1. Introduction

Most of the high grade iron ores mined in the world come from extensive deposits of enrichment ores derived from the Precambrian banded iron formations (BIFs). The BIF-hosted high grade hematite deposits exceed one billion tons and are the most important sources of iron ore on the planet. The BIFs in the Hamersley Iron Formation are the world’s most extensive banded iron formations, contributing to about 10% of the total world iron ore production. However, some of the usable reserves in the Hamersley Iron Formation are contaminated by the presence of phosphorus. The lack of understanding on the existence of phosphorus coupled with the erratic distribution within some of the ore bodies in the Hamersley Iron Formation has limited the development of appropriate dephosphorization techniques, since some of the BIF-hosted iron ores are composed of secondary minerals produced through the weathering of primary rocks and the degree of association of the phosphorus-containing gangue and the iron oxides is not always clear. As a result, the cheap and abundant high phosphorus iron ore reserves in the Hamersley Iron Formation have remained largely unexploited. Therefore, it is important to exploit the cheap and abundant high phosphorus iron ore as a resource in iron making. The main objective of this research is to investigate the behavior of phosphorus in the solid state pre-reduction and dephosphorization treatment processes of high phosphorus iron ore by mechanical crushing and screening methods were investigated in the present work. The reduction behavior of high phosphorus iron ore by carbonaceous materials was evaluated as a function of reduction temperature, reduction time and carbon mixing ratio. Most of the phosphorus compounds were not reduced in the low temperature reduction process of high phosphorus iron ore and remained as oxides in the gangue phases. The gangue phase size increased from 5 µm order before pre-reduction up to 20-30 µm after pre-reduction, and most of the phosphorus was still concentrated in the gangue phases even when the degree of sintering and agglomeration of the phases proceeded with increasing the reduction temperature. The dephosphorization treatment of the pre-reduced iron ore by mechanical crushing and screening methods was evaluated as a function of the initial reduction condition, screen size, and the mechanical property of the reduced iron ore phase.

KEY WORDS: high phosphorus iron ore; dephosphorization treatment; solid state reduction; mechanical crushing; screen separation.

2. Experimental Work

2.1. Sample Characterization

Table 1 shows the chemical composition of the Hamersley high phosphorus iron ore used in this investigation. The chemical composition was determined by ICP-AES method, and the sulphur and carbon contents were analyzed by inert gas fusion-infra-red absorptiometry. The fundamental characterization of the as-received high phosphorus iron ore samples was carried out by using powder X-ray diffraction and scanning electron microscopy analyses (SEM-EDX) methods. The X-ray diffraction analyses of the

<table>
<thead>
<tr>
<th>Composition</th>
<th>T-Fe</th>
<th>Fe₂O₃+(FeO)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>P₂O₅</th>
<th>TiO₂</th>
<th>S</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (mass %)</td>
<td>61.27</td>
<td>87.74</td>
<td>2.45</td>
<td>1.77</td>
<td>0.265</td>
<td>0.033</td>
<td>0.021</td>
<td>7.72</td>
</tr>
</tbody>
</table>

Other oxides (mass %): Na₂O, K₂O, TiO₂, CaO, MgO and S
as-received iron ore samples were carried out using a copper Kα X-ray source with a nickel monochromator. The scans were measured from 2θ: 0°–90° at a rate of 4°/min and sampling 0.02°. A voltage of 40 kV and a current of 30 mA were used. In the SEM-EDX analyses, grainy ore (5–10 mm) particles were selected at random and mounted in epoxy resin. The mounted samples were then polished by SiC paper from #320 up to #4000, followed by 1 μm, 0.5 μm and 0.25 μm diamond paste on a polishing wheel and then osmium was coated for 20 s on the polished samples. An accelerating voltage of 20 kV and magnification of 2000 was used to perform qualitative and semi-quantitative chemical analysis of the mounted iron ore samples.

2.2. Isothermal and Non-isothermal Reduction Behavior

2.2.1. Non-isothermal Reduction Behavior by TG-DTA Method

The non-isothermal reduction behaviors of high phosphorus iron ore with carbonaceous materials were investigated by TG-DTA method. The iron ore samples were mixed with 23 mass% graphite powders, that is, the calculated molar equivalent carbon requirement for iron oxides reduction. About 63.4 mg of the carbon-composited sample was heated from ambient temperature to 1350°C at a rate of 10°C/min. Argon gas was purged at a rate of 100 mL/min. The weight change (mass%), calculated as the ratio of the total weight loss to the initial weight of the carbon-composited sample, and DTA changes (μV) were plotted as a function of temperature.

