

Thermal Characterization of Mixing Extracted $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ from Iron Sand and Limestone Precipitated- CaCO_3 by DTA-TGA

Mastuki*, Department of Mechanical Engineering, Faculty of Engineering, 17 Agustus 1945 University Surabaya, Indonesia.

E-mail: mastuki@untag-sby.ac.id

Sugeng Priyandokohadi, Department of Mechanical Engineering, Faculty of Engineering, 17 Agustus 1945 University Surabaya, Indonesia.

Abstract--- Iron sand contains a lot of Fe_3O_4 from which Fe_2O_3 and limestone can be produced which contain CaCO_3 . Both of these materials are very plentiful in Indonesia. Because of the plentiful of these two materials, research was carried out for the management and development of products with the initial step of analyzing the thermal characterization of mixing of these two materials, namely Calcium Ferrite. Mixing Extracted $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ from Iron sand and limestone precipitated using solution mixing method has been conducted. Extraction of limestone as the raw material of precipitated calcium carbonate (PCC) and iron sands as that of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ was prepared. The PCC and $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ each are dissolved in 1 M HNO_3 and mixed to be most homogeneous with mole ratio of Ca/Fe is 1/4, 1/8 and 1/12. The results of the mixing are characterized by DTA/TGA. The test results showed that there was a drastic decrease in mass to a temperature of 5000C and decreased slowly. In this case it can be said that there are a process of dehydration and calcination before the temperature of 5000C and the subsequent diffusion process occurs.

Keywords--- $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, PCC, Solution Mixing Method, DTA-TGA.

I. Introduction

The use of magnetic materials in the industrial world began around the 18th century. The industrial revolution that occurred at that time encouraged scientists to develop research for industrial purposes. Electrical and electronic components, for example small DC motors, loudspeakers and others use permanent magnetic materials as magnetic energy sources. The military industry is also not left behind in the use of the benefits of magnetic materials. Magnetic materials used in almost all aspects of industry in practice can be divided into several types, one of which is a ferrite magnet. [1] Ferrite is a type of magnet that is synthesized using iron oxide. It is quite encouraging that the material of iron oxide is abundant in Indonesia, and in the form of iron sand. In iron sand, there are several of iron oxides such as Fe_3O_4 , Fe_2O_3 and (Ni, Zn) Fe_2O_3 . One type of commercially behavior ferrite is Barium Ferrite ($\text{BaO} \cdot 6\text{Fe}_2\text{O}_3$) and Strontium Ferrite ($\text{SrO} \cdot 6\text{Fe}_2\text{O}_3$). This type of ferrite powder can be synthesized by mixing Hematite (Fe_2O_3) with Barium Carbonate (BaCO_3) or Strontium Carbonate (SrCO_3)[2][3].

On the other hand, in addition to abundant iron sand, Indonesia is also rich in rocks which mostly contain Calcium Carbonate (CaCO_3) that is known as limestone. Calcium is a group of elements with Barium and Strontium. This similarity allows it to be synthesized by Calcium Ferrite which will become a candidate for low-cost permanent magnet materials or become a potential candidate for materials with certain chemical and physical properties that can be used in certain fields according to the properties that will be obtained.[4][5].

Considering the abundant amount of iron sand and limestone, and has not been used optimally, while the opportunity for the material to be processed into industrial material is wide open, it is necessary to conduct research oriented to the processing of Indonesian natural resources, namely iron sand and limestone, with the consideration that from these materials it will be able to be synthesized into a number of Calcium Ferrite products. In this study, Thermal characterization of mixing extracted $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ from iron sand and precipitated CaCO_3 from limestone is studied.

