High purity hematite (Fe$_2$O$_3$) from beach sands for soft ferrite magnetic materials application

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Abstract. Actually, the potential and deposits are rich and spread in many place, but the process from raw material to industrial product is not optimal yet. In this work, the manufacture of iron sand was done using direct reduction technique by compact coals as reductor. The carbon compound of coals were using for releasing oxide in magnetite compounds (Fe$_3$O$_4$) of iron sand, so it could be transformed to Fe phase. The iron sand was firstly milled using high energy ball mill (HEBM) for 0, 10, 20, and 40 hours. Then the iron sands samples were mixed with coals, bentonite and compacted using hydraulic press. Then, loaded into furnace and sintered at 700 °C, 800 °C, and 900 °C. As the results, it was identified (using XRF) that the major phase was Fe$_2$O$_3$ (75.40 %). Consistent with XRF results, the phase composition observation by using XRD was shown that the major phase of sample was Fe$_2$O$_3$ (hematite). It was also shown that the crystallite size of the sample was around 8 nm, as calculated using Scherrer formula. The magnetic behavior investigation was showed that the decreasing in magnetic saturation value (Ms) and remanent (Br) and followed by increasing the coercivity value (Hc).

1. Introduction

The increase in the price of steel raw materials in the international market has triggered the government and mining authorities to start using local raw materials. One of the local minerals that is currently being actively studied as a raw material for the steel industry is iron sand. Iron sand which is a mineral that has compounds that are useful for the industrial world such as magnetite (Fe$_3$O$_4$) which is used for the steel industry [1], as well as other compounds it has. For this reason, along with the development of the industrial world, efforts to process iron sand and other metallic minerals are being intensively investigated.

Aceh province is known to have abundant iron sand deposits. One of them is located on the coast of Syiah Kuala, Banda Aceh. The results of identification with XRD show that the magnetite (Fe$_3$O$_4$) phase is the main phase in this iron sand with a content of up to 86.55% [2]. Looking at the content, it is necessary to conduct further studies so that this mineral can be increased its added value.

In this study, iron sand processing will be carried out into semi-finished products, namely iron pellets (pig iron) by the direct reduction method. Here, the reduction process is carried out using a solid reducing agent in the form of coal and bentonite as a binder so that iron oxide compounds (Fe$_3$O$_4$) can transform...
into Fe[3]. Coal contains more carbon compounds in it than lime or other minerals. This carbon compound contained in coal is used as a reducing agent in the direct reduction process. Furthermore, the sample in the form of a combined pellet of iron sand, coal and bentonite, was sintered with temperature variations of 700°C, 800°C, and 900°C in the furnace. Next, the samples were characterized by phase composition using X-Ray Diffraction (XRD), as well as observations of magnetic properties using Permagraph.

2. Materials and Method
The iron sands was collected from the coast of Dayah Raya village, Syiah Kuala District, Banda Aceh. The iron sand was dried for 4 hours. Then the separation process was carried out using a permanent magnet. Furthermore, to obtain iron sand in the form of a fine powder, it is carried out using a mechanical alloying technique using a ball mill apparatus. The sand sample was put into a planetary ball mill (Fritsch, P6) with a ball-to-powder ratio of 10:1 and milled for 10, 20, and 40 hours with a rotation speed of 450 rpm. The milled samples was sieved, and the ingredients were mixed with coal and bentonite. Mixing of materials was carried out with a ratio of 3:1 sand and coal while the added bentonite is slightly useful as a binder in the direct reduction process. The next process was pelletization using a hydraulic press machine. The pellet process was carried out by applying pressure of 7 tons with a holding time 1 hour. The results of the pelletizing material in the form of a cylinder, then dried for 15 minutes at room temperature. Then, the heating process (sintering) was applied using a furnace with a temperature variation of 700°C, 800°C - 900°C and a heating time of 30 minutes. The sintered samples were then identified by XRF, XRD and Permagraph to obtain data on chemical composition, crystal structure and magnetic properties.

3. Results and Discussion
3.1. Identification of mineral content with XRF
Identification of the mineral content in the iron sand pellet sample is carried out using an XRF (X-Ray fluorescence) tool, where with this technique the levels of elements contained in the sample will be known. From this analysis, it is known that the composition of iron pellets formed from unmilled iron sand is reduced by carbon from coal, where from the XRF test results a Fe2O3 phase is formed with a percentage reaching 75.40% and is followed by other elements as shown in Table 1.

