



Pore structures and methane sorption characteristics of coal after extraction with tetrahydrofuran



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ARTICLE INFO

Article history:

Received 4 April 2014

Received in revised form

21 May 2014

Accepted 22 May 2014

Available online 14 June 2014

Keywords:

Methane

Extraction with THF solvent

The small organic molecule

Pore structure

Sorption characteristics

ABSTRACT

An anthracite and three bituminous coals were extracted with tetrahydrofuran (THF) solvent at 50 °C and atmospheric pressure by microwave-assisted extraction. Low-temperature nitrogen sorption and high-pressure methane sorption isotherms on raw coals and their residues were tested, and their extracts were analyzed via the Gas Chromatography/Mass Spectrometry (GC/MS). The pore structure (specific surface area, pore size distribution, pore volume, etc.) and the gas adsorbance of coals and their residues were comparatively analyzed. The results indicate that the mesopore volumes of all residues were increased compared to the raw coal, whereas the increase or decrease of the specific surface areas and micropore volumes was correlated with their ranks. Meanwhile, the pores of raw coals and their residues were mainly distributed in the range of 3–4 nm. Although the capability of gas adsorption by coal was strengthened after solvent extraction, the ability to adsorb methane was reduced because the amount of space for the dissolution of small organic molecules where methane condensed was reduced. This behavior is caused by two aspects: (1) The enhanced ability of gas sorption due to the enlarged pore structure resulting from the solvent extraction; (2) the weakened ability of gas sorption because of space reduction for dissolving or adsorbing of methane. Therefore, after extraction, the methane sorption characteristics of the coal were jointly dependent on the enlargement of the pore structure and the reduction of small organic molecules.

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1. Introduction

The porosity of coal itself has the capability of methane sorption. Under certain conditions, the adsorption gas becomes free gas through desorption and diffusion, and then emission from coal after the seepage in the pores and cracks of coal (Busch and Gensterblum, 2011). Coal seam Gas (mainly methane) is a kind of clean and unconventional energy of high-efficiency. However, in the process of coal mining, the abnormal emission of gas may lead to coal and gas outbursts even gas explosion to endanger coal mine safety. Meanwhile, the methane plays a major part in the greenhouse effect. The gas-adsorption characteristic is closely connected with coal composition and pore structure (Dutta et al., 2011). Solvent extraction can well change the pore structure of coal and adsorption characteristic (Li et al., 2009). Thus, research focusing on

the change of pore structure and adsorption characteristic of gas after solvent extraction is performed. And its outcome can surely be a great help to master coal seam gas occurrence mechanism, control micropore structure of coal, improve adsorption/desorption characteristics of gas in coal and promote coal-bed methane (CBM) development. At the same, it can be of a great significance to prevent serious gas problems (especially coal and gas outbursts) in coal mining.

As is well known, the storage of methane in coal is not only in the free or sorption state in pore spaces, but also it occurs in the solid solution state especially for high pressures of >2 MPa (Ailuni, 1992; Alexeev et al., 2004a,b; Cheng, 2010). Many parameters, including internal factors (Bustin and Clarkson, 1998; Clarkson and Bustin, 1999; Clarkson and Marc Bustin, 1996; Crawford and Mainwaring, 2001; Crosdale et al., 1998; Day et al., 2008; Gamson et al., 1993; Laxminarayana and Crosdale, 1999, 2002; Levy et al., 1997) (e.g., coal rank, maceral content, mineral matter composition, ash, moisture, etc.) and external conditions (Krooss et al., 2002; Zhong et al., 2002; Zhong, 2004) (e.g., temperature,

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pressure, etc.), influence the methane sorption characteristics of coal. It is widely recognized that coal is a complex mixture (Chen and Iino, 2001; Krzesińska, 2002; Marzec, 2002; Rusianova et al., 1990) with an organic macromolecular phase and a small organic molecules phase, which can be dissolved in organic solvent. Coal also includes a large number of aromatic compounds, some aliphatic compounds and a small amount of heterocyclic compounds (Chen et al., 2009). Zhu et al. (Xie, 2002; Zhu and Gao, 1984) found that the higher degree of coalification is, the lower ratio of soluble organic matter to the total amount of matter in coals would be. And the very ratio can be 10–23%, even up to 30% in bituminous coal. Therefore soluble organic matter certainly can be treated as an important part of coal. Due to the comparatively large amount of soluble organic matter, which provides an important sorption site for adsorption, methane can be adsorbed/dissolved under high pressure along with affecting pore structure of coal. So the changed pore structure can be reasonably speculated and severe impact on gas sorption characteristics can be foreseen, with the removal of soluble organic matter.