II. Theoretical Background

2.1. Hematite (Fe_2O_3)

Fe_2O_3 is obtained by heating the magnetite (Fe_3O_4). In the heating process, particles with Fe_3O_4 phase get thermal energy from the heating process in the furnace. The higher the heating temperature, the higher the thermal

energy is given so that the atoms vibrate and will rearrange themselves. Phase transformation from magnetite to hematite occurs at a temperature of $<300^{\circ}\text{C}$, further heating will make the sample transform to form a hematite phase at a temperature of $>320^{\circ}\text{C}$. This phase transformation into hematite runs slowly to a temperature of $<450^{\circ}\text{C}$. At a temperature of 500°C a hematite core will be created and will grow into a hematite phase quickly. The hematite phase begins to form on temperature $>320^{\circ}\text{C}$ to high temperatures The formation of this phase is very fast at a temperature of $>520^{\circ}\text{C}$, is 70-90% of the sample becomes a hematite phase within 60 minutes. When the sample is heated at a temperature of 600°C , 700°C and 800°C , the phase change from magnetite to fast hematite can even be even faster if the sample form is a pellet, the distance between particles is very close so that the results obtained by the hematite phase are 100%. This phase change process starts when Fe^{2+} and Fe^{3+} in magnetite are heated to the critical point (585 K), the more unstable Fe^{2+} from Fe^{3+} oxidizes to Fe^{3+} and diffuses so that Fe_2O_3 forms. At a constant temperature for example 600°C , diffusion occurs between particles at the grain boundary so that the grain formed becomes larger. The magnetite phase will transform more quickly into the hematite phase at a higher temperature of around 800°C with a longer holding time.[2][5].

2.2. Calcium Carbonate (CaCO_3)

Calcium Carbonate (CaCO_3) is a phase formed due to sediment deposits from marine orgasm. Most of the Calcium Carbonate used in industry is the result of direct extraction from rocks known as GCC (Ground Calcium Carbonate). Calcium carbonate is also made by crude calcination of CaCO_3 then dissolved in water and precipitated by giving carbon dioxide. The precipitate is known as PCC (Precipitate Calcium Carbonate).

PCC has three types of crystalline phases, namely: rhombohedral calcite with rhombic (sloping box) and scalenohedral morphology, orthorhombic aragonite with needle-like morphology, and hexagonal vaterite with porous spherical morphology. The fundamental difference of the three structures above lies in the number of oxygen atoms that surround each calcium atom. Calcite and Vaterite have CaO_6 and CaO_8 formations, while Aragonite has CaO_9 formation.[4][5]

2.3. Calcium Ferrite

Calcium Ferrite Material is a type of ceramic material made from a mixture of Ca oxide and Fe oxide. There are several phase forms of Calcium Ferrite such as CaFeO_3 , CaFe_2O_4 , $\text{Ca}_2\text{Fe}_2\text{O}_5$, CaFe_4O_7 , $\text{Ca}_4\text{Fe}_9\text{O}_{17}$, and $\text{Ca}_4\text{Fe}_{14}\text{O}_{25}$. Ferritic Calcium is applied to optical memory devices, manetoplumbite structures, biomaterials and the steel industry. Calcium Ferrite CaFe_4O_7 was developed to achieve an iron mineral material. However, to get CaFe_4O_7 in the form of iron minerals there are obstacles. CaFe_4O_7 tends to easily form ceramic material. Research on Calcium Ferrite has long been carried out. One of them is $\text{Ca}_2\text{Fe}_2\text{O}_5$. $\text{Ca}_2\text{Fe}_2\text{O}_5$ is referred to as a thermoelectric p-type material which has recently been studied by Emily from the USA. $\text{Ca}_2\text{Fe}_2\text{O}_5$ has a tetrahedral structure with a pnma chamber group. $\text{Ca}_2\text{Fe}_2\text{O}_5$ is synthesized by mixing CaCO_3 and Fe_2O_3 which is sintered at 1573K . [6]

