The effect of addition of sodium sulphate (Na₂SO₄) to nickel slag pyrometallurgical process with temperature and additives ratio as variables

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Abstract. Nickel industry is one of the most strategic industries because its widely used. Nickel slag as a by-product of nickel processing presents the potential for improving process efficiency. In this study aim to determine the effect of the addition of sodium sulfate additives and also the temperature in the reduction process of nickel slag. The research was preceded by preparation of nickel slag samples with crushing and sieving up to 200 mesh. The nickel slag is then reduced at 800°C, 900°C and 1000°C temperature without adding sodium sulfate and by adding sodium sulfate with 1 hour holding time. Furthermore, the results of the reduction is done XRD and AAS testing to see changes in the content of elements and compounds in nickel slag that has been tested. The results of the study explain that the content of the dominant impurities which is in the form of SiO₂ decreases as the temperature of the reduction and iron from Fe-rich Forsterite compounds will be liberated and will bind to sulfur derived from sodium sulfate to form troilite (FeS). This results in an increasing content of valuable minerals present in the nickel slag.

1. Introduction

We can say that industry of metal in Indonesia is the catalyst of other industries. Nickel industry is one of the most important metal industries that have many uses in our daily life. There are a variety of nickel products, 62% of nickel metal is used in stainless steel, 13% of them is used in super-alloys and non-ferrous alloys because it has good corrosion resistance properties and also has good resistance to applications in high temperatures [1].

Nickel ores can be classified into two groups: sulfide ores and laterite ores (oxides and silicates). In fact, 70% of the nickel mine has a base of laterite ore, but 60% of the primary nickel production has a sulfide ore base [1]. Processing of nickel ore that is done in Indonesia is nickel in laterite form. This lateritic nickel ore comes from ferro-magnesium silicate minerals commonly found in Sorowako, South Sulawesi[2]. The products of this nickel ore processing process also produce byproducts. This by-product of nickel ore is commonly referred to as nickel slag. Nickel slag is one of the result of processing and smelting of nickel ore. In Indonesia, there is still need for a deeper understanding of the further utilization of nickel slag especially on the

processing of the valuable elements contained therein.

The nickel slag, which is the result of the smelting, usually contains some valuable elements such as cobalt, nickel and copper where these valuable elements can exist in the form of sulphides, oxides or free elements [3]. However, the content of these non-ferrous elements is lower when compared to the iron content in the slag so as to enhance this non-ferrous element can be done by the reduction method[3]–[5].

Another content which contained in the nickel slag is fayalite (Fe₂SiO₄) in which the nickel and copper element distribution is spread evenly on this silica iron matrix which makes it difficult for the process of increasing the nickel and copper content. The addition of sodium sulfate as additive (Na₂SO₄) serves to bind the silica so it can be used as an alternative method to increase the nickel and copper element content in nickel slag[6]. Additive expected to bind Fe then form FeS according to the equation (1), (2), (3), and (4) so that content of Fe will decrease causing the Ni content to increase.

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• Binding of Fe form FeS

Almost all slags of nickel smelting have the following content of 0.04 - 1.2% Ni, 0.21 - 0.7% Co, and 0.6 - 3.7% Cu. While the slag generated from the converter contains 2.87 - 4.8% Ni, 0.77 - 1.59% Co, 0.17 - 1.4% Cu. The content of valuable mineral content of both processes has a higher value compared to laterite nickel ore of 1.05 - 2.3% Ni and 0.05 - 0.3% Co. The slags derived from nickel contain more than 98% Fe and Co, and 54 - 95% Ni and Cu in the oxide form depending on the treatment method and the type of the furnace. Whereas, there are less than 2% Fe and Co, and 4 - 5% Ni and Cu in sulfide form[7]. Based on these data, when compared with laterite ore, nickel slag can be one source of precious metals because it has a high content of nickel and copper.

2. Materials and method

2.1. Materials

The sample used in this research is nickel slag powder originating from Sulawesi. The sample preparation is the initial characterization process using XRF, ICP, and XRD. Preparation of samples to be performed before undertaking the study is a reduction in the size of the nickel slag using a milling machine by inserting the sample into a sample tube previously weighed in advance with a ratio of nickel slag samples to a ball mill of 1: 4. Then the weighted nickel slag is inserted into the tube along with the ball mill. The tube is then placed on a milling machine. When the size of the slag nickel has been reduced, the sieving process continues using a sieve shaker up to # 200.

After reducing the size of the nickel slag, proceed with the analysis of compounds and elements using XRD, ICP, and XRF.

