



Full Length Article

The influence of mineral matter on moisture adsorption property of Shengli lignite



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HIGHLIGHTS

- Variations of pore structure and oxygen-containing functional groups of coals during leaching procedures were analyzed.
- Mineral matters were confirmed to have influence on moisture adsorption performance of lignite.
- Mineral-water interactions in lignite were also discussed.

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ABSTRACT

A typical Chinese lignite was subjected to H₂O, CH₃COONH₄/HCl and HCl/HF/HCl leaching procedures, to study the influence of water-soluble salts, alkali and alkaline earth metals (AAEMs) organically bound to the coal substance or occur as acid-decomposable minerals and discrete mineral matters on moisture adsorption property of lignite. Variations of pore structure and chemical functional groups of coal samples during leaching procedures were determined by the nitrogen adsorption measurements and Fourier transform infrared spectroscopy (FTIR), respectively. Possible interactions between different types of minerals and moisture in lignite were also discussed. The results showed that the specific surface area and porosity of the coal treated by HCl/HF/HCl method increased significantly, while other leaching procedures had slight effect on coal pore structure. The FTIR spectrum of treated samples displayed similar bands of the organic part as those of raw coal. Water-soluble minerals in coal have adversely influence on the sorption behaviour of water molecules. The ionic cross-links forces and the hydration of ions, gradually disappeared with the removal of AAEMs result in the evident decrease of the capacity of moisture adsorption of lignite. The increase of specific surface area and the concentrations of oxygen-containing functional groups by removing discrete mineral particles could cause the increased equilibrium adsorption moisture content (EMC). On the other hand, a poorer cohesive structure of adsorbing moisture resulted from the presence of discrete mineral matters, raw lignite revealed lower EMC.

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1. Introduction

China has large resources of low rank coals (LRCs). Although abundant reserves, easier mining, cheap cost, low sulphur content, high moisture content severely limits the application of LRCs [1,2]. Efficient and safe dewatering or drying technologies are in urgent demand to sustainably utilize lignite. Thus, it is necessary to have a better understanding of the fundamental physical-chemical structure of lignite, particularly in relation to lignite-water interactions.

Coal as an organic sedimentary rock contains different inorganic mineral components. A typical Chinese LRC, Shengli lignite in east of Internal Mongolia, contains a significant amount of mineral matter [3]. Mineral matter in low-rank coals can be present as discrete mineral particles, as salts dissolved in water in the pores, as inorganic elements incorporated within the organic compounds of the coal macerals [4–6]. The latter two forms are perhaps best described as non-mineral inorganics, which are usually prominent in the mineral matter of LRCs [4,6–11]. Mineral matter as an integral part of the coal may significantly influence the moisture holding ability of lignite. However, considerable amounts of research have focused on the relationship of water in lignite with oxygen-containing functional groups and pore structure [1,2,12–14]. Furthermore, investigation on the lignite-water

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interactions was limited to the low-ash lignite in most previous studies. And additionally, some conclusions of these studies may not be readily applied to Chinese high-ash lignite. Therefore, insight into mineral-water interactions in coal is of great importance in order to provide theoretical foundation for the development of efficient dewatering technology of Chinese LRCs.

As for chemical coal cleaning or coal demineralization, using various reagents to dissolve or to react with the inorganic components of the coal have attracted many researchers' attention [15–18]. Conceptually, the different inorganic species in coal can be leached selectively by using appropriate reagents. According to the mode of occurrence of mineral matter in lignite, three types of mineral matter removed from lignite by specialized leaching agents. The nitrogen adsorption and FTIR analysis are applied to characterize the variations of pore structures and functional groups of treated samples respectively. The present study aims to explore the effects of the mineral matter on the moisture adsorption property of lignite, and to analysis interactions of different types of minerals in lignite with moisture.

2. Experimental

2.1. Lignite

A typical Chinese lignite from Shengli coal field in eastern region of Inner Mongolia was used in this study. The raw coal was ground to pass a 177 μm sieve. The proximate analysis and ultimate analysis are listed in Table 1. It shows that the ash content in Shengli lignite is as high as 25.63%.

2.2. Demineralized treatment

2.2.1. Soluble salts

100 mL of deionized water solution was added to 5 g raw coal and the mixtures were magnetically stirred at 60 °C for 4 h. The suspension was filtered and the coal residue was washed several times by deionized water.

