

The effect of time variation on the results of increasing titanomagnetite in iron sand at magnetization temperature (800°C) with Na₂SO₄ addition as additive

Hedi Eka Maulana¹, Agung Nugraha¹, Ahmad Maksum^{1,2}, Haidir Juna², Bambang Priyono¹, Johny Wahyuadi Soedarsono^{1,*}

¹Center of Minerals Processing and Corrosion Research, Department of Metallurgical and Materials Engineering, Universitas Indonesia, Depok 16424, Indonesia

²Department of Mechanical Engineering, Politeknik Negeri Jakarta, Depok 16425, Indonesia

Abstract. Indonesia has rich deposit of Iron Sand that can be found along of the Java southern part island. Iron sand contains some Ti-Rich minerals such as *ilmenite*, *titanomagnetite* dan *rutile*. This study aims to determine the effect of time variation on the results of Increasing titanomagnetite in iron sand and addition of 15% Na₂SO₄ as a catalyst. Variation of this reasearch was respectively 10 minutes, 20 minutes and 30 minutes with reduction temperature at 800°C. It takes the stage of roasting to condition the ore to be more easily reduced and increase the metal content so that it can maximize the iron sand purity with addition of Na₂CO₃ additive with mass ratio 1:0.4 . Based on the XRD and Semi-Quant equation using *Software HighScore Plus*, optimal time for reducing iron sand with coal at 800°C is 30 minutes, which produce content of *titanomagnetite* as much as 36%.

1. Introduction

Indonesia which is an archipelago country definitely has many river estuaries. Iron sand is widely spread along the south coast of java and generally has a very high Titanium content[1]. There are some minerals found in iron sand consist of magnetite, hematite, titanomagnetite and ilmenite. Titanium widely use for application in aeronautics and biomedical science[2]. However, some industry also use titanium in the form of rutile (TiO₂) as “White Pigment” especially for plastic and paper industry [3].

In this research, the process of increasing Ti content by reduction of iron sand which aims to form magnetite followed by magnetic separation with assumption that Ti bonded with Fe, which will form Pseudobrookite (Fe₂TiO₅), Ilmenite (FeTiO₃), and Ulvospinel (Fe₂TiO₄).

The process of formation of Titanomagnetite (xFe₂TiO₄(1-x)Fe₃O₄) will occur when there is a solid solution between Magnetite (Fe₃O₄) and Ulvospinel[4]–[6].

2. Materials and method

2.1. Materials

The Iron sand samples used in this experiment were characterized using X-Ray Diffraction Spectrometry to observe the compund contained in a mineral semi-quantitatively as seen as Figure 1. After that, Proximate and Ultimate Test have been done to determine the composition of Carbon in order to calculate total carbon required in this experiment.

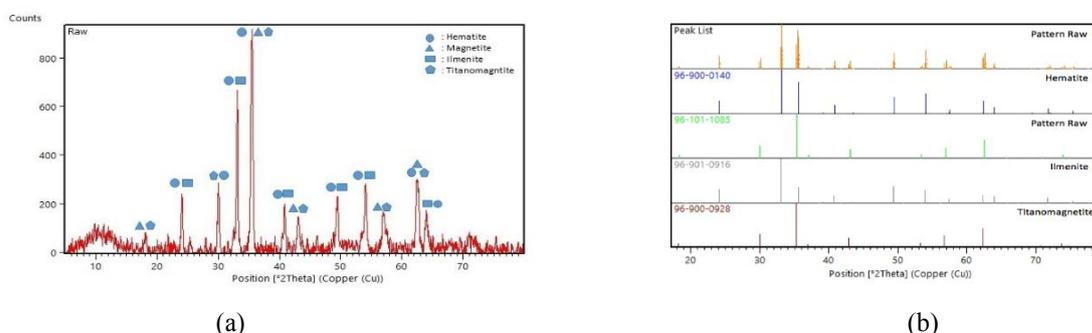


Fig. 1. (a) XRD result and (b) XRD patterns of iron sand initial samples

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

Tabel 1. Semi-quantitative analysis of initial samples

Compound Name	Chemical Formula	Semi-Quant (%)
Hematite	Fe ₂ O ₃	30
Magnetite	Fe ₃ O ₄	24.2
Ilmenite	FeTiO ₃	29.3
Titanomagnetite	xFe ₂ TiO ₄ (1-x)Fe ₃ O ₄	16.4

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 is done using a muffle furnace. Samples of iron sand are processed by crushing and grinding up to 200 mesh. Then continued roasting at 800°C for 2 hours with Na₂CO₃ addition with 1:0.4 ratio followed by quench. The water content of iron sand sample is removed by heating into oven at 120°C for 20 hours. Before the reduction process, experiment is done by adding 5% Coal and Na₂SO₄ 15% as fixed variable then continued by reduction with variation 10,20 and 30 Minutes at 800°C.

