EFFECT OF ADDITIVES ON THE ASH FUSION TEMPERATURE

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Abstract - the high contents of alkali metals in coal may induce ash-related problems, e.g., slagging, fouling and corrosion while it combusts in a circulating fluidized bed boiler. As an important indicator, the ash fusion temperature is widely used for characterizing coal ash deposition and slagging, which is strongly dependent on mineral matter distribution. To increase the ash fusion temperature, different additives, such as sio_2 and al_2o_3, are added into the coal.

In this work, a coal containing high alkali metals was mixed with one of the three additives (SiO_2, Al_2O_3 and kaolin). Both experiment and thermodynamic simulation were carried out to study the coal ash fusibility including the ash fusion temperature (DT, ST, HT, FT) and liquidus temperature (LT). The experimental results show that the ash fusion temperatures increase with the mixing ratio of SiO_2, Al_2O_3, or kaolin at different extents. The variation of the temperature with the mixing ratio of kaolin shows better linearity (average 40 K rise with 1% mixing ratio increment). The simulation was performed using Factsage 5.2. The simulation results agree well with the experimental results, especially for kaolin mixing ash. X-ray diffraction (XRD) analysis also conducted to study the mineral evolution.

INTRODUCTION

Heat and power generation by combustion in circulating fluidized beds is advantageous for burning a variety of coals and lowering pollutant emissions. However, several ash-related operational problems appear, such as slagging, fouling and corrosion, when utilizing the coal with high contents of alkali and alkaline earth metals (Li et al., 2015). Summarizing the previous results, these problems are due to primarily two reasons: (1) low-temperature eutectics containing alkali metals will form at high-temperature region, which is easily adhered in the heating surface; (2) re-condensing of evaporated alkali metals at lower gas temperature in the convection heating surface region will adsorb flying ash particles (Wang et al., 2015). Adding additives is an effective method to control these ash-related problems. Previous literature reports show that additives have a higher adsorption capability for alkali metals in the gas phase (Xu et al., 2014; Si et al., 2014). In addition, additives will improve the ash fusibility. In this study, we focus on the influence of additives at the fusion temperature.

As an important indicator, the ash fusion temperature is widely used to estimate the deposition and slagging behavior in a boiler. Ash fusibility is strongly affected by the mineral matter distribution. Generally, the acidic ash constituents (SiO_2, Al_2O_3 and TiO_2) are considered to increase the fusion temperature, whereas the basic oxides (CaO, Na_2O, MgO and K_2O) will decrease the fusion temperature. Vassilev et al. (1995) revealed that the relative influence of the oxides for increasing coal ash HT is normally TiO_2>Al_2O_3>SiO_2>K_2O, whereas that for decreasing HT is SO_3>CaO>MgO>Fe_2O_3>Na_2O. Dyk et al. (2006) investigated the effects of SiO_2, Al_2O_3 and TiO_2 addition on ash flow temperature of South African coal and confirmed that Al_2O_3 has the greatest effect on the ash flow temperature. Typically, SiO_2, Al_2O_3 and kaolin ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$) are widely used to increase the fusion temperature. However, Niu et al. (2016) found that the fluidized temperatures of biomass ash show 'V' shaped distributions with increased SiO_2, Al_2O_3, and K_2O, which is different from the flow temperature variation of coal ash. The content of alkali metals is high in this coal, and its ash components differ from that of other coals. Thus, the influence of additives is unknown and may be different with the coal of low alkali content. Consequently, it is necessary to study the ash fusibility to find the desired additives to increase the fusion temperature.

The thermodynamic computer package, FactSage, has been used to make predictions of multiphase equilibrium, liquidus temperature, the proportion of liquid and solid phases for a multicomponent system (Song et al., 2009). Kong et al. (2011) reported that fusion temperatures of three Chinese coal ashes decrease and then increase with increasing CaO addition, which is consistent with the change of liquids temperature calculated by FactSage. Song et al. (2010) revealed that ash fusion temperature of four Chinese coal ashes first decrease with increasing CaO, Fe_2O_3 and MgO contents, and increase once more, which are correlated closely with liquid temperature for the appropriate pseudoternary phase diagrams by FactSage. In this work, FactSage was used to predict the liquid temperature and mineral transformation, these values were compared with the tested ash fusion temperatures.