2.2.2. Isothermal Reduction Behavior

The isothermal reduction behavior by carbonaceous materials was investigated in the temperature range 900–1200°C under argon gas flow rate of 100 mL/min and designated reaction time. The carbon mixing ratio was varied from 10 to 23 mass% carbon. Graphite powder was used as the reductant. The reduction experiments were conducted in a vertical tube LaCrO3-heated electric furnace. Sample temperature was calibrated using a Pt–6%Rh/Pt–30%Rh thermocouple. The pre-reduced samples were quenched with helium gas impinging and then prepared for chemical analysis. The chemical composition of the reduced samples was determined by ICP-AES method. Sulphur and carbon were analyzed by inert gas fusion-infra-red absorptiometry. The microstructures of the phases after reduction reaction were determined by XRD, SEM-EDX and EPMA methods. The reduction behavior was evaluated as a function of reduction temperature, reduction time and carbon mixing ratios. The degree of reduction was evaluated as a function of the change in the total iron (mass%) after reduction.

2.3. Behavior of Phosphorus in the Solid State Reduction Process

The vaporization behavior of phosphorus in the non-isothermal reduction process of the high phosphorus iron ore was investigated by using a quadrupole mass spectrometer coupled to an electric furnace. The carbon-composited sample was pressed into a tablet and then heated from 400 to 1200°C at a rate of 10°C/min under vacuum conditions. The system was evacuated and controlled to maintain vacuum conditions of about 3×10⁻⁴ Pa by use of rotary and diffusion pumps. Further details on the mass spectrometer gas analysis experiments are available in the literature. The chemical behaviour of phosphorus in the isothermal reduction process was evaluated by SEM-EDX method on samples pre-reduced using conditions described in Sec. 2.2. The samples were prepared using standard techniques of mounting in resin and polishing as described Sec. 2.1.

2.4. Dephosphorization Treatment by Pre-reduction, Mechanical Crushing and Screening Methods

The dephosphorization treatment of high phosphorus iron ore before and after carbothermic reduction was evaluated by mechanical crushing and screening methods. As received and pre-reduced samples were mechanically crushed in an agate mortar and screened using 25, 45 and 75 μm screen sizes. The screen sizes were selected to evaluate the effect of fine, medium and course screen separation on the dephosphorization behavior. Mass balance calculations were carried out to determine the separation behavior of the respective components in each size fraction. The iron total yield and partition ratio of gangue to the respective size fractions were calculated from the initial amount of iron and gangue (P₂O₅, SiO₂, Al₂O₃, K₂O, etc.) per ton of the initial sample treated. In order to eliminate the variable effect of the initial carbon amount and the degree of reduction on the dephosphorization behavior of pre-reduced samples, a carbon mixing ratio of 23 mass% and reduction time of 3 h were maintained in pre-reduced samples subjected to mechanical crushing and screening treatment.

2.5. Mechanical Properties of Pre-reduced Phases

The effect of mechanical properties of the pre-reduced phases on the dephosphorization behavior was investigated by using Vickers micro-hardness test. Pre-reduced samples were prepared for micro-hardness test by using the standard techniques of grinding with SiC emery paper (#320–#4000) followed by diamond paste polishing as described in Chap. 2. The micro-hardness measurements were performed using an indentation load of 50 mN and dwell time 20 s. About ten data points were collected for each phase, and the average value was plotted as a function of reduction temperature. The micro-hardness values were correlated to the micrographic observations and the dephosphorization treatment behavior of the pre-reduced samples.

3. Results and Discussion

3.1. Sample Characterization

Hematite and goethite are the main phases identified by powder XRD, as shown in Fig. 1. The phosphorus was observed to be concentrated in the aluminio–silicate gange phases as shown in Fig. 2. The average size distribution of the phosphorus-containing aluminio–silicate gange phase was in the order of 5 μm, implying that the effective dephosphorization treatment of the as-received high phosphorus iron ore would require ultra-fine milling to size fractions less than 5 μm.
3.2. Isothermal and Non-isothermal Reduction Behavior

