Thermal characteristics of ferronickel slag on roasting process with addition of sodium carbonate (Na$_2$CO$_3$)

A B Prasetyo$^{1,3}$, A Maksum$^{1,2}$, J W Soedarsono$^1$, and F Firdiyono$^3$

$^1$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
$^3$Research Center For Metallurgy and Materials, Indonesian Institute of Sciences, Serpong, Tangsel, Indonesia

Email: chencen_abp@yahoo.com

Abstract. Thermal characterization of ferronickel slag waste has been studied using TG / DTA, XRD, and SEM-EDX. The characterization of the initial samples of ferronickel slag was carried out TG / DTA to 1200°C. The result obtained is at a temperature of 800°C, there is an increasing mass and up to 4.68% at a temperature of 1200°C. At temperature of 807.4°C to 845.8°C, an exothermic reaction occurs. The increasing mass is due to the ferronickel slag which is originally in the form of metal, and then it was roasted to undergo an oxidation reaction so that the metal that has been formed, it returned into oxides. So that the weight of the sample mass increase. Samples of ferronickel slag added with sodium carbonate were also analyzed using TG / DTA. The results obtained are 2 endothermic peaks at temperatures of 90.6°C and 858.9°C with a total mass reduction of 49.3%. At a temperature of 90.6°C, there is a heavy loss caused by 2.38% loss of surface water. The XRD result of ferronickel slag is composed of enstatite (MgSiO$_3$), forsterite (Mg$_2$SiO$_4$), fayalite (Fe$_2$SiO$_4$), and quartz (SiO$_2$) structures. From the XRD analysis, the composition of silica oxide associates with magnesium and iron in the form of enstatite, forsterite, and fayalites is a very dominant composition. The roasting process of a mixture of ferronickel slag with sodium carbonate was carried out by heating at a temperature of 800-1000°C for 1 hour, and the sample result of roasting were analyzed using XRD. The result of roasting shows that the roasting process takes place more perfectly at higher temperature; it is indicated by the increasing phase intensity of SiO$_2$ and the formation of sodium silicate (Na$_2$SiO$_3$). The result of SEM shows that the higher the temperature, the distribution of Na, Si, and O elements tend to cluster in the same place or spot, while the elements of Mg, Si, and O are less bonded.

1. Introduction
The depletion of world mineral reserves has led researchers to try to reuse waste from the mining industry, such as tin slag [1] and ferronickel slag, as alternative sources of high value metals. Ferronickel slag is a by-product of the metals separation from ore in nickel smelting with pyrometallurgical processes. During this time, ferronickel slag is only used as a material layer for the manufacture of mine road access and as a material to increase soil carrying capacity [2, 3]. Nearly 38% of ferronickel slag is used for road construction, 48% is used for the cement industry mixture and the remainder is used for fertilizer, geopolymer, hydraulic technique, and so on [4-7]. There is not much further utilization of ferronickel slag, so if the technology is not found to process it, the slag will accumulate in the waste
storage pond which will eventually disrupt the surrounding environment. Ferronickel slag waste is B3 waste (Hazardous and Toxic Material). So, it requires special handling [8].

As an effort to support the increase of minerals value and the implementation of sustainable mining, it is by utilizing the slag. Therefore, it becomes more valuable. The use of ferronickel slag can be done by extracting it in order to extract valuable elements from the slag. The biggest elements contained in ferronickel slag are 30% silica, 20% magnesium, 12% iron, 1-2% aluminum, and so on [9]. In addition, ferronickel slag is also indicated that it contains of rare earth metal elements. The rare earth elements contained in ferronickel slag include lanthanum, cerium, neodymium, yttrium, and so on. Soil metal elements rarely have special characteristic, namely being able to react with other elements to produce something new. Rare earth metals are able to increase the ability of materials in the form of strength, hardness, and resistance to heat; so that these elements are added to the manufacture of high-strength steel. Almost all today's high-tech products, from televisions, cell phones, hybrid cars, and nuclear missile guidance devices require rare earth metals [10, 11]. Extractions that have been carried out by several researchers from slag include magnesium, nickel, cobalt, chromium, zinc, cadmium, copper, and silica [12-14]. Indications of rare earth metals contained include lanthanum, cerium, neodymium, yttrium, and so on. Therefore, the study of rare earth extraction from ferronickel slag will be very interesting. With the presence of valuable elements in ferronickel slag, a preliminary study of the characteristics and roasting experiments of ferronickel slag are needed to determine the suitable process or technology for the extraction of precious metals in ferronickel slag.

