



Influences of different fractions of extracellular polymeric substances on the co-slurrying properties of sewage sludge with coal and petroleum coke



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ABSTRACT

Coal–sludge–slurry (CSS) and petroleum coke–sludge–slurry (PCSS) can be used as liquid fuel or gasification material, thus providing a new approach for recycling sewage sludge without pre-drying. Given that slurrying properties directly influence the industrial application of CSS and PCSS, this study investigated the influences of different fractions of extracellular polymeric substance (EPS) on the slurrying viscosity (η_{100} , average viscosity at a shear rate of 100 s^{-1}), maximum solid concentration (SC_{\max}), and rheological behaviors of CSS and PCSS. Sodium methylene bis-naphthalene sulfonate (NNO) and sodium lignosulfonate (SLS) were used as the dispersants during CSS and PCSS preparation. At the two dispersants conditions, when raw sludge was mixed with coal slurry at a sludge-to-coal ratio of 17:100, SC_{\max} decreased from 52.40% (coal slurry without sludge) to 42.99% and 42.32%, respectively. Similarly, when raw sludge was mixed with petroleum coke slurry with NNO and SLS as the dispersants, SC_{\max} decreased from 72.25% to 61.59% and 61.28%, respectively. The high amounts of trapped water in the sludge and the strong linkage between sludge flocs decreased the SC_{\max} of the slurry. After loosely and tightly bound EPS (LB-EPS and TB-EPS, respectively) were removed, the SC_{\max} of CSS and PCSS increased again because dead water, which increased the water content of the slurry system but did not act as a lubricant or buffer, was removed with the removal of EPS. LB-EPS had more influence on SC_{\max} than TB-EPS because LB-EPS trapped more water than TB-EPS. Thus, more trapped water was removed with the removal of LB-EPS. Shear stress versus shear rate curves were fitted using the Herschel–Bulkley model. The rheological parameters of CSS and PCSS with a η_{100} of 1000 mPa s were obtained by linear interpolation method. The rheological behaviors of CSS negligibly changed after the removal of EPS. The yield stress and pseudoplasticity of PCSS, however, increased and decreased, respectively. The rheological behaviors of PCSS likely changed after the removal of EPS because sludge particles could no longer link easily to form a spatial structure. Moreover, hydrophobic agglomerations between petroleum coke particles increased in the PCSS system.

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1. Introduction

Sewage sludge is composed of solid particles, microbes, and organic matter. These components flocculate and settle down during municipal wastewater treatment. Sludge is potentially harmful because in addition to its high content of water, organic matrices, and microorganisms, it also contains pathogens, heavy metals, salts, and organic toxins. Hence, sludge must be properly handled to avoid secondary environmental pollution. Energy recovery, which converts energy-containing sludge substances while simul-

taneously controlling sludge pollution and recycling sludge, is the most popular method for sludge disposal. The main methods for energy recovery from sludge include thermal utilization (combustion [1], gasification [2], and pyrolysis [3]), digestion for biogas [4,5], carbonization for solid fuel [6,7], and utilization as coal–sludge–slurry (CSS) [8,9].

In CSS technology, sludge is mixed into coal water slurry (CWS), which can be used as liquid fuel to replace oil or as gasification feed material, i.e., sludge is simultaneously disposed and recycled in the form of slurry fuel. CSS technology has a distinct advantage over other methods: the moisture content of sludge does not require strict control. Therefore, sludge does not require drying and deep dewatering prior to its preparation into CSS, thus decreasing the

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cost of sludge treatment. In addition, when CSS is used in combustion or gasification, some synergistic effects occur between the sludge and coal. In the mono-combustion of coal, the addition of sludge to coal enhances fuel combustion by decreasing fuel ignition time, reducing the ignition temperature of the fuel [10,11], and increasing the conversion rate of the combustible materials in the fuel [12]. Sludge can partly replace coal during combustion with a remarkable energy-saving cost [13,14]. The co-gasification of sludge with coal may be energetically advantageous because the tar yield decreases and H₂ and CO yields increase in the gas [15]. Zhao et al. [16] investigated gaseous pollutant emissions from the combustion of CSS with different sludge ratios in a commercial circulating fluidized bed incinerator. When the sludge ratio was less than 30%, the emitted flue gases contained nitrogen oxide (NO_x), sulfur oxide (SO_x), PAHs, PCBs, and PCDD/Fs at levels that meet local and EU standards. Liu et al. [17] showed the good operating characteristic of oil sludge co-fired with CWS in an industrial internal circulating fluidized bed boiler. The combustion efficiency of the boiler was 92.6% and boiler efficiency was 82.2%. Meanwhile, all SO_x, NO_x, carbon monoxide (CO), and heavy metal emission levels met the local current environmental requirements. Therefore, CSS is a technically feasible, energy-saving, and environmentally friendly method for sludge recycling.

