Binders and Bonding Mechanism for RHF Briquette Made from Blast Furnace Dust

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Blast furnace dust is a kind of solid waste that produced in the process of iron smelting and it contains large amount of Fe and non-ferrous metal elements. It’s not only a very good Fe-contained resource, but also a very important non-ferrous metal resource. Application of blast furnace dust to RHF (Rotary Hearth Furnace) briquette is an effective and comprehensive utilization method. However the strength of the briquettes is low, therefore the application of binder to the briquette should be developed. In this study, physical and chemical characteristics of blast furnace dust were investigated firstly. And the experiments of different binder used in the briquettes were studied. Then the bonding mechanisms of binders were discussed. The experiment results showed that different binder has different bonding mechanism of the briquettes. According to the application effect of binders, it should be priority to use the composite binder, and the excellent collocation pattern is starch binder together with silicon-containing binder, such as sodium silicate.

KEY WORDS: Rotary Hearth Furnace; agglomeration; carbon composite briquette; blast furnace dust; strength; bonding mechanisms.

1. Introduction

Blast furnace dust is a kind of solid waste generated in the process of blast furnace ironmaking. It’s treated as a kind of precious secondary resources, because its main components are C, Fe and a spot of recyclable non-ferrous metal elements, such as Zn, Pb, K, Na, etc.1,2) However it is harmful to human health, because it is characterized by easily floating in the air, due to its small particle size and low density. Therefore, the comprehensive utilization of blast furnace dust, not only has the good economic benefits, but also has the considerable social and environmental benefits.3)

At present, most of companies utilize blast furnace dust directly or indirectly through mineral processing such as sintering process, in order to recycle the iron and carbon in it. However, some companies sent it to cement plant as ingredient or directly store it. These methods can’t obtain the purpose of reasonable use of blast furnace dust resources.1,5) Considering the cyclic economy, the blast furnace dust should be regarded as precious secondary resources and get fully comprehensive utilization and recycling.6) Application of blast furnace dust to RHF (Rotary Hearth Furnace) briquette is an effective and comprehensive utilization method,7,8) however, RHF has a high standard of the material strength, a series of treatments such as drying, burden distribution and discharging is necessary, the strength of material in each part affect the smooth and efficient production of RHF.9,10) Therefore, adding suitable binder to improve strength of the briquettes is a key issue.

But there are less studies on binder that is suitable for blast furnace dust in China and abroad, and some researches on binder in metallurgical field mostly focused on the iron ore concentrate briquettes.11–13) Binder used in briquetting process can be divided into inorganic binder, organic binder and compound binder, and all of them have respective advantages and disadvantages:14) (1) The inorganic binder such as bentonite has a long history and mature experience of using it, and it has significant effect on the performance of briquettes, however, due to it’s many impurities, the appropriate control of supplying amount is necessary, such as the 1.5%–2.0% mass fraction of bentonite is appropriate. (2) Adding organic binder will not increase the content of harmful elements in the briquettes, but its performance at high temperature is poor, which has a great influence on the decrepitation temperature of briquettes, and its price is high. (3) The use of compound binder can reduce the supplying amount of inorganic binder, reduce the cost of briquettes, improve the quality of briquettes, and get better performance of briquettes. Therefore, considering the development direction of binder, organic binder and organic-inorganic compound binder has become the focus of research and development.

However, the effect of using these binders to produce the briquettes made from blast furnace dust and quality assessment for production should be further discussion through...
2. Materials and Methods

2.1. Experiment Materials

2.1.1. Blast Furnace Dust

Blast furnace dust used in the experiment were from a Chinese steel plant. The chemical composition and mineral component measured by X-ray diffraction of blast furnace dust is shown in Table 1 and Fig. 1, respectively. The particle size is shown in Table 2. The blast furnace dust not only contains T.Fe and C, but also contains some Zn, Pb, K, Na, etc. The content of Zn has reached more than 13%. The particle size of blast furnace dust is relatively fine, mass% of the dust under –200 mesh reached 62.75% and the average particle size is 0.103 mm. In addition, the carbon content is 32.21%, the carbon/oxygen is 1.8, and the carbon content is extremely excess. Based on this, in order to make full use of excess carbon in the blast furnace dust, 20% of iron oxide should be added into the briquettes, and the carbon/oxygen ratio is regulated to 1.2.

2.1.2. Binder

In order to detect the bonding properties of different binder in the briquettes, three kinds of binders were used in this study as shown in Table 3.