3. Result and discussion

3.1. Roasting process

The Roasting Process convert the entire magnetite phase into a hematite phase caused by the oxidation process of iron [7]–[9]. Based on XRD result, hematite phase is dominant phase formed on iron sand followed by the formation of Ilmenite with percentage of mineral as Table 4.

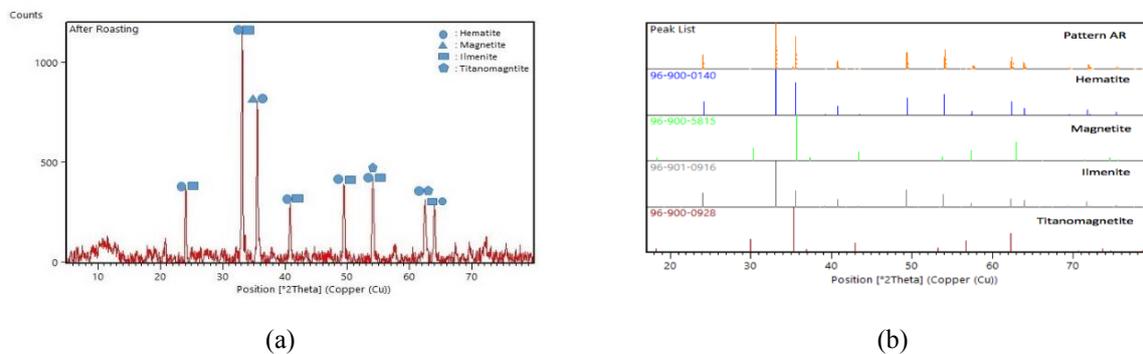


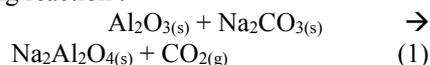
Fig. 2. (a) XRD result and (b) XRD pattern of after roasting samples

Table 4. Semi-quantitative analysis of after roasting samples

Compound Name	Formula	Semi-quantitative (%)
Hematite	Fe ₂ O ₃	49,0
Ilmenite	FeTiO ₃	49,9
Titano-magnetite	Fe ₂ TiO ₄ -Fe ₃ O ₄	1,1
Total		100

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

Addition of additive Na₂CO₃, not only aims to form alkaline complex phase when carried out, but also aids the separation of Fe₂O₃ with alumina by following reaction :



Then proceed with leach using aquadest so that it will increase the pH of the water to 12-14 by the following reaction :

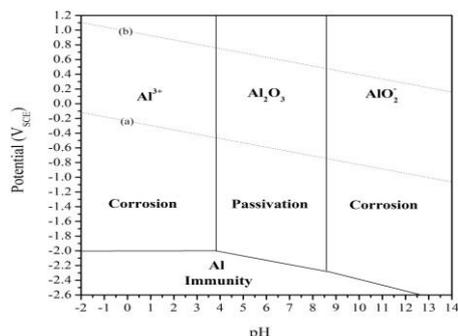
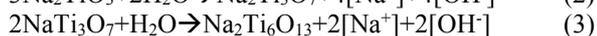


Fig. 3. Pourbaix diagram of Al₂O₃

After water quench process, the water itself was tested by pH meter. it shows that the acidity level is 12. In the pourbaix diagram which can be seen in Figure 3, Al₂O₃ shows that it can change to its ionic form AlO₂⁻ so that the predicted alumina on the sample will dissolve during water quench process. We can conclude that the Al impurities is eliminated and it is in accordance with the literature.

3.2. Reduction process

From the XRD result and semi-quantitative data obtained from High Score Plus Software on the reduction process there is an increase of magnetite and titanomagnetite compounds due to reduction process which influenced by %FeO. It can be seen from ternary diagram FeO-TiO₂-Fe₂O₃ in Fig. that increasing %FeO will initiate the form of Magnetite and Ulvospinel.

