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The behaviour and reactions of sodium containing minerals in ash melting process

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ABSTRACT

The flux effect of Na_2O in synthetic ash samples has been experimented and explained. Based on the ash fusion temperature (AFT) tests, X-ray diffraction (XRD) and the Gibbs principle of minimum free energy, the behaviour and reactions of Anorthite ($CaAl_2Si_2O_8$), Albite ($NaAlSi_3O_8$) and Nepheline ($NaAlSiO_4$) have been studied to explain the flux effect of Na_2O in this paper. The results show that the flux effect of Na_2O is due to three reasons: the generation of low melting temperature minerals such as Albite and Nepheline; the reduction of a high melting temperature mineral Anorthite; and the most important one, the generation of eutectics formed by them will reduce the ash fusion temperature significantly.

1. Introduction

With the rapid development of the Chinese economy and power industry, the demand of coal in China has experienced a significant growth in the past ten years [1]. Although the utilization of renewable energy including wind energy and biomass energy has obtained considerable development, coal still seems to be the main source of energy for a long time in China [2]. Meanwhile, because of the more and stricter demand of environment protection as well as the safety and economic operation of power industry, “efficient” and “clean” become two keywords in the process of coal utilization [3].

Ash melting and slagging, are the major problems in the efficient and clean utilization of coal [4]. The characteristics of ash melting and slagging definitely have an influence on the safety and economic operation of boilers. Thus, ash melting characteristics have drawn extensive attention of both Chinese and foreign researchers. Ash melting characteristics are closely related to ash composition, which is mainly composed of 8 oxides: SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, TiO_2, Na_2O and K_2O. In general, these oxides are roughly divided into two categories, the acidic oxides which increase the melting temperature and the alkaline oxides which decrease the melting temperature. Among these oxides, the effects of high content oxides in coal ash include SiO_2, Al_2O_3 and CaO that have already obtained attention by researchers and made important achievements [5–11]. However, the effects of alkaline oxides in ash components, such as Na_2O and K_2O, have not caught enough attention. Guangyu Li and Chang'an Wang have discussed the release and transformation of sodium during combustion of coals [12], while the effect of sodium on ash melting temperature as well as the behaviour and reactions of sodium containing minerals are still not clear.

However, the effects of alkaline oxides cannot be ignored. In spite of the smaller proportion of alkaline oxides in coal ashes, they are considered to lower the ash melting temperature, although the mechanism is still unclear [13,14]. What's more, in some areas, there are coals with higher percentage of alkaline oxides contents than the average level. For example, in Zhundong, Zhunbei and Zhunnan districts of Xinjiang province, China, the coal reserves account for 30% of the country's total predicted coal reserves, which makes Xinjiang another important coal base in China [15]. However, the Zhundong coals are rich in alkaline metals especially sodium, and the Na_2O in coal ashes can reach a proportion of more than 5% [16]. Unique ash compositions make unique characteristics of combustion, melting and slagging [17].

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Therefore, it is of great importance to make a research of the melting characteristic of high alkali coal in depth, especially the mechanism that Na_2O influences the ash melting process.

In ash melting which is a high-temperature process, component oxides in ashes react with each other at different temperatures to generate different minerals and eutectic mixtures, thus influencing the ash melting temperature. Therefore, minerals' reactions and behaviour can be researched to explain the effects of ash components on ash melting process [18]. In this research, the effect of Na_2O on ash melting temperatures is tested, and then explained by the behaviour of sodium containing minerals and eutectic mixtures produced in ash melting process and their reaction mechanisms.

Both experimental and theoretical methods are used in the research. The ash fusion temperature tests illustrate the effect of Na_2O on ash melting temperatures. The XRD peaks are used to detect the minerals in ash melting process. In thermochemistry, Gibbs free energy minimization principle is used to analyze the minerals' behaviour and reactions [19]. Thermodynamic database FactSage is used to establish multiple components of Na_2O–SiO_2–Al_2O_3–Fe_2O_3–CaO to simulate the melting process of ashes [20]. The system is analyzed by thermodynamic calculation and phase diagrams to illustrate the behaviour of the sodium containing minerals and eutectic mixtures in ash melting process.