2.2. Experiment Methods

2.2.1. Preparation of Briquettes

The flow chart of test process is shown in Fig. 2. At first, in order to remove the water in the materials, blast furnace dust should be dried in an oven as seen in Fig. 3(a) under the condition of 105°C for 12 h. After drying, blast furnace dust were mixed with a selected binder, iron oxide and water, then charged into the horizontal twinroller forming machine (as seen in Fig. 3(b)) with the pressure as...
20 MPa. Diameter of formed briquettes was 30 mm. Finally, the green briquettes were dried in an oven as seen in Fig. 3(a) at 200°C for 60 min for the next experimental process.

Roasting experiments were conducted in a high temperature electric resistance furnace as seen in Fig. 3(c). Temperature was measured with a Pt-Pt/Rh thermocouple, which was placed inside the furnace. Dried briquettes were put into the furnace and the experiment was started. When temperature had reached the design value, the experiment finished. After finishing roasting process, roasted briquettes were naturally cooled to room temperature.

2.2.2. Testing of Mechanical Strength of Briquettes

Mechanical strength consists with compressive strength of briquettes and falling strength of green and dried briquettes. Twenty briquettes were used for testing the mechanical strength in each test. The value for mechanical strength of every briquettes was recorded and used for average value. Compressive strength was measured by compressive strength test apparatus as seen in Fig. 3(d). Falling strength was measured through counting the drop number. The briquettes were dropped on the 10 mm thickness steel plate from the height of 0.5 m repeatedly, when crack or burst generated after drop, drop number is then obtained as the falling strength.

2.2.3. Observation of Binders Behavior

In order to identify the binding mechanism of different binders, the behavior of binders in the heating process has been observed by optical microscope. The drying oven has been used for heating process in the lower temperature range (<200°C), and the high temperature electric resistance furnace has been used for heating process in the relatively higher temperature range (>200°C). The photographs of binders behavior in different stages were obtained by using an image analysis system. These results will be useful to master the bonding properties of binders at different temperatures, and guide the determination of the collocation pattern.

3. Results and Discussion

3.1. Strength of Blast Furnace Dust Briquettes with Single Binder

Bentonite, sodium silicate, corn starch, silicone resin, and epoxy resin were blended by 3% addition ratio respectively with blast furnace dust and iron oxide. Strength of the green briquettes, dried briquettes and the briquettes after roasting at high temperature were measured. The comparison of compressive strength of the briquettes at room temperature, 200°C and 1000°C is shown in Fig. 4, and the falling strength of the briquettes at room temperature and 200°C is shown in Fig. 5. The comparison of compressive strength of the briquettes after roasting at 1100°C, 1200°C and 1250°C is shown in Fig. 6.

From the result of the experiment, the falling strength and compressive strength of the briquettes without binder are very poor, so does the compressive strength of briquettes after roasting at high temperatures, which can not meet the requirement of production (The requirement of production are as follows: falling strength is above 3 times, compressive strength of green and dried briquette is above 40 N, and the compressive strength of roasted briquette is about 1800 N). However, the strength of the briquettes can be improved by using every binder.

At room temperature, the compressive strength of the briquettes used binder is more than 40 N and the falling strength is more than 4 times. The adhesive effect of corn
starch is relatively better, the compressive strength and falling strength indices are 72 N and 5.9 times, which is the result from good viscosity of corn starch. It makes the blast furnace dust particles bonding closer, so the strength is relatively high. Silicone resin and epoxy resin have a relatively small improvement of the strength of the green briquettes, and the effect of the epoxy resin is relatively better. The improvement of strength is mainly result from the good bonding strength of the two kinds of resin binder. The effect of bentonite and sodium silicate for strength of the briquettes is not obvious, this is mainly determined by the properties of the binders and the blast furnace dust.

When the temperature reaches 200°C, water evaporates, bonding properties of organic matter decreases, and the compressive strength and falling strength of the briquettes is generally lower, considering the adhesive effect, the best is starch, then is epoxy resin, and the silicon-containing binder has a relatively small effect.

Above 1100°C, the reduction reaction of iron oxides started, the metallization rate of the briquette increased, and the strength increased. Adding bentonite, silicone resin and sodium silicate binder can get a relatively high strength of the briquettes, which resulted from the framework role of silicon. Sodium silicate can promote the reduction of briquettes, so the strength of the briquettes is higher than others. The corn starch and epoxy resin have the property of high temperature volatile, which makes the strength of the briquettes is relatively low. Although using the single binder can enhance the compressive strength of the roasting briquettes, the strength is lower than 1800 N, and it is hard to meet the production requirement.

