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Surface performance of carboxy methyl amylopectin for improving strength of pellet①

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[Abstract] Using synthesized carboxy methyl amylopectin as organic binders for pelletizing, the dry pellet compressive strength goes up to 322.8 N per ball, dropping strength is 6.67 times per 0.5 m, and the green pellet shock temperature reaches up to 820 ℃. The influence of the carboxy methyl amylopectin on the contact angle of iron ore surface was investigated. Compared with that having no organic binder, the surface tension increases 48 times and the capillary attraction increases 43 times. These results were obtained by using the quasi-particulate model calculation. The analysis demonstrated that the behavior of polar group and organic chain structure are the reasons of improving the strength of pellet. XPS analysis indicated that polar group bonded on iron ore surface make the electron energy of 2p orbit of Fe decreases from 711 eV to 710.2 eV. The results showed that the special spatial reticular structure of organic chain can improve pellet strength and green ball shock temperature.

[Key words] pellet; organic binder; surface action; pellet strength.
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1 INTRODUCTION

The substitution of inorganic binder by organic binder for pellet and agglomeration is now necessary[1~3], but there is a difficulty in using organic binder which causes the dried ball strength of the cold-bonded pellet and the shock temperature of green oxidized pellet to decrease. To solve this problem, it is necessary to carry out further research about the performance of organic binder on the iron ore surface. Based on References[4~6], carboxy methyl amylopectin (CMA) was synthesized and was used as the organic binder for pelletizing, and studies on the surface behavior of CMA was also carried out.

2 EXPERIMENTAL

2.1 Preparation of CMA

The materials used mainly included starch, ethanol, choleric ethyl acid and sodium hydroxide, all in chemical purity.

Add certain proportion of starch and ethanol in a three necked flask, and agitate homogeneously. Then add a solution consisting of 30% sodium hydroxide. Stir for 1.5 h at room temperature, drop a certain amount of choleric ethyl in and raise the temperature to 60 ℃. After 7 h, decrease the temperature to ambient temperature slowly, then filter. Add HCl to make the system neutralized, filter again, then wash the solid powder with 30% ethanol in order to get rid of impurity choleric sodium.

2.2 Pelletizing experiment

The iron ore concentrate was supplied by Beijing Mine Corporation, the chemical composition is shown in Table 1. The concentrate in research was re-milled firstly, and the size of ninety percent of the particles was under 0.074 mm, the properties are shown in Table 2.

Table 1 Chemical composition of iron ore concentrate (%)

Fe_T	FeO	SiO_2	Al_2O_3	CaO	MgO	P	S
66.05	28.14	4.62	0.91	0.36	0.31	0.026	0.03

Pelletizing experiment was done in a pelletizer disc with diameter of 800 mm, its angle of inclination was 49°, and speed of rotation was 20 r/min. 4 kg concentrate was used for the experiment. The mass of added water was 7.8% and the mass of additives CMA was 0.4%, and the pelletizing time was 18 min. Twenty green balls with diameter of 10~15 mm was selected for measuring drop strength, shock temperature, and for static drying respectively. The static drying was done in FN200-1 model electricity heat box under 120 ℃ for 4 h. The green and dried pellet strength was measured by ISO standard. The experiment results are shown in Table 3.

3 SURFACE PERFORMANCE OF CMA

3.1 Surface energy model of particles in pellet

It is proposed that forces existing in the pellet

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Table 2 Re-milled iron ore concentrate forming and proportion superficial area

True specific gravity/ $(g \cdot cm^{-3})$	Pile specific gravity/ $(g \cdot cm^{-3})$	Maximum molecular water/ %	Maximum capillary water/ %	Pellet forming index/ %	Proportion superficial area/ $(cm^2 \cdot g^{-1})$
4.58	2.36	6.2	14.24	0.771	1 680

