Optimizing the Mass Ratio of Two Organic Active Fractions in Modified Humic Acid (MHA) Binders for Iron Ore Pelletizing

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The aim of this present paper was to systematically optimize and determine the mass ratio of two organic active fractions (fulvic acid and humic acid) in a type of novel organic binder (named Modified Humic Acid (MHA)) developed in China for iron ore pelletizing. The experimental data demonstrated that the mass ratio of Na-HA to Na-FA had an obvious influence on the performance of MHA binders. The drop number of green pellets grew to reach a plateau of 11.7 times when the mass ratio of Na-HA to Na-FA was increased to 7:3. Obviously, the crushing strength of dried and fired pellets was increased with the increase of mass ratio of Na-HA to Na-FA. Especially, dried or preheated pellets remarkably increased their crushing strength after the mass ratio of 6:4. From these results, the optimum mass ratio Na-HA to Na-FA in MHA binders for iron ore pellotizing was concluded to be 7:3. The pelletizing performance of MHA binders could be undoubtedly improved by optimizing the mass ratio of Na-HA to Na-FA. The explanation for improving the pelletizing performance of MHA binders by optimizing the mass ratio of two fractions lies in that the influencing factors (acidic groups and viscosity) for deciding the pelletizing performance of MHA binders can be optimized and balanced by changing mass ratio of Na-HA to Na-FA. The reason for that mechanical strength of fired pellets was influenced by mass ratio of active fractions in MHA binders, was considered to be attributed to the thermal stability difference of active fractions.

KEY WORDS: iron-making; fired pellets; pelletizing; organic binder; iron ore; fulvic acid; humic acid.

1. Introduction

Presently, blast furnace iron-making is still the main technique for the production of pig iron. It was reported that the percent of the output of pig iron from blast furnace iron-making exceeds 95%. The reasonable burden structure for blast furnace comprising of acidic fired pellets and high-basicity sinter has been widely acknowledged. Iron ore fired pellets are characterized by good mechanical and metallurgical properties. The blast furnace iron-making operation displays that the benefits of extended blast furnace life, productivity and fuel savings associate with increasing the consumption of iron ore fired pellets. Therefore, lots of iron-making plants are enlarging the production scale of iron ore fired pellets so as to meet the increasing need of modern large-scale blast furnaces in China.

One of critical issues for the production of iron ore fired pellets is the optimization for iron ore pelletization. For a fixed production process, the primary concern for iron ore pelletization lies in the selection of an effective binder. Binders can perform physical or chemical roles both in the process of granulation and in the finished pellets. In particular for wet green pellets, the category and the content of binder are the important influencing factors for deciding the mechanical strength of pellets. Binders are generally chosen according to their functionality, cost, safety and environment concerns. For instance, good organic binders must be characterized by improving the wettability of iron ore particles, and possessing good adsorption capacity, great binding property, and good thermal stability. Bentonite has been widely employed to improve the mechanical strength of pellets in the process of iron ore pelletization. However, the negative effects of using bentonite as binder involve in decreasing total iron (TFe) grade and worsen the metallurgical properties of the fired pellets. The effects of bentonite on the chemical composition had been well illustrated by the silica and iron content of final products. Based on the above shortcomings of bentonite, many studies have been carried out on the development and application of organic binders to overcome the weakness of inorganic binders. Fired pellets production in foreign countries had shown that organic binder can substitute for inorganic bentonite because of better mechanical strength of green pellets in the pelletization process. Compared with inorganic bentonite, in fact, one of the biggest advantages of organic binders is attributed to residual silica-free. However, the existing studies show that the addition of foreign organic binder (such as Peridur) into pellets gives rise to some problems in iron ore pelletization. For example, the crushing strength of fired pellets is too low, resulting in powder/dust generation and ring-formation in the Grate Kiln process.
The huge advantages promote the development of domestic organic or organics-based binders with the rapid development of iron and steel industry in China. A type of novel organic binders, namely modified humic acid (MHA) binders, with high binding property and economic benefits were developed by Central South University (CSU) in China.\textsuperscript{21) Comparatively, the price of MHA binders is only one tenth of a typical organic binder with a trade mark of Perdur price and about 3 times of bentonite price. The addition of MHA binders can obviously improve the mechanical strength of green pellets.\textsuperscript{22,23) Therefore, the MHA binders can be considered as promising substitute for bentonite in iron ore pelletization. The MHA binders are comprised of two organic active fractions (fulvic acid/FA and humic acid/HA), which are generally in the form of sodium humates (Na-FA and Na-HA). Properties and adsorption behavior of active fractions in MHA binders onto iron ore particles had been partly examined in former documents.\textsuperscript{24,25) Preliminary research had revealed that the properties of MHA binders vary with both the categories and the mass ratios of organic active fractions.\textsuperscript{25–27) The aim of this present paper was to systematically optimize and determine the mass ratio of two organic active fractions of MHA binders in the field of iron ore pelletization. Mechanical strength of pellets balled with different mass ratios of two active fractions was tested to understand the difference between Na-HA and Na-FA, as well as the influence of the mass ratio of Na-HA to Na-FA on the performance of MHA binders.

