



The effect of alkali treatment on some physico–chemical properties of Xilinhaote lignite



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ABSTRACT

Studies of the simultaneous removal of minerals and acidic functional groups from Xilinhaote lignite were carried out using NaOH solution to identify how the alkali concentration affects some physico–chemical properties of Xilinhaote lignite. Changes in total acidity and carboxylic acid values measured by modified barium ion exchange were investigated along with the ash content. Pore size distribution in the lignite was determined by mercury intrusion porosimetry and N₂ adsorption. Adsorption water content was measured by desiccator method. The results show that at low alkali concentrations, NaOH reacts primarily with the acidic functional groups in lignite samples, and the changes in pore volume and adsorption water content are small. At high alkali concentrations, NaOH reacts with the minerals and organic matter simultaneously. A large amount of the elimination of minerals and organic matter causes significant change in increasing macropore volume which may lead to an increase in adsorption water content.

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1. Introduction

Lignite mostly occurs in some countries such as Australia and China. It is a very complex and heterogeneous material with a macromolecular structure [1], which is also highly porous and contains low molecular weight organic molecules [2,3]. Lignite is a low energy fuel with a high percentage of moisture and wide variations of ash contents [4–7]. It is known that the high water content of lignite has limited its utilization. For heterogeneous systems, porosity and the oxygen-containing functional groups can play an important role in the high water content of lignite [8,9].

The importance of alkaline degradation in the studies of lignite is well-known. Some workers removed minerals and sulfur from lignite by alkali treatment [10–14], and others obtained humic acids from lignite by alkali treatment [15–18]. The works focus on the effect of alkali treatment on either removal of minerals or organic matter. Few detailed investigations focus on the changes of some physico–chemical properties, including pore size distribution, and water absorptivity. Attempts to correlate physico–chemical properties with alkali treatment are significant because such properties may play an important role in the utilization, storage and handing properties of the lignite.

The paper aimed to assess the effect of alkali concentration on some physico–chemical properties of Xilinhaote lignite treated by NaOH solution and discuss the possible reasons. Of particular interests were the effects of the changes in pore size distribution and acidic functional groups on water absorptivity of the treated lignite.

2. Experimental

2.1. Materials

The lignite sample examined in this study was taken from Xilinhaote, Inner Mongolia, China. The lignite was ground to pass a 178 μm sieve for these experiments. The raw lignite was analyzed for proximate analysis according to the Chinese Standard Method [19], which adopted International Standard No. ISO 11722: 1999. The results are collected in Table 1.

2.2. Alkali treatment

A series of 6.00 g portions of raw lignite was prepared each with 100 ml of NaOH solution. The different concentrations were 0, 0.001, 0.005, 0.010, 0.050, 0.100, 0.500, and 1.000 mol/L NaOH, which were called XLHT0, XLHT0.001, XLHT0.005, XLHT0.010, XLHT0.050, XLHT0.100, XLHT0.500 and XLHT1.000, respectively. Xilinhaote raw lignite itself is called XLHTR. According to Song [20], each mixture was stirred for 2.5 h at room temperature, and then the sample was filtered and washed with distilled water until the filtrate was neutral. As to sample XLHT0, it was filtered and washed with distilled water until the pH was constant. The residue was vacuum dried for at least 6 h at 373.15 K. The treated products were then stored for further analysis.

2.3. Characterization

Macropore and mesopore size distributions were obtained by mercury intrusion porosimetry (MIP), using an AUTOPORE IV 9500 mercury porosimeter (Micromeritics instruments). Micropore size distribution,

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Table 1
Proximate and ultimate analysis of the lignite sample.

lignite	Proximate analysis (wt%)			
	M _{ad}	V _{db}	A _{db}	FC _{db}
XLHTR	22.23	34.27	14.59	51.14

for pores with diameters ranging between 6 and 20 Å, was determined by N₂ adsorption using an Autosorb-1 (Quantachrome Instruments). Image analysis was performed using scanning electron microscopy (SEM, Quanta™ 250, FEI Company). The number of carboxyl groups, and the total acidic values, were measured by an improved barium exchange technique [21]. Adsorption water content was determined by the desiccator method. Briefly, vacuum dried samples (1.0000 g db) were separately placed in weighing bottles (m₁ is the mass of weighing bottle, lid and lignite). Then the open weighing bottles were positioned in a desiccator with distilled water in its bottom. After several hours the weighing bottles were taken out, closed with lids and weighed (m₂). Experiments were repeated until equilibrium had been attained. The adsorption water content, on a dry basis, was calculated using the following equation: adsorption water content = [(m₂ - m₁)/1.0000]%.

