Indication of the Measurement of Surface Area on Iron Ore Granulation

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The characterization of the surface area of iron ore is of vital importance for the studies of the mineral processing. The specific surface area of iron ore particles can be measured by nitrogen adsorption, laser diffraction, and mathematical models based on the size distribution. The difference among these three methods and its indication on the granulation process were discussed. It was found that the shapes of the particles influences the specific surface area apparently. The roughness of the particle influences the specific surface area apparently, and the samples with like-slice and like-layer particles have high specific surface area. The granulation experiments shows that the efficiency of granulation increases with increasing the water saturation and the iron ore with more fine adhesive particles can get a higher efficiency of granulation easily. The usage of iron ore with big and rough particles can improve the permeability of the bed of granules. The iron ore with smooth and sphere particles has poor ability of granulation.

KEY WORDS: specific surface area; roughness; morphology; iron ore; particles.

1. Introduction

The granulation process before the iron ore sintering, by which the iron ore particles join together with the water among the particles, is of vital importance for getting a good permeability of the bed of granules in the sintering strand. The previous studies have approved that the particle bigger than 0.7 mm is regarded as the nuclear particle and the particle smaller than 0.2 mm is considered to be the cohesive particle during the granulation. The particle of 0.2–0.7 mm is the medium, neither as the nuclear nor the cohesive. The more particles of 0.2–0.7 mm, the worse granulation result. In addition, the surface feature of the particles also have a great effect on the granulation behavior. In general, the smooth and sphere particles are hard to attach or be attached, while the rough and irregular ones are easily to join together. Therefore, The characterization of the particle size and the surface features of iron ores is of vital importance for the studies of mineral processing. The specific surface area of iron ore particles can be measured by nitrogen adsorption, laser diffraction, and mathematical models based on the size distribution. However, what is the difference among these methods and what is the indication of the results were less discussed on the iron ore granulation, which is the right topic of the present study.

2. Experimental

The specific surface area of the particle samples were measured by ASAP2020 produced by Micromeritics, The principle of the ASAP 2020 is the adsorption of nitrogen at low temperature, the mass of nitrogen absorbed can be measured, thus, the surface area can be calculated with this data based on the theoretical absorption models like the BET model or the Langmuir model. All the iron ores were measured using nitrogen at the temperature of 77 K. For the measurement of particle size, the sieve sizing method and the laser diffraction method were used. The series of screens used in the sieve sizing are classified as 0.038 mm, 0.2 mm, 0.7 mm, 1 mm, 3 mm, 5 mm, 8 mm, and 10 mm. The laser diffractometer used in this study is MS 2000 which is produced by Malvern Instruments. The valid measuring range is from 0.02 μm to 2 000 μm. The bulk density and the real density of the samples were measured by the drainage method. In order to investigate the effect of the micro-morphology on the specific surface area of the particles, the samples of materials smaller than 0.038 mm were observed by SEM with two magnifications, named 200 times magnification for checking the homogeneity of the size and the shape of particles and 1 000 times magnification for the clear view of the surface morphology of the particles. The conception and the measurement method of the moisture capacity, which represent the ability of the water absorption of the iron ore, were suggested by the authors of this papers in the previous studies. The moisture capacity of the samples were also measured in this study. Before all the measurements, the iron ores samples were first pretreated by drying with the high temperature air of about 200°C in a rotating drum for 30 minutes for avoiding the agglomeration of the particles.

In order to investigate the relationship between the surface features and the ability of granulation, the granulation experiments were carried out, which was divided into two steps, named the step of mixing, in which the water is firstly added and the materials are mixed well for keeping the chemical composition and the size distribution homogeneously, and the step of granulating, in which the water is
complemented to reach a level desired and the particles grow up as moving with the rotating mixer. Before the experiments of granulation, the water content in the iron ore samples was measured, and the total water content can be got by adding the original water measured and the water added during the experiments.