For this work, coal samples with high alkali content were used. We measured the ash fusion temperature of coal ashes with SiO_2, Al_2O_3, and kaolin additives. The computer software package FactSage was also used to calculate the liquidus temperatures of ash samples, as well as the proportions of the various phases present as a function of increasing the amount of additives. XRD analysis was also conducted to study the mineral evolution.

1. EXPERIMENTAL SECTIONS

1.1 Coal and additive samples

In this work, one high-sodium coal was used. Proximate analysis, ultimate analysis of coal samples and chemical composition of ash according to the Chinese standard GB/T 212-2008, GB/T 476-2008 and GB/T 1574-2007, respectively, are shown in Table 1 and 2. Table 2 reveals that the coal sample contains high Na_2O (3.13%), Fe_2O_3 (12.76%) and MgO (6.96%).

First, coal ashes were sampled at the temperature of 815°C with the method of the Chinese standard GB/T 1574-2007. Pure SiO_2, Al_2O_3 and kaolin were well mixed with coal ashes as the additives, whose diameters range from 0.088 mm to 0.125 mm. The primary constituents of the mixed ash samples are given in Table 3. These ash samples were prepared for the fusion temperature test.

Table 1 Proximate and Ultimate Analysis

Proximate Analysis /%				Ultimate Analysis /%				
A_{ar}	V_{ar}	FC_{ar}	M_t	C_{ar}	H_{ar}	N_{ar}	$S_{t,ar}$	O_{ar}
7.56	26.16	20.03	46.24	32.24	2.31	0.62	1.02	10.00

Table 2 Coal Ash Composition and Fusion Temperature

Ash composition/%								Ash Fusion Temperature/°C			
SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	DT	ST	HT	FT
30.42	17.46	12.76	12.11	6.96	0.29	3.13	14.02	1134	1145	1162	1192

Table 3 Composition of Ash Samples

Sample		Composition in ash					
	Blending ratio m(additive)/m(ash) %	SiO_2/%	Al_2O_3/%	CaO/%	Fe_2O_3/%	MgO/%	Na_2O/%
SiO_2 mixed	0	30.42	17.46	12.11	12.76	6.96	3.13
	16	40.00	15.06	10.44	11.00	6.00	2.70
	39	50.00	12.55	8.70	9.17	5.00	2.25
	74	60.00	10.04	6.96	7.34	4.00	1.80
Al_2O_3 mixed	0	30.42	17.46	12.11	12.76	6.96	3.13
	10	27.64	25.00	11.00	11.59	6.32	2.84
	18	25.80	30.00	10.27	10.82	5.90	2.65
	27	23.96	35.00	9.54	10.05	5.48	2.46
kaolin mixed	12	31.04	20.58	10.84	11.43	6.23	2.80
	21	31.45	22.62	10.01	10.55	5.76	2.59
	28	31.74	24.06	9.43	9.94	5.42	2.44
	35	31.95	25.12	9.00	9.48	5.17	2.33
	40	32.11	25.95	8.66	9.13	4.98	2.24

1.2 Fusion Temperature Test

We performed the fusion temperature tests by following the Chinese standard GB/T 219-2008. The ash cone of specified geometry was first heated to 900°C at 15°C /min. Next, the ash cone was heated at a rate of 5°C /min in a mild reducing atmosphere. The following temperatures were recorded for each sample: deformation temperature (DT), softening temperature (ST), hemispherical temperature (HT), and flow temperature (FT). The fusion temperatures of the raw coal ash without additives are given in Table 2.

1.3 XRD analysis

To evaluate the effect of additives on mineral evolution during the process of ash melting, the above mixed ash samples were heated to 1100°C. The experimental results showed that some ash was fused and difficult to remove from the crucibles when the temperature exceeded 1200°C; thus, 1100°C was selected as the proper temperature. All the ash samples with different additives were analyzed by using XRD.

