The effect of calcination temperature on the structure of iron oxide phase from west Sumatra

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Abstract. This research aimed to investigate the effect of calcination temperature on phase changes and the structure of iron oxide contained in iron ore from the area of West Sumatra. Complex geological regions in West Sumatra contribute to the characteristics of iron ore in the area. The calcination temperature used is 260°C, 300°C and 500°C. The characterization tools used are X-ray powder diffractometer (XRD) and X-ray Fluorescence (XRF). The results of the analysis using XRF showed that this iron ore contained Fe content of 69.59% and after being purified at 87.50%. The results of the analysis using XRD indicate that the calcination temperature affects the iron oxide phase formed. At the calcination temperature of 300°C, the iron oxide phase that appears is Magnetite, Hematite, and Maghemite. At the calcination temperature 500°C the iron oxide phase that appears is Maghemite and hematite. The calcination temperature also affects changes in iron oxide structure. Structural changes that occur from cubic to cell units a = b = c = 8.3985 Å for Tetragonal structures with unit cells a = b 8.3460 Å and c = 25.0340 Å then to Rhombohedral structure a = b = 5.0320 Å and c = 13.7362 Å.

1. Introduction
Iron ore is a mine material containing iron oxide which has the potential to be developed as an industrial material. The iron oxide content in iron ore varies in each region. The iron oxide content found in iron ore has its own characteristics, such as phase and structure. The iron oxide phase can be in the form of magnetite, maghemite, and hemite. Magnetite can be known as black iron oxide, magnetic iron ore, iron II, III oxide, iron tetroxide, ferrous ferrite, Hercules stone and magnetiteiserzer (German) [1]. Magnetite (Fe₃O₄) has a curie temperature of 580°C which is a titanomagnetic (Fe₃-xTiₓO₄) series [2]. Black magnetite, classified as ferrimagnetic mineral containing Fe²⁺ and Fe³⁺. Magnetite influences the magnetic properties of rocks. The general nature of magnetite includes, the hematite crystal system is Cubik, with its cell dimensions a = 0.8396 nm. The density of magnetite is 5.18 g cm⁻³, and the type of attraction is Ferri-magnetic and the space group is Fd3m [1].

Maghemite has a chemical formula that is often identified with hematite. Maghemite has a brownish red color [1]. Maghemite is an unstable mineral and changes to hema-tit at a temperature of 300°C-500°C [2]. The maghemit crystal system is Cubik or Tetragonal, with cell dimensions a = 0.83474 nm. Maghemite density is 4.87 g cm⁻³, and the type of attraction is Ferrimagnetic and Cubic (P4₃₂₁) or Tetragonal (P4₁2₁₂) space groups [1]. Hematite is an iron oxide mineral that has long been known and is widely distributed in rocks and soil. Hematite is blood red if it is divided slowly and is black or shiny gray if it is roughly crystalline. Hematite can be obtained one of them by phase transformation.
from magnetite to hematite. Hematite ($\alpha$-Fe$_2$O$_3$) has a Curie 680°C temperature [2]. The crystal hematite system is Rhombohedral or Hexagonal, with cell dimensions $a = 0.503$ nm and $c = 1.375$ nm. Hematite density of 5.26 g cm$^{-3}$, and the type of attraction is antiferromagnetic and its space group is R3C [1].

All types of iron oxide phases have wide applications in the industry. At present, magnetite is used as dry ink (toner) on photo-copy machines and laser printers. Maghemite is the main ingredient for tapes and dyes in paint. Hematite can also be used as a major component in the manufacture of photoelectrochemical solar cells [3], the main ingredient in the manufacture of sensor gas acetone, and also as a catalyst in oil production [4].

The magnitude of the benefits of iron oxide makes researchers make efforts to get it. One way is to remove impurities found in iron ore. Magnetic minerals can be obtained using a permanent magnet (magnetic separator). The hematite phase can be obtained by heating from the magnetite phase. The magnetite phase can be a hematite phase at temperatures above 700°C [5].

