Characterization of Preparing Cold Bonded Pellets for Direct Reduction Using an Organic Binder

Guanzhou QIU, Tao JIANG,1) Zhucheng HUANG, Deqing ZHU and Xiaohui FAN

Department of Mineral Engineering, Central South University, Changsha, Hunan 410083, PR China.
1) Department of Metallurgical Engineering, University of Utah, 135S 1460E, Salt Lake City, UT 84112, USA.
E-mail: tjiang@mines.utah.edu

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This paper involves the preparation technologies of cold bonded pellets for direct reduction using an organic binder-Funa. Investigation shows that the binder possesses excellent adhesive abilities to iron ore concentrates and is the key to the preparation of cold bonded pellets. Pretreatment on the binder-bearing iron concentrates prior to balling operation is essential to the maximization of adhesion of the binder to ore particles. Roll drum milling was found to be an effective method for the purpose. Investigation also shows that iron ore concentrate containing the organic binder has a lower balling kinetics than bentonite concentrate due to the increased viscosity by the binder. A balling time of 20 min is needed to ensure the pellet strength. It is found that the appropriate drying and hardening conditions for wet balls are 200–250°C of temperature and 0.8–1.0 m/s of airflow rate. TGA and DTA detection shows that the organic binder is thermally stable below 250°C in either neutral or oxidative atmosphere. Under above conditions, cold bonded pellets with a compressive strength of 250–300 N/Pellet, a drop strength of 7–10 times/1.0 m and a resistance to abrasion over 98% (+3 mm) have been attained from magnetite concentrates by using 1.5% of the organic binder. Tests show that the cold bonded pellets present a greater reduction rate and a higher iron grade of products than fired pellets made with bentonite as binder.

KEY WORDS: iron ore; pelletization; binder; cold bonded pellet; direct reduction.

1. Introduction

Direct reduced iron has been found an excellent substitute for scrap in steelmaking in electric arc furnace over past years. The DRI capacity and production have steadily increased.1–3) According to Lungen et al.3) the total DRI capacity had reached 60.599 million tons annually by the end of 2000 and 43.2 million tons of DRI were produced in 2000 over the world. A further increase of capacity and production is expected in the future.

In China, the EAF production capacity has exceeded 22 million tons annually; however, the DRI production in the country is less than 1 million tons per year. Many of EAF have to operate with molten iron as feed because of the lack of DRI and scrap. It is definitely necessary to augment DRI production in the country.

It is generally accepted that coal based rotary kiln process of iron pellets are appropriate for the development of DRI in China in consideration of the lack of natural gas and high grade iron lumps in the country. These processes, of which oxidative or preheated pellets are commonly used as reduction feed, are found to suffer from the drawbacks of low productivity and high-energy consumption, etc. Cold-bonded pellet direct reduction (CBP) process has been developed and put into industrial practice in China to reduce energy consumption and increase productivity of DRI.4) It has been shown that the preparation of cold-bonded pellets is the critical step in CBP process. In this regard, this paper mainly involves characterizations of preparation of cold bonded pellets using an organic binder.

2. Experimental

In this investigation, a sample of magnetite concentrate was used. Its chemical composition is shown in Table 1. It was tested to have a fineness of 86.10% of −0.074 mm and a specific area of 1 820 cm²/g. A bentonite was used as binder in tests for comparison, which has a composition of 72.91% SiO₂, 13.59% Al₂O₃ and a particle size of −0.074 mm. The properties of the organic binder, Funa, will be described in following section. The composition of the binder used in this paper is shown in Table 1. The binder has a fineness of −140 mesh.

The balling of mixed material was carried out inside an experimental balling disc with a diameter of 800 mm, an edge height of 150 mm and a tilt angle of 45 degrees. Screening method was used to measure the diameter of green balls.

Drying and hardening tests were completed in a φ65×200 mm electrically heated furnace with air as drying medium. A thermal control unit was used to control temperature. A φ50×150 mm sample basket was used. Bed height of wet pellet feed was kept at 150 mm. The diameter of feed pellets ranges from 11–13 mm.