In a sintering plant, the time of granulation is about 3–5 minutes, and the filling rate of the mixer is about 15%. Therefore, the granulation time in this experiment was 4 minutes, and the filling rate was 15%. The rotating rate of the mixer was defined according to the Froude dimensionless number which is expressed as:

$$Fr = \frac{D \cdot n^2}{g}$$ ................................. (1)

where D, n, and g represent the diameter of the rotating mixer (m), rotating rate of the mixer (rad/min), and the gravity acceleration (m/s²). In the sintering plant studied, the d and n equal 600 mm and 16 rad/min. The d in the experimental mixer is 4.4 m and 16 rad/min. The mass of the mixture used in each experiment is about 60–70 kg. After the experiments of granulation, the size of the granules were measured as produced with the size screening method. The method in which the granules with the liquid nitrogen was not adopted because some granules always adhered together and hard to screen down. It is necessary to point out that though the granules may break down during the screening, the breakage ratio can be controlled in a low range by shaking the screens lightly.

3. Results and Discussion

3.1. Characterization of the Iron Ore Particles

In the present study, six samples of the iron ore were selected for the measurements. The chemical compositions of the samples are shown in Table 1. The size distributions were measured by dry screening without prior wet screening and the data are shown in Table 2. In four of the six cases, more than 50% of the material was smaller than 0.2 mm. The particle size distribution of the samples under 0.2 mm and their surface area was measured with the laser diffractometer, the results are shown in Fig. 1 and Table 3.

According to Fig. 1 and Table 2, samples C, E, and F are fine ores, and samples A, B, and D are the coarse. The surface area of the iron ore samples of unit mass can be calculated by Eq. (2), with the assumption of sphere particles in the samples which is expressed by:

$$S = 4\pi \sum \frac{n_i \cdot r_i^2}{\rho}$$ .......................... (2)

where S is the total surface area of all particles of unit mass, r_i is the radius of the particles. The number of particles with the size of r_i can be calculated by:

$$n_i = \frac{m_i \cdot 3}{\rho \cdot 4\pi r_i^3}$$ .......................... (3)

where m_i is the mass fraction of particles with the size of r_i in the raw materials of 100 g.

Replacing the n_i in Eq. (2) by Eq. (3) gives:

$$S = \sum \frac{m_i \cdot 3}{\rho \cdot r_i^2}$$ .......................... (4)

The bulk and the real density of the iron ore samples are shown in Table 4. According to Eqs. (2)–(4) and the data in Tables 2 and 4, the surface area can be calculated, the results are shown in Table 5.

The specific surface area of the samples measured by ASAP2020 are shown in Table 6. Samples A, C, and E have small surface area, from 1 to 4 m²/g, samples B and D have

| Table 1. Composition of the four iron ores selected, mass%. |
|---------------|--------|--------|--------|--------|--------|--------|--------|
| Ore | Water | LOI | TFe | FeO | SiO₂ | CaO | MgO | Al₂O₃ | S | P |
| A | 2.81 | 0.66 | 62.64 | 28.01 | 7.52 | 1.22 | 4.54 | 1.14 | 1.61 | 0.010 |
| B | 3.16 | 3.61 | 62.23 | 0.53 | 4.38 | 0.10 | 3.59 | 0.01 | 0.046 |
| C | 2.70 | 0.97 | 61.19 | 23.35 | 6.26 | 0.40 | 5.98 | 0.98 | 0.010 |
| D | 0.36 | 2.22 | 63.33 | 1.26 | 3.71 | 0.21 | 1.61 | 0.09 | 0.060 |
| E | 7.04 | 4.86 | 56.00 | 7.60 | 12.45 | 1.75 | 1.53 | 1.64 | 0.49 | 0.160 |
| F | 8.10 | 3.50 | 59.53 | 14.14 | 6.40 | 4.80 | 2.42 | 0.78 | 0.48 | 0.680 |

| Table 2. Size distribution (mm) of iron ores, mass%. |
|---------------|--------|--------|--------|--------|--------|--------|
| Ore | >10 | 8–10 | 5–8 | 3–5 | 1–3 | 0.7–1 | 0.2–0.7 | 0.038–0.2 | <0.038 |
| A | 1.5 | 0.3 | 4.6 | 9.3 | 3.8 | 1.8 | 10.9 | 49.7 | 18.2 |
| B | 4.0 | 3.2 | 10.0 | 11.6 | 11.1 | 7.1 | 26.3 | 17.8 | 8.9 |
| C | 3.9 | 1.6 | 11.1 | 12.5 | 11.6 | 5.8 | 15.7 | 28.4 | 9.4 |
| D | 0.0 | 0.7 | 1.0 | 0.8 | 0.9 | 1.1 | 13.8 | 51.6 | 30.1 |
| E | 0.0 | 0.4 | 0.2 | 0.2 | 0.4 | 0.4 | 3.9 | 55.1 | 39.4 |
| F | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.3 | 61.5 | 38.1 |

