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Wetting process and surface free energy components of two fine liberated middling bituminous coals and their flotation behaviors

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ABSTRACT

The hydrophobicity of bituminous coal surface has a significant effect on the separation of coal and mineral matter during flotation process. In this paper, the thermodynamic characterization of the two kinds of liberated fine middling bituminous coal measured by Washburn dynamic method and its influence on flotation have been investigated. Wetting rate and Lipophilic Hydrophilic Ratio (LHR) was calculated by linear regression analysis method according to the wetting process of different density fractions of coal samples wetted by *n*-hexane, α-bromonaphthalene, formamide and water. Washburn equation and Van Oss–Chaudhury–Good theory were used to estimate the surface free energy components of samples. The LHR value of Xiqu (XQ) coal is higher than that of Qianjiaying (QJY) coal, and it decreases with the density level. Density fraction of 1.5–1.6 $g \cdot cm^{-3}$ and 1.6–1.8 $g \cdot cm^{-3}$ for XQ coal is hydrophobic with similar wetting rate and LHR (7.18 and 6.58), which is consistent with its poor selectivity from the regressive release flotation test. Disperse part of surface free energy reduces slightly with the coal density increase; the base part of coal is increased and all lower than that of the hydrophobic kaolinite (58.27 $mN \cdot m^{-1}$). Furthermore, there is a corresponding relationship between the base part and LHR. Results of elemental analysis and FTIR coincide well with the coal surface property.

1. Introduction

High ash content of the clean coal and poor selectivity are the prominent issues of the fine coal flotation. Wettability of mineral surfaces is paramount, which affects the separation efficiency of flotation. Coal is intrinsically hydrophobic because of its chemical composition (surface aromatic and aliphatic groups) [1]. Poor coal flotation can happen due to the decrease of coal particle surface hydrophobicity or the similar wettability between coal-rich and mineral-rich particles [2]. Hydrophilic mineral (clay, carbonate etc.) exposed at the coal particle surfaces can make the decrease of coal surface hydrophobicity. Wettability refers to the surface properties and interaction of solid, gas and liquid phases. Contact angle is a useful indicator providing the wettability of the solid mineral surfaces. For flat surfaces, available contact angle measurement techniques include drop shape analysis method, atomic force microscopy method and confocal microscopy method. For non-ideal surfaces or particles, there are axisymmetric drop shape analysis method, Washburn dynamic method, namely capillary penetration methods, Bartell static method [3,4] and surfactant adsorption isotherm method [5]. These techniques above are applicable to mineral surfaces, especially.

Washburn equation relates the capillary rise height or weight of a liquid through a compact vertical bed. The bed was composited by many capillary clusters and wetted by the liquid of laminar flow through particle bed [6,7]. This method has advantages over most other techniques used to measure the contact angle of powder solids [8,9]. Surface energy and its component measurement by Washburn dynamic method were widely used including wetting behavior of mineral dust [10], material compound and modification [11–13], filter media for water treatment [6,14] and explosives [15] in the chemical engineering and environmental engineering filed. Surface energy can also be determined using the film flotation and measuring the induction time of the material [16,17].

The total surface free energy of solid is composed of the non-polar part (i.e., Lifshitz-van der Waals) and polar part (i.e., Lewis acid–base) according to the Van Oss–Chaudhury–Good theory. The former consists of the sum of the terms heretofore ascribed to London, Debye, and Keesom forces. The latter contains acid part and base part, which was due to H-bonds [18,19]. LW referring to Lifshitz-van der Waals; AB refers to short range acid–base interaction forces. *n*-Hexane with low viscosity and surface tension of 18.4 $mN \cdot m^{-1}$ at 20 °C is the probe to test the geometric factor of powder packed bed. α-Bromonaphthalene with disperse part only is the probe of the non-polar components of surface free energy. Surface tension of formamide and water contains the two parts.

In this paper, the wetting process and components of surface free energy, namely, thermodynamic characteristics of density fractions of the two kinds of fine liberated middling bituminous coal particles

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Table 1
Physical parameters of probe liquids (at 20 °C).

Probe liquids	Density ($g \cdot cm^{-3}$)	Viscosity ($mPa \cdot s$)	Surface tension ($mN \cdot m^{-1}$)	γ_s^{LW} ($mN \cdot m^{-1}$)	γ_s^{+} ($mN \cdot m^{-1}$)	γ_s^{-} ($mN \cdot m^{-1}$)
n-Hexane	0.661	0.326	18.4	18.4	0	0
α-Bromonaphthalene	1.483	5.107	44.4	44.4	0	0
Formamide	1.133	3.812	57.4	39.0	2.28	39.0
Deionized water	0.998	1.002	72.8	21.8	25.5	25.5

were investigated. These results have been related to performance of the coal in regressive release flotation test and particle characterization. The relationship between wettability of particles and its component of the surface free energy was also studied.