Using following methods tested viscosity of binder solu-
Table 1. The chemical composition of the magnetite concentrate and organic binder used in this investigation (%).

| Material       | T<sub>FeO</sub> | FeO | Humate | SiO<sub>2</sub> | Al<sub>2</sub>O<sub>3</sub> | CaO | MgO | S | P | C |
|----------------|-----------------|-----|--------|-----------------|-----------------|-----|-----|---|---|---|
| Iron Concentrate | 68.11           | 21.25 | -      | 165             | 0.42             | 0.98 | 2.21 | - | 0.004 | - |
| Binder         | 2.65            | - | 45.20  | 12.11           | 5.92             | 4.69 | 0.10 | 0.03 | 0.03 | 28.40 |

-^*; Not containing this component

1. Viscosity

A Stormer viscometer was used to measure the viscosity of binder solutions. It consists of two concentric cylinders, the inner of which rotates while the outer is held stationary. Viscosity is determined by measuring the rate of rotation of the inner cylinder under the application of a known torque. The solution was prepared by fully dissolving binders in water followed by centrifugal separation of impurities.

2. Compression Strengths

To measure the compression strength of a ball, it is subjected to uniform loading between two parallel plates until the ball is ruptured. A total of 20 balls with the average diameter of 12 mm for wet balls and 11 mm for dry balls are measured. The average of compressions at which the balls break down is measured in N as the compression strength.

3. Drop Strengths

The drop strength is measured by means of letting a ball hit a steel plate repeatedly from a height of 0.5 m for wet ball and 1.0 m for dry ball. The numbers of drops the ball is able to withstand without damage is measured as the drop strength of the ball. A total of 20 balls with the average diameter of 12 mm for wet balls and 11 mm for dry balls are tested. The average value of the drop number is used as the drop strength.

4. Resistance to Heat Shock

The resistance to heat shock is expressed as a temperature at which 90% of the balls remains undamaged. The test is made on 20 green balls, which are placed in a preheated furnace. The residence time in the furnace is 10 min.

5. Resistance to Abrasion

The resistance to abrasion is tested on dry balls in a heated furnace. The residence time in the furnace is 10 min. The drop strength in 10 min at a speed of 52 rpm. The resistance is stated in wt% of the part of particles more than 3 mm.

6. Porosity

The porosity is measured on dry pellets. Total porosity of a material is expressed as the ratio of pore volume to total volume of the material and is calculated using the difference between the true density and apparent density:

\[ \varepsilon = (1 - \rho_a / \rho_t) \times 100, \% \]

where \( \varepsilon \) is the porosity (%), \( \rho_a \) is the apparent density, (g cm\(^{-3}\)), and \( \rho_t \) is the true density, (g cm\(^{-3}\)).

7. Reducibility and Swelling Rate

JIS M8713 and JIS M8715 standard test methods were used to determine the reducibility and swelling rate of pellet product respectively. The reduction conditions are identical for both: 75 mm internal diameter of retort, 500 g sample, 10–12.5 mm pellet size, 30%CO/70%N\(_2\) composition of reducing gas, 900 l/h gas amount and 180 min reduction duration.

3. Results and Discussions

3.1. Preparation and General Properties of Organic Binder

Bentonite is the most commonly used binder in iron ore pelletizing. However, there are some drawbacks with the use of bentonite. It contaminates the product with gangue and reduces the iron grade of the product. If bentonite is used for the preparation of pellets for direct reduction, the green pellets have to be subject to preheating or oxidative roasting to meet the requirements of direct reduction for strengths.

In contrast to bentonite, organic binders have the inherent advantage of being eliminated during firing. They do not contaminate the product. This obvious advantage provided the incentive for the development of organic binder. Overt 20 organic binders have been reported so far. In addition to not contaminating product, many of organic binders are found to create greater mechanical strengths than bentonite. The great dry strengths might enable the pellets to be directly used in direct reduction or steelmaking without the requirement for preheating or firing. However, most of organic binders are expensive than bentonite and have unfavorable thermal stability. Lowering cost and improving thermal stability are major subjects for the successful industrial application of organic binders.

