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Investigation of fluctuation behavior in viscosity of coal slags used in entrained-flow gasifiers

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ABSTRACT

Entrained-flow gasification has attracted extensive attention because of its clean and efficient utilization of coal as well as flexible application in industry for power generation and chemical production. Numerous theoretical and experimental investigations on slag flow in entrained-flow gasifiers have been performed to ensure a smooth operation, but an unscheduled shutdown due to slag tap blockage remains an ongoing challenge. A fluctuation phenomenon of slag viscosity gives a rise in the risk of slag tap blockage. In this work, three Chinese coal slags with low silicon content and high iron content were used to investigate the viscosity fluctuation phenomenon. It was found that the crystalline phases and suspended bubbles can cause the fluctuation phenomenon. The fluctuation degree is related to the volume fraction of crystalline phases and the crystallization rate. In the search for the mechanism of the viscosity fluctuation, an in-situ observation using a high temperature stage microscope system (HTSM) in combination with XRD and SEM analyses was carried out. In addition, the viscosity of investigated slags with the suppression of solid phases as well as the phase distribution at high temperatures was calculated. Based on a comprehensive analysis of the results, a possible mechanism has been proposed that the viscosity fluctuation is attributed to an instant local change in the macrostructure such as the deformation of suspended bubbles, the change of the orientation of acicular crystals and the interaction of the acicular crystals and suspended bubbles.

1. Introduction

Entrained-flow gasification is considered as a promising coal gasification technology because of its high efficiency and environment-friendly feature [1]. Entrained-flow gasifiers usually operate at high temperatures, so it is necessary to ensure the stability of equipment as well as the smooth slagging condition [2]. Viscosity is an important parameter to determine the slagging situation, the viscosity of < 25 Pa·s is desirable for entrained flow gasifiers [3]. Considerable efforts have been made to study the factors which influence the slag viscosity [4]. At a given temperature above the liquidus temperature, slag viscosity mainly depends on the bulk composition of slag [5]. At temperatures below liquidus temperature the slag type is generally divided into glassy and crystalline slag according to the viscosity-temperature characteristics. For glassy slag, the viscosity gradually increases with decreasing temperature. In contrast, the viscosity of crystalline slag increases rapidly when the temperature decreases to the temperature of critical viscosity [6,7]. Kong et al. [8] investigated the effect of cooling rate on both glassy and crystalline slag viscosity. The gasification atmosphere is another variable which may affect slag viscosity. Schobert et al. [9] found that atmosphere can also influence the viscosity of slags containing iron.

The presence of crystalline phases may cause a slag tap blockage, so it is necessary to study the crystallization characteristics. Francis et al. [10] used differential thermal analysis (DTA) to investigate crystallization kinetics of blast furnace slags. Seebold et al. [11] studied the crystallization of coal ash-slags by means of DTA. Wang et al. [12] studied crystallization behavior of glass ceramics by means of differential scanning calorimetry (DSC). Xuan et al. [13] investigated crystallization characteristics using DSC and the single hot thermocouple

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technique (SHTT) to observe crystalline morphology. Confocal laser scanning microscopy (CLSM) has been widely used in many fields [14] for in-situ studies on crystallization. Another method for in-situ study was high temperature stage microscope system (HTSM) [15].

Based on the complexity of Fe which has various valence states, many researchers also investigated the influence of Fe [16–18]. Shen et al. [19] studied the effect of cooling rate on the crystallization process of iron-rich slags. Xuan et al. [13] used six synthetic slags with different Fe_2O_3 contents to study the influence of Fe_2O_3 and atmosphere on crystallization characteristics. It was found that increasing iron oxide could strengthen crystallization tendency, whereas the reducing atmosphere could weaken crystallization tendency.

In addition to the investigation of crystallization, much research has been conducted to estimate the viscosity of solid-liquid mixtures by developing models [20–22]. In those models, the suspension viscosity is described by linking the volume fraction of solid to the relative viscosity. The influence of the shape and size of solid particles on suspension viscosity was also investigated [23–25]. Zhou et al. [26] found that non-spherical particles had remarkable effect on suspension viscosity and with the increase of aspect ratio, the suspension viscosity markedly increased.

Aside from the model development for solid-liquid mixtures, many researchers studied the viscosity of gas-liquid two-phase even gas-solid-liquid three-phase mixtures [27–29]. Mitrias [30] found that bubbles could play different roles in the rheology of the suspension. When the bubbles are assumed to be rigid fillers, the presence of bubbles could increase the viscosity. On the contrary, deformable bubbles could lead to a decrease in the viscosity. Pang et al. [31] investigated the mechanism how bubbles influence the apparent viscosity. The studies showed that volume fraction and capillary number were two factors that have a great effect on the apparent viscosity. Zhang et al. [32] studied the effects of bubbles in coal ash slag. It was found that bubbles inside slag could decrease the slag viscosity. Therefore modified models are required to predict the liquid slag viscosity. Vona et al. [33] investigated the multiphase rheology of magmas and demonstrated that the presence of pores has a major impact on the rheological response and may produce a remarkable decrease of the viscosity.

