A preliminary study on the reduction of limonite ore by using rice husk as a reducing agent

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Abstract. The abundant of rice husk in Indonesia has encouraged researchers to study the feasibility of rice husk for substituting material that is more expensive or dangerous. In previous study, silica with a purity of 99.9\% has been obtained from rice husk with calcinations process. Nevertheless, the gases resulting from the process were not used and left useless. Therefore, in this study, those gases derived from rice husk calcinations process were used as reducing agents during the ferronickel (Fe-Ni) production through a direct reduction process. The objective of this study was to investigate the effect of the amount of rice husk in the pellets on the increase of nickel content in the limonite reduction process. The limonite ore were crushed to the size of less than 150 mesh using disc-mill, and then were mixed with rice husk powder (10, 20, 30 in wt \% mass) before being pelletized using bentonite as a binder. The resulted pellets were roasted at 500°C for 60 minutes and then quenched in water media. After drying process, the reduction process of 40g pellets was conducted at 1000°C for 90 minutes with 20g rice husk in furnace. The effects of additional rice husk on the direct reduction of limonite ore pellets were qualitatively analyzed by using X-ray powder diffraction (XRD) and quantitatively by Atomic absorption spectroscopy (AAS). Both analysis results showed that the reduction process followed the reaction scheme: Fe\textsubscript{2}O\textsubscript{3}→Fe\textsubscript{3}O\textsubscript{4}→FeO and NiO phase was detected in the sample with 20\% rice husk addition. The optimum concentration of Ni 1.23\% was obtained for 20\% rice husk addition.

Keywords: Direct reduction, Ferronickel, Limonite, Quenching, Rice husk.

1. Introduction
Nickel, as one of the commercially important metals in modern life, is widely used in the industrial manufacture of stainless steel, both for steel construction and household purposes, and the battery industries as well. In addition, nickel is also used in a wide variety of metal alloys and nickel plating [1]. At this time, the nickel was obtained from primary sources in the form of nickel sulfide ore (nickel associated with copper) and lateritic ore (nickel associated with iron and/or magnesium silicate) [2]. Approximately 60\% of the total nickel production in the world uses a nickel sulfide ore as raw material. Its existence, however, is only about 30\% of total world reserves of nickel [3]. With the
depletion of nickel sulfide ore reserves caused by continuous exploration, the world industries are forced to find other sources that can be used in nickel production industries as an alternative raw material to substitute nickel sulfide.

For the last few years there has been an increase in the investigation of low-grade lateritic ore to substitute nickel sulfide as the nickel resource [4,5]. Lateritic ore is more difficult to be processed due to the lower nickel content and more complexity of its mineralogy structure as a result of their isomorphism crystal structure goethite and serpentine [6,7].

In the metallurgical extraction methods, nickel lateritic ore is generally processed through hydrometallurgy [8–10], pyrometallurgy [11], or a combination of both pyro- and hydrometallurgy [12]. Until now, the hydrometallurgical process, especially High Pressure Acid Leaching (HPAL), has been effective for dissolving nickel lateritic ore with the high recovery of nickel and cobalt [13]. However, this method requires higher investment costs mainly for the autoclave procurement. In addition, this method is also less effective when the content of magnesium in the lateritic ore is higher than 15%, and sometimes can cause problems for the environment and health as well.

The widely used nickel ore in Indonesia is the one with high nickel content above 1.5%, which is then used to produce ferronickel or nickel matte [14]. Various studies to increase levels of nickel from lateritic ore have been done, ranging from thermodynamic calculations for the reduction [15], the characterization of the microstructure and phase changes during the process of reduction and leaching [16], the mechanism of its reduction with coal as a reducing agent [17], and the effect of sodium sulfate [18] or sodium chloride [19] addition in the nickel lateritic ore reduction roasting process, to further increase the nickel content of the result of the reduction, magnetic separation and microwave [20].

Recently, many researchers have been using coal as reducing agent on the reduction process of nickel lateritic ore in order to produce ferronickel or nickel matte. Based on the above discussion, this study investigated the effect of the amount of rice husk in the pellets on the increase of nickel content in the limonite reduction process. The characteristics of limonite ore and reduction product were analyzed by using X-ray diffraction (XRD) and Atomic Adsorption Spectroscopy (AAS). The results of this preliminary study may provide a reference for further investigation in related reduction process, and furthermore, it can answer the feasibility of rice husk as a sustainable alternative reducing agent.