1.4 Factsage modeling

Factsage, a thermodynamic software package, is the fusion of two well-known software packages, i.e., Fact-Win and ChemSage, whose calculation method is based on Gibbs' energy minimization. Equilib and Phase Diagram are the two major modules. The Equilib module allows for calculating the multiphase equilibria, as well as the proportions of liquid and solid in a multi-component system. Phase Diagram allows for predicting the liquidus temperature (LT).

For this study, the Phase Diagram module was chosen to calculate the liquidus temperature. Five main oxides (SiO_2, CaO, Al_2O_3, Na_2O, and MgO) were selected as the initial components; the proportion of each of the oxides was obtained from Table 3. The calculating temperature ranged from 1000~1500°C and was maintained at atmospheric pressure.

2. ASH FUSION CHARACTERISTICS

2.1 Effect of SiO_2 addition

Experimental and simulation results regarding the effects of SiO_2 content on the fusion temperature are shown in Fig. 1 and Fig. 2. As shown in Fig. 1, with increasing SiO_2 content, four characteristic temperatures

(DT, ST, HT, and FT) first decrease and then increase. The lowest fusion temperature appears when the SiO_2 content is 40%. As the SiO_2 content reaches 60%, FT is only 40°C higher than the raw coal ash without addition. However, the simulation results exhibit a slight difference. Fig. 2 illustrates the liquidus temperature (LT) in the SiO_2-Al_2O_3-CaO-Na_2O-MgO system. The lowest LT appears for the SiO_2 content of 50%. The value of LT increases rapidly when the SiO_2 content exceeds 50%, leading to a 200°C interval between the raw coal ash and the ash with 60% SiO_2 content. In short, the fusion temperature transformation becomes complicated when SiO_2 is mixed in the coal ash. However, a larger blending ratio of SiO_2 is useful for controlling the slagging and fouling problems during combustion.

Fig. 2 also displays the mineral distribution of different SiO_2 contents by Factsage. When the SiO_2 content rises from 40% to 50%, Mg_2SiO_4 may react with SiO_2 to form $MgSiO_3$. As the melting point of $MgSiO_3$ (1550°C) is lower than that of Mg_2SiO_4 (1897°C); as a result, the LT decreases. When the SiO_2 content exceeds 50%, SiO_2 exists in the compound and does not react with other mineral. Thus, the ash fusion temperature increases because of the high melting point of SiO_2.

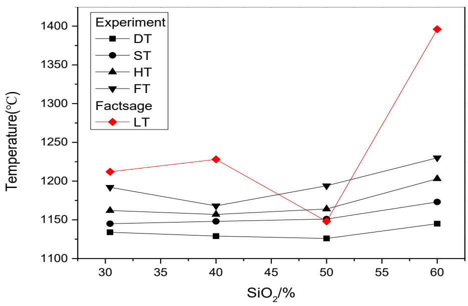


Fig. 1. Effect of SiO_2 on the fusion temperature and the liquidus temperature

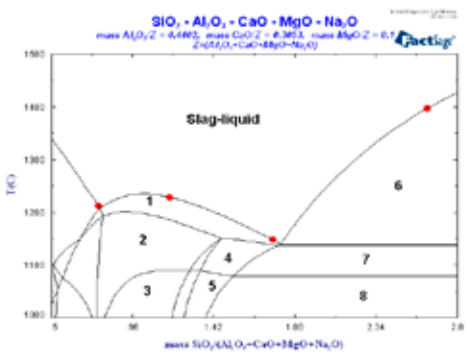


Fig. 2. Liquidus temperature in the SiO_2-Al_2O_3-CaO-Na_2O-MgO system

1. $CaAl_2Si_2O_8$ 2.$CaAl_2Si_2O_8$+Mg_2SiO_4 3. $CaAl_2Si_2O_8$+Mg_2SiO_4+$MgOCaOSi_2O_4$