2.2. Experiment

The process included the sample preparation (initial characterization and ball milling), the reduction, and The roasting process that performed in this study using coke as reductor. Preparation was done by weighing 2 grams of reductor as well as nickel slag and additives Na₂SO₄ 20 gram each for a ratio of 1: 1 and weighing for comparison between slag nickel and additives of 1: 2 and 2: 1. Each of the weighed samples was mixed and separated into 6 reaction tubes comprising 3 additive-free tubes and 3 test

tubes with additives according to their ratio ratios. Each tube is then inserted into the plastic and stirred so that the reducing agents, additives and nickel are evenly mixed. After the mixture is evenly mixed, the sample is put into crucible and on the top of it closed using glasswool which is aimed so that the sample contained in crucible is not directly oxidized.

Crucible which has been covered by glasswool then given charcoal on the top so that the roasting process can occur evenly. Then, crucible is placed inside the muffle furnace with operating temperature of 800°C, 900°C and 1000°C for 1 hour. After the roasting process finish, crucible is removed from the muffle furnace using iron bars and allowed to stand before the samples contained therein are then removed and weighed.

3. Result and discussion

3.1. Slag Nickel Characterization

Phase identification of nickel slag is carried out using XRF, ICP OES, and XRD. This nickel slag has been done size reduction and sieved with a size of 200 mesh. The result of the XRF test can be seen in Table 1.

Table 1. Result of XRF test Nickel Slag

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

XRF testing will produce list of elements that is contained in the nickel slag. From the table, we can see that the dominant elements are Si and Fe. Another test that used to identify phase contained in nickel slag is ICP OES. The result of nickel slag testing by ICP OES can be seen in Table 2.

Table 2. Result of ICP OES Test Nickel Slag

Element	Content (%)
Si	0,004112
Fe	6,460345
Co	0,0042
Ni	0,101
Mg	13,0383

The data obtained by XRD PANaliticalc Empyrean

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testing is processed using software named HighScore Plus and the result can be seen in Figure 1 and Table 3. In this test, there is a restriction in the search of compound contained in slag nickel. The compound sought in *HighScore Plus* software are only compounds that containing iron, magnesium, and silica.

The results of this test will produce peaks indicating the compounds contained in the nickel slag. The higher peak formed indicates more phases found in nickel slag, so from the peak analysis the dominant phase in the nickel slag is Fe-rich Forsterite (FeMgSiO_4). There are also Olivine ($\text{NiMg}_2\text{SiO}_4$), Quartz (SiO_2) and Fayalite (Fe_2SiO_4).

Fig. 1. Result of XRD Test of Nickel Slag

Table 3. Semi-Quant Data Calculation of Nickel Slag by *HighScore Plus*

Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO_4	42,7
<i>Olivine</i>	$\text{NiMg}_2\text{SiO}_4$	22,8
<i>Quartz</i>	SiO_2	4,7
<i>Fayalite</i>	Fe_2SiO_4	29,8

3.2. Characterization of Coal as Reductor

Nickel slag pyrometallurgy process in this research is done by coal as the redactor where its composition is got from BATAN and can be seen in Table 4. The pyrometallurgy process is also done by Na_2SO_4 as additive.

3.3. Effect of Temperature

3.3.1. Effect of Temperature to Nickel Slag

The temperature of roasting process has great effect to the change of compound composition which contained in nickel slag. The change of compound

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composition determined by activation energy each compound to get free then form a new compound.

Tabel 2. Coal Specification That is Used as Reductor

Komponen	Zat Terbang	Abu	Fixed Carbon	S	Moisture	Calories Value (Cal/g)
%	36,26	14,39	36,92	0,91	14,4	6047

Fig. 2. Result of XRD Test Nickel Slag that is done in Different Temperature

Table 5. Composition of nickel slag roasted at 800°C

800°C		
Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO ₂	21,40%
<i>Forsterite</i>	Mg ₂ SiO ₄	19,90%
<i>Olivine</i>	NiMg ₂ SiO ₄	25%
<i>Fayalite</i>	Fe ₂ SiO ₄	29%
<i>Quartz</i>	SiO ₂	4,60%

Table 6. Composition of nickel slag roasted at 900°C

900°C		
Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO ₂	21,50%
<i>Forsterite</i>	Mg ₂ SiO ₄	20,70%
<i>Olivine</i>	NiMg ₂ SiO ₄	22,90%
<i>Fayalite</i>	Fe ₂ SiO ₄	30,10%
<i>Quartz</i>	SiO ₂	4,70%

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Table 7. Composition of nickel slag roasted at 1000°C

1000°C		
Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO ₂	21,40%
<i>Forsterite</i>	Mg ₂ SiO ₄	22,10%
<i>Olivine</i>	NiMg ₂ SiO ₄	23,10%
<i>Fayalite</i>	Fe ₂ SiO ₄	28,40%
<i>Quartz</i>	SiO ₂	5,00%

From the data above, can be seen the change of the composition of compounds contained in the slag nickel with temperature as variables without additive. As temperature increases, the composition of the compounds present in the nickel slag does not show significant changes and tends to remain. According to Rinanda et. al [8], the reduction process with temperature as variable with 1 hour holding time with increasing temperature, the composition of SiO₂ compounds tends to remain, comparable with other compounds present in nickel slag which tend to remain in line with the increasing of reduction temperature. This is because the SiO₂ compound undergoes a change reaction from silica to silicon according to equation 4.

