

The effect of NaOH (natrium hydroxide) to slag nickel pyrometallurgy in different temperature and additive ratio

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Abstract. Nickel slag is one of the output from nickel ore smelting. In Indonesia itself, further utilization of valuable elements in it is needed to be processed. Nickel slag also has Fayalite (Fe_2SiO_4) content where nickel and copper are spread evenly on the iron matrix silica which then complicate the process of increasing nickel and copper content. The addition of Sodium Carbonate (Naoh) is used as a silica binder and as an alternative way to increase nickel and copper content. In this research, pyrometallurgy is done by coal as a reductor in 800°C, 900°C and 1000°C operating temperature and ratio between nickel slag and additive equal to 1:1, 1:2, and 2:1. Based on this study, it is obtained that with the increasing of temperature without additive, there is still found the presence of silica in a form of Fe-rich Forsterite (FeMgSiO_4) and Olivine (NiMgSiO_4). Whereas with the presence of additive in slag nickel pyrometallurgy with a different temperature and ratio, it is seen that there is a phase formation of Sdoium Magnesiosilicate ($\text{Na}_2\text{MgSiO}_4$), Magnesium Oxide (MgO) and Wustite (FeO) which proved the binding of silica and has liberate iron that helps the process of increasing nickel and copper content.

1 Introduction

Indonesia is one of the countries with nickel reserves in the world's largest laterite ore. The nickel ore processing can be separated from byproducts [1]. The byproducts found in this nickel slag are cobalt, nickel, and copper. Other content contained in nickel slag is fayalite (Fe_2SiO_4) where nickel and copper elements are distributed evenly on this silica iron matrix which then complicates the process of increasing nickel and copper levels [2], [3]. Considering to previous studies that several authors already used sodium hydroxide to eliminate silica from nickel laterite [4]–[6] and tin slag [7] in their experiment, the addition of sodium hydroxide additives (NaOH) which aims to bind silica in nickel slag has been investigated in this research. Therefore, this research will examine how the increase of the precious metal with the effect of adding additives to nickel, cobalt and copper metal reduction methods. With this research, the authors hope to contribute to future research.

2 Materials and method

Table 1. Result of XRF test Nickel Slag

| Element | Content |
|---------|-----------|
| Si | 25,02% |
| Fe | 7,20% |
| Co | 64 ppm |
| Ni | 430,6 ppm |

Table 2. ICP OES of initial sample

| Element | Content (%) |
|---------|-------------|
| Fe | 6,460 |
| Ni | 0,101 |
| Mg | 13,038 |
| Cu | 0,004 |

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2.1. Materials

In this research XRF, ICP, OES, and XRD are used to know the characterization of initial samples which

aims to know what compounds are contained in nickel slag.

In this research the reductor used is coal. Coal serves to reduce the oxide compounds present in the nickel slag. The specification data of coal used for the pyrometallurgical process is obtained from BATAN.

