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The crystalline and microstructural transformations of two coal ashes and their quenched slags with similar chemical compositions during heat treatment

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ABSTRACT

The crystalline and microstructural transformations of two laboratory ashes and their quenched slags (from a gasifier) with similar chemical compositions (one with high silicon dioxide (SiO_2) concentrations and the other with high aluminum oxide (Al_2O_3) concentrations) were systematically characterized using X-ray diffraction, multinuclear solid-state nuclear magnetic resonance, and a high-temperature viscometer. The results show that the content of SiO_2 and Al_2O_3 in ash has significant influence on the crystal types and size of cristobalite clusters in the liquid slag during heat treatment. Consequently, the formed cristobalite clusters was the crucial to the viscosities and rheological properties of liquid slags.

Introduction

During high-temperature gasification processes, organic material in coal is gasified to produce synthesis gas (syngas), and inorganic mineral matter in the coal is converted to slag and flows down the refractory walls of the gasifier into a water quenching system [1–4]. The efficient operation of such gasifiers strongly depends on steady and reliable discharge of slag, and the fusion and rheological properties of slag are crucial to establish the operational conditions of the gasifier [5,6]. Generally, the slag viscosity should be controlled within the range of 15–25 Pa s at operating temperatures of 1200–1500 °C to maintain high energy efficiency and prolong the life of the refractory wall [5,7].

The slag viscosity strongly depends on temperature and chemical compositions. Traditionally, higher temperatures reduce slag viscosity. Acidic silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) as a network of former cations increases viscosity, while basic oxide calcium oxide (CaO) and iron oxide as modifier cations can decrease the fusion temperature and viscosity of ash and slag [8]. Generally, SiO_2, Al_2O_3, CaO, and iron oxide are predominant in coal ash [9]. Based on the ternary system SiO_2–Al_2O_3–CaO (or iron oxide) and the quaternary system SiO_2–Al_2O_3–CaO–iron oxide, numerous synthetic coal ashes have been prepared and used to investigate the relationship between the viscosity and composition of ash and/or slag [8,10,11]. Various empirical and semiempirical models such as Urbain, Riboud, and Kalmanovitch–Frank have been proposed to predict the viscosity of ash and slag [8,12]. However, these empirical models have a common disadvantage in that their application has a limited chemical composition range. Moreover, deviation of the predicted viscosity at specific temperatures is greater than 5%, which is too high for commercial and gasifier use.

The viscosity–temperature curve obtained from laboratory ash is an effective tool to determine the operational temperatures of gasifiers. However, a significant viscosity difference exists between laboratory ash and their quenched slag from the gasifier. Lin et al. reported that the three laboratory ashes and their quenched slags

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have different viscosities [13]. For example, the viscosities of Datong ash and its slag were 43.0 and 25.8 Pa s at 1550 °C, respectively. Song et al. also reported a similar result, showing that the viscosity of slag was lower than the corresponding ash within a slag tapping temperature range of 1400–1500 °C [14].

Quenched slag from the gasifier has three distinguishing characteristics compared to its parent ash. First, slag consists mainly of distorted aluminosilicate with high concentrations of SiO_2 and Al_2O_3 and lower amounts of Na and K cations [15]; the parent coal ash is composed mainly of quartz, metakaolinite, and other mineral matters. Second, slag has suffered a severe thermal shock within a short time, but laboratory ash is produced under relatively moderate conditions (815 °C) for longer times. Third, the aluminosilicate in the slag is an amorphous structure, while the inorganic mineral matter in ash is crystal or has a vitreous structure. Based on these three characteristics, ash and its slag should have different viscosities and rheological properties.

In this study, we compared laboratory ash and quenched slag during the heat treatment process. We also analyzed the correlation between rheological properties and local structures of two laboratory ashes and their quenched slags with similar chemical compositions (one with high concentrations of SiO_2 and the other with high concentrations of Al_2O_3) using X-ray diffraction (XRD) and multinuclear solid-state nuclear magnetic resonance (SS NMR). The effects of excessive SiO_2 and Al_2O_3 on the crystal, structure, and rheological properties of ash and slag were evaluated. The Q^n theory, where n denotes the number of bridging oxygens linked to other Si atoms for each Q unit (SiO_4, the compound form of SiO_4) was used to interpret variations in microstructural aluminosilicates. Their viscosities and rheological properties at different shear rates were measured using a high-temperature viscometer from 1700 °C to their resolidification temperature.

Experimental

Samples

The two representative laboratory coal ashes, including Coal Valley and Tanito Harum (CVA and THA, respectively) and their rapidly quenched slags from the gasifier (CVS and THS, respectively) were examined. The both of slags were discharged out of the industrial gasifier at 1500 °C. The two laboratory low-temperature ashes were prepared in a muffle furnace at 300 °C for 2 months, and two standard ashes were prepared at 815 °C for 24 h under air atmosphere. The preparation of ashes using different heat treatments was performed as follows: 600 °C for 24 h using low-temperature ash, 900 °C for 24 h, and 1000 °C, 1100 °C, 1200 °C, 1300 °C, 1400 °C, 1500 °C, and 1600 °C for 30 min using standard ashes. Their slags were heat-treated at 300 °C, 600 °C, and 815 °C for 24 h, and the heat treatment of slags at other temperatures was performed using the same treatment procedure like the two ashes as described above.