The purpose of the study is to observe the changes in phase and mass; morphology and distribution of elements contained and the structure of ferronickel (FeNi) slag minerals by adding sodium carbonate (Na2CO3) additives then roasted at temperature variations of 800°C, 900°C, and 1000°C for 1 hour. With the addition of sodium carbonate, it is expected a decomposition reaction between magnesium silicates as the main compound in slag with sodium carbonate to form sodium silicate compound.

2. Materials and Experimental

The raw material used in this study is ferronickel slag from smelted nickel at PT Morowali Industrial Park. The preparation stage was done by smoothing the ferronickel slag to get the size of -100 meshes. The sample was crushed using a crusher then mashed again using a disk mill to get the size of -100 meshes. The characteristics of ferronickel slag were analyzed using XRF, TG / DTA, SEM EDX, and XRD analysis. The chemical composition (wt. %) of ferronickel slag which was analyzed using XRF is listed in Table 1. TG/DTA was used to analyze the phase changes and mass of ferronickel slag at a certain temperatures. The analysis of TG / DTA was carried out using the TG/DTA with brand name of SETARAM ex France type Setsys in the temperature range of 100°C -1200°C with a heating rate of 10°/minute and air atmosphere. The analysis of SEM EDX was used to determine the morphology and distribution of the elements contained in ferronickel slag. SEM used is the SEM with JSM 6390 A. Jeol brand. The structures of ferronickel slag minerals were analyzed using XRD of the Schimadzu MAXima XRD-7000 brand with Cu Kα radiation (λ = 1.54). Operation of the generator was done at 40 kV and 30 mA, with a measurement speed of 2 degrees / minute, 0.020 degree pitch sampling.

Ferronickel slag roasting experiments were carried out by adding sodium carbonate (Na2CO3) additive. Raw materials of ferronickel slag which have been crushed to grain the size of 100 meshes were then mixed with additives in the mixer. The composition of the mixture between ferronickel slag and sodium carbonate is 50:50. Roasting was done by heating the sample in crucible graphite in a carbolite type of muffle furnace at temperatures of 800°C, 900°C, and 1000°C for 1 hour. Roasting with the addition of sodium carbonate is expected to be able to bond silicates which are the most elements that are contained in ferronickel slag.

The reactions that occur in the binding of SiO2 with the addition of Na2CO3 (reaction 1, 2, and 3) are as follows[15]:

\[
\text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2
\]  
(1)

The reaction is preceded by the process of decomposition of Na2CO3 to Na2O and CO2. When the temperature is increased there will be a reaction between Na2O and SiO2:

\[
\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2
\]  
(2)

The reactions that occur in the binding of SiO2 with the addition of Na2CO3 (reaction 1, 2, and 3) are as follows[15]:

\[
\text{Na}_2\text{CO}_3 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{CO}_2
\]  
(1)

The reaction is preceded by the process of decomposition of Na2CO3 to Na2O and CO2. When the temperature is increased there will be a reaction between Na2O and SiO2:
The products between Na$_2$O and SiO$_2$ depend on the temperature and composition of the Na$_2$O and SiO$_2$ mixtures. The reactions that occur are as follows:

$$\text{Na}_2\text{O} + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 \quad (3)$$

3. Result and discussion

3.1. XRF Analysis
The analysis results of chemical composition with XRF are presented in table 1. The results of the analysis show that in the ferronickel slag based on table 1, the most abundant element contained is silica at 25.02%. Other contained elements are iron and aluminum as much as 7.20% and 3.61% respectively. While the Ni element is detected very small at ppm, namely 430.6 ppm, this indicates that the Ni element has been extracted all into ferronickel metal as a product in smelting. Rare earth metals are also detected in this XRF analysis. The detected elements of rare earth metals are lanthanum, cerium, yttrium, neodymium, samarium, and so on. With the potential for rare earth metals, separate research can be done for rare earth metal extraction which has very high economic value.

