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Release characteristic of different classes of sodium during combustion of Zhun-Dong coal investigated by laser-induced breakdown spectroscopy

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Abstract Serious fouling and slagging problems are associated with the combustion of Chinese Zhun-Dong coal due to its high content of sodium (Na). Understanding the release characteristic of Na during the combustion is essential to viable utilization of this coal. In this work, coal samples were treated with a sequence of solvents: water (H_2O), ammonium acetate (NH_4Ac), hydrochloric acid (HCl), and the release characteristics of various classes of Na during coal combustion were investigated using the technique of laser-induced breakdown spectroscopy. The relative contribution of various Na classes to the Na release during each combustion stage was found to be similar, in the order of H_2O-soluble Na > NH_4Ac-soluble Na > HCl-soluble Na > insoluble Na. Sodium released during the devolatilization stage can be attributed to each of the sodium classes. After the devolatilization stage, H_2O-soluble Na and NH_4Ac-soluble Na dominated the Na release during both char and ash stages. Over 64 % of the total Na released during combustion comes from the H_2O-soluble Na, which suggests that the Na release during the combustion of Zhun-Dong coal can be reduced effectively after treatment by H_2O washing.

Keywords Zhun-Dong coal · Laser-induced breakdown spectroscopy (LIBS) · Sodium release · Combustion · Online measurement

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1 Introduction

Because of the abundant reserves, coal is still the main energy source for power generation in China [1] despite the numerous associated pollutants, e.g., sulfur dioxide (SO_2), nitrogen oxides (NO_x), and particulate matter (PM) [2–4]. Besides the combustible organic component, coal also contains several kinds of mineral matter including sodium (Na) compounds. During coal combustion, the released Na species are linked to the severe problems of fouling and corrosion of heat transfer surfaces in industrial boilers [5, 6]. Zhun-Dong coal, produced in the Xinjiang Uygur Autonomous Region of China, is a coal reserve of 390 billion tons and is expected to be one of the most widely used low-rank coals over the next several decades. However, due to its high Na content, serious fouling and slagging problems have been associated with its use in industrial power plants [7]. Understanding the release behavior of Na and designing strategies to limit Na release during the combustion process is essential to the practical utilization of Zhun-Dong coal.

Sodium exists in two forms in coals. One is present in the inorganic compounds, i.e., inorganic sodium, and the other is bound to the organic structure of coal, i.e., organic sodium [8–10]. In practice, Na compounds in coals are classified using the chemical fractionation technique according to their solvation in a sequence of solvents, typically water (H_2O), ammonium acetate (NH_4Ac), and hydrochloric acid (HCl) [8, 11, 12]. The Na compounds leached out by H_2O can be sodium salts, such as sodium chloride, sulfate and carbonate, or sodium acetate. The Na that is removed by NH_4Ac is likely linked to organic groups. HCl can dissolve the Na associated with ionic sites of clays. Na that remains in the coal after the fractionation procedure is bound in highly stable compounds, such as sodium silicate.

The release of Na during coal combustion is a subject that has received much attention from various research groups in the last few decades [13–20]. Although these studies improved the understanding of the Na release mechanism, the release characteristics of the various Na compounds were seldom discussed. Recently, Van Eyk et al. [10] studied the release behavior of water-bound and organic Na from brown coals by removing a fraction of the inherent moisture and concomitant dissolved salts using mechanical and thermal expression. However, Na release during the devolatilization stage could only be inferred by extrapolation of experimental data at the char and ash stages due to the limitation of their experimental method. Further investigation into the Na release during all stages of coal combustion is needed to understand the release mechanism of various Na compounds, with the overall goal of discovering strategies to prevent their release.

In this study, laser-induced breakdown spectroscopy (LIBS) was employed to measure the Na release during the combustion of Zhun-Dong coal. The benefits of the LIBS method over alternative methods have been mentioned in Ref. [21]. Detailed principles of this method can be found in previous publications [22–24]. Specifically, the release behavior of different classes of Na was studied systematically by washing coal samples using deionized H_2O, NH_4Ac, and HCl successively. Based on these experiments, a possible way for limiting the Na release during the combustion of Zhun-Dong coal was suggested.

2 Experimental methods

2.1 Sample treatment

The basic properties of the Zhun-Dong coal used in this study including the proximate and ultimate analyses and the ash composition are given in Table 1. The standard ashing procedure was followed to prepare the sample for the ash composition analysis. In order to study the release behavior of different Na compounds, the coal sample was treated with the chemical fractionation technique as follows.

The first step of the fractionation process is the removal of water soluble Na by rinsing with water. Samples of pulverized Zhun-Dong coal weighing 1 g were added to a beaker containing 100 mL deionized water at room temperature (298 K) and thoroughly stirred. Washing was performed for 2, 5, 30, or 60 min, resulting in four sample subsets. The reason for choosing such four washing time conditions is that 2 min is the shortest washing time including the filtering procedure and the other three durations are set for studying the effects of different washing times. According to the measured sodium release curves as shown in the next chapter, 5-min washing was found to be long enough for removing the related sodium. Thus, 30- and 60-min washing was carried out to verify this conclusion. After washing for the specified time, the suspension was filtered. In order to guarantee that the related sodium has been removed, samples that were used in subsequent fractionation steps were taken from the 30-min washing subset in the last step. After water washing, the coal sample was treated by 100 mL NH_4Ac solution (1 mol/L) and 100 mL HCl solution (1 mol/L) in turn in a similar way with the first step.

The residual coal sample after filtration in each step was then air-dried in an oven at 323 K at least for 12 h before use. The resulting solutions were analyzed with inductively coupled plasma-atomic emission spectrometry (ICP-AES) to determine the contents of different classes of sodium in the raw coal. With repeating the measurements three times in each step, the uncertainty of the decided contents of different sodium classes was estimated to be lower than 10 %.

The coal samples to be used for combustion were compressed into spherical coal pellets weighing 50 mg with a diameter of 4 mm. During each combustion measurement, the coal pellet was carried into the methane/air flame and suspended on two ceramic rods (d = 1 mm) at

Table 1 Properties of Zhun-Dong coal

Proximate analysis (wt%, dry basis)									
Volatile matter					Fixed carbon				Ash
30.86					64.79				4.35
Ultimate analysis (wt%, dry basis)									
C		H		N		S		O (by difference)	
75.39		3.48		1.19		0.42		15.17	
Ash composition (wt%)									
SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	Na_2O	K_2O	TiO_2	SO_3	MnO
10.79	9.62	36.83	9.21	3.95	3.42	0.41	0.68	24.74	0.35