Fuel 181 (2016) 951–957

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Improved sequential extraction method for determination of alkali and alkaline earth metals in Zhundong coals

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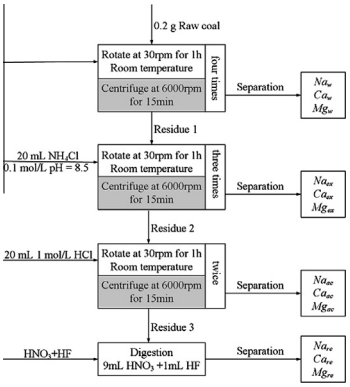
HIGHLIGHTS

- Effects of extraction condition on AAEM determination in were experimentally studied.
- An improved sequential extraction method was proposed with clearly defined conditions.
- The new method has higher accuracy and is less time consuming.
- AAEM occurrence modes and contents in three Zhundong coals were determined by the new method.
- Mineral patterns in raw coal and extraction residues were analyzed by XRD.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 March 2016
Received in revised form 17 April 2016
Accepted 5 May 2016
Available online 17 May 2016

Keywords:
Zhundong coal
Alkali and alkaline earth metal species (AAEMs)
Sequential extraction method
Occurrence modes

ABSTRACT

Zhundong coal is one of the most important coals in China due to its huge reserve, but it causes severe fouling and slagging problems when it is burnt in boilers for its high AAEMs (alkali and alkaline earth metal species) contents. Accurately determination of the occurrence modes and contents of AAEMs in Zhundong coals is a necessary step to overcome the ash-related problems. Nowadays, different researchers used different methods or procedures to determine AAEMs in Zhundong coals, and the data were scattering. Based on a series of experiments on the effects of extraction conditions, an improved extraction method with clearly defined conditions for each extraction step was proposed. 0.1 mol/L NH_4Cl (pH = 8.5) instead of 1 mol/L NH_4OAc (pH = 7) was used to extract the exchangeable AAEMs in Zhundong coals to avoid the high solubility of carbonates in the extraction solution. The improved method was more accurate and took much less time than the conventional one. With the proposed extraction method, the occurrence modes and contents of AAEMs in three Zhundong coals were measured. The results revealed that Na is mainly water soluble (Na_w/Na_{total} = 50–85%) which is halite or in the form of surface bound Na^+, while Ca and Mg are mainly acid soluble (Ca_{ac}/Ca_{total} = 60–90%, Mg_{ac}/Mg_{total} = 45–90%) which are carbonates together with a little amount of sulfates. Exchangeable AAEMs organically bonded to the coal matrix are not the main occurrence mode of AAEMs. Acid insoluble Ca-species could be rankinite. The amounts of AAEMs in the same occurrence mode could be remarkably different among coals from different Zhundong district. The improved sequential extraction method can be extended to determine AAEMs in high carbonate-containing coals.

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http://dx.doi.org/10.1016/j.fuel.2016.05.014
0016-2361/

1. Introduction

Zhundong coal, which is produced in Zhundong district, Xinjiang, China, is a kind of sub-bituminous coal characterized by the features of low ash and sulfur contents, medium volatile content and heating value, promising to have high reactivity [1,2]. With the forecast reserve of ~390 billion tons [3], Zhundong coals can meet the coal consumption of China for the next 100 years according to the current coal consumption, regarding as one of the most important coals in China [4–6].

However, applications showed that Zhundong coal often caused severe slagging and fouling problems, endangering the safety and increasing the operation cost of facilities [4–7]. High contents of alkali and alkaline earth metals (AAEMs) have been found to be responsible for the ash-related problems [8–11]. Generally, content of Na is 0.2–1 wt% and content of Ca is 0.6–2.5 wt% in raw Zhundong coals. Occurrence modes and contents of AAEMs are the basic data for the facility design and operation. Usually, these properties are determined by sequential extraction method [12–14], which is a four-step procedure using four kinds of extraction solutions: deionized water, ammonium acetate (NH_4OAc), hydrochloric acid (HCl) and acids for digestion (e.g. HNO_3 and HF). Accordingly, the AAEMs are categorized into four occurrence modes: water soluble, exchangeable, acid soluble and acid insoluble AAEMs [15], and contents of AAEMs in the four occurrence modes are respectively determined by analyzing the extraction solutions collected in each step.

