Thermal characteristics and phase transformation of iron ores containing varied crystalline water with coal mixtures

M M F Sinuhaji¹, S Harjanto¹, and A Hapid²

¹Department of Metallurgical and Materials Engineering, Universitas Indonesia, Depok, Indonesia
²Geostech-Badan Pengkajian Penerapan Teknologi, Serpong, Indonesia

E-mail: sri.harjanto@ui.ac.id

Abstract. Iron ore, with high combined water such as goethite, is widely spread in Indonesia. This is not commonly used as the main raw material in iron and steel making process. However, as iron ore resources are getting limited and decreasing in number, iron making industries have to seek other iron ore sources, such as low-grade iron ore goethite ore. The purpose of this research is to investigate the thermal characteristics of composite iron ore containing high combined water, coal, and synthetic goethite ore as comparing samples using the thermogravimetric method. This research is conducted with several experimental conditions: heating from 25-1200°C; heating rate 10°C/minute; nitrogen (inert) furnace atmosphere. The composition is divided into two parts, which are composite A and composite B with 24% and 16% coal, respectively. The results showed that wustite and solid iron formations at a temperature of 973°C; 1050°C and 990°C; 1060°C, respectively. This is because there is more coal composition on composite A so that composite B needs a higher temperature to produce CO as reducing agent. In general, for all mixtures, the reactions occurred from lower temperature are dehydration, dehydroxylation, the formations of Fe₂O₃ (hematite), Fe₃O₄ (magnetite), wustite (FeO), and Fe Metal.

1. Introduction

Indonesia is one of the major mine-producing countries with several sources, such as iron ore, gold, nickel, coal, tin and so on. This potential can provide benefits for Indonesia’s economy, either directly or indirectly. Iron ore is the main raw material in iron and steel manufacture as well as one of the most widely used metals in the world because the amount is greatly abundant. Its fabrication process is also relatively cheap and easy, and the resulting mechanical properties are quite good. The steel industry is the basis that sustains the development of a country. Large iron and steel production of a country will have an impact on the country's economy Indonesia is one of the countries in the world which has many iron ore reserves with lateritic iron ore species. This type is generally not the main raw material in iron and steel manufacture, but due to the limitation and decrease of primary iron ore, laterite is strived as raw material, especially in the formation of the composite pellet.

Murakami et al. conducted research on lateritic iron ore reduction which states that at the same temperature, the reduction degree of goethite iron ore is higher than that of primary iron [1]. This indicates that the energy to reduce goethite iron ore is low. Strezov et al. also say that during the reduction pr0Cess, goethite material will undergo free-water release or dehydration and hydroxide component or dehydroxylation during the heating pr0Cess [2]. Kawigraha also conducted research on goethite ore reduction saying that free-water release comprised on goethite ore happens below the
temperature of 100⁰C, and OH component release or hydroxide happens at the temperature of 260-425⁰C, and the change of Fe₂O₃ into Fe₃O₄ takes place after hydroxylation [3].

Based on the earlier discussion, this research is conducted on lateritic iron ore containing high combined water. This research uses bituminous coal as the reducing agent and CaCO₃ as flux. In general, this research aims to identify the thermal characterization of a composite pellet containing high combined water by using TG-DTA method.

2. Experimental method
Sebuku iron ore from Kalimantan is characterized using the XRD and XRF tests to find out the qualitative and quantitative content in it. Iron ore is pulverized and sieved to obtain a very fine grain size below 140 mesh. The reducing agent used is coal (sub-bituminous coal), which is carried out on proximate and ultimate tests to determine the content of moisture, ash, volatile water, and fixed carbon. All raw materials are weighed according to the dose using a digital scale and then mixed until homogeneous and finally forming a pellet. After that, the pellet will be dried again in an oven (dryer) for 120 minutes at a temperature of 120⁰C. Next, the pellet is taken out from the oven and mashed with mortar so that the composite is obtained in the form of fine powder. Then the powder is sieved again to obtain the same size which is below 140 mesh. The mass of each powder composition is taken 2 grams, which will be reduced using TG-DTA to analyze the thermal characteristics of ore composite iron ore containing high crystal water and coal. In the same condition, the pellet is heated in a tube furnace from the temperature of 25-1200⁰C; heat rate of 10⁰C/minute; and an inert atmosphere. The nitrogen is then characterized using XRD to determine the phase formed at the temperature of 1000⁰C, 1100⁰C; 1200⁰C.