2. Experimental

2.1. Materials

One of the coal samples was middling of heavy medium coal preparation of Xiqu (XQ) coking coal preparation plant in Shanxi Province of China, and the other one was middling of the two stage flotation process from Qianjiaying (QJY) coking coal preparation plant in Hebei Province of China. Middling of XQ coal sample was dry ground first in a jaw crusher to −1 mm and then in a porcelain ball mill of laboratory type for 2.5 min with 200 rpm, 45% filling rate to −0.5 mm. QJY coal sample was crushed to −0.5 mm using the porcelain ball mill. The two kinds of coal sample were screened to −0.5 mm and further purified with the heavy liquids with density of 1.3 $g \cdot cm^{-3}$, 1.4 $g \cdot cm^{-3}$, 1.5 $g \cdot cm^{-3}$, 1.6 $g \cdot cm^{-3}$, and 1.8 $g \cdot cm^{-3}$, which were prepared by mixing carbon tetrachloride, benzene or bromoform at appropriate ratio. Density fractions were dried for 3 h at 70 °C and then were stored in bottles filled with nitrogen.

Kaolinite and chemical reagents, including *n*-hexane, α-bromonaphthalene and formamide, were analytical grade. Water used in experiments was distilled before further purification through ion-exchange resins (Milli-Q). The characteristics of the probe liquids at 20 °C were listed in Table 1 [20–22].

2.2. Methods

2.2.1. Wetting process measurement

KRUSS Tensiometer K100 with range of 1–1000 $mN \cdot m^{-1}$, ±0.001 $mN \cdot m^{-1}$ was used in this measurement. A different density fraction of 2.000 g was weighed and put into a clean Washburn tube. A filter paper is placed between the tube and sample particle to avoid the particles falling down. Strike the Washburn tube for the same times with strict uniform force lightly until sample compaction height was the same with each other to ensure reproducible results. Then Washburn tube was fixed on the hook assembly of the Tensiometer K100. The automatic elevator-platform which was loaded with a glass beaker filled with no less than 30 mL probe liquid rose slowly until about 2 mm from the bottom of the solid samples. The temperature was kept strictly around 20 ± 0.5 °C. As soon as the surface of liquid got in touch with the bottom of the Washburn tube automatically, the rising of the elevator-platform stopped immediately and the Tensiometer K100 started to detect the mass change of the Washburn tube for 200 s. In each case, five measurements were conducted for the reproducible result.

2.2.2. Regressive release flotation test

As seen in Fig. 1, XFDM flotation cell was used for coal flotation test with 150 g coal in 1.5 L water. The suspension was conditioned at 1800 rpm for 2 min at room temperature. Afterwards, *n*-dodecane (200 g/t for XQ coal and 800 g/t for QJY coal) and 2-octyl alcohol at a dosage of 200 g/t was added. Air flow rate was 0.2 m^3/h. The froth concentrates and flotation tailings were filtered, dried (in an oven at 105 °C), weighed and taken for ash determination.

2.2.3. Particle characterization

Size distribution of coal samples and kaolinite was tested by Microtrac S3500 laser particle size analyzer.

Elemental analysis of the XQ and QJY coal was conducted with Vario MACRO cube.

Thermo Nicolet 380 of the Nicolet was used. FTIR is an important and widely used analytical tool for determining the structure of coal material and functional groups. Density fractions stored in bottles of 2 mg and spectrographic KBr of 300 mg were mixed in the agate mortar and ground homogeneously until the powder particle size was about 2 μm. The powder was dealt with 30–40 MPa pressure to form a pellet. FTIR spectra were recorded on a Nicolet Nexus IR 6700 with KBr pellet in the range of wave numbers 4000–400 cm^{-1}. Scans were collected at a resolution of 4 cm^{-1}. Sample scanning frequency is 64. Background and vapor influence was deducted in the Map analysis.

3. Results and discussion

3.1. Size distribution and density analysis

Effective capillary radius of each density grade was close to each other as the particle size of the two kinds of coal sample was concentrated in

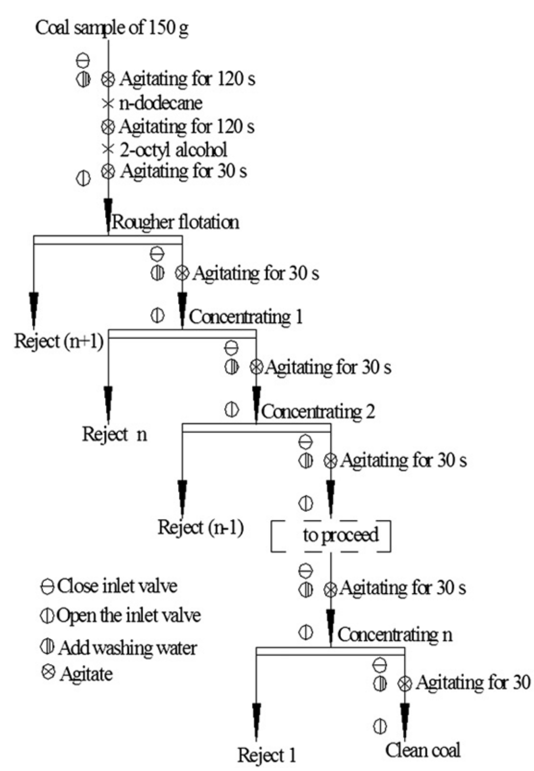

Fig. 1. Coal flotation test by progressive release.