Nowadays, a number of studies using the sequential extraction method have been conducted to determine occurrence modes and contents of AAEMs in Zhundong coals. However, the extraction conditions are very different among the existing studies. For example, Fu et al. [16] extracted Zhundong coals using deionized water, 1 mol/L NH_4OAc and 1 mol/L HCl solutions sequentially with solution/coal ratio (SCR) = 50 mL/g. Under these settings, experiments were conducted at various agitation duration (t) and temperature (T). Based on the results, the best condition of T = 60 °C and t = 24 h was suggested for each step. Chen et al. [17] extracted Zhundong coals by adding 1 g coal into 30 mL deionized water, 0.1 mol/L NH_4OAc, 0.1 mol/L HCl in turn, agitating at T = 60 °C for 2 h in each step. Wang et al. [18] conducted the extraction experiments at SCR = 120 mL/g, agitating at T = 60 °C for 24 h in each step. Dong et al. [19] extracted Zhundong coals at SCR = 75 mL/g, agitating at T = 20 °C for 12 h in each step. Based on the existing studies, Na is mainly water soluble which accounts for more than 60% of total Na, while Ca is major exchangeable which accounts for 40–65% of total Ca in Zhundong coals [16–19]. However, these data were inconsistent and meaningless for comparison unless the effect of extraction conditions is clarified.

Moreover, most of the existing studies about AAEMs in Zhundong coals are focused on Na, while Tao et al. [20] revealed that original minerals in Zhundong coals also contained a large amount of calcium sulfate hydrate, calcite, quartz, kaolinite and pyrite. Accurately determination of Ca content in Zhundong coals is necessary for the Ca-species is regarded as another important factor to the ash-related problems [21]. In conventional measurements, exchangeable AAEMs organically bonded with carboxyl groups in coal matrix are extracted by 1 mol/L neutral NH_4OAc solution, which was firstly introduced by Benson and Holm [12]. However, as Matsuoka et al. [22] reminded, besides the exchangeable Ca, some Ca-containing minerals such as calcite ($CaCO_3$) and anhydrate ($CaSO_4$) might dissolved in NH_4OAc solution as well. The high solubility of $CaCO_3$ and $CaSO_4$ in NH_4OAc solution could result in an over-estimation of exchangeable Ca in high carbonate-containing Zhundong coals.

Consequently, in this paper, the effects of extraction conditions on AAEMs determination in Zhundong coals were studied by a series of experiments under different agitation duration, extraction times, solution/coal ratio and using different types of solutions. Based on the experimental results, an improved sequential extraction method with improved accuracy and of less time consuming was proposed. Subsequently, occurrence modes and contents of AAEMs in three Zhundong coals were determined by the proposed sequential extraction procedure. And mineral patterns in each occurrence mode were simply discussed according to X-ray diffraction analyses of the ash samples.

2. Experiments

2.1. Coal properties

Three coals from Sha'erhu, Tianlong and Zhongnengshihua coal mines in Zhundong region, Xinjiang China, named as ZD-1, ZD-2 and ZD-3 separately were tested in this paper. The coal samples as received were firstly dried at low temperature (T < 50 °C), then they were grounded and sieved to particle size between 60 μm and 105 μm. Before experiments, all the sieved samples were dried again in an oven at 105 °C in N_2 atmosphere for 2 h. Properties of the coals are listed in Table 1. The coals have high moisture and high volatile contents, but very low ash content (<5%). Chloride (Cl) content in ZD-1 is higher than in ZD-2 and ZD-3, while sulfur content in ZD-1 is lower than in the other two coals. Chloride in Zhundong coals were measured by ICS-1000 ion-chromatography made by DIONEX.

For ash composition analyses, coal samples were slowly heated up to 500 °C at a heating rate of 10 °C/min in a muffle furnace, and kept at 500 °C for 1 h. Low oxidizing temperature can reduce the effect of organic matters and minimize the change of minerals (only decomposition of kaolinite and dehydration of hydrates could happen at 500 °C [20]) in ash analysis process. The ash samples were then analyzed by X-ray fluorescence (XRF), and main ash compositions are listed in Table 2. Obviously, Zhundong coal ashes are characterized by high Ca and Na content. Since the amount of K is much lower than that of Na, no discussion on K is given in this paper.

2.2. Sequential extraction procedure

As schematically shown in Fig. 1, a four-step sequential extraction method was employed based on previous studies [12,15–19].

Step 1 (water soluble): 0.2 g coal and 20 mL deionized water were mixed in a 50 mL polyethylene centrifuge tube. Then, the tube was placed in an agitation device and rotated at 30 ± 2 rpm

Table 1
Properties of tested Zhundong coals.

Samples	ZD-1	ZD-2	ZD-3
Proximate analysis (wt%)			
M_{ad}	18.61	13.24	12.87
A_{ad}	4.12	6.10	6.85
V_{daf}	36.28	30.89	28.28
FC_{ad}	49.23	55.74	57.58
$Q_{ad,net}t$ (MJ/kg) (LHV)	20.42	23.31	24.59
Ultimate analysis (wt%, ad)			
C	1.00	0.84	0.94
H	66.14	67.63	65.80
N	3.53	3.48	3.85
Cl	0.75	0.09	0.04
S	0.08	0.44	0.32
O[a]	5.76	8.18	9.33

[a] By difference.