3. Result and discussion
3.1. Phase analysis on composite ore A and synthetic A

![Figure 1. XRD results from ore A and synthetic A at a temperature of 1000, 1100, and 1200⁰C](image)

Based on Figure 1, composite ore A and synthetic A at the temperature of 1000⁰C have formed Fe (Iron) crystals. On ore A, there is a spinel compound as the increase of the compound’s temperature becomes more invisible. However, on synthetic A, a spinel compound is not formed. Based on the intensity, reduction temperature of 1100⁰C has the highest Fe (Iron) intensity, whereas, at the temperature of 1000⁰C, the intensity is lower. In synthetic A, with increasing reduction temperature,
the intensity of Fe is lower. It can be analyzed that, or A at the temperature of 1100°C formability Fe is more thorough than at 1000°C. Nevertheless, on synthetic A, the intensity of Fe is lower as the temperature rises. This is because the crystallinity of Fe is more stable at the temperature of 1000°C.

3.2. XRD results on composite ore B and synthetic B

Figure 2. XRD results on ore B and synthetic B at temperature 1000, 1100, and 1200°C

Based on Figure 2, on both ore B and synthetic B, Fe (Iron) crystal is formed at the temperature of 1000°C. On ore B at the temperature of 1000°C, wustite is still can be found, but as the temperature rises, the whole wustite has transformed into Fe. On synthetic B, there is also wustite which decreases in intensity as the temperature increases. Ore B and synthetic B also have spinel (slag). Based on its intensity, composite ore B has the highest Fe intensity at 1100°C and the lowest Fe intensity at 1000°C. On synthetic B, at a temperature of 1000 and 1100°C, the intensity of Fe formed tends to be in the same size, but later decreases with the increasing temperature. This is because the crystallinity of Fe is stable at the temperature of 1100°C.

3.3. Thermal characteristics Iron Ore Coal Composite High Combined Water at 25-400°C

Figure 3 and Figure 4 are the results of the STA test on composite A and B with an initial mass of 5,303 mg and 5,612 mg. Based on the DTA curve, composition A and B are at the same peak, which is at the temperature of 70°C while 263°C is the endothermic peak. This indicates the existence of a dehydration reaction or the release of free water molecules and dehydroxylation. Based on TG curve, at that temperature, there is a mass reduction of 53.002 μg or as much as 0.99% of the total mass on composition A. Meanwhile, on compositions B the amount of mass reduction is 44.60 μg or 0.79% of the total mass. The second peak is at the temperature of 263°C. TG curve shows a very significant mass change in a very short time. This shows that there is goethite dehydroxylation reaction by the formation of magnetite with a weight loss of 7.01% of the total mass on composition A while on composition B 394.21 μg or about 7.024% of the total mass.

Figure 5 and Figure 6 are the results of the STA test on synthetic A and B with an initial mass of 5,437 and 6,326 mg. The results show that at the temperature of 25-400°C, there is a peak which is at the temperature of 288°C and 291°C with a weight loss of 6.68% and 6.53% on synthetic A and synthetic B.
Table 1. Thermal characterization of lateritic iron ore and goethite at a temperature range of 25-400°C

| Reaction             | A   | B   | A'  | B'  |
|----------------------|-----|-----|-----|-----|
| Dehydration          | 70°C| 70°C| -   | -   |
| %weight loss         | 0.99| 0.74| -   | -   |
| Dehydroxylation      | 263°C| 263°C| 288°C| 291°C|
| %weight loss         | 7.01| 6.68| 6.68| 6.53|

Note: A/B lateritic iron ore with 24% and 16% coal
      A'/B' synthetic goethite iron ore with 24% and 16% coal