Fig. 1. Particle size distribution of the eight iron ore samples (≤0.2 mm).
Table 3. From the size distribution measured by laser diffraction.

| Factors | A | B | C | D | E | F |
|---------|---|---|---|---|---|---|
| True density | 4.14 | 4.09 | 4.17 | 4.54 | 4.15 | 4.02 |
| Bulk density | 2.03 | 2.06 | 2.11 | 2.49 | 2.15 | 2.04 |

Table 5. Surface area of the samples calculated with the size distribution.

| Factors | A | B | C | D | E | F |
|---------|---|---|---|---|---|---|
| <0.2d(50) | 20787.7 | 9409.5 | 27743.7 | 11069.1 | 35908.7 | 40344.7 |
| 0.2–0.7d(50) | 356.3 | 851.8 | 437.0 | 421.4 | 121.2 | 10.8 |
| 0.7–1d(50) | 31.3 | 120.8 | 18.4 | 81.8 | 6.4 | 0.5 |
| 1–3d(50) | 28.2 | 81.0 | 6.7 | 69.8 | 2.6 | 0.0 |
| 3–5d(50) | 34.5 | 42.4 | 2.7 | 37.7 | 0.8 | 0.1 |
| 5–8d(50) | 10.4 | 22.4 | 2.1 | 20.6 | 0.5 | 0.0 |
| >8–10d(50) | 0.5 | 5.1 | 1.1 | 2.2 | 0.6 | 0.0 |
| Total | 21250.2 | 10536.8 | 28211.7 | 11705.7 | 36040.7 | 40356.1 |

d_{50} the mean diameter of the particles in the size range; data of d(50) from Table 3.

Table 8. Shape factors of the sample.

| Factors | A | B | C | D | E | F |
|---------|---|---|---|---|---|---|
| N.A. (external & all particle) | 134.5 | 1432.9 | 98.2 | 629.1 | 42.9 | 65.7 |
| L.D. (<0.2 mm) | 0.254 | 0.256 | 0.269 | 0.313 | 0.444 | 0.442 |
| Calculations (<0.2 mm) | 0.031 | 0.035 | 0.034 | 0.029 | 0.038 | 0.041 |
| Calculations (all particles) | 0.021 | 0.011 | 0.028 | 0.012 | 0.036 | 0.040 |

large surface area, from 9 to 20 m²/g. The results by different methods which can be classified as mathematical models, laser diffraction and nitrogen absorption are shown in Table 7, in which N. A., L. D., Cal. represent the value by nitrogen absorption, laser diffraction and the calculation by the model. It indicates that the specific surface area measured by the ASAP2020 is much larger than that by the laser diffraction and the mathematical models. It is important to point out that the specific surface area measured by the nitrogen absorption should be close to the real value of the particle surface area according to the theory of physical adsorption. The size sieving and the laser diffraction methods are both based on a very important assumption that all the particles are dense smooth spheres. However, the real iron ore particles are never smooth spheres, but very irregular shape with much roughness. Both of the roughness and the irregular shape can increase the specific surface area of the particle. In the method of size sieving, the very fine particles can agglomerate or adhere to the big particles, resulting in some errors in measuring the size distribution. However, in the method of laser diffraction, all the particles are hopefully fully dispersed in the medium used to obtain a suspension of the particles.

The above discussion explains why the surface area measured by nitrogen adsorption is larger than that calculated from the size distribution measured by laser diffraction.

