Dephosphorization Treatment of High Phosphorus Iron Ore by Pre-reduction, Air Jet Milling and Screening Methods

Elias MATINDE1) and Mitsutaka HINO2)

1) Formerly Graduate Student, Tohoku University. Now Private Consultant (Metals, Minerals and Energy Resources), 2079 Sogwala Road, Mkoba 6, Gweru, Zimbabwe.
2) Formerly Tohoku University. Now at Hokkaido Polytechnic College, 3-190 Zenibako, Otaru, Hokkaido 047-0292 Japan.

(Received on September 24, 2010; accepted on January 12, 2011)

This paper proposes a novel process for the pre-treatment of high phosphorus iron ore by pre-reduction, air jet milling and screening methods. The dephosphorization behavior was evaluated as a function of such parameters as the milling gas kinetic energy, $E_K$ and specific energy consumption, $E_{sp}$. At a fixed milling gas kinetic energy, the dephosphorization treatment behavior was highly dependent on the solids feed rate and the degree of sintering of the pre-reduced phases. The proposed pre-treatment process involves a pre-reduction process by carbonaceous materials at 1200°C, and air jet milling using $E_K$ of 325.24 kJ and $E_{sp}$ of 3.24 kJ kg⁻¹ h⁻¹ followed by fine screen separation using a 25 μm screen size.

KEY WORDS: high phosphorus iron ore; solid state carbothermic reduction; sintering degree; dephosphorization treatment; air jet milling; specific energy consumption; milling gas kinetic energy; solids feed rate.

1. Introduction

The behavior of phosphorus in the solid state carbothermic reduction process and the dephosphorization treatment of high phosphorus iron ore by pre-reduction, mechanical crushing and screening methods were discussed in the previous work.1,2) The reduced iron ore phases were characterized according to their behavior under uni-axial mechanical loading. Mechanical crushing of the reduced iron ore resulted 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 screening methods.1,2) Therefore, the application of uni-axial direct mechanical pressure was avoided in the present investigation. The main objective of this work is to investigate the dephosphorization treatment of high phosphorus iron ore pre-reduction, air jet milling and screening methods. Processing parameters to improve the total iron yield and the dephosphorization behavior are also proposed.

2. Fundamentals of Air Jet Milling

The size reduction in an air jet mill takes place either by inter-particle collision or by impact against the solid surfaces such as the mill lining.3–6) The main breakage mechanism in the air jet milling process is destructive breakage due to impact, but other breakage mechanisms, such as abrasion, primary cleavage and secondary cleavage, also play important roles depending on the design and operating conditions of the jet mill.3–6) Although numerous models have been proposed for the breakage of single component systems in a jet mill,7–10) a limited set of empirical models have been reported on the breakage behavior of multi-component particulate systems due to the lack of applicable experimental data on the breakage mechanism, and the different behavior of each particulate component during the milling process.11–13) As a result, in this paper our focus is only on operational parameters in the jet milling process of a multi-component particulate sample. Although jet mills have widespread applications in the chemical and pharmaceutical industries, little information is available on their applications in mineral processing and extractive metallurgy. As such, it would be of particular interest to have a better understanding of the milling mechanism in order to exploit the unique size reduction mechanism inherent to air jet mills in the processing the pre-reduced high phosphorus iron ores.

3. Dimensional Analyses of Air Jet Milling Parameters

The grinding mechanism in a pressurized air jet mill depends mostly on the design and operating parameters of the mill, such as the gas pressure used for grinding, the solids feed rate, and the number and geometry of the nozzles.5,6) In the present work, the dephosphorization treatment of pre-reduced high phosphorus iron ore was evaluated using the air jet milling parameters such as the kinetic energy of the milling gas, $E_K$, and the specific energy consumption, $E_{sp}$. The grinding power, supplied as gas kinetic energy, $E_K$, is given by the Eq. (1).5,6)

$$E_K = \frac{1}{2} M_g v_g^2$$

where $M_g$ is the mass of milling gas (kg) and $v_g$ is the velocity of milling gas (ms⁻¹). The velocity of gas, $v_g$, is given by
\[ v_k = k \frac{2P}{\rho_k} \] .......................... (2)

Where \( k \) is a constant, \( \rho_k \) is the density of milling gas (kg/m³) calculated from the ideal gas equation, \( P \) is the milling gas pressure (Pa). For simplicity, \( k = 1 \) was applied in the present consideration. Eqs. (1) and (2) can be combined to give

\[ E_k = P \left( \frac{M_k}{\rho_k} \right) \] .............................. (3)

From Eq. (3), the gas kinetic energy is a linear function of the milling gas pressure, since \( M_k \) and \( \rho_k \) can be considered constant for any given operating condition.