2. Materials and Methods

2.1. Iron Ore Concentrates Sample

The iron ore concentrates sample is the same one previously introduced,\textsuperscript{28) and it was obtained from Baima mining plant, China and used without further purification. The main chemical composition of the iron ore concentrates sample used for pelletizing was firstly analyzed and is shown in Table 1.

The concentrates sample contained 55.36 mass% TFe, 10.00 mass% TiO\textsubscript{2}, 4.40 mass% SiO\textsubscript{2}, 5.23 mass% Al\textsubscript{2}O\textsubscript{3} and 0.72 mass% V\textsubscript{2}O\textsubscript{5}. Particle size distribution and specific surface area of the iron concentrates sample were separately tested by water sieving method and an air permeability method (FBT-9FBT-9 model, Hongyu Corporation, Hebei, China). The content of the sample below 0.074 mm was only 39.60%. The specific surface area of the sample was 993 cm\textsuperscript{2}·g\textsuperscript{−1}. Particle morphology of the iron ore concentrates was measured by a scanning electron microscope (SEM) (JSM-6360LV model, JEOL) analysis and is presented in Fig. 1.

2.2. Two Organic Active Fractions of MHA Binders

The two active fractions of MHA binders refer to sodium fulvic acid (Na-FA) and sodium humic acid (Na-HA) according to the categories and functionality of humic substances.\textsuperscript{29) They were prepared from fulvic acid (FA) and humic acid (HA) by adopting sodium treatment with alkali. The pH of these two sodium humates were both 9.0. The main elemental compositions of the two active fractions of MHA binders are displayed in Table 2.

Meantime, the content of total acidic groups (—COOH and —OH) and the viscosity values of single active fraction and MHA binders with different mass ratios of two active fractions were also tested by standard methods as recorded as former literatures.\textsuperscript{29) Each testing was repeated twice and an average value was reported. The related results are displayed in Fig. 2. The changing curves in Fig. 2 showed that the content of total acidic groups of MHA binders was decreased with increasing the mass ratio of Na-HA to Na-FA. However, the viscosity values of MHA binders were increased with increasing the mass ratio of Na-HA to Na-FA.

2.3. Preparation of Unfired (Green and Dried) Pellets

The experimental procedure included blending, wet-grinding and balling. Firstly, 5 kg of the iron concentrates were mixed with a given binder. Because of high viscosity of the sodium humates, the mixing feed was further dispersed in a type of ball mill (called Damp Mill in China) with dimensions of 1 000 mm diameter and 500 mm length.

### Table 1. Chemical composition of the iron ore concentrate (mass%).

<table>
<thead>
<tr>
<th>TFe (%)</th>
<th>FeO (%)</th>
<th>SiO\textsubscript{2} (%)</th>
<th>Al\textsubscript{2}O\textsubscript{3} (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>TiO\textsubscript{2} (%)</th>
<th>V\textsubscript{2}O\textsubscript{5} (%)</th>
<th>P (%)</th>
<th>S (%)</th>
<th>LOI* (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.36</td>
<td>21.36</td>
<td>4.40</td>
<td>5.23</td>
<td>0.81</td>
<td>0.72</td>
<td>0.018</td>
<td>0.045</td>
<td>0.65</td>
<td>60 min</td>
<td></td>
</tr>
</tbody>
</table>

*LOI means loss on ignition, which was tested in air atmosphere at 1 000°C for 60 min.

