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**Research Paper** 

## Alkali metal transformation and ash deposition performance of high alkali content Zhundong coal and its gasification fly ash under circulating fluidized bed combustion



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#### HIGHLIGHTS

- Zhundong (ZD) coal and its gasification fly ash are high alkali fuels.
- The transformation of Na and K during high alkali fuels combustion was studied.
- The release of Na during fly ash combustion was less pronounced than it was in the ZD coal.
- Variation in the bed temperature did not greatly affect the conversion of K.
- The ash deposition behavior during ZD coal and fly ash combustion were different.

#### ARTICLE INFO

Keywords: CFB Zhundong coal Gasification fly ash Sodium Ash deposition

#### ABSTRACT

Alkali metal transformation and ash deposition during combustion of Zhundong (ZD) coal and its gasification fly ash (ZDf) were studied in a 0.4 t/d circulating fluidized bed. The Na in ZD coal was present primarily as Na<sub>2</sub>SO<sub>4</sub>. NaAlSi<sub>3</sub>O<sub>8</sub> and KAlSi<sub>3</sub>O<sub>8</sub> were the main compounds of Na and K in ZDf. Variation in the bed temperature had a significant effect on the transformation of Na, but it did not greatly affect the conversion of K. During combustion of the ZD coal, Na was mainly in flue gas, the Na in fly ash was mainly in the water soluble form, but in bottom ash it was mainly in the insoluble form. During combustion of the ZDf, Na was found mainly in the fly ash and flue gas, insoluble Na and K accounted for above 80.0% of Na and K in ashes. The release of Na during the ZD f combustion occurred primarily as a result of the agglomeration and bonding of the ash particles that were rich in Na<sub>2</sub>SO<sub>4</sub>, and the deposition propensity was high. However, the ash deposition during the ZDf combustion propensity was high. However, the ash deposition during the ZDf combustion propensity was high. However, the ash deposition during the ZDf combustion propensity was low.

#### 1. Introduction

The growing demand for energy in China has led to an increase in the use of low quality-coal as a fuel. Zhundong (ZD) coal is usually characterized by a high volatile content, good reactivity and low ash and sulfur content, which makes it a promising fuel for power generation [1]. The ZD coal reserve in China has been estimated to be in excess of 3.9 Gt [2]. However, because of the high sodium concentration in ZD coal, a series of ash-related problems including ash deposition and slagging occur during the combustion of ZD coal [3,4]. The sodium content in ZD coal is usually about 0.2–0.9% [1,5]. To decrease the sodium base ratio and mitigate the ash-related problems, at present, high sodium ZD coal is utilized by blending it with low sodium coal, but this approach cannot solve the basic ash-related problems [6,7].

Employing low temperatures (850–950 °C) in the gasification/ combustion process in a circulating fluidized bed (CFB) is a good method for the clean use of ZD coal [8,9]. Zhang et al. [10] found that supercritical water gasification was an effective way for the utilization of ZD coal. Alkali metal could not only play a catalytic effect in the gasification process, but also finally enriched in the solid residue in the form of aluminosilicate salt which was stable. Application of CFB gasification to ZD coal would produce a large quantity of gasification fly ash with a high carbon content. Song et al. [9,11–13] conducted a series of gasification experiments using ZD coal in a 0.4 t/d CFB gasifier. Their

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experimental results showed that the sodium content in ZD coal gasification fly ash (ZDf) was as high as 1.0–4.0%. Therefore, ZD coal and the corresponding ZDf are both high-alkali content fuels, so re-burning of the ZDf is needed to reuse this waste resource [14]. Combustion of ZD coal and ZDf in a CFB can help to reduce the contamination and slagging caused by the sodium in the fuels. Consequently, it is quite important to fully understand the transformation of alkali metals during the combustion of high alkali fuels in a CFB.

In recent years, studies of the release and transformation behaviors of alkali metals during thermal conversions of ZD coal have been very popular. Sodium and potassium are the predominant alkali metals in various coals, and sodium is more predominant in ZD coal than potassium [5,15]. In general, sodium in coals can be divided into four categories: water soluble sodium, NH4Ac soluble sodium, HCl soluble sodium and insoluble sodium [10,16]. Water soluble and NH<sub>4</sub>Ac soluble sodium are easily released and are harmful during combustion [16,17]. During CFB gasification of ZD coal, some of the water soluble sodium released from the coal is condensed and enriched in the fly ash, whereas a portion of sodium can combine with the coal matrix and is preserved in the unburned carbon that is present in the fly ash. The quantities of alkali metals in the ZD coal gasification fly ash are far more concentrated than in the ZD coal. The mass fraction of HCl soluble and insoluble Na in the gasification fly ash are found to increase and the water soluble Na mass fraction usually decreased in comparison to the native ZD coal. Moreover, the gasification fly ash is usually in the form of ultrafine sized particles that contain high concentrations of ash and carbon [14]. Therefore, compared to the normal combustion of ZD coal, the unique properties of ZDf may result in new chemical transformation reactions of sodium during its combustion process.

Song et al. [14] studied the release and chemical transformation of sodium in ZDf during its combustion in a vertical tube furnace. These authors found that the sodium in this fly ash was more tightly bound to the fly ash as a result of different chemical reactions that had occurred in the ZD coal during its combustion. Yang et al. [18] studied the sintering and fusion characteristics of anthracite gasification fly ash in a fluidized bed. Their results showed that the slagging tendency of the fly ash was affected by the chemical transformation of the minerals in the fly ash. The content of the fluxing components, including Fe, Ca and Mg, was higher in this fly ash, so that the ash fluid temperature of the fly ash was higher than it was in the raw coal.

