Study of the mechanism for improving green pellet performance with compound binders

Caixia Li，Yang Bai，Ruichen Ren，Gaoquan Liu，Jingyu Zhao

College of Mining, Liaoning Technical University, Fuxin 123000, Liaoning, China

Corresponding author: by9211@163.com (Yang Bai)

Abstract: In this study, the characters of bentonite organic binders were investigated by analytical methods, including X-ray diffraction, zeta potential, and scanning electron microscope. The results showed that the surfaces and the edges of montmorillonite layers reacted with carboxyl groups or oxhydryl groups of expanded starch or carboxymethyl cellulose (CMC), enhancing the surface electronegativity of the bentonite. The addition of organic binders reduced the contact angle between the bentonite and magnetite and enhanced the hydrophilicity of bentonite surfaces. Based on the polymer chains of organic binders, the house-of-cards structure formed by a compound binder was more stable than when formed by bentonite alone. The non-stripped layers in bentonite were peeled off under the action of chemical bonds. At the same time, improved bentonite dispersion in pellets was observed, with decreased bentonite particle size and increased surface area. The solid bridges produced by the reaction between magnetite and Mg^{2+} in the montmorillonite layer restrained pellet expansion, which thus improved the decrepitation temperature during the heating process.

Keywords: pelletization, Mg-bentonite, expanded starch, CMC, house-of-cards structure

1.   Introduction

As the biggest importer of iron ore in the world, China's demands for ore from foreign resources have been increasing sharply every year. Domestic ore has great potential value as it enjoys a well-found category and abundant iron resources, but ore's the average grade is only 32-34% and ≥50% rich ore represents only 2.7% of the total proven resources, which is well below the proportions of other major producer countries (Cui et al.,2012). As one kind of agglomerated iron ore, pellets become a powerful method for relieving the pressure on in-country provisions and ore grade requirements, with characteristics of high grade, uniform particle size, and good reducibility (Liu, 2006).

The quality of binders is a key factor in production that decides the pellet performance. Bentonite as a binder is easily obtainable, offers good cohesiveness, good spherical shape, and low costs (Eisele et al., 2003). According to the traditional theory, bentonite has two reasons to improve the strength of green pellet (Kawatra et al., 2001; Kawatra et al., 2002). One is that the colloidal substances in the bentonite particles reduce the distance between the layers in the bentonite, which thus increase the Van der Waals forces among the layers (Kawatra et al., 2003; Alince et al., 2001). Additionally, bentonite particles form a solid bond bridge, which strengthens the interaction between particles. Moreover, organic binders (such as CMC and expanded starch, etc) which wholly or substantially burn up under high temperature, have been developed (Eisele et al., 2003; Sivrikaya et al., 2010). However, there are various kinds of organic binders in different forms. Therefore, the mechanism in the pellets is more complex. In general, it is believed that the functional groups in organic binders can bond with Fe^{2+} or Fe^{3+} on the surface of iron ore, which can enhance the surface hydrophilicity of the iron ore particles and provide benefits for the formation of pellets (Haas., 1989; Chizhikova et al., 2003;). The net structure formed by long molecular chains in organic binders will encapsulate iron ore particles tightly in the pelletizing process. In the meanwhile, moisture will be removed from the capillary and make the connection between iron particles more closely (Murr et al., 1989). However, when the organic binder

exceeds a certain additive amount, the high viscosity of organic binder may have a negative effect on the performance of the green pellets. Due to the low profit of domestic steel mills in China, organic binders will not only increase production costs, but also might affect the grate-kiln-cooler process which requires higher preheating temperatures. This presents significant obstacles to organic binder applications in China.

In recent years, the compound binder that combines the advantages of bentonite and organic binders has become the focus of research and development. Nevertheless, the mechanism of compound binders is not well understood. However, it is certainly that the mechanism of compound binder is not simple summation of the mechanism of organic binder and bentonite, which is closely associated with a variety of factors, such as the selection of organic binder and the compound method (Guanzhou et al., 2004). In this study, bentonite was compounded with organic binders. Based on the comparison of the resulting green pellets added different binders, the mechanism for improving green pellet performance with compound binders was described.