Sample characterization

The chemical compositions of the ash and slag samples were determined using X-ray fluorescence (XRF; Shimadzu EDX800). The ash fusion temperatures were determined under oxidizing and reducing atmosphere according to Japanese standard JIS M 8801. The XRD pattern was recorded over 5–90° with steps of 0.01° s^{-1} using CuKα radiation at 40 kV and 30 mA at room temperature (RINT Ultima III; Rigaku). ^{29}Si magic angle spinning (MAS) SS NMR spectra were measured at a Larmor frequency of 79.43 MHz with a JEOL ECA-400 multinuclear spectrometer equipped with a magnetic field of 9.4 T at a 15 kHz MAS speed in zirconia rotors using a 3.2 mm CPMAS probe. ^{29}Si single-pulse spectra were obtained using π pulses with a length of 6.8 μs and a recycle time of 10 s, collecting up to 10,000 free induction decay (FID) signals. The ^{29}Si chemical shift scale was referenced to external polydimethylsiloxane (PDMS). ^{27}Al MAS SS NMR spectra were measured at a frequency of 208.48 MHz with a JEOL ECA-800 spectrometer equipped with an 18.8 T standard bore magnet at a 20 kHz MAS speed. The ^{27}Al radio frequency (RF) field strength was 96 kHz, verified using a 1.0 M aqueous $AlCl_3$ solution. Chemical shifts were referenced to the $AlCl_3$ signal.

Viscosity and rheology measurement

Viscosity measurements were performed using a homemade rotary viscometer and a high-purity alumina rotational bob [13]. The 50–80 g sample was placed in an alumina crucible, which was then placed in a sacrificial graphite sleeve to consume free oxygen under constant nitrogen gas flow. Before measuring the viscosity of ash and slag, the viscometer was calibrated using a reference material (717a, borosilicate glass) certified by the American National Institute of Standard and Technology. The measurement deviation was controlled to less than 5%. Measurements were conducted at a cooling step from 1700 °C to the solidification temperature at an interval of 50 °C, with at least 10 min to equilibrate temperatures and compositions inside the crucible. Both the heating and cooling rates were 5 °C min^{-1}. The viscosity at each temperature was measured four times to ensure repeatability. The average of these measurements was used as the viscosity value [16].

The rheological behaviors of the ash and slag at high temperatures were determined based on a rheological diagram (variations in the apparent viscosity versus shear rate) obtained using a high-temperature viscometer. Based on the "Power-Law" model, which can be described as $\eta(\dot{\gamma}) = m|\dot{\gamma}|^{n-1}$, the shear rate at the rotor surface can be calculated by $\dot{\gamma} = 2\omega(R_0^2)/[n(R_0^2 - R_i^{2/n})]$, where $\gamma^{\bullet}$ is the shear rate (s^{-1}), ω is the angular velocity (s^{-1}), R_0 is the crucible radius (cm), R_i is the rotor radius (cm), m is the consistency coefficient (Pa s), and n is the flow index ($n = 1$ for Newtonian flow and $0 < n < 1$ for the non-Newtonian flow with shear thinning) [13]. In this experiment, the crucible and rotor radius are 1.85 and 0.30 cm, respectively. The flow index n was calculated and optimized by plotting the log (torque) versus log (ω). Different shear rates were applied by adjusting the rotational speed to 1, 3, 5, 7, 10, 15, 20, 30, and 50 rpm.

Table 1
Properties of the two ashes and their slags.

	Weight percentage (wt%)			
	CVA	THA	CVS	THS
SiO_2	57.00	47.00	58.78	50.40
Al_2O_3	18.30	24.24	25.18	32.18
CaO	11.20	10.9	8.20	8.03
Fe_2O_3	5.08	5.34	3.84	4.03
Na_2O	0.37	2.14	ND[b]	ND
K_2O	1.57	0.92	1.01	0.68
TiO_2	0.52	1.25	0.47	0.95
SO_3	3.46	3.10	ND	ND
P_2O_5	0.26	0.94	ND	0.41
MgO	1.63	2.83	2.07	3.00
Others[a]	0.61	1.34	0.45	0.32
Sum ($SiO_2 + Al_2O_3$)	75.30	71.24	83.96	82.58
Ratio (SiO_2/Al_2O_3)	3.11	1.94	2.33	1.57

[a] Others mean the trace metal oxides including BaO, Cr_2O_3, CuO, MnO, $R_{b2}O$, SrO, V_2O_5, ZrO_2, Y_2O_3, and ZnO.
[b] ND means not detected.