3. Results and discussion

3.1. The effect of alkali treatment on acidic functional groups

Table 2 shows the effects of NaOH concentrations on the contents of carboxyl groups and total acidic functional groups. The increase in NaOH concentration is associated with the decrease in the total numbers of carboxyl groups and acidic functional groups. When the concentration of alkali is very low, the reaction between alkali and acidic functional groups is limited, which leads to the amount of acidic functional groups removed from the surface of lignite is small. Up to the concentration of 0.500 mol/L, NaOH reduces the carboxyl groups and the total acidic values significantly compared to XLHTR. The change between XLHT0.500 and XLHT1.000 is not significant, which suggests that above an alkali concentration of 0.500 mol/L, no more amount of acidic functional groups could be removed from lignite. In other words, there is a small change in the removal of acidic functional groups with the significantly increase in alkali concentration.

3.2. The effect of alkali treatment on the ash content

The effects of alkali concentrations on the ash contents of all samples are presented in Table 3.

It can be seen from Table 3 that the ash content of XLHT0 is lower than that of XLHTR, since some soluble minerals are removed [22]. The ash contents of all samples are increased by alkali treatment compared to XLHT0. Allard [23] stated that during alkali treatment organic material was removed from lignite. These suggest that the amount of removed organic matter exceeds that of the removed minerals. Up to an alkali concentration of 0.500 mol/L, the increase in alkali concentration is accompanied by the increase in the ash content, which shows that changes are mainly transformations of the organic matter. Above an alkali concentration of 0.500 mol/L, the increase in alkali concentration is associated with the decrease in ash content. This is because NaOH

Table 2
Carboxyl groups and total acidity in raw lignite and alkali treated lignite.

Sample	Carboxyl groups (mmol/g db)	Total acidity (mmol/g db)
XLHTR	14.50	17.24
XLHT0.001	14.38	17.06
XLHT0.010	14.18	16.82
XLHT0.100	13.66	16.04
XLHT0.500	7.63	10.56
XLHT1.000	6.89	9.85

Table 3
The effect of alkali treatment on ash content (wt% db).

Sample	Ash content	Sample	Ash content
XLHTR	14.50	XLHT0.100	16.69
XLHT0	12.68	XLHT0.500	18.51
XLHT0.001	13.61	XLHT1.000	14.29
XLHT0.010	13.95		

reacts with a large amount of the minerals which is dissolved from the lignite in this region. So removal of a considerable amount of organic matter will lead to corresponding gain in the ash content and a decrease in ash content is observed as more and more of the minerals dissolve from the lignite.

3.3. The possible reactions between NaOH and lignite samples

The chemical changes which take place during alkali treatment can be characterized by the pH values, as is shown in Fig. 1. A 0.10 mol/L NaOH solution was used as the titrant for the measurements of pH values, and the pH values were read by pH meter.

The pH values of each sample treated by different concentrations of NaOH solution are increasing with the increasing concentration of NaOH solution, but the increase is becoming slow during the titration process. There are only small changes in the samples treated by high alkali concentrations (0.100, 0.500 and 1.000 mol/L) during titrating. The results indicate that there are a small amount of acidic functional groups on the surface of lignite which could react with NaOH, and the quantity of surface acidic functional groups of samples decreases slowly with the significant increase of the NaOH concentration treated lignite. When the NaOH concentration in the treated samples is high enough, the residual amount of surface acidic functional groups is smaller, NaOH in turn reacts with minerals. These results are consistent with Sections 3.1 and 3.2.

According to the upper results, XLHTR, XLHT0.010, XLHT0.500 and XLHT1.000 were selected for the following experiments.

3.4. The effect of alkali treatment on pore size distribution

Mercury porosimetry is based on that the liquid mercury is gradually injected into an evacuated pore system by means of an external pressure, so that artificial pores, the diameters of which have been set to bigger than 60 μm, will be induced [24]. Ultra-micropores which are smaller than 3 nm are inaccessible to MIP. Thus, macropores and mesopores have been set to range from 0.05 μm to 60 μm and from 3 nm to 50 nm, respectively, as is shown in Fig. 2. The micropores in turn were determined considering adsorption of N₂, whose pore diameters were

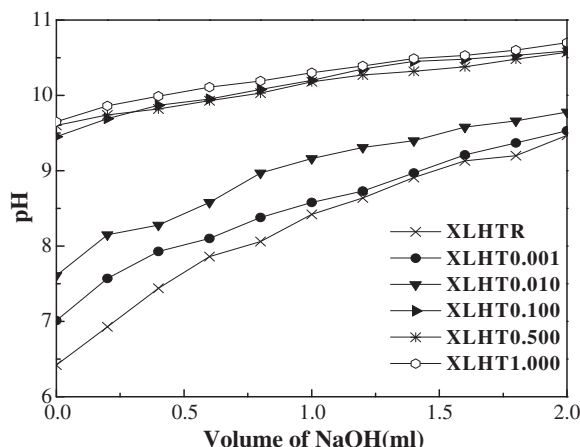


Fig. 1. Potentiometric titration results of all samples.

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