2. Materials and methods

2.1. Materials

Bentonite was obtained from Jianping, Liaoning province, China and had a particle size of 80% passing -0.074 mm (200 mesh). The montmorillonite content was only 62.32% in the bentonite. Low-grade montmorillonite was not appropriate for industrial applications because montmorillonite was the effective component of bentonite based metallurgical pellet binders. The little awl corner hydrocyclones (Gosdel and Technology co., Beijing, China) were selected for bentonite purification, being a highly precise separator and commonly used for nonmetallic mineral processing (Gong et al.,2016). The overflow of Φ75 hydrocyclone as purified bentonite for next step of the pelletizing. X-ray diffraction patterns (Fig. 1) and clay cation exchange capacity (Table 1), showed that the bentonite was Mg-bentonite with a belonged to the dioctahedral structure and cheto montmorillonite characteristics (Grim et al., 1961). The schematic diagram of little awl corner hydrocyclones purification is shown in Fig. 2 and chemical analyses of purified bentonite in Table 2.
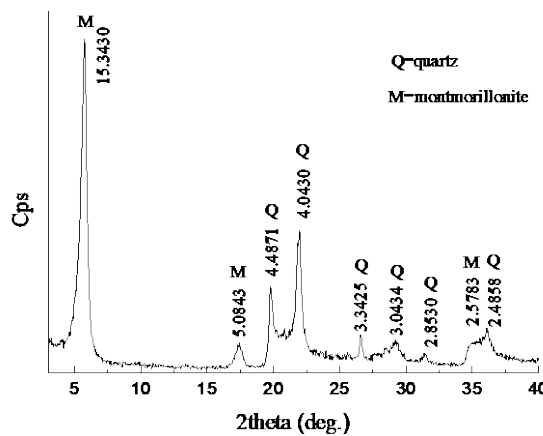
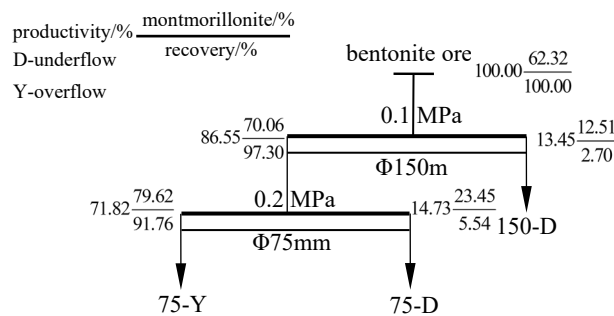

Fig. 1. X-ray diffraction diagram of purified bentonite

Fig. 2. The schematic diagram of little awl corner hydrocyclones purification

Table 1. Purified bentonite cation exchange capacity

Material	ΣE_c, (mmol $\cdot100g^{-1}$)	Each exchange cation in total account, %			
		E_{Na}^+	E_K^+	E_{Mg}^{2+}	E_{Ca}^{2+}
Purified bentonite	78.10	13.76	2.61	57.35	26.28

Magnetite concentrate in these experiments was obtained from Bajiazi Iron Concentration Plant located in Fuxin, Liaoning province, China. The concentrate had 5% moisture, a particle size of 80% passing -0.074mm (200mesh) and 51% passing -0.045mm (325mesh). Ballability index K is commonly defined as the ability to form pellets during agglomeration, which has been widely used in the countries from former Soviet Union and China to evaluate the natural ballability of powder materials (Guanzhou et al., 2004). The formula of ballability index K:

$$K = \frac{W_m}{W_c - W_m} \tag{1}$$

where K is the natural ballability index of material; Wm the maximum molecular water content of the material (%) and Wc is the maximum capillary water content of the material (%).

According to the method of ballability index K of iron ores, the K of this magnetite concentrate was 0.26 and its ballability was poor. The main chemical composition is shown in Table 2.