The ratio between the measurements by the nitrogen absorption and the laser diffraction which is shown in Table 8 gives the information of the shape and the roughness of the particle. The ratio varies greatly among the samples. For samples B and D, the surface area measured by ASAP is as high as 1 432 and 629 times of that calculated by the model. For the other samples like E, the measurements by ASAP2020 are as high as about 42 times of the calculations. For the others, the value varies from 60 to 130 times. In order to study the reason why the values change so largely, the particles were observed under the SEM machines, the morphology of the samples are shown in Figs. 2 and 3. Figure 2 which was observed with the magnification times of 200 indicates the homogeneity of the particle size and the shape. For the homogeneity of the particle shape, it was found that sample B looks closed to sphere; samples A and C have like-layer or like-slice particles; other samples have no very apparent features and are hard to be classified. For the homogeneity of the particle size, samples B and E have a better homogeneous size of the particles than others. This conclusion agrees well with Fig. 1 and Table 3 from which samples B and E have a related narrow zone of the size distribution while the samples A and F have a relative wide distribution range in the size of very small size. Fig. 3 which was observed with the magnification times of 1 000 indicates the micro-morphology of the particle in the samples, from which it can be seen that the size distribution in samples B and D are much rougher than the other samples. There are many humps on the surface of the particles. For the other samples, the rough surface which was formed during the crash is clear.

In theory, the roughness of the surface of the particle influences the specific surface area of the particle greatly. As shown in Fig. 4(A), there are many half sphere humps on the surface of the cubic body. It is assumed that the radius and the number of the half sphere humps on one surface are n and rₕ individually, a, which is the length of the side of the cubic body, equals to n⋅rₕ. The increase of n will decrease the rₕ for keeping the consistent of a, which is shown in Fig. 4(B). It means that the rₕ will be very small if n is big enough. Therefore, it can be assumed that the small humps have no effect on the size and the volume of
the cubic body. The surface area of the new body can be expressed as:

\[ S_n = 6\left(a^2 + n^2\pi r_n^2\right) \] ........................ (5)

and the ratio of the specific surface area between the new body and the original body is:

\[ f = \frac{(a^2 + n^2\pi r_n^2)}{a^2} = 1 + \pi \] ........................ (6)

The calculations indicate that the surface area increases by about 4.14 times with the sphere humps on the surface.

A further case, in which a secondary layer humps formed, is considered according to Fig. 4(C). A very special case of Fig. 4(C) is that the secondary half sphere on the surface of the first half sphere is very small, and the overlay of the first half sphere can be regarded as a flat circle of the same diameter with the second half sphere. In this case the surface area of the first half sphere will increase by 2 times. If the third layer is continued to add on the body, the ratio of the specific surface area between the final body (m layers) and the original body can be expressed as:

\[ f = (1 + \pi) \cdot 2^{m-1} \] ........................ (7)

According to Eq. (7), the surface area of the body increases by about 16 times with the three layer humps, and about 128 times with 6 layer humps.

The ratio between the measurements by the nitrogen adsorption and the laser diffraction gives the information of the shape and the roughness of the particle which is shown in Table 8. The ratio varies greatly among the samples. The effect of the particle shape on the specific surface area can be roughly evaluated by comparing the measurements by nitrogen absorption with the measurements by laser diffraction of the samples except B and D due to their specific sur-
face area greatly influenced by high roughness. For the other samples, the high value means that the particles have a greater ratio between their length and the cross section, or more closed to a needle shape. Comparing Fig. 3 with Table 8, there indeed are some agreements. For example, samples A and C have great ratio from calculations, and their SEM patterns also approve the calculation. Comparing with other samples, the particles of these two samples have more clear like slice or like-layer particles. Samples B and D have very large specific surface areas and there is indeed much roughness on the surface of the particle from the SEM images.

If the increase of the average specific area due to the shape of the particles could be roughly assumed as 7.7 times (Because the roughness of the samples A, C, E, and F is very low, their average value (11.1+10.2+3.5+5.9)/4=7.7, see Table 8) can be roughly used to represent the effect of particle shape, the effect of the roughness on the increase of specific surface area can be calculated roughly as 8.0 for sample B (61.6/7.7≈8 from Table 8) and 3.12 for sample D (24.1/7.7≈3.12 from Table 8). According to the mathematical models like Eq. (7), it can be evaluated that there are about 1–2 layer humps on the particles which was also observed clearly from their SEM image.