The specific energy consumption, \( E_{sp} \), is the ratio of the kinetic energy of the milling gas flow, \( E_k \), to the solids feed rate, \( Q_{solids} \) (kg/s), and is given by

\[ E_{sp} = \frac{E_k}{Q_{solids}} \propto \frac{P}{Q_{solids}} \] .............................. (4)

Eqs. (3) and (4) can be combined to give

\[ E_{sp} = k \frac{P}{Q_{solids}} \] .............................. (5)

where \( k = \frac{M_k}{\rho_k} \) is a constant specific to the \( E_{sp} \) value of the milling gas. The relation between the specific energy consumption and milling gas kinetic energy shown in Eq. (4) provides an expression for the operating conditions independent of different mill types and working conditions. The effects of different parameters on the efficient operation of a pressurized air jet mill have been extensively studied by several researchers. Ramanujan and Venkateswarlu concluded that the solids feed rate and mass flow rates of the grinding air were the most important factors influencing the particle breakage in a jet mill. Tuunila and Nystrom concluded that the solids feed rate and mass flow rates of the grinding air were the most important factors influencing the particle breakage in a jet mill. Tuunila and Nystrom concluded that the most significant variables in jet mill grinding were the solids feed rate, the volumetric flow rate of the grinding air and the height of inner classification tube when grinding at constant pressure. In the present work, the variables for investigation were selected after careful consideration of these important parameters cited in the literature.

4. Experimental Work

4.1. Isothermal Pre-reduction of High Phosphorus Iron Ore

The samples were prepared from the solid state reaction of high phosphorus iron ore by carbonaceous materials. The isothermal carbothermic reduction behavior was investigated in the temperature range of 1100–1300°C under an argon gas flow rate of 100 ml/min, and designated reaction time. The as-received iron ore samples were pulverized to 100% passing 75 \( \mu \)m sieve, and thoroughly mixed with 23 mass % graphite powders (100% passing 45 \( \mu \)m sieve), that is, the calculated molar equivalent carbon requirement for iron oxides reduction. The iron ore-carbon composited sample was then pressed into a tablet of 10 mm in diameter and 10 mm in height. The reduction experiments were conducted in a vertical tube LaCrO₃-heated electric furnace. The 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 pre-reduced samples was determined by the ICP-AES method. Sulphur and carbon were analyzed by inert gas fusion-infrared absorbptometry. The microstructures of the phases after pre-reduction were determined by XRD, SEM-EDX and EPMA. The reduction behavior was evaluated as a function of the reduction temperature, reduction time and carbon mixing ratios, and the degree of reduction calculated from the results obtained from the chemical analysis by the ICP-AES and LECO methods.

4.2. Air Jet Milling Experiments

Air jet milling experiments were performed in an aluminina-lined jet mill. Figure 1 shows the schematic diagram of the jet milling apparatus used in this investigation. Batch milling experiments were performed using a classifying gas pressure of 0.64 MPa and milling gas pressures of 0.30 MPa, 0.50 MPa and 0.64 MPa. The solids feed rate was controlled at 0.021, 0.029 and 0.046 kg/hr using a vibrating feed controller. The milled products were collected from the bag filter and mill chamber, thoroughly mixed and prepared for chemical, particle size distribution and screen separation analyses. The experimental parameters were evaluated in terms of the kinetic energy of the milling gas, \( E_k \), and the specific energy consumption, \( E_{sp} \), as derived in Eqs. (1)–(5). From the results discussed in our previous work, the 25 \( \mu \)m screen size was tentatively selected for evaluation in the present work.