Table 2. Chemical composition of purified bentonite and magnetite concentrate

Material	SiO_2	Al_2O_3	Fe	CaO	K_2O	Na_2O	MgO	MnO_2	TiO_2	P_2O_5	S
Purified bentonite	64.82	15.88	1.39	2.38	0.25	0.34	4.35	0.05	0.15	0.01	0.01
Magnetite concentrate	1.24	0.81	69.59	1.33	0.23	0.05	0.12	—	—	0.01	0.18

CMC and expanded starch in this study were tested as organic binders. The expanded starch was a fine powder with a particle size of -0.074 mm which was made by rice and corn in a certain proportion and extruded by food expander under the condition that temperature was 240~270 ℃ and pressure was 1.1~1.2 MPa. CMC was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. The viscosity of CMC at 20 g/L and 25 ℃ was 800~1200 mPa·s.

2.2. Equipment

Elemental analyses of purified Mg-bentonite and magnetite concentrate were determined by Bruker X-ray fluorescence (XRF) spectrometer (S8 TIGER, Bruker Corp., Billerica, MA, USA). Phase analyses of the purified Mg-bentonite and burst pellet were carried out using a Shimadzu X-ray diffractometer (XRD) spectrometer (6100, Shimadzu Corp., Tokyo, Japan). Pelletization tests were performed on a 600mm diameter by 150mm depth balling disc with a rotating speed of 32r/min and tilt angle of 45°. The contact angles of different binders were measured using a dynamic contact angle instrument (OCA20, Data Physics Instruments GmbH, Filderstadt, Germany). Micrographs were obtained using a JEOL 35C scanning electron microscope (SEM; JEOL Ltd., Tokyo, Japan). Zeta potentials were measured using a Counter-Delsa440sx dynamic potential analyzer (Beckman Coulter, Inc., Brea, CA, USA).

2.3. Preparation of compound binder

In preparing the compound binder, 3% (by mass) organic binder was added to purified bentonite and mechanically stirred. Then, supplementary water was added up to 30% (by mass). Next, the mixture was squeezed twice in a screw extrusion machine and aged for 2 d. Finally, CMC-bentonite and expanded starch-bentonite were obtained respectively.

2.4. Pelletization experiments

Pelletization experiments were performed on an experimental pelletizing disc with a diameter of 600 mm, an edge height of 150 mm, a rotating speed of 32r/min and a tilt angle of 45°, as shown in Fig. 3.

The pH of experimental water is 6.9. It is well known that it is very difficult to accurately control the water content of green pellets in pelletizing process. According to the standard of industrial production, the water content of green pellets in this paper was controlled at about 9%. The test procedure includes:

(1) Mixing binder with the magnetite concentrate followed by the addition of desired quantity of water. The magnetite concentrate was found to have a water content of 5%, which was raised to about 8% in this step.

(2) Balling the moist mix in a batch manner. At first, 100 g of sample was taken from the mix and used to make the seed by stirring the sample after adding additional water. The duration time of this stage (seed formation) was 1min. The mix and additional water were added alternately to maintain the growth of pellets after the seeds were added into the pelletizing disc. The time of seed-growing was about 15min. When most of the pellets were in the diameter of 10~12.5 mm, stop adding additional water and continue rolling 3 min to make the pellets close tightly. A total mix of 1.5 kg was used for each batch pelletizing.

(3) Screening out the qualified pellets which were in the diameter of 10~12.5 mm after the experiment and measuring the mechanical strength of green pellets. The water content of the qualified green pellets is about 9% (drying the 500g green pellets at 105℃ for 4 h to obtain water content).
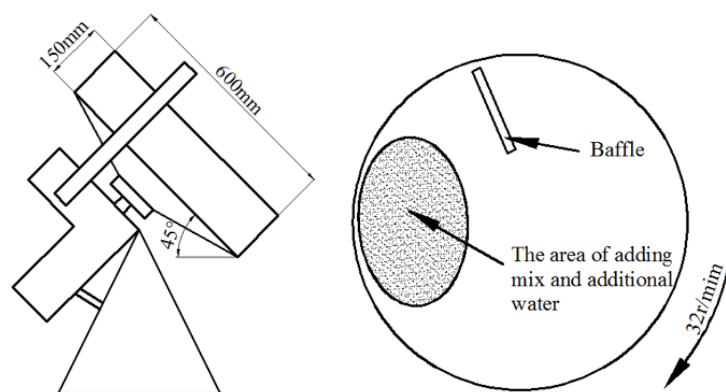

