The effect of sodium sulfate (Na$_2$SO$_4$) and sodium carbonate (Na$_2$CO$_3$) addition on the reduction-roasting process of titania iron sand

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Abstract. This study aims to determine the effect of sodium sulfate (Na$_2$SO$_4$) addition on the reduction proses of tiania iron sand. The sample that used in this research are the iron sand that taken from Sukabumi, West Java, coal as reductor, sodium carbonate (Na$_2$CO$_3$), and sodium sulfate (Na$_2$SO$_4$) as additive and primary parameter. From the result of XRD characterization and semi-quantitative analysis the addition of sodium carbonate (Na$_2$CO$_3$) on roasting process remove the impurities like alumuniom oxide (Al$_2$O$_3$). In the other hand, the content of titano-magnetite (Fe$_2$TiO$_4$-Fe$_3$O$_4$) in the iron sand increase with addition of sodium sulfate (Na$_2$SO$_4$). Meanwhile, from semi-quantitative analysis result with the variation of sodium sulfate (Na$_2$SO$_4$) in 5%, 15%, and 25% have an optimum point on the addition of 15% sodium sulfate (Na$_2$SO$_4$) with 46,9% of titano-magnetite (Fe$_2$TiO$_4$-Fe$_3$O$_4$) content.

1. Introduction

Iron sand in Indonesia has been known to spread along the coastal area of Sumatra, Java, Lesser Sunda Island and Sulawesi. Iron sand is also a mineral that contains many oxide compounds, such as ilmenit (FeTiO$_3$), magnetite (Fe$_3$O$_4$), titano-magnetite (F$_3$O$_4$-Fe$_2$TiO$_4$) hematite (Fe$_2$O$_3$) and so many more[1]. The titanium content contained in the iron sand that makes it has more value. This is due to the titanium can make the selling price becomes higher, because to process and get titanium requires a fairly complicated process and requires considerable cost. Recent studies have shown that direct iron ore reduction was investigated after adding sodium sulfate (Na$_2$SO$_4$), an increase in Fe Content in the addition of sodium sulfate (Na$_2$SO$_4$) [2, 3].

In this research, pyrometallurgical extraction aims to make iron sand has different magnetic properties, so that later able to be separated magnetically. This is done because it assumes that titanium in iron sand generally binds to iron (Fe). The bonds between titanium and iron can be in the form of ilmenit (FeTiO$_3$), pseudobrokite (Fe$_2$TiO$_5$), ulvospinel (Fe$_2$TiO$_4$), etc. So if the ulvospinel (Fe$_2$TiO$_4$) binds to the magnetite (Fe$_3$O$_4$) compound will form a titano-magnetite (Fe$_2$TiO$_4$-Fe$_3$O$_4$) compound that has different magnetic properties, because the titano-magnetite is a ferrimagnetic compound [4], [5].

2. Materials and Method

2.1 Materials

Iron sand samples used in this study carried out initial characterization by X-Ray Diffraction (XRD) test. Figure 1 provides the XRD result of iron sand.

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In the other hand, the semi-quantitative test is used to see the content of each compound on the XRD result. The semi-quantitative test result can bee seen in Table 1. While for coal that used as a reductor was also tested with proximate and ultimate test to see the composition of the coal. The result of proximate and ultimate test can be seen in Table 2 and Table 3.
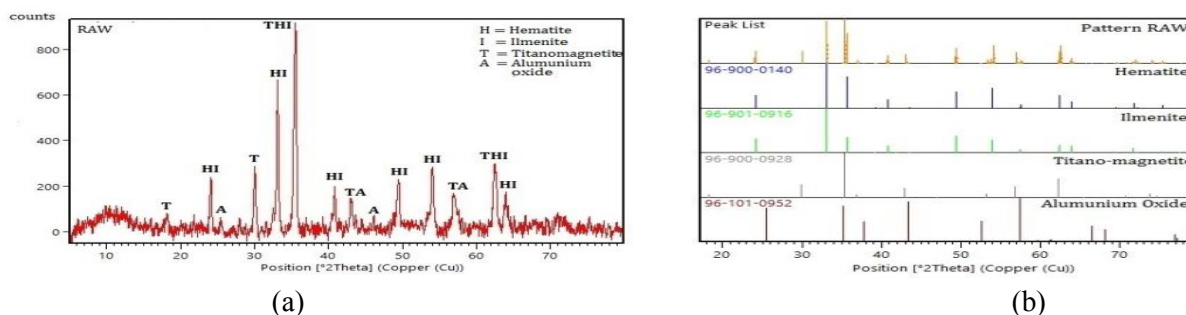

(a)

(b)

