Effect of Surface Properties of Iron Ores on their Granulation Behavior

Hongxia MAO, Rende ZHANG,* Xuewei LV, Chenguang BAI and Xiaobo HUANG

College of Materials Science and Engineering, Chongqing University, Chongqing, 400044 China.

(Received on November 30, 2012; accepted on January 10, 2013)

The granulation property of iron ores was generally influenced by their wettability, surface roughness and shape of the iron ore. In this study, the surface roughness and shape of iron ores were characterized by the ratio of BET specific surface area ($S_{\text{BET}}$) to specific surface area ($S_{\text{LS}}$) calculated using size distribution obtained by a laser diffraction method. Wettability of ores was characterized by measuring the contact angle ($\theta$) between iron ore and water. Bed permeability was used as an evaluation index of granulation effect. A variety of materials were subjected to a granulation test under an actual production condition. Special attention was paid to four ores with different surface properties and wettabilities. Nine groups of mixtures were obtained by linear programming taking the basicity as the objective function. Granulation results showed that the optimum bed permeability of nine mixtures have a good linear relation with mass fraction of four ores studied. Slopes ($k$) of fitting lines were used to characterize the granulation properties of ores, binary linear regression equation was derived with the $k$ used as dependent variable, $\theta$ and $S_{\text{BET}}/S_{\text{LS}}$ used as independent variables: $k=16.443–0.277\times\theta+0.058\times(S_{\text{BET}}/S_{\text{LS}})$. Granulation performance of iron ore gets better with decreasing the contact angle and increasing the ratio of $S_{\text{BET}}$ to $S_{\text{LS}}$.

KEY WORDS: granulation property; surface roughness; wettability; permeability.

1. Introduction

Many kinds of iron ores were used together in the modern steel mill with increasing demand and depletion high grade resources. The granulation performance of ores seems particularly important in order to get a good permeability of the packed bed of granules during sintering process. Many studies were carried out on the granulation properties of iron ores from different respects and acquired series of achievements. Khosa1) found that the optimum moisture could be described accurately by knowing the ore’s SiO$_2$, LOI and Al$_2$O$_3$ content, as well as the $\sim0.15$ mm and percentage of intermediate (0.1 to 1 mm) size fractions. It was also found that for most iron ores, an increase in particle size close to the size of 0.1 mm has the greatest effect of reducing permeability and increasing granulating moisture. Maeda2) got the conclusion that when iron ore with high wettability was used for nuclei particles, it can be granulated under all conditions, and for ores with low wettability used as nuclei particles, it was necessary to increase the adding moisture in order to obtain the granulated particles of the same grade using iron ore with high wettability for nuclei particles. The fracture strength of granulated particles increased with decreasing the contact angle. Bergstrand3) found that the mineralogical and textural characteristics of the superfine particles are likely to be an important factor in the granulation behavior of an ore or a blend of ores. Kasal4) found that pre-ignition permeability of the mixes was unequivocally related to the mean size of the granules. Control of moisture content in the mix is a reliable and convenient way to obtain an appropriate pre-ignition permeability. Lv5) studied the effect of moisture capacity of iron ore on granulation, and gained the conclusion that the moisture capacity and the optimum water content have a highly positive correlation. Iron ores which have high moisture capacity need more water added in the granulation process in order to get high permeability. The above studies focused mainly on chemical composition, size distribution, wettability, mineralogical characteristics and moisture capacity. However, research on surface morphology of iron ore is far from sufficiency.

The surface properties of iron ore powders include mainly two aspects: surface morphology and wettability. Surface morphology of iron ore refers to roughness and the shape of the particle which can be got by comparing the specific surface area measured with the laser diffraction method and the liquid nitrogen absorption method.6,7) The value of laser diffraction method shows the particle size distributions by measuring the angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample. Large particles scatter light at small angles relative to the laser beam and small particles scatter light at large angles. The angular scattering intensity data is then analyzed to calculate the size of the particles responsible for creating the scattering pattern. The particle size is reported as a volume equivalent sphere diameter. Assume that the iron particle is spherical, non-porous and opaque particles, specific surface area of iron ore can be got by geometrical calculations.8)
The BET model based on liquid nitrogen absorption technique determines the specific surface area of a powder by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces between the adsorbate gas molecules and the adsorbent surface of the test powder. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure.9,10) The mathematical model used to calculate the specific surface area from the laser diffraction methods is based on the important assumption that all particles are fully dense smooth spheres. However, real iron ore particles are never smooth spheres but are rather irregularly shaped with great roughness; both characteristics can increase the specific surface area of the particle. The specific surface area measured by nitrogen adsorption should be close to the real value of the particle specific surface area according to the theory of adsorption. The specific surface area measured by BET method is much larger than that by combining the size distribution determined by laser diffraction and the mathematical model calculation. Thus the ratio of $S_{BET}$ to $S_{LS}$ can characterize the surface roughness of iron ore because of the fact that the roughness of the particle influences the specific surface area apparently.6,7) Contact angle between iron and water is used to characterize the wettability of iron ore particles. In this work, the determination of contact angles of ores by liquid penetration rate is used.11,12)

The aim of this study was to investigate the permeability of the green granules bed of nine groups of iron ore sinter mixes, and the particular emphasis was given to examining how the characteristics of the ores such as surface roughness, shape and wettability affect granulation and the resulting bed properties.