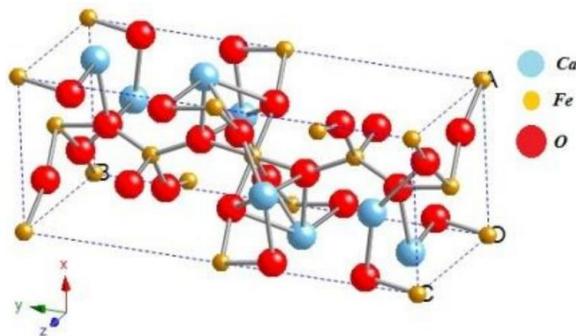


Fig. 1: Tetrahedral crystal structure of $\text{Ca}_2\text{Fe}_2\text{O}_5$ (Crystal Maker, Ltd)

III. Methods

3.1. Synthesis $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

$\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is synthesized by coprecipitation method. Iron sand have been extracted to be dissolved in HCl 37% and stirred at a temperature $\pm 65^{\circ}\text{C}$ for 1 h by a magnetic stirrer ± 650 rpm. Then a solution was formed, it was filtered by filtering paper. By NH_4OH was added into this solution while stirring at temperature $\pm 65^{\circ}\text{C}$, precipitation particle of Fe_3O_4 was formed. Fe_3O_4 precipitation was washed by distilled water repeatedly to result in pH 7, then

filtered, dried and calcined at 800⁰C for 2 h. Fe₂O₃•H₂O formed is tested with XRD to ensure the phase formed is Fe₂O₃•H₂O phase.

3.2. Synthesis PCC

The precipitated calcium carbonate (PCC) or CaCO₃ is synthesized by carbonation method. Limestone was calcined at 900⁰C for 6 h then produced CaO. CaO is dissolved in distilled water to form Ca(OH)₂ and then carbonated by CO₂ gas. In this case, PCC was formed, than finally filtered and dried. CaCO₃ precipitated formed is tested with XRD to ensure the phase formed is CaCO₃ phase.

3.3. Synthesis Ca-Fe-O (Mixing Fe₂O₃•H₂O from Iron Sand and PCC from Limestone Precipitated)

The mixing of extracted Fe₂O₃•H₂O from iron sand and PCC from limestone is mixed by solution mixing method. Fe₂O₃•H₂O and PCC each one are dissolved in HNO₃ solution that Ca/Fe mole ratio is 1/4, 1/8, and 1/12. The solution of Fe(NO₃)₃ and Ca(NO₃)₂ are mixed until homogeneous, then is heated treatment process at 80-90⁰C to slurry and dried at 80⁰C for 8 h. The slurry is dried and crushed to be powder. The powder is analyzed thermal characterization by DTA-TGA.

IV. Results and Discussion

The results of Fe₂O₃ synthesis from iron sand were confirmed by XRD testing. Fe₂O₃ was precipitated again to Fe₂O₃•H₂O and confirmed by XRD testing as well. Re-precipitation is done so that later Fe₂O₃ dissolves easily in HNO₃ during the synthesis of Calcium Ferrite. XRD test results show that what is formed is Fe₂O₃ and Fe₂O₃•H₂O. XRD patterns of Fe₂O₃ and Fe₂O₃•H₂O are shown in Figure 2 and Figure 3.

