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Viscosity temperature properties from molecular dynamics simulation: The role of calcium oxide, sodium oxide and ferrous oxide

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ABSTRACT

For the long-term stable operation of the entrained flow gasifier in the coal chemical industry, the flux agents are generally adopted to adjust the fusibility of coal ash. Therefore, it is necessary to understand the underlying mechanism for the impact of typical oxide flux agents on viscosity temperature properties of coal ash from structures and thermodynamics. In this work, the role of calcium oxide, sodium oxide and ferrous oxide on viscosity temperature properties is investigated by a combination of molecular dynamics simulations and thermodynamic calculations. The variations of viscosity and temperature of critical viscosity are obtained for different ternary coal ash systems by thermodynamic calculation. Ternary phase diagrams are applied to evaluate the effect of different flux agents, which are also found to cause mineral transformation from high-temperature minerals to low-temperature minerals. Oxygen bond species are employed as the indicator of the structural evolution originating from addition of different flux agents. The sodium atoms may more readily weaken the tricluster oxygen bonds than calcium or ferrous atoms according to the results. Higher content of bridging oxygen bonds in the sodium oxide ternary coal ash system can enhance the stability of the structures and induce higher viscosity. Stability coefficients are defined here and a function to describe the relationship between the viscosity and flux agent content is established. The results from the current work are expected to provide new clues to find strategies controlling the fusion behaviour of coal ash systems.

1. Introduction

The viscosity temperature properties are significant for the long-term stable operation of the entrained flow gasifier [1]. Generally, the expected viscosity range is 2.5 Pa·s–25 Pa·s under the operation temperature of an entrained-flow gasifier. Viscosity higher than that range may cause blockage at the reactor bottom near the slag tapping hole, and consequently, lead to unscheduled emergency shutdown of the process [2]. When the viscosity is lower than 2.5 Pa·s, however, the problem of refractory wear may arise [3,4]. Therefore, the adjustment of the fusibility, by addition of flux agents to the coal ash system or coal blending, to control viscosity in the appropriate range is one of the most important aspects for running the entrained flow gasifier in both theory and practice. To date, limitations in the coal blending scheme remain such as restrictions in the availability of suitable coal in the neighbouring region. Thus, the method using flux agents is most commonly adopted under the gasification condition. Accordingly, it is essential to understand the impact of flux agents at high temperatures.

Calcium oxides and ferrous oxides are major flux agents widely chosen in the entrained-flow gasifiers. Besides, there is high content of

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sodium oxide in the Zhundong coal, which is the largest intact coal field in the world [5]. Much research has been conducted to investigate the mechanism by which these flux agents affect viscosity [6–8]. The effect of calcium oxide on the pattern of viscosity-temperature was investigated macroscopically by varying the amount of solid minerals in the slag [6]. The role of ferrous oxides in the viscosity varies depending on the chemical valences of iron [9]. The analyses of structural characteristics of molten slags reveal sodium oxide plays a role on the viscosity-temperature behavior of coal ash slag [4,8]. Although the general effect of fluxing agents on viscosity has been reported, the underlying fluxing mechanism for a complicated coal ash system remains unaddressed due to insufficient knowledge of the detail of structural variation in the molecular scale [10]. Moreover, it is meaningful to recognize the difference in the fluxing mechanisms among ferrous oxide, calcium oxide and sodium oxide since these flux agents may coexist in the coal ash. Therefore, it is highly important to understand the fluxing mechanism from the microscopic perspective.

In practice, the influence of flux agents on the chemical and mineral composition can be analyzed by the spectroscopies of X-ray diffraction (XRD), X-ray photoelectron, FTIR and Raman. FactSage is a software package that consists of a thermodynamic database, and various calculation and manipulation modules which enables one to perform thermodynamic calculations using the databases of pure substances and solutions [11]. The ternary phase diagram, predicted by FactSage, is frequently used to investigate the thermodynamics and mineral transformation [11–13]. Molecular dynamics (MD) simulation has been widely applied to investigate the variations of mineral compositions and structures microscopically, which helps illustrate the nature of physical properties of materials in-depth [14–17]. The structural features, such as the radial distribution functions, coordination numbers, mean square distances and oxygen bond species, are commonly considered as the key to understand the mechanism of microscopic viscosity variation [16]. Li et al. uncovered the mechanism of the coke reaction at high temperatures by analyses of the structural evolution with the SiO_2 content [14]. The role played by alkalis was investigated by the radial distribution function and oxygen bond species. Both Si-O and Al-O networks de-polymerize into simple structures with increasing basicity, causing increased atomic diffusion coefficients and decreased viscosities [17]. The alkalis show different influence on the total diffusivity for various ions in K_2O and Na_2O bearing systems, leading to distinctive trends in viscosities [15]. Furthermore, mineral transformation in the high-temperature or high-pressure process can also be understood by MD simulation. Molten anorthite was studied from first-principles calculations on the diffusion and viscosity as a function of pressure and temperature [18].

