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EFFECT OF CaO/Fe_2O_3 ON SLAG VISCOSITY BEHAVIOR UNDER ENTRAINED FLOW GASIFICATION CONDITIONS

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ABSTRACT

The entrained flow gasification is becoming a predominant and efficient way for coal clean utilization. And the steady and reliable removal of the ash slag is the key factor for smooth operation of entrained gasifiers. For the purpose of reducing the additive amount of flux and improving gasification efficiency, the influence of CaO/Fe_2O_3 (weight ratio of CaO/Fe_2O_3) on the viscosity-temperature behavior was studied in this work. Slag structure at high temperatures, and crystallization behavior of the coal ash slag with different CaO/Fe_2O_3 were studied in detail. As the CaO/Fe_2O_3 of the slag decreased, viscosity of the slag decreased at same temperatures. And Fe_2O_3 has a more decreasing effect on slag viscosity compared with CaO. Si-O-Si proportion is the key factor to influence slag viscosity when CaO/Fe_2O_3 is over 6:4, for other CaO/Fe_2O_3, Al-O structure should be considered. Both positive and negative mutual effect exist between CaO and Fe_2O_3. When CaO/Fe_2O_3 is lower than 2:8, they have negative mutual effect for breaking Si-O-Si bond. In addition, Sample 10C0F and 2C8F are suitable for the smooth operation of entrained flow gasification.

Keywords: Entrained flow gasification; Slag viscosity behavior; CaO/Fe_2O_3; Network structure; Crystallization

1. INTRODUCTION

The efficient and clean utilization of the coal is increasingly urgent for sustainable development [1]. Coal gasification is becoming the main clean coal utilization technology. Typically, based on the flow mechanism of feedstock, coal gasification technology can be divided into fixed bed, fluid bed and entrained flow gasification [2]. The last one has becoming the most promising choice for the advantages of high throughput, high carbon conversion and fuel feedstock flexibility [3].

The entrained flow gasifier is slagging gasifier, the smooth slag tapping is the key factor to ensure long-term operation of the gasifier, which is largely dependent on slag viscosity behavior [4]. Therefore, the slag viscosity behavior becomes the first principle for smooth operation of the entrained flow gasification.

Most of coals in China are not suitable for slag tapping because of the high slag viscosity at high temperatures [5]. To broaden the range of coals that can be processed in entrained flow slagging gasifiers, the fluxes which usually contains network modifiers are always used to blend the feedstock to produce a feed with appropriate slag viscosity behavior [6].

In this work, the viscosity behavior of the slags with same $CaO+Fe_2O_3$ content, different CaO/Fe_2O_3 were proceeded to investigate the mutual effect of different metal oxides. The structure of molten slags was studied by solid-state nuclear magnetic resonance (SS-NMR) and Raman. In addition, the crystallization behavior of the slags was analyzed by thermochemical calculation and the mineral compositions were studied by X-ray diffraction (XRD).

2. MATERIAL AND METHODS

2.1 Synthetic ash materials

To eliminate negative impact caused by irrelevant elements, the ash samples were simplified via using the

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synthetic ash. The ashes were composed of SiO_2-Al_2O_3-Na_2O-CaO-Fe_2O_3, which accounted for more than 90% (mass fraction) in a real coal ash. Analytic reagents SiO_2, Al_2O_3, Fe_2O_3, CaO were chosen and Na_2CO_3 instead of Na2O was selected. These five reagents were ground to less than 75 μm (200 mesh) and then mixed thoroughly in a ball milling. Chemical compositions of the synthetic ashes are listed in Table 1. The samples had same Si/Al (1.5) (mass ratio of SiO2/Al_2O_3), Si+Al (65%) (total content of SiO_2+Al_2O_3), and same CaO+Fe_2O_3 (34%) (total content of CaO+Fe_2O_3), but different CaO/Fe_2O_3 (mass ratio of CaO/Fe_2O_3).

Table 1 Chemical compositions of the materials (wt%)

Sample	SiO_2	Al_2O_3	Na_2O	CaO	Fe_2O_3
10C0F[1]	39.0	26.0	1.0	34.0	0.0
8C2F[2]	39.0	26.0	1.0	27.2	6.8
6C4F	39.0	26.0	1.0	20.4	13.6
4C6F	39.0	26.0	1.0	13.6	20.4
2C8F	39.0	26.0	1.0	6.8	27.2
0C10F	39.0	26.0	1.0	0.0	34.0

[1]: 10C0F: 34% (mass fraction) CaO in the synthetic ash without Fe_2O_3;

[2]: 8C2F: mass ratio of CaO and Fe_2O_3 is 8:2.

