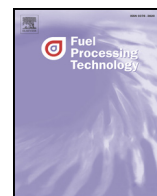




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Research article

# Volatilisation and transformation behavior of sodium species at high temperature and its influence on ash fusion temperatures

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## ABSTRACT

Zhundong coalfield is one of the superhuge coalfields newly mined in the Xinjiang Autonomous Region of China. However, operational practices have shown that power plants frequently encounter ash deposition problems during combustion of Zhundong coals because of the volatilisation of sodium species. To address such an issue, in this paper, volatilisation levels of sodium species of different coal ash samples in different conditions were studied. The effects of atmosphere and ratio between the major elements in coal ash were also studied to find the resolvent for prohibiting volatilisation. The results show that two Zhundong coals both with a higher sodium content but different calcium and silicon content induce different ash fusion temperatures (AFTs). The volatilisation levels of Wucaiwan (WCW) coal ashes which have higher calcium but lower silicon content were much higher than XHS coal ashes during ashing and AFTs test process. Further studies found that most of the sodium species in XHS coal ash which have a higher silica content transform to  $\text{Na}_6\text{Ca}_2\text{Al}_6\text{Si}_6\text{O}_{24}(\text{SO}_4)_2$  at high temperature. However, fewer sodium aluminosilicate but greater amount of  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$  was found in WCW coal ash of 1200 °C. By analyzing the coal ash compositions, it was found that the volatilisation of sodium species was insignificant for the samples with a  $\text{SiO}_2/\text{Na}_2\text{O}$  ratio of more than 20 or with a  $(\text{SiO}_2 + \text{Al}_2\text{O}_3)/\text{Na}_2\text{O}$  ratio of more than 25. Calcium species promoted the volatilisation of sodium species, and the volatilisation was insignificant for the samples with a  $\text{SiO}_2/\text{CaO}$  ratio of more than 4.

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## 1. Introduction

Zhundong coal field, located in the east of Junggar Basin, Xinjiang, China, is the largest intact coalfield in the world with a forecast reserve of 390 billion tons. According to the current coal consumption in China, the Zhundong coal could meet the needs for coal consumption in China for the next 100 years [1,2]. However, Zhundong coal has high contents of active sodium species [3] which will cause serious fouling and agglomeration in boilers or on tail heating surface, and even affect the safe operation of the boiler [4,5]. Up to now, the coal could not be used on a large-scale in Xinjiang, due to its special property, geographical location, economic and traffic conditions.

In the past decades, there were many pioneer researches and findings on the volatilisation of alkali and alkaline earth metallic (AAEM) species in coal. Li and co-workers [6,7] found that significant proportions of the AAEM species in the coal samples were volatilised during pyrolysis even at temperatures as low as 300 °C. The volatilisation of AAEM species was not sensitive to changes in heating rate but was strongly influenced by increasing temperature. The monovalent species (Na) was

always volatilised to a much larger extent than the divalent species (Mg and Ca) under similar pyrolysis and gasification conditions. Na and K vaporized during gasification and the interaction with inherent minerals was insignificant. Almost all the Ca and Mg were retained in the gasified char even if a major part of the carbon disappeared due to the gasification [8]. The  $\text{CO}_2$  volatile ratio affects the retention of Na during devolatilisation of coal, but does not affect the retention of Ca or Mg [9].

Furthermore, there were studies that investigated AAEM ash reaction. The extent of interaction between the sodium and silica/silicates was reduced by the presence of chlorine and sulfur and this effect was greater with kaolin than with quartz. At gas temperatures of 1200–1400 °C, sodium was volatilised from the coal before significant reactions occurred with the silica. At 1000 °C the sodium was not fully released prior to the commencement of the silicate formation reaction [10]. Aluminosilicate sorbents with a preferable  $\text{Al}_2\text{O}_3/\text{SiO}_2$  ratio of about 1/8 is sufficient to remove alkali metal vapors from the hot flue gas at about 1400 °C under pressurized pulverized coal combustion conditions [11]. Kaolin is well known as a good sorbent to chemically absorb sodium compounds at high temperature [12,13,14,15]. The kaolin particles contribute to depressing the formation of fine particulates and sodium compounds even under actual coal combustion conditions [16]. Wang et al. [17] studied on the ash deposition mechanism in

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**Table 1**  
Proximate analysis of coals (wt.%).

Coals	WCW	XHS	HLJ
Moisture	9.97	9.21	8.38
Ash, (db)	4.08	7.73	17.11
Volatile, (db)	30.95	32.64	36.66
Fixed carbon, (db)	64.97	59.63	46.23

boilers burning Zhundong coal. It was found that from 400 to 800 °C, 80% of sodium, and 100% of chlorine are released; from 800 °C to 1000 °C, all the left sodium evaporates and sulfur started to release with the formation of partial aluminosilicates; from 1000 to 1200 °C, all of the remaining sulfur is released through the decomposition of calcium sulfates and then calcium starts to evaporate, while silicon oxides disappear due to the formation of new complex silicates. Ma et al. [18] found that with the increase of combustion temperature, minerals in Zhundong coal transform into fusible minerals such as fayalite and calcium silicate. The dispersed Ca species were converted into submicron particles upon pyrolysis and then they interacted with clay minerals to form complex aluminosilicates of low-melting points [8]. At 500 °C and 600 °C, the main form of sodium is NaCl for Zhundong coal. At 700 °C, NaAlSi<sub>3</sub>O<sub>8</sub> is observed. Further increasing the ashing temperature will promote the appearance of NaAlSiO<sub>4</sub> [19].