### Table 2. Main elemental compositions of two active fractions in MHA binders.

<table>
<thead>
<tr>
<th>Elemental composition (mass%)</th>
<th>Atomic ratio</th>
<th>Na (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Na-FA</td>
<td>55.31</td>
<td>6.93</td>
</tr>
<tr>
<td>Na-HA</td>
<td>68.49</td>
<td>4.05</td>
</tr>
</tbody>
</table>

Fig. 1. Particle morphology of the iron ore concentrates measured by SEM.
The milling conditions were fixed as follows: the moisture content of raw materials 7.0%, milling time 5 min, rotary ratio 35 r·min⁻¹. Thereafter, the mixture was balled to green pellets in laboratory with a disc pelletizer of 1000 mm diameter, 500 mm length and inclined at 45° to the horizontal (as seen in Fig. 3-b). The time required for pelletizing was 10 min, and another 2 min was needed to compact the green pellets after finishing adding the mixed feed and water. The diameter of wet green pellets was controlled at 12–15 mm. The moisture content was kept with 8.5±0.2%. Finally, the wet green pellets were dried in an oven at 110°C for 4 h for the next experimental process.

2.4. Preparation of Fired (Preheated and Roasted) Pellets

Preheating and roasting experiments were both conducted in an electric heated horizontal tube furnace. The tube furnace was characterized by 50 mm internal and 70 mm external diameters, as well as natural opened at both ends for air circulating (as seen in Fig. 3-c). Temperature was measured with a Pt-Pt/Rh thermocouple, which was placed inside the furnace. Dried pellets were put into a corundum crucible, which was pushed into the central portion of the furnace, in which an oxidizing atmosphere (air) was kept. Experiments were started when temperature profile had reached the desired value. After finishing preheating and roasting process, the preheated and roasted pellets were naturally cooled to room temperature.

2.5. Testing of Mechanical Strength of Pellets

The equipments for testing of mechanical strength of pellets were all developed by CSU. The apparatus for testing the crushing strength of fired pellets is shown in Fig. 3-d. The measurement errors of equipments range from 2% to 5%. Mechanical strength containing wet drop number and crushing strength of pellets was tested as mentioned as related documents.⁴,²³ Each time, twenty pellets were used for testing the mechanical strength. The value for mechanical strength of pellets was recorded by taking the average reading.

3. Results

3.1. Mechanical Strength of Green Pellets Balled with Single Active Fraction

The wet drop number and the crushing strength of green pellets balled with single active fraction were firstly obtained and are shown in Fig. 4.

As seen from Fig. 4, the mechanical strength of green pellets balled with single active fraction was generally increased with increasing the dosage. The difference in the mechanical strength of green pellets balled with different active fractions was embodied mainly as the drop number. The results clearly showed that the drop number of green pellets balled with Na-FA was lower than that of green pellets balled with Na-HA. Under the condition of 0.5 mass% Na-FA, the drop number of green pellets was nearly 6.1 times (as seen in Fig. 4-a). When it came to the green pellets balled with 0.5 mass% Na-HA, the drop number could reach 8.2 times (as seen in Fig. 4-c).

3.2. Mechanical Strength of Unfired Pellets with Varying Mass Ratio of Na-HA to Na-FA

The mechanical strength of green and dried pellets with varying mass ratio of Na-HA to Na-FA is shown in Figs. 5 and 6, respectively.

It can be seen from Fig. 5, the drop number of green pellets changed obviously with varying mass ratio of Na-HA to Na-FA. The relation between the drop number of green pellets and the mass ratio of Na-HA to Na-FA was in the form of parabola. The drop number of green pellets grew to reach a plateau with a peak of 11.7 times when the mass ratio of Na-HA to Na-FA was increased to 7:3. Interestingly, the drop number of green pellets was decreased when the mass
ratio of Na-HA to Na-FA was further increased or decreased.

The results in Fig. 6 clearly showed that the crushing strength of dried pellets also changed with varying mass ratio of Na-HA to Na-FA. The crushing strength of dried pellets was nearly 20 N when the dosage of Na-FA was 0.5 mass%. When it came to the dried pellets balled with 0.5 mass% Na-HA, the crushing strength could reach 307 N. It was obvious that, the crushing strength of dried pellets was increased with increasing the mass ratio of Na-HA to Na-FA. It is also worth mentioning that the crushing strength of dried pellets was increased intensely after the mass ratio of Na-HA to Na-FA exceeded 6:4.

3.3. Mechanical Strength of Fired Pellets with Varying Mass Ratio of Na-HA to Na-FA

In this part, the dried pellets balled with varying mass ratio of Na-HA to Na-FA were preheated at different temperatures in air atmosphere for 10 min. And the related results are shown in Fig. 7.

As seen from Fig. 7, the crushing strength of preheated pellets balled with Na-FA alone was lower than that of preheated pellets balled with Na-HA alone. It was obvious that the crushing strength of preheated pellets was increased with increasing the mass ratio of Na-HA to Na-FA. Under the condition of 0.5 mass% Na-FA alone, the maximum value of crushing strength of preheated pellets was nearly 329 N at 950°C. When it came to the preheated pellets balled with 0.5 mass% Na-HA, the maximum value of
crushing strength could reach 488 N at 920°C. Similarly, the crushing strength of preheated pellets was increased obviously after the mass ratio of Na-HA to Na-FA was above 6:4.

