Synthesis and characterization of high purity $\text{Fe}_3\text{O}_4$ and $\alpha$ - $\text{Fe}_2\text{O}_3$ from local iron sand

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Abstract. The synthesis and characterization of high purity of $\text{Fe}_3\text{O}_4$ and $\alpha$-$\text{Fe}_2\text{O}_3$ from iron sand has been carried out. Iron sand samples retrieved from Banten, Indonesia. The iron sand powder was milled for 10 hours at room temperature by using high energy milling (HEM) and then was separated according to its type using magnetic separator. The iron sand powders are dissolved in acid chloride solution so that is formed a solution of iron chloride, and this solution is sprinkled with sodium hydroxide to obtain fine powders. The fine powders which formed were washed again with de-ionized water and sintered in the electric chamber furnace at 750 °C in the air at atmosphere pressure for 5 hours. The elemental analysis results using neutron activation analysis (NAA) is obtained that the fine powders contain the dominant of iron (Fe). The refinement results of X-ray diffraction pattern shows that the fine powders have a single phase of $\text{Fe}_3\text{O}_4$, and then after sintering changed to $\alpha$-$\text{Fe}_2\text{O}_3$ single phase. The microstructure analysis showed that the particle of $\text{Fe}_3\text{O}_4$ and $\alpha$-$\text{Fe}_2\text{O}_3$ shaped respectively like spherical and polygonal with the similarly particle sizes and homogeneously on the surface of the samples. We concluded that this study has successfully performed the process of purifying iron sand to obtain fine powders of $\text{Fe}_3\text{O}_4$ and $\alpha$-$\text{Fe}_2\text{O}_3$ with high purity. The first section in your paper

1. Introduction
Indonesia is an archipelago which has a long coastline is endowed with rich natural resources, especially iron sand. The iron sand is generally to be found around the coastal area and which is also rich in various minerals such as iron and titanium. The iron sand in Indonesia has a huge potential with a proven reserve of up to 83 million tons with an average Fe content of around 59% is are dispersed almost throughout the coastlines of Indonesia, especially in Java, Sumatra and Nusa Tenggara. One of the iron sand reserve with a huge potential and having a very high Fe content is the iron sand found on the coast of Banten. According to the previous research results which have been carried out by Wisnu et al. there are some indications that based on the elemental test results of the iron sand by using neutron activation analysis method, the iron content in the iron sand of Banten is very high as shown in table 1 [1].
Table 1. The result of elementer analysis of the iron sand from Banten [1]

| No. | Element | Content (µg/g) | Concentration | Uncertainty |
|-----|---------|----------------|---------------|-------------|
| 1.  | Fe      | 585,223.43     | 103.85        |             |
| 2.  | Ti      | 70,051.89      | 4,250.25      |             |
|     | M (impurity) | < 1,000       |               |             |

From table 1 shows that the elemental constituents are iron and titanium with around 58.52 and 7.01 wt% respectively which also implies that the iron sand has an economic potential to be processed in the future.

One of iron mineral compound comes in the form of iron oxide. Iron oxide is a popular material because of its wide-ranging applications such as absorber materials [2-4], in sensors [5], as catalysts [6], and in biomedical applications such as imaging- and drug delivery devices [7]. In addition Iron oxide has many advantages, such as: oxidation stability, non-toxicity and compatible liquid system. There are four variety of commonly known crystalline iron oxides, namely α-Fe₂O₃ also known as hematite, β- Fe₂O₃ and γ- Fe₂O₃ also known as maghemite, ε- Fe₂O₃ and Fe₃O₄ also known as as iron (II, III) crystalline [4].

Many methods of synthesis have been carried out to obtain iron oxides and the type of procedures chosen will determine the quality and quantity of the product material. Synthesis of iron oxides utilizing different processes will produce compounds with different magnetic and electrical properties.

Several synthesis methods of iron oxide powders have been reported, among them the hydrothermal [8] the sol gel [9], the micro-emulsion [10], the co-precipitation [11], and the ultrasonic method [12]. In this work, the authors will focus on the extraction of iron oxide from local raw materials of iron sand through two stages. The first stage (top-down method) is iron sand particles that are large will be broken down into smaller sizes by using mechanical, chemical, or with other energy forms. Techniques commonly used in the top-down method is mechanical milling, followed by magnetic separation process with the aim to separate the powder of magnetic and non magnetic (impurities) of iron sand.

