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Full Length Article

Coal ash fusion properties from molecular dynamics simulation: the role of calcium oxide

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ABSTRACT

The role of calcium oxide on ash fusion properties was investigated in this work by molecular dynamics simulations and thermodynamics calculations. The variation of volume was used to identify the melting points, which was compared with the liquidus temperature calculated by the FactSage codes. The phase diagram was calculated to explain the variation of melting points with the content of calcium oxide. The radial distribution functions and species of oxygen bonding were employed to characterize the structural evolution with the different fraction of calcium oxide. The melting point of anorthite is lower than that of mullite due to less tricluster oxygen atoms. The content of CaO with high flux efficiency in $(SiO_2)_2$-Al_2O_3-CaO is found from 5.00% to 15.00%. The current modelling work on melting behaviors of minerals containing various amount of CaO may provide new insight into the mechanism of ash fusion influenced by flux.

1. Introduction

Integrated gasification combined-cycle (IGCC) technology has aroused increasing interest due to its long-term stable operability, high power generation efficiency and low greenhouse gas emission [1–3]. One of the kernel parts in IGCC is the entrained-flow gasifier, running at high temperature. The organic matter in coal reacts with the gasification agent immediately above 1673 K and the carbon conversion is usually over 99%. Mineral matters, around 20.00% in coal, transform into ash and melt to be slag, which flow down the inner wall of the gasifier and finally out of the gasifier from the bottom. The coal ash melting behavior is therefore regarded as one of the key issues for running the entrained flow gasifier and slag tapping in both theory and practice. In general, the expected slag tapping temperature range for various gasifiers is 1573–1673 K [4,5]. Currently, the ash fusion temperatures (AFTs) of most coal in China are not satisfactory for direct slag tapping. As a remedy, the flux added to the coal can adjust the AFTs to an appropriate temperature range. Thus, it is essential to understand the role of the major flux components such as calcium and iron oxides at high temperatures for guiding the addition of flux agent.

Calcium oxide or calcium carbonate is widely used as flux agent for entrained-flow gasifiers [6]. Many works have been performed to investigate the fluxing mechanism of calcium oxide. The fusibility, which reflects both the accessibility of ash fusion and ash mobility in the gasifier, essentially depends on the chemical and mineral composition in coal ash. In order to analyze the mineral components of coal ash at high temperatures as well as the influence of calcium oxides on AFTs, the spectroscopies of X-ray diffraction (XRD), Electron Bean, Micro-Ramana, FTIR and Raman have been used [7–11]. FactSage, the thermodynamics calculation tool, is also widely applied to study slag composition and mineral properties at high temperatures, which helps to understand the mineral transformation [6,12]. Generally, the AFTs decrease with the addition of calcium oxides for the formation of anorthite, but increase with the enhanced amount of calcium oxides due to the formation of gehlenite [2,3,6,12–15]. Although the anorthite and gehlenite were the key calcium containing mineral in the coal ash slag at high temperatures, their effect on fusibility is not clear yet. Unfortunately, the information by XRD, FTIR, Raman and FactSage may not provide a complete picture for explaining the evolution of mineral structure before/after melting since the influences of calcium oxide on AFTs only take place in the transformation of mineral phases when the structure can be hardly described as an ordered phase. Besides, the role

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of calcium oxide in the network of aluminosilicates has not been understood in-depth up to now.

The molecular dynamics (MD) simulation is a powerful method to study the behavior of the minerals and materials at the molecular level, and is widely utilized to reveal the nature of physical properties from the evolution of microscopic structures [16–26]. For melting, the results from MD simulations can reflect the continuous variation of structures and properties in the whole heating process [27]. The detail structural and property information in phase transformations including self-diffusion and viscosity change can be analyzed from the calculation results such as the atomic trajectory, the radial distribution function and the average coordination number. For example, first principle MD simulation has been used to obtain the details in structural change of anorthite and Mg_2SiO_4 as a function of pressure and temperature [19–21]. Bouhadja et al. applied the classical MD simulation to investigate the structural characteristics of the calcium aluminosilicate system and validate their empirical potential applied to the system [17]. Furthermore, the MD results from the molecular level help to understand the role of each composition in the system. As an example, the oxygen bond analysis defined by the coordination number of oxygen atoms, was used to describe the network structure of aluminosilicate and was found closely related with fluidity of the liquid phase [20,21].

In this work, computational investigations by the MD approach with the comparison to thermodynamics calculations are conducted on the role of calcium oxide in aluminosilicate, and especially the effect on fusibility of aluminosilicate at high temperatures. The paper aims to interpret the fluxing mechanism of the calcium oxide on ash fusion of anorthite which is one of the most important minerals generated with the addition of calcium oxide to the aluminosilicate system.

