Extraction of Iron from Refractory Titanomagnetite by Reduction Roasting and Magnetic Separation

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The abundant refractory titanomagnetite (TTM) provides a cheap alternative source of iron, but this ore contains impurities and is difficult to process to make suitable concentrates for the blast furnace. In this study, reduction roasting of a primary TTM concentrate followed by magnetic separation was investigated to understand the effects of reduction time, coal dosage, and CaF$_2$ addition on the reduction behavior of TTM and growth mechanism of iron particles. The phase composition of reduced samples was characterized by X-ray diffraction. The size distribution of iron particles was quantitatively examined using image analysis. Results showed that CaF$_2$ can help improve the reduction degree and particle size of metallic iron. The metallization degree increased from 85.5% to 89.5% when the CaF$_2$ dosage increased from 0% to 4%, while a minor increase was observed when the CaF$_2$ dosage exceeded 4%. Accordingly, the TTM samples were treated by reduction roasting with 4% CaF$_2$ and 25% coal at 1 200°C for 60 min followed by magnetic separation. A magnetic concentrate with an iron content of 91.1% and a recovery of 92.9% was achieved. In addition, the relationship between the size distributions of iron particles and grinding fineness was also studied. The size distribution using data from the diameter of iron particles was found to be close to the actual grinding fineness.

KEY WORDS: reduction roasting; magnetic separation; titanomagnetite; CaF$_2$; size distribution.

1. Introduction

The exploitation of refractory iron ores has become increasingly important across the world owing to the fast depletion of easy-to-process iron ores.1) Ironsand is extensively distributed in coastal areas, such as Indonesia and New Zealand, and can provide an alternative source for conventional iron ores.2) Although the composition of ironsand is partially dependent on its origin/location, it approximates that of titanomagnetite (Fe$_3$-$_x$Ti$_x$O$_{4}$) containing ~60% total Fe (TFe). The major impurities in ironsand are MgO, Al$_2$O$_3$, and SiO$_2$. All but SiO$_2$ are typically associated with the titanomagnetite (TTM) grains and are present as solid solution components within the lattice.3,4) Thus, it is difficult to separate major impurities and obtain high-quality iron concentrates using conventional beneficiation methods such as specific gravity and magnetic separation.5) To efficiently utilize the TTM, many pyrometallurgical processes, including blast furnace smelting and direct reduction–electric furnace smelting, have been investigated.5–8) The conventional smelting routes have, to some extent, achieved recovery of iron, but they still have several disadvantages. For example, ironsand needs to be incorporated into sinter for ironmaking because its small particle size precludes direct charging into a blast furnace, and sinter blend only allows the addition of a small amount of ironsand to ensure the desired sintering characteristics.3) Recent research has shown it is feasible to recover metallic iron from refractory iron ores by reduction roasting followed by magnetic separation.9–11) This technology combines metallurgy and mineral processing, in which iron oxides are primarily reduced to metallic iron with grain growth. The reduced product is then ground to its liberation size followed by magnetic separation.12–14) In addition, it is widely believed that the reduction characteristics or separating result is not good without using the aid of additives, so additives such as CaF$_2$ and CaCO$_3$ are often used. However, previous studies on the reduction roasting of ironsand have primarily focused on the influential factors, such as reaction temperature, and reaction time.15,16)

In this study, the feasibility of reduction roasting followed by magnetic separation to extract iron from refractory TTM was investigated. The effects of reduction time, coal dosage, and CaF$_2$ addition on the reduction behavior of TTM...
and growth mechanism of iron particles were analyzed and clarified. The correlation of the size distribution of iron particles with the grinding fineness was also evaluated in this study, based on the grinding fineness and magnetic separation tests.

2. Experimental

2.1. Materials

The raw TTM used in this study was obtained from the Indonesian coast. After drying, grinding, and magnetic separation, the chemical composition of the TTM concentrate was as follows: 57.29% TFe, 26.08% FeO, 12.04% TiO₂, 1.69% SiO₂, 1.74% MgO, and 1.23% Al₂O₃. The X-ray diffraction (XRD) pattern (Fig. 1) of the TTM sample showed that the main crystalline phases were TTM as well as small amounts of ilmenite and quartz. Bituminous coal was used as the reductant, and it was ground to < 1 mm prior to the reduction tests. A proximate analysis showed that the coal was composed of 56.66% fixed carbon, 29.54% volatiles, 6.55% ash, and 7.25% moisture. Analytical-reagent grade CaF₂ was used as an additive. The size distributions of the TTM sample and CaF₂ were analyzed by a laser interferometer (SEISHIN LMS-30). As shown in Fig. 2, the size of the TTM sample was the range from 0 to 52 μm, and the average size was about 17 μm. The size of the CaF₂ particles was the range from 0 to 50 μm, and the average size was about 12 μm.