Table 3 Property of pellet

CMA additive/ %	Green ball			Dry ball		Abrasion / %
	Compressive strength / N per ball	Dropping strength / times per 0.5 m	Shock temperature / ℃	Compressive strength / N per ball	Dropping strength / times per m	
0.4	21.8	6.67	820	322.8	16.18	98.5

among particles include capillary attraction, chemical adsorption force, magnetic gravitation, electrostatic force, van der Walls force, and viscosity stagnant force[4,5]. The energy model can be described as

$$A_T = A_c + A_{vd} + A_h + A_m + A_v + A_e$$

where A_c is the capillary force, A_v the viscosity stagnant force, A_h the chemical adsorption force, A_m the magnetic gravitation, A_{vd} the van der Walls force, A_e the electrostatic force. The analysis shows that in the green pellet the A_c, A_v and A_h play important roles; but in the dry pellet, A_h is the most important force, others such as A_e, A_m, A_{vd} can be ignored[4,5].

3.2 Effect of CMA on hydrophilicity of iron concentrate surface

The investigation indicated that when the CMA was in present, the hydrophilicity of iron ore surface was improved dramatically. The effect of CMA on the contact angle of ore surface is shown in Fig.1. If the additives are absent, the contact angle of water to the magnetite iron ore surface is 48°. Increasing additives, the contact angle reduced rapidly, and the hydrophilicity of the iron ore was improved. It could enhanced the liquid bridge viscosity existing among fine particles and improved A_c and A_v. So the pellet strength was improved. From Fig.1, we also know that the influence of CMA was more affective than CMC.

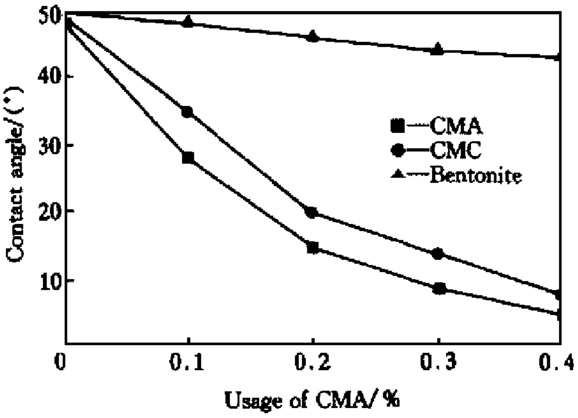

Fig.1 Influence of organic binder on contact angle of magnetite iron ore

3.3 Quasi-particulate model calculation

The CMA has many hydrophilic groups (—OH) and polar groups ($—COO^-$). They can improve hydrophilicity of fine magnetite ore rapidly, so the surface tension and capillary gravitation is improved besides affecting the water migration and formation of a liquid bridge between particles. In addition, the chain of the organic binder can also influence the water migration, viscosity and the formation of a liquid bridge among the particles. The liquid phase can be formed as shown in Fig. 2. In the quasi-model, where O and O' denote particle center, A denotes contact point, and B is the cross point.

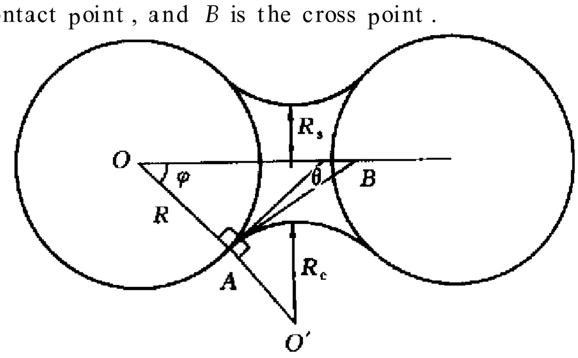

Fig.2 Quasi-particles model

We can ignore the variation of forces caused by the particles themselves, so the factors affecting the strength of the pellet are only surface tension, capillary gravitation and viscosity stagnant force of liquid bridge[6~8].

1) Surface tension F_1

The F_1 performances lie in moistening the periphery of three phase of liquid-solid-vapor, it is calculated by

$$F_1 = 2\pi Rr \sin\varphi \sin(\theta + \varphi) \quad (1)$$

where R denotes the particle radius, r the liquid tension, φ the adhere angle of liquid bridge to particle, and θ the moisten angle between the liquid bridge and particles.