However, after the mechanical alloying process was carried out on iron sand with variations in milling time (10, 20 and 40 hours), then it was formed into iron sand pellets with coal as a reducing agent which was sintered in a furnace at a temperature of 900°C. it turned out that after the reduction process occurred in the furnace the Fe2O3 phase reached 72.23% and was followed by other elements as shown in Table 2.

From Table 1 and 2, there was a decrease in the level of Fe in the sample after the milling process occurred. The longer the milling time which reaches 40 hours, the percentage of Fe2O3 phase decreases, but the phase decrease is not drastic, only 3% occurs. Based on previous work [2], the iron sand milling process was yielded a maximum percentage of Fe3O4 of 86.55% when the milling time reached 20 hours. But when the milling time for the material reached 40 hours the percentage of Fe3O4 decreased again. The decrease in Fe3O4 phase was caused by unwanted oxide crystals starting to form again. From this study, it affects the reduction results of iron sand pellets so that the Fe2O3 phase formed from iron sand which is milled with a time of 40 hours has decreased.

3.2. Phase Identification with XRD
This XRD test uses a Shimadzu D6000 X-ray diffractometer, CuKα radiation (λ= 1.54060) at an angle of 10°-80°, the generator is operated at a voltage of 40 kV with a current of 30 mA. The XRD test aims to identify the mineral phase of the iron sand pellet sample that has been reduced with a solid reducing agent, namely coal with various sintering temperatures (700, 800 and 900°C). From the XRD results that have been carried out for variations in milling time (0, 10, 20 and 40 hours) then
a comparison is made with the data base that has been issued by the Joint Committee for Powder Difraction Standard (JCPDS) so that the research data is more accurate. This identification is approximated by the value of d of certain minerals as stated in the JCPDS. The results of this test are shown in Figure 1.

Table 1. XRF observation results for un-milled iron sand pellets.

| No. | Compound  | Percentage (%) |
|-----|-----------|----------------|
| 1   | Fe$_2$O$_3$ | 75.40%         |
| 2   | SiO$_2$    | 10.0%          |
| 3   | Al$_2$O$_3$| 4.90%          |
| 4   | TiO$_2$    | 4.59%          |
| 5   | NiO        | 1.18%          |
| 6   | CaO        | 0.83%          |
| 7   | Cr$_2$O$_3$| 0.794%         |
| 8   | MnO        | 0.48%          |
| 9   | V$_2$O$_5$ | 0.48%          |
| 10  | P$_2$O$_5$ | 0.3%           |
| 11  | Rb$_2$O    | 0.28%          |
| 12  | Br         | 0.18%          |
| 13  | K$_2$O     | 0.14%          |
| 14  | CuO        | 0.12%          |
| 15  | Re$_2$O$_7$| 0.15%          |
| 16  | ZnO        | 0.087%         |

Table 2. XRF observation results for 40 hours milled iron sand.

| No. | Compound  | Percentage (%) |
|-----|-----------|----------------|
| 1   | Fe$_2$O$_3$ | 72.23%         |
| 2   | SO$_3$     | 17.6%          |
| 3   | TiO$_2$    | 4.98%          |
| 4   | SiO$_2$    | 1.3%           |
| 5   | NiO        | 0.948%         |
| 6   | Cr$_2$O$_3$| 0.815%         |
| 7   | CaO        | 0.58%          |
| 8   | V$_2$O$_5$ | 0.49%          |
| 9   | MnO        | 0.46%          |
| 10  | Br$_2$O$_7$| 0.32%          |
| 11  | Br         | 0.19%          |
| 12  | ZnO        | 0.11%          |
| 13  | K$_2$O     | 0.016%         |
| 14  | CuO        | 0.090%         |
Based on image observations and X-Ray Diffraction (XRD) data, a phase identification analysis was carried out by taking into account the intensity, phase, hkl, lattice spacing (d) and grain size. Samples analyzed in powder form were analyzed to determine the composition of the detected phase. Seen from Figure 1 for samples of iron sand pellets formed from un-milled iron sand sintered at a temperature of 900ºC reduced by coal. It shown the peaks of iron (Fe), hematite (Fe2O3), magnetite (Fe3O4), and other compounds. Fe2O3 as the main phase which has the highest peak. The addition of the heating period will provide more time for carbon (C) to react to form carbon monoxide (CO) [4,5]. As a result, with increasing carbon monoxide gas, the tendency to form Fe will be higher. However, it must also be noted that the excessive heating period will have the opposite effect that the formed Fe will be reduced back to Fe3O4 and Fe2O3 [6].