However, the transformation of AAEMs is more associated to coal types. For Zhundong coal as a newly found, low-rank lignite with extremely high sodium and quite different calcium and silicon content, the understanding of AAEMs transformation and melting or fusion of eutectics is still insufficient. Therefore, this study aims to find the possible resolvent to restrain the volatilisation of sodium species, via investigating the volatilisation behavior and transformation of AAEM species at high temperature. And finally make guidance for the use of Zhundong coals.

## 2. Experimental

### 2.1. Samples

WCW and XHS coal used in this study were obtained from Xinjiang province, which was a typical type of Zhundong coal with high sodium content. The coal was crushed and pulverized to obtain a particle size of less than 0.2 mm for blending and ashing to produce ash samples. HLJ

coal which has a higher silica content was used to blend with WCW and XHS coal to obtain samples with a greater quantity of silicon, aluminum for study. The proximate analysis of WCW, XHS and HLJ coals are presented in Table 1.

High sodium coal ashes produced at 400 °C, 500 °C, 600 °C, 700 °C, 815 °C from WCW and XHS coal as well as HLJ coal were used for this study. The ashes were named according to their respective coal samples and the temperature they were produced. For example, ash sample WCW-HLJ(5:5)-400 means the ash was produced at 400 °C from WCW and HLJ blend coal with a ratio of 5 to 5 by weight. To study the effects of calcium on the volatilisation level of sodium, another special ash sample with high calcium content was produced at 815 °C by blending and then ashing of XHS coal and CaCO<sub>3</sub>. The composition and AFTs of those ash samples are presented in Table 2 and Table 3.

### 2.2. Apparatus and experiment

#### 2.2.1. Ashing process

The ashing process was operated as follows: a coal sample was placed on the combustion boat with a thickness of less than 0.05 g/cm<sup>2</sup>. A muffle furnace was heated to the target temperature of 400 °C, 500 °C, 600 °C, 700 °C, 815 °C, and then the boat was placed within and kept for 2 h at the designed temperature in an atmosphere of air.

#### 2.2.2. Ash fusion temperature test

The AFTs were tested by following the Chinese standard procedures (GB/T219-2008). This test involves heating a cone shape sample at a rate of 17 K/min before 900 °C, 5 K/min after 900 °C in an oxidizing atmosphere (in air), or a mild reducing atmosphere obtained by sealing 12 g of carbon and 9 g of graphite into the furnace. Four temperatures which describe the softening and melting behaviour of ash were recorded for each sample, corresponding to specific shapes of the ash cones: deformation temperature (DT), spherical temperature (ST), hemispherical temperature (HT), and fluid temperature (FT). Each experiment was carried out twice to ensure repeatability of the results. In addition, to analyse the escape of sodium species at high temperature, the cone ash sample was placed in the AFTs tester and then heated to the target temperature of 1100 °C, 1300 °C in oxidizing or mild reducing atmosphere and then cooled to room temperature. The residual ash was collected carefully from the sample supporter for ash composition analysis.

**Table 2**  
Analysis of WCW and XHS coal ash samples.

Ash	WCW-400	WCW-500	WCW-600	WCW-700	WCW-815	XHS-400	XHS-815
Ash(ad), %	3.91	3.84	3.51	3.3	3.26	6.64	6.14
Ash composition, wt.%							
P <sub>2</sub> O <sub>5</sub>	0.04	0.05	0.06	0.07	0.07	2.04	2.41
Fe <sub>2</sub> O <sub>3</sub>	7.58	8.18	8.86	9.6	10.71	5.65	6.24
SiO <sub>2</sub>	8.24	9.68	9.79	9.96	10.35	31.9	32.64
MgO	6.87	7.43	7.85	8.34	8.7	6.41	7.58
CaO	28.81	31.3	33.6	35.68	36.41	14.23	17.05
TiO <sub>2</sub>	0.31	0.33	0.36	0.37	0.38	0.67	0.73
Al <sub>2</sub> O <sub>3</sub>	5.93	6.41	6.82	7.39	7.51	15.76	17.37
Na <sub>2</sub> O	6.45	6.71	6.42	5.83	4.88	7.32	7.12
K <sub>2</sub> O	0.25	0.31	0.45	0.47	0.69	0.78	1.07
AFTs test in mild reducing atmosphere, °C							
DT	1280	1290	1300	1310	1300	1130	1140
ST	1410	1410	1420	1420	1380	1140	1150
HT	1420	1420	1430	1420	1390	1150	1150
FT	1420	1440	1440	1440	1420	1170	1180
AFTs test in oxidizing atmosphere, °C							
DT	1330	1340	1340	1340	1340	1330	1290
ST	1340	1350	1350	1350	1340	1330	1300
HT	1340	1350	1350	1360	1340	1340	1310
FT	1360	1360	1380	1390	1360	1350	1320

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