Takanohashi et al. (2000) proposed the mechanism of isotherm for methanol vapor sorption through an analysis of the impact of solvent extraction on the sorption properties of coal. Zhang et al. (Wang et al., 2003; Zhang et al., 2004) investigated the effect of solvent extraction on the pore structure, granularity, and sorption behaviors of nitrogen by the residues, and claimed that, it could change the pore structure (e.g., specific surface area, pore volume, etc.) and leave pore expanded and increased. Jiang (2013) believed that different methane sorption characteristics of coal before and after extraction ascribe to metamorphism degree of coal, pore structure and moisture content. And they focus on the difference of sorption characteristics of raw coal and residual coal, neglecting a fact that the sorption methane in coal is in various formation, which is determined mostly by pore structure of coal, while the methane of solid solution state is mainly stored in sealed pores of coal (Alexeev et al., 2004b). Thus, this paper tries to investigate the change rule of pore structure and its influence on methane sorption characteristics after removing soluble organic matter in coal.

To investigate the effect of extraction on the pore structure and the role small organic molecule plays in the formation of methane sorption mechanism of coal, four Chinese coal samples (one anthracite and three bituminous coals) were extracted with tetrahydrofuran (THF) solvent at 50 °C and atmospheric pressure by microwave-assisted extraction. Low-temperature nitrogen sorption and high-pressure methane sorption isotherms were measured for coals and their residues, and the extracts were analyzed via GC/MS. The research is of great significance to build up the foundation of controlling pore structure of coal and mastering relevant technique, method and equipment. Meanwhile, it will promote the gas drainage and reduction of gas emission.

2. Experimental

2.1. Sample preparation

An anthracite and three bituminous coals were adopted as the experimental coal samples from the north of China. The anthracite was selected from No.3 coal seam of Changping mine (CP No.3). Three bituminous coals were selected from No.5 coal seam of Yangzhuang mine (YZ No.5), No.9 coal seam of Zhangji mine (ZJ No.9) and No.8 coal seam of Xiegou mine (XG No.8). Information about the source of the coal samples is shown in Table 1.

Fresh coal samples were first collected and sealed in the underground colliery, and then were transported back to the laboratory. After the treatment of stripping, breaking and screening, the coal samples between –60 and +80 mesh size (0.180–0.250 mm)

Table 1
General information about coal samples.

Sample	Sample location	The geological age of coals	Depth (m)
YZ No.5	Yangzhuang Mine of Huaibei City in Anhui Province	Shihezi Formation	682
CP No.3	Changping Mine of Gaoping City in Shanxi Province	Shanxi Formation	417
ZJ No.9	Zhangji Mine of Xuzhou City in Jiangsu Province		1265
XG No.8	Xiegou Mine of Lvliang City in Shanxi Province		273

were used for extraction, low-temperature nitrogen sorption and high-pressure methane sorption experiments, and which also were utilized for determining the maceral group composition and minerals in the coal according to the GB/T 8899-1998 method (China standard). These samples were dried at 80 °C for 12 h in vacuum. Approximately 10 g of the coal samples –80 mesh were used for proximate analysis following the test methods for proximate analysis of coal by instruments (MT/T 1087-2008, China standard). The proximate and petrographic analysis of these samples are listed in Table 2

2.2. Experimental procedures

2.2.1. Extractions

The extraction experiments were conducted via a CW-2008 multi-microwave reaction/extraction device, Zeming Tech Co., Ltd. The 60 g coal sample and 900 ml THF solvent (analytic reagent) were mixed and put them into an extraction vessel afterward. Then, the extraction device was started at 50 °C and atmospheric pressure after checking the connections. Four hours after extraction experiment, the mixtures were shifted from the extraction vessel into a 10,000 ml beaker and filtered with a vacuum filter device. Afterward, the liquor and residues (residual coals) were separated. Finally, the residues were further dried at 80 °C for 12 h in vacuum. The extracts were obtained by vaporizing THF with a RE-52AA rotary evaporator. The extraction yield ($E_{(wt\%,daf)}$) was calculated according to the following equation, with the results listed in Table 2.

$$E_{(wt\%,daf)} = \frac{\text{coal(g)} - \text{residue(g)}}{(1 - \text{ash}_{(wt\%,daf)}) / 100} \times \text{coal(g)} \times 100 \quad (1)$$

2.2.2. Low-temperature nitrogen isotherm method

The pore-structure parameters of coal were obtained from the method of low-temperature nitrogen isotherm, which were performed on a 3H-2000PS4 type surface-area-analyzer, Beishide

Table 2
Analyses of coals and extraction yield with THF solvent.

Sample	M_{ad}	Proximate analysis (wt%)			$R_{v, \max}$ (%)	Mmf, %		$E_{(wt\%, daf)}$ (THF)
		A_d	V_{daf}	FC_d		Vitrinite	Liptinite	
CP No.3	1.81	19.55	8.95	71.34	2.64	55.4	44.6	0.813
YZ No.5	1.58	46.16	10.15	43.52	1.7	66.3	33.7	2.164
ZJ No.9	1.26	4.17	28.97	66.49	0.93	46.2	46.1	2.428
XG No.8	2.37	31.83	20.31	47.36	0.82	42.4	49.1	2.085

wt = weight; daf = dry ash free; $R_{v, \max}$ = Maximum vitrinite reflectance; M_{ad} = air-dried moisture; A_d = dry ash; FC_d = dry fixed carbon; Mmf = mineral matter free.

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