At this stage the iron oxide produced still has the size and shape of the particles that have not yet become homogeneous and their purity level is still low [1]. Therefore it is now necessary to undertake the second step, namely the bottom-up method. This second method is the synthesis by way of homogeneous nucleation of the liquid, namely binding by chemical reaction. The advantages of this method is homogenization of all the particles size, shape or morphology, the chemical composition and the intended crystal structure as was originally desired, such as the composition and the same surface, individual dispersionor mono-dispersion, and no agglomeration. Among all the bottom-up techniques so far, chemical co-precipitation is the most superior method in the synthesis of iron oxide particles because the procedure is straightforward and uncomplicated. The main objectives of this study is to obtain high purity Fe₃O₄ and α- Fe₂O₃ oxide samples by processing and purifying iron sand into iron oxides. The discussion will be focused on the results of processing and purifying the iron sand, the phase analysis includes structure parameters of the synthesized Fe₃O₄ and α- Fe₂O₃, their particle morphology and the elemental content of the synthesized oxides.

2. Materials and Methods

The iron sand raw material was extracted in Banten province Indonesia. The purifying process of iron sand into iron oxide product in the form of Fe₃O₄ and α- Fe₂O₃ with high purity is shown in figure 1.
During the first stage, iron sand was milled by using high energy milling (HEM). Then proceed with the separation of iron sand using a magnetic separator with weak magnetic fields in order to obtain fine powder of type of titanomagnetite which has a high Fe content. In the second stage the fine powder of titanomagnetite was dissolved in a technical grade chloride acid (HCl) solution with the ratio of 0.25Kg/L HCl to produce a solution of iron chloride. Next, technicalgrade Sodium hydroxide (NaOH 5M) was added slowly to a solution of iron chloride while stirring continuously using a magnetic stirrer. Stirring was performed at 80 °C for 1 hour. The precipitate was washed with demineralization water until reaching the neutral pH state, in order to removeresidual salts and other impurities from the sample. The precipitate is then separated from the solvent using permanent magnets (Nd2Fe14B magnet) and after that dried in an oven at 100 °C. The dry powder sample was milled by using an agate mortar to homogenize the particle size of the sample and then heated at 750 °C in a furnace for 5 hours. Finally, the sample was milled again by using an agate mortal.

The iron sand purification result was analyzed by X-ray diffractometer (XRD) method using a Miniflex Rigakuapparatus with CuKα radiation ($\lambda = 1.5406 \ \text{Å}$). The qualitative and quantitative phaseanalysis was performed by applying a GSAS program using Rietveld method. The morphology of the powder samples was observed by the scanning electron microscope (SEM) method employing the JED 2300 JEOL scanning electron microscope. Finally, the elemental composition analysis was performed by using neutron activation analysis (NAA) method. The standard reference material from NIST is usedas the internal quality control standardand Au alloyobtained from the Institute for Reference Materials and Measurement (IRMM) is used as flux monitor standard. The irradiation has been performed at thermal neutron flux about 1013 n.cm$^{-2}$.s$^{-1}$ in the irradiation facility of Multi Purpose Reactor GA. Siwabessy in Serpong, Indonesia.

3. Result and Discussion
Fine powder of titanomagnetite type which has a high Fe content from the milling process and magnetic separator has been obtained from the first stage process. Then in the second stage, the
The fine powder of titanomagnetite type with high Fe content is characterized by XRD method and compared with the Fe₃O₄ and α-Fe₂O₃ fine powder resulting from the purification process. In figure 3 are shown the results of measurements of XRD reflection pattern of the third of powders both before and after the purification process.

| No. | Mineral name       | Phase                  | Mass fraction (%) |
|-----|--------------------|------------------------|-------------------|
| 1.  | Ilmenite           | (Fe, Ti, M)₂O₃         | 11.67 ± 0.01      |
| 2.  | Hematite           | α-Fe₂O₃                | 15.96 ± 0.01      |
| 3.  | Titanomagnetite    | (Fe₃, Ti, M)₃O₄       | 72.37 ± 0.04      |

M : Impurities (Na, Sc, Cr, Co, Zn, Ga, As, La, Sm, Eu, Ho, Yb, Hf, W, Pt, U, Sb, Th, Ce, Mg, Mn, V, Al, and Ta)
Table 1 indicates that the phases contained in the iron sand is rich in titanomagnetite phase, moreover there are still ilmenite and hematite phases left over in the sample. However, in both the titanomagnetite- and ilmenite phase some minute (in ppm) amount of impurity elements M are also found.

