnetic separation process.

1. Introduction
Nickel is a commercially important metal and used mainly in the production of stainless steel. About 68% of the nickel consumed to make stainless steel and another 32% goes into alloyed steels, castings, electroplating, and rechargeable batteries. About 70% of world land-based nickel resources are contained in laterites, they currently account for only about 40% of the world nickel production [1]. Thus, nickel laterite ore processing has attracted much greater attention in recent years and economical processing of nickel laterite ores is becoming imperative due to the increasing demand for nickel which is driven by the rapid development of stainless steel industry [2].

Nickel is closely associated with a complex compound in lateritic nickel ore, such as olivine (magnesium and silicate oxide) and goethite (iron hydroxide). The complex compound of nickel ore makes their inability to improve its metal oxide concentration using physical beneficiation process, thus pyrometallurgy or hydrometallurgy is a must. Pyrometallurgy includes a processing with a blast furnace or rotary kiln-electric arc furnace smelter [3], while hydrometallurgy includes high-pressure acid leaching and Caron process [4]. Nevertheless, it is costly and produces a lot of chemical waste.
A reduction process of nickel ore was conducted at lower than smelting process temperature had been conducted. A small amount of additives were involved in this reduction process to enhance the nickel grade and recovery at low reduction temperature [5]. Therefore, a low cost and less chemical waste in nickel ore processing can be realized. Sodium sulfate is commonly used as an additive in the selective-reduction of nickel ore processing. Jiang et al. (2013) reported that the addition of 10 wt. % of sodium sulfate and 2 wt.% of coal in the reduction of nickel ore containing 1.49% Ni at 1200°C for 50 minutes resulted in 10.86% and 88.56% for nickel grade and recovery, respectively [6].

However, there is still less information for the using of others sodium-based additives in selective-reduction of nickel ore processing. In this present work, the addition of sodium carbonate and sodium chloride were used as additives in the selective-reduction process. The effect of both additives on nickel grade and recovery was investigated clearly comparing with the sodium sulfate additives. The ferronickel growth during the reduction process was also observed carefully.

2. Material and Methods
The nickel laterite ore was from South East Sulawesi, Indonesia. The X-ray fluorescence (XRF) was performed to determine the chemical compositions of the nickel ore, as showed in table 1.

| Element | Fe | Ni | Al | Si | Ca | Mg | Cr | Mn | Co |
|---------|----|----|----|----|----|----|----|----|----|
| wt. %   | 50.5| 1.4| 4.86| 6.5| 0.18| 1.81| 2.68| 0.85| 0.07|

The nickel laterite was ground to less than 0.147 mm and mixed together with 10% wt. of palm shell charcoal as reductant and 5-15% wt. sodium-based additives. The proximate and calories analysis of the reductant were listed in table 2. The additives were sodium carbonate, sodium chloride and sodium sulfate. The mixture was agglomerated into 10-15 mm in diameter of pellets. The pellets were drying at 100°C for 4 hours in an oven and continued with the reduction process, which took place in a muffle furnace at 1050°C for 60 minutes.

| Proximate analysis (wt. %) | Fixed carbon content | Calories (cal/g) |
|---------------------------|----------------------|------------------|
| Moisture                  | Volatile matter      | Ash content      |                |
| 0.43                      | 22.57                | 21               | 77             | 6,244 |

The reduced pellets were cooling rapidly in a water and then dried at 100°C for 4 hours. The pellets were ground again into less than 74 µm before the wet magnetic separation process was performed and separated into the concentrate (magnetic) and the tailing (non-magnetic).

The iron and nickel grade of concentrate were analyzed by using X-ray Fluorescence (XRF), while the morphological of ferronickel was observed using Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS). The X-ray Diffraction (XRD) was used to analyze the mineralogical phases in the reduced pellet.
3. Results and Discussion

3.1. Effect of additives on nickel and iron grade and recovery
Figure 1(a-d) presents the result of various types and amount of additives on iron-nickel grade and recovery in the concentrates resulting from the reduction process at 1150°C for 60 minutes followed by the magnetic separation process. The reduction of nickel limonite ores without additives only produced nickel grade and recovery of 2.5% and 29.3%, respectively. The nickel grade and recovery significantly increased by adding 15% wt. of sodium sulfate additive which was 5.3% and 83.7%, respectively. Nevertheless, the nickel grade tended to be constant, while the recovery seemed to be decreased during the addition of sodium carbonate and sodium chloride additives.