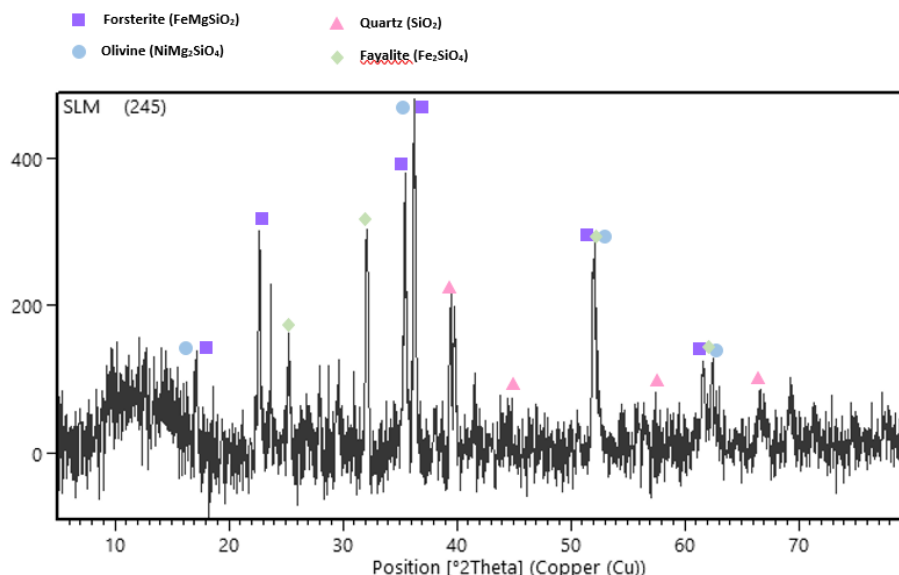


Fig. 1. XRD results of initial sample

Table 3. Semi-quantitative analysis of initial sample

| Compound Name | Chemical Formula | Semi-Quant (%) |
|--------------------|----------------------------------|----------------|
| Fe-rich Forsterite | FeMgSiO ₄ | 27,8 |
| Olivine | NiMgSiO ₄ | 32,1 |
| Quartz | SiO ₂ | 2,3 |
| Fayalite | Fe ₂ SiO ₄ | 37,8 |

Table 4. Coal component as reductor

| Component | Volatile Matter | Ash | Fixed Carbon | S | Moisture | Calories Value (Cal/g) |
|-----------|-----------------|-------|--------------|------|----------|------------------------|
| % | 36,26 | 14,39 | 36,92 | 0,91 | 14,4 | 6047 |

2.2. Experiment

The first step taken in this study is the reduction of the size of the nickel slag using a milling machine by entering the sample into the tube along with the ball mill. The tube is then placed on the milling machine. The next process is sieving using a sieve shaker up to # 200. After the reduction of size, the slag nickel is incorporated into the crucible and added the coal

reducer where the research has 2 variables namely temperature and ratio ratio between slag nickel with NaOH additive. In the temperature variable, pyrometallurgy was performed with the addition of coal and additives of 2 grams and 20 grams at 800°C, 900°C and 1000°C for 1 hour, respectively. The weight ratio between nickel slag and additives is 1:1, 1:2, and 2:1, while the pyrometallurgy temperature is at 1000°C for 1 hour in a muffle furnace.

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3 Result and discussion

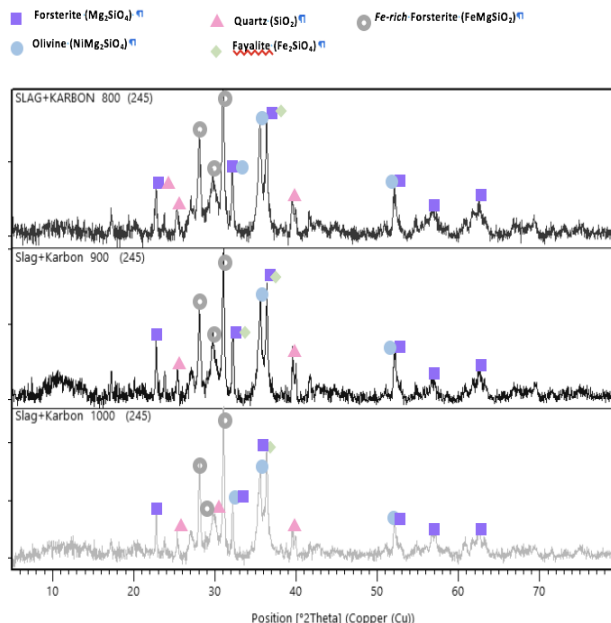


Fig. 2. XRD result of nickel slag pyrometallurgy process in different temperature without additive

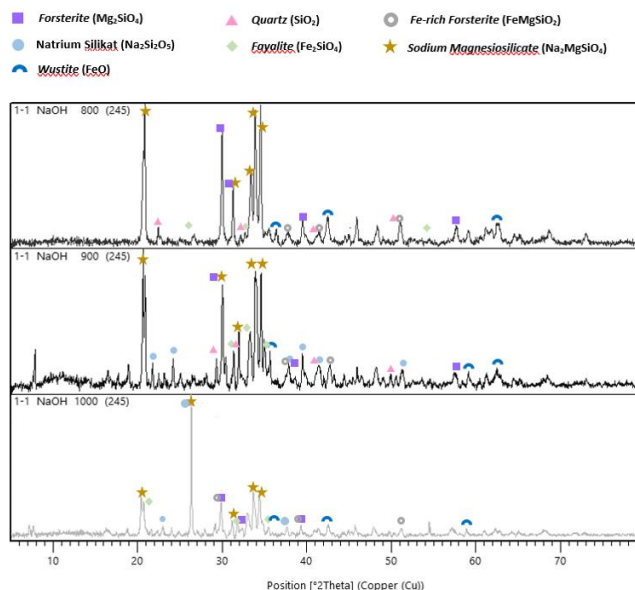
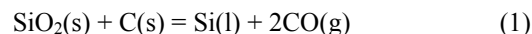


Fig. 3. XRD result of nickel slag pyrometallurgy process in different temperature with NaOH addition.

