Effects of Na$_2$SO$_4$ addition on the selective reduction of limonite ore from Southeast Sulawesi

Rinanda Rahmat$^1$, Ahmad Maksum$^{1,2}$, Delfiendra$^3$ and Johny Wahyuadi Soedarsono$^1$

$^1$Center of Minerals Processing and Corrosion Research, Department of Metallurgical and Materials Engineering, Universitas Indonesia, Depok 16424, Indonesia
$^2$Department of Mechanical Engineering, Politeknik Negeri Jakarta, Depok 16425, Indonesia
$^3$Center for Testing and Identification of Goods, Directorate General of Customs and Excise, Jakarta, Indonesia

Email: jwsono@metal.ui.ac.id

Abstract. In terms of its process, although only about 40% of the world's nickel reserves are classified as lateritic ore, nickel sulfide still dominates nickel laterite for its practicality. Because of the high demands on nickel, development and research on nickel mineral processing are needed to ensure that the demands are fulfilled from year to year. On this research, a study will be conducted on the effect of adding Na$_2$SO$_4$ to increase the level of nickel content in limonite by selective reduction process. The reduction process is done by heating limonite ore and coal as reducer from room temperature to 1000°C with temperature rising to 10°C/minute in mini furnace on varying addition of 0%, 5%, 10%, and 15% Na$_2$SO$_4$. After that, the reduction result is tested on XRD and AAS. It has been found that the nickel content has decreased, which is likely due to the excessive reduction time resulting in the magnetite being re-oxidized to hematite. Therefore, based on recovery calculations, the optimal addition of Na$_2$SO$_4$ is 5% by weight where the obtaining nickel content is 1.09%.

1. Introduction

Indonesia has become the sixth country to have the most nickel reserve for about 4.5 million ton. The composition of nickel in the world is divided in to nickel laterite for 60% and nickel sulfide for 40%. One of the nickel processes is pyrometallurgy process. In Indonesia, processing nickel itself still relies on nickel sulfide because the processing of nickel laterite is quite complex and cost more money [1,2]. Subsequently, nickel laterite process was developed with selective reduction by adding sulfur additives. In a study, it is mentioned that adding sodium sulfate in a selective reduction of limonite has increased the nickel content in ferronickel from 2.3% to 9.48%. After that, through the magnetic separation process, the nickel recovery has increased from 56.97% to 83.01%. This study shows that the sulfur in Na$_2$SO$_4$ reacts with Fe to form FeS (troilite) which acts as an activation agent to accelerate the melting phase and increase the displacement rate to gain more aggregation of ferronickel particles during the reduction process [3]. Based on the aspects above and previous study [4], this study will discuss the effect on adding Na$_2$SO$_4$ in the selective reduction process with limonite ore using the coal reducer.
2. Materials and method

2.1. Materials
Limonite ore samples used in the study carried out initial characterization by XRD test. Figure 1 provides the XRD test result of nickel ore.

![Figure 1. XRD pattern of nickel ore’s initial sample.](image)

While for the quantity test, the AAS test is performed to see the Fe and Ni contents in the limonite ore. The AAS test result can be seen in Table 1.

Beside the limonite, coal as a reductor was also tested with proximate and ultimate test to see the composition of the coal. The test results can be seen in Table 2.

| Table 1. Atomic absorption spectroscopy analysis of iron, nickel, and cobalt content from limonite ore. |
|-------------------------------------------------|
| **Element** | **Content (%)** |
| Fe       | 41.46            |
| Ni       | 1.16             |

2.2. Experiment
This selective reduction process takes place in a mini furnace. The limonite ore samples which has been processed into a fine powder (#300) were mixed with 6% of coal with the same mesh size and Na$_2$SO$_4$ with 0%, 5%, 10%, and 15% levels, and added by 3% of bentonite. After that, the samples were shaped into pellets with a small amount of water. The water content was removed by heat in the oven at 100°C for about 2 hours. After it dries, the samples can be put into a mini furnace. The reduction process of limonite ore is done in the range of 1000°C with constant temperature rise of 10°C /minute. According to the furnace procedure, the temperature is raised up to 60% of the target temperature and held for about 10 minutes, and then raised again until the target temperature that is 1000°C and held again for an hour. The cooling process is done inside the furnace. After the reduction process, AAS test was performed to determine the level of Fe and Ni on the limonite which has been under reduction. Also, XRD test is being held to analyze the compounds and nickel contents which were contained in the laterite ore.
### Table 2. Proximate and Ultimate Analysis of Coal.

