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Research article

Transformation behavior of alkali metals in high-alkali coals

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ABSTRACT

Burning a coal containing a high content of alkali metals (Na, K) in utility boilers may result in ash-related problems such as slagging, fouling and corrosion on the heat transfer surfaces. This study investigated the transformation behavior of Na in four typical high-alkali coals including one Zhundong (ZD) coal and three Taer (TR) coals during combustion. The Na content in the coal is much higher than the K content, and different high-alkali coals have difference in the aspect of their existing forms. Measurement results of the tested coals showed that most of the Na in the coal is H_2O-soluble Na. During combustion, the released alkali metals increase with the elevated temperature. The H_2O-soluble Na and NH_4Ac-soluble Na in the ash decrease after the coal is burnt. This indicates that the released Na is originated from the H_2O-soluble and NH_4Ac-soluble Na, with the H_2O-soluble Na being the dominant constituent. The investigation also reveals that some of the H_2O-soluble Na in the ash might be converted into HCl-soluble Na and insoluble Na through reacting with Si-Al minerals. Furthermore, the low volatility of Na for ZD and TR coals is closely associated with the content of Cl, Si and Al in the coal.

1. Introduction

Coal, as an important source of primary energy, will continue to play an important role in worldwide energy consumption over the next few decades. However, the high-grade good quality coal has been excessively consumed; thus, low-grade coal has been attracting increasing attention. Unfortunately, some of these coals can give rise to several serious economic and safety problems in coal-fired power plants, including many ash-related problems, such as fouling, slagging, and corrosion [1]. One important factor causing these issues is the high content of alkali metals in coal, especially Na. During the thermal utilization of high-alkali coals, part of the alkali metals (Na, K) are released into the flue gas. Subsequently, the released alkali metals can condense on the heat transfer surface with a relatively low temperature and form a sticky layer, which results in the growth of an ash deposition layer [2]. Therefore, the transformation behavior of alkali metals is a very important stage for the formation of ash deposition, and better understanding their behavior is necessary.

According to the literature review, the transformation behavior of alkali metals is influenced by the reaction conditions and coal properties. The reaction conditions are referred to the reaction atmosphere (combustion, gasification, or pyrolysis), reaction time, temperature, pressure etc. [3–6]. The coal properties include the particle size, coal composition/coal type, existing forms (chemical forms) of alkali metals etc. [7–13]. With respect to various alkali metals in the coal, not all of them would result in ash deposition, while water-soluble and organic alkali metals are considered the most harmful [14]. Presently, the alkali metals in coal are classified as water-soluble (H_2O-soluble), ammonium acetate-soluble (NH_4Ac-soluble), hydrochloric acid-soluble (HCl-soluble) or insoluble by using the chemical extraction method [3,7,14,15]. Li et al. [3] investigated the release and transformation of Na during combustion of Zhundong coals in a laboratory-scale reactor. It was found that H_2O-soluble Na is the dominant form in the coal, and most Na in the form of NaCl is released into gas phase with increasing temperature. Apart from those released into the gas phase, some part of H_20-soluble alkali metals would convert into other forms [7,14]. Quyn et al. [8] probed the effect of chemical form and valence of alkali and alkaline earth metallic (AAEM) species on their volatilisation in a fluidized-bed/fixed bed reactor and a thermogravimetric analyser. The chemical and/or physical form of Na in the brown coal has a remarkable effect on the volatilisation of Na during pyrolysis, and the Na in the form of NaCl in the coal substrate volatilize more easily than that in the form of carboxylate.

Besides, the volatilisation of alkali metals also strongly depends on the coal composition/coal type. Many researchers have found that chlorine (Cl) has a close relation with the release of alkali metals [9,11,12,16–18]. Oleschko et al. [17,18] analysed the combustion products of German brown coals on line. Na- and K-species release

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mainly in the form of NaCl and KCl, and their release content is strongly dependent on the Cl-content of the coals. Gottwald et al. [11] found that the amount of Cl is decisive for the level of alkali emitted in fluidized bed combustion as well. Nevertheless, the release of Na and Cl from coal containing NaCl is disproportionate [4]. The influence of other elements, such as Si, Al and even S etc., on the release of alkali metals could not be ignored [9,11,16,19]. Naruse et al. [9] proposed a cross-correlation method to evaluate the evolution of Na from four different coals. Coals with higher cross-correlation coefficients between Na and Si/Al in raw coal have lower volatilisation fractions of Na in combustion. Glazer et al. [16] observed that the release of gaseous alkali species is not only related to the K/Cl, but also K/Si during the co-combustion of coal and biomass. However, the inhibiting effect of Si and Al on Na release might be restricted by Ca-species [20]. Blasing et al. [10] investigated the release of Na-, K-, Cl-, and S-species during gasification and combustion of German hard coals, and the release of NaCl depends on the S/Cl and Na/Cl ratios.