In this part, those preheated pellets oxidized at 950°C for 10 min were further roasted at different temperatures in air atmosphere for 10 min. And the related results are presented in Fig. 8.

As clearly shown in Fig. 8, the crushing strength of roasted pellets balled with Na-FA alone was also lower than that of roasted pellets balled with Na-HA alone. Also, the crushing strength of roasted pellets was increased with the increase of mass ratio of Na-HA to Na-FA. The crushing strength of roasted pellets was nearly 2721 N at 1280°C when the dosage of Na-FA was 0.5 mass%. The crushing strength of roasted pellets balled with 0.5 mass% Na-HA alone could reach 3371 N at 1280°C. Again, the crushing strength of roasted pellets was enhanced intensely after the mass ratio of Na-HA to Na-FA was above 6:4.

3.4. Effect of Binder Dosage on Mechanical Strength of Pellets Balled with Optimized Mass Ratio of Na-HA to Na-FA

Based on the above data, the optimized mass ratio of Na-HA to Na-FA could be established for this pelletizing feed. Using the combined fractions with the optimized mass ratio (Na-HA to Na-FA 7:3), the mechanical strength of green and dried pellets can be found from Table 3. And the crushing strength of fired pellets is shown in Fig. 9.

The data in Table 3 obviously showed that, the mechanical strength of pellets balled with the optimized binder, especially for the drop number of green pellets and the crushing strength of dried pellets, were enhanced with the increase of the binder dosage. With an addition of the optimized binder 0.25 mass%, the drop number of green pellets and the crushing strength of dried pellets were higher than those of green and dried pellets separately balled with 0.5 mass% Na-HA and 0.5 mass% Na-FA alone. It can be concluded that the performance of MHA binders could be undoubtedly improved by optimizing the mass ratio of the two active fractions.

The results in Fig. 9 displayed that, the mechanical

<table>
<thead>
<tr>
<th>Dosage of binder (mass%)</th>
<th>Green pellets</th>
<th>Dried pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Drop number</td>
<td>Crushing strength (N)</td>
</tr>
<tr>
<td>0</td>
<td>3.6</td>
<td>10.5</td>
</tr>
<tr>
<td>0.25</td>
<td>8.2</td>
<td>10.9</td>
</tr>
<tr>
<td>0.50</td>
<td>11.7</td>
<td>11.3</td>
</tr>
<tr>
<td>0.75</td>
<td>13.5</td>
<td>11.5</td>
</tr>
<tr>
<td>1.0</td>
<td>17.9</td>
<td>11.5</td>
</tr>
</tbody>
</table>
strength of fired pellets balled with the optimized binder was decreased with increasing the binder dosage. The crushing strength of fired pellets balled with the optimized binder fell in between those of pellets separately balled with Na-HA and Na-FA alone in the same level of binder dosage.

4. Discussion

4.1. Influence of Mass Ratio of Active Fractions on Mechanical Strength of Unfired Pellets

Pelletizing experiments of iron ore concentrates using MHA binders demonstrated that the mass ratio of active fractions in MHA binders had an obvious influence on mechanical strength of unfired pellets, especially on the drop number of green pellets and the crushing strength of dried pellets. These phenomena can be explained as follows. The molecular structural characteristics and the physical/chemical properties of organic fractions determine the performance of organic binder in the field of iron ore pelletization. For instance, the functions and molecular structure of an ideal organic binder for iron ore pelletization had been expounded. And the ideal structure and physical/chemical properties of organic binders can be summarized by the following key points: (1) Acidic groups involving —COOH and —OH are ideal polar and hydrophilic groups of organic binders; (2) The cohesive force and adhesive force of organic binder are the most important indexes for deciding the binding strength of iron ore particles and binder; (3) The higher molecular weight, the greater cohesive force and mechanical strength of organic binder itself; (4) Good wettable of organic binder solution to the surface of iron ore particles is precondition for achievement of great adhesive force. Based on those four points above, it can be found that the most two factors influencing the performance of organic binder in iron ore pelletization refer to its acidic groups and molecular weight. Increasing the content of acidic groups and increasing the molecular weight of binder will be favor for improving the performance of organic binder. Because the viscosity of organic polymer solution can positive-linearly reflect its molecular weight, the viscosity is generally considered as an alternative influencing factor.