3.2.1. TG-DTA and Mass Spectrometer Gas Analysis

Figure 3 shows the non-isothermal carbothermic reduction profiles obtained from TG-DTA. The variation of CO and CO$_2$ gas composition evolved from the mass spectrometer gas analysis results is shown in Fig. 4. These results were used to clarify the mechanism of reaction occurring in the carbothermic reduction of high phosphorus iron ore. The reduction behavior was characterized by a small but continuous TG weight loss and endothermic DTA change in the temperature range 400 to 1 000°C. From Fig. 4, a gradual increase in the intensity of CO and CO$_2$ gas species was observed from the start of analysis around 500°C. The intensity of CO$_2$ gas species peaked at about 850°C, and gradually decreased to zero at around 1 200°C as shown in Fig. 4. The evolution behavior of CO and CO$_2$ gas species shown in Fig. 4 was expected since the reduction of hematite to metallic iron is known to occur in stages.5–10)

The stepwise reductions of hematite to magnetite and magnetite to wüstite by CO gas in the temperature range 400–1 000°C are shown below.5,6)

\[
\begin{align*}
3\text{Fe}_2\text{O}_3(s) + \text{CO}_{(g)} &= 2\text{Fe}_3\text{O}_4(s) + \text{CO}_{2(g)} \\
\Delta G°^\circ &= 19 105 - 69.13T \text{ J mol}^{-1} \text{K}^{-1} \\
\text{Fe}_3\text{O}_4(s) + \text{CO}_{(g)} &= 3\text{FeO}_{(s)} + \text{CO}_{2(g)} \\
\Delta G°^\circ &= 10 610 - 17.80T \text{ J mol}^{-1} \text{K}^{-1}
\end{align*}
\]

Magnetite can also be reduced directly to metallic iron since wüstite is not thermodynamically stable below 570°C.7)

\[
\text{Fe}_3\text{O}_4(s) + 4\text{CO}_{(g)} = 3\text{Fe}_{(s)} + 4\text{CO}_{2(g)} \quad T < 570°C
\]

Rapid TG changes and DTA peaks were observed in the temperature range 1 000 to 1 200°C, and only a small rate of weight loss was observed above 1 200°C. In addition, a sharp increase in the CO gas evolution rate was also in the temperature range 1 100 to 1 200°C. In the later stages of reduction, the TG-DTA profiles and the CO–CO$_2$ gas evolution behaviors are characteristic of the conversion of magnetite to wüstite followed by the final reduction of wüstite to metallic iron and the carbon solution loss reaction, as shown below.5,6)
3.2.2. Isothermal Reduction Behavior

The isothermal reduction behavior of high phosphorus iron ore by carbonaceous materials is shown in Figs. 5–7. Figure 5 shows the effect of pre-reduction temperature on the isothermal reduction behavior. The rate of reduction and, therefore, the degree of reduction of iron oxides mixed with 23 mass% graphite powders increased with increasing the reduction temperature. The observed rate of increase in the degree of reduction was not significant when the reduction time was increased from 3 to 12 h, regardless of the increase in the reduction temperature.

Figures 6 and 7 show the effect of carbon mixing ratio on the degree of reduction in the iron ore–carbon composite reacted at 1 100°C for 3 h. The degree of reduction increased significantly with increasing the carbon mixing ratio from 10 to 15 mass%, and further increasing the carbon mixing ratio from 15 to 23 mass% had no significant effect on the degree of reduction. From the XRD patterns shown in Fig. 7, the complete reduction of iron oxides was achieved at 15 mass% carbon mixing ratio. The reduction behavior shown in Figs. 6 and 7 was due to the increase in the contact area between solid carbon and iron oxide, and the resulting increase in the amount of in-situ generated CO gas. Therefore, at lower carbon mixing ratios, the rate of reduction of iron oxides was limited not only by the direct reduction by contact carbon but also by the amount of CO gas generated at the reaction interface.8–11)

3.3. Behavior of Phosphorus in the Solid State Reduction Process

Figure 8 shows the vaporization behavior of phosphorus gas species in the solid state carbothermic reduction process of high phosphorus iron ore. The vaporization behavior of phosphorus from the solid state carbothermic reduction of phosphorus compounds in the high phosphorus iron ore at 1 100°C is shown in Fig. 8.
iron ore to form unstable PO, PO₂ and P gas intermediates is shown by Eqs. (6)–(8).

\[
P_2O_5(s) + 3C(s) = 2PO(g) + 3CO(g) \quad \text{(6)}
\]
\[
P_2O_5(s) + C(s) = 2PO_2(g) + CO(g) \quad \text{(7)}
\]
\[
P_2O_5(s) + 5C(s) = 2P(g) + 5CO(g) \quad \text{(8)}
\]

From the vaporization behavior shown in Fig. 8, it is possible to remove the phosphorus by vaporization as unstable PO and PO₂ gas intermediates in the solid state reduction process of high phosphorus iron ore, but the extent of phosphorus vaporization was not significant enough to consider as a dephosphorization treatment at process levels.