2. Experimental

2.1. Materials

Chemical composition and surface properties data are reported in Table 1. Ore A is a high-grade soft hematite ore which is beneficial to sinter process. Ore B and Ore D are all limonite, which contain high grade of combined water and LOI. Ore C is a hematite ore which contains high silica and low alumina.

Table 1. Chemical composition and surface properties for materials studied.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Chemical composition (%)</th>
<th>Surface properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TFe</td>
<td>SiO$_2$</td>
</tr>
<tr>
<td>Ore A</td>
<td>65.29</td>
<td>1.36</td>
</tr>
<tr>
<td>Ore B</td>
<td>58.27</td>
<td>5.55</td>
</tr>
<tr>
<td>Ore C</td>
<td>64.51</td>
<td>4.3</td>
</tr>
<tr>
<td>Ore D</td>
<td>59.14</td>
<td>4.38</td>
</tr>
</tbody>
</table>

Fig. 1. Size distribution of ores studied.

SEM images of fines from the four ores are given in Fig. 2. Ore B shows the extremely rough and heterogeneous nature of the particles, while the micrographs of Ore C shows angular and smooth surface.

The laser diffraction analysis and isotherm linear plots of fines from the iron ores are given in Figs. 3 and 4. The particle size (~0.125 mm) of four iron powders are same for laser diffraction analysis and liquid nitrogen adsorption analysis. Figure 3 shows that the size distribution of Ore A is dispersive, as for Ore C, it is concentrated. The $S_{LS}$ is obtained by combining the size distribution determined by laser diffraction and the mathematical model. From Fig. 4 it is evident that desorption curve is above the adsorption curve, Ores B and D have larger surface area for their adsorption qualities are much bigger than Ores A and B, the $S_{BET}$ are calculated by combining the date of adsorption experiment and the mathematical model. The specific surface area measured by las diffraction and BET methods are show in Table 1. The specific surface area measured by liquid nitrogen adsorption methods is much larger than that by combining the size distribution measured by laser diffraction and the mathematical model calculation. This difference due to the assumption that iron powder is spherical and smooth for laser diffraction analysis. The specific surface area mea-
The wettability of iron ore powders are characterized by measuring the contact angle between iron ore and water with the penetration method. Example of penetrating rate measurement obtained for packed bed of Ore A powders are given in Fig. 5, the two curves represent pressure difference versus time for cyclohexane and water text respectively, and the corresponding plots of pressure difference squared against time are liner as expected, the slopes were used to calculate contact angle. A fit range from 50 to 100 s was fixed for all calculations. The range of the early stage of penetration was neglected since it is governed by inertial forces with very fast rates of liquid uptake, expanding the range of calculations beyond 150 s results in high errors in contact angle determination due to increasing deviation from linearity, Table 1 shows contact angles of four iron ores calculated by formula (1).

\[
\theta_i = \arccos \left( \frac{K_i \eta_i \gamma_i}{K_0 \eta_0 \gamma_0} \right) \quad \text{............... (1)}
\]

\(K_0\) and \(K_1\) represent two slopes measured by cyclohexane and water respectively, \(\gamma_0\) and \(\gamma_1\) are surface tension of cyclohexane and water, \(\eta_0\) and \(\eta_1\) are viscosity of cyclohexane and water.

### 2.2. Experiment

A variety of materials including natural fine ores and return fines from screening operations, flue dust, and other iron bearing materials of small particle size were used according to the actual production condition. All materials were used at as received moistures. Linear programming was used to blend ores by taking the basicity (R=2) as the objective function. Table 2 shows the constraints which includes chemical composition and size distribution of mixtures. Mass fractions of each material were also considered.
For materials studied (Ores A, B, C and D), the mass fraction ranged in a broad span. And for other materials, the amounts were limited to a narrow range in order to lessen the influence of other factors. Sinter mix weight compositions of nine groups were given in Table 3.