2.2.2. AAEMs

Coal sample was sequentially demineralized by ammonium acetate and hydrochloric acid solution. 100 mL of 1 M ammonium acetate was mixed with 5 g coal in a plastic bottle and then magnetically stirred at 60 °C for 4 h. Then coal sample was filtered and the residue was washed with an additional 100 mL of 1 M hydrochloric acid solution following the same procedure as with the ammonium acetate extraction. Finally, the coal residue was washed several times with deionized water until there is no chlorine detected in the solute.

2.2.3. Discrete mineral particles

Coal sample was sequentially demineralized with 5 M hydrofluoric acid, full-strength (29 M) hydrofluoric solution, and full-strength (12 M) hydrochloric acid under the same condition as described above. After these three demineralized procedures, all the residue was dried at 70 °C for 24 h under vacuum for moisture adsorption experiments and stored under nitrogen to avoid

oxidation. The samples demineralized by H_2O , $\text{CH}_3\text{COONH}_4/\text{HCl}$ and $\text{HCl}/\text{HF}/\text{HCl}$ leaching procedures are denoted as De-W, De-A and De-F, respectively.

2.3. Moisture adsorption experiments

Moisture adsorption experiments were carried out by Aquadyne DVS dynamic water vapor sorption analyzer under the condition of 20 °C and a relative humidity of 90%. About 100 mg of treated coals was transferred to the instrument and weighed. Adsorption kinetics curves and the equilibrium adsorption moisture content (EMC) of coals under this condition were obtained. The moisture adsorption contents (ψ_i) were calculated on a dry basis by means of the following equation, $\psi_i = (m_i - m_0)/m_0$ (g water/g dry coal) where m_0 is initial dried coal mass, m_i is the wet coal weight at time intervals.

2.4. Analysis method

A Bruker S8 Tiger X-ray fluorescence (XRF) spectrometry was employed to quantify major elements in coal ash. Ionic species in the extract solution were determined by ICS-1100 Dionex ion chromatograph. In order to identify crystalline phases in the coal, X-ray diffraction (XRD) analysis was performed by means of a Panalytical Empyrean X-ray diffractometer with $\text{Cu K}\alpha$ radiation at voltage 40 kV and current 30 mA. The infrared absorption spectrums ($4000\text{--}500\text{ cm}^{-1}$) of samples were recorded on a Nicolet iS5 FTIR spectrometer. KBr pellets were prepared by grinding about 2 mg of dried coal with 200 mg KBr. Nitrogen adsorption/desorption isotherms measurements were carried out with a Belsorp-Max commercial instrument to determine coal surface area and pore size distribution.

3. Results and discussion

3.1. Characterization

Data from Table 1 displays that Shengli lignite had a high ash content and a high mineral concentration accordingly. The mineral elements detected by XRF for high-temperature coal ash are presented in Table 2. The high temperature coal ash was obtained in a muffle furnace at 575 °C (to avoid loss of sodium, etc.) for several hours until reached a constant mass. As shown in Table 2, the coal ash mainly consisted of silicon, aluminium, ferrum, sulphur and AAEMs. Among those, the total content of AAEMs oxides was as high as 18.97%. These results were consistent with a previous report that the predominant amounts of Ca and Mg were contained in LRCs [19]. AAEMs present in lignite primarily as cations bonded to the maceral matrix by means of oxygen-containing functional groups and other organic functional groups, which exerted important effects on the water holding ability of lignite [20–22].

Discrete minerals in Shengli lignite were investigated with low-temperature ashing and quantitative X-ray diffraction techniques. Oxygen plasma asher (Quorum K1050, England) was adopted to separate the mineral matters from the coal macerals without altering them. XRD analysis of the low-temperature ash (LTA) from the Shengli lignite showed the material consisted mainly of quartz

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

Sample	Proximate analysis			Ultimate analysis				
	M_{ar}	A_{d}	V_{daf}	C_{daf}	H_{daf}	S_{daf}	N_{daf}	O_{daf}
Raw coal	31.91	25.63	47.59	67.18	4.96	1.65	0.97	25.24

ar: as-received basis; ad: air-dry basis; d: dry basis; daf: dry and ash-free basis; *: by difference.

Table 2
Chemical composition analysis of raw coal ash (in wt%).

SiO_2	Al_2O_3	CaO	Fe_2O_3	S	MgO	K_2O	Na_2O
46.907	20.932	10.153	6.033	5.686	5.040	1.905	1.871
TiO_2	P	Sr	Ba	Mn	Cu	Cl	Zn
0.786	0.316	0.127	0.111	0.057	0.028	0.023	0.017

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