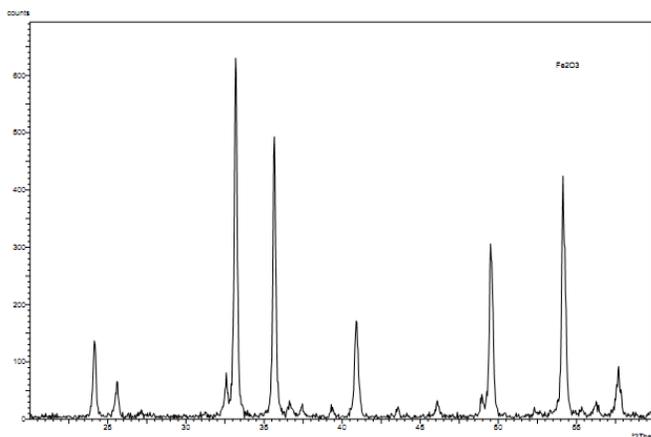


Fig. 2: Diffraction Pattern of Fe₂O₃

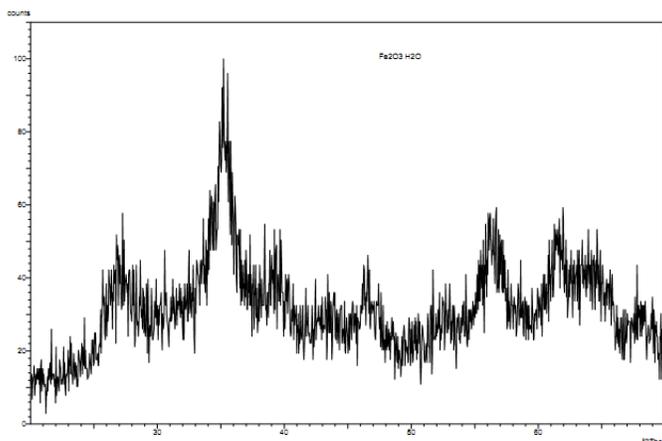


Fig. 3: Diffraction Pattern of Fe₂O₃•H₂O

The results of CaCO₃ synthesis from limestone were also confirmed by XRD testing. The XRD test results show that CaCO₃ is formed. The XRD pattern of CaCO₃ is shown in Figure 4.

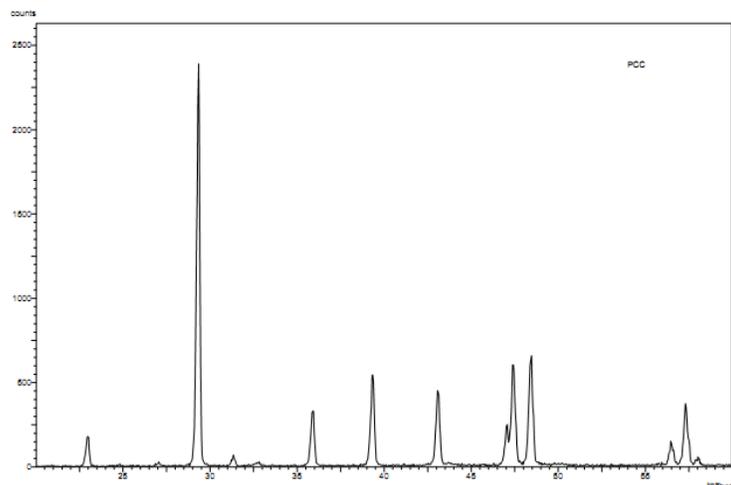


Fig. 4: Diffraction Pattern of CaCO₃ Precipitated

DTA-TGA testing is carried out with heating speed 20⁰C per minute. Heating is carried out from room temperature up to 1000⁰C. Data from DTA-TGA testing for samples with mol ratio 1: 4, 1: 8, and 1:12 respectively are shown in Figure 5, Figure 6, and Figure 7.