| Parameter               | Content (% adb) |
|-------------------------|-----------------|
| **Proximate Analysis**  |                 |
| Moisture in air dried sample | 7.26           |
| Ash                     | 15.87           |
| Volatile Matter         | 16.44           |
| Fixed Carbon            | 60.43           |
| **Ultimate Analysis**   |                 |
| Carbon                  | 64.02           |
| Hydrogen                | 3.11            |
| Nitrogen                | 0.60            |
| Oxygen                  | 16.32           |

#### 3. Result and discussion

The XRD pattern of samples which has been under selective reduction on all Na$_2$SO$_4$ addition variations can be seen on Figure 2. It was shown that after undergoing reductions, the phases which present in the initial sample like lizardite, goethite, and kaolin was no longer seen. During the reduction process, goethite, and lizardite phase were facing dehydroxylation for the first time [5]. Dehydroxylation is a structural transformation or change that leads to the destruction of OH-group structures or the loss of water bonds in the crystalline of mineral. This process occurs naturally during reduction as a result of heat, and the next step is re-forming of the other crystalline structures.

From the XRD results above, there were four types of samples that contain hematite and magnetite compounds. This results showed that the reducer was not yet capable of reducing all hematite to become magnetite, wustite, or metallic iron. Furthermore, while SiO$_2$ was still in the reduction sample, the SiO$_2$ content will decrease as the temperature goes higher. This reduction was done at 1000°C where silica reduction starts at 1200°C. Regardless of the various temperature, the reduction temperature from SiO$_2$ could be decreased by the milling process [6]. It was predicted that the milling process of coal and nickel was done least from perfect because it was only done for 30 minutes. Moreover, the mix between Na$_2$SO$_4$ and bentonite was done manually and without the milling process. Consequently, the SiO$_2$ that were formed are still quite a lot.

The present of MgO in each reduced samples indicate that the MgO has not been fully reduced and reacts with other elements. Anyhow, some MgO reacted with other elements and formed a forsterite.

The formation of forsterite allowed oxide grains closure and prevented further reduction of nickel and iron. Also, sulfur had a major impact in this forsterite phase.

The presence of forsterite in XRD samples are possible due to the mixing of limonite, coal, and Na$_2$SO$_4$ were not yet formed as a well physical and chemical bond, thus making the samples less smooth and less reactive. As what has been mentioned above, only the mixing of limonite and coal used ball mill while the mixing of Na$_2$SO$_4$ was done manually. It was known that the ball milling was one of the mechanical activities which could improve the surface area, improve the surface reactivity, and reduce the particle size of powder [6]. As the mechanical was activated during the milling, the reduction reaction rate would increase and the sample would be optimized to 1000°C.

The AAS test also aims to see the Fe and Ni contents after the reduction is done which later lay out the recovery calculation. The AAS samples results which have been reduced can be seen in Table 3.
Figure 2. XRD pattern of initial nickel lateritic ore.

Table 3. Comparison of nickel and iron content of limonite between ore and after reduction samples.

| Element | Ore | After reduction | Unit |
|---------|-----|----------------|------|
|         |     | 0% Na₂SO₄ | 5% Na₂SO₄ | 10% Na₂SO₄ | 15% Na₂SO₄ |
| Fe      | 41.46 | 8.38   | 16.34   | 13.49    | 7.64    | % w/w   |
| Ni      | 1.16  | 0.32   | 1.09    | 1.00     | 0.67    | % w/w   |

The comparison data can be seen in Table 3. From the table above, it can be seen that after being reduced, there is a content decrease both in Fe and Ni. This can happen because of the time and duration during the reduction which have an important role in the reduction process [7]. Using the reduction time including the cooling phase for about 5 hours will have an effect on the level or concentrate of the results in reduction. This decrease also can be caused due to the weary reducer that has been used quite long. Moreover, the long the reduction goes, there will be an increase in CO₂ concentrate that cause the limit in gas-solid reaction to be filled by CO₂ which later can obstruct the reduction process [7].