The relations between total acidic groups and viscosity of binder and mechanical strength of green and dried pellets balled with MHA binders with different mass ratios of active fractions are separately presented in Figs. 10 and 11.

As clearly shown in Fig. 10, the drop number of green pellets was dependent on total acidic groups and viscosity of binder which were influenced by mass ratio of active fractions in MHA binders. A peak of the drop number of green pellets appeared when the content of acidic groups and the viscosity were separately 6.454 mmol·g⁻¹ and 77.3 mPa·S corresponding to the optimized mass ratio of Na-HA to Na-FA (7:3). The explanation for the changing trend can be given as follows. As demonstrated in Fig. 2, the content of acidic groups in MHA binders was decreased with the increase of mass ratio of Na-HA to Na-FA, while the viscosity became bigger. Therefore, it is reasonable that a parabolic relation appeared between the drop number of green pellets and the influencing factors for the pelletizing performance of MHA binders in Fig. 10.

The results in Fig. 11 showed that, total acidic groups and viscosity of binder also had an obvious influence on the crushing strength of dried pellets. The crushing strength of dried pellets was decreased with increasing the total acidic groups, as well as decreasing the viscosity of binder. A sharp decrease of crushing strength of dried pellets appeared when the content of acidic groups and the viscosity were separately 6.9 mmol·g⁻¹ and 72 mPa·S corresponding to the mass ratio of Na-HA to Na-FA (6:4). The explanation for the results is that increasing the viscosity of MHA binder was more beneficial for improving the crushing strength of dried pellets although total acidic groups of binder was decreased simultaneously. As displayed in Fig. 2, the viscosity of MHA binders was increased more obviously when the mass ratio of Na-HA to Na-FA is above 6:4. Therefore, an obvious increase of crushing strength of dried pellets took place after the mass ratio of Na-HA to Na-FA 6:4. And this reason could be applicable to expound Fig. 6, which showed that the crushing strength of dried pellets was increased obviously after the mass ratio of Na-HA to Na-FA 6:4.

These combined results in Figs. 10 and 11 both confirmed that the nature for improving the pelletizing performance of MHA binders by optimizing the mass ratio of two fractions is that the influencing factors (acidic groups and viscosity) for the pelletizing performance of MHA binders can be optimized and balanced by changing mass ratio of the two
active fractions.

4.2. Influence of Mass Ratio of Active Fractions on Mechanical Strength of Fired Pellets

Preheating and roasting experiments displayed that the mass ratio of active fractions in MHA binders also had an obvious influence on mechanical strength of fired pellets. These results can be explained as follows. It has been widely agreed that thermal decomposition characteristics of binder during firing could have an impact on the preheating and roasting process of pellets. Former studies had revealed that Na-FA was characterized by a lower thermal stability due to lower molecular weight and aromatization degree compared to Na-HA. Because of a higher thermal stability, therefore, the mechanical strength of fired pellets was increased with increasing the mass proportion of Na-HA in MHA binders. This can explain that the crushing strength of fired pellets balled with the optimized binder was situated between those of pellets separately balled with active fraction alone in the same level of binder dosage.

5. Conclusions

The mechanical strength of pellets balled with different mass ratios of two active fractions was tested to understand the difference between Na-HA and Na-FA, as well as the influence of the mass ratio of active fractions in the field of iron ore pelletization in this study. The following conclusions were drawn from the results of this work:

(1) The performance of MHA binders vary with both the categories and mass ratio of organic active fractions. The obvious difference was found from the mechanical strength of pellets balled separately with Na-HA and Na-FA alone.

(2) The relation between the drop number of green pellets and the mass ratio of Na-HA to Na-FA was in the form of parabola having a maximum value at a mass ratio of 7:3. The crushing strength of dried pellets and fired pellets was increased with increasing the mass ratio of Na-HA to Na-FA. Especially, the dried or preheated pellets remarkably increased their crushing strength after the mass ratio of 6:4. From these results, the optimum mass ratio Na-HA to Na-FA in MHA binders for iron ore pelletizing was concluded to be 7:3.

(3) The mechanical strength of unfired pellets balled with the optimized binder (Na-HA to Na-FA 7:3) was higher than those of unfired pellets separately balled with 0.5 mass% Na-HA and Na-FA alone. The crushing strength of pellets balled with the optimized binder was between those of pellets separately balled with active fraction alone in the same level of binder dosage.

(4) The nature for improving the pelleting performance of MHA binders by optimizing the mass ratio of two fractions is that acidic groups and viscosity of MHA binders can be optimized and balanced by changing mass ratio of active fractions.

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