

Effect of ash components and atmospheres on slagging characteristics of high-AAEM lignite gasification

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Abstract. Two kinds of high alkali and alkaline earth metal (AAEM) lignite (TTc and ZDc) were used as fuels, and three atmospheres of CO₂, CO/CO₂, and H₂O (g) were used in the horizontal tube furnace experiments to simulate the gasification conditions in different parts of the boilers. The relevant thermodynamic calculations on the atmospheres and ash compositions were conducted in FactSage 7.2. The results show that both two coals have a high risk of slagging. Decreasing the relative content of SiO₂ or increasing the relative content of Al₂O₃ can increase the ash fusion temperatures (AFTs) of TTc; increasing the relative content of CaO can increase the AFTs of ZDc. Besides, it is not recommended to adjust the relative content of Fe₂O₃. The proportion of the liquid phase of ZDc ash in CO/CO₂ atmosphere is much higher than that of CO₂ and H₂O (g) in a typical circulating fluidized bed (CFB) gasification temperature interval, while the generation of liquid phase of TTc ash is less affected by atmospheres. The bottom of boilers is the most severe slagging zone, and purging with H₂O (g) is a good way to alleviate the low-temperature slagging of the return feeder.

1 Introduction

Low-rank lignite is widely distributed in China, the United States, Australia, Indonesia, and Germany, and it plays an integral role in primary energy production and consumption [1]. In China, the excavation and application of the high-AAEM coalfield in the Xinjiang area with a detected reserve of 390 billion tons could ensure the coal demand for the next 100 years [2, 3]. AAEMs (mainly referring to Na, K, Ca, and Mg) in low-rank lignite can act as good catalysts during coal gasification, while, the different migration and transformation characteristics of AAEM elements and complex reactions between AAEMs and other minerals such as Al, Si, and Fe, will low the AFTs and lead to slagging [1-5].

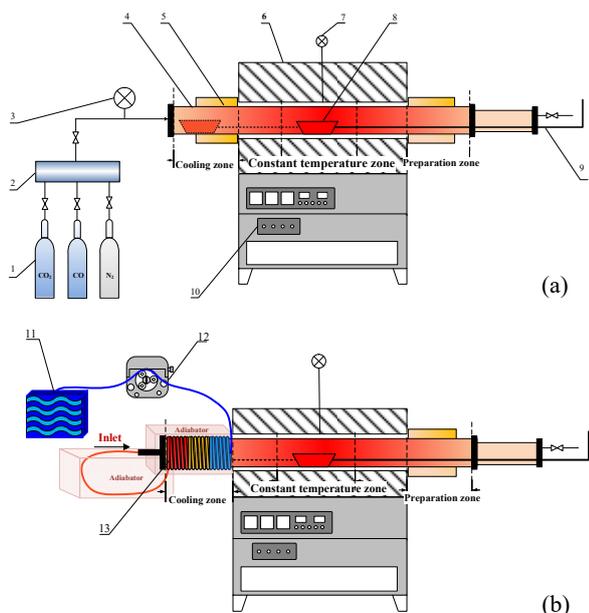
The CFB gasification technology is extensively applied in the coal chemical process and power generation for their high gas production and low environmental pollution. In the circulation process, coal particles will experience different atmospheric conditions, in which the bottom of the boiler can be approximately regarded as a high concentration CO₂ atmosphere, the upper of the boiler as a reducing atmosphere (CO/CO₂), and the segment of feeder mainly as H₂O (g) atmosphere. The migration and transformation of AAEMs and the interactions between different mineral components have certain differences under different atmospheres. Due to the insufficient knowledge of high-AAEM lignite, boilers exhibit a clear incompatibility during the coal utilization process, serious slagging occurred during the gasification process and the normal operation of boilers are affected.

To date, some studies have been conducted on the impact of the equivalence ratio on slagging and fouling characteristics of high-AAEM lignite, there is still lacking a systematic study to explore the influence of gasification agent types in different segments of boilers on slagging and ash fusion characteristics of lignite.