The granulation experiments were carried out in the laboratory rotating mixer at a defined rotating rate for 4 min with various water content added. The rotating mixer is with a diameter of 416 mm and a length of 940 mm. The granules were loaded into the permeability measurement device, which is with a diameter of 210 mm and a height of 300 mm. For the permeability tests, the compressed air passed through the bed, and the pressure indicator located in the base of the device recorded the pressure drop across the bed. Several water content levels were selected for granulation and the negative pressure of the granules in the measurement device were measured to compare the permeability. The water content with the lowest negative pressure of the burden is the optimal water content for granulation. Bed permeability of green sinter feeds was calculated using the widely accepted equation.\(^{(14)}\)

\[
JPU = \frac{Q}{A} \left( \frac{H}{\Delta P} \right)^{0.6}
\]

where \(Q\) is the air flow rate (m\(^3\)/min), \(A\) is the cross-sectional area of the bed (m\(^2\)), \(H\) is bed height (mm) and \(\Delta P\) is the pressure drop across the bed (mm H\(_2\)O).

### 3. Results and Discussions

For each group, raw mixtures of materials were granulated at varying moistures and the bed permeability was measured. The results of four groups are presented in Fig. 6 and show a quadratic equation fitted to the experimental data. In accordance with the previous studies, the bed permeability initially increases with increasing moisture before beyond a maximum and then decreasing at higher moistures.\(^{3,5,14,15}\)

The water content with the maximum permeability from the fitting curves is the optimal value.

#### Table 3. Mixing ratios of materials used (mass percentage, %).

<table>
<thead>
<tr>
<th>Group No.</th>
<th>Ore A</th>
<th>Ore B</th>
<th>Ore C</th>
<th>Ore D</th>
<th>Other ores</th>
<th>Return fines</th>
<th>Flux</th>
<th>Coke breeze</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.97</td>
<td>0.00</td>
<td>5.28</td>
<td>16.16</td>
<td>30.15</td>
<td>30.67</td>
<td>9.51</td>
<td>3.23</td>
</tr>
<tr>
<td>2</td>
<td>12.51</td>
<td>16.19</td>
<td>3.13</td>
<td>10.29</td>
<td>10.01</td>
<td>30.72</td>
<td>9.14</td>
<td>3.23</td>
</tr>
<tr>
<td>3</td>
<td>9.09</td>
<td>0.00</td>
<td>5.69</td>
<td>27.07</td>
<td>14.78</td>
<td>30.69</td>
<td>9.46</td>
<td>3.23</td>
</tr>
<tr>
<td>4</td>
<td>12.46</td>
<td>20.99</td>
<td>3.11</td>
<td>0.00</td>
<td>24.90</td>
<td>30.69</td>
<td>9.40</td>
<td>3.23</td>
</tr>
<tr>
<td>5</td>
<td>4.98</td>
<td>0.00</td>
<td>5.29</td>
<td>25.92</td>
<td>20.48</td>
<td>30.69</td>
<td>9.40</td>
<td>3.23</td>
</tr>
<tr>
<td>6</td>
<td>4.98</td>
<td>0.00</td>
<td>4.08</td>
<td>18.10</td>
<td>29.47</td>
<td>30.69</td>
<td>9.46</td>
<td>3.23</td>
</tr>
<tr>
<td>7</td>
<td>4.81</td>
<td>3.88</td>
<td>9.42</td>
<td>22.27</td>
<td>14.33</td>
<td>30.49</td>
<td>11.57</td>
<td>3.23</td>
</tr>
<tr>
<td>8</td>
<td>6.17</td>
<td>0.00</td>
<td>9.61</td>
<td>28.19</td>
<td>10.69</td>
<td>30.49</td>
<td>11.60</td>
<td>3.23</td>
</tr>
<tr>
<td>9</td>
<td>4.82</td>
<td>1.43</td>
<td>2.41</td>
<td>23.48</td>
<td>22.67</td>
<td>30.50</td>
<td>11.48</td>
<td>3.23</td>
</tr>
</tbody>
</table>

Table 2. Composition and size distribution limiting of mixtures (mass percentage, %).

<table>
<thead>
<tr>
<th>TFe</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>MgO</th>
<th>LOI</th>
<th>0.25–1 mm</th>
<th>&lt;0.25 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>59–62</td>
<td>3.4–4.2</td>
<td>1.3–1.7</td>
<td>1.45–1.60</td>
<td>4.5–6</td>
<td>18–21</td>
<td>21–29</td>
</tr>
</tbody>
</table>

For group 2, the mass fraction of Ore A was 12.51% which was the highest percentage of Ore A content among the nine groups, this group get optimum permeability at lowest moisture content among four groups and the optimum permeability is only second to group 4; the mass fraction of Ore B was the highest in group 4 which reached 20.99%, From Fig. 6, it is indicated that the shape of the permeability–moisture curves is also dependent on the composition of the mixture, group 4 displaying narrower curves than other three groups, A possible explanation is that a faster rate of granule size enlargement with moisture addition contribute to the rapid increase and a significant losses in bed voidage caused by granule deformation lead to a fast drop, thereby narrowing the permeability–moisture curve; Group 7 has the highest Ore C content (9.42%) among nine groups, From Fig. 6, it is indicated that the group 7 achieved optimal permeability at highest moisture content in four groups, Ore C has a low wettability and a large content of fine, it was necessary to increase the adding moisture in order to obtain a good permeability; Group 8 has the lowest optimal permeability among four groups in which the mass fraction of Ore D is the highest. The major reasons for the lowest permeability may due to the fact that Ore D has a lower wettability whose contact angle can be up to 79.47°.