Therefore, different binders play the different role, starch binders can improve the low temperature strength of the briquettes, the silicon-containing binders can improve the high temperature strength of the briquettes, in order to make full use of the advantages of all kinds of binder, the starch binders should be used accompanying with silicon-containing binder to develop the appropriate compound binder.

3.2. Strength of Blast Furnace Dust Briquettes with Compound Binder

In order to make sufficient use the characteristics of each binder, bentonite, sodium silicate, corn starch and silicone resin were chosen to combine compound binder,” and the influence on the strength of the briquettes were studied. The percentage of compound binder is 3%. There combinations of compound binders were made as follows.

A: corn starch (2/3) + silicone resin (1/3)
B: corn starch (2/3) + sodium silicon (1/3)
C: corn starch (1/3) + sodium silicon (1/3) + bentonite (1/3)

The compressive strength of the briquettes added compound binder at room temperature, 200°C and 1000°C is shown in Fig. 7, the falling strength of the briquettes at room temperature and 200°C is shown in Fig. 8, the compressive strength of the briquettes at 1100°C, 1200°C and 1250°C is shown in Fig. 9. The experimental samples are indicated by the English letters that represent the compound binder.

From the experimental results, the compound binder can effectively improve the strength of the briquettes.

At room temperature, the compressive strength of the briquettes added compound binder is more than 55 N, and falling strength is more than 5.3 times, especially the briquettes added compound binder of corn starch and silicone resin, whose compressive strength is 66 N and falling strength is 5.8 times.

After drying at 200°C, because of water evaporates and low bonding properties of the carbon, the falling strength
especially the compressive strength of the briquettes added which makes the strength of the briquettes greatly improved, the role of silicon-containing compound binder is obvious, than 2.9 times.

Table 4.

<table>
<thead>
<tr>
<th>Binder proportion</th>
<th>Compressive strength/N</th>
<th>Falling strength/ times</th>
<th>Compressive strength/N</th>
<th>Falling strength/ times</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%</td>
<td>49</td>
<td>5.3</td>
<td>44</td>
<td>2.7</td>
</tr>
<tr>
<td>2%</td>
<td>54</td>
<td>5.5</td>
<td>46</td>
<td>3.1</td>
</tr>
<tr>
<td>3%</td>
<td>60</td>
<td>5.5</td>
<td>55</td>
<td>3.4</td>
</tr>
<tr>
<td>4%</td>
<td>67</td>
<td>5.7</td>
<td>62</td>
<td>3.7</td>
</tr>
<tr>
<td>5%</td>
<td>72</td>
<td>6.0</td>
<td>69</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Under the condition of high temperature, the framework role of silicon-containing compound binder is obvious, which makes the strength of the briquettes greatly improved, especially the compressive strength of the briquettes added corn starch and silicone resin or sodium silicate compound binder has been improved relatively larger, the strength is about 2000 N. This is because the iron oxide in the briquettes have been reduced in great quantities at the high temperature, the connection between the particles becomes the connection between the metal iron or iron whisker, and silicone resin has excellent bonding strength and superior thermal oxidation stability and the effect of the silica framework, which makes the briquettes added silicone resin-containing compound binder obtain a higher compressive strength. At the same time, sodium silicate promotes the reduction, so the carbon-containing briquettes added sodium silicon-containing compound binder gets high metallization rate, the compressive strength of the briquettes is relatively high due to the close bond between the metal irons.

In a word, strength of the briquettes added compound binder is greatly improved. But the price of bentonite and sodium silicate is relatively low, and the price of silicone resin is relatively high. Considering economy and strength of the briquettes, the excellent collocation pattern is the corn starch and sodium silicate.

3.3. Strength of Blast Furnace Dust Briquettes with Different Binder Proportion

The different binder proportion affected strength of the briquettes. The appropriate proportion of corn starch and sodium silicate compound binder has been studied through the determination of strength. And results were shown in Table 4.

