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Effect of carboxymethyl cellulose on the drying dynamics and thermal cracking performance of iron ore green pellets

Xiao-hui Fan, Gui-ming Yang *, Xu-ling Chen, Xiang-ning He, Xiao-xian Huang, Lu Gao

School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, Hunan, China

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ABSTRACT

Carboxymethyl cellulose (CMC) is an efficient organic binder in iron ore pelletization. However, the addition of CMC will reduce the anti-thermal cracking performance of the green pellets prepared. The objective of this article is to investigate the effect of CMC property on the drying dynamics and thermal cracking performance of green pellets. The results show that as the degree of polymerization (DP) and degree of substitution (DS) of CMC increase, drying rate declines and apparent activation energy of second drying stage goes up. When more CMC or CMC with larger DP and DS is added, the green pellets possess better mechanical strength but worse anti-thermal cracking performance. Although CMC decomposes during drying at 300–350 °C, which may destroy the reticulate structure of organic chains, thermal cracking is attributed to high resistance of water/vapor diffusion caused by compact structure of the pellets rather than CMC decomposition.

1. Introduction

Binders are essential to the pelletization of iron ore concentrate in iron & steel industry. The predominant binder applied in preparing green pellets is bentonite owing to its high water adsorption capacity, high binding strength and relatively low market price [1–3]. However, the presence of acid constituents such as silica and alumina is considered undesirable for iron making operations [4,5]. The advantages of organic binder including low dosage and being eliminated during firing provide huge incentives for the development of organic binder. Based on the material source, organic binder for iron ore agglomeration can be mainly divided into coal/petrochemical products [6,7] and natural/modified saccharides. Being natural renewable and friendly to environment, saccharides have been extensively developed, including glucose, corn starch, modified starch, lactose monohydrate, hemicellulose, Peridur, HPMC (hydroxypropyl methylcellulose), CMC (carboxymethyl cellulose), etc. [5,8–12].

CMC has a widespread use in many industrial fields such as food industry, pharmacy, textile and architecture. It is an important cellulose derivative with carboxymethyl groups ($-CH_2-COOH$) bound to some of the hydroxyl groups of the glucopyranose monomers that make up the cellulose backbone [4]. Green pellets added with CMC have good mechanical strength but their anti-thermal cracking performance is not satisfying. At the same iron ore concentrate, binder dosage and pellet moisture content, thermal cracking performance is determined by the CMC property. Literatures on the application of CMC in iron ore pelletization mainly concern the process [13,14] and the interaction mechanism between organic groups and iron ore interface based on colloidal theory [15–17], the quantitative discussions on drying dynamics and thermal cracking performance of green pellets added with different types of CMC have not been reported in details. Since thermal cracking is an outstanding problem for pellets added with CMC especially in shaft furnace process, the essence of thermal cracking should be elucidated as well.

In the present work, one typical magnetite concentrate and three types of CMC were chosen to investigate the effect of CMC property on the drying rate together with drying activation energy of green pellets. In addition, green pellets at different types of CMC and different CMC dosage were prepared to analyze the comprehensive effect of CMC on green pellet quality including mechanical strength and thermal cracking performance. Finally, the essence of thermal cracking was discussed based on our experimental data.

2. Experimental

2.1. Materials

2.1.1. Iron ore concentrate

One iron ore concentrate provided by a particular pelletizing plant in China was used to prepare green pellets for the drying test. Since the raw iron ore in that plant went through milling and magnetic separation during ore beneficiation, the concentrate produced has a fine particle size distribution. Hydraulic sieving result shows that more than 95% of the concentrate has a particle size of −74 μm. The specific surface area was measured at 1730 cm^2/g using Blaine

* Corresponding author. Tel.: +86 731 8830542; fax: +86 731 8710225.
E-mail address: csuygm@sina.com (G. Yang).

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Table 1
Chemical composition and size distribution of iron concentrate (wt. %).

TFe	FeO	SiO_2	CaO	MgO	Al_2O_3	S	LOI	+74 μm	−74 + 44 μm	−44 μm
67.45	26.15	5.07	0.22	0.19	0.24	0.068	0.25	4.95	11.05	84.00

method (National standard GB/T 8074–2008). Main chemical composition and size distribution of the concentrate were given in Table 1, showing a relatively high content of FeO.

2.1.2. Carboxymethyl cellulose

Three types of domestic CMC (CMCD, CMCS and CMCT) were used as binder in the preparation of green pellets. CMCD was supplied by a chemical plant where it was applied to the suppression of iron dust and coal powder. CMCS was purchased from Shanghai Shan-Pu chemical agent company and CMCT was purchased from Tianjin Kermel chemical agent company. DP (degree of polymerization) and DS (degree of substitution) are two important properties of CMC. In this study, DP was measured by an UbbeloHde viscometer using copper ethylenediamine (CED) as a good solvent at 25 °C. This method is based on an empirical formula derived from Poiseuille's law that liquid viscosity is proportional to its flowing time in capillary tube. This empirical formula describes the correlation between liquid viscosity and polymer concentration, and is given in Eq. (1),

$$\eta_{SP}/C = [\eta] + \kappa[\eta]^2 C \tag{1}$$

where η_{SP} is the specific viscosity, $[\eta]$ is the intrinsic viscosity, C is the mass concentration of polymer and κ is a constant. The intrinsic viscosity of three different CMCs was calculated as the intercept of corresponding fitted linear curve in Fig. 1. The DP of three different CMC was afterwards estimated by Mark–Houwink Equation $[\eta] = K(DP)^{\alpha}$, where K and α are the empirical constants. Referring to the Cellulose–CED system, K was taken to be 1.7×10^{-3} g/L and α was taken to be 0.8.