Surface roughness and the shape of the iron ore can be characterized by SEM photos qualitatively and \(S_{\text{BET}}/S_{\text{LS}}\) quantitatively. The contact angle between iron ore and water can characterize the wettability of iron. The contact angle
and $S_{\text{BET}}/S_{\text{LS}}$ of four ores studied are shown in Fig. 7. It is evident that Ore A has the highest wettability and Ore D has the lowest, the differences between the maximum and minimum of contact angle value reached 30°. Form the $S_{\text{BET}}/S_{\text{LS}}$ value it is obvious that the surface roughness of Ore B is the largest and then are Ore D, Ore A, Ore C in turn.

Through the comparison between the contact angle and $S_{\text{BET}}/S_{\text{LS}}$ of four ores is clearly shows that there are uncertain relationship between wettability and surface roughness, the contact angle of the iron ore depend on the chemical composition in a great extent. The relationship between the mass fraction of four ores studied in mixtures and permeability are shown in Fig. 8. From Fig. 8, it is indicated that the bed permeability has a good linear relation with mass fraction of ore. The bed permeability get better with increasing the mass fraction of Ores A and B in the mixture, while Ores C and D act opposite role. The more content of Ores C and D in mixture, the worse the bed permeability. A straight line represents the relationship between permeability and ore content is obtained by fitting the experimental data based on least square method. The slope represents the granulation property of ore. Ore A is conducive to granulation because it has the lowest contact angle among the four ores and proper surface roughness; As for Ore B, although its wettability is not as good as Ore A for the contact angle reached 76.30°, it has an extremely rough surface for $S_{\text{BET}}/S_{\text{LS}}$ reached up to 116.32. It is also beneficial to granulation; For Ore C, it is evident that its wettability is better than Ore B, but it has a smooth surface through both $S_{\text{BET}}/S_{\text{LS}}$ value and SEM photo, It goes against the granulation; Ore D also has adverse impacts on granulation because it has the lowest wettability for the contact angle reached up to 79.47°. Based upon the above analysis, it is indicated that the surface granulation properties of iron ore is under the joint action of wettability, shape and surface roughness.

Binary linear regression Eq. (3) was derived with the $k$ used as dependent variable, $\theta$ and $S_{\text{BET}}/S_{\text{LS}}$ used as independent variables, resulting a multiple correlation coefficient $R^2=0.904$ which can pass the F inspection at very high display level. The standardized regression coefficients of $\theta$ and $S_{\text{BET}}/S_{\text{LS}}$ were $-1.19$ and $1.09$ respectively, the influence of wettability of iron ore was slightly notable than shape and surface roughness. It is demonstrated that there is an increase in $k$ when the decrease of $\theta$ and the increase of $S_{\text{BET}}/S_{\text{LS}}$ value.

$$k = 16.443 - 0.277 \times \theta + 0.058 \times (S_{\text{BET}} / S_{\text{LS}}) \quad \ldots \ldots (3)$$

4. Conclusions

The surface granulation properties were influenced by surface properties such as wettability, surface roughness and shape in common. In this study, Wettability of ores was
characterized by measuring the contact angle ($\theta$) between iron ore and water, the surface roughness and shape of iron ore were characterized by the ratio of $S_{BET}$ to $S_{LS}$. Bed permeability was used as an evaluation index of granulation effect. Granulation results showed that the optimum bed permeability of nine mixtures have a good linear relation with mass fraction of four ores studied, slopes ($k$) of fitting lines were used to characterize the granulation properties of ores. Binary linear regression equation was derived with the $k$ used as dependent variable, $\theta$ and $S_{BET}/S_{LS}$ used as independent variables: 

$$k = 16.443 - 0.277 \times \theta + 0.058 \times \left( \frac{S_{BET}}{S_{LS}} \right),$$

resulting a complex correlation coefficient $R^2 = 0.904$. The standardized regression coefficients of $\theta$ and $S_{BET}/S_{LS}$ were $-1.19$ and $1.09$ respectively, thus the influence of $\theta$ and $S_{BET}/S_{LS}$ were almost equal, the effect of wettability was slightly more notable.

Acknowledgements

The authors are especially grateful to National Natural Science Foundation of China (Grant No. 51104192).

REFERENCES