The results of X-ray diffraction pattern refinement of the Fe$_3$O$_4$ sample obtained from the purification process are shown in figure 4.

![Figure 4. The refinement result of XRD profiles on the Fe$_3$O$_4$ sample after purifying process.](image)

Phase identification of Fe$_3$O$_4$ sample employs the crystallography open database (COD: 9013529) as a reference. According to the COD data the results obtained could be identified as the single phase of magnetite. Since the Hanawalt table can only be used for qualitative analysis, then the rietveld method (GSAS program) will be used for quantitative analysis.

The refinement result obtained are of excellent quality, the fitting converges to small reliability R factor and with a goodness of fit value $\chi^2$ (chi-squared) in good agreement with the standard value set by rietveld method. The structure parameter, factor R and goodness of fit ($\chi^2$) are shown in table 3.

| Space group : F d -3 m (227), crystal system : Cubic |
| a = 8.380(3) Å, b = 8.380(3) Å, c = 8.380(3) Å, α=β=γ=90° |
| V = 588.5(7) Å$^3$ and $\rho$ = 5.226 gr.cm$^{-3}$ |
| R factor $wR_p = 17.12$ Rp = 13.26 $\chi^2$ (chi-squared) = 1.245 |

Based on the obtained results of XRD refinement, it could be safely established that Fe$_3$O$_4$ sample synthesized using the purification process is a single magnetite phase.

In the next step, the Fe$_3$O$_4$ sample is set to undergo heat treatment to obtain a sample of α- Fe$_2$O$_3$. In figure 5 are shown the refinement results of X-ray diffraction pattern of the α- Fe$_2$O$_3$ sample after the heat treatment process.
The refinement result has also produced excellent quality of fitting. The phase identification refers to the crystallography open database (COD: 9000139) for the hematite phase. Figure 5 shows that the sample is a hematite single phase. The structure parameter, factor R and goodness of fit ($\chi^2$) are shown in table 4.

**Table 4.** Structure parameter, factor R, goodness of fit ($\chi^2$).

| Sample after purifying and sintering | $\alpha$-Fe$_2$O$_3$ phase |
|-------------------------------------|-----------------------------|
| Space group : R -3 c (167), crystal system : Hexagonal |                                  |
| $a = 5.0323(3)$ Å, $b = 5.0323(3)$ Å, $c = 13.730(1)$ Å, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$ |                                  |
| $V = 301.14(4)$ Å$^3$ and $\rho = 5.283$ gr.cm$^{-3}$ |                                  |
| R factor | $wR_p = 18.26$ | $R_p = 11.67$ | $\chi^2$ (chi-squared) = 1.106 |

The SEM micrograms of the sample before and after purifying process are shown in figure 6.

(a) Iron sand after milling by HEM

(b) After separating by magnetic separator
Figure 6. Surface morphology of samples before and after purifying process

In figure 6(a) is shown the particle morphology of the (mechanically) milled iron sand sample. The collision of the milling steel balls causes the particles of iron sand to be flattened and thus the fracture forming smaller particles. Figure 6(b) shows the fine powder of iron sand from separation process results using a magnetic separator, so the particles seem to appear in the shape of aggregates and are almost uniform. Figure 6(c) is a particle morphology of Fe₃O₄ from purification process results and the particles appear in the form of spherical and are uniform. Spherical shape is thought to originate from the droplets NaOH at low speed. Figure 6(d) is a particle morphology of α-Fe₂O₃ with uniform polygonal shape. Specific form and nature of α-Fe₂O₃ particles follow the shape of a hexagonal structure. Uniform shape indicates that microscopically the samples have similar phase. These results are consistent with the results of refinement X-ray diffraction pattern of the sample of Fe₃O₄ and α-Fe₂O₃ obtained from purification process.