2.2. Experimental Procedures

The reduction of TTM by bituminous coal was conducted in a vertical tube electric furnace whose schematic is shown in Fig. 3. The reaction chamber was an alumina tube with an inner diameter of 56 mm and a height of 82 cm. A homogeneous temperature zone in this furnace was about 30 mm. The sample was prepared by mixing 10 g of the TTM concentrate, a certain amount of coal and CaF₂, and then the mixtures were placed in a corundum crucible.

To conduct the reduction experiments, the furnace was preheated to the temperature of 1 200°C, and then purged with N₂ for 20 min. The corundum crucible with the sample was then placed in the hot zone of the furnace. The flow rate of N₂ was maintained at 3.0 L/min, and the concentrations of CO and CO₂ in the outlet gas were analyzed online by an infrared CO/CO₂ analyzer (Vario Plus, MRU). After
a specific reaction time, the sample was quickly removed from the hot zone to the cool top part of the furnace for quenching.

The reduced samples under optimum conditions were treated by grinding and magnetic separation. Grinding was performed using a rod mill (RK/BM-1.0L) at a solid density of 60 wt% with a rotation speed of 289 r/min for different times (5–20 min). An XCGS-73 magnetic tube with a magnetic field intensity of 1 250 Oe was used to recover metallic iron. The magnetic concentrate designated direct reduced iron (DRI) was obtained by a two-stage magnetic separation process, namely, the rough concentrate obtained from the first separation step was magnetically separated again. The main evaluation indexes of the test results were the iron grade and the iron recovery of DRI. The iron recovery refers to the percentage of the total iron contained in the ore that is recovered into the DRI.

2.3. Analysis and Characterization

The reduced samples were analyzed by X-ray diffraction (XRD, D/Max 2200, Rigaku) with Cu Kα radiation. The metallization degree ($\eta$) of the reduced sample was calculated as follows:

$$\eta = \left( \frac{MFe}{TFe} \right) \times 100\% \quad \text{........................(1)}$$

where MFe is the weight percent of metallic iron in the reduced sample (%), and TFe is the weight percent of total iron in the reduced sample (%).

To study the morphological changes and size distribution of iron particles, the reduced samples were mounted in epoxy resin and polished for optical microscopic observation (Leica DM64500P Optical Microscope) and scanning electron microscopy (SEM, S360-EVO18) analysis. Fifty optical microscope images (each containing > 300 iron particles) for each reduced sample were obtained in reflected light and analyzed using Leica QWin (Leica Microsystems, Germany) software, which can provide a series of image-analysis tools for microscopy applications, such as image detection, processing, and measurement. For every image, the properties (such as length, width and area) of each iron particle were automatically measured by QWin software. Taking the images shown in Fig. 4 for instance, different colors in the image (Fig. 4(b)) processed by the QWin software denote different size distributions of iron particles. In the end, the data were exported to an Excel file for categorization and calculation.

3. Results and Discussion

3.1. Effects of Coal Dosage and Reduction Time

The phase transformations of reduced samples were identified in the presence of different coal dosages. The reduction experiments were conducted at 1 200°C for 60 min without CaF₂. The XRD analysis (Fig. 5) shows that the main phases of the sample with the addition of 15% coal were metallic iron and TTM. When the coal dosage increased to 20%, the phase of TTM disappeared, while FeTiO₃, Ca₃Al₂O₆, and (Fe, Mg)Ti₂O₅ peaks were observed. The peak intensities of FeTiO₃ gradually decreased, whereas those of metallic iron increased with increasing coal dosage. When the coal dosage increased from 25% to 30%, no new phase was observed. Therefore, the coal dosage was fixed at 25% in the subsequent experiments.

The effect of reduction time on the reduction of TTM was also investigated. Figure 6 shows the XRD patterns of the samples reduced at 1 200°C without CaF₂ for different times. When the reduction time was 20 min, the main phases included metallic iron, FeTiO₃ and FeO. After reduction for 40 min, the FeO phase disappeared, and new phases of Ca₃Al₂O₆ and (Fe, Mg)Ti₂O₅ were observed. When the reduction time was further extended, no new phase was observed. Therefore, the reduction time was fixed at 60 min in the subsequent experiments.