Although many research efforts have been made on the release and transformation of alkali metals in high-alkali coals, the understanding on influence mechanisms of coal compositions is still insufficient and there are some debates among different researchers. Moreover, the investigated high-alkali coals to date mainly come from Victorian in Australia, Rhineland in German, and Zhundong in China etc. [3,6–8,12,13,17,20,21]. The research work about Taer coal is not reported, not to mention its transformation behavior. Taer coalfield is the largest coalfield in Pakistan with a reverse of 175 billion tons. However, it has the characteristics of high Na-content as well, which will cause serious ash deposition in boilers. Due to the obvious difference between the primitive plants, coal-forming processes and geological environments in different coalfields, the properties of coals are diverse and complicated [22]. Thus, it is challenging to explore the ash deposition of this coal directly using the existing findings on behavior of alkali metals.

The aim of this article is to understand the transformation behavior of Na in high-alkali coals including Taer and Zhundong coals during combustion. The combustion experiments were conducted in an electrically heated tube reactor at a temperature of 500–1000 °C. The existing forms of alkali metals (Na and K) in coal/ash were measured by the chemical extraction method. The ashes were analysed with X-ray diffraction (XRD). Meanwhile, to gain a better understanding of the transformation behavior of Na species, the equilibrium calculation was used by FactSage 5.2.

2. Experimental method

2.1. Sample preparation

Four kinds of coals with high-alkali metals (Na, K) were investigated in this article. Among these, ZD coal comes from the Zhundong (ZD) coalfield, which was discovered in China. This coalfield has caused great concern because of its huge reverse, low-ash content and excellent combustibility etc. [23,24]. The other coals come from the Taer (TR) coalfield, and they are referred to as TR-1, TR-2 and TR-3, respectively. These four coals all have serious ash deposition propensity due to the high Na content.

The received coal was put in an electric thermostatic drying oven with the temperature set as 50 °C, and the air drying process lasted for 2 h. Then, the air-dried coal was crushed and sieved to obtain particles with a size of ≤ 200 μm. These coal samples were used for further analysis. Additionally, the proximate, ultimate and ash composition analysis are given in Tables 1 and 2.

Table 1
Proximate and ultimate analysis of coals.

		ZD	TR-1	TR-2	TR-3
Proximate analysis [w_{ad}%]	M	11.17	9.24	7.97	8.86
	A	6.43	12.77	21.15	13.36
	V	27.91	44.17	40.62	44.9
	FC	54.49	33.82	30.26	32.88
Ultimate analysis [w_{ad}%]	C	62.89	54.43	46.82	54.72
	H	3.04	3.9	3.7	4.02
	O	15.41	16.89	16.85	16.07
	N	0.55	1.04	0.84	1.11
	S_t	0.51	1.73	2.67	1.86
	Cl	0.019	0.014	0.011	0.02

Table 2
Ash composition analysis of coals.

		ZD	TR-1	TR-2	TR-3
Ash composition [w%]	SiO_2	41.57	30.42	45.55	36.91
	Al_2O_3	11.16	17.46	18.55	16.75
	Fe_2O_3	4.79	12.76	14.13	13.27
	CaO	16.21	12.11	4.75	11.47
	MgO	6.48	6.96	6.06	6.23
	K_2O	0.51	0.29	0.22	0.14
	Na_2O	3.5	3.13	1.76	2.91
	SO_3	8.05	14.02	6.51	11.06

2.2. Measurement of alkali metals (Na, K)

The chemical extraction method was widely used to measure the content of alkali metals (Na, K) [3,7,13,14]. First, H_2O-soluble, NH_4Ac-soluble and HCl-soluble alkali metals were extracted sequentially from coal or ash by H_2O, NH_4Ac (1 mol/L) and HCl (1 mol/L). Then, the residue was digested with a microwave digestion system. Lastly, the extraction and digestion solutions were analysed with inductively coupled plasma optical emission spectrometry (ICP-OES), and the content of alkali metals in different existing forms was obtained.

2.3. Combustion experiment

The combustion experiments were conducted in an electrically heated tube reactor (as shown in Fig. 1). To investigate the transformation behavior of alkali metals during the coal combustion, 2 g of coal was loaded in an alumina boat that was positioned in the centre of the tube reactor. The inner diametre of the tube reactor is 54 mm, and the total heating length is 600 mm. During each experiment, the air was continually supplied by a gas cylinder, and the flowrate was set as 1.0 L/min via the mass flow metre. Temperature is an important parameter for coal combustion. It was increased from room temperature to the setting temperature at a rate of 10 °C/min, and then maintained for 1 h in order to ensure that the coal sample was completely combusted. After combustion, the ash was collected and analysed. It is well known that the content of alkali metals complies with the conservation law. They are partly released into the gas phase, the other remainder is retained in the ash. Thus, the content of alkali metals in the gas phase can be obtained when those retained in ash are analysed. In addition, the minerals in ash were identified by XRD.

2.4. Equilibrium calculation on the transformation of Na species

Thermodynamic equilibrium calculations were carried out using the FactSage 5.2 to simulate the transformation behavior of Na species during combustion. The calculation method was based on the principle of minimization of Gibbs free energy. The calculated temperature range was set as 500–1200 °C, which corresponded with the experimental temperature, and the temperature step was 50 °C at normal pressure. The required data for the calculations included: C, H, O, N, S, Cl, Si, Al, Fe, Ca, Mg, K and Na. The theoretical air volume was calculated using the equation: $V^0 = 0.0889([C] + 0.375[S]) + 0.265[H] - 0.0333[O]$, and the excess air coefficient was 1.2. In addition, the solution database