Funa is a kind of carbonaceous composite binder with humate as its major constituent. It was developed in Central South University and patented in China. It is made from weathered coal or lignite by extraction of caustic solution. The major reaction can be shown as following:

\[ (\text{OH})_n R(COOH)_m + n\text{NaOH} = (\text{OH})_n R(COONa)_m + n\text{H}_2\text{O} \]
The molecule has a chain skeleton of netty structure with aromatic rings, which allows the binder great cohesive strength and good thermal stability.

Investigations show that the binder displays the characteristic of surfactant and colloid. It reduces the surface tension of water from 73 to 65 dyn cm⁻¹ and reduces contact angle of water on the surface of magnetite concentrates sharply from 46° to zero. In addition, it makes the surfaces more negatively charged. IRS detection indicates that the molecules of the binder chemically bond on the surface of magnetic concentrate.

Moreover, the binder is cheaper than any other organic binder reported so far and has found industrial use in agglomeration of coal, phosphate and iron ores in China.

3.2. Balling of Organic Binder Bearing Iron Concentrate

3.2.1. Effects of the Binder Dosage on Pellet Strength
Investigation shows that the binder dramatically improves drop strength of wet pellets to above 20 times/0.5 m at 1.5 % dosage. The compressive strength of wet pellet increases with the addition of the binder and keeps at the same level as bentonite wet pellets. Effects of binder dosage on dry strength of pellets are shown in Figs. 1 and 2. It can be seen that strengths of organic binder bearing dry pellets are much greater than those of pellets made with bentonite. It is worth noting that pellet strengths reach the maximum at about 1.5–1.7 % dosage of the organic binder and no longer increase or even go down beyond the range.

As mentioned above, the organic binder chemically bonds on the surface of iron, therefore, the more the binder, the more the reaction site between the binder and the surface and consequently the greater pellet strengths.

The stopping increase or decrease in pellet strengths with the further addition of the binder in the range over 1.7%, which responds to a concentration of the binder of about 20% inside green pellets assuming that water content in green pellets is 8.5% and the binder is completely dissolved, is due to its excess viscosity. Figure 3 shows relationships between concentration of binders and their viscosity. The viscosity of the organic binder solution increases dramatically with the concentration in the range over 15%. The wettability of the solution is hence seriously retarded according to Washburn equation. In this regard, the binder will not be able to fully disperse inside the iron ore concentrate, which in turn causes the decrease of pellet strengths.

3.2.2. Pretreatment of Mixing Material
It is found that the appropriate pretreatment on mixing material of concentrate and the binder prior to balling operation is of great importance to the achievement of high quality cold bonded pellets. Continuous Muller, single-rotor turbulent mixer, roll drum mill, etc. were tested in laboratory and roll drum milling was found to be the most effective. Unlike dry ball grinding for reducing particle size, the purpose of roll drum milling is to make the organic binder disperse more evenly and the binder and ore particles contact more tightly. The compared results of roll milling and single-rotor turbulent mixing are shown in Table 2. It can be seen the mechanical strengths of cold-bonded pellets are clearly improved through milling treatment.

The effects of milling time on strengths of dry pellets are shown in Figs. 4 and 5. It is again shown that the milling

![Fig. 1. The effects of binder addition on drop strength of dry pellets.](image1)

![Fig. 2. The effects of binder addition on compressive strength of dry pellets.](image2)

![Fig. 3. The relations between the viscosity of binder solutions and their concentrations.](image3)

| Pretreatment Methods | Compressive strength (N/Pellet) | Drop strength (times/1.0 m) | Resistance to abrasion (+2mm), % |
|---------------------|-------------------------------|-----------------------------|---------------------------------|
| Roll Drum Milling   | 257                           | 8.04                        | 98.34                           |
| Single-Rotor        | 234                           | 6.25                        | 96.68                           |
| Turbulent Mixing    |                               |                             |                                 |
pretreatment clearly improves pellet strengths and about 10 min of milling time is needed under the tested conditions. The resistance to abrasion (+3 mm) is found over 98.5% under these conditions.