3.2. Effect of CaF₂ Dosage

To compare the effects of CaF₂ on the reduction of TTM,

![Fig. 5. XRD patterns of samples reduced at 1 200°C for 60 min with different coal dosages. (Online version in color.)](image)

![Fig. 4. Image acquired for image analysis. (Online version in color.)](image)
the reduction degree (R) can be calculated from the composition and flow rate of the outlet gas according to Eq. (2), given as:

$$ R = \frac{16\int_0^t V_o dt}{M_{OFe}} $$

where $M_{OFe}$ (g) is the total mass of removable oxygen from iron oxide to metallic iron in theory, and $V_o$ (mol/min) is the mole generation rate of oxygen at reduction time t (min).

According to the weight percentages of FeO and Fe$_3$O$_4$ in the iron sand sample, the oxygen content combined with Fe can be calculated by Eq. (3). Thus, when 10 g of the sample was added, the theoretical amount of oxygen loss was 2.21 g.

$$ \omega_{ox} = \text{mass}\% \text{FeO} \times \frac{MW_{O}}{MW_{FeO}} + \text{mass}\% \text{Fe}_2\text{O}_3 \times \frac{3MW_{O}}{MW_{Fe}_3\text{O}_4} $$

$$ = 5.80\text{mass}\% + 16.41\text{mass}\% = 22.21\text{mass}\% $$

The mole generation rate of oxygen at reduction time t can be calculated according to the following expression:

$$ V_o (mol/min) = \frac{\varphi_{CO}}{\varphi_{N_2}} \times V_{N_2} \times \frac{1mol}{24.5L} $$

$$ V_{co}(mol/min) = \frac{\varphi_{CO}}{\varphi_{N_2}} \times V_{N_2} \times \frac{1mol}{24.5L} $$

$$ V_{o}(mol/min) = v_{co} + 2v_{co} = \frac{3}{24.5} \left( \frac{\varphi_{CO} + 2\varphi_{CO}}{\varphi_{N_2}} \right) $$

where $V_{CO}$ and $V_{CO}$ represent the formation rates of CO and CO$_2$, respectively, which can be calculated using $N_2$ as a reference gas via Eqs. (4) and (5). $\varphi_{CO}$, $\varphi_{N_2}$ and $\varphi_{CO}$ represent the measured volume percent of CO, CO$_2$ and N$_2$ in the outlet gas. The number 24.5 indicates that the volume of 1 mol ideal gas is 24.5 L at 25°C (298 K), calculated using gas state equation ($PV = nRT$). The flow rate of N$_2$ ($V_{N2}$) was fixed at 3 L/min.

Therefore, Eq. (2) can be rewritten as:

$$ R = \frac{16\int_0^t \frac{3}{24.5} \left( \frac{\varphi_{CO} + 2\varphi_{CO}}{\varphi_{N_2}} \right) dt}{2.21} $$

$$ = \frac{16}{2.21} \int_0^t \left( \frac{\varphi_{CO} + 2\varphi_{CO}}{\varphi_{N_2}} \right) dt $$

The experiments were conducted at 1 200°C with a reduction time of 60 min and a coal dosage of 25%.

Figure 7 shows the reduction degree curves at different CaF$_2$ dosages, viz, 0%, 4%, 8% and 12%. From Fig. 7, it can be found that CaF$_2$ obviously influenced the reduction degree, and the reduction degree increased with increasing CaF$_2$ concentrations. This indicates that the addition of CaF$_2$ played a positive role in increasing the reduction degree of TTM. Furthermore, in general, the reduction of TTM progressed according to the following path: Fe$_{1-x}$Ti$_x$O$_3$→FeO→Fe$_2$TiO$_4$→Fe+$\text{Fe}_2\text{Ti}_2\text{O}_5$→Fe+$\text{Fe}_2\text{Ti}_2\text{O}_5$. Thus, it can be clearly observed from Fig. 7 that in the later stage of reduction, the reaction rate decreased because the reductions of Fe$_2$TiO$_4$ and Fe$_2$Ti$_2$O$_5$ by coal were more difficult than that of FeO. Moreover, it is shown that the final degree of reduction slightly exceeded 1.0 when the addition of CaF$_2$ was 8% and 12%, probably because the volatile matter generated a small amount of CO and CO$_2$.

The effect of CaF$_2$ dosage on the metallization degree of reduced samples is shown in Fig. 8. As the CaF$_2$ dosage increased, the metallization degree first increased quickly and then slowed down. The metallization degree increased from 85.5% to 89.5% when the CaF$_2$ dosage increased from 0% to 4%, and only increased from 89.5 to 91.3% as the CaF$_2$ dosage increased from 4% to 12%. The above results show that the presence of CaF$_2$ can easily promote the reaction of TTM, but the promoting effect weakened when the dosage of CaF$_2$ was more than 4%.