2 Experimental

Gasification experiments were conducted in a horizontal tubular furnace. Fig. 1 depicts the schematic diagram of the present experimental system. The system mainly comprises a reactor, gas or water intake system, flow control system, sample injector, and exhaust system. The inside diameter of the alundum-tube reactor is 70 mm, and the length of the constant temperature zone is 150 mm. The maximum working temperature is 1400 °C with the furnace temperature measured by an S-type thermocouple with an accuracy of 1 °C. The cylinder of CO₂ and cylinder containing 60% CO in CO₂ were used to provide the gas agents (Fig. 1(a)), and the water was introduced to the heating zone of the reactor via a peristaltic pump to provide vapor agent (Fig. 1(b)). In each experiment, 5 (±0.005) g sample was put in a corundum boat and the corundum boat with the sample was placed in the isothermal zone.

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1-gas cylinder group; 2-flow control and distribution system;
3-pressure gauge; 4-tube reactor;5-fixed bracket;
6-electric furnace; 7-thermocouple; 8-corundum boat;
9-pushrod; 10-temperature control system;
11-water tank; 12-peristaltic pump; 13-heat tracing device

Fig. 1. Schematic diagram of the horizontal tube furnace.

It is noted that the TTc belongs to typical high-sodium coal with 10.58 % Na₂O. ZDc is rich in AAEMs, i.e. 10.95 % CaO, 2.72% MgO, and 7.86% Na₂O. Besides, the Fe₂O₃ content in ash is 18.26 %. The coals were milled, air-dried at room temperature, and the size range of 0.18~0.355 mm was sieved.

3 Test Results and Discussions

3.1 Influence of typical mineral components on AFTs

The calculated ternary and pseudo ternary phase diagrams are shown in Fig. 2 and Fig. 3. Percentages of Al₂O₃, SiO₂ and Na₂O and percentages of Al₂O₃, SiO₂, CaO/Fe₂O₃, and Na₂O of the coal ash samples were normalized to 100 %, respectively, and plotted in the corresponding phase diagrams. The line of the same colour are isotherms which illustrate all components that have the same given liquid temperature.

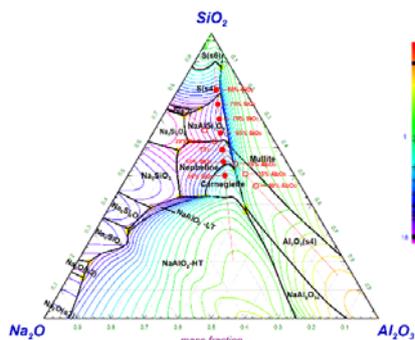
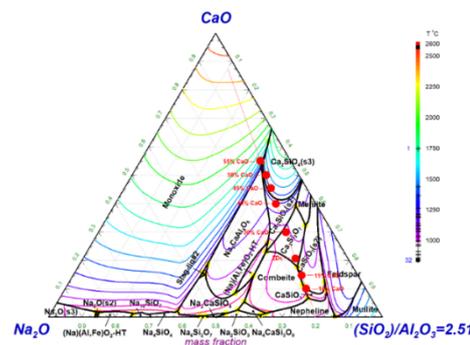
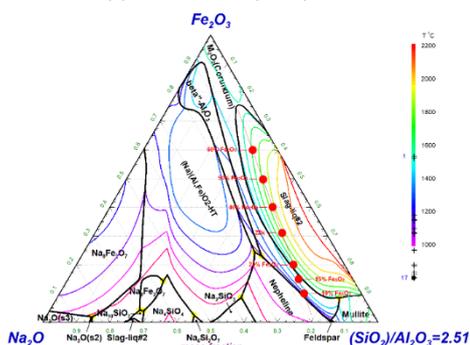


Fig. 2. SiO₂-Na₂O-Al₂O₃ ternary phase diagram of TTc.

TTc ash located in the primary crystallization region of Nepheline that closes to the region of Albite, indicating that a large number of low-temperature eutectic systems could be generated at a relatively low temperature. Reducing the relative content of SiO₂ in coal ash will promote the position move toward to the high-temperature melting region of Camegiet, and the risk of slagging of TTc is reduced. It should be mention that the content of SiO₂ is suggested to be controlled under 55%. Adjusting the relative content of Al₂O₃ in a small range can greatly increase the melting temperature of the entire coal ash. It is believed that increasing the AFTs of coal ash by increasing the relative content of Al₂O₃ is better than reducing the SiO₂ content.