4.3. Mass Balance Calculation

It was shown in our previous work that the dephosphorization treatment by pre-reduction, mechanical crushing and fine screening using the 25 \( \mu \)m screen size achieved a good total iron yield but resulted in low total gangue separation. After pre-reduction, the gangue phases were completely encapsulated by the reduced iron particles, and the mechanical crushing resulted in the entrapment of gangue within the elongated reduced iron particles thereby hindering effective separation by screening methods. In order to
achieve an economic balance between the total iron yield and dephosphorization efficiency, a screen size of 25 μm is applied in the present investigation. The mass balance for the dephosphorization treatment process was determined from the grade equations for each separation process, as shown in Eqs. (6)–(8).15)

\[ \frac{dM_i(x)}{dx} = \frac{dM_{ic}(x)}{dx} + X_{if} \frac{dM_{ic}(x)}{dx} \]

\[ X_{ic} = T - Fe, SiO_2, Al_2O_3, P_2O_5 etc \]

where \( M_i, M_{ic} \), and \( M_{if} \) refer to the mass of feed, coarse product and fine product, respectively. The subscript index \( x \) refers to the quantities of particles with size \( x \). \( X_{ic} \), \( X_{ic} \), and \( X_{if} \) are the mass distribution of the components in the initial feed, coarse and fine size fractions, respectively (mass %).

The distribution of the component \( X \) to the respective size fractions is given by

\[ X_{ic(x)} = \left( \frac{m_i}{m_f} \right) \times X_{ic} \quad \text{(7)} \]

\[ X_{if(x)} = \left( \frac{m_i}{m_f} \right) \times X_{if} \quad \text{(8)} \]

Where \( m_f \) is the total mass of sample treated in kilograms, and \( m_i \) and \( m_f \) is the mass distribution in kilograms to the screen oversize and undersize fractions, respectively. The grade equations shown in Eqs. (6)–(8) were applied to determine the mass balance of the total iron and the partition of gangue to the screen oversize and undersize fractions per ton of pre-reduced iron ore treated.

4.4 Particle Size Distribution of Feed and Air Jet Milled Materials

After air jet milling, the samples were analyzed as compound samples collected from the bag filter and mill chamber. A laser diffraction particle measurement was performed to determine the particle size distribution of the feed and product materials. The effects of the air jet milling parameters on the milling and dephosphorization behavior of the pre-reduced iron ore were analyzed from the particle size distribution data, which was interpreted from the median particle size, \( D_{50\%} \), values. The parameter, \( D_{50\%} \), which refers to the median particle size for which 50 volume % of the particles analyzed lie above or below this value, was preferred as a measure of the mean particle sizes because it is less prone to statistical scatter caused by few coarse particles.

5. Results and Discussion

5.1. Effect of Pre-reduction Temperature

The effect of the pre-reduction temperature on the dephosphorization treatment was investigated for the samples pre-reduced for 3 h and separated using 25 μm sieves. The samples were milled with 542.07 kJ gas kinetic energy and specific energy consumption of 7.24 kJ kg\(^{-1}\) h. The pre-treatment behavior was evaluated in terms of the iron yield and the partition of gangue to the screen oversize and undersize fractions per ton of reduced iron ore treated, as shown in Fig. 2. The increase in the iron yield as the reduction temperature increased from 1100 to 1200°C can be attributed to the increase in the degree of reduction of the reduced iron ore samples with increasing reduction temperature.1,2) Figures 3(a) and 3(b) further show the mass distribution of each component in the respective size fractions. After pre-reduction at 1100°C, a high P\(_2\)O\(_5\) removal ratio (55%) and high removal ratios of SiO\(_2\) (57%), Al\(_2\)O\(_3\) (69%) and other gangue components (K\(_2\)O, Na\(_2\)O, K\(_2\)O, TiO\(_2\), CaO, MgO and S) were achieved, but with only 63% of the total iron yield achieved under these pre-treatment conditions. When the reduction temperature was increased to 1200°C, the total iron yield increased from 63% to 81%, while the dephosphorization ratio and the ratio of SiO\(_2\) removal decreased from 55% to 38% and 57% to 39%, respectively. The results shown in Figs. 3(a) and 3(b) indicate the importance of the role played by the pre-reduction conditions in the dephosphorization treatment of the pre-reduced iron ore.1,2)

5.2. Effect of Gas Kinetic Energy

The effect of gas kinetic energy on the dephosphorization behavior was investigated in samples pre-reduced at 1100°C for 3 h and separated using 25 μm sieves. Gas kinetic energy, \( E_k \), was varied from 325.24, 542.07 to 693.84 kJ, and the specific energy consumption, \( E_{sp} \), was fixed at 7.24 kJ kg\(^{-1}\) h. Figure 4 shows the effect of milling gas kinetic energy on the median particle size, \( D_{50\%} \). The size distributions of particles produced under varied gas kinetic energies is shown in Table 1. The milling process in a jet mill is a function of the energy of inter-particle collisions and the probability of particle collisions, as shown in Eqs. (3)–(5). Therefore, increasing the gas kinetic energy leads to the increased particle velocity, and consequently, the energy of inter-particle collisions.