Fig. 1. (a) XRD result and (b) XRD patterns of iron sand initial samples

Tabel 1. Semi-quantitative analyisis of intial samples

Compound Name	Formula	Semi-quantitative (%)
Hematite	Fe_2O_3	28,0
Ilmenite	$FeTiO_3$	24,3
Titano-magnetite	Fe_2TiO_4-Fe_3O_4	35,5
Alumunium oxide	Al_2O_3	12,2
Total		100

Tabel 2. Proximate analysis of coal

Parameter	Result
Moisture	7,26%
Ash	15,87%
Volatile metter	16,44%
Fixed Carbon	60,43%

Tabel 3. Ultimate analysis of coal

Parameter	Result
Carbon (C)	64,02%
Hydrogen (H)	3,11%
Nitrogen (N)	0,60%
Oxygen (O)	16,32%

2.2 Experiment

This reduction-roasting process take place in a muffle furnace. The samples of iron sand crushed to size up to 200 mesh. The samples were mixed with sodium carbonate (Na_2CO_3) at a ratio 1 : 0,4 for roasting process. After that the samples were roasted with 800^OC for 2 hours, than quenching in aquadest. The water content was removed by heat in the oven at 120^OC for 20 hours. After it dries, 10 grams of samples were mixed with 5% coal and Na_2SO_4 with 5%, 15%, and 25% levels for reduction process. The reduction process is carried out for 30 minutes with a temprature of 800^OC. The cooling process is done by quenching it again in aquadest than dried in the oven with the same treatment as after roasting process. After roasting and reduction process, XRD test is being to held analyze the compounds in the samples and the semi-quantitative analysis is done by using *X'pert High Score Plus* software.

3. Result and Discussion

3.1 Roasting process

At Figure 2, XRD test results after roasting process indicate that there is no impurity compound such as alumunium oxide (Al_2O_3), but also accompanied by significantly reduced titano-magnetite compounds, so that the compounds formed after the roasting process are hematite (Fe_2O_3) and ilmenite ($FeTiO_3$). This is supported by semi-quantitative analysis data which can be seen in Table 4.
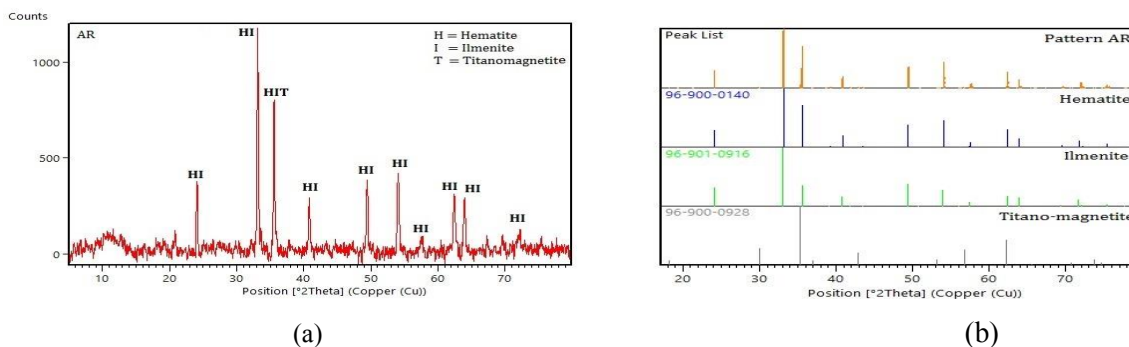
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(a)   (b)

Fig. 2. (a) XRD result and (b) XRD pattern of after roasting samples

Table 4. Semi-quantitative analysis of after roasting samples

| Compound Name	Formula	Semi-quantitative (%)
Hematite	Fe_2O_3	49,0
Ilmenite	$FeTiO_3$	49,9
Titano-magnetite	Fe_2TiO_4-Fe_3O_4	1,1
Total		100

The loss of the alumunium oxide (Al_2O_3) compound is due to binding to sodium carbonate (Na_2CO_3) forming the $NaAlO_2$ compound by the following reaction [6] :

$$Na_2CO_3 = Na_2O + CO_2 \qquad (1)$$

$$Na_2O + Al_2O_3 = 2NaAlO_2 \qquad (2)$$
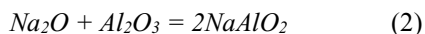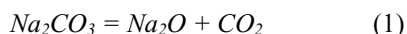
A highly soluble $NaAlO_2$ compound in water causes it to dissolve during the quenching process using aquadest.