2. Thermodynamics and molecular dynamics simulation

2.1. Thermodynamics calculation

In this work, FactSage software packages [28,29] have been adopted to predict the liquidus temperature and ternary phase diagram of Al_2O_3-SiO_2-CaO by the FactPS and FToxid databases in the FactSage 6.4. The calcium oxide content covered is 0.00–40.00 wt% and the temperature range is 300 K–3000 K under 100 kPa in the argon atmosphere.

2.2. Molecular dynamics simulation

Molecular dynamics simulations are conducted by the LAMMPS software package [30]. The inter-atomic interaction is modelled by Born-Mayer-Huggins (BMH) function [31,32], including Columbic, repulsive and Van der Waals interactions as shown below:

$$U_{ij} = \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}} + A_{ij}\exp\left(\frac{-r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{6}_{r_{ij}} \quad (1)$$

where i, j are the atomic identities, and r_{ij} is the distance between atom i and atom j The coefficients of A_{ij}, ρ_{ij}, and C_{ij} are some parameters to simulate the inter-atomic interaction. The three terms in the Eq. (1) denote Coulombic, repulsive and Van der Waals interactions respectively. The potential coefficients in the above equation are listed in the Table 1 [33].

Table 1
Coefficients for Bertrand's Potential for the Al_2O_3-SiO_2-CaO system.

Atom type	q(e)	A(kJ/mol)	ρ(Å)	C(Å^6 kJ/mol)
Al	1.4175	2753544	0.172	3336.26
Ca	0.945	15019679	0.178	4077.45
O	-0.945	870570	0.265	8210.17
Si	1.890	4853816	0.161	4467.07

The potential used in the simulation was developed to describe nine-component system including the Al_2O_3-SiO_2-CaO amorphous systems [34]. Bertrand et al. validated the force field coefficients by comparing the bulk moduli, thermodynamic, and transport properties with experimental values [33]. The equation of state from their numerical model was in good agreement with high-pressure data obtained from sink/float experiments or shock-wave compression [35]. Thus, these coefficients are adopted to simulate the current Al_2O_3-SiO_2-CaO amorphous systems in coal ash.

The original compositions of the systems are chosen to be the same as that used in the FactSage calculation. All the atoms in the systems are placed randomly for the amorphous structures and the total atom number depends on the number density. Besides, the anorthite structure is constructed according to the XRD data in a 3 × 3 × 3 periodic supercell [36]. All the simulation process is as follows. The initial structure is relaxed in the canonical ensemble (NVT) at 300 K for 200 picoseconds (ps) for the thermodynamic equilibrium. The equilibrium structure is adopted in the following simulation with the timestep of one femtosecond (fs). 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. The system heated from 300 to 3000 K at the rate of 1 K/ps in the isothermal-isobaric (NPT) ensemble. Nose-Hoover [37] thermostat and barostat [37,38] for the temperature and pressure control is used, respectively. The velocity integration is carried out by the Verlet-leapfrog algorithm.

3. Results and discussion

3.1. The melting point (liquidus temperature) calculation

The liquidus temperature (melting point) was generally estimated by the volume variation. The corresponding data for anorthite (with 15% w.t. CaO) calculated by the MD simulation are shown in Fig. 1. The melting point is obtained from the inflection point on the first differentiation curve of the volume. The experimental liquidus temperature of anorthite is 1826 K, and the predicted value by MD simulation is 2004 K. They can be considered in reasonable agreement [39], though the deviation up to 9.74% exists. The difference between the calculated and experimental values can be attributed to two factors. One is the heating rate of MD simulation is generally much higher than the heating rate used in the experiments. The other is the approximations introduced in the force fields that cannot fully reproduce the potential energy surface of the system.

To investigate the fluxing effect of calcium oxide, both the MD simulation and FactSage calculations are applied to predict the liquidus temperature of Al_2O_3-SiO_2-CaO amorphous systems with calcium oxide

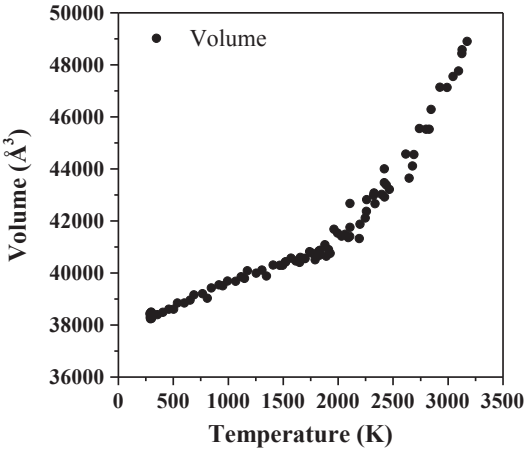

Fig. 1. Variation of volume as a function of the temperature of the anorthite system.