THE EFFECT OF IRON OXIDE ON INTERACTION BETWEEN RESIDUAL CHAR AND ASH AT HIGH TEMPERATURE AND ITS INFLUENCE ON ASH FUSIBILITY

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ABSTRACT

Residual char is often found in slag. The coal ash fusion behavior is essentially affected by the interaction between ash and residual char. In this work, the effect of Fe₂O₃ on ash fusibility were investigated. It was found that when the ashes have same content of residual char, ash fusibility increases as the Fe₂O₃ increases. The exist of Fe₂O₃ leads the formation of Fe and Fe₃Si. The reaction between the Fe₂O₃ and residual char is not benefit to the formation of SiC at high temperature.

Keywords: gasification, coal ash, fusibility, iron oxide.

1. INTRODUCTION

Due to the advantage of suitability of feedstocks and the high syngas yields, the entrained flow gasification technology is currently the most successful the gasification technology [1]. In the gasifier, the ash fusion temperatures (AFTs) is used to directly determine the operating temperature and to ensure the stable ash discharge condition [2]. The AFTs are essentially dependent on chemical compositions of coal ash. Residual char is widely found in the slag from gasifier [3]. Several studies have been made on the interaction between carbon and slag [4]. The content of Fe₂O₃ also showed an important effect on ash fusibility [5]. However, few studies were carried out about the effect of ash compositions on the carbothermal reaction and its influence on the ash fusibility. So, this paper mainly investigate the effect of Fe₂O₃ on the ash fusibility contained residual char.

2. MATERIAL AND METHODS

2.1 Synthetic ash samples

In order to simplify the system and eliminate the effect of trace elements, the four major components, SiO_2 , Al_2O_3 , Fe_2O_3 and CaO, were used to prepare a synthetic ash. The chemical compositions of the synthetic ashes are listed in Table 1.

Table 1 Chemical compositions of the ash sample (wt %)

Sample	SiO ₂	AI_2O_3	Fe_2O_3	CaO	
1	52.17	26.09	4.00	17.74	$Fe_2O_3=4$
2	50.00	25.00	8.00	17.00	$Fe_2O_3=8$
3	47.83	23.91	12.00	16.26	$Fe_2O_3=12$
4	45.65	22.83	16.00	15.52	Fe ₂ O ₃ =16

2.2 Residual char(denoted as RC)

A Chinese anthracite coal, ZhaoZhuang, was selected to prepare RC. The coal sample was ground to less than 200 μ m and dried. The coal was treated by acid leaching to eliminate the minerals from coal according to GB/T7560-2001. Then the treated coal was heated to 1400 °C under N₂ and stayed for 2 hours in a horizontal tube furnace. The proximate analyses and total sulfur contents of RC are shown in Table 2.

Table 2: Ultimate analysis of RC (wt %)								
Sample	С	Н	Oª	Ν	Sb			
Coal char	95.82	0.1	3.31	0.64	0.03			

2.3 Preparation of blended ash

In this work, the RC was added into the above synthetic ash samples based on the Fe_2O_3 content. The blended ashes with 4%, 8%, 12% and 16% Fe_2O_3 were prepared. Then, the blended ashes were thoroughly grinded in an agate mortar, and stored in the desiccator after heating at 110 °C for 2 h.

2.4 Mineral composition of ashes at high temperature

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The blended ash was heated to the target temperature and kept for 10 min under an Ar atmosphere in a horizontal tube furnace, and then cooled at 8 °C/min in flowing Ar at 300 ml/min. The XRD patterns of the ashes were recorded on a Bruker D2 X-ray powder diffractometer with Cu K α radiation (30 kV, 450 mA). Powder samples were mounted on a sample holder and scanned with a step size of 0.03° varying 2 θ from 10° to 90°.

2.5 TG-MS

The thermal behavior of ash with different Fe_2O_3 were characterized in thermogravimetric analysis (TGA, SETSYS Evolution 16/18, France) to 1450 °C under argon. The heating rate is 8°C/min. The gas line between TGA and MS was heated to 150 °C to prevent the condensation of gaseous products. Although other ionic species were detected during pyrolysis, special attention was paid to the following m/z signals: 18, 28, and 44. The m/z signals of 18, 28, and 44 were analyzed by MS (Omnistar, GSD-300).