Iron grade increased towards the increasing of sodium sulfate additive, as shown in figure 1(c). The optimum iron grade was 81.9% resulted from 10% wt. sodium sulfate addition. For sodium carbonate additive, the optimum iron grade was 72.1% resulted from the addition of 5% wt. of additive. Nevertheless, the addition of sodium chloride additive decreased the iron grade. From figure 1(d), the increasing of additives from 5% wt. to 15% wt. decreased the iron recovery. The addition of 15% wt. of additives produced iron recovery of 46.2%, 45.4%, and 35.2% for sodium chloride, sodium carbonate, and sodium sulfate, respectively. The low recovery of iron indicated a low of iron metalization in the selective reduction process of nickel laterite ore, thus the concentrate contains a small amount of iron and resulted in high nickel grade.

![Figure 1](image1.png)

**Figure 1.** Effect of different additives on nickel and iron grade in concentrate

3.2. Characterization of reduced laterite by XRD and SEM-EDX
The XRD analysis was performed in nickel laterite for reduction temperature at 1150°C for 60 minutes with various additives in 5, 10, and 15% wt. as given in figure 2. From the XRD patterns of
reduced nickel laterite without additives, as given in figure 2(a), showed that there is only two dominant peaks, they are fayalite ((Mg, Fe)₂SiO₄) and iron nickel (FeNi). Fayalite was formed due to the lizardite dehydroxylation (Mg₃(Si₂O₅)(OH)₄) and silicate mineral recrystallization of nickel laterite ore [7]. Moreover, goethite (FeO(OH)) and olivine (MgNiSiO₄) in nickel laterite were reduced to be ferronickel in the reduction process. The 2.5% of nickel grade in concentrate was resulted from the selective reduction of nickel ore without additives.

![Figure 2. XRD pattern of the reduced laterite with different additives: (a) without additive, (b-d) sodium carbonate, (e-g) sodium chloride, and (h-j) sodium sulfate.](image)

In addition of 5% wt. of sodium carbonate additive, the peak of fayalite (Fe₂SiO₄) diffraction in reduced ore decreased and replaced by the peak of magnetite (Fe₃O₄). By increasing the sodium carbonate additive, the intensities of wustite (FeO) and ferronickel (FeNi) peaks were increased, as presented in figure 2(b-d). It was explained that by adding the sodium carbonate additive, the
decomposition of sodium carbonate producing CO₂ occurred and promotes the boudard reaction producing CO gas. The CO gas could increase the reduction of oxides in laterite ores [8]. However, if the sodium carbonate additive increased up to 15% wt., the peak of quartz (SiO₂) was found in the reduction process of nickel laterite due to the reduction of fayalite into wustite and quartz at high temperature. Quartz as an impurities inhibit the reduction of nickel oxide, thus the nickel recovery at the reduction process with 15% wt. sodium carbonate at 1150°C was very low.

Figure 2(e-g) presents the XRD pattern of the reduced nickel laterite ores with the addition of sodium chloride additive. The peak diffraction of 5%, 10%, and 15% wt. sodium chloride had a tendency of having the similar peak diffraction consists of fayalite (Fe₂SiO₄), magnetite (Fe₃O₄), and ferronickel (FeNi).

The XRD patterns with 5%, 10%, and 15% wt. of sodium sulfate additive are given in figure 2(h-j). The increasing of wustite and troilite was observed in the increasing of sodium sulfate thus it was decreasing the iron recovery in concentrate. Wustite was more difficult to reduce than nickel oxides and troilite. In addition, the sulfur, resulting from decomposition of sodium sulfate, reacted with iron to form troilite which was non-magnetic thus increasing nickel concentration in concentrate while undergoing beneficiation through the magnetic separation process [6]. Furthermore, there was a decrease in peak diffraction of nickel along the increased temperature as shown in figure 2(h-j). This indicated that ferronickel in concentrates containing more nickel than iron and it also confirm that the decrease of iron recovery in the increasing dose of sodium sulfate.

Figure 3 and figure 4 shows the micrograph of reduced nickel laterite using sodium carbonate additive at temperature 1150°C for 60 minutes performed by SEM and phase identification of microstructure using EDX analysis. The white area, which is shown by point A, C, and G, indicated as ferronickel (FeNi) particles.

**Figure 3.** SEM analysis of reduced laterite in presence of sodium carbonate additive (a) 5% wt., (b) 10% wt. and (c) 15% wt. (magnification 1000BSE)
In the addition of 5% wt. sodium carbonate additive, the particle size of ferronickel was fine and distributed uniformly. The increasing of sodium carbonate addition to 10% wt. had an effect on transforming the ferronickel particle size to be larger. The average optimum size of ferronickel particles was found at 10% wt. of sodium carbonate which was 12.8 µm. Nevertheless, the increasing to 15% wt. of sodium carbonate would lead to the dispersion on ferronickel particles as shown in figure 3(c). More sodium carbonate addition will result in more CO₂ gas. As reported by Zhou et al. (2017), that the CO₂ gas resulted in the expansion of volume, so the structure of polluters and particles in the ores resulting from reduction was exposed to the tension due to the expansion of volume and particle shapes started to decay and be dispersed [8].

