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Effect of oily sludge on the rheological characteristics of coke-water slurry

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HIGHLIGHTS

- Oily sludge and high-sulfur-petroleum coke are mixed to prepare coke-oily-sludge slurry (COSS).
- Different methods of adding oily sludge have great influence on the slurryability.
- A modification method for oily sludge is introduced.
- Added modified oily sludge (MOS) increase viscosity, yield stress, thixotropy, and stability of COSS.
- The MOS transforms the COSS from a dilatant fluid to a pseudoplastic fluid.

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ABSTRACT

In this study, the co-slurryability of hazardous solid waste—oily sludge and high-sulfur-petroleum coke (HSPC), in an oil refinery was evaluated. The effects of pre-treatment and method of adding oily sludge, on the co-slurryability of coke-oily-sludge slurry (COSS); maximum solids loading, rheological characteristics, and stability of slurry, were thoroughly investigated. The experimental results showed that with 5.0 wt% adding ratio of modified oily sludge (MOS), COSS with a maximum solids loading of 68.7 wt% was obtained, and mostly corresponded to coke-water slurry (CWS) with a maximum solids loading of 68.5 wt%. As the percentage of MOS increases, the yield stress and thixotropic loop area of COSS also gradually increases. COSS is a pseudoplastic fluid, and shows a different behavior as compared to CWS (with shear-thickening behavior). MOS played the role of a stabilizing agent, and therefore the storage time of COSS could be prolonged to more than 15 days.

1. Introduction

Oil is one of the most important sources of energy in the world. However, with the exploitation and utilization of oil, an excess of oily sludge is being produced [1,2]. Oily sludge contains a lot of heavy metals and toxic substances such as benzene, phenol, anthracene, and pyrene [3,4]; therefore, it is hard to dispose them and has been listed as a hazardous organic waste by regulating agencies [5]. The common disposal methods for oily sludge include solvent extraction [6,7], biological treatment [8–10], combustion, landfill, and dehydration [11]; however, these methods have several disadvantages such as high costs of waste disposal, complicated processes, and secondary pollutions. Further, oily sludge contains a lot of unused petroleum ingredients, and therefore it will be a huge waste of resources if they are not used properly.

Petroleum coke is an important by-product of oil refinery process, and its properties are similar to oily sludge; it is produced by delayed coking process, and often used for producing electrodes and fuels [12]. The annual production of petroleum coke increases every year due to the increasing demand for heavy oil. However, common disposal methods for petroleum coke are inefficient to handle such a growth [13–16]. In particular, for high-sulfur-petroleum coke (HSPC) with a sulfur content of 2–7 wt%, large amounts of toxic sulfur dioxide (SO_2) are produced during its combustion [17]. Consequently, the large-scale production of HSPC is restricted because of air pollution.

A new concurrent disposal method for oily sludge and HSPC may involve the preparation of coke-oily-sludge slurry (COSS), which could be processed in entrained-flow gasifiers to achieve the co-gasification. This method is expected to provide a good strategy for solving the waste disposal problems of both these

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hazardous organic wastes. HSPC has a high calorific value and low ash and volatile contents, which are beneficial to its combustion and gasification [14,18]. Moreover, the sulfur content in HSPC can be effectively reduced by converting it into hydrogen sulfide (H_2S) through gasification, which can then be further recycled as brenstone. Thus, gasification can effectively reduce the production of SO_2, and thereby eliminate the secondary pollution hazards. The preparation of COSS does not require dehydration and fractionated treatments of oily sludge, because anyway a certain amount of water is needed during the slurry gasification. Furthermore, heavy metals present in oily sludge can be effectively removed as ash [19]. Therefore, HSPC and oily sludge can be utilized together in an environmentally friendly manner, and not only could reduce the environmental load, but also could bring huge economic benefits.

The studies on the application of sewage sludge in forming co-slurries with coal, and using petroleum coke as a partial substitution for coal in fuel slurry have been reported [22–27]. However, studies related to COSS has not been reported yet. Further, COSS should exhibit suitable rheological behaviors and good stability during its storage and transfer through pipelines [20,21]. Herein, we have prepared COSS by mixing oily sludge and HSPC with the help of additives and used different methods for adding oily sludge. Further, the effects of modified oily sludge (MOS) on apparent viscosity, yield stress, thixotropy, rheological type, and stability of COSS have been evaluated. Finally, the formation mechanism of coke-oily-sludge slurry has been discussed.