Fig. 3. The schematic diagram of the experimental pelletizing disc

After the pelletization experiment, qualified green pellets were tested for various performance characteristics (drop numbers, decrepitation temperature and compressive strength) described below. Three parallel tests were performed for performance characteristics of green pellets. Each parallel test was tested on a certain number of pellets according to the requirements of different performance characteristics, and the mean value of which can be used to improve calculation precision was taken.

(1) Drop numbers: The drop numbers was measured by letting a green pellet hit a 10mm steel plate repeatedly from a height of 0.5 m. The average value of 10 green pellets which were able to withstand without damage was measured as the drop numbers.

(2) Decrepitation temperature: The dynamic drying method was used to measure the decrepitation temperature. A drying pot was packed with 20 qualified pellets and placed into a vertical tube furnace with 1.5 m/s heated air for 5 min. The maximum temperature of 4% green pellet cracking was the decrepitation temperature.

(3) Compressive strength (green pellets): The compressive strength was measured by letting a green pellet subjected to uniform loading between two parallel plates until the pellet is ruptured. A total of 60 pellets were measured with a compression speed of 50 mm/min. The average value was considered as the compressive strength of green pellets.

3.   Results and discussion

3.1.   The mechanism for preparing compound binder

3.1.1 XRD and SEM

The interplanar spacing of compound binder became smaller and its diffraction peak wider and smoother than that of purified bentonite alone (Fig. 4). The organic molecules were found not to have

entered the montmorillonite interlayers. As CMC and expanded starch are amorphous substances, which produce scattering effects alone, organic binders might have been attached to the surfaces or edges of montmorillonite by chemical adsorption or electrostatic interaction, which decreased the montmorillonite's crystallinity and diffraction peak intensity.

Comparisons of SEM images showed that the magnetite particle edges were indistinct in pellet with added compound binder (Fig. 5 and Fig. 6). Compound binder was also found to be on magnetite surfaces, and small magnetite particles were evenly packed in the middle of large particles. Appearing just the opposite, most of the purified bentonite existed in the form of monomers.
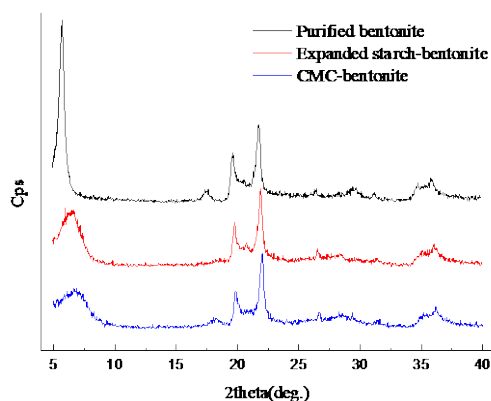
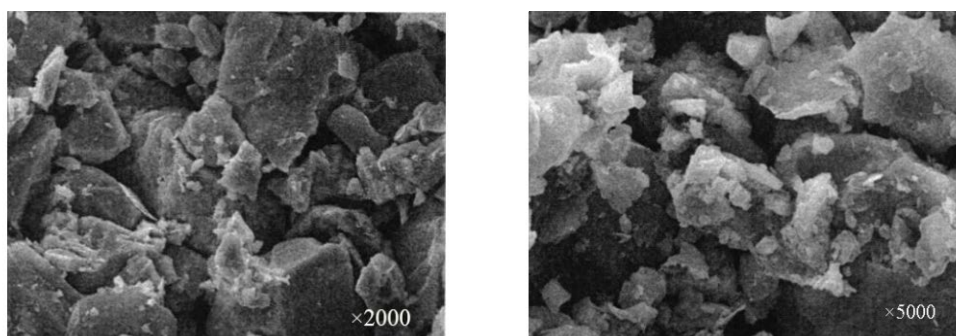Fig. 4. X-ray diffraction spectrum of compound binder