Based on data from Figure 2 and Table 5 the most common compound in slag is fe-rich forsterite. The composition of SiO₂ compounds in this nickel slag decreases with increasing temperature.

In Table 5 it can be seen at temperatures of 800°C quartz content of only 1.4%. When compared with the initial slag that has not been given the

pyrometallurgical treatment in Table 4.3, there is a decrease in the levels of Silica Dioxide. This occurs because of the reduction of silica into silicon by the addition of coal as a reducing agent, it can be seen from Reaction 1.



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The decrease in SiO₂ levels in the nickel slag has led to an increase in the precious mineral content in the increased nickel slag. So, the most optimal temperature of this test is 1000 °C. In Figure 2 it can be seen that the addition of temperature, the effect of this temperature addition informs that not much phase change occurs with some changes in semi-quantity based on Table 5. It can be seen also that the decrease in Fe-rich Forsterite levels in the presence

of an increase in temperature of 800°C , 900°C, and 1000°C each have levels of 71%, 67.8%, and 55.7% respectively.

In Table 5 it can be seen that fayalite and olivine levels do not show significant change. This indicates that the compound belongs to the silicate-bearing group in which to reduce the compound requires a complicated condition.

Table 6. Semi-quant results of nickel slag pyrometallurgy process in different temperature without additive

| Compound Name | Chemical Formula | Semi-Quant (%) | | |
|----------------------|----------------------------------|----------------|-------|--------|
| | | 800°C | 900°C | 1000°C |
| Fe – rich Forsterite | FeMgSiO ₄ | 71 | 67,8 | 55,7 |
| Olivine | NiMgSiO ₄ | 9,2 | 8,1 | 8,2 |
| Forsterite | Mg ₂ SiO ₄ | 7,6 | 7,2 | 6,8 |
| Quartz | SiO ₂ | 1,4 | 6,4 | 19,7 |
| Fayalite | Fe ₂ SiO ₄ | 11,0 | 10,5 | 9,7 |

Table 7. Semi-quant result of nickel slag pyrometallurgy process in different temperature with addition of NaOH

| Compound Name | Chemical Formula | Semi-Quant (%) | | |
|-------------------------|------------------------------------|----------------|--------------|---------------|
| | | 800°C + NaOH | 900°C + NaOH | 1000°C + NaOH |
| Fe – rich Forsterite | FeMgSiO ₄ | 20,4 | 6,3 | 18,5 |
| Olivine | NiMgSiO ₄ | 12,0 | 6,8 | - |
| Forsterite | Mg ₂ SiO ₄ | 25,9 | 12,3 | 23,2 |
| Quartz | SiO ₂ | 1,3 | 18,2 | 2,7 |
| Fayalite | Fe ₂ SiO ₄ | 16,8 | 9,2 | - |
| Sodium Magnesiosilicate | Na ₂ MgSiO ₄ | 22,8 | 36,2 | 29,4 |
| Magnesium Oksida | MgO | 0,8 | 0,4 | 1,1 |
| Hematit | Fe ₂ O ₃ | - | 10,6 | 25,1 |

It can be seen in Figure 3 the dominant compound with the addition of NaOH additive both at temperature 800°C, 900°C, and 1000°C with holding time for 1 hour ie Sodium Magnesiosilicate (Na₂MgSiO₄) and Forsterite (MgSiO₄) compounds. At the temperature of 800 ° C can be seen the dominant compounds are Sodium Magnesiosilicate and forsterite. With the addition of temperature from 800oC to 900°C the previous phase is Forsterite turns phase into Sodium Magnesiosilicate. This indicates that an increase in temperature and the addition of a 7u additive of NaOH may increase the effectiveness of the binding of Magnesium Silicate where the addition of NaOH can bind Magnesium Silicate in the form of Sodium Magnesiosilicate before finally turning phase into Sodium Silicate and freeing Mg[8].

