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Viscosity of coal ash slag containing vanadium and nickel

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ABSTRACT

The viscosity–temperature behaviors of ashes with different ratios of V_2O_5 and NiO were studied. XRD, FTIR, XPS, Raman and SEM-EDX were applied for investigating the mechanism of influences on viscosity by V and Ni based on the formation of crystalline phase and the change of molecule network structure of liquid phase. Under reducing atmosphere, V_2O_5 was reduced to V_2O_3 which forms V – O – Al bond with Al_2O_3. The penetration of Al^{3+} into the original tetrahedral $[SiO4]^{4-}$ skeleton was blocked and the framework size of aluminosilicate reduces, so the viscosity of liquid slag decreased significantly. However, the formation of vanadium-rich spinel increased the viscosity of slag and type of slag transformed into crystalline type for spinel precipitating at high temperature. When the temperature was below the melting temperature of Ni, the existence of metal Ni changed slag into crystal type, and viscosity increased sharply. During coexistence of V and Ni, Ni particles were covered by vanadium-rich spinel, which caused T_{cv} (temperature of critical viscosity) of slag containing VNiO to be lower than that of slag containing V or Ni.

1. Introduction

The entrained-flow gasifier of high efficiency has been a main development tendency for the key of coal based fuel and chemicals in the recent years [1]. The multiple feedstock including biomass, petroleum coke and wastes is important in reducing the consumption of coal. With the continuous increasing demand of crude oil supply worldwide, the amount of petroleum coke, a by-product of the oil refining industry, has been increasing and is expected to continue to increase. Gasification of petroleum coke has many merits including lower gaseous emissions and less solid waste. The petroleum coke is of low reactivity and high gasification temperature is required, so entrained-flow gasification running at high temperature and high pressure is more suitable for petroleum coke [2]. For entrained-flow gasifier, the membrane wall of the gasifier will be smoothly covered by a layer of solid slag in the operation process. The membrane wall requires well controlled slag flow behavior and also certain ash content of raw material [3]. The ash content of petroleum coke is generally lower than 1.2%, so it is hard to apply directly in entrained-flow gasifier. Meanwhile, ash of petroleum coke is mainly composed of vanadium and nickel. Vanadium in petroleum coke ash is generally about 20%, and some are even higher. Also, the content of nickel is usually higher than 10% [4]. The unique ash composition of petroleum coke also causes the problem for slag tapping in entrained-flow gasifier. Petroleum coke blended with coal is a better method for the utilization of petroleum coke in entrained-flow gasification [5].

For entrained-flow slagging gasifier, continuous slag tapping is the key for successful operation [3]. Viscosity–temperature of slag is the fundamental parameter for slag tapping in the membrane wall gasifiers, such as Shell and GSP gasifiers. Generally, three characteristic temperatures, such as the temperature of 25 Pa s (T_{25}), the temperature of 2.5 Pa s ($T_{2.5}$), and the temperature of critical viscosity (T_{cv}), are obtained from the viscosity–temperature curve for evaluating the flow behavior of slag in entrained-flow gasifier.

Slag viscosity is well controlled in a certain range for slag tapping by setting the suitable operation temperatures [6]. For example, the viscosity of 2.5–25 Pa s is required at temperatures from 1300 to 1500 °C for Shell gasifier. Besides, the temperature of critical viscosity (T_{cv}) from slag viscosity curve is another key parameter for slag tapping. T_{cv} should be at least 150 °C lower than that of the temperature at 2.5 Pa s, because it is regarded as the lower limit of operation temperature. The flow properties of slag are determined by the ash composition and temperatures. The constituents of coal ash are classed as either basic or acidic. The acidic constituents are silica, alumina, and titania, and they are considered to increase the viscosity. The basic constituents are iron, calcium, magnesium, and alkalis, and they are accepted to lower viscosity effectively [7]. However, ash composition of petroleum coke is classified into acid or basic constituent. The network theory is used for explaining the relationship of viscosity liquid slag with compositions [8]. Liquid slag components can be classified into three categories according to the different influences on viscosity. Si, as a network former, increases viscosity. Na, K, Mg and Ca, as network modifiers decrease viscosity. Al and Fe, as an amphoteric can act either as network former or modifier. However, the roles of V and Ni in slag are not clear. During slag tapping, the slag is

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cooled down and the formation of crystalline phases also can significantly change the viscosity [9]. The viscosity–temperature behavior was dependent on the amount and size of the solids in the slag, and compositional changes of the liquid phase are caused by solid phase precipitation at the same time [10]. The influence of coal ash composition on slag viscosity was widely discussed, but the large difference that exists between ash composition of petroleum coke and coal may cause problems for slagging in the gasifier, because the transformation of V and Ni is very different from the general coal ash composition at high temperatures. Park and Myongsook [4] indicated that V_2O_3 in coke ash remained solid at typical gasification temperatures, and the solid V_2O_3 caused the increase of slag viscosity. In the study of Nakano et al. [11], synthetic slag mixtures were investigated by a series of quench experiments. It seems that karelianite (V_2O_3) formed a solid solution with Al_2O_3 and Fe_2O_3. Duchesne et al. [12] measured the slag viscosities of coal, petroleum coke and coal/petroleum coke blends. Petroleum coke ash is mainly composed of vanadium and nickel. Vanadium, one of the major components of petroleum coke ashes, also promotes the formation of vanadium-rich spinels which increases slag viscosity. However, the mechanism of influences on viscosity by V needs to be clarified further, and the effect of Ni and the synergistic effect of V and Ni on slag viscosity have not been reported before.