Figure 5 shows the effect of gas kinetic energy on the total iron yield and the partition of gangue to the screen oversize and undersize fractions. It is interesting to note that no significant change in the total iron yield and gangue partition to the screen fractions was observed when \( E_k \) was...
increased from 325 to 694 kJ. Although the mean particle size, D_{50\%}, of the mill product decreased from the initial value of 87 μm to 77 μm and 46 μm after milling at E_k of 325 kJ and 694 kJ, respectively, the mean product size did not affect the overall dephosphorization ratio when the cut-off size of the sieve was 25 μm.

An inverse relation was found between the gas kinetic energy and the product particle size, as shown in Fig. 4. However, the change in the mean particle size was only about 30 μm despite more than doubling the gas kinetic energy from 325 kJ to 694 kJ. This means that milling gas pressure may be considered as a non-critical parameter under the present experimental conditions, provided the classifier gas pressure was optimized to avoid the settling or the cascading of the solid particles within the milling chamber. In other words, a gas kinetic energy of 325 kJ can be applied in the dephosphorization treatment process when all the other parameters are kept constant.

5.3. Effect of Specific Energy Consumption

The effect of specific energy consumption was evaluated in samples pre-reduced at 1100°C for 3 h, and separated using a 25 μm screen size. The specific energy consumption, E_{sp}, was varied from 3.24, 5.28 to 7.24 kJkg^{-1}h, i.e., at solids feed rate of 0.047 kg h^{-1}, 0.029 kg h^{-1} and 0.021 kg h^{-1}, respectively. The milling gas kinetic energy, E_k, was fixed.
Figure 6 shows the effect of the specific energy consumption, which was expressed in terms of the solids feed rate, on the mean particle diameter of the mill product. The mean particle size increased as the solids feed rate was increased from 0.021 kg/h to 0.047 kg/h. Since the specific energy consumption is defined as the amount of energy consumed to reduce the particle size per unit mass, increasing the solids feed rate resulted in a decrease in the specific energy consumption per unit particle, and therefore, resulted in the larger mean product sizes.

The iron yield and the partition of gangue to the screen oversize fractions decreased when the specific energy consumption was increased from 3.24 to 5.28 kJ/kg·h, as shown in Fig. 7. The effect of specific energy consumption on the total iron yield shown in Fig. 7 is further summarized in Fig. 8. Since the specific energy consumption is inversely related to the solids feed rate, a high solids feed rate results in a low specific energy consumption per unit particle, and therefore, poor destructive breakage by impact. On the other hand, a low solids feed rate may lead to the low accumulation of solids in the mill chamber (and therefore, high specific energy consumption per particle), resulting in finer product sizes, as is shown by the solids feed rate of 0.021 kg/h in Fig. 6. At constant gas kinetic energy and classifier pressure, a low solids feed rate may also result in the solid particles being fluidized into the classifying chamber without any meaningful destructive collision taking place. Therefore, it is important to experimentally determine an optimal solids feed rate for the stable application of the air jet mill in the milling process of the pre-reduced iron ore.

5.4. Effects of Pre-reduction Time and Temperature

The effect of pre-reduction temperature for shorter reduction periods was evaluated in samples pre-reduced at 1100, 1200 and 1300°C for 0.5 h, and milled under the following conditions: \( E_k = 325.2 \text{ kJ} \) and \( E_{sp} = 1.94 \text{ kJ/kg·h} \). From the...
results shown in Fig. 9, it is interesting to note that, with the exception of phosphorus, a high degree of total gangue separation, especially on SiO2, Al2O3 and other gangue components was successfully achieved with a high T–Fe yield. Although the T–Fe yield can be increased further by using higher pre-reduction temperature conditions, the dephosphorization degree decreases significantly, making it difficult to optimize the balance between the process yield and dephosphorization efficiency. Figure 10 further summarizes the effects of the pre-reduction time and temperature on the T–Fe yield and overall gangue removal after pre-reduction at 1100, 1200 and 1300°C for 0.5 h (mass %). $E_k$: 325.24 kJ, $E_p$: 1.94 kJkg⁻¹h. Other gangue components: Na2O, K2O, TiO2, CaO, MgO and S.