3. RESULTS AND DISCUSSION

3.1 AFTS





Normally, the Fe_2O_3 is a fluxing agent which benefits the ash fusibility. When the 10% RC exits in ashes ($Fe_2O_3=4\%-16\%$), the DT and ST maintain stable while the HT and FT decrease with the content of Fe_2O_3 increase. It is known that the HT is related to the considerable melting of most of the minerals as a result of intensive liquid formation, while the FT is the characteristic temperature at which most refractory minerals have melted. So, the result of AFTs imply that Fe_2O_3 will reduce the amount of refractory minerals, which lower the FT and HT.

3.2 MINERAL

In order to further explain the role of Fe_2O_3 in ash with RC. The XRD of samples ($Fe_2O_3=4\%-16\%$) with 10% RC were compared in Fig 2. As shown in Fig 2, the major mineral in slag caused by Fe_2O_3 is Fe and Fe3Si. Besides, the increase of Fe_2O_3 decreases the content of SiC in the ashes. The increased Fe_2O_3 reacted with RC, which lowers the content of the carbon in the ashes. As a result, the carbothermal reaction between the SiO₂ and residual char was lessened.



Fig 2 XRD patterns of the ashes with different Fe_2O_3 at 1400 °C

1: Fe₃Si; 2: Corundum (Al₂O₃); 3: Quartz (SiO₂); 4: Anorthite (CaAl₂Si₂O₈); 5: Moissanite (SiC); 6: Fe

3.3 TG-MS



Fig 3 the TG curves of ashes with different composition

As shown in Fig 3, the curve1 represent the TG of ash (sample 2) with 10% RC. In order to further investigate the role of Fe_2O_3 in ash at high temperature, the ash contained RC without Fe_2O_3 (curve2) and the mixture of Fe_2O_3 and RC (curve3) was tested by TG. Compared with curve1 and curve2, it can be observed that Fe_2O_3 lead the weight loss during 700-1300°C, which

was confirmed by curve3. The weight loss was mainly caused by releasing CO which is detected by MS. Combined with the mineral at high temperature in Fig 2, the possible reaction during 700-1300°C can be summarized as follows:

> $3C + 2Fe_2O_3 = 3CO_2 + 4Fe_3O_3$ (1)

$$C + CO_2 = 2CO (g)$$
 (2)

$$3Fe +SiO_2 +2C = Fe_3Si +2CO (g)$$
 (3)

 $3C + SiO_2 = SiC + 2CO (g)$

$$3C + SiO_2 = SiC + 2CO (g)$$
 (4)



Fig 4 the TG and DTG curve of ashes with different Fe₂O₃

The TG of ash with different Fe₂O₃ was compared in Fig 4. The increase of Fe₂O₃ will lead more weight loss during 900-1500 °C. In the main, the weight loss can be divided into three part according the DTG curve. As indicated by DTG, the main effect by Fe₂O₃ on carbothermal reaction focus on Part 1 and Part 2, which correspond with reaction (1) and reaction (3) respectively. When the surplus RC exist, the reaction (2) will occur that leads ash to release CO rather than CO₂.



Fig 5 The main reactions in ash

As discussed above, the carbothermal reaction of Fe₂O₃ in the ash with temperature can be concluded in Fig 5.

4. CONCLUSIONS

- (1) The Fe_2O_3 mainly affect the FT and HT, and ash fusibility increases as the Fe₂O₃ increases.
- (2) The exist of Fe_2O_3 in ash that contained residual char will lead the formation of Fe and Fe₃Si.
- (3) Carbothermal reaction of Fe₂O₃ and residual char occur during 700-1300°C. The Fe₂O₃ consume residual char firstly, which is not benefit to the formation of SiC at high temperature.

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REFERENCE

[1] Minchener A J. Coal gasification for advanced power generation. Fuel, 2005, 8417: 2222-35.

[2]Van Dyk J C, Waanders F B, Benson S A, et al. Viscosity predictions of the slag composition of gasified coal, utilizing FactSage equilibrium modelling. Fuel, 2009, 881: 67-74.

[3] Xu S, Zhou Z, Gao X. The gasification reactivity of unburned carbon present in gasification slag from entrained-flow gasifier. Fuel Processing Technology, 909: 1062-70.

[4]Kong L, Bai J, Li W, et al. (2015), The internal and external factor on coal ash slag viscosity at high temperatures, Part 2: Effect of residual carbon on slag viscosity. Fuel, 158: 976-982.

[5]He C, Bai J, Kong LX, et al. The precipitation of metallic iron from coal ash slag in the entrained flow coal gasifier: By thermodynamic calculation. Fuel Processing Technology, 2017, 162:98-104.