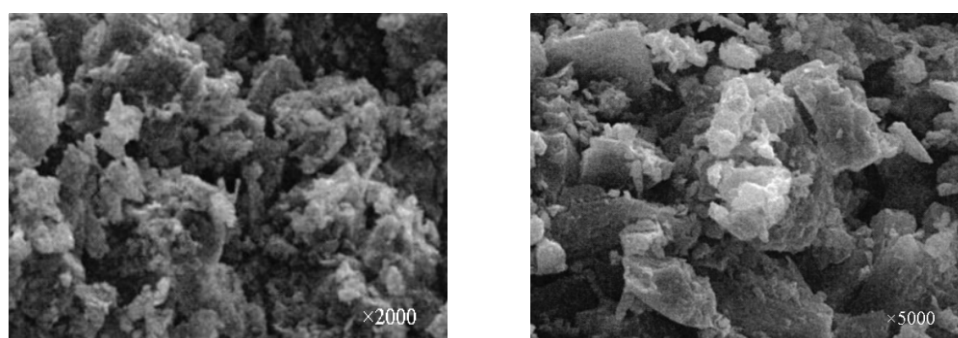Fig. 5. The SEM images of pellet with purified bentonite

Fig. 6. The SEM images of pellet with compound binder

3.1.2 Zeta-potential and contact angle

Based on the zeta-potentials of purified bentonite alone and compound binder, the zeta-potential of compound binder was lower than that of purified bentonite under all pH conditions. The lower zeta-potential of binders attracted more cations during pelletization. This also meant that water absorption rate and swelling rate were stronger and the diffusion layer thicker in the electric double layer. The contact angle on the surfaces of compound binder and magnetite were smaller in equivalent conditions.

As the binder concentration increased, the contact angle of purified bentonite changed little, but the compound binder did exactly the reverse. When the binder concentration increased from 0 to 0.5%, the contact angle of purified bentonite changed only 6.7° while CMC-bentonite and expanded starch-bentonite changed 32.8 and 26.9°, respectively. With the decreased contact angle, the surface hydrophilicity of magnetite was improved, which was beneficial to pellet formation. In addition, the viscosity of liquid bridges was increased, thereby enhancing the interface energy, capillary attraction energy, and viscous energy among the particles, which was beneficial to green pellet quality (Wang et al., 1997).
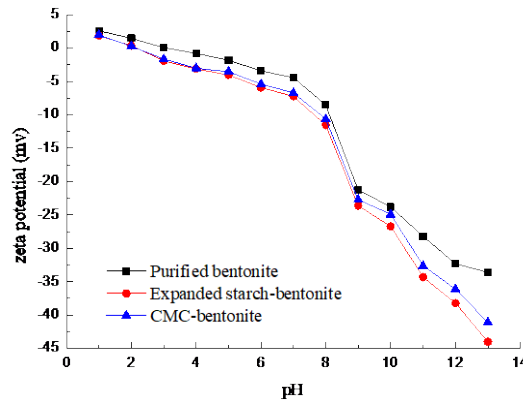

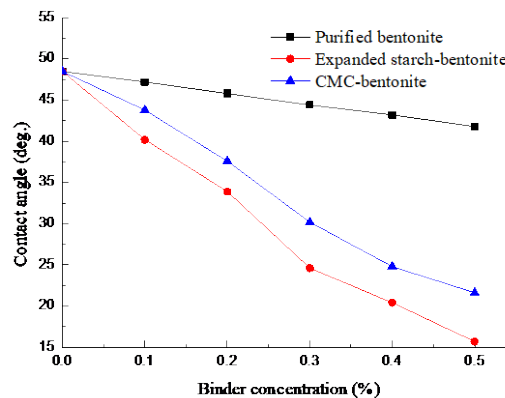Fig. 7. The relationship between pH and zeta potential of different binders

Fig. 8. The influence of binder content on the surface contact angle of iron concentrate