2. Material and method

2.1. Materials
The selected reducing agent is the rice husk from Kerawang, West Java, Indonesia. The proximate analysis of the rice husk is listed in Table 1. The rice husk is a good reducing agent because of high volatile matter, and relatively low harmful element (S, P) content.

| Analysis Parameters   | Value | Unit | Basis |
|-----------------------|-------|------|-------|
| Proximate             |       |      |       |
| Moisture              | 8.70  | %    | adb   |
| Ash                   | 23.85 | %    | adb   |
| Volatile Matter       | 54.10 | %    | adb   |
| Fixed Carbon          | 13.35 | %    | adb   |
| Ultimate              |       |      |       |
| Carbon                | 33.14 | %    | adb   |
| Hydrogen              | 5.14  | %    | adb   |
| Nitrogen              | 0.55  | %    | adb   |
| Total Sulfur          | 0.12  | %    | adb   |
| Oxygen                | 37.20 | %    | adb   |
A limonite ore from North Sulawesi Province in Indonesia was selected for this study. The chemical composition of the limonite ore has silica and alumina content as seen in Table 2.

Table 2. Main chemical compositions of the low-grade nickel lateritic ore sample (mass fraction, %).

|       | Fe$_2$O$_3$ | NiO  | CO$_2$O$_3$ | SiO$_2$ | Al$_2$O$_3$ | Cr$_2$O$_3$ | MnO  | MgO  | ZrO$_2$ | Others |
|-------|-------------|------|-------------|---------|-------------|-------------|------|------|---------|--------|
| Mass  | 75.3        | 1.69 | 0.315       | 10.8    | 6.04        | 2.59        | 1.25 | 0.94 | 0.701   | 0.374  |

2.2. Roasting reduction method

The limonite ore was crushed and sieved to 80 wt%, passing 0.074 mm, while rice husk was crushed and screened to a size range of 0.5–2. The sieved limonite ore sample was thoroughly mixed with bentonite (2 wt.%) and sieved rice husk (the amount of rice husk addition were varied from 0 wt.% to 30 wt.%) for preparing pellets with a diameter of 12–16 mms, as shown in Table 3.

Table 3. The mixture composition of pellets.

| Code | Limonite | Bentonite | Rice Husk |
|------|----------|-----------|-----------|
| Sample 1 | 98%    | 2%        | 0%        |
| Sample 2 | 88%    | 2%        | 10%       |
| Sample 3 | 78%    | 2%        | 20%       |
| Sample 4 | 68%    | 2%        | 30%       |

2.3. Characterization

The content of nickel and iron in the magnetic concentrate samples were determined by atomic absorption spectrometry (AAS, HITACHI 180/80, Japan). Meanwhile, the XRD patterns were recorded using a diffractometer (RIGAKU D/Max 2500, Japan) under the conditions of radiation: Cu Ka, tube current and voltage: 250 mA, 40 kV, scanning range: 10–80° 2θ, step size: 0.02° 2θ and scanning speed: 8°/minute.

3. Result and discussion

3.1. Initial characterizations

Before undergoing the roasting reduction, the chemical composition of the limonite ore was analyzed by XRF is given in Table 2.

Figure 1. The XRD Pattern of Limonite ore with (S) phases as Spinel (Al$_{1.835}$Cr$_{0.079}$Fe$_{0.221}$Mg$_{0.775}$Ni$_{0.014}$O$_4$Zn$_{0.007}$) and (G) phases as Goethite.
Based on that chemical composition, the XRD pattern resulted from XRD machine was analyzed by using Expert High Score Software to predict the phases that are presented in the limonite ore. And the result (Figure 1) showed that peaks from limonite ore sample matched with the goethite and spinel (Al1.835 Cr0.079 Fe0.221 Mg0.775 Ni0.014 O4 Zn0.007) phase patterns standard. So, it was confirmed that goethite and spinel were the main essential minerals in the limonite sample ore. Meanwhile, the invisibility of crystalline structure of nickel was suggested that nickel was associated with other elements and formed as spinel.

3.2. Effect of rice husk addition on phase transformation during reduction
The effect of rice husk addition on mineral transformation of limonite ores after roasting reduction at 1000°C is shown in Figure 2.

![Figure 2. XRD patterns of magnetic concentrates obtained from the pellets reduced at 1000°C for 60 minutes.](image)

In reference to Figure 2, the major phases that were present in sample 1 were magnetite, hematite, and trevorite. Meanwhile, NiO phase was not detected in the XRD pattern. It might happen due to the amount that was too small or existed in the trevorite form. Thermodynamically, trevorite phase, which might be formed due to the reduction of NiO by fixed carbon, was able to occur at low temperatures, namely 438 °C, as shown in Figure 3. In addition, NiO was easily reduced by CO. This was indicated by a negative value of the standard Gibbs free energy of reaction (3), and the curve of forming NiO was located above the forming of CO2, as shown in Figure 3.

\[
\begin{align*}
C + CO_2 &= 2CO \\
\Delta G^\circ &= 166550 - 171TJ/mol \\

NiO + C &= Ni + CO \\
\Delta G^\circ &= 124800 - 175TJ/mol \\

NiO + CO &= Ni + CO_2 \\
\Delta G^\circ &= -40590 - 0.42TJ/mol
\end{align*}
\]
Figure 3. Standard Gibbs free energy ($\Delta G^\theta$) of carbon oxide and nickel oxide.