2.2 Viscosity measurement

About 100-105 g the synthetic ash samples were firstly heated to 150 °C higher than T_{liq} and hold for 20 min to reach the equilibrium in an electric furnace. After that, part of the pre-melted slags was broken to less than 2 mm and others were ground to less than 75 μm for quenched experiment.

Viscosity measurement was performed by a Theta high temperature rotational viscometer (RV DV-III). About 50 g pre-melted slags were put into an alumina crucible and then fixed at the center of the furnace. The protect alumina tube was evacuated fully and a reducing atmosphere (CO/CO_2=6:4, volume fraction) was used to blow the slag sample with a rate of 50 ml/min. The furnace was gradually heated to 1200 °C at 10 °C/min and then to 1600 °C at 5 °C/min. To ensure the melting of all crystalline solids, this temperature was hold for 20 min. Then, the spindle was immersed into the molten slag and the measurement started at a cooling rate of 3 °C/min at a constant share rate of 2.5 s^{-1}. The slag viscosity and temperature were recorded at the interval of 0.1 °C.

2.3 Preparation of quenched slag

A horizontal electricity tube furnace was used to prepare quenched slags under a reducing atmosphere as viscosity measurements. The temperature program in quenching experiment was same with that in viscosity measurement. When the temperature was decreased to the set point, the ash sample was pulled out rapidly and quenched in ice water immediately. All quenched slag samples were crushed and ground to less than 75 μm for XRD analysis, Raman and NMR characterization.

2.4 Characterization of quenched slags

Quenched slag at 1500 °C (1773K, >Tliq) was chosen to analyze the structure of molten slag by Raman characterization. The quenched slags were ground to less than 75 μm. A Horiba LabRAM HR800 spectrometer equipped with a CCD detector was carried out to analyze the coordination of Si atoms. The 514.5 nm line of an Ar+ laser was used for sample excitation.

^{27}Al MAS–NMR spectra were measured at a Bruker Avance III 600 MHz Wide Bore spectrometer (magnetic field 14.1 T) using a 4 mm CPMAS probe under 13 kHz MAS speed in zirconia rotors. ^{27}Al radiofrequency field strength was verified by using a 1.0 M aqueous $AlCl_3$ solution. Chemical shift was referenced to the $AlCl_3$ signal.

To investigate mineral compositions of slag samples during cooling, a Bruker D2 X-ray powder diffractometer with Cu Kα radiation (40 kV, 40 mA) was employed. The quenched slags were placed on a sample stage and scanned with a step size of 0.02° at 4°/min range from 5° to 90° (2θ).

2.5 Thermal calculation

FactSage software is widely used to predict the equilibration of multiphase, liquidus temperature as well as the proportion of slag and solid. In this study, the FToxide and FactPs database were selected to calculate the phase diagram.

2.6 Results and Discussion

2.6.1 High-temperature viscosity behavior

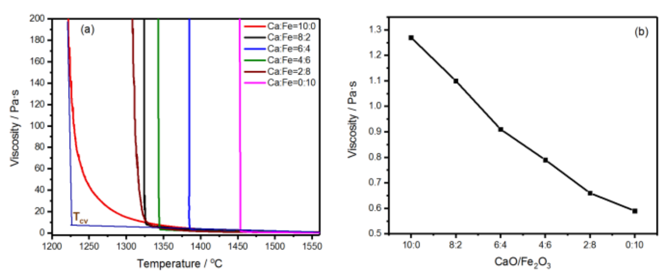

Fig. 1 (a) Viscosity-temperature curves of the ash slags with different CaO/Fe_2O_3

(b) Slag viscosity value at 1500 °C

From Fig. 1(a), as CaO/Fe_2O_3 decreased, the slag viscosity value at same temperatures decreased, and the difference of the slag viscosity was more obvious at low temperatures. For example, at 1500 °C, the viscosity values were 1.27, 1.1, 0.91, 0.79, 0.66, 0.59 Pa·s respectively for the sample from 10C0F to 0C10F. This suggested that Fe_2O_3 has a more decreasing effect on slag viscosity compared with CaO.

It also can be observed that the slag contained Fe_2O_3 exhibited crystal behavior, while sample 10C0F behaved as a glassy slag. The rapid increase of viscosity was usually attributed to the formation of the crystalline phases. This implies that the decrease of CaO/Fe_2O_3 is benefit to forming crystalline phases during cooling.