It shows that the results of the reduction of iron sand in Dayah Raya village, Syiah Kuala Sub-district with coal reductant analyzed produce the main phase material, namely hematite (Fe2O3). However,
from the three samples, the Fe phase was formed with the peak position increasing along with the fineness of the iron sand in the sample. The sample with unmilled iron sand has the lowest Fe intensity compared to the milled iron sand sample. The increase in the milling process in the sand causes the intensity of the Fe phase to increase in the reduced sample, but the milled iron sample is above 20 hours, the Fe phase formed from the reduction results in a decrease in intensity. This is because the milling time is too long so that unwanted oxide crystals are formed again [7-10]. The addition of the intensity of the Fe phase in the milling sample and after milling was found in the sample with 20 hours milling resulted in the highest peak with a position with $2\theta = 44.4260^\circ$, $d = 2.03756$ Å and $I/I_0 = 12$ were detected as the optimum Fe phase from the reduction results.

3.3. Magnetic Properties Analysis Results

Observation of the magnetic properties of the iron sand pellet sample which was reduced by a coal reducing agent resulted in a hysterical loop curve as shown in Figure 4. The resulting magnetic properties in the form of Saturation Magnetization ($M_s$) 0.8 T, Remanent Magnetization ($B_r$) 0.010 T and Coercivity ($H_c$) 7.90 kA/m have shown that this Fe phase has also been proven based on phase identification based on X-ray diffraction data. Figure 3 shows the loop hysteresis curve of un-milled iron sand sample mix with coal for sintering at temperature of 900°C.

![Figure 3. Loop hysteresis curve of un-milled iron sand sample with sintering temperature of 900°C.](image)

Furthermore, characterization of the magnetic properties of sand samples which were milled 10, 20 and 40 hours was also carried out with sintering temperatures of 700°C, 800°C and 900°C. The resulting hysteresis loop curve is shown in Figure 4.

The magnetic properties produces a hysteresis loop curve that shows magnetic properties in the form of saturation magnetization ($M_s$) of 0.025 T, while the remanent value ($B_r$) is 0.06 T and coercivity ($H_c$) is 7.36 kA/m. When compared, the magnetic properties of the pellet samples with iron sand before milling and after milling for 10, 20 and 40 hours, it is clear that changes in the magnetic properties of these samples have been seen. The changes include a decrease in the value of $M_s$ and $B_r$ accompanied by an increase in the value of $H_c$. This is due to the shrinking of the crystal size and the heat treatment that has been carried out [10-13]. It is clear that the sample does not meet the hysteresis loop curve where the saturation magnetization value is 0 T, the remanent value ($B_r$) is 0.001 T and the coercivity ($H_c$) value reaches >924.3 kA/m. Samples formed with milled iron sand will cause a finer powder size which will increase the empty space between particles in the pellet sample which is a source of demagnetization causing saturation magnetization ($M_s$) and remanent values ($B_r$) [15,16]. Then followed by an increase in the value of coercivity ($H_c$) which shows the finer the size of the magnetic...
crystal causing the Hc value to increase and be more stable [14]. It is noticed, that the milling process has shown an advantage in the finer powders processing [17-19].

Figure 4. Loop hysteresis curve after milling iron sand sample with sintering temperature of 900°C.

4. Conclusions
Based on the results of the reduction of iron sand pellets on the coast of Dayah Raya village, Banda Aceh shown the composition of the phase formed from iron sand pellets with X-ray diffraction technique obtained informed that the reduction results produce Fe2O3 phase as the main phase at a sintering temperature of 900°C for samples formed from un-milled and milling process. The formation of the Fe phase in the un-milled and milled iron sand pellet samples has the highest peak for the 20 hour milling sample. Furthermore, the magnetic properties shows a decrease in the magnetic saturation (Ms) and remanet (Br) values followed by an increase in the coercivity (Hc) value. From the magnetic properties obtained above, it is suitable for application of ferrite-based soft magnets.

Acknowledgments
Authors wish to thank Chandra Irwansyah, S.Si (Material Physics Lab., Syiah Kuala University) for assistance in the sample preparation and XRD testing.

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