### 3.2.3. Effects of Balling Time

The effects of balling time on average pellet diameter and pellet strengths are shown in Figs. 6 and 7. It can be seen that the organic binder clearly reduces the growth rate of green pellets. These results are similar to those obtained by Sastry et al., with Peridur and Woming bentonite as binders.22–24)

It is commonly accepted the migration rate of the capillary water inside green pellets determines the growth rate of green balls if the mechanical action from balling device is kept constant. Washburn investigated the dynamics of capillary flow and proposed the following equation to describe the migration rate of capillary water21,25):

\[
\frac{dl}{dt} = \frac{r \gamma \cos \theta}{\eta 4l}
\]

where
- \( r \) : the capillary radius,
- \( \eta \) : the viscosity of the liquid,
- \( \gamma \) : the surface tension,
- \( l \) : the length filled by liquid,
- \( \theta \) : the contact angle,
- \( t \) : the time,
- \( dl/dt \) : the rate of liquid flow through capillary.

Since the growth rate of green pellets is directly proportional to migration rate of capillary water, we may have:

\[
\frac{du}{dt} = k
\]

or

\[
\frac{du}{dt} = k \frac{r \gamma \cos \theta}{\eta 4l}
\]

where \( u \) is the growth rate of green pellets and \( k \) is the constant associated with mechanical force.

Equation (5) indicates that the growth rate of green pellets depends on the surface tension of the liquid, the viscosity of the liquid and the contact angle if the type, particle size and surface structure of raw materials as well as mechanical force are kept unchanged.

It has been known that the organic binder reduces the surface tension of water from 73 to 65 dyn cm\(^{-1}\) and the contact angle on magnetic concentrates from 46° to 0°.19) The former causes \( u \) to decrease and the latter makes it increase. However, these two are not significant affecting factors compared to viscosity. The viscosity of the organic binder solution increases sharply with its concentration. From Fig. 3 it can be found that the viscosity of the binder solution at the dosage of 1.5% (the corresponding concentration inside green pellets is 17.6%) and 1.7% (the concentration is 20%) is almost 10 and 100 times greater respectively than that without the binder. Therefore, the increase of viscosity caused by the binder is the major reason for the reduced growth rate of green pellets.

From Fig. 7 it can be found that the strength increases...
obviously with balling time below 20 min and slowly over the range. Hence the appropriate balling time for iron ore concentrates bearing the organic binder should not be below 20 min.

3.2.4. Effects of Moisture
It is also found that the amount of water during balling has apparent effects on balling behaviors of iron ore concentrates. The excessive water will cause wet pellets to cohere to each other and difficult to be discharged from the balling disc. The appropriate amount of water depends on the type, particle size; etc. of iron ore concentrates and needs to be determined by balling test. For the magnetite concentrate used in this investigation, the appropriate moisture is found to be 8.5–9.0%.

3.3. Drying and Hardening of Organic Binder Wet Pellets
Generally, drying and hardening are carried out in two phases in the production of fired or preheated pellets. In order to simplify treatment process, we incorporate the two into one in the preparation of cold bonded pellets. The wet pellets containing the organic binder are hardened while being dried. Investigation shows that drying patterns (blowing or drawing, one-step or multi-step drying) have not much effect on dry strength of pellets, while heating rate (temperature and flow rate of drying air) has clear effects on it as shown in Figs. 8 and 9. It is found that compressive and drop strength of dry pellet decreases with the flow rate of drying air, and decrease slightly with the temperature of drying air in the tested range. A lower drying temperature (200°C) allows a greater airflow rate (1.0–1.2 m/s) and a higher drying temperature (300°C) requires a smaller airflow rate (<1.0 m/s). It is found the resistance to abrasion of dry pellets increases at low flow rate and decreases at high flow rate with flow rate of drying air.

It is found that the natural curing on wet pellets at ambient temperature also produces product pellets with equivalent strengths to forced drying under above conditions. However, the natural curing is under control of climate and is not commonly feasible.