Thus, further analysis of the elemental content in the samples by using neutron activation analysis (NAA is required). NAA is both a quantitative and a qualitative method with high efficiency for the precise determination of a number of main-components and trace elements in different types of samples. NAA method is principally based on the nuclear reaction between neutrons and target nuclei. It is a useful method for the simultaneous determination of about 25-30 major, minor and trace elements of geological, environmental, biological samples in ppb-ppm range without or with chemical separation [1].

Figure 7 shows the gamma-ray spectrum of neutron activation analysis (NAA) measurement result on the sample after the purification process.

Figure 7. The elementary analysis of sample after purifying process by NAA
The spectrum of gamma energy as Figure 7 shows that the dominant elements are iron (Fe-59) at 1099.25 keV, this means that the sample is rich in content of iron. The detailed information on concentration of elemental content in the sample is given in Table 5.

Table 5. The result of elementer analysis of the Iron sand kind of titanomagnetite samples

| No. | Element | Iron sand kind of titanomagnetite Content (µg/g) | Uncertainty |
|-----|---------|-----------------------------------------------|-------------|
| 1   | Fe      | 580.677.03 | 2,773.38 |

| No. | M* (impurity) | M* (impurity) Content (µg/g) | Uncertainty |
|-----|---------------|-------------------------------|-------------|
| 1   | Ce            | 19.44                         | 0.53        |
| 2   | Yb            | 0.95                          | 0.15        |
| 3   | Th            | 0.70                          | 0.07        |
| 4   | La            | 8.14                          | 0.37        |
| 5   | Eu            | 0.39                          | 0.03        |
| 6   | Zn            | 561.65                        | 21.08       |
| 7   | Co            | 144.78                        | 1.48        |
| 8   | Sc            | 13.11                         | 0.06        |
| 9   | Cr            | 652.08                        | 7.53        |
| 10  | Sm            | 2.61                          | 0.07        |
| 11  | Sc            | 14.94                         | 0.88        |
| 12  | Na            | 536.13                        | 10.18       |
| 13  | La            | 9.36                          | 0.40        |
| 14  | Mg            | 7559.73                       | 2760.42     |
| 15  | V             | 3154.05                       | 83.31       |
| 16  | Mn            | 4534.03                       | 40.14       |
| 17  | Ti            | 4249.37                       | 512.42      |

According to the results of the elemental content analysis of the Fe$_3$O$_4$ sample, it is also a very complex sample. Table 5 displays the iron content in the sample of processing result, which in this case is around 58.07 wt%. It means that this sample has a very high iron content. These results show that in this work the processing of iron sand from local resources into high purity of Fe$_3$O$_4$ and α-Fe$_2$O$_3$ has successfully been carried out and because of its economic potential it is strongly recommended to continue with the production works.

4. Conclusion

This study has successfully performed the purifying process of iron sand from local resources to obtain fine powders of Fe$_3$O$_4$ and α-Fe$_2$O$_3$ with high purity. The co-precipitation method is a simple and an effective technique for preparing fine powder of Fe$_3$O$_4$ and α-Fe$_2$O$_3$. The refinement results of x-ray diffraction pattern shows that both Fe$_3$O$_4$ and α-Fe$_2$O$_3$ have a single phase. Fine powder of Fe$_3$O$_4$ has a structure of cubic (F d -3 m) with lattice parameters a = b = c = 8.380(3) Å, α = β = γ = 90o, V = 588.5(7) Å$^3$ and ρ = 5.226 gr.cm$^{-3}$. Meanwhile fine powder of α-Fe$_2$O$_3$ has a structure of hexagonal (R -3 c) with lattice parameters a = b = 5.0323(3) Å, c = 13.730(1) Å, α = β = 90o and γ = 120o, V = 588.5(7) Å$^3$ and ρ = 5.226 gr.cm$^{-3}$. SEM micrograms of the sample show that the particle of Fe$_3$O$_4$ and α-Fe$_2$O$_3$ are shaped like spheres and polygons respectively with similar particle sizes and homogeneously on the surface of the samples. The spectrum of gamma energy shows that the dominant elements are iron (Fe-59) at 1099.25 keV around 58.07 wt%, this means that the sample is rich in content of iron. The purifying process used is economical and environmentally friendly, as it involves technical quality materials, which make Fe$_3$O$_4$ and α-Fe$_2$O$_3$ as a promising material for industrial applications.
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