2. Material and methods

2.1. Synthetic ash samples

For the convenience of variable control, synthetic ash samples were chosen to replace coal ashes. To simulate the composition of coal ash, SiO_2, Al_2O_3, Fe_2O_3 and CaO were chose as high content components in synthetic ash. S/A means the mass ratio between SiO_2 and Al_2O_3 (wt.%), and it is settled at 2.00 as a constant. Low content oxides and oxides hardly react with Na_2O in coal ash like TiO_2, MgO and K_2O were not chosen. Along with Na_2O as variable, 6 groups of five-component synthetic ashes were prepared, as shown in Table 1. The synthetic ash samples were first mixed in deionized water to make muddy water. Then the muddy water was stirred by magnetic stirrers for 4 h before being dried to make sure the mixture is sufficient.

2.2. Experimental methods

The high-temperature ash melting tester was used to measure the ash fusion temperature which describes the melting process of ash when it is heated, as shown in Fig. 1: initial deformation temperature (IDT), softening temperature (ST), hemispherical temperature (HT), and flow temperature (FT). According to Chinese standard GB/T 219-2008, AFT tests were carried out in weak reducing atmosphere which was achieved by filling graphite and activated carbon in the corundum boat. The AFT results are presented in Table 1.

A high-temperature tube atmosphere furnace which can be heated to 1700 °C was used to provide the conditions needed in the ash melting process including temperature, pressure and atmosphere. The synthetic ashes were heated to target temperature in an air atmosphere for 4 h to make sure the reactions were sufficient. The pressure was maintained at −100 Pa to simulate furnace draft. All experimental data were recorded by the paperless recorder to ensure the reliability of the conditions. The samples were quenched with water and collected for later testing after reaching the target temperature. The mineral compositions of ash samples were detected by XRD. The XRD peaks were analyzed by the computer software package MDI Jade 5.0. The whole experiment process is shown in Fig. 2.

2.3. Theoretical methods

The Gibbs principle of minimum free energy and the multiple phase equilibrium theory were applied to research the minerals' reactions and behaviour in the melting process. Based on Gibbs energy, different thermodynamic parameters of minerals and reactions between them can be calculated by mathematical manipulations like Fourier transform. According to the Gibbs principle of minimum free energy, a reaction whose Gibbs energy is negative can happen and a reaction with a lower Gibbs energy is prior to that with a higher Gibbs energy. Based on this theory, the products of a reaction can be calculated by minimizing the Gibbs energy of the reaction to achieve multiple phase equilibrium.

Multiple components system of Na_2O–SiO_2–Al_2O_3–Fe_2O_3–CaO was established by thermodynamic database FactSage 6.4 to simulate the synthetic ashes in ash melting process. FactSage is a thermodynamic database contains the Gibbs energy of thousands of substances as well as a platform on which mathematical manipulations can be made to achieve the multiple phase equilibrium. In terms of the components, FToxid was chosen as the database. In calculation, temperature, pressure and content of reactants can be settled as variations to research their effects on the reactions. By achieving the reaction equilibrium, products of a reaction can be calculated and predicted. To give a visual description of the reaction equilibrium at different reactant contents, a phase diagram can be figured by FactSage.

Table 1
Chemical composition and AFTs of synthetic ash samples.

Ash samples	Content of oxides (wt.%)						The AFTs (°C)			
	SiO_2	Al_2O_3	S/A	CaO	Fe_2O_3	Na_2O	IDT	ST	HT	FT
1	50.00	25.00	2.00	17.00	8.00	0.00	1240	1260	1270	1290
2	49.50	24.75	2.00	16.83	7.92	1.00	1240	1270	1280	1300
3	48.50	24.25	2.00	16.49	7.76	3.00	1200	1270	1280	1300
4	47.50	23.75	2.00	16.15	7.60	5.00	1160	1220	1240	1290
5	46.00	23.00	2.00	15.64	7.36	8.00	1110	1160	1170	1200
6	45.00	22.50	2.00	15.30	7.20	10.00	1100	1120	1130	1170

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