The chemical transformation reactions of alkali metals in coal are closely related to the operating temperatures of the combustion process. Kosminski et al. [19] found that the combustion temperature directly affected the reactions between the resident Na compounds and the resident SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, which directly affected the Na release process. Zhang et al. [20] reported that when ZD coal was gasified at 850–1050 °C, the sodium retention ratio in the ash initially decreased, but then increased as the temperature of combustion increased. Wang et al. [21] concluded that as the combustion temperature increased from 400 °C to 800 °C, 80% of the sodium was released from the coal. Jiang et al. [22] found that during the pyrolysis of biomass at 900 °C, 53–76% of resident alkali metals escaped from the pyrolyzed char. The operating temperature of the CFB was lower than the coal ash fusion temperature, and many studies have been conducted on the release behaviors of sodium during gasification of ZD coal in CFBs [5,8,9,13]. Unfortunately, little work has been conducted on the chemical transformation characteristics of alkali metals during combustion of high alkali fuels in a CFB. This is especially true in the case of alkali metals during the re-burning of ZDf. Song et al. [8] studied the chemical transformation of sodium in coal under different atmospheres in a 0.25 t/d CFB reactor. These authors found that more sodium was released into the gas phase with an increase in temperature, and the sodium existed primarily as Na<sub>2</sub>SO<sub>4</sub> in the combustion fly ash and as NaCl in the gasification fly ash. Qi et al. [23] found that sodium induced aggregation of ash particles and defluidization in the furnace were more pronounced when ZD coal was gasified in the CFB gasifier. In addition,

the ash deposition and corrosion of the tail heating surfaces were more pronounced during the combustion of ZD coal. These results suggest that a study of the ash deposition behaviors during combustion of ZDf is needed.

The goal of the presently reported work is to clarify the chemical transformation behaviors of sodium and potassium during the combustion of ZD coal and ZDf, and provide the basic data concerning the combustion of high alkali fuels (these are ZD coal and ZDf) in a CFB. The combustion experiments of high alkali fuels were conducted at 860 °C, 910 °C and 960 °C in a 0.4 t/d CFB reactor. The basic properties of the alkali metals in ZD coal as well as ZDf and the effects of the bed temperature on the chemical transformation behaviors of alkali metals during combustion were studied using a series of analytical techniques. The differences in chemical transformation of alkali metals and the ash deposition behaviors during combustion of the ZD coal and ZDf were also discussed.

#### 2. Experimental

#### 2.1. Experimental system

The combustion experiments of ZD coal and ZDf were conducted in a CFB test system, respectively, where the fuel feed rate of the system was 0.4 t per day. A schematic diagram of the system is shown in Fig. 1. The 0.4 t/d CFB test system was comprised of a riser, a cyclone separator and a loop seal. The height of the riser was 4200 mm and the inner diameter was 150 mm. The bottom of the riser was wrapped with a section of heating wire for ignition of the fuel in the initial stage. The air required for the experiment was provided by an air compressor. The flue gas temperatures and wall temperatures were adjusted by the slagging probes (A-G) equipped with a cooling system. In addition, the ash deposition characteristics during ZD coal and ZDf combustion were tested through the slagging probes.

The schematic diagram of the slagging probes (A-G) is shown in Fig. 2. The slagging probes were composed of Cr25Ni20 (GB/T20878-2007). Two thermocouples were set on the outside and inside of the probe end to measure the wall temperature of the heating surface, the wall temperature was calculated from the average temperature of the two thermocouples. The slagging probes were cooled by different mediums (air or water) to adjust the flue gas temperatures and wall temperatures of the heating surfaces, Probe A and Probe B were cooled by water, and the remaining probes were cooled by air. The length of Probe A was 1150 mm, while the length of the remaining probes was 400 mm. The flue gas temperatures were measured with the thermocouples ( $T_8-T_{13}$ ). All of the data, including pressures, temperatures and air volume flow rates, were collected and displayed real-time by a Programmable Logic Controller (PLC) data acquisition system.

#### 2.2. Fuels and operating conditions

A typical ZD coal and a sample of gasification fly ash from ZD coal (ZDf) were used as the fuels in the combustion experiments. The ZD coal was obtained from the Xinjiang Zhundong area of China, and ZDf was obtained from the ash collection can from a 0.4 t/d CFB gasifier as shown in Fig. 1, following a 950 °C gasification experiment using ZD coal. ZD coal was crushed and sieved to a size range of 0.1-1.0 mm, and the median particle size of ZDf was about 35  $\mu$ m. The properties of ZD coal and ZDf were determined based on the Chinese standards including GB/T212-2008, GB/T476-2008, GB/T219-2008, and GB/T1574-2007, etc. As shown in Table 1, the Na<sub>2</sub>O content in ZD coal ash was as high as 3.92% [5]. The properties of ZDf were significantly different from those of ZD coal, where the volatile matter content and water content were both lower, and the ash content was greater. The Na<sub>2</sub>O content in ZDf was 2.39%. It should be noted that the K<sub>2</sub>O content in ZDf ash was as high as 2.29%, and was much higher than it was in the ash from the ZD coal.

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