3.1.3 Structural analysis of compound binder

In the preparation of compound binder, bentonite formed a gelatin structure by absorbing water and swelling. Owing to the effect of shearing and extrusion forces, an uncertain number of layers were dispersed from the original montmorillonite crystal structure. The layer surfaces were negatively charged, but, in contrast, layer edges were positively charged in water as a result of the fracture of silicon-oxygen and aluminum-oxygen bonds in the montmorillonite crystal. Al^{3+} has an inert electronic structure, which has a low electronegativity, and thus it easily reacts with oxygen. Driven by Brownian motion, flaky bentonite particles flocculated in the direction in which system energy tended to be the lowest, which was produced from quasicrystals by edge-to-face, face-to-face, and edge-to-edge forms (Kroon et al., 1998). Face-to-face flocculation was mainly produced by the sharing of diffuse electric double layers of two negatively-charged layers. However, surfaces possessed larger electrostatic repulsions, such that the occurrence of face-to-face flocculation was low. Negatively-charged surfaces attract positively charged edges to form face-to-edge flocculation in terms of electrostatic interactions. Edge-to-edge flocculation might also have occurred, because the layer edges had less negative charge and thus less electrostatic repulsion. As the result of the co-action of edge-to-edge and edge-to-face flocculation, the house-of-cards structure was formed (Gungor et al., 2001).The process of the house-of-cards structure formation in bentonite gel is shown Fig. 9.The connection between bentonite and

magnetite particles was enhanced because of the formation of this special structure and the viscosity resistance between particles in liquid increased, thus improving the shear resistance and compressive capacity of liquid-bonded bridges.
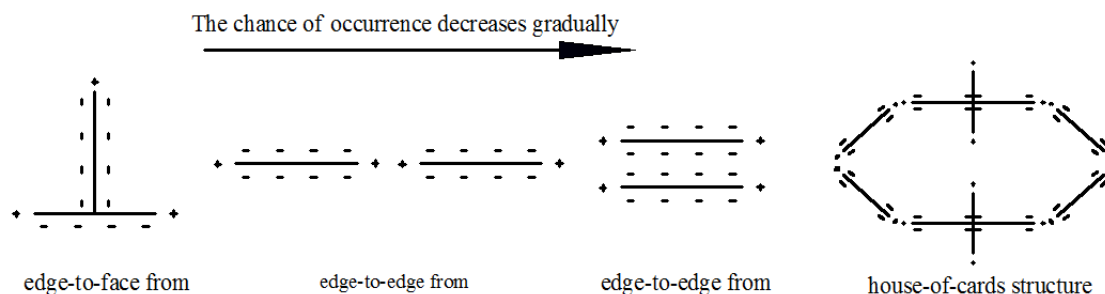

Fig. 9. The process of house-of-cards structure formation in bentonite gel.
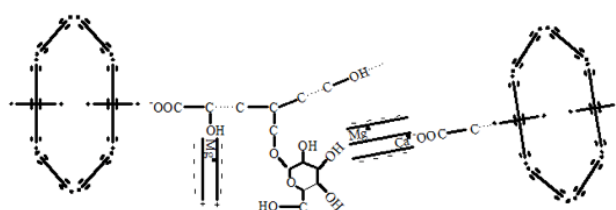

Fig. 10. The house-of-cards structure in compound binder

CMC and expanded starch are macromolecular organic materials that possess a variety of branched chain structures and large numbers of carboxyl and hydroxyl functional groups (Fig.10). According to correlative references (Wang et al., 1986), the electro negativities of carboxyl and hydroxyl groups were calculated to be 4.1 and 3.9, respectively. Chemical adsorption occurred between Al^{3+} on layer edges and organic binders with anionic functional groups, caused by carboxyl groups of <4 electronegativity. Furthermore, interlaminar Mg^{2+} and Ca^{2+} formed chelates with carboxyl and hydroxyl groups, such that anionic groups entered into the layers to make montmorillonite's zeta potential more negative. Based on the organic binder's polymer chains, the house-of-cards structure formed by the compound binder was more stable than that formed by bentonite alone. The bentonite's non-stripped layers were further peeled off under the action of chemical bonds. In the meanwhile, improved bentonite dispersion in the pellets was observed as well as decreased bentonite particle size and increased surface area.