2. Experimental

2.1. Materials and preparation

HSPC and oily sludge from Gaoqiao Petrochemical Company (located in Shanghai, China) were chosen for this study. Proximate and ultimate analysis and properties of the oily sludge are shown in Tables 1 and 2, respectively. The moisture content of the oily sludge is approximately 60.0 wt%, and its ash and volatile matters are significantly higher than those of HSPC. However, the calorific value of oily sludge as-received basis is so high that it can be reused, and therefore has a strong potential to significantly enhance the economic returns. Sodium naphthalene sulfonate formaldehyde condensate (MF) was used as the dispersing agent with a constant dosage of 1.0 wt% (on the basis of the weight of HSPC).

First, HSPC was ground to less than 3 mm particles in a hammer crusher, and then dried in a dry oven at 105 °C for 2 h. The dried HSPC was comminuted in a ball mill for 5 min and 2 h to obtain two particle size distributions. Iron sulfate ($Fe_2(SO_4)_3$, 3.0 wt% of oily sludge) was added to oily sludge in order to damage the stable water–oil-solid-multiphase structure. The resulting sludge was named as MOS. The maximum solids loading is defined as the solids content of slurry with a apparent viscosity of (1000 ± 100) mPa s at a shear rate of 100 s^{-1}. The water in oily sludge is accounted for the quantity of water in the resulting COSS. The solids content of COSS is defined as:

Table 2
Properties of oily sludge.

Parameters	Values
Viscosity/mPa s	273.6
Volatile hydrocarbon content (105 °C)/wt%	17.63
Nonvolatile hydrocarbon content/wt%	14.98
Solids content/wt%	7.53
pH	7.4

$$s = 1 - w, \tag{1}$$

where s is the solids content of COSS (wt%), and w is the water content of COSS (wt%). Because of the high calorific value of oil, the oil of oily sludge contributes to the total solids content of COSS.

2.2. Analytical procedure

The rheological property measurements of COSS were performed using Malvern Bohlin CVO rheometer. The temperature was controlled at 25 ± 0.1 °C. The apparent viscosity of COSS was measured as follows: shear rate was smoothly increased from zero to 100 s^{-1}, and then kept constant at 100 s^{-1} for 30 s for further viscosity measurements. The yield stress of COSS was determined as follows: the critical stress at which the suspension begins to flow was measured, such as the point at which slope of the strain (as a function of shear stress) changes from a very low value to a high value, or a rapid reduction in the measured viscosity occurs [28]. The thixotropy of COSS was determined as follows: the shear rate was gradually increased from zero to 170 s^{-1}, and then decreased from 170 s^{-1} to zero. The area of thixotropy loop was automatically calculated by the computer.

Another important property of slurry is its stability over a time period. The stability of slurry was measured according to “glass rod penetration test” described by Qiu et al. [29]. The COSS was poured into a glass cylinder (3 cm in diameter) to 15 cm in height at room temperature. A glass rod (5 mm diameter, 20 g) was spontaneously dropped from the slurry surface to the bottom of cylinder at a certain time interval, and it stopped when the tip got in contact with the hard sediment. The time taken by slurry to hold without hard sediment is defined as the storage time. Li et al. [20] using a apparatus defined the settling index as:

$$\eta = c_1/c_4, \tag{2}$$

where η is the stability index, c_1 is the top layer (120 mm), and c_4 is the bottom layer (60 mm) after a certain period (%). The device is made from Plexiglass, with a diameter of 25 mm and a height of 300 mm. Samples can be withdrawn from four different sections using the interlinking between adjacent sections. If the stability index approaches a value of 1, the slurry has better stability characteristic. The top and bottom layers were dried and weighed for calculation of the solids ratio according to Eq. (2).

Table 1
Proximate analysis and ultimate analysis of HSPC and oily sludge.

Sample	Proximate analysis (wt%)				Ultimate analysis (wt%)[c]				Q_d[d] (MJ kg^{-1})
	M_{ar}[a]	A_d[b]	V_d[b]	FC_d[b]	C_d	H_d	N_d	$S_{t,d}$	
HSPC	13.01	0.15	10.68	89.16	91.08	2.54	1.08	4.88	35.02
oily sludge	59.86	8.61	88.09	3.30	33.16	7.18	0.45	0.68.	17.73

[a] M_{ar} refers to moisture on a received basis.
[b] $A_{d,}$ V_d and FC_d refer to ash, volatile and fixed carbon on a dried basis.
[c] Ultimate analysis is also on a dried basis.
[d] Q_d refers to the calorific value: HSPC is on a dried basis, oily sludge is on a received basis.