The viscosity fluctuation phenomenon may occur due to the complex dependence of suspension viscosity. Liu et al. [34] observed the viscosity fluctuation behavior of coal slags with high content of calcium and low content of silicon, and they found that adding silica could practically eliminate the viscosity fluctuation phenomenon. However, the mechanism of viscosity fluctuation phenomenon still remains unclear. Investigation of viscosity fluctuation is limited in the literatures. In this paper, under continuous cooling condition the viscosity fluctuation was investigated for three Chinese coal slags ZF (Zhengfang), TKX (Tuokexun) and NH (Nanhu), all of which contain high content of iron and low content of silicon. The slag TKX displayed a fluctuation phenomenon during the whole cooling process and was employed to further study the influence of different cooling rates and atmospheres on viscosity fluctuation phenomenon. The viscosity of the investigated slags without suspended crystals and gases (i.e. the crystalline phases are assumed to be fully suppressed and the suspended gases are also assumed to be completely removed) was calculated as a reference viscosity. In order to study the mechanism of viscosity fluctuation during the viscosity measurement, we also observed the crystallization process under different atmospheres by means of an in-situ high temperature stage microscope (HTSM). Crystalline phases were identified by X-ray diffraction (XRD) and the morphology was observed by scanning electron microscope (SEM). The phase distribution with respect to temperature was also calculated with FactSage using the thermodynamic databases of FToxid and FactPS.

Table 1
Chemical composition of different coal ashes.

Samples	Chemical composition/*wt*%							
	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	K_2O	Na_2O	SO_3
ZF	29.81	17.56	18.08	15.71	7.81	0.10	3.41	7.51
TKX	27.61	14.29	7.93	26.72	3.90	0.68	8.53	10.33
NH	17.69	12.96	28.24	11.15	5.87	0.30	3.73	20.05

2. Materials and methods

2.1. Preparation of coal ash samples

In this study, three Chinese coals ZF, TKX and NH were chosen. A muffle furnace (Germany, Nabertherm, LVT 15/11/P330) was used to prepare coal ash samples at 815 °C under air atmosphere. The ash powders of smaller than 0.1 mm were prepared for further analysis. According to Chinese standard procedure GB/T1574–2007, the chemical compositions of coal ash samples were analyzed by X-ray fluorescence (America, Thermo Fisher Scientific ARL Advant'X Intellipower TM 3600) and the results were summarized in Table 1. To obtain the temperature for the pre-melting process, ash fusion temperatures (AFTs) were also analyzed by a 5E-AF4000 ash fusion point determination meter (Changsha KaiYuan Instruments Co. Ltd), as shown in Table 2.

2.2. Viscosity measurements

A RV DVIII high temperature rotational viscometer (American firm Theta Industries) was used to determine the viscosity, and the schematic diagram for the experimental setup is shown in Fig. 1. The viscosity resolution is ± 1%. The experiments were carried out under nitrogen and reducing ($V(CO_2)$: $V(CO)$ = 40:60) atmosphere respectively according to Chinese standard procedure GB/T31424–2015.

As a first step, coal ash sample of 80–90 g was placed into a corundum crucible and pre-melted in a high-temperature furnace under air atmosphere. The slag sample obtained (about 40–45 g) was placed into another corundum crucible fixed by the corundum stents inside the furnace. Then the entire system kept vacuum-pumping for about 5 mins. Nitrogen was subsequently injected into the sample chamber at a flow rate of 100 mL/min for the viscosity measurement under nitrogen atmosphere. For the reducing atmosphere it was achieved by injection of CO_2 and CO respectively at the flow rate of 40 mL/min and 60 mL/min into the sample chamber. The furnace was heated at 20 °C/min up to 1200 °C, kept for 5 mins, heated at 10 °C/min up to 1500 °C, then heated at 5 °C /min up to 1580 °C and kept for 30 mins. The spindle was slowly immersed into the molten slag and the viscometer recorded the viscosity value every 5 s when the temperature cooling program started. The cooling rate was set at 1, 2, 5 °C/min respectively under reducing atmosphere, and set at 2 °C/min under nitrogen atmosphere. When the magnitude of the viscosity was small, the initial rotational speed of the spindle was 15 rmp. With increasing viscosity, the speed would decrease. When the viscosity increased to 35 Pa·s, the speed decreased to 13 rmp. The speed was further decreased by about 1.5 rmp when the viscosity was increased by 10 Pa·s. The measurement stopped when the

Table 2
Ash fusion temperatures of different coal ashes.

Samples	Characteristic temperature/°C			
	DT	ST	HT	FT
ZF	1076	1092	1104	1152
TKX	1115	1154	1180	1206
NH	1254	1329	1334	1338