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Research article

Effect of CaO/Fe_2O_3 on fusion behaviors of coal ash at high temperatures

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ABSTRACT

The ash fusibility, usually investigated and evaluated by the ash chemical composition, is widely used for guiding the coal utilization in boiler and gasifier. The ratio of basic and acidic oxides (B/A) in coal ash is the most important parameter for ash fusibility evaluation. While the coal ash has the identical B/A ratio, SiO_2/Al_2O_3 and CaO/Fe_2O_3 ratio also show significant influence on the ash fusibility. However, the researches on CaO/Fe_2O_3 on ash fusibility are rare. In order to quantify the influence of CaO/Fe_2O_3 on the ash fusibility, thermal mechanical analyzer (TMA) is applied to investigate the ash fusion behavior of coal ash with various CaO/Fe_2O_3 ratios. XRD, FactSage and DSC are combined to explore the ash fusion characteristics and mechanisms. The results showed that AFTs increased with the increasing of CaO/Fe_2O_3 ratio, which was attributed to variation of Fe_2O_3 content and iron valence. However, the ash with low CaO/Fe_2O_3 ratio trended to form mullite, increasing AFTs. Hence, the optimal CaO/Fe_2O_3 ratio for fluxing effect existed to balance the mineral component and iron valence. The different shrinkage curves were attributed to the different fusion events and different mechanism. The fusion process of ash ($CaO/Fe_2O_3 = 0.25$) exhibited as the behavior of a pure substance, which has the narrow fusion range. And the fusion range was dominated by the low temperature eutectics including spinel, quartz, corundum, and anorthite, which were beneficial for preventing ash sintering. Meanwhile, the fusion process of ash sample ($CaO/Fe_2O_3 = 4$) occurred step by step, and it had a wide fusion range. The low-melting point minerals such as wollastonite, clinopyroxene, calcium silicate induced and manipulated the fusion process. These ash samples with the wide fusion range were favored for slagging process. Besides, the shrinkage rate of ash was mainly determined by the slag formation rate when viscosity was low, but it was dependent on slag formation rate as well as viscosity for the high viscosity slag. Two correlated relations between shrinkage rate and ratio of liquid phase formation rate and viscosity for ash with $CaO/Fe_2O_3 < 1$ and $CaO/Fe_2O_3 \geq 1$ were established to prevent ash sintering at high temperatures.

1. Introduction

Coal gasification is a relatively clean and effective method to produce syngas that can be used for power directly or as a raw material for chemicals [1]. Among various gasification technologies, entrained flow gasification is a preferred one as they can feed both solid and liquid [2]. Besides, entrained flow gasifier is running at high temperatures (> 1400 °C) and pressures (20–30 atm) [3], which is beneficial for a high-quality syngas free of tars and phenols. In the entrained flow gasifier, organics in the coal almost completely transform into syngas. Most of minerals become a molten slag flowing down against the refractory wall under the gravity and tap out from the bottom of the gasifier [4]. Thus, a growing interesting has been issued on its application. However, sintering of ash in fly ash filters and slagging blockage caused significant problems in industrial practice, which given rise to safety concerns and economic losses. Therefore, the entrained flow gasifiers generally require flow temperature (FT) of the coal ash below 1350 °C to ensure slag tapping successfully. Meanwhile, the temperature at the entry of syngas cooler should be lower than 2/3FT-150 °C to prevent ash sintering [2,5].

Ash fusion temperatures (AFTs) are widely used to characterize the ash fusibility. Many works have been done to test and predict AFTs of the coal ash. Some investigations have been attempted to correlate AFTs to chemical compositions. For example, Seggiani et al. [6] used the partial least-squares regression method to predict the AFTs, and Thulasi et al. [7] developed a neural network model to correlate AFTs.

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Some works focused on the effect of oxides on AFTs [8,9], but the effect of C/F has not been found in the previous work to our knowledge, especially TMA method. TMA has become a powerful tool to investigate ash fusion behavior in recent years, which is able to characterize the sintering and melting process. Besides, the accuracy of shrinkage temperature corresponding to particular shrinkage extent (± 10 °C) is far better than AFTs test (± 40 °C) [10]. Gupta et al. [11] investigated the effect of potassium on the fusibility of coal ash and confirmed that TMA test offers a more accurate alternative for characterizing the ash fusibility. Bryant et al. [12] also used the TMA to qualify the effect of flux addition for coals in slagging gasifiers. Yan et al. [13] indicated that the TMA curve provided more information on fusion process and found that DT and FT were closed to the sintering completion and the initial primary fusion temperature, respectively.