From the experimental results, the compressive strength and falling strength of the briquettes increase with increasing the binder proportion. When the binder proportion is more than 2%, the comprehensive strength of green briquettes is above 54 N, and the falling strength of green briquettes is above 5.5 times; After drying, the briquettes comprehensive strength is above 46 N, falling strength is above 3.1 times, and strength at high temperature reaches 1796 N, and all of these has met the mentioned requirement of production. Therefore, the appropriate proportion of corn starch and sodium silicate compound binder is 2%

and compressive strength of the briquettes decrease, the compressive strength of the briquettes added compound binder is more than 54 N, and the falling strength is more than 2.9 times.

3.4. The Bonding Mechanism of Binders

According to the experiments results, different binders have different function. The binders, such as corn starch and epoxy resin, can improve the strength of the briquettes at low temperature, and the silicon-containing binder can improve strength of the briquettes at high temperature. Based on these facts, the two better binders selected in this study are sodium silicate and corn starch, and the bonding mechanisms are investigated.

3.4.1. The Mechanism of Sodium Silicate Addition

1) The Mechanism of Enhancement of Solid Phase Bonding

The general chemical formula of sodium silicate is Na2O·mSiO2·nH2O, where m is called the modulus, the molar ratio of SiO2 to Na2O, n means moisture content of sodium silicate. In this study, m=2.3, n=9.

Appropriate sodium silicate and water are blended to blast furnace dust, a layer of sodium silicate bond film will be formed on the blast furnace dust particles surface (silicate bond film), and the blast furnace dust particles are connected by this film, which improves strength of the briquettes at room temperature. However, the amounts of sodium silicate are relatively small, the bond film is very thin, and the range of the increased strength is also relatively small. With the increase of temperature, sodium silicate condensation and water evaporation, sodium silicate separates out the silica acid gel after dewatering and hardening as shown in Fig. 10.

Newborn gel particles have intensive activity, they will enter the briquettes and block capillary pores inside the briquettes, and the connection between blast furnace dust particles is enhanced by the silica acid gel particles. However, the briquettes lose water after being heated, and the cohesive strength between carbon particles has decreased, which lead
to the loose of briquette structure, and a relatively small range of the strength increase. Even the strength of briquettes is lower than the strength at room temperature as shown in Fig. 11.

More Si–OH bonds exist in the silica acid gel, with higher temperature, dehydration and condensation take place between Si–OH bonds, and form a reticular formation of Si–O–Si bond, which is a three-dimensional structure of the curing system with excellent water resistance.21) Curing reaction under the condition of heating is as follows:

\[ \text{Na}_2\text{O} \cdot n\text{SiO}_2 + (2n+1)\text{H}_2\text{O} \rightarrow 2\text{NaOH} + n\text{Si(OH)}_4 \ldots (1) \]

\[ \text{NSi(OH)}_4 \rightarrow [\text{Si(OH)}_4]_m \rightarrow \ldots \ldots (2) \]

Si–O–Si bonds generated between silica acid gel particles after the curing reaction have the effect of connection bridge (negative ion connection bridge), connect the gel particles and mineral particles into a complex reticular formation, make the structure of briquette more compact, thus improve the strength of briquettes. Under the condition of high temperature, silica acid gel can be dried, and K, Na, Pb, Zn and other elements in the briquettes volatilized, but strength of the briquettes also be improved because of the existence of high temperature resisting silicon and its reticular formation as shown in Figs. 12 and 13.

2) The Mechanism of Promotion of Reduction

Sodium silicate is comprised of ionic compound, and the sodium ions have good hydrophilicity. Therefore the sodium ions will leave the original position when contact with aqueous solution, and the water molecules take the original place, and the displacement reaction starts. In weak alkaline environment, sodium silicate forms bond film of silicic acid \([n\text{Si(OH)}_4]_n\), thus sodium ions can promote the curing of sodium silicate.

In the process of briquettes reduction, due to a small size of the sodium ion, the free sodium ions can easily spread to the blast furnace dust particles and enter into the lattice of \(\text{Fe}_3\text{O}_4\), and the amount of sodium ions will be increased.
Fig. 13. Bonding mechanism of sodium silicate.

Fig. 14. Change of corn starch in the bonding process.
when $\text{Fe}_2\text{O}_3$ generates in the reduction process.\textsuperscript{22)} In this process, the sodium ions can greatly promote the spread of iron ions inside the blast furnace dust, which promotes the two transformation reactions, such as $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$. With the progress of reduction reaction, the number of sodium ions entered into the lattice is growing, so the reduction process of $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$ is promoted more greatly.

The metallization rate of the briquettes with sodium silicate as binder and without sodium silicate after roasting at high temperature is shown in Table 5.