TGA and DTA analysis of the organic binder in neutral and oxidative atmosphere has been made in order to investigate the behaviors of the organic binder in drying and hardening. Results shows that, in neutral atmosphere, the binder loses its free moisture at 110°C and does not present clear heat effect between 200–250°C. The total weight loss is about 120°C and has not clear heat effect between 200–250°C as in neutral atmosphere. The total weight loss is observed to be 13.5% below 200°C and 1.5% between 200–250°C. It is also found that, the rate of weight loss markedly increases when temperature is over 300°C.

TGA and DTA results show that the organic binder is thermally stable below 250°C in either neutral or oxidative atmosphere. The drying and hardening of wet pellets at 200–250°C is another important technological character for the preparation of cold bonded pellets.

3.4. Physical–Chemical Characters of Cold Bonded Pellets
Table 3 lists the mechanical strengths, partial physical properties and reduction behaviors of cold bonded pellets made with 1.5% the organic binder. For comparison, it also lists the characters of oxidative pellets made from the same iron ore concentrate with 1.5% bentonite as binder and fired at 1250°C. Generally, the cold-bonded pellets have a

| Table 3. Physical–chemical characters of cold-bonded pellets and comparison to oxidative fired pellets. |
|---------------------------------|----------------|-----------------|-----------------------------|-----------------|-----------------|
| Type of Pellets                | Compressive Strength N/Pellet | Drop Strength (times/1.0 m) | Resistibility to Abrasion (>3mm), % | Porosity, % | Reducibility, % | Reduction Swelling Rate, % |
| Cold-Bonded                    | 268              | 8.7             | >98                         | 29.32          | 72.76           | -3.24                  |
| Oxidative Fired                | 2200             | >50             | >99                         | 22.78          | 68.88           | 8.16                   |
compressive strength of 250–300 N/Pellet, a drop strength of 7–10 times/1.0 m and resistibility to abrasion (+3 mm) over 98%. The porosity of cold bonded pellets is markedly greater than that of oxidative-fired pellets, which commonly present a porosity of 21–23%. From Table 3, it can be seen that cold-bonded pellets are clearly superior to oxidative fired pellets in reduction behavior (reducibility, swelling rate) although their mechanical strengths are lower than those of the latter are. The excellent reduction behavior of cold bonded pellets is mainly due to their great porosity. Moreover, the carbon inside pellets brought by the organic binder will speed up the reduction of the pellets. In addition, it is found that total iron content of reduction product from cold bonded pellets is always higher than that from oxidative fired pellets made from the same iron ore concentrate with bentonite as binder, because the organic binder is mostly volatilized out and bentonite is kept inside pellets during reduction.

The excellent reduction behavior and medium mechanical strength of cold bonded pellets offer the possibility for the pellets to be used as feed in direct reduction rotary kiln or shaft furnace. The process of coal-based rotary kiln reduction with cold bonded pellets as feed has been put into industrial use in China after a series of batch, pilot and field experiments and investigations. New direct reduction processes (coal-based or gas-based shaft furnace, etc.) with cold bonded pellets as feed are being developed.

4. Conclusions

This paper has involved the preparation of cold bonded pellets for direct reduction using an organic binder-Funa. Results show that the binder is the key to the preparation of cold bonded pellets. The proper dosage of the binder is found to be about 1.5%. Stopping increase or decrease in cold bonded pellets is mainly due to their great porosity. Pretreatment of organic binder bearing iron ore concentrates prior to balling is essential to the maximal adhesion of the binder to ore particles. Roll drum milling is found to be an effective treating method. It is found that the binder causes balling rate of the concentrate to drop markedly also due to the viscosity increased by the binder. A balling time of 20 min is needed to ensure the pellet strengths. The appropriate drying conditions are found to be 200–250°C temperature and 0.8–1.0 m/s airflow rate. TGA and DTA detection shows that the binder is thermally stable below 250°C in either neutral or oxidative atmosphere. The cold bonded pellets with a compressive strength of 250–300 N/Pellet, a drop strength of 7–10 times/1.0 m and a resistibility to abrasion over 98% (+3 mm) have been achieved with 1.5% the organic binder. Investigations show that the cold bonded pellets present a greater reducibility, a negative swelling rate and a higher iron grade of reduction product than oxidative fired pellets with bentonite as binder. The cold bonded pellets have been used in the production of direct reduction iron in China.

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