Characterization of Calcium Ferrite Phase from Fe$_2$O$_3$ and CaCO$_3$ Based on Iron Sand and Limestone Using XRD and SEM-EDX Analysis

Mastuki, P U Gatut, A W Brata, A G Istiawan, B Aditya and H Masrufi
Mechanical Engineering, Faculty of Engineering, University of 17 Agustus 1945 Surabaya, Indonesia

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

Abstract. Synthesis of Ca-Fe-O using coprecipitation method employing CaCO$_3$ and Fe$_2$O$_3$ has been conducted. Extraction of limestone as the raw material of precipitated calcium carbonate (PCC) and iron sands as that of Fe$_2$O$_3$ was prepared to explore various compound of Ca-Fe-O. PCC and Fe$_2$O$_3$ are dissolved in HCl then mixed into homogeneous and precipitated using NH$_4$OH. Mixing is resolved by the mass ratio of PCC and Fe$_2$O$_3$ with a ratio of 1/4, 1/6, 1/8, 1/12. The results of synthesis are sintering at temperature of 700°C. The sintered samples were characterized by XRD and SEM-EDX. The results of XRD is indicated the formation of Ca-Fe-O phases that is dominated by Ca$_2$Fe$_2$O$_5$ and Ca$_2$Fe$_9$O$_{13}$ phases, and results of SEM/EDX indicate nanoscale particle size that is composed of Ca, Fe, O, and Si elements.

1. Introduction
Iron sand is one of the natural resources which is quite abundant in Indonesia. Almost all of the big islands in Indonesia have iron sand with different qualities. There are three types of iron sand ore, they are hematite magnetic iron ore, lateritic iron ore, and titan iron ore. Generally, iron sand is widely applied as a concrete aggregate in civil construction field[1], as a basic material in steel industrial field, and as a basic material in the manufacturing magnetic materials in developing advanced materials[2]. Research on the development of advanced materials that mostly use iron sand is the manufacture of soft and permanent magnets. One of permanent magnet that utilization of iron sand is magnet type Barium Ferrite and Strontium Ferrite.

Barium Ferrite can be synthesized by some methods, they are powder metallurgy (milling, annealing, and sintering mechanisms)[3] and coprecipitation method (acid-base technique) by extracting iron sand to be pure and small dan be easily diffused with BaCO$_3$ or SrCO$_3$. Iron sand was extracted by coprecipitation method to getting Fe$_3$O$_4$ that was then sintered into Fe$_2$O$_3$[4]. Barium or Strontium that using to synthesis Barium Ferrite is Barium or Strontium in the form of carbonate[5].

Besides abundant iron sand, there is abundant natural resources else, that is limestone. Limestone is a sedimentary rock which has high CaCO$_3$ phase content. In Indonesia, limestone is in various regions with a total 2,156 billion tons, which are spread in Aceh Darussalam (131.12 billion tons (Mt)), North Sumatra (3.24 Mt), West Sumatra (68.1 Mt), Riau (53.2 Million tons (Million)), Bengkulu (137.1 Million), Jambi (157 Million), South Sumatra (294 Million), Lampung (2 Million), Banten (61.6 Million), West Java (660.3 Million) Mt, Central Java (6 Mt), DI Yogy (10M), East Java (3,069Mt), Bali (154.64Mt), NTB (1.2Mt), NTT (132.82M), Central Kalimantan (449Mt), South Kalimantan...
(8.33Mt), East Kalimantan (57 Mt), North Sulawesi (18.8M), Gorontalo (18.5Mt), Central Sulawesi (696Mt), South Sulawesi (31.33Mt), Southeast Sulawesi (1.527Mt), North Maluku (8.87Mt), and Papua (2.6 Mt).

Generally, limestone is applied as a basic material for construction materials, the main material for portland cement production, and as an additive in the metal smelting industry. Limestone (dominated by CaCO$_3$ phase) is one of the potential that has not been considered as an alternate Ba and Sr that is both form the carbonate phase.

Calcium is one of alkaline earth elements and so is same group with Barium and Strontium. The physical and chemical properties of Calcium aren’t much different than Barium and Strontium. This allow a Calcium Ferrite formed. Research on Calcium Ferrite has been carried out that is a type material p-Type thermolectric properties of the oxygen-defined Ca$_3$Fe$_2$O$_5$ perovskite. Considering the abundant of iron sand dan limestone that not yet be developed maximally, and so, this study is conducted to analyze the types of Calcium Ferrite phases formed by synthesizing them based on local natural materials of iron sand and limestone.

2. Experimental

2.1. Synthesis

Calcium Ferrite samples were synthesized by a fusion of Fe$_2$O$_3$ and CaCO$_3$ with mass proportions ratio 1/4, 1/6, 1/8, and 1/12 for CaCO$_3$/Fe$_2$O$_3$. Calcium Ferrite is synthesized by coprecipitation method. Fe$_2$O$_3$ is obtained by extraction from iron sand and than be synthesized by coprecipitation method. Iron sand is dissolved in HCl 37% and the resulting solution was precipitated by NH$_4$OH. The precipitation is sintered at 800°C for 2 hours. And CaCO$_3$ is obtained by extraction from limestone and than be syntesized by carbonation method. Limestone is calcined at 900°C for 6 hours to produce CaO. CaO is dissolved into distilled water and than be carbonated by CO$_2$ gas. Calcium Ferrite samples were synthesized using the coprecipitation method by dissolving in HCl 37% each Fe$_2$O$_3$ and CaCO$_3$. The each resulting solution are mixed till homogeneous and than be precipitated by NH$_4$OH. The resulting mixture sample is then sintered at 700°C for 1 hour.