From the experimental results, sodium silicate is conducive to the promotion of metallization rate of the briquettes. Compared with the pallets without sodium silicate, the metallization rate increased by 4.6%. In addition, more iron oxide was reduced to metallic iron due to the increase of metallization rate, so does the strength of briquettes.

3.4.2. The Mechanism of Corn Starch Addition

The general chemical formula of corn starch is $[(\text{C}_6\text{H}_{10}\text{O}_5)_n]$. And corn starch has semi-crystalline particle structure, the internal area is non-crystalline area, while the outer area is crystallized area. At the same time, the high relative molecular mass of corn starch and the close reticular formation generated from hydroxyl synthesis by hydrogen bond result in large viscosity.\textsuperscript{23)}

The bonding mechanism of corn starch is shown in Figs. 14 and 15. In the mechanical blending process, due to the effect of mechanical force, the crystal structure of corn starch has been destroyed. The degree of lattice ordering of crystal in crystalline area reduces gradually, which creates a good fluidity of corn starch.

After adding water, corn starch granules swell, and viscosity increases, so the briquettes get a high strength at room temperature. With an increase of temperature, the lattice of corn starch granular in crystalline area is broken gradually, so the non-crystalline area becomes larger. When the temperature reaches gelatinization temperature, corn starch granules unceasingly expand, the volume can reach several times or dozens of times of the original volume. Due to the expansion of the particles, the crystal structure disappeared, the volume swelled, corn starch became the translucent and sticky liquid. The gelatinization of starch can produce a large number of hydrogen bond with high activity, that’s the reason why the water absorption of starch has increased since the gelatinization process. In the compound binder of corn starch and sodium silicate, hydrogen bonds enter into the sodium silicate, and accelerate the dehydration condensation reaction of sodium silicate, then strength of the briquettes improve greatly.

With the temperature rising, the water molecules enter into the corn starch, combine with starch molecular and start irreversible swell. When the temperature reaches $110^\circ\text{C}$, the gelatinization complete, the original morphological structure of corn starch granules are broken and the intermolecular interaction is weakened, so the compatibility between the corn starch granules and blast furnace dust particles increase, density and strength of the briquettes are improved.

After $200^\circ\text{C}$ corn starch gradually transform into a continuous solid connection bridge, which connected the blast furnace dust particles closely, and strength of the briquettes increases. With the temperature rise further, the element Pb, Zn, etc. in the briquettes begins to evaporate, Metallic iron begins to generate gradually, and holes in briquette surface become larger, the solid connection bridge between blast furnace dust particles gradually evaporates. When the temperature above $1\,000^\circ\text{C}$, the solid connection bridge disappears gradually and strength of briquettes decreased. Therefore, the corn starch is very hard to improve the strength of the briquettes at high temperatures.

4. Conclusions

(1) Without binder, the strength of RHF briquette made from blast furnace dust both after dried and roasted is very low, so they can’t meet the requirements of the production, thus the binder for the briquettes need to be developed.

(2) The different binder plays the different role, corn
starch binders can improve the low temperature strength of the briquettes, the silicon-containing binders can improve the high temperature strength of the briquettes. Therefore, the starch binders should be used accompanying with silicon-containing binder to develop the appropriate compound binder.

(3) The compound binder can make full use of the advantages of all kinds of binder, consequently it can greatly improve the strength of green briquettes, dried briquettes and roasted briquettes. The excellent collocation pattern of compound binder is the corn starch and sodium silicate, and the appropriate proportion is 2%.

(4) At low temperature, sodium silicate generates bond film and separates out silica acid gel particles, which enhances the strength of briquettes. And the gel particles and blast furnace dust will be connected with each other like reticular formation through the Si–O–Si bonds generated from silica acid gel particles at high temperature, which is the key of cured bonding effect. Besides, Na⁺ diffuses into the crystal lattice of Fe₃O₄ and improves the reduction process of iron oxides. Simultaneously, it’s conducive to the further increasing of strength of the briquettes.

(5) Corn starch can improve the briquettes strength at room temperature and the strength after drying because of the expansibility after absorbing water, viscosity and compatibility after gelatinization of corn starch. After 200°C corn starch gradually transform into a continuous solid connection bridge, which connected the blast furnace dust particles closely. But when the temperature above 1000°C, the solid connection bridge disappears gradually and strength of the briquettes decreased.

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