(a) CaO-Na₂O-(SiO₂)/Al₂O₃



(b) Fe₂O₃-Na₂O-(SiO₂)/Al₂O₃

Fig. 3. Pseudo ternary phase diagrams of ZDc.

The located position of ZDc ash in CaO-Na₂O-SiO₂-Al₂O₃ phase diagram is near the junction of Ca₃Si₂O₇, CaSiO₃, and Combeite with the melting temperature around 1100~1200 °C. It is found that increasing the relative content of CaO will increase the melting temperature of ZDc. The located position of ZDc ash in the Fe₂O₃-Na₂O-SiO₂-Al₂O₃ phase diagram is in the region of the high temperature melting region of Slag-liq#2. Reducing the content of Fe₂O₃ in ash will cause a monotonous reduction in melting temperature, however, increasing the content of Fe₂O₃ in ash will cause the first increase and then decrease trend of ash melting temperature. It is not recommended for ZDc to adjust the AFTs by adjusting the relative content of Fe₂O₃ in ash.

3.2 Slagging characteristics under different atmospheres

As shown in Fig. 4, the slag-liquid formations of mineral compositions were calculated to illustrate the state that the

input components are completely reacted and the reaction attainment of equilibrium. The liquid phase in ash is comprised of two parts. One is low melting point compounds that are prone to direct melting, and the other is low-temperature eutectics formed by the interactions between the components. The liquid generation tendency of TTc in three atmospheres is basically the same, which indicates that the melting process of TTc ash is less affected by atmospheres. The main substances in ash are Albite ($\text{NaAlSi}_3\text{O}_8$) and Nepheline (NaAlSiO_4), with the total amount accounts for more than 50 % of the residual ash. The contents of Ca- or Fe-based components are relatively low. Therefore, the formation of liquid slag under three types of atmospheres is mainly derived from the low-temperature co-melting effect of Nepheline and Albite. A large amount of low-temperature eutectic will increase the ratio of liquid slag in ash rapidly, and the mineral components containing Ca and Fe are melted in a short time by the infiltration of the liquid slag.

As for ZDc, FeS has strong fluxing properties, especially when it exists in the form of FeS-FeO (melting point about 940 °C) in coal ash. Under the reducing conditions, the overall growth trend of liquid-slag is relatively stable. In the other two atmospheres, Albite and Na_2SO_4 in coal ash will melt at about 900 °C, resulting in a large increase in liquid-slag. However, the molten Na_2SO_4 will further react with other components to produce other substances with a relatively higher melting point, therefore the proportion of liquid phase in coal ash decreased. It is worth noting that in the typical CFB gasification operation temperature interval, the proportion of liquid phase in a CO/CO_2 atmosphere is much higher than that of CO_2 and $\text{H}_2\text{O}(\text{g})$, and the growth trend of liquid phase under $\text{H}_2\text{O}(\text{g})$ conditions is relatively slow.

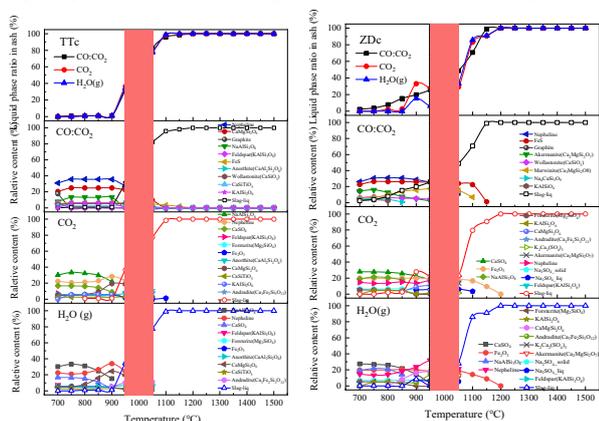


Fig. 4. Slag-liquid formation of TTc and ZDc under different atmospheres.