In this study, thermodynamic calculations combined with MD simulations were conducted on the comparison of the roles of calcium oxide, ferrous oxide and sodium oxide on the behavior of the coal ash, especially their influence on viscosity temperature properties. The current work aims to reveal the viscosity variation mechanism for various flux agents and quantify the corresponding dependence of viscosity temperature properties on calcium oxide, ferrous oxide and sodium oxide contents.

2. Methodology

2.1. Thermodynamic calculation method

The FactSage software package [19,20] has been used to predict the viscosity and ternary phase diagram for various coal ash systems including silicon oxide, aluminum oxide, ferrous oxide, calcium oxide and sodium oxide using the FactPS and FToxid databases in FactSage 6.4. The silicon and aluminum ratio is 2:1 and the flux agent content covered is 0.00–20.00 wt%. The temperature range is 1000 K-2000 K under 1 atm in the argon atmosphere. The thermodynamic calculations are based on the Gibbs Free Energy minimization.

Table 1
Coefficients for Bertrand's Potential for the various ternary coal ash systems.

Atom type	q(e)	A(kJ/mol)	ρ(Å)	C(Å^6 kJ/mol)
Al	1.4175	2,753,544	0.172	3336.26
Ca	0.945	15,019,679	0.178	4077.45
O	-0.945	870,570	0.265	8210.17
Si	1.890	4,853,816	0.161	4467.07
Fe^{2+}	0.945	1,257,488	0.19	0
Na	0.4725	11,607,587	0.17	0

2.2. Molecular dynamics simulation process

MD simulations were performed using the LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) software package [21]. The Born-Mayer-Huggins (BMH) function is used to model the inter-atomic potential [22,23], including Columbic, repulsive and Van der Waals interaction terms as shown below:

$$U_{ij} = \frac{q_i q_j}{4\pi \in_0 r_{ij}} + A_{ij}\exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} \quad (1)$$

Here i, j are the atomic identities, and r_{ij} is the distance between atom i and atom j. The coefficients of q_i, q_i, A_{ij} and ρ_{ij}, and C_{ij} are empirical parameters (atomic charges) used in the Coulombic, repulsive and Van der Waals interactions, respectively, as denoted in Eq. (1) with the values listed in Table 1 [24]. The transferable potential model used in the simulation was developed to describe nine-component crystals or liquids, including SiO_2-Al_2O_3-CaO-Na_2O-FeO [25]. Previous researchers have validated the force field coefficients and equation of state by comparing the bulk moduli, thermodynamic, transport properties and high-pressure data with experimental values [24,26]. Therefore, these coefficients are adopted to model the various ternary amorphous systems in coal ash.

The original compositions are chosen corresponding to those used in the FactSage calculation. All the atoms in the amorphous ternary systems are placed randomly and the total atom number depends on the experimental density. All the simulation processes are as follows. The initial structure is relaxed in the canonical ensemble (NVT) at 3000 K for 200 picoseconds (ps) for thermodynamic equilibrium and then cooled down to 300 K with the cooling rate of 10 K/ps. Subsequently, the equilibrium structure is adopted in the following simulation with the timestep of 1.0 fs (fs). The temperature of the configurations relaxed in canonical ensembles at 300 K is then increased from 300 K to 2000 K with the rate of 1 K/ps in isothermal-isobaric (NPT) ensembles. In both ensembles above, Nose-Hoover thermostat and barostat algorithms were adopted [27,28]. The time integration is carried out using the Verlet-leapfrog method with a periodic boundary condition. The cutoff of the short range interaction is 12 Å, while the electrostatic interaction is calculated by the Ewald method with the cutoff of 8 Å.

3. Results and discussions

3.1. Effect of flux agent on the coal ash viscosity

Viscosity temperature properties, including viscosity and the temperature of critical viscosity, are important aspects for the steady operation of large-scale entrained-flow gasifiers. The viscosity variation as a function of temperature and flux agent contents calculated by FactSage is shown in Fig. 1(a)-(c). The composition mole ratio of SiO_2 and Al_2O_3 in the model is 2.0 (the typical value for coal ash) which is also adopted in the following sections. The viscosity can be found to decrease with both the increased temperatures and contents of ferrous oxide, calcium oxide and sodium oxide in the system. As mentioned, the viscosity should be in the range of 2.5 Pa·s–25 Pa·s at the slag tapping temperature (such as 1350–1450 °C). To meet this requirement, the