3.2. The mechanism for improving green pellet strength with compound binder

3.2.1 The influence of binder content on drop numbers

The drop numbers increased with increased binder content, but the increase in drop numbers of green pellets with added compound binder was much larger than that of pellets with purified bentonite alone (Fig. 11). In spite of that, pellets were cut by high-speed shearing action in the course of collision and the house-of-cards structure was formed by bentonite enhanced interactions between bentonite and magnetite particles, which raised the viscous resistance between the particles in liquid phase. The house-of-cards structure was then damaged and the shear stresses in liquid bridges reduced accordingly under the action of high-speed shearing forces. Reposing for a period of time, the lamellar structure rearranged to edge-to-edge and edge-to-face under the influence of thermal motion and electrostatic attractions, such that the house-of-cards structure was recovered. Compared with the structure formed by purified bentonite alone, compound binder further enhanced its stability. Tracing it to the cause, not only did the binder have electrostatic interactions, but it also formed chemical bonds in the house-of-cards structure. Because of the macromolecular chains of the organic binders, the attached functional groups absorbed bentonite particles and the non-peeling layers were further stripped, which made bentonite particles distributed more uniformly. The grain size of bentonite

became smaller, surface area increased, and degree of separation improved. Small particle magnetite, which was absorbed onto bentonite surfaces, was uniformly filled into large particle magnetite and, hence, it decreased the pellet pore diameters, decreased porosity, and raised the strength of these green pellets.
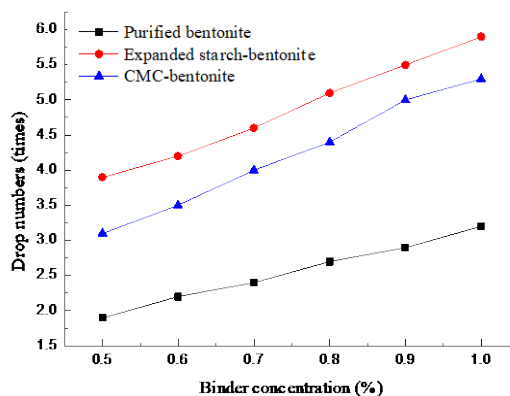

Fig. 11. The influence of binder content on drop numbers

3.2.2 *The influence of binder content on decrepitation temperature*

The decrepitation temperature increased with increased binder content, but, in green pellets with added compound binder, decrepitation temperature growth slowed significantly (Fig.12). Whether it was purified bentonite alone or compound binder, a house-of-cards structure formed in water, which was the equivalent of forming pipelines that eased water diffusion into the pellets. However, the water holding capacity of organic binders was much larger than that of bentonite. Compared with pellets with purified bentonite alone, adsorbed water in pellets with added compound binder was more difficult to evaporate, eventually forming dried, water-free shells. At the same time, soluble ions in magnetite migrated on pellet surfaces during the drying process and blocked the capillary channels because of the high ion adsorption capacity of the organic binders. This contributed to internal pressure build up, which eventually led to pellet decrepitation. Furthermore, CO_2 and H_2O produced by oxidation of organic binders flowed from pellet interiors. This effect not only destroyed the pellets' internal structure but also reduced the O_2 concentration on the pellet surfaces, which had an unfavorable effect on magnetite oxidation. Mg^{2+} in the montmorillonite interlayers were in the form of replacement or interstitial material that became part of a ferric oxide lattice under high temperature. Na^+ or Ca^{2+} which in the montmorillonite interlayers, differ in their ionic radii and, as the ionic radius of Mg^{2+} is only 0.66×10^{-10} m, which close to the ionic radius of Fe^{2+} and Fe^{3+}, and it does not cause lattice distortion. Mg^{2+} reacted with magnetite to form minerals, such as magnesioferrite and pleonast, under high temperature conditions (such as 650℃) (Fig. 13). These minerals, adsorbed to bentonite, were closely cemented and corroded reciprocally to form strong solid bridges, which inhibited pellet expansion.