DS of CMC was measured by acid–base titration using pH electrode. 0.200 g purified and dried CMC sample was dissolved carefully in 80 mL distilled water in a beaker under magnetic agitation. After being agitated for 30 min, the pH of solution was modified to be 8 to guarantee that all carboxyl groups existed as –COONa. Then 0.05 mol/L H_2SO_4 was applied to titrate the solution with titration end-point of pH = 3.74 detected by pH electrode. The acid amount needed for the transformation of all –COONa into –COOH can be used to calculate the DS by Eq. (2),

$$DS = \frac{0.162B}{1-0.08B} \quad \text{with} \quad B = \frac{2M(V_1 - V_2)}{m} \tag{2}$$

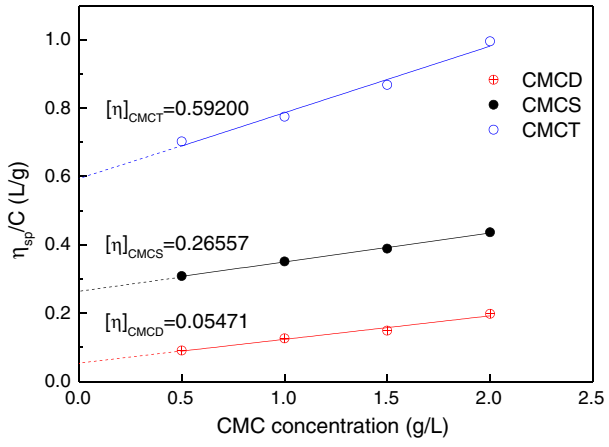

Fig. 1. Correlation between viscosity of CMC–CED solution and mass concentration at 25 °C.

where M is the H_2SO_4 concentration (mol/L), V_1 is the acid volume for titration of CMC solution (mL), V_2 is the acid volume for titration of 80 mL distilled water (mL), and m is the sample mass (g).

Main properties of these CMCs were detected delicately before pelletization and the results were given in Table 2, which shows that CMCT has the largest DP and DS while CMCD is a starch-level CMC.

2.2. Methods

2.2.1. Balling

Preparation of green pellets was conducted in a Φ400 mm disk-balling machine with the side height of 130 mm. Throughout the pelletization, inclination angle was fixed at 45° and rotation speed was fixed at 40 r/min. Weight of each batch was about 1 kg, the balling duration was controlled at 13 min including 1 min for initial nucleation and 2 min for terminal consolidation. During balling, moisture content of each batch was controlled manually at 10.5 ± 0.5% based on our experience (the precise moisture content was obtained by desiccating the sampled green pellets at 105 °C overnight). Green pellets were afterwards screened and sampled to detect mechanical strength and thermal cracking percentage at certain conditions. Meanwhile, one smooth green pellet was selected for drying test on a uniquely designed device. The detail of the drying test is explained in the following part.

2.2.2. Drying of individual pellet

Drying test was conducted in a self-equipped device, the schematic figure of which was shown in Fig. 2. This device, differing from the equipment described in Section 2.2.3, was set to investigate the drying dynamics of a single pellet rather than pellet bed. A Φ20 mm × 1500 mm quartz tube containing heat-conducting porcelain balls was placed into a horizontal tube furnace. One end of the quartz tube was connected to a mini air-blower and the other end aimed closely at the pellet which was put onto an electronic balance with 0.001 g accuracy. The air flow rate was controlled at 1.0 m^3/h by a rotameter between air-blower and quartz tube. Prior to drying, air-blower was started and the quartz tube was heated by the furnace at certain heating power to obtain hot outlet gas. After a period of heating time, a thermometer was placed at the exit end of quartz tube to detect the outlet gas temperature. Drying of individual green pellet would not begin until the temperature became steady. For each batch of pellets, one smooth green pellet of Φ12.5 ± 0.1 mm detected by a vernier caliper was selected and quickly placed onto the electronic balance, and the weight of this pellet varying with time during drying was then recorded.

Since blowing air toward the pellet impacts the balance reading, the weight of pellet varying with time was calibrated by the reading difference between a dried pellet having the same diameter at the absence and the presence of blowing air.

2.2.3. Thermal cracking detection

Thermal cracking was detected in a Φ650 × 1000 mm vertical tube furnace (simulate the shaft furnace process), as shown in Fig. 3. A Φ80 × 1200 mm stainless steel pipe containing porcelain balls was

Table 2
Main properties of three CMC.

Binder type	Degree of polymerization	Degree of substitution
CMCD	76	0.46
CMCS	552	0.51
CMCT	1504	0.65