The chemical behavior of phosphorus in the solid state reduction process of high phosphorus iron ore evaluated by qualitative SEM-EDX is shown in Figs. 9(a)–9(d). Although the quantitative determination of phosphorus was inconclusive due to the low concentration of phosphorus in the initial sample, it is clear from the qualitative analysis shown in Figs. 9(a)–9(d) that most of the phosphorus compounds were not reduced in the solid state carbothermic reduction of high phosphorus iron ore, and remained as oxides concentrated in the gangue phases. Extensive growth and agglomeration of the phosphorus-rich gangue phases was observed in samples pre-reduced at 1 100°C and 1 200°C for 3 h. The average gangue phase size increased from the 5 μm order before pre-reduction to 20–30 μm in pre-reduced samples, providing the motivation to separate the phosphorus-rich gangue from reduced iron ore by mechanical crushing and screening methods. Most of the phosphorus compounds were still concentrated in the gangue phase, even when the reduction temperature was increased to 1 200°C. The Gibbs free energies of reaction for the reduction of hematite and phosphorus compounds considered to exist as apatite by solid carbon are shown in below.12)

\[
\Delta G°(J) = 586 390 - 508.57° \quad \text{(9)}
\]
\[
\Delta G°(J) = 3 615 500 - 1 311.80° \quad \text{(10)}
\]

From the value of the Gibbs free energies of reactions calculated in equations above, the phosphorus-compounds are more stable than iron oxides, and the complete reduction of iron oxides to metallic iron would proceed. Previous research also supports the conclusion that phosphorus compounds are not reduced in the low temperature reduction process of high phosphorus iron ore and remain in the form of oxides in the gangue phases.13)

3.4. Phase and Microstructure Analyses of Pre-reduced Phases

From the quantitative analyses of the reduced phases after reduction at 1 200°C for 3 h, the metallic iron phases consisted of about 98.5 mass% T-Fe and 1.5 mass% C, while the gangue phases consisted of about 62 mass% SiO₂, 33 mass% Al₂O₃ and 5 mass% K₂O. Liquid phase-controlled sintering of the gangue phases was expected above 1 000°C, since the temperature for the initial liquid-phase formation in the gangue phases was 985°C based on the quantitative phase analyses as shown in Fig. 10. No significant liquid-phase controlled sintering was expected in the reduced iron phase, since the reduction temperatures were kept below the eutectic temperature for the Fe–C phases at less than 1.5 mass% C. Therefore, the sintering of the reduced iron phases was controlled mainly by the solid state

![Fig. 9. SEM micrographs after pre-reduction at (a) 900°C, (b) 1 000°C, (c) 1 100°C and (d) 1 200°C for 3 h.](image-url)
diffusion in reduced iron particles.

3.5. Dephosphorization Treatment of the As-received Iron Ore by Mechanical Crushing and Screening Methods

Figure 11 shows the effect of screen sizes on the yield of iron oxides and the partition of gangue to screen fractions per ton of mechanically-crushed as-received sample. Mechanical crushing and screen separation using the 25 μm and 75 μm screen sizes achieved good dephosphorization ratios of 61% and 51%, respectively, but it resulted in over 50% loss of iron oxides. Although a relatively good total iron oxides yield was achieved by medium size screen separation, that is the 45 μm screen size, resulted in low dephosphorization ratios. The dephosphorization behavior observed in Fig. 11 is closely related to the mineralogy of the as-received iron ore.1,2) Table 2 shows the Moh’s hardness values of some of the common minerals associated with iron bearing minerals.14) For example, the Moh’s hardness value for apatite, a major phosphorus-bearing contaminant in iron ore, is close to that of hematite, magnetite and goethite. Therefore, the mechanical crushing of the phosphorus-bearing gangue interlocked within the iron oxides would result in the iron oxides being milled in the process. In the present case, the phosphorus-rich alumino-silicate gangue observed in Fig. 2 was in the order of 5 μm. Therefore, the effective dephosphorization treatment would require ultra-fine milling to size fractions less than 5 μm. However, ultra-fine milling is energy intensive, and the iron oxides are milled in the process, resulting in low process yield.