Recent research shows that the magnetite phase derived from iron sand can be a hematite phase at temperatures above 800°C [1]. the magnetite phase (Fe$_3$O$_4$) can turn into maghemite phase ($\gamma$-Fe$_2$O$_3$) at calcination temperature 200°C and the macemite phase ($\gamma$-Fe$_2$O$_3$) becomes hematite phase ($\alpha$-Fe$_2$O$_3$) at calcination temperature 300-600°C [5]. The difference in the temperature of calcination in the formation of magnetcite into hematite, is influenced by other content obtained in magnetite as well as containing small amounts of Co, Ni, Zn, Cu, Mn, Al, and Cr. Other elements in iron ore are influenced by the structure or location of the iron ore found.

Calcination temperatures other than causing phase changes can also cause changes in crystallography, microstructure and grain size of crystals of iron oxide [6][7][8]. This can be seen in the heating of magnetite with a temperature of 300°C the structure formed is cubic but at a temperature of 800°C the structure formed is hexagonal [6].

This article explains the effect of calcination temperature on the phase formed and the structure of iron oxide from the Sumatra region.

2. Research Methods

2.1. Preparation of Iron Oxide

The iron ore samples used came from the West Sumatra region. The iron ore that has been obtained is separated from the impurity by washing and drying. Then iron ore is crushed using steel mortar. The size of the iron ore produced is ± 0.5 cm. Furthermore, iron ore is mashed using bowl mill. To obtain magnetite minerals, finely ground iron ore is drawn using a permanent magnet. Powdered iron ore that has been mashed, placed into a wide container. A plastic-coated magnet is inserted into the container and rotated centrifugal so that the magnetite material attaches to the magnet. The powder attached to the magnet is taken and separated. Each of the refined iron ore is calcined using furnace at temperatures of 300°C, and 500°C with a length of holding time of 3 hours.

2.2. Characterization

Iron ore samples before purification and after purification, are then paraded using the Epsilon 3 type XRF to determine the content and content of iron ore constituents. Extract samples, 300°C samples, and 500°C each were characterized using CubiX3 Cement XRD (1.5606 Å CuKa, 40 mA, 45 kV) to determine the characteristics of iron oxide in terms of the phase and crystal structure that emerged. Measurements are made from the angle of 10° to 90° with step size 0.010. The process of identifying phase and structure is obtained from the search match using the high score plus program.

3. Results and Discussion

3.1. Fe content of Iron Ore
Table 1 shows that the iron content of iron ore in the West Sumatra region is 69.59%, followed by other elements as impurities. The iron content of iron ore is high when compared to other studies [10]. The high Fe content in iron ore in West Sumatra is caused by the formation process, namely contact metasomatis with hydrothermal contact type. The process of forming this ore begins with a solution of magma which is rich in ore breaking through the layers of rock. The intruded stone undergoes chemical changes due to the exchange of ions and elements from magma.

| No | Elements | Concentration (%) | Elements | Concentration (%) |
|----|----------|--------------------|----------|--------------------|
| 1  | Zn       | 0.292              | Zn       | 0.208              |
| 2  | Si       | 9.833              | Si       | 4.793              |
| 3  | Al       | 1.934              | Al       | 1.279              |
| 4  | Fe       | 69.596             | Fe       | 87.509             |
| 5  | K        | 0.283              | K        | 0.071              |
| 6  | Ag       | 0.885              | Ag       | 0.248              |
| 7  | Mn       | 16.395             | Mn       | 4.832              |
| 8  | P        | 0.34               | P        | 0.26               |
| 9  | Pb       | 0.103              | Pb       | 0.029              |

Table 1 also shows that after purification using permanent magnets, the Fe content increases to 87.509%.

3.2. Effect of Calcination Temperature on Phase Changes of Iron Oxide

The amount of iron oxide contained in iron ore can be seen from the increase in iron content in the XRF results, also can be seen from the results of XRD analysis. Based on the processing of XRD analysis data in Figure 1, the iron ore constituent mineral content indicated from the high intensity was dominated by the magnetite phase (symbol M) with PDF (01-089-4319) and low intensity phases namely hematite (H) PDF (01-073-2234) and quartz (Q) PDF (01-070-8054).