From the XRD pattern of sample 2 in Figure 2, it could be observed that the presence of magnetite phase in sample 2 was noticeably increased if compared to the first sample. This was suspected due to the utilization of rice husk in the limonite ore during the reduction process. The rice husk helped to produce more CO gas used in the reduction process. The utilization of rice husk in the pellet assured that the limonite ore would be in contact with the rice husk and when the rice husk in the pellet was starting to produce CO gas, it came in contact with the limonite ore optimizing the process working in tandem with the rice husk used as the reduction agent.

The increased amount of the rice husk has impacted significantly with the XRD pattern of sample 3 compared with the XRD pattern of sample 1 and sample 2. Although the major phases that were present in sample 3 were hematite, magnetite, and trevorite, NiO started to appear clearly. The magnetite phase that existed in sample 3 was also more intense and existed in more angles than the magnetite phase in the XRD pattern of the previous samples. This was due to the trevorite phases that had been further reduced to NiO and magnetite, triggered by the increased amount of CO that was caused by the utilization of higher amount of rice husk in the limonite ore.

In Figure 2, the number of trevorite phase peaks (from sample 1 to sample 3) was increased with the increasing of rice husk amount; and the NiO phase had even been detected in sample 3. However, the trend was not observed in the XRD pattern sample 4 in which the amount was the largest rice husk. It was suspected that the amount of rice husk was too much. This caused NiO trapped in premature melt of silica husks (rice husk ash) and then separated as a tail in magnetic separation process [21].

3.3. Effect of rice husk addition on the Ni and Fe contents of magnetic concentrates after reduction

The Ni and Fe content of magnetic concentrate in each sample was detected by using AAS, as given in Table 4. As shown in the Table 4, the highest Ni content was obtained from samples 3, which was prepared by using 20% additional RH. In the range of 0-20%, the increasing of additional RH amount would lead to higher iron contents in magnetic concentrate. These results were similar to the effects of sawdust [22–24], where the addition of sawdust as reducing agents would increase the amount of magnetic iron ore concentrate in the form of magnetite phase.
Table 4. Nickel and iron contents in magnetic fraction as a function of rice husk addition.

| Code                      | Fe (wt.%)| Ni (wt.%) |
|---------------------------|----------|-----------|
| Limonite Ore              | 39.68    | 1.19      |
| Concentrate sample 1 (without RH) | 9.48    | 0.55      |
| Concentrate sample 2 (10% RH) | 8.28    | 0.61      |
| Concentrate sample 3 (20% RH) | 19.81   | 1.23      |
| Concentrate sample 4 (30% RH) | 7.47    | 0.27      |

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The amount of nickel content corresponding to the amount of iron content in various amounts of rice husk indicates a strong bond between nickel and iron in a compound. So it is more convinced that the Ni is incorporated in magnetite substance of one Fe atoms to form trevorite (NiFe$_2$O$_4$), as seen in the XRD pattern. Meanwhile, the relatively small nickel content in all concentrates indicates that most of the nickel content is in the tailings, so it is not attracted by magnets because of their smaller magnetic properties.

The interesting phenomenon was the decreasing Ni content in sample 4. This low amount of the Ni content in sample 4 was suspected due to the excess amount of the rice husk used in the process, which generated an excess tar and silica which act as a barrier for CO to reduce hematite. So, the fraction of magnetite and trevorite become low and affect to Ni recovery.

4. Conclusion
In this study, beneficiation of nickel from limonite ore was carried out by roasting reduction and magnetic separation. The increasing of Ni content was a result of the transformation of hematite into magnetite phase during roasting reduction by using rice husk as pellet addition and reducing gas agent. A small amount of nickel detected in the concentrate may be due to too strong a magnet being used. This causes a small amount of trevorite that should not be attracted by the magnet getting into the concentrate bin.

The optimum result, 1.23 % Ni, was reached in magnetic concentrate sample which was obtained from reduction of pellet with 20% additional RH. Nevertheless, it is still necessary to analyze the composition and the phase of the obtained tailings fraction to ascertain where the largest concentration of nickel, whether in concentrate or in tailings.

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