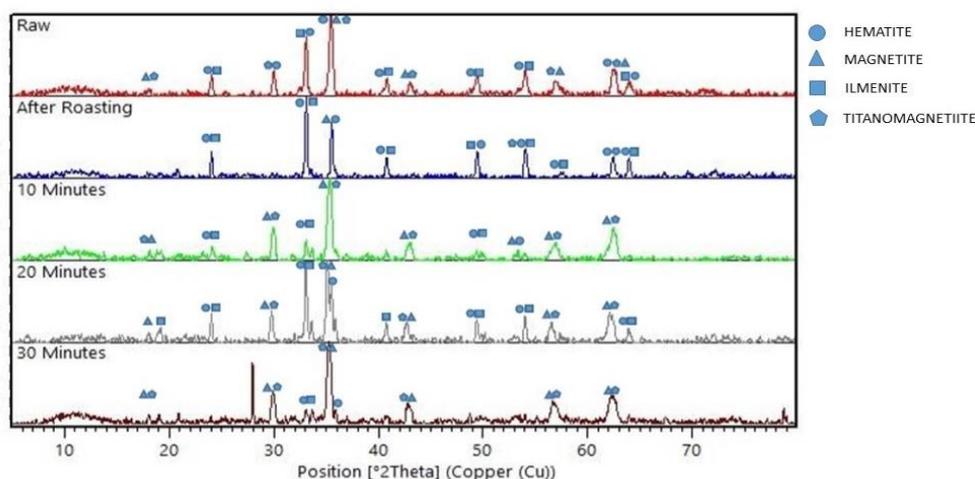


Fig. 5. XRD results of after reduction samples at all variation

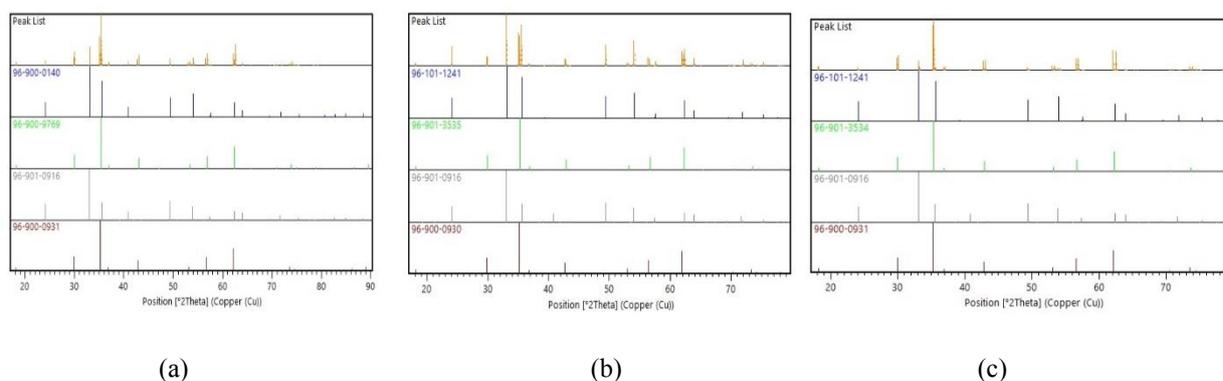


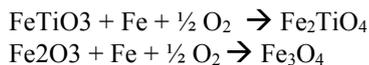
Fig. 6. XRD pattern of after reduction samples. (a) 10 Minutes, (b) 20 Minutes, (c) 30 Minutes

The initiation of Magnetite and Ulvospinel leads the form of Titanomagnetite which Titanomagnetite is

formed by solid solution mechanism between Magnetite and Ulvospinel. Its formation can be seen based on

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

reaction below :



The reduction process leads to a partial transformation of the hematite-ilmenite phase into a magnetite-titanomagnetite phase since both are co-existent minerals.

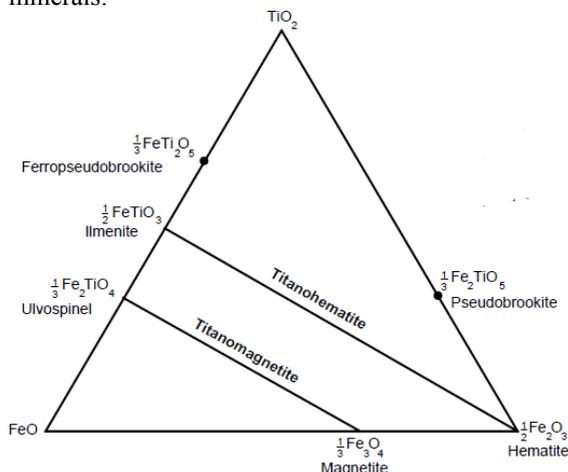


Figure 7. Ternary diagram TiO₂-FeO-Fe₂O₃ [10]

On the other hand, an increased level of magnetite from initial iron sand at variable 20 Minutes and 30 Minutes with magnetite concentration are 24.2%, 25.9% and 51.1% respectively. While, titanomagnetite concentration are 16.4%, 22.7% and 36% respectively. Anomaly was shown in variable 10 minute with magnetite and titanomagnetite level are 51.6% and 28.4%, it is caused by the difference of working procedure so that the pyrolysis last longer than 20 Minute variable.