3.2.3 *The influence of binder content on compressive strength*

The compressive strength of green pellets with compound binder was higher than that of green pellets of purified bentonite with the identical binder content (Fig. 14). For green pellets, its compressive strength was probably influenced by capillary attraction and viscous energies and chemical functions (Li et al., 2001). Compound binder and colloidal particles in the mineral could have formed a colloidal structure with water, which meant that it had a higher viscosity and surface tension compared to purified bentonite alone. Free water in pellets was squeezed out to form high surface tension and solid particles drawn closer. A movable gelatinous structure further coated or filled the gap between the magnetite particles, which greatly increased the contact area and intermolecular forces between the solid particles. Chemical adsorption on surfaces between the compound binder and magnetite were increased. When pressure was exerted on the pellets, both friction in the solid phase and capillary forces in the liquid bridges were increased, thus improving the compression strength of the green pellets.
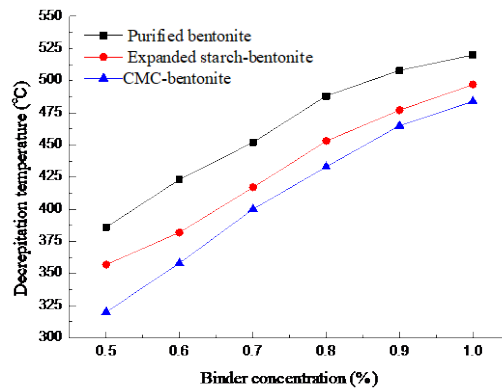
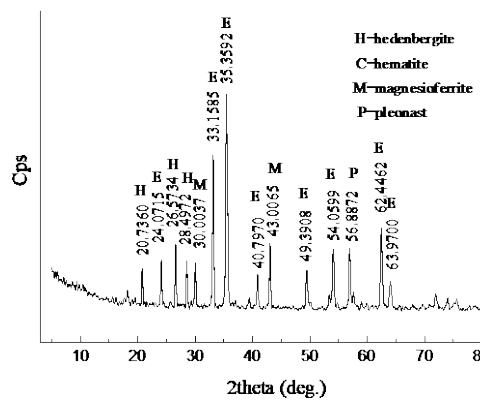Fig. 12. The influence of binder content on decrepitation temperature

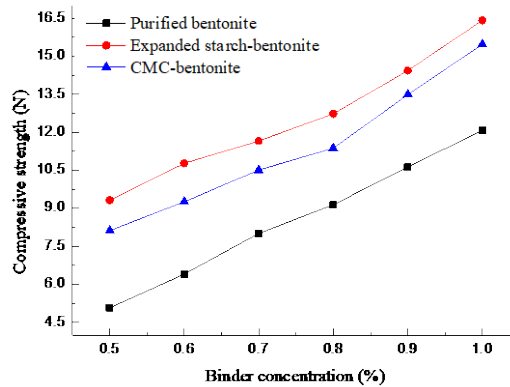Fig. 13. X - ray diffraction pattern of burst pellets (650℃)

Fig. 14. The influence of binder content on compressive strength

4. Conclusions

Pelletization experiments were carried out with bentonite and compound binders to examine the mechanism for improving green pellet performance with compound binders. The pelletization experiments showed that compound binder can greatly improve the green pellets performance (drop numbers, decrepitation temperature and compressive strength) compared with bentonite. The zeta potential of compound binder was lower than that of bentonite under all pH conditions and the contact angle on the surfaces of compound binder and magnetite were smaller in equivalent conditions, which meant the interface energy, capillary attraction energy and viscous energy among the particles were enhanced. Based on the organic binder's polymer chains and the formation of chemical bonds, the house-of-cards structure formed by the compound binder was more stable than that formed by bentonite alone and the bentonite's non-stripped layers were further peeled off which decreased

bentonite particle size and increased surface area. The grain size of bentonite became smaller, surface area increased, and degree of separation improved. Compared to Ca-bentonite or Na-bentonite, Mg-bentonite can increase the decrepitation temperature of green pellets. Mg^{2+} in the montmorillonite interlayers reacted with magnetite during the heating process and formed solid bridges that inhibited the pellet expansion which increased the decrepitation temperature.

Acknowledgments

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