While iron (Fe) contained in Fe-rich forsterite is released into Wustite this is because the phases

originally Fe-rich forsterite (FeMgSiO₂) become Sodium Silicate (Na₂SiO₅).

As is well known, the nickel slag used in this study also contains Silica in the form of Fayalite (Fe₂SiO₄) compounds in Fig. 3 with the addition of NaOH to the conversion of the compound into Na₂Si₂O₅ and FeO. Based on Table 6, there is the presence of Sodium Silicate where based on semi-quant data seen at increasing temperature of 800 °C, 900°C and 1000°C of Sodium Silicate content respectively 21.6%, 35.4% and 28.4%. In addition to these compounds, it can be seen that there is a Wustite presence at temperatures of 800 ° C, 900 ° C and 1000 ° C each 0.3%, 1.2% and 0.3%. Can be seen from Figure 3 at temperature 1000°C it is seen that the formation of sodium silicate and wustite decreased when compared to the previous temperature that is 900°C which has increased significantly indicates ineffective use of adding

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NaOH additives at 1000 ° C at nickel slag extraction. From the data obtained can be concluded that the effectiveness of adding additive NaOH with temperature change is present at temperature 900°C.

Based on Figure 4 it can be seen that there is an increase in NaOH additive content by comparison ratio between slag nickel and its additive. It can be seen in the 2:1 ratio that the dominant compound is Fe-rich Forsterite of 60.1%. With the addition of NaOH additives, Fe-rich Forsterite phase has turned phase into Forsterite which has liberated iron in the

form of Wustite (FeO) with the binding of silica in the form of Sodium Silicate (Na₂Si₂O₅). This can be seen in the calculation of semi-quant where the ratio ratio of 1: 2, 1: 1 and 2: 1 showed that Fe-rich Forsterite content of 60.1%, 7.7% and 4.6% respectively Wustite respectively 0.2%, 0.3% and 18.9% respectively. The reaction of FeO formation can be seen in the following equation:

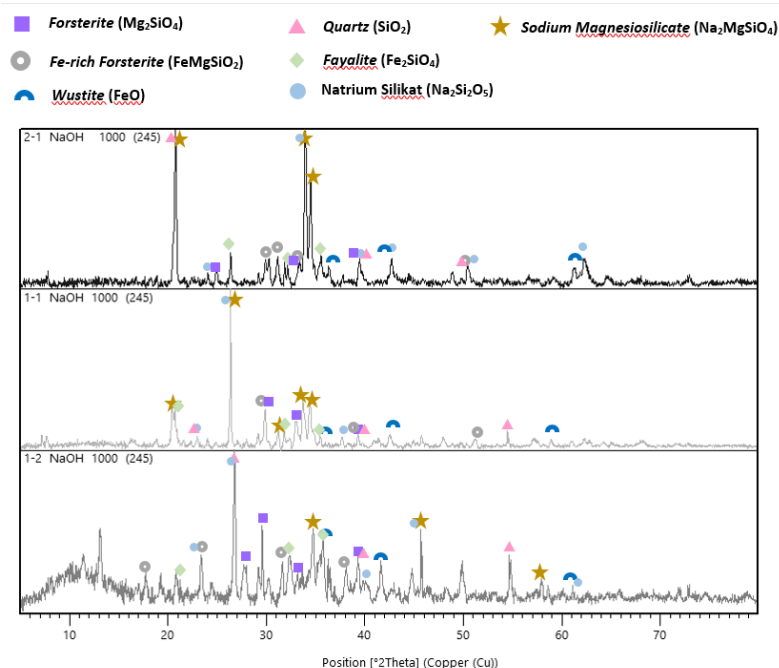
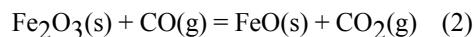


Fig. 4. XRD result of nickel slag pyrometallurgy process different ratio between nickel slag and NaOH addition