Fig. 8. Effect of milling gas pressure and solids feed rate on the T–Fe yield, mass % (1100°C, 3 h).

Fig. 9. Partition of components to the screen size fractions after pre-reduction at 1100, 1200 and 1300°C for 0.5 h (mass %). $E_k$: 325.24 kJ, $E_p$: 1.94 kJkg⁻¹h. Other gangue components: Na2O, K2O, TiO2, CaO, MgO and S.

Fig. 10. Comparative effects of pre-reduction time and pre-reduction temperature on the T–Fe yield and gangue removal, mass %. $E_k$: 325.24 kJ, $E_p$: 1.94 kJkg⁻¹h.

Fig. 11. SEM images after pre-reduction at 1100–1300°C for 0.5 h (a–c), 1100–1200°C for 3 h (d–e) (Accelerating Voltage: 20 kV, Magnification: ×1000).

improve the efficiency of the dephosphorization process, it is important to control the degree of sintering and agglomeration of the reduced iron phases, and this is possible by using a pre-reduction time of 0.5 h in the reduction temperature of 1200–1300°C.

5.5. Comparative Dephosphorization Treatment Behavior by Mechanical Crushing and by Air Jet Milling Methods after Pre-reduction at 1100°C

Table 2 shows the comparative effects between the air jet milling method and mechanical crushing in an agate mortar after pre-reduction at 1100°C for 3 h. The air jet milled samples were milled using gas kinetic energy of 542 kJ and specific energy consumption of 7.24 kJg⁻¹h. A T–Fe yield of about 92% was observed after mechanical crushing in an agate mortar, and a T–Fe yield of about 63% was observed after air jet milling. After air jet milling and screen separa-
over 60% gangue removal ratio was achieved but the T–Fe yield was low. Therefore, further work is required to optimize the balance between the total iron yield and overall gangue removal in order to improve the economic value of the pre-reduced iron product.

The difference in the milling and dephosphorization behavior observed from the two size-reduction methods applied in the present work can be attributed to the different particle breakage mechanism, as shown in Fig. 12. Figure 12 shows the scanning electron microscopy (SEM) micrographs of the sample pre-reduced at 1100°C for 3 h and mechanically-crushed in an agate mortar, (b) milled using gas kinetic energy of 542 kJ, and, specific energy consumption of 3.24 kJkg⁻¹h⁻¹, and (c) milled using gas kinetic energy of 542 kJ and specific energy consumption of 5.28 kJkg⁻¹h⁻¹.

6. Conclusion

The dephosphorization of high phosphorus iron ores by pre-reduction, air jet milling and screening methods was investigated in the present work. At a fixed milling gas kinetic energy, the milling and the pre-reduced iron ore-gangue separation behavior was highly dependent on the solids feed rate. The degree of sintering and agglomeration of the reduced iron grains was critical in controlling the dephosphorization treatment process of the pre-reduced iron ore by air jet milling and fine screening methods. The simplified breakage mechanism occurring during the mechanical crushing or air jet milling process of pre-reduced iron ore is shown in Fig. 13.

![Fig. 12. SEM micrographs of the samples pre-reduced at 1100°C for 3 h and, (a) mechanically-crushed in an agate mortar, (b) milled using gas kinetic energy of 542 kJ, and, specific energy consumption of 3.24 kJkg⁻¹h⁻¹, and (c) milled using gas kinetic energy of 542 kJ and specific energy consumption of 5.28 kJkg⁻¹h⁻¹.](image)

![Fig. 13. Proposed size reduction mechanism occurring during the mechanical crushing or air jet milling process of pre-reduced iron ore.](image)
kJ and specific energy consumption of 3.24 kJ/kg·h, and screen separation using a 25 μm sieve.

Acknowledgments

The present authors would like to express their appreciation to Prof. Takahiro Miki and Prof. Fumio Saito, both of Tohoku University, and Dr. Naoya Sato of Hitachi Metals, for valuable discussions. This work was in part sponsored by the Global COE Program of Tohoku University. The authors gratefully acknowledge their support.

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