![XRD measurement results from iron ore at a temperature of 26 °C](image)

**Figure. 1.** XRD measurement results from iron ore at a temperature of 26 °C

Comparison of XRD measurement data with matching databases in the 300 °C sample is shown in Figure 2. After a search match on iron ore samples based on Fig. 2, it was found that in the 300°C
sample found 2 types of iron oxide phases including magnetite with PDF (01-089-4319), hematite with PDF (01-073-2234), and maghemite with PDF (01-089-5894).

Figure 2. XRD measurement results from iron ore at calcination temperature 300°C

Comparison of XRD measurement data with matching databases in 500°C samples is shown in Figure 3.

Figure 3. XRD measurement results from iron ore at calcination temperature 500°C

Based on Figure 3, there are 2 types of iron oxide phases in the 500°C sample such as maghemite with PDF (01-089-5894) and hematite with PDF (01-089-0599). The XRD analysis that has been done can be obtained information that changes in calcination temperature cause phase changes. As a result of the increase in the calcination temperature it results in phase changes from magnetite to maghemite and to hematite. The occurrence of this phase change is because during the heating there is a transformation of the iron oxide phase from magnetite to maghemite and to hematite. The occurrence
of phase changes due to changes in temperature is caused by the growth and change of one phase in iron ore. Just as in the extract sample magnetite and hematite phases were found, but when heated at 300°C a new maghemite phase appeared. The formation of the maghemite phase is caused by the occurrence of the magnetite oxidation process to maghemit [1].

The reaction of magnetite transformation to maghemite, beginning with magnetite is built on Fe$^{3+}$ ions arranged in tetrahedral patterns and Fe$^{2+}$ ions arranged octahedral. As a result of giving heat energy causes atoms, in iron ore in particular magnetite to vibrate. At that time there is a transfer of cations to the crystal surface and together with that there is a cation vacuum. On the surface the crystals of Fe$^{2+}$ ions are oxidized to Fe$^{3+}$ ions. The Fe$^{3+}$ ion interacts with binding oxygen to form the edge of maghemite [1]. Such conditions cause Fe$^{3+}$ ions with tetrahedral geometry and if there are Fe$^{3+}$ ions with hokta-hedral geometry in pairs with oxygen this is a feature of maghemite.

On heating the iron ore sample at 500°C the magnetite phase does not appear again. The appearance of the magnetite phase is not caused by all the magnetite being transformed into maghemite. This is in accordance with the study. At a temperature of 500°C no magnetite phase was found but only the maghemite and hematite phases were found.

The emergence of the overall hematite phase due to the maghemite phase has undergone transformation into hematite as a whole. The process of transforming the maghemite phase into hematite is the same as the process of transforming magnetite into maghemite. The occurrence of this transformation process results from an increase in heat and a continuous oxidation process, resulting in more Fe$^{3+}$ ions being formed. The amount of Fe$^{3+}$ ions formed causes the phase to turn into hematite. Hematite has a hexagonal structure containing a small portion of Fe$^{2+}$ ions and is composed mostly by Fe$^{3+}$ ions, this is confirmed by the ternary diagram. In the ternary diagram the ratio of Fe$^{3+}$ increases with the ratio of Fe$^{2+}$ from magnetite to hematite.

Based on XRD data analysis for each sample, it can be seen that the calcination temperature variations affect the iron oxide phase formed. The iron oxide phase formed for each temperature is shown in Figure 4.