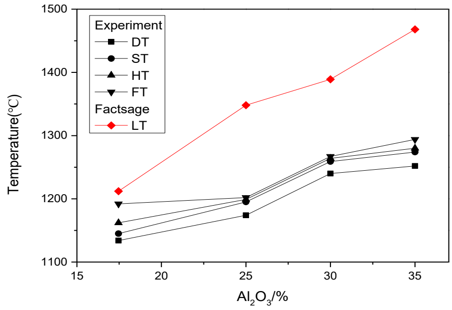
4. $CaAl_2Si_2O_8$+$MgSiO_3$ 5. $CaAl_2Si_2O_8$+$MgSiO_3$+$MgOCaOSi_2O_4$

6. SiO_2 7.$CaAl_2Si_2O_8$+$MgSiO_3$+SiO_2 8. $CaAl_2Si_2O_8$+$MgSiO_3$+SiO_2+$MgOCaOSi_2O_4$

2.2 Effect of Al_2O_3 addition

Fig. 3 and Fig. 4 show the effects of Al_2O_3 addition on the fusion temperature. Experimental and simulation results display the same tendency. Four characteristic temperatures and LT all increase with the Al_2O_3 addition increasing. From Fig. 3, LT is higher than FT during the process of Al_2O_3 content increasing. This observation is reasonable because the coal ash has not fused completely when the FT is reached, and all minerals turn into liquid at the LT. When the content of Al_2O_3 rising from 17.5% to 35%, LT experiences a larger increasement of 250°C, while the four characteristic temperatures experience a smaller increase (approximately 100°C). Anyway, experimental and simulation results indicate that Al_2O_3 addition is efficient to raise ash fusion temperature and is useful for controlling the slagging and fouling problems during combustion. Dyk et al. (2006) also indicated that Al_2O_3 has a better effect on the ash flow temperature than SiO_2 and TiO_2.

Fig. 4 displays the mineral transformation of different Al_2O_3 contents in the SiO_2-Al_2O_3-CaO-Na_2O-MgO fusion system. When the Al_2O_3 content rises from 17.5% to 30%, Mg_2SiO_4 will react with the Al_2O_3 to form $MgAl_2O_4$. Because the melting point of $MgAl_2O_4$ (2130°C) is higher than Mg_2SiO_4 (1897°C), the value of LT increases. When the Al_2O_3 content exceeds 30%, the compound contains large amount of Al_2O_3, which induces the increase of the LT.



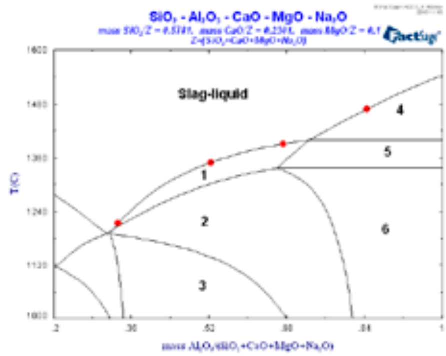


Fig. 3. Effect of Al_2O_3 on the fusion temperature and the liquidus temperature

Fig. 4. Liquidus temperature in the SiO_2-Al_2O_3-CaO-Fe_2O_3-MgO system

1. $MgAl_2O_4$ 2.$MgAl_2O_4$+$CaAl_2Si_2O_8$ 3. $MgAl_2O_4$+$CaAl_2Si_2O_8$+Mg_2SiO_4

4. Al_2O_3 5.Al_2O_3+$MgAl_2O_4$ 6. Al_2O_3+$MaAl_2O_4$+$CaAl_2Si_2O_8$

2.3 Effect of kaolin addition

The effects of kaolin addition on fusion temperature are shown in Fig. 5. Experimental and simulation results display the same tendency, which is similar to that of the raw coal ash mixed with Al_2O_3 additive. The four characteristic temperatures and LT all increase with the kaolin addition increasing. LT is higher than FT for various amounts of kaolin addition. However, compared with the fusion temperature of Al_2O_3 addition, LT is closer to FT (averaged 20°C) when kaolin is mixed. Moreover, the variation of the temperature with the mixing ratio of kaolin shows better linearity. Kaolin addition results in average 40°C rise with 0.1 increase in the blending ratio, which is higher than the rise with the SiO_2 addition (0.5°C/0.1 blending ratio) and slightly lower than the rise of the Al_2O_3 addition to the ash (43°C /0.1 blending ratio). Therefore, kaolin and Al_2O_3 are promising additives to increase the fusion temperature.