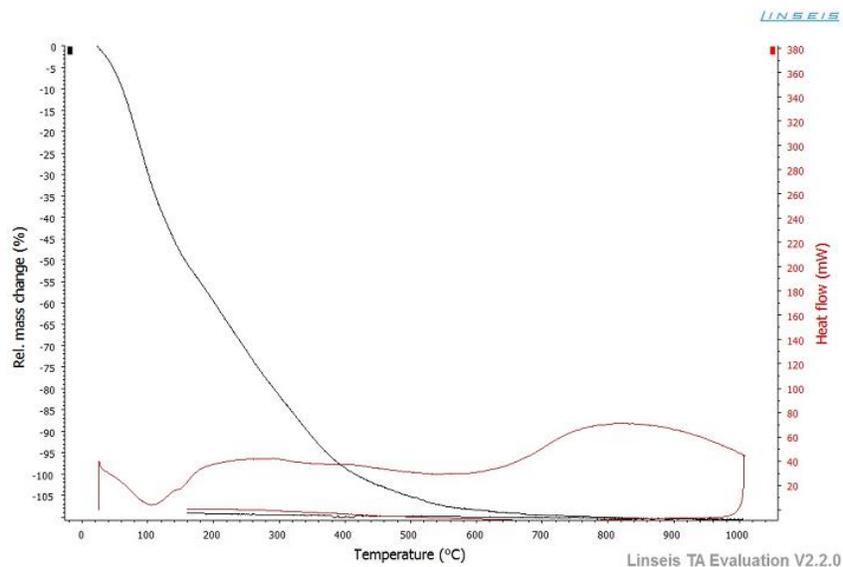


Fig. 5: DTA-TGA Curve for 1: 4 Mole Ratio

On the DTA curve, a decrease and increase in the curve shows the existence of an atomic release process or a new bond is formed between atoms or better known as the diffusion process. The determination of the atomic release process or diffusion process is confirmed by the TGA curve.

If there is a decrease and an increase in the DTA curve which is accompanied by a decrease in mass which is indicated by the decrease in the TGA curve, it can be concluded that there is a process of dehydration or calcination. If there is a decrease and increase in the DTA curve without being accompanied by a decrease in mass, then it can be concluded that there is a diffusion process.

In Figure 5, the TGA line curve indicates that there is a dehydration process and calcination up to about 500⁰C and began to slow down to a temperature of 1000⁰C which was marked by a significant reduction in mass followed by a slow decline. On the DTA line curve, there are 2 exothermic point peaks at temperatures around 100⁰C and 575⁰C.

This has explained the dehydration process at 100⁰C and the calcination process at 575⁰C. The process above 575⁰C shows exothermic and endothermic followed by reduced mass slowly. In this region explained that there is a diffusion process between Ca and Fe forming a new phase of Ca and Fe.

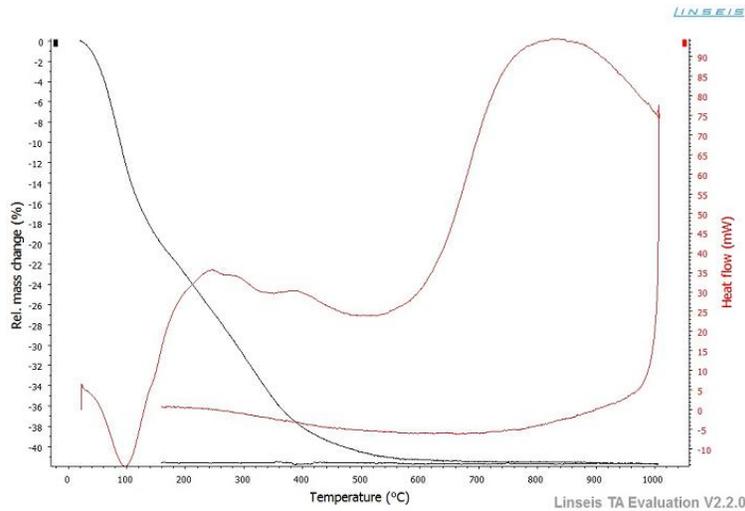


Fig. 6: DTA-TGA Curve for 1: 8 Mole Ratio

In Figure 6, the dehydration process occurs at a temperature of 95⁰C and the calcination process occurs at a temperature of 545⁰C. The process above 545⁰C shows exothermic and endothermic followed by a slow decrease in mass. In this region, it is explained that there is a diffusion process between Ca and Fe forming a new phase for mol ratio 1: 8.