![Figure 4. XRD pattern of iron ore at temperatures of 26 °C, 300 °C, and 500 °C.](image)
Based on Figure 4, phase changes can be seen from the XRD pattern with each calcination temperature variation. These phase changes are seen from the loss and appearance of the iron oxide phase peaks in the XRD pattern. Phase changes begin at the calcination temperature of 300°C, where the magnetite phase in the plane (111) undergoes phase transformation to maghemite with the plane (113). At the calcination temperature of 500°C all phases of magnetite undergo phase transformation to maghemite as a whole, this can be seen from the absence of magnetite peaks in the XRD pattern. At 500°C calcination temperature there is also a transformation of the maghemite phase to hematite, this can be seen from the higher peak of hematite in the plane (104), plane (116), and plane (024). Phase changes that occur occur due to the provision of different temperatures for each sample. Phase changes can be seen from the emergence of new phases and the loss of certain phases such as the magnetite phase.

3.3. Effect of Calcination Temperature on Structural Changes of Iron Oxide

Increasing the temperature of calcination causes changes in the phase of a material, this also causes the structure of the material to change. When transformation of the magnetite phase to maghemite then to hematite, there was also a change in the structure of the iron ore. The structural changes that occur are the magnetite phase with a cubic structure with unit cells $a = b = c = 8.398$ Å to the Tetragonal structure of the maghemite phase with unit cells $a = b = 8.346$ Å and $c = 25.034$ Å then to the hematite phase with a Rhombohedral structure $a = b = 5.032$ Å and $c = 13.736$ Å. This change in structure is caused by the continuous oxidation process in the sample. The oxidation process causes the appearance of Fe$^{3+}$ ions, each pair of Fe$^{3+}$ ions is accompanied by a cation void, so this affects the coordination of atoms in their cell units which causes the crystal structure to change from maghemit to hematite.

In the XRD measurement data that has been matched with the database, the iron ore sample phase is obtained. In addition, crystal structures are also included which include lattice parameters ($\alpha, \beta, \gamma, a, b, c$), space groups, crystal systems found in each iron ore sample. Iron ore before calcination contained magnetite phase with cell cubic unit structure $a = b = c = 8.395$ Å and hematite phase Rhombohedral unit cell $a = b = 5.032$ Å, $c = 13.740$ Å. The iron ore samples calcined at a temperature of 300°C contained the magnetite phase and hematite phase which had the same structure as the sample without calcination, and also contained the maghemite phase with the cell unit Tetragonal structure $a = b = 8.346$ Å and $c = 25.034$ Å. In iron ore calcined with a temperature of 500°C, the maghemite phase appears, whose structure is the same as the 300°C sample and hematite phase with the structure of the Rhombohedral unit cell $a = b = 5.032$ Å and $c = 13.733$ Å.

In the results of the study it was found that the calcination temperature affected the structure of iron oxide formed. Increasing the calcination temperature causes the structure of iron oxide to change from Cubic to Tetragonal then to Rhombohedral. In addition, in the results of the study for samples before calcination, and 300°C, 500°C, there was a change in lattice unit cell parameters for hematite. The change can be seen from the unit value as long as the sample before calcination and the sample 300°C unit cell $a = b = 5.032$ Å and $c = 13.740$ Å, but the sample is 500°C, there is a decrease in cell units $a = b = 5.032$ Å and $c = 13.733$ Å. This change occurs due to the coordination conditions of the atoms making up the iron ore, besides that it can also be caused at the calcination temperature of 500°C, the maghemite phase has been transformed into hematite.

4. Conclusion

The results showed that the calcination temperature affected the iron oxide phase formed. At the calcination temperature of 300 OC, the iron oxide phase that appears is Magnetite, Hematite, and Maghemite. At the calcination temperature of 500 OC the iron oxide phase that appears is Maghemite and hematite. The calcination temperature also affects changes in iron oxide structure. Structural changes that occur from cubic to cell units $a = b = c = 8.3985$ Å for Tetragonal structures with unit cells $a = b = 8.3460$ Å and $c = 25.0340$ Å then to Rhombohedral structure $a = b = 5.0320$ Å and $c = 13.7362$ Å.
Acknowledgment
The authors thank to Universitas Negeri Padang for financial support through Hibah Kerjasama Internasional PNBP 2020 for this work.

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