Full Length Article

Correlating the sodium release with coal compositions during combustion of sodium-rich coals

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HIGHLIGHTS

- Six typical sodium-rich coals were selected as the testing samples.
- The SR has a strongly positive correlation with the Na/(Si + Al) ratio.
- The promoting effect of Cl on SR is insignificant for sodium-rich coals.
- High content of calcite in ash has an obviously promoting effect on SR.

ARTICLE INFO

ABSTRACT

Sodium release (SR) has caused a series of severe problems during combustion of the special sodium-rich coals. An enhanced understanding of SR is crucial for designing the appropriate control measures. Thus, with a special focus on the sodium-rich coals, the correlations between compositions and SR, including the underlying mechanisms, are investigated on an atmospheric lab-scale tube furnace at 1000 °C. Some properties of coal compositions, such as the occurrence modes of Na, the mass ratios of Na/Cl, Na/S, Na/Ash and Na/(Si + Al), were quantitatively correlated with SR, respectively. The results show that the inhibiting effect of Si-Al minerals played a dominant role on the SR compared with the promoting effect of Cl. A strongly positive correlation was observed between Na/(Si + Al) and SR. Besides, the high content of calcite in the ash could obviously promote the SR, whereas the formation of thenardite in the residue markedly inhibited it. The comparison between combustion and gasification has been conducted, and it indicates that the SR also has a strongly positive correlation with the Na/(Si + Al) during steam gasification. In addition, the promoting effect of calcite on the SR could be mitigated by SO_3 due to the formation of anhydrite.

1. Introduction

Sodium-rich coals are widely distributed around the world, such as North Dakota in the United States, Victorian in Australia and Zhundong in China [1–3]. Due to the huge reserves and low mining cost, those coals are currently used as a fossil fuel for power generation. However, severe problems, such as fouling, slagging and corrosion, encountered frequently during combustion [4–6]. It is generally believed that sodium release (SR) at high temperatures should be responsible for the above problems [4–7]. Moreover, the released sodium species was found to be involved into the formation of fine particulates [6,8,9]. Thus, for developing appropriate control technologies, it is very essential to acquire some useful information on the characteristics of SR during combustion of sodium-rich coals [10].

Currently, the vast majority of researchers focused more interests on the effect of operating conditions on SR, such as reaction temperature, pressure, atmosphere, and even reactor type [11–18]. However, only few of them have reported the vital role of coal compositions on SR [7,19–23]. According to the limited reports, under a definite combustion condition, the SR was depended greatly on coal compositions, especially the elements of Na, Cl, S, Si and Al [7,20,21]. To find out the underlying mechanisms, a series of on-line measurement methods were employed [7,19–22]. For instance, by using an excimer laser-induced fluorescence (ELIF), Glazer et al. observed that the release of alkali metals depended greatly on the K/Cl and K/Si ratios during biomass combustion [22]. In addition, by using a molecular beam mass spectrometry (MBMS), Blasing et al. found that the release of NaCl depended

negative correlations with the ratio of S/Cl and the content of Si + Al during lignite combustion [12]. In another study on the hard coals, it was found that the release of NaCl depended greatly on both the Na/Cl and S/Cl ratios [20]. Furthermore, by using a high pressure mass spectrometry (HPMS), Oleschko et al. realized that Cl in coal promoted the release of alkali species, whereas Si and Al in ash inhibited it during combustion of hard coals [7].

So far, the on-line methods have performed well as the release of Na-species can be finely analyzed with changes of residence time during all the stages of combustion. However, it should be noticed that the on-line methods still have a few deficiencies of nature. On the one hand, their accuracy is not as high as the traditional methods. For this reason, the on-line methods can only provide semi-quantitative analyses. On the other hand, among the various released Na-species, only some special forms of them, such as NaCl and Na_2SO_4, can be well detected by the on-line methods. For the other forms, such as NaOH, it is hardly detected due to the same mass-to-charge ratio with carrier gas Ar, although NaOH has been identified as the crucial released form during combustion [12,20,24].

To overcome the known deficiencies of on-line methods, a traditional off-line method combined with ICP-OES analysis was adopted to quantitatively determine SR. In consideration of the lack of available information on the harmful sodium-rich coals, six sodium-rich coals from different regions of China and Australia were selected as testing samples. Some composition characteristics, such as the occurrence modes of Na, the mass ratios of Na/Cl, Na/S, Na/Ash and Na/(Si + Al), were correlated with SR, respectively. In addition, the residues were characterized by XRD analysis, providing some evidence for correlation analyses. Moreover, a detailed comparison of SR was made between oxygen combustion and steam gasification. The objective of this work is to find out the underlying correlations between coal compositions and SR during the combustion of sodium-rich coals. Meanwhile, those findings could provide some useful information for developing appropriate control technologies.