The phase transformations were identified by XRD. As shown in Fig. 9, the main phases of the reduced sample without adding CaF$_2$ were metallic iron, (Fe, Mg)Ti$_2$O$_4$ and FeTiO$_3$. When the CaF$_2$ dosage was increased to 4%, no new phase was observed. When the dosage of CaF$_2$ was more than 4%, the diffraction peaks of CaF$_2$ were observed, which indicates there were lots of residual CaF$_2$ in reduced sample that did not react.
In generally, one ion may replace another if the difference between their ionic radii does not exceed 15% of the radius of the smaller ion.\textsuperscript{15,16} Fluorine ions and oxygen ions have similar ionic radii (0.133 and 0.144 nm, respectively). This indicates that F\textsuperscript{−} can easily replace the position of O\textsuperscript{2−}, and an O\textsuperscript{2−} ion tends to replace two F\textsuperscript{−} ions to maintain local electrical neutrality.\textsuperscript{17,18} As a result, F\textsuperscript{−} can break the TTM network and reduce the stability of the lattice structure, thus accelerating the reduction process. Therefore, the induced structural changes facilitated the reduction of the TTM, and also can decrease the melting point, which will be beneficial to the growth of metallic iron grains. However, combined with the XRD analysis, it was found that when the CaF\textsubscript{2} dosage was increased to 4%, no new phase was observed, and titanium existed mainly in the form of (Fe, Mg)Ti\textsubscript{2}O\textsubscript{5} and FeTiO\textsubscript{3}. These results show that even in the present of CaF\textsubscript{2}, the reductions of FeTiO\textsubscript{3} and (Fe, Mg)Ti\textsubscript{2}O\textsubscript{5} by coal were still difficult. Therefore, with the increasing of CaF\textsubscript{2} dosage, only a certain amount of F\textsuperscript{−} can diffuse into the TTM lattice, but more F\textsuperscript{−} will exist in the form of CaF\textsubscript{2}. This also explains why peaks of CaF\textsubscript{2} were observed when the dosage of CaF\textsubscript{2} was more than 4%. Besides, excessive CaF\textsubscript{2} also caused lower melting point, which hindered the diffusion of reducing gas and weakened the promoting effect of CaF\textsubscript{2}.

3.3. Growth Characteristic of Metallic Iron Particles

With the exception of metallization degree, the sizes of iron particles should be controlled because they considerably affect the results of magnetic separation. In general, the size characterization can be expressed by mean size. Therefore, mean size parameters (diameter and length) were first studied in this study to determine the effect of CaF\textsubscript{2} on the growth behavior of iron particles. The mean diameter represents the average value of the equivalent diameter of the measured iron particles, and the mean length represents the average value of the length of the measured iron particles.

Figure 10 shows that both the mean diameter and length of the iron particles first increased quickly and then their growth rates slowed down as the dosage of CaF\textsubscript{2} increased. Figure 10(a) shows, when the CaF\textsubscript{2} dosage increased from 0% to 8%, the mean diameter increased from 13.2 \(\mu\text{m}\) to 18.9 \(\mu\text{m}\), and corresponding increased from 18.9 \(\mu\text{m}\) to 20.8 \(\mu\text{m}\) as the CaF\textsubscript{2} dosage increased from 8% to 16%. Figure 10(b) shows that the mean length increased from 25.3 \(\mu\text{m}\) to 39.0 \(\mu\text{m}\) when the CaF\textsubscript{2} dosage increased from 0% to 8%, while a minor increase was observed when the CaF\textsubscript{2} dosage exceeded 8%. These results suggest that adding CaF\textsubscript{2} can facilitate the growth of iron particles.

To gain insights into the effect of CaF\textsubscript{2} addition on the growth of iron particles, the reduced samples were analyzed by SEM. Figure 11 shows that the addition of CaF\textsubscript{2} resulted in an increase in the particle sizes of iron grains compared to the sizes in the case at which no additive was present. Therefore, combined with the XRD analysis, the content of CaF\textsubscript{2} should be maintained at a proper level of 4% because the addition of excessive amounts of CaF\textsubscript{2} will lead to the presence of excessive amounts of residual CaF\textsubscript{2} in the reduced sample that will not react.