The ash fusion behaviors are determined by components of the coal ash and interaction among them [14]. Coal ash consists of mineral matters including silicate, sulphide, carbonate and sulphate [15]. However, the mixture of minerals with different crystallization degree is difficult to identified and quantified, especially at high temperatures. Thus, the chemical compositions are usually used to character the composition of coal ash. The chemical compositions of the coal ash could be divided into two groups based on their roles on fusibility, acidic oxides (SiO_2 and Al_2O_3) and basic oxides (Fe_2O_3, CaO, K_2O and Na_2O). The acidic oxides usually form a polymer structure to increase AFTs, while the basic oxides tend to break the network structure, decreasing the AFTs. Therefore, the ratio of polymerization and depolymerization compositions, basic/acidic (B/A), is widely used to judge the ash fusion behaviors [16]. For example, Vassilev et al. [17] found that the AFTs decreased with the increasing B/A ratio, but the relation was not linear. When the coal ashes have the same B/A ratios, the contents of basic or acidic oxides could also be different. Another index, SiO_2/Al_2O_3 (S/A), is applied to evaluate the ash fusibility. CaO and Fe_2O_3 are the main fluxing agents in the coal ash. Nigel et al. [18] found that CaO/Fe_2O_3 ratio showed a significant influence on ash deposit, but the researches on the effect of CaO/Fe_2O_3 on ash fusion behavior at high temperatures were rare. Hence, the ratio between basic oxides, such as CaO/Fe_2O_3 is required, and the better understanding of CaO/Fe_2O_3 on the ash fusibility could help to develop the binary fluxing agents.

In this work, the synthetic ash samples with various C/F ratios were prepared, and the thermal mechanical analyzer (TMA), differential scanning calorimeter (DSC), X-ray diffraction (XRD), heating stage-microscope (HSMP) and FactSage software were combined to investigate the effect of C/F on the fusion characteristics and the mechanism.

2. Experimental

2.1. Samples preparation

The synthetic ash sample was widely used to investigate the ash fusion behavior at high temperatures [8,9,19]. The oxides of SiO_2, Al_2O_3, Fe_2O_3, and CaO are the major compositions of the coal ash, so the coal ash could be simplified into these four constitutes [5]. The purpose is to adjust the composition accurately and eliminate the influence of other minor compositions. In this work, the synthetic ashes are used by mixing pure oxides. The purity of SiO_2, Al_2O_3, Fe_2O_3, and CaO is 99.7%, 99.5%, 99.8%, 98%, respectively. All oxides were grinded to finer than 75 μm after heated in muffle furnace at 900 °C and mixed thoroughly in a ball milling. The chemical compositions of the samples are designed and shown in Table 1. The B/A and S/A of sample are same, but C/F ratio range is from 0.25 to 4.00.

2.2. Ash fusion temperature test

The AFTs measurements were carried out following the Chinese standard procedures (GB/T 219-2008) under argon atmospheres. The aim is to prevent the effect of atmosphere on iron valence. The shape changes of ash cone which is loaded in a furnace are recorded by an auto video camera during the heating process. The four characteristics temperatures, deformation temperature (DT), soft temperature (ST), hemispherical temperature (HT) and flow temperature (FT), were recorded in turn by the definition of the AFTs.

Table 1
Chemical compositions of the synthetic ash samples.

Samples	Chemical compositions (wt%)				B/A	S/A	C/F
	SiO_2	Al_2O_3	Fe_2O_3	CaO			
1	42.00	28.00	24.00	6.00	0.43	1.50	0.25
2	42.00	28.00	20.00	10.00	0.43	1.50	0.50
3	42.00	28.00	15.00	15.00	0.43	1.50	1.00
4	42.00	28.00	10.00	20.00	0.43	1.50	2.00
5	42.00	28.00	6.00	24.00	0.43	1.50	4.00

2.3. Thermal mechanical analysis

The TMA test was conducted on a SETARAM thermal mechanical analyzer. A tablet was prepared under 1 MPa pressure for 1 min and placed into a corundum crucible with a flat end. A load of 2.0 g was applied on the top of ram to ensure the ram and tablet touching tightly. The tablet was heated from ambient to 600 °C at a rate of 8 °C/min and then 7 °C/min to 1500 °C under argon atmosphere. During the shrinkage process, penetrating ram moves down and finally touches the bottom of the crucible when the slag becomes a fully liquid slag. The shrinkage curve by the position of ram describes the fusion process of ash sample precisely.

2.4. Differential scanning calorimeter

A NETZSCH STA 449F5 DSC was used to investigate the heat exchange of samples. About 15 mg synthetic ash was placed in a platinum crucible. The experimental condition was same with that in TMA measurements. The peaks of exothermic and endothermic are recorded, which will be used to characterize the mineral reaction and phase transition.

2.5. In-situ heat stage microscope

The morphology of ash during heating was observed by a high temperature stage microscope. The ash particle was placed on a sapphire piece and heated from ambient temperature to 1100 °C at rate of 30 °C/min and then 5 °C/min to 1500 °C in argon atmosphere. A rapid heating rate was selected in the initial stage, because no obvious change occurred below 1100 °C. The images were taken in-situ by a high resolution digital camera.

2.6. Quenched slag and XRD analysis

To explore the impact of C/F ratio on mineral transformation and mineralogy at high temperatures, the quenched slags were prepared in a horizontal electricity tube furnace with a 5 °C/min heating rate in argon atmosphere. When the temperature reached 1300, 1400 and 1500 °C, the slag was taken out and quenched in an ice water immediately. Afterwards, the slags were grinded to < 75 μm after heating at 105 °C for 2 h and used to do the XRD analysis. The XRD was conducted by a D2 powder diffractometer from BRUKER. The diffraction conditions were Cu target, 0.1540 nm, 40 kV and 40 mA.