The mineral transformation during kaolin addition is difficult to obtain in the SiO_2-Al_2O_3-CaO-Na_2O-MgO fusion system by Factsage because of the complexity of the thermodynamic model when both SiO_2 and Al_2O_3 content increase. Therefore, we do not provide the calculation results of mineral distribution with varied kaolin contents; this will be provided later.

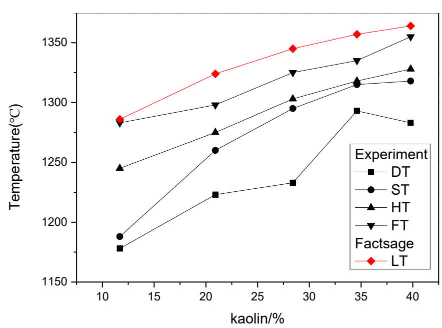


Fig. 5. Effect of kaolin on the fusion temperature and the liquidus temperature

2.4 Effect of S/A ratio

The mass ratio of SiO_2 and Al_2O_3 (S/A) is an important factor to evaluate the ash fusibility (Xuan et al., 2015). When SiO_2, Al_2O_3 and kaolin are mixed with the coal ash, the S/A (SiO_2/Al_2O_3) ratio changes.

Previous literature shows that a high SiO_2/Al_2O_3 ratio accounts for the high fusion temperature of most Australian bituminous coal ash (Patterson et al., 2000; Hurst et al., 1999). Fig. 6 shows the effect of S/A ratio on one of the characteristic temperature (FT) and the liquidus temperature (LT), with the S/A ratio ranging from 1 to 4.5. Curve fitting shows that, with the increasing of S/A ratio, both FT and LT decrease initially and subsequently increase. The lowest FT appears when the S/A ratio is approximately 4, and the ratio value reduces to 3.5 for that of LT. S/A ratio of the raw coal ash is approximately 1.7. Consequently, FT and LT first decrease and then increase as the S/A ratio increases, whereas lowering the S/A ratio leads to a straight increase of FT and LT. Hence, Al_2O_3 and kaolin is more efficient to improve fusibility, i.e., Al_2O_3 and kaolin may be the better additives.

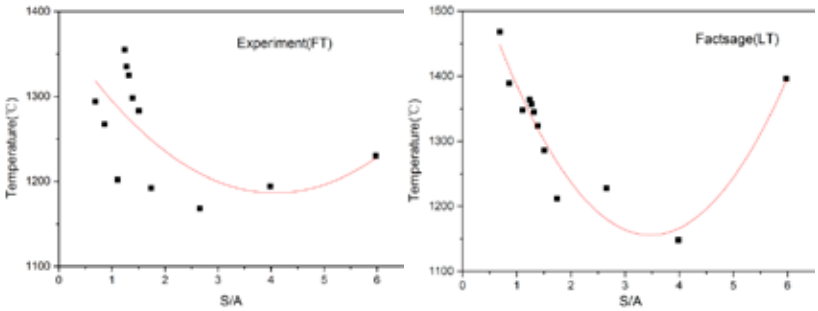


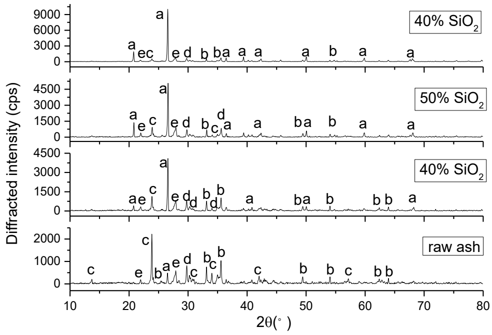
Fig.6. Effect of S/A on the fusion temperature and the liquidus temperature

3. MINERAL TRANSFORMATION MECHANISM

Fig. 7 shows the mineral composition of coal ash with different amounts of SiO_2 addition at 1100°C. Some hematite is present in the ash due to the high content of Fe_2O_3. With the SiO_2 addition ratio increasing, more quartz is found in the ash, which will increase the fusion temperature. The Na-based mineral hauyne is also found in the ash due to the high content of sodium in this coal. Moreover, the content of hauyne decreases with the SiO_2 addition increasing, which will induce the better fusibility because of the low melting point of hauyne. Diopside and anorthite are also found in the ash, whose contents remain nearly constant. From the above, the coal-ash fusion temperature will increase with increasing SiO_2 addition.