Based on table 1, between composite A and composite B, there are dehydration and dehydroxylation at the same temperature of 70°C and 263°C. This indicates that the content of free water molecule and hydroxide group are stable. This means that composite A and composite B have almost the same crystallinity. Based on the TG curve, the content of water crystallinity is about 7%. Compared to lateritic ore, there is no dehydration peak found on synthetic goethite ore. There is only one susceptible peak temperature of 25-400°C. This suggests that synthetic iron ore does not contain free water or free molecules because it uses high FeOOH. Between lateritic iron ore and synthetic goethite iron ore, the highest dehydroxylation temperature is on the synthetic one. This is because synthetic iron ore contains OH group, which means that releasing all OH group, a higher temperature is needed.

3.4. Reduction reaction products
3.5. at 400-1200°C

This research also observes the different behaviors of lateritic iron ore containing goethite and synthetic iron ore containing coal at the temperature of 400-1200°C. According to TG-DTA test results on composite A, at the temperature of 438°C, which is the exothermic peak or hematite formation of the TG graph, there is a mass loss of 12.7% of the total mass. The second peak is at the temperature of 973°C showing a mass decrease of 26.8% of the total mass. The third peak is at the temperature of 1050°C, where a mass loss occurred as much as 34.12%.

On the other hand, results on composite B shows that the first peak of the TG graph occurs at the temperature of 438°C, causing a mass decrease as much as 12.7% of the total mass. The second peak occurs at 990°C showing there is a mass loss of 26.8% of the total mass. The third peak is at the temperature of 1060°C; there is a mass loss of 26.8% of the total mass.

Meanwhile, on Synthetic A, the first peak is at the temperature of 475°C, indicating a loss as much as 12.46% of the total mass. The second peak occurs at the temperature of 921°C where there is a mass decrease of 26.7%. The third peak is at the temperature of 1079°C where there is a loss as much as 37.7% of the total mass. Lastly, on synthetic B, the peak of the TG curve is at the temperature of 477°C where a mass loss happens as much as 12.96% of the total mass. The second peak is at the temperature of 923°C while the third peak is at 1099°C, causing a decrease in mass as much as 2128.3 µg or 33.6% of the total mass. The comparison is as seen below in Table 2.
Table 2. Thermal characterization of lateritic iron ore and goethite iron ore at 400-1200°C

|                         | A       | B       | A'      | B'      |
|-------------------------|---------|---------|---------|---------|
| Magnetite formation (°C)| 438     | 438     | 475     | 477     |
| % wl                    | 12.7    | 12.7    | 12.46   | 12.96   |
| Wustite formation (°C)  | 973     | 990     | 921     | 923     |
| % wl                    | 26.8    | 25.6    | 26.7    | 25.67   |
| Fe metal formation (°C) | 1050    | 1060    | 1058    | 1079    |
| % wl                    | 34.12   | 26.6    | 37.7    | 33.6    |

Note: A/B: lateritic iron ore containing 24/16% coal  
A'/B': synthetic iron ore containing 24/16% coal

According to table 2, between composite A containing 24% coal and composite B containing 16% coal. The temperature at which there are wustite, and Fe metal formations on composition A is lower than that of composition B. Likewise, on synthetic A and synthetic B, wustite and Fe metal formations occur at higher temperature, which is on synthetic A. This is because on iron ore with higher percentage of coal will supply more CO formation since carbon will highly react to form carbon monoxide gas or in other words, the gasification rate increases. In contrast, for iron ore containing a lower percentage of coal, it needs a higher temperature to form more CO also to increase the gasification rate. This is confirmed by research conducted by Willman [21], stating that the lower quantity of coal needs a higher temperature to supply CO formation.