The addition of Na₂SO₄ will accelerate the reduction process, due to the mechanism of sodium sulphate crystallization damage which will lead to the formation of micropores in iron sand [11], [12].

Table 5. Semi-quantitative analysis of after reduction for 10, 20 and 30 Minutes

Compound Name	Formula	Semi-quantitative (%)		
		10 Minutes	20 Minutes	30 Minutes
Hematite	Fe ₂ O ₃	15.3	38.7	7.4
Magnetite	Fe ₃ O ₄	51.6	25.9	51.1
Ilmenite	FeTiO ₃	4.7	12.7	5.5
Titanomagnetite	Fe ₂ TiO ₄ .Fe ₃ O ₄	28.4	22.7	36

4. Conclusion

The optimum point of Titanomagnetite formation is shown at the time of iron sand reduction for 30 minutes with semi-quant level by 36%, so it could be understood the longer time reduction process of solid solution formation between ulvospinel and magnetite will be maximal. Addition of Na₂CO₃ to the alkaline roasting process followed by wuenching process using aquadest aims to remove impurities in the form of aluminium. Then the addition of Na₂SO₄ to reduction serves as a catalyst in the reduction process

The authors also wish to thank the Ministry of Research Technology and Higher Education and Directorate of Research and Community Engagement, Universitas Indonesia, under PITTA Research Grants Contract No. 2459/UN2.R3.1/HKP05.00/2018 for the financial support of this research.

References

1. P. A. Nugraha, S. P. Sari, W. N. Hidayati, R. Dewi, and D. Y. Kusuma, "The Origin and Composition of Iron Sand Deposit in the Southern Coast of Yogyakarta," in *AIP Conference Proceedings*, 2016, vol. 20028, pp. 1–5.
2. M. Kulkarni, A. Mazare, E. Gongadze, Perutkova, V. Kralj-Iglic, I. Milošev, P. Schmuki, A. Iglič, and M. Mozetič, "Titanium nanostructures for biomedical applications," *Nanotechnology*, vol. 26, no. 6, 2015.
3. T. A. Lasheen, "Soda ash roasting of titania slag product from Rosetta ilmenite," *Hydrometallurgy*, vol. 93, no. 3–4, pp. 124–128, 2008.
4. Y. ran Liu, J. liang Zhang, Z. jian Liu, and X. dong Xing, "Phase transformation behavior of titanium during carbothermic reduction of

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

- titanomagnetite ironsand,” *Int. J. Miner. Metall. Mater.*, vol. 23, no. 7, pp. 760–768, 2016.
5. D. S. Chen, B. Song, L. N. Wang, T. Qi, Y. Wang, and W. J. Wang, “Solid state reduction of Panzhihua titanomagnetite concentrates with pulverized coal,” *Miner. Eng.*, vol. 24, no. 8, pp. 864–869, 2011.
 6. P. Halli, P. Taskinen, and R. H. Eriç, “Mechanisms and Kinetics of Solid State Reduction of Titano Magnetite Ore with Methane,” *J. Sustain. Metall.*, pp. 1–16, 2016.
 7. M. Azif and A. Maksum, “Effect of pellet size addition on the selective reduction of limonite ore from Southeast Sulawesi,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 105, 2017.
 8. A. Maksum and J. W. Soedarsono, “Effects of temperature on the direct reduction of Southeast Sulawesi ’ s limonite ore,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 105, 2017.
 9. R. Rahmat and A. Maksum, “Effects of Na₂SO₄ addition on the selective reduction of limonite ore from Southeast Sulawesi Effects of Na₂SO₄ addition on the selective reduction of limonite ore from Southeast Sulawesi,” *IOP Conf. Ser. Earth Environ. Sci.*, vol. 105, 2017.
 10. R. L. Butler, *Ferromagnetic minerals*, vol. 1. Blackwell Scientific Publication, 1992.
 11. M. Jiang, T. Sun, Z. Liu, J. Kou, N. Liu, and S. Zhang, “Mechanism of sodium sulfate in promoting selective reduction of nickel laterite ore during reduction roasting process,” *Int. J. Miner. Process.*, vol. 123, pp. 32–38, 2013.
 12. E. xia Gao, T. chang Sun, Z. guo Liu, C. Geng, and C. yan Xu, “Effect of Sodium Sulfate on Direct Reduction of Beach Titanomagnetite for Separation of Iron and Titanium,” *J. Iron Steel Res. Int.*, vol. 23, no. 5, pp. 428–433, 2016.