3.6. Dephosphorization Treatment by Pre-reduction, Mechanical Crushing and Screening Methods

Figure 12 shows the effect of reduction temperature on the dephosphorization treatment of reduced iron ore by mechanical crushing and separation using the 45 μm screen size. The reduction temperature was varied from 900 to 1200°C and the carbon mixing ratio and reduction time were fixed at 23 mass% carbon and 3 h, respectively. Increasing the reduction temperature favors both the total iron

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemistry</th>
<th>Relative Density (g/cm³)</th>
<th>Hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>α-Fe₂O₃</td>
<td>5.25</td>
<td>5.5-6.5</td>
</tr>
<tr>
<td>Magnetite</td>
<td>Fe₃O₄</td>
<td>5.20</td>
<td>6</td>
</tr>
<tr>
<td>Goethite</td>
<td>α-FeOOH</td>
<td>4.3</td>
<td>5-5.5</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al₂Si₂O₅(OH)₄</td>
<td>2.63</td>
<td>2-2.5</td>
</tr>
<tr>
<td>Apatite</td>
<td>Ca₃(PO₄)₂(OH,FCl)</td>
<td>3.2</td>
<td>5</td>
</tr>
</tbody>
</table>
yield and the separation of the phosphorus-rich gangue from reduced iron ore. Figure 13 shows the effect of screen sizes on the total iron yield after pre-reduction at 1 100°C and 1 200°C for 3 h. As shown in Fig. 13, a high total iron yield was achieved by pre-reduction at 1 100°C and 1 200°C and fine screen separation using the 25 μm screen size. The mass balance analyses shown in Fig. 14 highlights further the effect of screen sizes after pre-reduction at 1 100°C. The total iron yield decreased from 92 to 84% when the screen size was increased from 25 to 45 μm, indicating substantial iron losses with increasing the screen size. However, the dephosphorization and degree of SiO₂ and Al₂O₃ removal from the screen oversize fractions increased from 26 to 38%, 19 to 31% and 33 to 54%, respectively. It is clear from these results that increasing the screen size increased the total gangue removal. However, the overall dephosphorization degree resulted in the low yield of total iron. Therefore, it is important to optimize the cut-off screen size for the economic dephosphorization pre-treatment by these methods.

3.7. Effect of Mechanical Properties of Pre-reduced Phases

The dephosphorization treatment behavior shown in Figs. 13 and 14 can be explained in terms of the mechanical strength of the reduced phases as shown in Fig. 15. From the SEM-EDX analysis results shown in Fig. 9, a low degree of agglomeration of the reduced phases was observed after pre-reduction at 900°C and 1 000°C, corresponding to the observed low micro-hardness values, and therefore the low total iron yield. As explained in Sec. 3.4, liquid phase-controlled sintering of the gangue phases was expected to be dominant above 1 000°C and the increase in the degree of sintering and agglomeration of the reduced phases with temperature resulted in the observed increase in the micro-hardness values. Although higher reduction temperatures and fine screen separation using the 25 μm screen size favored the total iron recovery and gangue removal, the separation of the phosphorus-rich gangue from the reduced iron ore fell below expectation. The mechanical crushing and fine screen separation of samples pre-reduced at 1 100°C and 1 200°C for 3 h achieved good iron yield but with low total gangue removal ratios. After pre-reduction, the gangue phases were completely encapsulated by the sintered reduced iron particles. From the quantitative analyses of the reduced phases, the reduced iron phase was considered a ductile material, and the gangue phase was a brittle mate-
rrial. Therefore, mechanical crushing of the reduced iron ore would result in the elongation of the ductile reduced iron particles and the entrapment of the gangue within the elongated reduced iron particles, thereby hindering effective separation by mechanical crushing and screening methods as summarized in Fig. 16.

4. Conclusions

The dephosphorization treatment of the as-received high phosphorus iron ore by mechanical crushing and screening methods resulted in the low recovery of iron oxides. Phosphorus was vaporized as unstable PO and PO₂ gas intermediates in the reduction process of high phosphorus iron ore. However, the extent of phosphorus vaporization was not significant enough to consider as a dephosphorization treatment at process levels. Most of the phosphorus compounds were not reduced in the solid state carbothermic reduction process of high phosphorus iron ore and remained as oxides in the gangues. The gangue phase increased from 5 to 20–30 μm after pre-reduction thereby providing the motivation to separate of the phosphorus-rich gangue from the pre-reduced iron ore by mechanical crushing and screening methods. The degree of sintering of the reduced phases was observed to be a critical parameter in the dephosphorization treatment of high phosphorus iron ore by these methods.

REFERENCES
8) E. Kawasaki, J. Sanscrante and T. J. Walsh: J. AIChe, 8 (1962), 49.