Regarding wustite formation on lateritic iron ore and synthetic iron ore, the temperature of synthetic iron ore is lower because its total %Fe is higher compared to that of lateritic iron ore. Therefore, with the same amount of coal, synthetic iron needs a lower temperature to form wustite. Nevertheless, regarding solid iron formation, the temperature of synthetic iron ore is higher compared to that of lateritic iron ore. This is because, on that temperature, the reducing agent is about to finish reducing magnetite iron ore into wustite and to reduce wustite into Fe metal, there is on half of the reducing agent left, so the temperature needs to be higher. Another factor which possibly allows higher synthetic iron temperature is because it is affected by porosity; distribution size and particle form; and specific gravity. On synthetic iron ore, there are probably size and distribution of particle which are not equal that obtained porosity is deficient, so it is more difficult to be reduced. Based on the weight loss occurred on each sample from carbon, volatile matter, ash, and coal moisture also oxides which are on iron ore. According to weight loss percentage, the biggest is synthetic A; synthetic B; composite B respectively 43.52%; 39.2; 35.7%; 26.8 of each total mass.

Figure 3. Results of STA test on composition A composite
3.6. Phase transformation of iron ore coal composite high combined water

To see the average carbon monoxide gas formed by the metal and iron formation, the temperature of each sample is plotted into a boudouard diagram to see the comparison. Based on Figure 4.5, the plot of each wustite and metal iron formation temperature can indicate the CO content as the required reducing agent. Wustite formation on composite A at 973°C requires approximately 17% gas fraction [CO / CO + CO2]; on composite B at 990°C requires 15% gas fraction [CO / CO + CO2]; on synthetic A at 921°C requires 19% gas fraction [CO / CO + CO2; on synthetic B at 923°C 18% gas fraction [CO / CO + CO2]. To conclude, the higher the temperature, the less the reducing gas necessary to reduce the iron ore, or the less the reducing agent, the higher the temperature required to reduce the magnetite to wustite.
Figure 7. Temperature plot showing wustite and solid iron formations on each sample

Fe metal formation on composite A at 1050°C requires around 76% gas fraction [CO/CO+CO₂]; on synthetic A at 1058°C requires around 77% gas fraction [CO/CO+CO₂]; on composite B at 1060°C requires around 78% gas fraction [CO/CO+CO₂]; on synthetic B at 1079°C requires around 75% gas fraction [CO/CO+CO₂]. With the same amount of coal on lateritic ore and synthetic ore, synthetic needs a higher temperature to reduce wustite to iron. This is because the reducing agent, right before reducing magnetite to wustite, is about to react thoroughly, and there are only a few lefts. Therefore, a higher temperature is needed to reach stability.

4. Conclusion
1. According to a research on reduction of lateritic iron ore containing high combined water (goethite) and synthetic iron ore with the thermogravimetric method, the reaction 0ccurred at temperature range 25-400°C are dehydration or free water molecule release and dehydroxylation. Both reactions on lateritic iron ore are obtained at the same temperature, which is 70°C and 263°C. This indicates that free water molecule content and hydroxide group are stable. Based on the TG curve or mass loss, it is counted that water crystallinity content is about 7%. On synthetic goethite iron ore, there is no dehydration. This indicates that synthetic iron ore does not contain free water molecule because it uses high pure FeOOH.
2. At temperature range 400-1200°C, composite A containing 24% coal and composite B containing 16% coal, the temperature for wustite and Fe metal formations on composite A is lower than that of composite B. Likewise, on synthetic A and synthetic B, temperature of synthetic A is lower than that of synthetic B. This is because iron ore containing more coal will supply more CO formation. Carbon will react more to form carbon monoxide gas, or the gasification rate increases.
3. Based on the temperature plotting into boudouard diagram, estimated wustite formation on composite A at 973°C requires approximately 17% gas fraction [CO / CO + CO₂]; on composite B at 990°C requires 15% gas fraction [CO / CO + CO₂]; on synthetic A at 921°C requires 19% gas fraction [CO / CO + CO₂]; on synthetic B at 923°C 18% gas fraction [CO / CO + CO₂]. To conclude, the higher the temperature, the less the reducing gas necessary to reduce the iron ore to wustite, or the less the reducing agent, the higher the temperature required to reduce the magnetite to wustite. Given the same amount of coal between lateritic iron ore and synthetic iron ore, synthetic needs a higher temperature to reduce wustite to iron. This is because the reducing agent,
right before reducing magnetite to wustite, is about to thoroughly react that there is only a few amounts left, so higher temperatures are required to reach stability.

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