| Element | Wt(%) | Element | Wt(ppm) | Element | Wt(ppm) |
|---------|-------|---------|---------|---------|---------|
| Si      | 25.02 | S       | 402     | Pr      | 70.9    |
| Al      | 3.61  | Cl      | 267.1   | Zn      | 142.1   |
| Na      | 0.22  | Sc      | 40.6    | Y       | 102.1   |
| P       | 0.09  | V       | 218.5   | La      | 346.7   |
| K       | 0.10  | Zr      | 211     | Ce      | 1109    |
| Ca      | 0.65  | Co      | 64      | Nd      | 303.3   |
| Ti      | 0.09  | Mn      | 5511    | Nb      | 26.1    |
| Fe      | 7.20  | Ni      | 430.6   | Sm      | 116.7   |
| Cr      | 0.95  | Ba      | 62.7    | Sr      | 39      |

3.2. TG/DTA Analysis
TGA analysis (Thermo Gravimetric Analysis) / DTA (Differential Thermal Analysis) was carried out to see the thermal kinetics of ferronickel slag when heated, so that the temperature can be determined effectively in the roasting process and to determine the phase changes that occur at a certain temperatures. TGA/DTA was carried out on ferronickel slag samples without the addition of other substances, and the ferronickel slag added with sodium carbonate.

The results of TGA / DTA Analysis can be seen in Figures 1 and 2. The TG / DTA analysis of ferronickel slag samples without the addition of other substances can be seen in Figure 1. The results of TG / DTA analysis in Figure 1 show that heating to ferronickel slag samples shows exothermic peaks at temperature of 807.4°C to temperature of 845.8°C. The exothermic reaction occurs at the maximum peak at a temperature of 824.7°C. The occurrence of exothermic reactions is also followed by an increasing sample mass in the TG / DTA analysis of ferronickel slag without the addition of another substance of 4.68%. This increasing mass is probably due to the reaction between the slag and oxygen from the outside during roasting. This is because the TG / DTA analysis was carried out on a small number of samples with an atmosphere that did not use inert gas or with an open system, so the metal on the surface might react with oxygen.
The TG / DTA curve of the mixture of ferronickel slag and sodium carbonate can be seen in Figure 2. In Figure 2 shows 2 reaction peaks that are quite clear. Those are at temperatures of 90.6°C and 849.5°C. The first endothermic peak on the curve of figure 2 begins at temperatures of 68.4°C to a temperature of 101.6°C and the peak of endothermic reaction 1 occurs at a temperature of 90.6°C. At a temperature of 90.6°C, there is a heavy loss of 2.38% because the surface water in the ferronickel slag begins to vaporize. At a temperature of 849.5°C, the formation of an endothermic reaction begins and ends at a temperature of 865.4°C. The endothermic peak reaction occurs at a temperature of 858.9°C accompanied by a very drastic loss of mass of 49.34%. This is because at the temperature interval there is a released CO₂ like reaction 2 above, namely the decomposition reaction of Na₂CO₃ to Na₂O + CO₂. By increasing the temperature of process, an endothermic reaction occurs which does not cause a
decrease in mass. At this temperature, the possibility of Na₂O to SiO₂ binding becomes Na₂SiO₃ (sodium / sodium silicate) as seen in reaction 3 above. This is in accordance with the phase diagram of the formation of sodium silicate from Na₂O and SiO₂ that can occur at temperatures of 800°C to 900°C, with 1: 2 to 2: 3 mole ratios of Na₂O and SiO₂ [16].