Slag structure and crystallization behavior were main factors which affect slag viscosity-temperature behavior. Therefore, the effect of CaO/Fe_2O_3 on slag structure and crystallization behavior was investigated and discussed in the following study.

2.6.2 Effect of CaO/Fe_2O_3 on Si-O structure

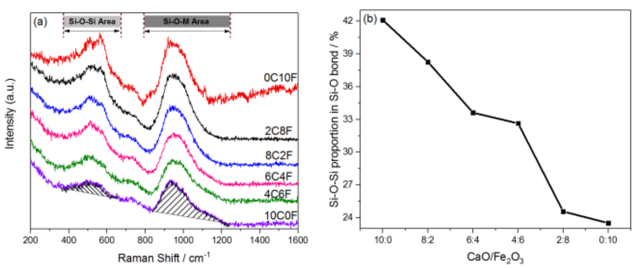

Fig. 2 (a) Raman spectra of the quenching ash slags at 1500 °C (b) Si-O-Si bond proportion among all Si-O bonds

From Fig. 2(a), the raman shift of 400-600 cm^{-1} was assumed as Si-O-Si bond, and the range of 800-1200cm^{-1} was defined as Si-O-M (Al, Ca, Fe, Na) bonds. The calculated Si-O-Si proportion was presented in Fig 2(b). The results showed that with decreasing CaO/Fe_2O_3, Si-O-Si ratio decreased, which caused low polymerization degree of molten slag. Consequently, a low viscosity value was obtained at high temperatures.

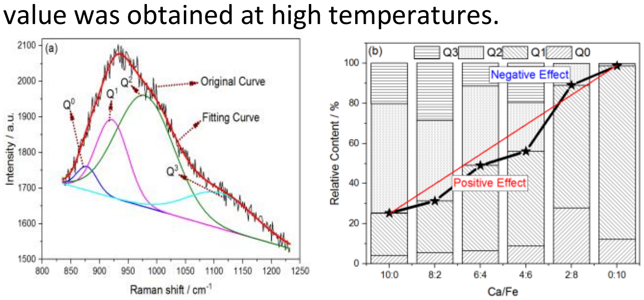

Fig. 3 (a) A typical deconvolution of raman spectra (b) Contents of Q^n units based on deconvolution results

In Fig. 3(a), to further investigate the influence of CaO/Fe_2O_3 on Si-O-M bonds (Q^0, Q^1, Q^2, Q^3 species), the method of deconvolution was applied to analyze the extensively overlapped individual peak by gaussian method around 800-1200 cm^{-1}. The results was depicted in Fig 3(b). With decreasing Ca/Fe, Q^0+Q^1 contents increased, which meant ferrous ion has higher ability to break Si-O-Si bond than Ca^{2+}. As for breaking Si-O-Si bond, when CaO/Fe_2O_3 is over 4:6, CaO and Fe_2O_3 has a positive mutual effect. While the ratio is less than 2:8, CaO and Fe_2O_3 has a negative mutual effect.

2.6.3 Effect of CaO/Fe_2O_3 on Al-O structure

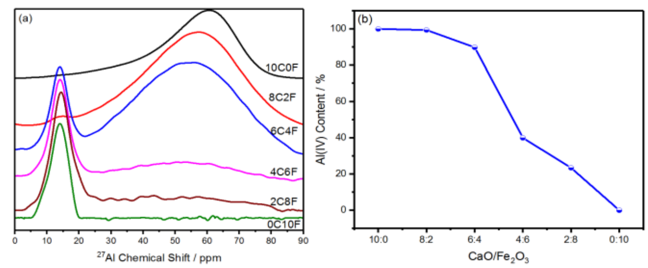

Fig. 4 (a) ^{27}Al NMR spectra of quenching ash slags at 1500 °C (b) Al(IV) content as a function of CaO/Na2O

The influence of CaO/Fe_2O_3 on Al-O structure was also discussed, and the results were drawn in Fig. 4. Generally, the range around 50-100 ppm was Al-IV ($[AlO_4]^{5-}$, tetrahedron structure) and the range around 10-20 ppm was responsive for Al-VI ($[AlO_6]^{9-}$, octahedral structure). It can be observed that chemical shift of $[AlO_4]^{5-}$ moved to lower frequency with the decreasing CaO/Fe_2O_3. And Al-VI structure appeared gradually with decreasing CaO/Fe_2O_3, while Al-IV vanished gradually. From Fig. 4(b), Al-IV content decreased with decreasing CaO/Fe_2O_3. The results indicated that low CaO/Fe_2O_3 was benefit for the formation of Al-VI, which decomposed slag polymerization degree, resulting in low viscosity.

