Powder Technology 340 (2018) 17–25

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Binding mechanisms of polysaccharides adsorbing onto magnetite concentrate surface

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ARTICLE INFO

Article history:
Received 19 April 2018
Received in revised form 8 August 2018
Accepted 9 September 2018
Available online 10 September 2018

Keywords:
Binding ability
AFM
Carboxymethyl starch
Carboxymethyl cellulose
Guar gum
Pelletization

ABSTRACT

Polysaccharides have been widely investigated in past decades as alternative binders in iron ore pelletization. This study aims to further clarify adsorption mechanisms and binding characteristics of three representative polysaccharides: carboxymethyl starch (CMS), carboxymethyl cellulose (CMC) and guar gum (Guar). FTIR analysis and zeta potential measurements indicate that CMS and CMC can adsorb onto magnetite concentrate via carboxymethyl and hydroxyl groups, while guar gum through the hydroxyl group. Chemical interaction and hydrogen bonding are dominant interactions between binders and magnetite. AFM images show that a continuous thick film is generated after the adsorption of CMS. CMC adsorbs onto magnetite surfaces in the shape of fibrous structure, forming a much thinner layer. The adsorption layer of Guar is the thinnest. Chemical interaction force is the main contribution for adhesive force. Equilibrium adsorption data of these binders can be described by the Freundlich isotherm. Chemical adsorption is the dominant mechanism and adsorption capacity can represent adhesive force. Pelletization results verify that wet strengths of pellets produced with Guar are the largest, followed by CMC and CMS. Viscous force rather than adhesive force is the determining contribution to wet strength. Binder cohesive force and adhesive force are significant contributions to dry strength. Solution viscosity and adsorption capacity are primary criteria to evaluate binders. The combination usage of these binders is recommended to reach the required wet and dry strengths at a lower cost.

1. Introduction

Low grade iron ores contain a great deal of gangue minerals, particularly silicates but potentially including carbonates as well. Fine grinding is typically required to liberate the magnetite from associated gangue minerals. Pelletization is a method of agglomerating fine-grained, iron-rich concentrates into an adequate product (pellet) for blast furnaces and direct reduction furnaces [1]. Binder is an essential material for improving mechanical strengths of pellets in pelletization [2]. Bentonite is the traditional binder for iron ore pellets due to its high binding ability and relatively low market price. However, acid constituents in bentonite such as silica and alumina are considered as contaminants for iron making [3,4]. Therefore, organic binders are promising substitutes for bentonite as they burn out during roasting with virtually no residue [5,6].

Starch, cellulose and guar gum (Guar) are three typical polysaccharides, which have been extensively used in mineral processing due to their low-cost, renewability and nontoxicity [7–10]. Starch is made of the α-D-glucose and cellulose of β- D-glucose [7]. Carboxymethyl starch (CMS) and carboxymethyl cellulose (CMC) are chemically modified starch and cellulose through etherification reactions, respectively. Guar gum (Guar) is a branched polysaccharide in which galactomannan is the basic unit [11,12]. These polysaccharides have also been tested as organic binders in pelletizing according to previous studies [13,14]. Hasas et al. investigated the relations of plate water absorption test (PWAT) value, slurry viscosity and tensile strength to physical strengths of pellets with the addition of CMC, corn starch or Guar [15]. They found the most effective organic binders were characterized by medium PWAT values (>500 and < 10,000), high slurry viscosities (>75 cP at 6 pct solids) and high adhesive tensile strengths (>4 kg/cm^2). Yang et al. studied two CMC with different substitution degrees and found that CMC with a higher substitution degree exhibited a better binding performance [16]. Yuan et al. modified the CMS with nano-$CaCO_3$ and obtained better binding results [17]. Besides, the applications of corn starch and CMC were also conducted in conjunction with bentonite [18,19].

Nevertheless, above studies mainly focus on strengths of pellets with CMS, CMC or Guar. The differences in function groups, electrical properties, solution viscosities and adhesion abilities of binders have not been fully investigated. What's more, the differences in adsorption capacity, adsorption mechanism and morphological changes after the adsorption

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https://doi.org/10.1016/j.powtec.2018.09.021
0032-5910/

are rarely mentioned. Besides, binders are required to provide sufficient drop strength of wet pellets and compression strength of dry pellets to survive in handling, transporting, drying in grate-kiln process or travelling grate process [20]. However, the relations of adsorption capacity and adhesion properties of binders to wet and dry pellet strengths have not been specified. Thus, it's necessary to ascertain the contributions of two different forces to strengths of dry and wet pellets (e.g. particle-binder forces and internal cohesive forces between binder molecules).

Therefore, in our present study, our objectives here are to (1) characterize the function groups, zeta potentials, solution viscosities and adhesion properties of CMS, CMC and Guar; (2) determine surface properties of magnetite concentrate adsorbed with these binders, such as zeta potential and morphological changes; (3) measure adhesion abilities of magnetite concentrate coated with different binders and deduce adhesive forces between particles and binders; (4) obtain the adsorption mechanism of CMS, CMC and Guar onto magnetite surfaces and confirm the relation between adsorption capacity and adhesive force; (5) ascertain which interaction forces (capillary force, adhesive force, viscous force, cohesive force and so on) are main contributions to strengths of wet and dry pellets, acquire criteria to evaluate the binding ability of binders and provide the guidance for rational usage of CMS, CMC and Guar at a low cost.