2. Material and methods

2.1. Coal samples

Six typical sodium-rich coals were chosen as samples. Among them, ZD-1, ZD-2 and ZD-3 were collected from Zhundong (Xinjiang province, China); AU, JL and HC were respectively collected from Victorian (Australia), Yili (Xinjiang province, China) and Yidong (Inner Mongolia, China). The method for collecting the above samples accords with GB/T 482-2008 [25]. The proximate and ultimate analyses are listed in Table 1, which are in accordance with GB/T 30733-2014 and GB/T 476-2008 [26,27]. The content of sulfur is determined according to GB/T 214-2007 [28]. The content of oxygen is calculated by the difference. Ash chemical composi-

tions are determined by an X-ray fluorescence spectrometer (S8 TIGER, Bruker, Germany), and the results are listed in Table 2.

The samples were dried at a room temperature, then pulverized and sieved to less than 74 μm. Prior to combustion, samples were dried at 110 °C for 2 h to eliminate the moisture disturbance. The above coals were selected due to the high content of Na in ash and the significant difference in the amounts of Na, S, Cl, Si and Al, which are of interest for this investigation.

2.2. Coal combustion and gasification

All combustion and gasification experiments were conducted in a lab-scale tube reactor housed in an electrically heated furnace. The schematic diagram of test system is illustrated in Fig. 1. The total heating length of furnace is 670 mm with a 150 mm flat-temperature zone. The inner diameter of tube reactor is 32 mm. The temperature of furnace was measured by a K-type thermocouple with the accuracy of 1.5 °C. The gas flow of oxygen and nitrogen was controlled by two gas mass flow meters with the accuracy of 2%. The flow of steam vapor was controlled by a double plunger pump with the accuracy of 0.5%. Prior to experiments, the rate of gas flow was revised by a soap-film flowmeter. To avoid the disturbances of air, a magnetic injection device was designed to push or pull the corundum boat into or out of flat-temperature zone by a heat-resisting nickel wire.

A typical produce of combustion experiment is as follows. Firstly, the furnace was heated to the preset temperature of 1000 °C and held for 30 min. Meantime, a gas flow of 80 vol% N_2 and 20 vol% O_2 was fed into the reactor at a rate of 500 mL/min for 15 min to remove the inside air. Secondly, a corundum boat loaded with ca. 1.00 g coal was placed at the cold side of tube for 5 min. Then, the sample boat was quickly pushed into the flat-temperature zone by the nickel wire. A steep temperature gradient was generated between the sample and its surrounding areas, which caused the violent release of volatiles in a short time. The released species were immediately carried out by gas flow. This process was similar with the real situations in the industrial furnaces. Subsequently, the residual char was burned under a controllable rate to prevent the runaway of combustion temperature. Finally, after residence for 15 min, the boat was pulled out and cooled to room temperature under the gas flow. For steam gasification, the operating procedure is almost same with that in the oxygen combustion. The only difference is that the gas flow changes to 60 vol% H_2O and 40 vol% N_2. After coal combustion and gasification, the obtained residues were collected for the following analysis.

2.3. Sequential chemical extraction

The occurrence modes of sodium were determined by the traditional method of sequential chemical extraction [29–31]. Sodium in coal are mainly classified into three forms: water-soluble

Table 1
Proximate and ultimate analyses (wt%) of coal samples.

Sample	Proximate analysis			Ultimate analysis (daf)				
	M_{ad}	A_d	V_{daf}	C	H	O^a	N	S_t
ZD-1	10.65	3.82	28.93	82.06	3.47	13.25	0.87	0.35
ZD-2	3.93	8.17	39.67	75.88	4.87	18.02	0.91	0.32
ZD-3	8.97	19.04	29.44	77.30	4.00	17.79	0.73	0.18
AU	12.56	27.71	52.84	67.22	5.16	21.21	0.93	5.47
JL	16.01	4.41	42.33	74.48	5.18	18.36	1.16	0.82
HC	5.29	6.44	33.55	79.01	4.48	15.15	0.97	0.39

ad, air-dried base; d, dry base; daf, dry and ash free base.
[a] By difference.