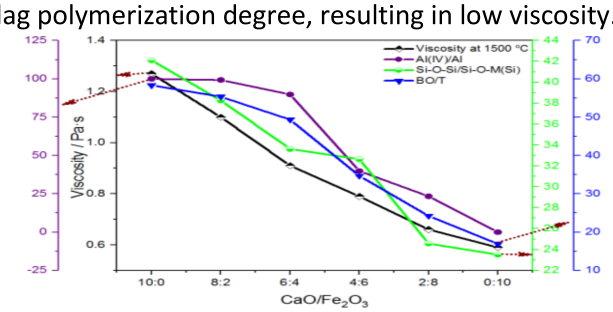

Fig. 5 Correlation between slag viscosity and Al-IV proportion, Si-O-Si proportion, BO/T (considering both Si-O and Al-O)

To further illustrate the main aspect for influencing slag viscosity at high temperatures. The relationship between three slag structure parameters tested by quenching slag at 1500 °C and slag viscosity value at 1500 °C was shown in Fig. 5. All the curves had same tendency. However, when CaO/Fe_2O_3 is over 6:4, slag viscosity was mainly determined by Si-O structure. While CaO/Fe_2O_3 is lower than 4:6, BO/T is the main parameter to influence slag viscosity due to the change on Al-O structure caused by CaO/Fe_2O_3. Therefore, both Si-O and Al-O structure should be considered when CaO/Fe_2O_3 is low.

2.6.4 Effect of CaO/Na2O on crystallization behavior of slag during cooling

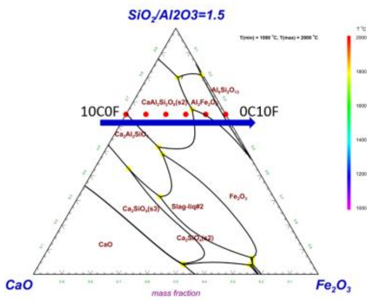

Fig. 6 Phase diagram with different CaO/Fe_2O_3

To investigate the most stable phase in SiO_2-Al_2O_3-Na_2O-CaO-Fe_2O_3 system, FactSage 7.2 was introduced to calculate the phase diagram. From Fig. 6, The primary phase of the slag transformed from gehlehite ($Ca_2Al_2SiO_7$) to anorthite ($CaAl_2Si_2O_8$), spinel ($Al_2Fe_2O_6$) and mullite ($Al_2Si_6O_{13}$) with decreasing CaO/Fe_2O_3.

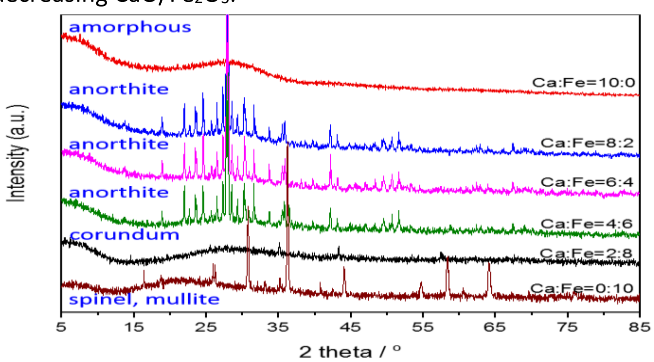

Fig. 7 The XRD patterns of quenched slag (Tcv-50 °C) with different CaO/Fe_2O_3

From Fig. 7, sample 10C0F is a glassy slag. And for sample 8C2F, 6C4F and 4C6F, the crystal phase is anorthite, which is accordance with the FactSage calculated results. For sample 0C10F, the crystal phase is spinel and mullite. Spinel is much easier to grow up and afford nucleation center for mullite. The crystal phase of corundum is difficult to grow up, therefore, sample 2C8F has lower Tcv than other crystal slags and sample 0C10F has the strongest crystal tendency.

2.7 Conclusions

(1) With decreasing CaO/Fe_2O_3, viscosity value of molten slag at same temperatures decreased. Fe_2O_3 has a more decreasing effect on slag structure compared with CaO.

(2) For the effect of Si-O bond, when CaO/Fe_2O_3 is over 4:6, CaO and Fe_2O_3 has a positive mutual effect, otherwise, they have a negative mutual effect.

(3) With high CaO/Fe_2O_3, Si-O-Si proportion is the main factor to influence slag viscosity, while CaO/Fe_2O_3 decreased, Al-O structure should be considered.

(4) Crystal phase affect crystal tendency of ash slag during cooling. Sample 10C0F and 2C8F are favor of slag tapping.

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