XRD patterns of ash with Al_2O_3 addition at 1100°C are shown in Fig. 8. Note that, at the Al_2O_3 content of 27%, kyanite and aluminum oxide are both found in the ash, both of whose melting points are extremely high and will increase the fusion temperature. In addition, the content of hauyne displays a tendency that is similar to that of SiO_2 addition in Fig. 7. Obviously, Al_2O_3 will also improve the ash fusibility.

Fig. 9 shows the XRD patterns of ash with kaolin addition at 1100°C. The composition of mineral is more complex than that in Fig. 7 and Fig. 8. With the increasing in addition ratio, the content of quartz first increases and then decreases. Note that more anorthite, whose melting point is high, is found when the addition ratio increases. Moreover, the content of hauyne decreases with the SiO_2 addition increasing. Therefore, kaolin addition will increase the fusion temperature. When the addition ratio reaches 28%, anhydrite is present in the ash due to the decomposition of hauyne.



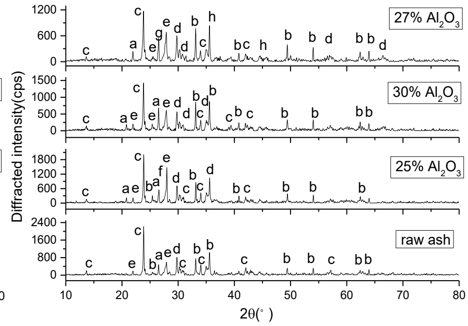


Fig.7. XRD patterns of ash with SiO_2 addition at 1100°C   Fig.8. XRD patterns of ash with Al_2O_3 addition at 1100°C

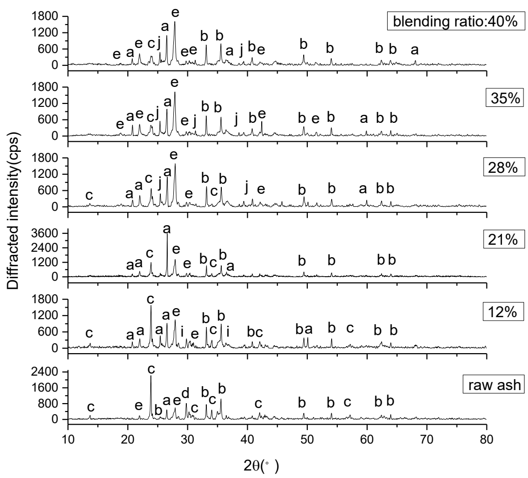


Fig.9. XRD patterns of ash with kaolin addition at 1100°C

a-quartz; b-hematite; c-hauyne; d-diopside; e-anorthite; f-albite; g-kyanite; h-aluminum oxide; i-uklonskovite; j-anhydrite

4. CONCLUSION

In this work, experiment and thermodynamic simulation were performed to study the coal ash fusion characteristics, and the mineral transformation. The main conclusions are as follows:

(1) Experiment results show that the coal-ash fusion temperature will increase with the blending ratio increasing of the three additives (SiO_2, Al_2O_3, and kaolin). However, Al_2O_3 and kaolin are more efficient to enhance the ash fusibility. With increasing S/A ratio, the fusion temperature drops initially and then increase.

(2) Regarding Al_2O_3 and kaolin addition, simulation results (LT) show the same variation tendency as the experimental results (DT, ST, HT, FT). The LTs rise with the blending ratio increasing for Al_2O_3 and kaolin additives, which is different from that of SiO_2 addition.

(3) XRD patterns show that, mounts of minerals with high melting point (quartz, aluminum oxide and anorthite) are found in the ash, when the mixing ratios of three additives reach higher. In addition, the content of the Na-based mineral hauyne decreases as the amount of additives increase. Hence, all of the three additives will enhance the ash fusion characteristics.

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