In summary, the high-AAEM lignite faces the highest risk of slagging under CO/CO_2 atmosphere, and the lowest under $\text{H}_2\text{O}(\text{g})$ condition. Combined with the actual operation of the condition of CFB gasification, although the CO_2 concentration at the bottom of the furnace is very high, the dense phase zone is still in a reducing atmosphere, therefore it is considered as the most severe slagging segment. As for feeder, it is an advantageous way to alleviate slagging by purging with $\text{H}_2\text{O}(\text{g})$.

3.3 Ash fusion characteristics

The microstructures and element contents on the surface of different samples are shown in Fig. 5. The surface of TTc gasification particles obtained under CO_2 and CO/CO_2 atmosphere have obvious melting areas. From the EDS results, Na, Al, and Si are the main enrichment elements of the melting part (a, b, and c_1), and they mainly exist in the forms of sodium silicate and aluminosilicate. The surface of $\text{H}_2\text{O}(\text{g})$ particle is rough (c_2), the main mineral elements on the surface are Mg and Ca, especially the Ca with content nearly 20 %. The contents of Na, Al, and Si are relatively low. As for ZDc gasification particles, a large amount of Fe is enriched on the surface under the $\text{H}_2\text{O}(\text{g})$ atmosphere, and the content AAEM metals like Na, Mg, and K are at a relatively low level. It is considered that the $\text{H}_2\text{O}(\text{g})$ atmosphere will reduce the enrichment of Na on the surface of the particles, thereby reducing the degree of melting on the surface and reduce the stickiness between the particles.

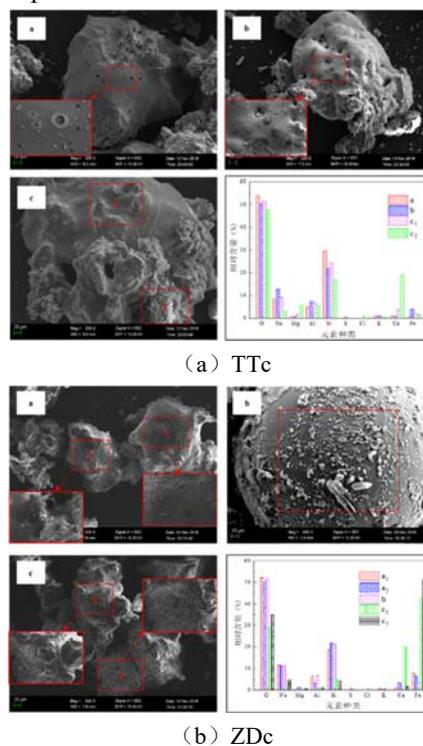
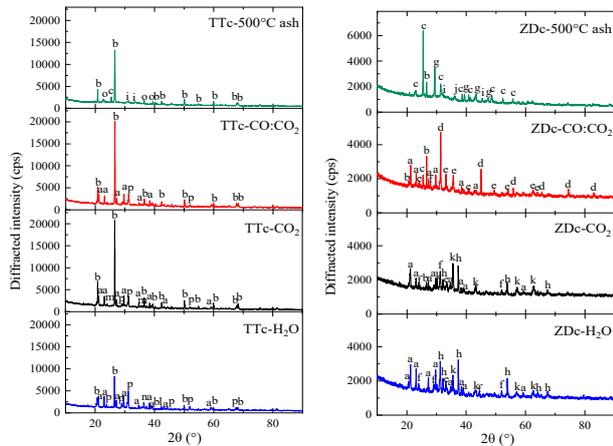


Fig. 5. Microstructures and element contents on the surface of gasification particles.