3.3. XRD Analysis
XRD analysis was conducted to determine the composition of the dominant chemical compounds and other compounds. The XRD analysis of the initial sample of ferronickel slag and the roasting process with temperature variables of 800°C, 900°C, and 1000°C is presented in Figure 3. The result of XRD analysis of ferronickel slag is identified that ferronickel slag is composed of forsterite (Mg₂SiO₄), fayalite (Fe₂SiO₄), quartz (SiO₂), and enstatite (MgSiO₃). From this XRD analysis, there is showed that the composition of silicate oxide which associates with magnesium and iron in the form of enstatite, forsterite, and fayalite is a very dominant composition. It can be seen in the graph of the highest peak diffraction, which is the composition of enstatite, forsterite, and fayalite. Based on the analysis with GSAS software, the composition of this ferronickel slag compound can be estimated to be 24.5% fayalite, 31.5% forsterite, 20.2% enstatite, and 25.5% quartz (in% mass). This condition is in accordance with the results of XRF analysis that the element with the largest content is silica which associates with magnesium and iron. This result is in accordance with the research that has been done before, namely the characterization of XRD on ferronickel slag shows that the dominant compositions are enstatite and forsterite [3, 9, 14].

The results of the roasting process with temperature variations of 800°C, 900°C, and 1000°C will be more clearly understood by comparing the XRD diffraction graph from roasting with the addition of sodium carbonate at various temperatures as in Figure 3. In figure 3 it is showed the XRD results of the initial samples of ferronickel slag contain of compounds with crystal structures consisting forsterite, enstatite, quartz, and fayalite as the dominant minerals. In figure 3, roasting at a temperature of 800°C with the addition of sodium carbonate as an additive causes the silica bound in enstatite, forsterite, and fayalite to start decomposing. Although the forsterite phase is still detected at a temperature of 800°C, but at this temperature, there are forsterite and enstatite which start to transform into MgO, and fayalite transforms into ferrosilite (FeSiO₃).

The result of roasting at a temperature of 900°C shows that sodium silicate is formed even though it does not show a high peak. This result is in accordance with the TG / DTA analysis shown in Figure 2 and in accordance with the phase diagram of Na₂O and SiO₂ that sodium silicate is formed at temperatures between 800°C-900°C as seen in Figure 3. At this temperature the enstatite phase (MgSiO₃) starts to separate into MgO and SiO₂, so that it dominates high peaks. The SiO₂ phase experiences an increase in intensity; this intensity change indicates that the roasting reaction is more perfect due to rising temperatures.

At the temperature of 1000°C, sodium silicate (Na₂SiO₃) has been formed and the SiO₂ phase has a very significant increase. It indicates that the addition of sodium carbonate is very influential on the process of sodium silicate formation and SiO₂ decomposition. With the very high intensity of SiO₂, it is expected that after the roasting process, a further process can be carried out, namely leaching with hot water to separate SiO₂ from ferronickel slag.
Figure 3. Curve of XRD Diffraction from the Initial slag and Roasting with the addition of Na$_2$CO$_3$ at various temperatures of 800°C, 900°C, and 1000°C.

### 3.4. SEM EDX Analysis

To find out the mineralogical structure and distribution of elements in ferronickel slag and the results of roasting, a SEM EDX analysis was done. The results of observations and mapping of elements using SEM EDX are shown in Figure 4. From figure 4 (a) it can be observed that silica and magnesium cover almost all parts of the ferronickel slag along with oxygen. This shows that indeed most silica is present in the form of silica oxide compounds and associates with magnesium. This corresponds to the XRD analysis that the dominant composition is silica that associates with magnesium and iron, namely enstatite, fosterite, and fayalite as seen in the XRD analysis of ferronickel slag. Calcium, aluminum, iron, and chromium elements are very small and evenly distributed in almost all parts. These results are in line with the research conducted by Mubarok et al. And Tangahu et al. which explains that in SEM analysis of ferronickel slag, the dominant distribution are magnesium, silica, and oxygen [3, 14].
In figure 4 (b) the results of 800°C roasting show that sodium is visible even though it is still in certain spots and the association between magnesium, silica, and oxide is still very strong which is shown by the red distribution of the three elements. In figure 4 (c), the results of 900°C roasting show the distribution of sodium is very high. It indicates that the red color of the distribution is greater and it blends with silica and oxide. Magnesium in its distribution has begun to decrease in association with silica. So it can be assumed that at this temperature sodium silicate (Na₂SiO₃) has been formed completely. It is indicated from the red color between the associations of sodium, silica, and oxide which are increasingly red, while magnesium has begun to appear, and its distribution is not too dominant. In figure 4 (d) shows the distribution of elements that are higher for the distribution of sodium, silica, and
oxide in one distribution / spot, whereas the distribution of magnesium begins to thin or decrease. This is consistent with the analysis of TG / DTA and XRD where the higher the temperature, the formation of sodium silicate will be stronger and can be separated from magnesium.