2.2. Phase Characterization

X-ray diffractometer (XRD) is used to obtain X-ray diffraction patterns. The XRD measurement results are used to analyze the phase content of the resulting sample. The phase identification process is carried out by the search and match process using the Xpert Identify Graph and Match! Software. XRD testing for Calcium Ferrite samples was carried out in the Material Engineering laboratory of the ITS campus in the range of 2theta : 5° - 90°.

2.3. SEM-EDX

Scanning Electron Microscope (SEM) is a type of electron microscope that depicts samples by scanning electrons in a raster scanning pattern. The electrons that interact with the sample-forming atoms produce a signal that gives information about the sample's topography, composition, and other properties. SEM combined with EDX informs the elements and their distribution from the sample. SEM-EDX testing was performed on Calcium Ferrite samples which had more Calcium Ferrite phase composition of XRD test data. SEM-EDX testing is carried out in the ITS Mechanical Engineering laboratory.

3. Results and Discussion

3.1. Phase and structural analysis

Calcium Ferrite phase formation occurs at temperatures above 500°C[8]. Fe$_2$O$_3$, which is the basic ingredient of Calcium Ferrite synthesis and also the result of extraction from iron sand, is analyzed for purity of the phase. This is important as confirmation that the extraction was successful and that Fe$_2$O$_3$
was actually obtained, as well as for CaCO$_3$. XRD test results of Fe$_2$O$_3$ and CaCO$_3$ are shown in figure 1 and figure 2.

Figure 1. X-ray diffraction pattern of Fe$_2$O$_3$ synthesized from iron sand

Figure 2. X-ray diffraction pattern of CaCO$_3$ synthesized from limestone
**Figure 3.** X-ray diffraction pattern of Calcium Ferrite synthesized by coprecipitation method

**Figure 4.** SEM of Calcium Ferrite samples with a ratio of 1/6
Figure 3 shows the X-ray diffraction pattern for Calcium Ferrite samples in the ratio of 4, 6, 8, and 12. The XRD test data obtained provides information that three types are formed Calcium Ferrite phase, they are CaFe$_4$O$_7$, Ca$_2$Fe$_2$O$_5$, and Ca$_2$Fe$_9$O$_{13}$. Each type of phase formed has different characteristics for each variation given. For the CaFe$_4$O$_7$ phase, this phase increases with increasing ratio of Fe$_2$O$_3$ given. That is because the CaFe$_4$O$_7$ phase requires more Ca elements and is formed at high temperatures. As for the other phases, namely Ca$_2$Fe$_2$O$_5$ and Ca$_2$Fe$_9$O$_{13}$, the pattern of large values of the phases formed is up and down. That is due to the growth of Fe$_2$O$_3$ phases which are indeed formed in the temperature range of 600°C to 800°C. From the overall data, there is still a lot of research to be done for other variations so that later can get information about properties of the phase formation and proportions in accordance with the desired phase needs.

3.2. Element composition, particle size, and sample shape analysis

Information on elemental composition, particle size, and sample shape of Calcium Ferrite was done by SEM-EDX testing. SEM-EDX testing is carried out on samples with a ratio of 1/6 by considering the volume fraction of the Ca$_2$Fe$_2$O$_5$ phase as a type of Brownmillerite Material which has attractive electrical properties. SEM results with various types of magnifications are shown in figure 4 and EDX results are shown in table 1.

| Element | Atomic % |
|---------|----------|
| Ca      | 2        |
| Fe      | 34       |
| O       | 58       |
| Si      | 6        |

Figure 4 shows an indication of the size of nano-sized particles. Besides, particles also appear agglomerated which indicate the magnetic properties of the particles. This is reasonable considering the basic material of the magnet itself is Fe$_3$O$_4$. Table 2 also shows that the constituent elements of the sample are Ca, Fe, O, and Si. These results confirm or explain the roughness formed in the background of the XRD test data.

4. Conclusion

Calcium Ferrite from the results of mixing of Fe$_2$O$_3$ extracted from natural iron sand and CaCO$_3$ extracted from natural limestone were successfully synthesized. The XRD test results showed three types of Calcium Ferrite phases namely CaFe$_4$O$_7$, Ca$_2$Fe$_2$O$_5$, and Ca$_2$Fe$_9$O$_{13}$ with CaFe$_2$O$_5$ phases, and Ca$_2$Fe$_9$O$_{13}$ as dominant phases. SEM test results show indications of nano-sized particle size and also the particles look agglomerated which indicates the magnetic properties of these particles. The EDAX results show that the elements making up the phase are Ca, Fe, O, and there is little impurity, Si. The EDAX results confirm or explain the background roughness level from the XRD test results.

5. Acknowledgments

This research was partially supported by “Hibah Internal PT 2018” research grant provided by University of 17 Agustus 1945 Surabaya, Indonesia.

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