3.4. Magnetic Separation

To extract iron from refractory TTM, the reduced samples with adding 4% CaF\textsubscript{2} were separated by grinding and magnetic separation. Figure 12 shows that the iron recovery...
increased gradually with an increase in the grinding time. When the grinding time increased from 5 min to 20 min, the iron recovery increased from 72.0% to 92.9%. Subsequently, the iron recovery increased slowly to 93.6% when the grinding time was extended to 25 min. The iron grade of DRI increased from 69.8% to 91.1% when the grinding time increased from 5 min to 20 min, but it decreased gradually as the grinding times exceeded 20 min. Therefore, the optimal grinding time was 20 min, which achieved an adequate liberation of iron particles. Under the optimal conditions, a magnetic product with an iron grade of 91.1% and an iron recovery of 92.9% was obtained. Besides, the mineral composition of the DRI was also determined. As shown in Fig. 13, the main mineral of the DRI was metallic iron, the diffraction peaks of FeTiO$_3$ and (Fe, Mg)Ti$_2$O$_5$ were not observed. Although there might be little impurities such as FeTiO$_3$ or (Fe, Mg)Ti$_2$O$_5$ in DRI, the content was very low.

To investigate the relationship between measured size distributions of iron particle and grinding fineness, the grinding fineness tests were carried out. From Fig. 11(b), it can be found that the size of iron particle was mainly distributed in the range of 0 to 50 $\mu$m, so the fineness of the powder after grinding was wet classified at a 400 mesh (37.4 $\mu$m). As shown in Fig. 14, the percentage in a -400 mesh first increased rapidly followed by a slower increase as a function of grinding time. The percentage increased from 43.2% to 95.4% when the grinding time increased from 5 min to 20 min, while it only increased from 95.4% to 96.5% as the grinding time increased from 20 min to 25 min. Hence, it is difficult to improve grinding fineness as well as the liberation of iron by continuing grinding. These results further suggest that the optimal grinding time may be 20 min, where the grinding fineness was about 95.4% in the case of the -400 mesh. Generally, a sample is ground to 95% through a 400 mesh, which means the percentage in a -400 mesh reaches 95% and the maximum particle size in the ground sample is close to the mesh size, namely about 37.4 $\mu$m. In other words, the reduced product with 4% CaF$_2$ is supposed to be ground to liberation size, i.e., about 37.4 $\mu$m.

The size and cumulative distributions of iron particles are important factors in the understanding of the mill performance, and they are displayed in Figs. 15(a) and 15(b). Figure 15(a) shows that the particle size was mainly distrib-
uted in the range of 0 to 48 μm. In addition, D_{50} and D_{95} can be used to describe the particle size and size distribution. For example, D_{95} represents the particle size when the percentage of cumulative distribution reaches 95%. Thus, from Fig. 15(a), it can be seen that the value for D_{95} was 43.3 μm. As shown in Fig. 15(b), iron particles have a wide length in the range of about 0 to 120 μm, and the value for D_{95} was 104.4 μm.

When the measured value for D_{95} was compared with the grinding fineness (95% through the -400 mesh), it can be inferred that the D_{95} value (43.3 μm) is closer to the optimal liberation size (37.4 μm). This also suggests that the measured value using data from the length of iron particles is considerably different from the actual grinding fineness. Therefore, the above-mentioned size analysis can not only be convenient to study the effect of additives on the growth of iron particles and size distribution, but also help predict the size range and suitable liberation size by using the diameter data of the iron particles.

4. Conclusions

To extract iron from refractory TTM, reduction roasting and the particle size of metallic iron were investigated. These procedures analyzed and clarified the effects of reduction time, coal dosage, and CaF₂ addition. The conclusions are summarized as follows:

1) CaF₂ can help improve the reduction rate of the TTM. The reduction degree increased with increasing CaF₂ dosage, but the promoting effect weakened when the dosage of CaF₂ was more than 4%. With the CaF₂ dosage of 4%, the main products were metallic iron, (Fe, Mg)Ti₂O₅ and FeTiO₃. The addition of an excessive amount of CaF₂ led to the formation of an abundant volume of residual CaF₂ in the reduced sample that did not react. Other factors such as reduction time and coal dosage can also affect the reduction of TTM.

2) It is observed that CaF₂ significantly promoted the growth of metallic iron. The particle size of metallic iron in the reduced samples increased when the CaF₂ content increased.

3) A comparison of the size distributions of iron particles with grinding fineness showed that size distribution using data of the diameter of iron particles was close to the actual grinding fineness. Based on the results, this method will be applied as an effective way to predict the size range and suitable liberation size.

4) The TTM samples were treated by reduction roasting with 4% CaF₂ and 25% coal at 1 200°C for 60 min, followed by magnetic separation. A magnetic concentrate with an Fe content of 91.1% and a recovery of 92.9% were achieved.

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Fig. 15. Size and cumulative distributions of the reduced samples with adding 4% CaF₂. (Online version in color.)