Considering the reactivity of co-feeding materials, petroleum coke should be blended with coal with low reactivity for entrained-flow gasification. The typical anthracite from Shanxi, China was selected for blending with petroleum coke for reactivity matching. Also, petroleum coke in the blending will decrease the ash content of the mixture since the ash content of Shanxi anthracite is usually over 30% before washing. In the study, viscosity while adding different ratios of V_2O_5 and NiO at reducing atmosphere was investigated. XRD and SEM-EDX were applied to account for mechanism of influences on viscosity by V and Ni. The content range of V and Ni in ash which was appropriate for slag tapping was indicated.

2. Experimental

2.1. Samples

The typical anthracite from Shanxi, China was selected for this study. Coal ash was prepared at 815 °C according to GB/T1574-2007. Inductively coupled plasma-atomic emission spectrometry (ICP-AES) was used to characterize ash composition based on ASTM D6349. Flux agent (CaO) is added on dry ash basis for satisfying slag tapping in entrained-flow gasifier. Raw ash and 12% CaO were blended in agate mortar and the mixture was denoted as CC. The chemical compositions of raw ash and CC are given in Table 1. CC was blended with different ratios of V_2O_5 and NiO respectively. The blends were stored in a desiccator after blending sufficiently.

2.2. Viscosity test

The viscosity of slag was analyzed with a theta high-temperature rotating viscometer under a reducing atmosphere ($CO/CO_2 = 6:4$). The test started above liquidus temperature for keeping the sample totally melted. The maximum temperature of the viscometer is 1680 °C, which is high enough to perform the test of almost all the coal ash samples. Viscosity measurements were started at the temperature at which the melt was Newtonian Àuid, and held for 30 min. The ramp rate was 1 °C/min. The viscosity and temperature were recorded continuously at interval of 0.1 °C, so the viscosity–temperature curve was obtained. The molybdenum rotors and cylinder crucibles were used and the parameters for the rotor crucible combination were calibrated with a standard reference material of 717A glass. The sample temperature was recorded using a type-B platinum thermocouple protected by an alumina pedestal. The temperature measuring system is corrected by the temperature calibration experiment [13].

Table 1
Ash compositions of samples.

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	SO_3	K_2O	Na_2O	P_2O_5
Raw ash	50.36	33.42	3.70	5.49	1.29	1.25	1.83	0.87	0.98	0.32
CC	45.18	29.99	3.32	15.64	1.16	1.12	1.64	0.78	0.88	0.29

2.3. Quenching experiment

The sample was heated in the vertical electricity tube furnace under reducing ($CO/CO_2 = 6:4$) atmosphere. The thermal profile is set based on the procedure of viscosity test. When the sample was heated to the target temperature in the crucible, the crucible was taken out and quenched in an iced water. Quenched slag is regarded as maintaining the composition and structure at high temperature. The quenched slag and the slag after viscosity test were determined by XRD. It is possible to reveal the formation of crystal minerals of slag during cooling in viscosity test by comparing XRD results of quenched slag and tested slag.

2.4. Instrumental analysis

Coal ash or slag samples were ground to less than 0.074 mm. A Rigaku D/max-rB X-ray powder diffract meter was applied for XRD patterns using Cu Kα radiation (40 kV, 100 mA, $K\alpha_1 = 0.15408$ nm). The samples were scanned with a step size of 0.02° at 4°/min over a 2θ range of 5–80°.

A JSM-7001F scanning electron microscope (SEM) was employed to assess the microstructure of the quenched slag. For SEM observations, the slags were mounted in liquid epoxy resin, pelletized, polished and finally sputtered-coated with carbon. Analysis of the quenched sample provides information about the amount of solid phase in slag at high temperatures. The microstructure of the quenched slags was observed using SEM in back-scattering mode (BSE), and Energy Dispersive X-ray (EDX) Spectroscopy was carried out to identify the composition of solid in the quenched samples.

FTIR spectra were recorded with a Bruker Vertex 70 Fourier transform infrared spectrometer. Slag sample was accurately weighed and then mixed with KBr with the ratio of 1:200. The mixture was finely milled in the agate mortar for 30 min and then pressed into pellets under 12 MPa. The spectral region from 4000 to 400 cm^{-1} was examined.

X-ray photoelectron spectroscopy (XPS) measurements were performed by means of Axis Ultra Dld (Kratos Group PLC) with Al Kα $h\nu = 1486.6$ eV at 150 W.

The Raman spectra were taken in Bruker Optics Senterra R200-L using 100 mW of the 785 nm excitation.

3. Results and discussion

3.1. Effect of V on viscosity

Fig. 1 shows the variation of slag viscosities versus temperature with different additions of V_2O_5 and the relation between viscosity and temperature above 1400 °C is isolated for comparison in Fig. 1b. Slag viscosity above 1525 °C decreased monotonously when the addition of V_2O_5 was not over 15%. Although the melting point of V_2O_3 is over 1910 °C and part of them remained as highly dispersed solid at high temperatures, the decrease should be caused by the interaction between V_2O_3 and aluminosilicate, because small amount of V_2O_3 dissolves in the liquid slag and V_2O_3 forms an equilibrium solid solution with Al_2O_3 [11]. Karelianite and alumina (corundum) form the solid solution at high temperature for sharing the same rhombohedral crystal structure, which decreased the quantity of Al as an amphoteric in the network structure in the liquid phase. V dissolved in the aluminosilicate plays a role by decreasing the network size of the slag structure. The interaction