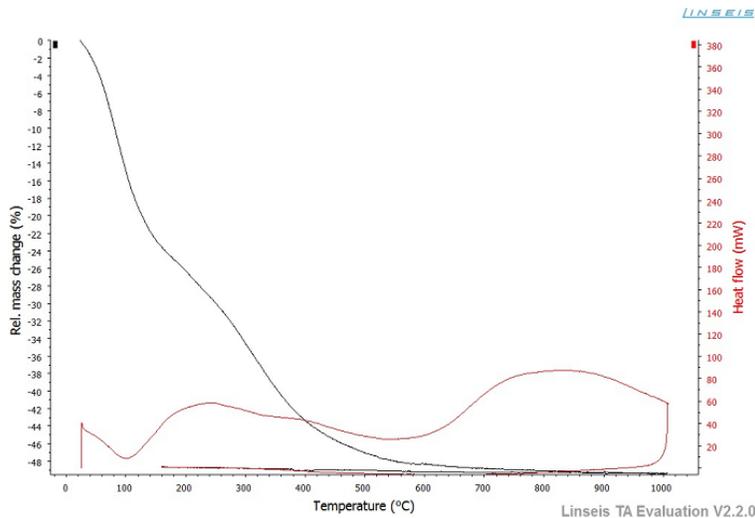


Fig. 7: DTA-TGA Curve for 1: 12 Mole Ratio

In Figure 7, the dehydration process occurs at a temperature of 98⁰C and the calcination process occurs at a temperature of 548⁰C. The process above 548⁰C shows exothermic and endothermic followed by a slow decrease in mass. In this region, it is explained that there is a diffusion process between Ca and Fe forming a new phase for mol ratio 1: 12.

V. Conclusion

The mixture of Fe₂O₃•H₂O and PCC has been successfully transformed. Based on the results of DTA-TGA, there are dehydration and calcination process before the temperature of 500⁰C and above 500⁰C the diffusion process occurs. And it can be said that sintering heat treatment can be carried out in these temperature regions (above 500⁰C).

Acknowledgment

This research was partially supported by “Hibah PDP” research grant provided by Simlitabmas, Ristekdikti, 2018.

References

- [1] B.D. Kulkarni, R.B. Jotania, A.S. Deshpande, R.B. Khomane, and C.C. Chauhan, "Physical and Magnetic Properties of Barium Calcium Hexaferrite Nano-particles Synthesized by Water-in-oil Reverse Micelle and Co-precipitation Techniques," *Journal of Scientific Research*, vol. 1, no. 1. pp. 1–13, 2009.
- [2] C.S. Prakash, V.M. Nanoti, and D.K. Kulkarni, "Magnetic characterization of substituted calcium hexafemte," *Mater. Lett.*, vol. 24, no. 1–3, pp. 171–173, 1995.
- [3] H.I. Hsiang and R.Q. Yao, "Hexagonal ferrite powder synthesis using chemical coprecipitation," *Mater. Chem. Phys.*, vol. 104, no. 1, pp. 1–4, 2007.
- [4] Darminto, M. Cholishoh, F. . Perdana, M. Baqiya, M. Cahyono, and Triwikantoro, "Preparing Fe₃O₄ nanoparticles from Fe²⁺ ions source by co-precipitation process in various pH," *AIP Conf. Proc.*, vol. 1415, no. September, pp. 234–237, 2011.
- [5] Mastuki, M.A. Baqiya, and Darminto, "Explorative Synthesis of Magnetic Ca-Fe-O Compounds by Mixing Precipitated CaCO₃ from Limestone and Iron Sand Extracted – Fe₂O₃.H₂O," *Mater. Sci. Forum*, vol. 827, pp. 203–207, 2015.
- [6] E. Asenath-Smith, I.N. Lokuhewa, S.T. Mixture, and D.D. Edwards, "p-Type thermoelectric properties of the oxygen-deficient perovskite Ca₂Fe₂O₅ in the brownmillerite structure," *Journal of Solid State Chemistry*, vol. 183, no. 7. pp. 1670–1677, 2010.