2. Materials and methods

2.1. Materials

The iron ore concentrate (magnetite concentrate) in this study is provided by Nanfen iron mine. Its main chemical compositions were described in our previous study [3]. The TFe of magnetite concentrate is 67.42% and silica is the main gangue constituent. It has a particle size of 87.90% passing 74 μm (200 mesh). Industrial grade CMS, CMC and Guar are obtained from domestic companies in China.

2.2. Methods

2.2.1. FT-IR spectroscopy

The FTIR analysis was carried out by Nicolet 380 FTIR spectrometer. Solid samples were evenly blended with potassium bromide and then compressed for 1 min to form uniform and transparent tablets. After that, tablets were scanned by infrared wave varying from 400 cm^{-1} to 4000 cm^{-1}.

2.2.2. Zeta potential measurements

Zeta potentials of samples were measured by Malvern Instrument Nano-ZS90 zeta potential analyzer. Concentrations of CMS, CMC and Guar solutions are 100 $mg \cdot L^{-1}$.The magnetite concentrate was finely ground further to 5 μm in an agate mortar prior to measurements. Suspensions of magnetite concentrate coated with different organic binders were prepared by adding 50 mg sample into 50 mL binder solution at different pH values. The solution pH was regulated with 0.10 $mol \cdot L^{-1}$ HCl or 0.10 $mol \cdot L^{-1}$ NaOH. The measurement procedure was described in previous study [3].

2.2.3. Viscosity measurements

A Brookfield-DV2T type viscometer was used to measure viscosities of different binder solutions. The solution was prepared by fully dissolving predetermined amount of binder in distilled water. Each measurement was repeated three times and the final viscosity was provided by the average value.

2.2.4. Atomic force microscopy imaging and force analysis

In the field of mineral processing, atomic force microscopy (AFM) is an established tool to analyze the surface properties of minerals [8,21]. To further characterize the morphological changes and surface force differences of magnetite concentrate particles coated with three different binders, AFM analysis was implemented. The magnetite particles (<2 μm) were firstly added into 40 $mg \cdot L^{-1}$ binder solution and dispersion was achieved by ultrasonic treatment for 5 min. The dispersed suspension was centrifuged at 8000 rpm for 5 min and the supernatant was discarded. Distilled water was then added into the remaining ore samples and the suspension was further dispersed for 5 min in the ultrasonic bath. The supernatant of above remaining ore samples was taken for AFM analysis to obtain mapping and force measurement results of magnetite concentrate coated with different binders. Several drops of the supernatant solution were deposited onto a clean mica slide. The mica slide was then placed in a dessicator at room temperature for 24 h. AFM analysis was conducted by Multimode 8 SPM (Brucker), which was operated in Peakforce Tapping QNM mode. Silicon nitride AFM probe (SNL-10 type) with spring constant of 0.233 N/m was used for AFM imaging and force analysis. The images were obtained at 512 lines\scan at 0.9 Hz scan rate to secure the high imaging resolution and mechanical properties mapping. Images were collected and presented as 2D Height and 3D Height images. Force curves between the AFM probe and magnetite concentrate coated with binders were acquired in dry air. The AFM measurements were conducted at room temperature.

In addition, to characterize adhesion properties of binders, several drops of the binder solution (40 $mg \cdot L^{-1}$) were deposited onto a clean mica slide. The mica slide was then placed in a dessicator at room temperature for 24 h. Force curves of binders deposited on mica substrate were also obtained by AFM in dry air.

2.2.5. Adsorption experiments

Adsorption studies were performed using the batch depletion method, which was described in our previous study [17]. The binder concentration was analyzed by the phenol-concentrated sulfuric acid method [22]. The binder concentration after adsorption was measured by a model 722 N visible spectrophotometer at a wavelength of 490 nm. The adsorption capacity (per gram of magnetite concentrate) of binder was calculated according to the following equation:

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (1)$$

where q_e is the equilibrium adsorption capacity of the sample ($mg \cdot g^{-1}$); C_0 and C_e ($mg \cdot L^{-1}$) are the concentrations of binders in the initial and equilibrium solution samples, respectively; V is the total volume of the binder solution (L) and m is the mass of the adsorbent (g).

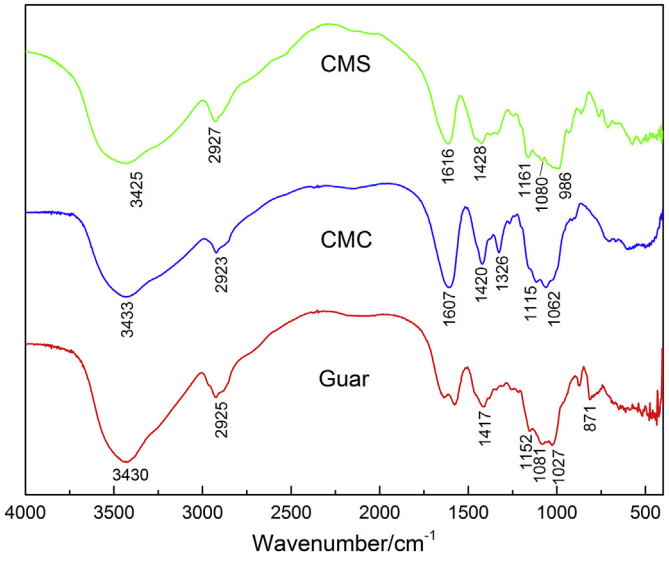

Fig. 1. FTIR spectra CMS, CMC and Guar.