With the separation between silica and magnesium, it is expected to facilitate the process of dissolving silica by using hot water, so that silica can be separated from the valuable elements contained in the ferronickel slag. Through these steps of process, it is hoped that it would facilitate the next process, namely the extraction of precious metals from ferronickel slag.

4. Conclusion
The result of TG / DTA ferronickel slag analysis shows that at temperatures of 807.4°C to 845.8°C, there is an exothermic reaction which causes the mass to increase by 4.68%. The result of TG / DTA analysis on ferronickel slag with sodium carbonate adds 2 endothermic peaks at a temperature of 90.6°C and 858.9°C with a total mass reduction of 49.3%. At a temperature of 90.6°C, there is a heavy decrease caused by 2.38% of surface water loss. In endothermic reaction the temperature of 858.9°C shows the release of CO₂ which results in significant mass loss. With increasing temperature, the formation of sodium silicate will be more perfect.

The result of XRD shows ferronickel slag is composed of enstatite, forsterite (Mg₂SiO₄), fayalite (Fe₂SiO₄), and quartz (SiO₂) structures. The result of XRD analysis on roasting of ferronickel slag added with sodium carbonate shows that the roasting process takes place more perfectly at higher temperature. This is indicated by the increasing of phase intensity of SiO₂ and the formation of sodium silicate (Na₂SiO₃). The result of SEM EDX shows that with higher temperatures, the distribution of Na, Si, and O elements tends to be in the same place or spot, while the elements Mg, Si, and O decrease.

The formation of sodium silicate is expected to facilitate the extraction process of precious metals contained in ferronickel slag. The next process is leaching with hot water to separate SiO₂ from ferronickel slag. So that by separating SiO₂ as the dominant element, it is expected that other valuable elements will be easy to extract.

References
[1] Permana S, et al. 2016 *IOP Conference Series: Materials Science and Engineering*. IOP Publishing
[2] Kang S S, K Park and D Kim 2014 *Materials* **7**(10) 7157-7172
[3] Tangahu B V, et al. 2015 *Adv. Chem. Engineer. Sci.* **5**(03) 408
[4] Maragkos I, Giannopoulou I P, and Panias D, 2009 *Miner. Eng.* **22**(2) 196-203
[5] Choi, Y.C. and S. Choi, 2015 *Constr. Build. Mater.* **99** 279-287
[6] Rahman M A, et al 2017 *Constr. Build. Mater.* **140** 194-202
[7] Sugiri S and D T S 2005 *Jurnal Infrastruktur dan Lingkungan Binaan* **1**(1)
[8] Shen H and Forssberg E 2003 *Waste Manage.* **23**(10) 933-949
[9] Demotica J S, et al. 2012 *Int. J. Environ. Sci. Develop.* **3**(5) 470
[10] Weber R J and Reisman D J 2012 *US EPA Region*
[11] Tsamis A and Coyne M 2015 Directorate General For Internal Policies Policy Department A: Economic And Scientific Policy
[12] Chu Y S, et al. 2010 *J. Korean Ceram. Soc.* **47**(6) 613-617
[13] Park J H, et al. 2016 *Wat Sci. Tech.* **73**(5) 993-999
[14] Mubarok M and Yudiarto A 2017 *Energy Technol.* 247-258
[15] Firdiomyono F, et al. 2016 *Maj. Metalurgi*, **27**(1) 15-26
[16] Holand W and Beall G H 2012 *Glass ceramic technology* (United States : John Wiley & Sons)

Acknowledgment
The author would like to thank the Ministry of Research and Higher Education as a provider of scholarships and financial support through the Postgraduate Team Grant with contract number 553 / UN2.R3.1 / HKP05.00 / 2018. In addition, this study is also supported by the Research Center for Metallurgy and Materials, the Indonesian Institute of Sciences with its laboratory facilities.