2) Capillary attraction F_2

$$F_2 = \pi R^2 r(1/R_c - 1/R_s)\sin^2\varphi \quad (2)$$

where R_c and R_s all denote the curvature radius(see

Fig.2).

3) Viscosity stagnant force of the liquid bridge F_3

$$F_3 = 3\pi \eta R^2 \omega / H \quad (3)$$

where η denotes the liquid bridge viscosity, ω the separating rate, and H the space between particles.

The total adhere force of the particles can be expressed by the formula

$$F = F_1 + F_2 + F_3 \quad (4)$$

The angle θ can be considered as contact angle, the adhere angle φ is shown by Quasi-particles model. In tri-angle ΔOAB, by sine and cosine alternation, we can get

$$\cos 2(\varphi + \theta) = \sin \varphi + \cos^2 \theta - 2\sin \varphi \cos \theta \sin(\varphi + \theta) \quad (5)$$

From Fig.2, we also know that

$$R_c = R(1 - \cos \varphi) / \cos(\varphi + \theta) \quad (6)$$

$$R_s = R\sin \varphi + R_c \sin(\varphi + \theta) \quad (7)$$

In the absent or present of CMA, the contact angle of powder is 48° or 43° respectively. The results show that the surface tension and capillary force were increased by 48 times or 43 times, respectively. Because of the increase in the surface tension (F_1) and capillary force (F_2), the particles became more closer than before, so the viscosity stagnant (F_3) is enhanced.

3.4 Influence of CMA on surface chemical energy

3.4.1 General performance of polar group of organic binder

The effect of organic binder molecular on iron ore surface is mainly chemosorption forces through hydrogen bond, chemosorptive bond and coordination bond. The hydrogen of the organic chain and active group can form hydrogen bonds with high electronegativity oxygen atom of iron oxide. This is favorable for improving the pellet strength. But the energy of hydrogen bond is only 8 ~ 40 kJ/mol, usually belongs to van der walls force. The polar groups of organic binder can bond on iron ore surface and form covalent bonds and ionic bonds with Fe. The energy of these bonds are always larger than 40kJ/mol, so they contribute to improve the surface energy of the pellet particles and the strength of the pellet.

The bonded atoms of the polar groups can form bonds with metal ions by coordination bonds. For example, the bio-bridge bond and mono-bridge bond groups can form coordination bonds with anode ions of the iron ore surface. So chemical energy can be improved.

It is known that when pelletizing, the chemical behavior of the polar group on the iron ore surface is very important for improving the strength of the pellet. The results also show that the most important selecting criterion of the organic binders is whether the organic binders have groups.

3.4.2 Behavior of polar groups of CMA on iron ore surface

CMA has many polar groups like COO^-. By the Leusies acid and alkali theory, the polar group COO^- can form an ion bond with Fe^{2+} and Fe^{3+}. Using the HMO method and by electroneganate calculation formula, we can get an index of group COO^- [1]: ionization potential I_p is 12.1, affinity energy E_n is 4.0, electroneganate X_g is 3.9. The electroneganate of Fe is 1.8, their deviation is 2.0, which shows that the group COO^- can bond with Fe^{2+} and Fe^{3+} [9,10]. When 0.4% CMA is present as the organic binder, the analysis results of XPS are shown in Fig.3. Comparing the two figures, we know that the electron energy of 2p orbit of iron atom in fines is reduced by 0.8 eV (from 711.0 eV to 710.2 eV). It is demonstrated that the polar groups of CMA have bonded on the iron ore particle surface and made the surface energy increased.