Slurrying properties are highly crucial during the preparation, pumping, atomization, and storage of coal slurry [18]. Wang et al. [8] and Li et al. [19] studied the solid loading, apparent viscosity, stability, and rheological and thixotropic behaviors of CSS. They found that CSS exhibits pseudoplastic behavior, thixotropic hysteresis, and good stability. These characteristics guarantee that solid–liquid separation does not occur easily during the storage of the two-phase slurry. However, CSS has high slurrying viscosity when directly prepared with untreated raw sludge and coal, hindering its disposal in a large volume. Wang et al. [8] added sludge (moisture content of ~75%) to CWS at a sludge-to-coal ratio of 15:100. They reported that the maximum solid concentration (SC_{max}) of the slurry decreased by 9.5–12.5%. Similarly, Li et al. [19] reported that SC_{max} decreased from 73% to 59% when sludge (moisture content of ~82%) was added to CWS at a sludge-to-coal ratio of 16.6:100. Wang et al. [20,21], Liu et al. [22], and Ma et al. [23] found that after the addition of sludge, petroleum coke–water slurry (PCWS) exhibited enhanced pseudoplastic and thixotropic behaviors and significantly improved stability. The apparent viscosity of PCWS, however, greatly increased whereas its slurrying ability decreased.

Previous studies have indicated that sludge flocs are the main factors that increase the viscosity and decrease the solid concentrations of CSS or petroleum coke–sludge–slurry (PCSS). To improve the slurrying ability of CSS, Wang et al. [24–26] and Liu et al. [27,28] pretreated sludge via ultrasonic, alkaline, thermal, and mechanical grinding methods to disrupt sludge flocs and decrease floc size, and then decreased the apparent viscosity of CSS. However, the action mechanisms of sludge flocs on the slurrying properties of CSS were not clearly revealed.

A sludge floc is composed of loosely bound EPS (LB-EPS), tightly bound EPS (TB-EPS), and core pellet fractions from the outer to the inner layers of the floc matrix [29,30]. These three components have drastically different morphology, volume, density, porosity, hydrophilicity, and water retention capacity [31–33]; therefore, they exert different influences on the co-slurrying properties of sludge with coal and petroleum coke. Information on the influences of the three fractions on the slurrying properties of CSS or PCSS, however, is limited. In the present study, the three sludge floc fractions were gradually removed, the slurrying performances of CSS and PCSS prepared with EPS-removed sludge were determined, and then the influences of different fractions of EPS on the slurrying properties of CSS and PCSS were evaluated. The

results obtained from this study will contribute to elucidating the slurrying mechanism of CSS and PCSS.

2. Experiment and methods

2.1. Materials

2.1.1. Sewage sludge, coal, petroleum coke

Dewatered sludge was selected as the sewage sludge sample and was collected from a municipal wastewater treatment plant located in Hangzhou, China. This plant treats approximately 500,000 m³/d of industrial and domestic wastewater using anaerobic–anoxic–oxic technique. The sludge sample was dewatered using a press filter and had a moisture content of 82.41%. The sludge sample was then stored at 4 °C before use. Brown coal mined from Xinjiang District, China, and petroleum coke from TANECO, Russia, were selected as slurrying components. Prior to preparation into slurry, coal and petroleum coke were ground and sieved to a particle size of less than 150 μm.

Proximate analyses were conducted using a drying oven and muffle furnace in accordance with the national standards of China (GB/T 212–91). Ultimate analyses were conducted using an element analyzer (Vario EL III, Elementar, Germany) in accordance with the national standards of China (GB/T 476–2001). Calorific values were determined using an automatic calorimeter (ZDHW-6G, Hebi Huatai, China) in accordance with the national standards of China (GB/T 213).

2.1.2. Dispersants

The dispersant is an important component of coal slurry or petroleum coke slurry. By decreasing aggregation forces between solid particles and increasing surface charges, the dispersant decreases the viscosity and enhances the stability of slurry. Sodium methylene bis-naphthalene sulfonate (NNO) and sodium lignosulfonate (SLS), the two most commonly used dispersants for coal and petroleum coke slurry preparation, were selected as the dispersants in this study. The chemical structure of the dispersants is shown in Fig. 1.

2.2. EPS removal

LB-EPS and TB-EPS were removed from sludge via a modified heat method [32,33]. An exact amount of 5.68 g sludge (with 1 g dry matter) was first diluted to a volume of 30 mL using 0.05% NaCl solution. The mixture was then stirred by an electric agitator (JB90-SH, Shanghai Biaomo, China) at 300 rpm for 5 min. The sludge mixture was then diluted with NaCl solution, which was pre-heated to 80 °C, to a volume of 100 mL. The sludge suspension was then immediately sheared by an electric agitator at 600 rpm for 2 min, and then allowed to stand for 30 min. Then, the upper liquid phase was cautiously poured out, and the remaining phases were resuspended to a volume of 100 mL. The upper liquid phase was again carefully poured out after 30 min of standing. The remaining phases were centrifuged at 4000g for 10 min by a centrifuge (H-1600RW, Shanghai Lixinjian Co., China). TP sludge, which was obtained after the removal of LB-EPS, remained at the bottom of the centrifuge tube. TP sludge was composed of TB-EPS and the core pellet. To further remove TB-EPS, TP sludge was resuspended to a volume of 100 mL using 0.05% NaCl solution. The sludge suspension was heated to 70 °C in a water bath oscillator at 150 rpm for 30 min. Then, the sludge suspension was allowed to stand for 30 min at room temperature. The transparent upper liquid phase was cautiously poured out, and the remaining phases were resuspended to a volume of 100 mL and allowed to stand for 30 min. The upper liquid phase was again carefully poured

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