Meanwhile, the loss of titano-magnetite compound is due to the high temprature oxidation process. The formation of ilmenite and hematite is the result of the oxidation of ulvospinel and magnetite which are the compounds of titano-magnetite. It can be seen based on the following reaction [5] :

$$6FeTiO_4 + O_2 \rightarrow 6FeTiO_3 + Fe_3O_4 \qquad (3)$$

$$2Fe_3O_4 + 1/2O_2 \rightarrow Fe_2O_3 \qquad (4)$$
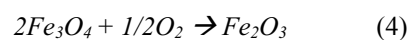
3.2 Reduction process

From the XRD result and XRD pattern on Figure 3 and Figure 4, this result showed that the re-emergence of titano-magnetite compound. This may due to the change of hematite to magnetite will increase FeO level which can be seen in ternary diagram TiO_2-FeO-Fe_2O_3 at Figure 5.
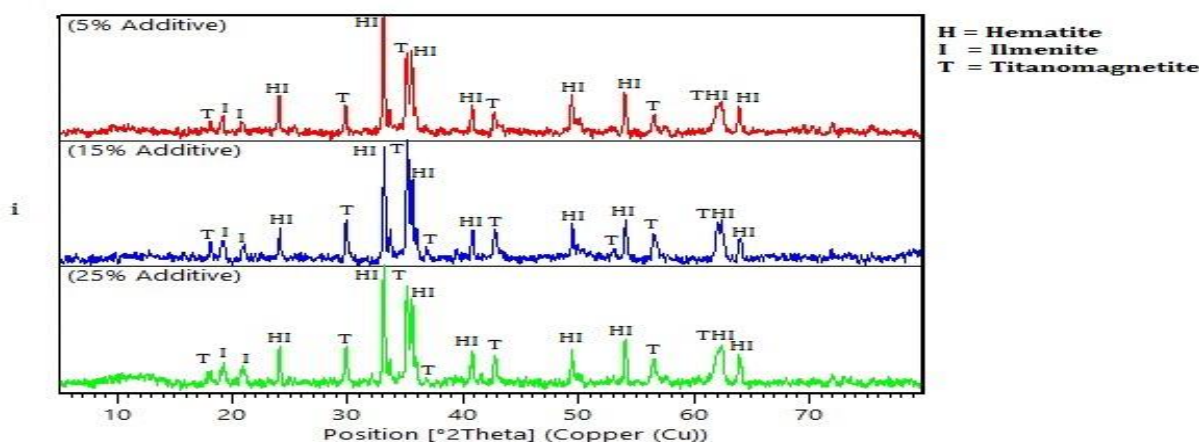

Fig. 3. XRD results of after reduction samples at 5%,15%, and 25% Na2SO4 addittion

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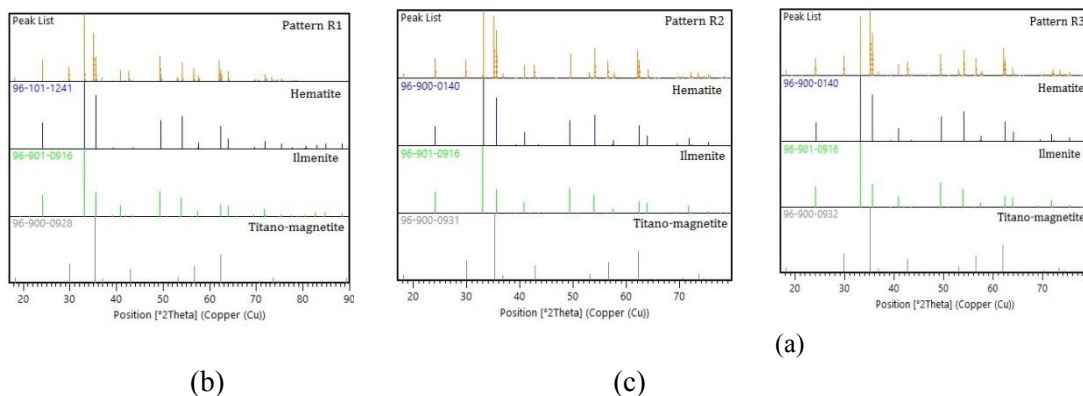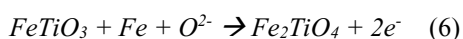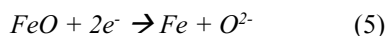* Corresponding author: jwsono@metal.ui.ac.id

Fig. 4. XRD pattern of after reduction samples. (a) 5% Na_2SO_4, (b)15% Na_2SO_4, (c)25% Na_2SO_4 addition