3.3.2. Effect of Temperature to Nickel Slag with additive (Na₂SO₄)

To see the effect of temperature to enhance grade of valuable element in nickel slag with use of Sodium Sulphate (Na₂SO₄) as additive by the ratio 1:1, reduction done with many temperature. The enhancement of valuable element expected to be done at optimum temperature.

Fig. 3. Result of reduction process with addition of Na₂SO₄ to nickel slag with ratio 1:1

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Table 8. Composition of nickel slag roasted at 800°C with addition of Na₂SO₄

800°C		
Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO ₂	16,5
<i>Troilite</i>	FeS	36,6
<i>Olivine</i>	NiMg ₂ SiO ₄	19,9
<i>Fayalite</i>	Fe ₂ SiO ₄	23,3
<i>Quartz</i>	SiO ₂	3,7

Table 9. Composition of nickel slag roasted at 900°C with addition of Na₂SO₄

900°C		
Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO ₂	16,8
<i>Troilite</i>	FeS	37,4
<i>Olivine</i>	NiMg ₂ SiO ₄	20,3
<i>Fayalite</i>	Fe ₂ SiO ₄	22,9
<i>Quartz</i>	SiO ₂	2,6

Table 10. Composition of nickel slag roasted at 1000°C with addition of Na₂SO₄

1000°C		
Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO ₂	17,5
<i>Troilite</i>	FeS	39,2
<i>Olivine</i>	NiMg ₂ SiO ₄	20,7
<i>Fayalite</i>	Fe ₂ SiO ₄	21,8
<i>Quartz</i>	SiO ₂	0,8

Based on data above, it can be seen that with the addition of Na₂SO₄ to nickel slag with the variation of the reduction temperature at 800°C, 900°C, and 1000°C with holding time of 1 hour, the higher the temperature there will be less SiO₂ present in nickel slag [9]. It can also be seen that the content of other compound which is Fayalite decreased. This is due to Fe being liberated at the time of reduction so that when Na₂SO₄ added, the liberated Fe will bond to S to form Troilite (FeS).

3.3.3. Effect of Ratio of Additive to Nickel Slag

In the previous test it can be seen that the most optimal temperature for reducing nickel slag is at 1000°C. Therefore, to see the effect of adding additive to the composition of compounds present in slag nickel, a reduction process done with a fixed temperature of 1000°C with a holding time of 1 hour.

Fig. 4. Result of Variation of Additive Added to Nickel Slag

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Table 11. Result of Composition Nickel Slag added by Na₂SO₄ by ratio 2:1

Slag : Additive = 2:1		
Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO ₂	17,4
<i>Troilite</i>	FeS	39,1
<i>Olivine</i>	NiMg ₂ SiO ₄	18,2
<i>Fayalite</i>	Fe ₂ SiO ₄	23,2
<i>Quartz</i>	SiO ₂	2,1

Table 12. Result of Composition Nickel Slag added by Na₂SO₄ by ratio 1:1

Slag : Additive = 1:1		
Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO ₂	17,5
<i>Troilite</i>	FeS	39,2
<i>Olivine</i>	NiMg ₂ SiO ₄	20,7
<i>Fayalite</i>	Fe ₂ SiO ₄	21,8
<i>Quartz</i>	SiO ₂	0,8

Table 13. Result of Composition Nickel Slag added by Na₂SO₄ by ratio 1:2

Slag : Additive = 1:2		
Compound	Chemical Formula	Semi-Quant (%)
<i>Fe-rich Forsterite</i>	FeMgSiO ₂	15,3
<i>Troilite</i>	FeS	46,3
<i>Olivine</i>	NiMg ₂ SiO ₄	16,3
<i>Fayalite</i>	Fe ₂ SiO ₄	21,4
<i>Quartz</i>	SiO ₂	0,7

4. Conclusion

The result of XRD test of slag nickel reduced at temperatures of 800°C, 900°C, and 1000°C without additive indicates no reduction of iron or nickel occurring from Fe-rich Forsterite (FeMgSiO₄) and Olivine (NiMg₂SiO₄). The result of XRD test of slag reduction which has been reduced at temperatures of 800°C, 900°C, and 1000°C with the addition of Na₂SO₄ shows that with the increase of temperature, Fe-rich Forsterite (FeMgSiO₄) phase changes into Troilite (FeS). The result of XRD test of slag reduction that has been reduced at 1000°C with ratio between nickel slag with Na₂SO₄ additive 2:1, 1:1 and 1:2 shows as Na₂SO₄ additive increase, the decrease of silica oxide (SiO₂) occurred.

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