The occurrence of this decline can also due to the wustite peak intensity weakened when the reaction time is extended. This extension can increase the nickel and iron accessions, yet decrease the contents of both materials. When the reduction time is shortened, the wustite reduction rate becomes slower and the hematite will block the diffusion from NiO resulting nickel with higher contents [8].

Even so, if it was seen from the four parameter that add the sulfur contents, the sulfur can actually capable of giving better nickel contents beside without an addition of Na₂SO₄.

The comparison of nickel and iron content can be seen from this graph at Figure 3 below.
Recovery calculation shows that by adding Na$_2$SO$_4$ for 5% can gives the maximum results compare to other vary additions. The recovery result can be seen in Table 4 and Table 5.

### Table 4. Nickel recovery.

| Sample  | Concentrate weight, C (gr) | Ni Concentrate, c (%) | Ore weight, F (gr) | Ni ore, f (%) | Ni recovery |
|---------|---------------------------|-----------------------|-------------------|--------------|------------|
| 0% Na$_2$SO$_4$ | 12.6581                  | 0.32                  | 20.6067           | 1.16         | 16.9%      |
| 5% Na$_2$SO$_4$ | 13.0191                  | 1.09                  | 21.6377           | 1.16         | 56.56%     |
| 10% Na$_2$SO$_4$ | 11.2490                  | 1.00                  | 20.0248           | 1.16         | 48.42%     |
| 15% Na$_2$SO$_4$ | 12.4028                  | 0.67                  | 20.3553           | 1.16         | 23.61%     |

### Table 5. Iron recovery.

| Sample  | Concentrate weight, C (gr) | Fe Concentrate, c (%) | Ore weight, F (gr) | Fe ore, f (%) | Fe recovery |
|---------|---------------------------|-----------------------|-------------------|--------------|------------|
| 0% Na$_2$SO$_4$ | 12.6581                  | 8.38                  | 20.6067           | 41.46        | 12.41%     |
| 5% Na$_2$SO$_4$ | 13.0191                  | 16.18                 | 21.6377           | 41.46        | 23.48%     |
| 10% Na$_2$SO$_4$ | 11.2490                  | 13.49                 | 20.0248           | 41.46        | 18.28%     |
| 15% Na$_2$SO$_4$ | 12.4028                  | 7.64                  | 20.3553           | 41.46        | 11.22%     |

From the Figure 4 below, it can be seen the comparison of recovery of nickel and iron after reduction by variation of Na$_2$SO$_4$.

**Figure 3.** Comparison of nickel and iron content of limonite between after reduction samples with variation of sulfur addition.

**Figure 4.** Comparison of nickel and iron recovery of limonite after reduction samples with variation of sulfur addition.
4. Conclusion

Adding extra sulfur in reduction process can increase the nickel and iron contents. It is mentioned before that the initial sample has 1.16% nickel. After the reduction for additional 0%, 5%, 10%, and 15% Na2SO4, each nickel contents obtained 0.32%, 1.09%, 1.00%, and 0.67%. Meanwhile, the iron contents in initial sample is 41.46% and after being reduced with additional 0%, 5%, 10% and 15% Na2SO4, the iron contents gain 8.38%, 16.34%, 13.49%, 7.64%.

Although limonite selective reduction is supposed to be able to increase the nickel content. However, this study shows that the selective reduction decreasing the nickel and iron contents compared to samples before they undergo reduction. One of the factors that may affect the result is the duration during reduction.

But, the nickel and iron value after the reduction tends to be better with sulfur addition. For nickel, when it is added 0% of Na2SO4, the value becomes 16.9%. As for the addition of 5%, 10% and 15%, the nickel obtains 55.56%, 48.42% and 23.61% respectively.

The fact that the contents and recovery have a decrease when sulfur was added for more than 5%, shows that adding sulfur has an optimal value for each reductions.

Based on XRD test result, there is no ferronickel in each samples. This may be caused of the imperfect reduction of hematite into magnetite, wustite, and metallic iron. As for iron oxide and nickel oxide, they react to sulfur and form NiS and FeS.

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