Table 8. Semi-quant result of nickel slag pyrometallurgy process in different ratio between nickel slag and NaOH addition

| Compound Name | Chemical Formula | Semi-Quant (%) | | |
|-------------------------|------------------------------------|----------------------------------|----------------------------------|----------------------------------|
| | | Slag Ratio dan Additive NaOH 1:2 | Slag Ratio dan Additive NaOH 1:1 | Slag Ratio dan Additive NaOH 2:1 |
| Fe – rich Forsterite | FeMgSiO ₄ | 9,2 | 18,5 | 14,9 |
| Olivine | NiMgSiO ₄ | 10,7 | - | - |
| Forsterite | Mg ₂ SiO ₄ | - | 23,2 | 24,3 |
| Quartz | SiO ₂ | - | 2,7 | 1,0 |
| Fayalite | Fe ₂ SiO ₄ | 12,7 | - | - |
| Sodium Magnesiosilicate | Na ₂ MgSiO ₄ | 51,7 | 29,4 | 30,0 |
| Magnesium Oksida | MgO | 0,6 | 1,1 | 1,0 |
| Hematit | Fe ₂ O ₃ | 15,1 | 25,1 | 28,8 |

The formation of wustite produces a side compound of Sodium Silicate which in the ratio of 1:2, 1:1 and 2:1 respectively have levels of 19.1%, 28.4%, and

40.5%. In addition, there was a decrease in SiO₂ levels at 1:2 and 1:1 levels initially having a 1.2% concentration based on semi-quantity calculations,

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and with the addition of NaOH additive there was a decrease in SiO₂ content to 0.8%. This shows that silica has been bound to form Sodium Silicate and the exemption of iron into a wustite shape.

4 Conclusion

The type of mineral used in this research is classified as silicate-bearing and to reduce this type of mineral needed more complicated condition. Addition of NaOH indicates the initial phase of Fe-rich Forsterite (FeMgSiO₂) undergoes phase change to Sodium Magnesiosilicate (Na₂MgSiO₄) and Magnesium Oxide (MgO) as well as Iron (Fe) reduction to Hematite (Fe₂O₃). The formation of Hematite in the increase of temperature and disappearance of fayalite in the increase of NaOH addition indicates the liberation of Iron (Fe) which is bonded to magnesium silicate in the form of Fe-rich Forsterite (FeMgSiO₄) and binding Magnesium Silicate in the form of Sodium Magnesiosilicate.

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References

1. K. Quast, J. N. Connor, W. Skinner, D. J. Robinson, and J. Addai-mensah, "Preconcentration strategies in the processing of nickel laterite ores Part 1 : Literature review," *Miner. Eng.*, vol. 79, pp. 261–268, 2015.
2. S. Wang, C. Wang, Q. Wang, W. Ni, and K. Li, "Optimization and microstructure study of the reduction of nickel smelting slag mixed with calcium carbide slag and coke dust for recovering iron," *Chem. Eng. Trans.*, vol. 62, pp. 55–60, 2017.
3. Z. Guo, D. Zhu, J. Pan, and F. Zhang, "Mineralogical Characteristics and Preliminary Beneficiation of Nickel Slag from Reduction Roasting-Ammonia Leaching," *Minerals*, vol. 7, no. 6, p. 98, 2017.
4. T. W. Samadhi, "Thermochemical analysis of laterite ore alkali roasting: Comparison of sodium carbonate, sodium sulfate, and sodium hydroxide," *AIP Conf. Proc.*, vol. 1805, no. 40008, pp. 1–5, 2017.
5. M. Hutton-ashkenny, D. Ibana, and K. R. Barnard, "Reagent selection for recovery of nickel and cobalt from nitric acid nickel laterite leach solutions by solvent extraction," *Miner. Eng.*, vol. 77, pp. 42–51, 2015.
6. Q. Guo, J. Qu, T. Qi, G. Wei, and B. Han, "Activation pretreatment of limonitic laterite ores by alkali-roasting using NaOH," *Int. J. Miner. Metall. Mater.*, vol. 19, no. 2, pp. 100–105, 2012.
7. Sulaksana Permana, J. W. Soedarsono, A. Rustandi, and A. Maksum, "Other Oxides Pre-removed from Bangka Tin Slag to Produce a High Grade Tantalum and Niobium Oxides Concentrate," in *IOP Conference Series : Materials Science and Engineering*, 2016, vol. 131, pp. 10–20.
8. T. Yang, X. Yao, and Z. Zhang, "Geopolymer prepared with high-magnesium nickel slag: Characterization of properties and microstructure," *Constr. Build. Mater.*, vol. 59, pp. 188–194, 2014.

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