3.2. Granulation

The particle size distribution of the granules after granulation experiments with various water content were measured. The relationship between the particle size distribution and the water content added were shown in Fig. 5. It was found that the curve of the size distribution of the particles move toward right side of the horizontal axis for all the samples measured, meaning that the particles grow up with the increase of the water content added. In order to get the ability of granulation of the iron ore, the efficiency of granulation can be calculated by comparing the distribution of the particles size before and after granulation, which can be expressed by:

$$\varphi = \frac{(m' - m)}{m'} \times 100\% \quad \text{ (8)}$$

where, $m'$ and m represent the mass fraction of the particles smaller than x mm before and after granulation. In this study, the x was fixed as 3 mm and 5 mm. The granulation

![Fig. 5. Accumulative mass fraction vs particle size with various water content.](image)
efficiency of the iron ore was influenced greatly by the saturation of the water content in the bed of iron ore particles. The ability of the water absorption of the iron ore particles varies a lot among the samples. Figure 6 shows that results of the moisture capacity measurement. The water saturation of iron ore particles, which was defined as Eq. (9), was used to compare the efficiency of the granulation.

\[ S = \frac{W_s}{W_i} \] ................................. (9)

where, \( W_s \) and \( W_i \) are the water content added and the water content when saturated. With the water saturation, the efficiency of the granulation for the samples were plotted in Figs. 7 and 8.

Figure 7 shows that the granulation efficiency increase with increasing the water saturation. For the iron ores A, C, and F, the efficiency of granulation increased very quickly once the water saturation reach a critical value, but for the ores B, D, and E, the efficiency of granulation were much lower. Combing the size distribution of the samples with their efficiency of granulation, it was found that the iron ores A, C, and F have many fine particles smaller than 0.2 mm which can be used as the adhesive particles. The granules can grow up quickly by the attachment of fine particles with the action of the water. For the ores B and D, there are less fine particles, therefore, the efficiency of granulation is lower. It is very strange that ore E has many fine particles but the efficiency of granulation is very low. From Table 8, it can be found the shape factor of ore E is the smallest, meaning the particles in ore E have less rough surface and the shape of the particle is more close to sphere than other ores. From the previous studies reported, the sphere particles with smooth surface are difficult to form big granules during the granulation. It should be the reason why the ore E has poor ability of granulation. The regularity of the granulation efficiency is very similar when the \( x \) in Eq. (8) was 5 mm, as shown in Fig. 8.

Although the ores B and D have poor efficiency of granulation, they have more big and rough particles which are beneficial for forming the big granules with high strength. In order to check the improvement of the granulation by adding ores B and D in the mixture, the granulation experiments were carried out. After granulation process, the granules were loaded into the sintering pot for measuring the negative pressure of the bed in a fixed gas flow rate. The gas flow rate, depth of burden, surface area of the bottom of the sintering pot are equal to 0.33 m³/min, 100 mm, 0.0177 m².

There were five cases with or without B and D in the experiments. Cases 1 and 2 were got without ores B and D, and the size distribution of the cases 1 and 2 was similar, in case 3, 29.7% ore D was added into the mixture of case 1, 10.8% ore B and 4.9% ore D, 3.1% ore B and 19.1% ore D were added into case 2 individually to form cases 4 and 5. The results was shown in Fig. 9. It shows that the perme-
ability of cases 1 and 2 have lower permeability, while it improved apparently with little water in case 3. In cases 4 and 5, the same conclusions can be got.

4. Conclusions

The characterization of the specific surface area of the iron ore particles by various methods and its indication on the granulation process were discussed in this study. The conclusions can be summarized as follows.

(1) The homogeneity of the particle size was studied by comparing the results of laser diffraction and that of SEM observation, the conclusions of the two measurements agree well. The shapes of the particles influences the specific surface area apparently, the samples with like-slice and like-layer particles have high specific surface area.

(2) The specific surface areas of the iron ore particles were measured by nitrogen adsorption and also calculated from the size distribution measurements-combining size sieving and laser diffraction. It shows that the roughness of the particle influences the specific surface area apparently.

(3) The granulation experiments shows that the efficiency of granulation increases with increasing the water saturation and the iron ore with more fine adhesive particles can get a higher efficiency of granulation easily.

(4) The usage of iron ore with big and rough particles can improve the permeability of the bed of granules. The iron ore with smooth and sphere particles has poor ability of granulation.

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