With increasing FeO levels will also help the process of reducing ilmenite ($FeTiO_3$) to ulvospinel (Fe_2TiO_4), according to the following two half-cell reacting [7]:

$$FeO + 2e^- \rightarrow Fe + O^{2-} \qquad (5)$$

$$FeTiO_3 + Fe + O^{2-} \rightarrow Fe_2TiO_4 + 2e^- \qquad (6)$$

Into a full cell reaction :

$$FeTiO_3 + FeO \rightarrow Fe_2TiO_4 \qquad (7)$$

With the formation of magnetite (Fe_3O_4) and ulvospinel (Fe_2TiO_4), then it will re-form the titano-magnetite (Fe_2TiO_4-Fe_3O_4) compound which is essentially a combination of magnetite and ulvospinel.
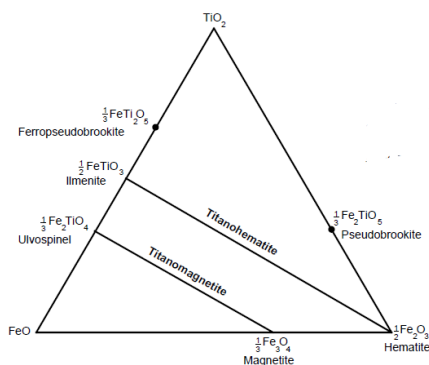

Fig. 5. Ternary diagram TiO_2-FeO-Fe_2O_3 [4]

On the other hand, an increased in titano-magnetite levels in all the reduction results by addition of additives when compared to initial samples. It can be seen from the result of semi-quantitative analysis in Table 5. At the addition of 5% additives, titano-magnetite content increased 0,8% to 36,3% when compared with initial sample. Then on addition of 15% additives, titano-magnetite content increased 11,4% to 46,9% when compared to the initial sample. On addition of 25% additives there was a decrease in titano-magnetite content when compared with the addition of 15% addititive, but still increased by 7,3% to 42,8% when compared with the initial sample.

A high increase in the addition of a 15% additive is due to Na_2SO_4 if it binds to a carbon reductor capable of producing CO gas that can help the reduction process. This is can be seen base on the following reaction [8] :

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO \qquad (8)$$
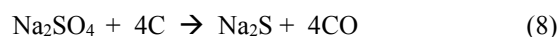
A decrease in the addition of 25% addtitives is due to the rapid reduction process, so that the carbon content in the reducing agent runs out quickly. The depletion of the carbon reducer will no longer be able to produce CO gas, so the reaction will turn into oxidation reaction in the reamaining time.

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Table 5. Semi-quantitative analysis of after reduction sample with addition 5%,15%, and 25% additives

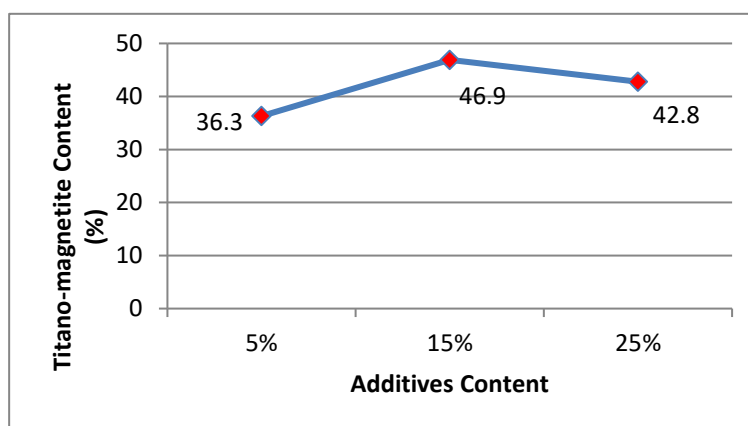| Compound Name	Formula	Semi-quantitative (%)		
		5% additives	15% additives	25% additives
Hematite	Fe_2O_3	14,6	50,0	34,9
Ilmenite	$FeTiO_3$	49,1	3,1	22,4
Titano-magnetite	Fe_2TiO_4-Fe_3O_4	36,3	46,9	42,8
Total		100	100	~100

4. Conclusion

Fig. 6. Comparison graph of additives and titano-magnetite content

Adding sodium carbonate (Na_2CO_3) to the roasting process is capable of binding alumunium oxide (Al_2O_3) as an impurity forming water soluble $NaAlO_2$, thereby increasing the titano-magnetite content after reduction process is performed.

At the reduction process, adding sodium sulfat (Na_2SO_4) can increase the content of titano-magnetite (Fe_2TiO_4-Fe_3O_4) formed. The increase that occured has an optimum point on the addition of 15% sodium sulfate with titano-magnetite content formed at 46,9% as can be seen in Figure 6. This may be due to Na_2SO_4 if binding to carbon is capable of producing CO gas which is useful for the reduction process. But a decrease in addition of 25% additives is due to the depletion of the carbon reducer will no longer able to produce CO gas, so the reaction will turn into oxidation reaction in the remaining time.

With known the optimum point of titano-magnetite formation, for further research can be done by magnetic separation and quantitative analysis because of titano-magnetite having different magnetic properties compared to hematite and ilmenite. So it is expected to also increase the content of titanium is higher than the initial sample

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