The detected results of XRD displayed in Fig. 6 show that during the gasification process Na-based substances in coal will react with Al_2O_3 and SiO_2 to generate a large amount of Nepheline. Limited by the reaction rate of the gasification process under the CO/CO_2 atmospheres, there is a certain amount of incompletely reacted coal left on the residues. Therefore, there are strong intensity peaks of SiO_2 show in the detection results. A large number of Fe_2O_3 peaks are monitored in ZDc residues, which are mainly caused by two reasons. One is the incompletely reacted coal itself contains Fe_2O_3 , the other is the generated FeS is re-oxidized during the low-temperature ashing process before the detection. It is worth noting that, the Ca mainly exists in the form of $\text{Ca}_2\text{Al}_2\text{SiO}_7$ in CO_2

atmosphere and in the form of CaO in H₂O (g) condition, which indicates a higher potential of slagging in CO₂ atmosphere.



a-K(Na,K)₃Al₄Si₄O₁₆; b-SiO₂;c-CaSO₄; d-NaCl;
e-Fe₂O₃; f-Ca₂Al₂SiO₇; g-CaCO₃;h-CaO; i-Na₂SO₄;
j-Na₇Al₃O₈; k-Fe₂MgO₄; l- FeO; m- KAlSi₃O₈; n-Fe₂Al₂O₄;
o-(Mg, Fe)₂SiO₄; p-Ca₂MgSi₂O₇

Fig. 6. Crystal phase of samples.

Fig. 7 shows the relationship between the softening temperature (ST) and the retention ratio of sodium (R_{Na}), where the R_{Na} is defined as the ratio of the sodium content in the gasification residues to the content in the raw coal [6], which can be calculated by the following equation:

$$R_{Na} = \frac{OV_{residue} \times A \times C}{OV_{coal}} \times 100\% \quad (1)$$

Where $OV_{residue}$ and OV_{coal} represent the original value of sodium in gasification residues ($mg \cdot g^{-1}$) and raw coal, respectively, A is the ash ratio (%), and C is the gasification residue ratio (%).

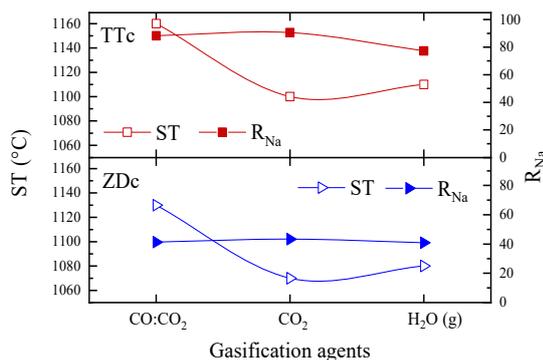


Fig. 7. Relationship between R_{Na} and ST under different atmospheres.

The R_{Na} of gasification residues under H₂O (g) condition is the lowest, which proves that the H₂O (g) atmosphere can indeed promote the release of Na during the gasification process. The R_{Na} under CO₂ and CO/CO₂ atmosphere are both at a relatively high level. However, the reasons for the high R_{Na} in the two types of gasification residues are different. Under CO₂ conditions, the Na-based components react with other mineral components to form silicate and aluminosilicate and be retained in the gasification residues, while under CO/CO₂

conditions, a certain amount of Na in the gasification residues is derived from the unreacted sample. Therefore, the existence forms and characteristics of Na under the two conditions are different. Besides, the refractory framework structure formed by carbon crystals in the residues greatly improves the AFTs of the entire gasified ash. Therefore, although the R_{Na} is high, the gasification residues still exhibit high melting properties in CO/CO₂ atmosphere.

4 Conclusion

Based on the results and discussions presented above, the conclusions are obtained as below:

(1) For TTe, increasing the AFTs by increasing the relative content of Al₂O₃ is better than reducing the SiO₂ content. For ZDc, increasing the content of CaO in ash will increase the AFTs, and it is not recommended to adjust the AFTs by adjusting the relative content of Fe₂O₃ in ash.

(2) The melting process of TTe ash is less affected by atmospheres. As for ZDc, the proportion of the liquid phase in a CO/CO₂ atmosphere is much higher than that of CO₂ and H₂O (g) in the typical CFB gasification operation temperature interval.

(3) The H₂O (g) atmosphere can promote the release of Na during the gasification process, and alleviate slagging. The dense phase zone in the bottom is considered the most severe slagging segment. As for the return feeder, it is an advantageous way to alleviate slagging by purging with water vapor.

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