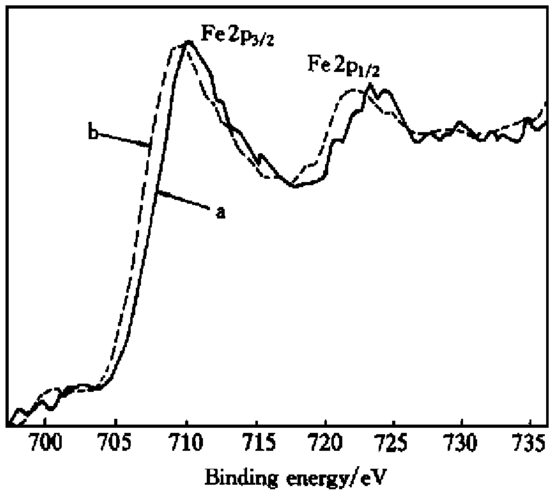

Fig.3 XPS analysis for iron ore powder
(a) —Iron concentrate with 0.4% CMA;
(b) —Dried pellet with out CMA

3.4.3 Influence of organic chain on thermal stability of green pellet[11,12]

The organic chair of CMA is cubic mesh structure. When pelletizing, many capillary and gelation pores are formed. These are not like the pores formed by CMC and polyacrylamide, which made internal system of the pellet or agglomerate closed. The pores formed in pellets are favorable for water vapor dispersing, and create the outside dispersion and internal dispersion at approximate the same speed, so the pellet could not break when heating, and the shock temperature of green pellet rises. Another reason that CMA can improve shock temperature is CMA has many polar groups, like COO^-, which bond on the iron ore surface and make the surface energy improved.

XPS analysis for the pellet fines heated by 800 ℃ wind is shown in Fig.4. Compared with Fig.3, the

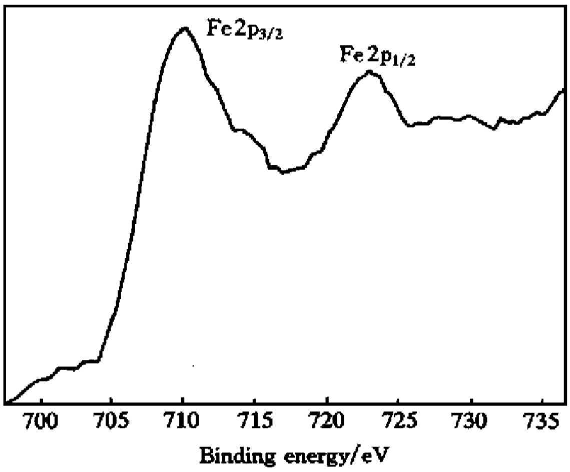

Fig.4 XPS analysis for pellet powder after heated at 800 ℃ by warm wind

2p orbit energy of iron has decreased 0.8 eV, equal to the value of 2p orbit energy of dried pellet powder when added 0.4 % CMA, but not heated to 800 ℃, which demonstrates that the group —COO— is still effective.

4 CONCLUSION

1) Using CMA as an organic binder, the pelletizing experiment was carried out with the dry ball compression strength reaching to 322.8 N per ball. The dry ball dropping strength is 6.67 times per 0.5 m and the green ball shock temperature is 820 ℃.

2) CMA can improve the strength of pellet through its contribution to the surface energy. When using CMA, the contact angle of iron ore surface decreases from 48° to 43°. Quasi-particulate model calculation indicates that when 0.4 % CMA is added, the surface tension F_1 increases by 48 times and the capillary gravitation F_2 increases by 43 times than before. Then the particles became more closely, so the viscosity stagnant force F_3 is also enhanced.

3) The organic binder CMA has many COO^- polar groups, which can bond on iron ore surfaces by a chemosorptive bond. It can enhance the surface energy of pellet particles. XPS analysis shows that the energy of 2p orbit of Fe atom has decreased 0.8 eV.

4) The space netty chain of organic binder can make itself well dispersed when pelletizing. They formed capillary and gelation pores, which make water vapor evaporate easily. So the internal dispersion and outside dispersion of vapor evaporating could keep the same speed; it makes the shock temperature of pellets and agglomerates improve dramatically.

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