From micrograph analysis (figure 3), the ferronickel particles were surrounded by impurities, which is shown by point B, E, D, F and H. From the XRD analysis, the impurities are wustite (point E) and fayalite (point B). At point H, it was found that the impurities contained high of silicon and oxygen. It was confirmed from the XRD analysis with 15% wt. of sodium carbonate additive which has found the peak diffraction of quartz. Figure 5(a-c) shows the micrograph in reduced nickel laterite ores with sodium chloride additive. The points A, C, and E show ferronickel as a white area which is dominated by Fe and Ni element (figure 6(a)). Meanwhile, the points B, D, and F are impurities minerals surrounding the ferronickel particles. The impurities consisted of Mg, Si, and O which indicated fayalite as the gangue mineral. This could confirm the result analysis of XRD pattern with the addition of additive sodium chloride, as shown in figure 2(e-f). The optimum size of ferronickel particles was 8.0 µm with the addition of 10% sodium chloride. The increasing of sodium chloride up to 15% wt. decreased the ferronickel particles size. This was occurred because there was an indication of pyrohydrolysis process towards sodium chloride to be HCl as an agent of chlorination that had been achieved. Thus, adding further additives up to 15% did not significantly affect the formation of ferronickel particles.
Figure 5. SEM analysis of reduced laterite in the presence of sodium chloride additive (a) 5% wt., (b) 10% wt. and (c) 15% wt. (magnification 1000BSE)

Figure 6. Spectrum of EDX analysis of reduced laterite in the presence of sodium chloride for point: (a) A; (b) B

Figure 7 shows the micrograph of reduced nickel laterite with the addition of sodium sulfate additive. The points B, D, and G presented the ferronickel particles enfolded by its impurities. There was found fayalite, wustite, and quartz as impurities, as shown in XRD pattern in figure 2(h-j), which is shown in point A, E and H. The addition of 10% until 15% wt. of sodium sulfate additive resulted the ferronickel particles which surrounded by troilite (FeS), which is shown by point C. The interaction of troilite and metallic iron was formed during the process of reduction to promote ferronickel particle growth due to the low Fe-FeS eutectic melting point (985°C). The liquidus state will promote the rate of mass transfer of metal ions during the process of reduction. Thus, ferronickel particles growth and agglomerates surrounded the troilite [5]. The increasing addition of sodium sulfate additive increases the reduction reaction of sodium sulfate with these following reactions in equation (1-2) [9].
1/4 Na\(_2\)SO\(_4\) + CO ↔ 1/4 Na\(_2\)S + CO\(_2\)  \hspace{1cm} (1)

Na\(_2\)S + FeO + 2SiO\(_2\) ↔ Na\(_2\)Si\(_2\)O\(_5\) + FeS  \hspace{1cm} (2)

Sodium sulfate was reduced by CO gas produced Na\(_2\)S which would react with wustite into troilite. This FeS would enfold the ferronickel particles as resulting from SEM-EDS analysis in figure 7.

Figure 9 showed the ferronickel size after selective reduction using various additives at a reduction temperature 1150ºC for 60 minutes. The ferronickel particle size was observed to be larger from 6.3 µm to 43.7 µm with the increasing sodium sulfate from 5% to 15%. While, the optimum of ferronickel particle size was around 12.8 µm and 8 µm with the addition of 10% sodium carbonate and sodium chloride additives, respectively. The further increasing amount of more than 10% additives sodium carbonate and chloride reduced the ferronickel particle size. The sodium sulfate additives resulted the optimum size of ferronickel due to the formation of FeS at the low melting point which promotes the agglomeration of ferronickel particles during the reduction process.

Figure 7. SEM analysis of reduced laterite in the presence of sodium sulfate additive (a) 5% wt., (b) 10% wt., and (c) 15% wt. (magnification 1000BSE)
Figure 8. Spectrum of EDX analysis of reduced laterite in the presence of sodium sulfate for point: (a) D, (b) E, (c) C

Figure 9. Ferronickel particle size of reduced laterite with different additives (reducing temperature 1150°C for 60 minutes)

4. Conclusion
The addition of additives was potentially increased the grade and recovery of nickel in concentrate compared with the nickel laterite ore resulting from the selective reduction process without additives. Adding additive sodium sulfate could significantly increase nickel and iron grade and recovery compared to the sodium carbonate and sodium chloride additives. At reduction temperature of 1150°C for 60 minutes, the nickel laterite ore with addition 15% wt. of sodium sulfate resulted in the optimum nickel grade and recovery, which was 5.3% and 83.7%, respectively. The addition of 15% wt. sodium sulfate also produced the optimum ferronickel particle size, which was 43.7 µm. Sodium sulfate promotes the FeS formation in the reduction of nickel laterite ore, thus increase the recovery of nickel and ferronickel particle size.

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