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Characterization of mineral composition and its influence on microstructure and sorption capacity of coal

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ABSTRACT

Mineral matter is widely accepts as one of the important factors influencing the gas sorption capacity of coal. By analyzing ash content and Langmuir volume of coals, studies have reported positive, negative, and poor impacts of mineral matter on sorption capacity without convincing reasons explaining the contradictory results. This paper proposes a new analysis method to correlate minerals and gas sorption capacity by connecting the mineral matter compositions to sorption capacity through the variations in the microstructure. In addition to mineral content, mineral occurrence modes and compositions were also studied to investigate their relations with gas sorption capacity.

A total of 22 coal samples are used to interpret the characterization of minerals, including mineral content by proximate analysis, mineral occurrence mode by scanning electron microscope (SEM) and energy-dispersive X-ray spectrometer (EDX) analyses, and mineral compositions by X-ray powder diffraction (XRD) analysis. Low-temperature nitrogen adsorption and high pressure methane adsorption analyses of selected samples are applied to characterize microstructure and gas adsorption capacity.

We found that mineral content, occurrence mode, and composition are three controlling factors that together determined the influence of mineral matter on gas sorption capacity. In fact, some factors have potential for both positive and negative influence. This is why both negative and positive influences have been previously observed. The direction and magnitude of influence depends on the relative weights of the driving factors. For samples in this study, clay mineral content showed the strongest positive relation to S_{BET}, total V_{BJH}, and V_L, compared to total mineral and brittle mineral content. The relation of other minerals to S_{BET}, total V_{BJH}, and V_L is weak. The final result indicated that mineral matter had a positive influence on gas sorption capacity.

1. Introduction

Coalbed Methane (CBM) is labeled as an unconventional natural gas due to its unique storage and flow mechanisms. Gas stored in coal seams occurs dominantly in an adsorbed state on the internal pore surfaces of coal, which can as account for as much as 95% of total gas content (Gray, 1987). Mineral matter is one of the most important factors influencing gas sorption capacity on coals, which also include coal rank, moisture, micro-pore structure, as well as maceral composition and type (Yee et al., 1993; Bustin and Clarkson, 1998).

Various studies have reported that the gas sorption capacity of coal is affected by mineral matter. By comparing ash content to Langmuir Volume, a negative correlation was commonly observed and accepted (Faiz et al., 1992; Yee et al., 1993; Crosdale et al., 1998; Laxminarayana and Crosdale, 1999; Liu et al., 2014; Ma et al., 2014). One interpretation of this effect was that mineral matter has less surface area compared to the microporous organic constituents of coal (Gan et al., 1972; Clarkson and Bustin, 1996). Another interpretation was that the mineral matter was essentially non-adsorbent to methane and acted as a simple diluent to the whole coal matrix (Crosdale et al., 1998; Laxminarayana and Crosdale, 2002). Thus, it was considered as counterintuitive when a positive correlation was found in Australian coals by Bustin (1997). Further, this opposite phenomenon was also found in Black Warrior coals by Carroll and Pashin (2003). On the basis of the

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interpretations for a negative relation, it is hard to understand the mechanisms of minerals for enhancing the sorption capacity of coal. In addition, Chalmers and Bustin (2007) reported poor correlation between gas sorption capacity and ash content in subbituminous coals. However, it should be noted that all these studies on the relation between minerals and gas sorption capacity only analyzed the mineral content in relation to gas sorption capacity, and these previous studies ignored the possibility that mineral occurrence and mineral composition may also have impacts on gas sorption capacity.

Studies on mineral occurrence in coal have mainly utilized qualitative analysis, and the studies have been focused on the pore and cleat-fill mineralogy as well as discussing their influence on CBM generation and production (Spears and Caswell, 1986; Daniels et al., 1996; Dai et al., 2006). Diagenetic and epigenetic minerals, such as calcite, pyrite, kaolinite, silica, boehmite, silica, and sphalerite, were commonly filled in cleats (Daniels et al., 1996; Dai et al., 2006). Laubach et al. (1998) and Gamson et al. (1996) concluded that the degree of mineral filling is one of the key factors that retard fluid conduction. Pitman et al. (2003) reported that minerals can affect the gas transmission and storage capacity of Black Warrior coals. Studies on mineral composition have mainly used quantitative analysis, and they have been focused on precisely determining the mineral species and composition ratios as well as discussing the abundance and origin of minerals or trace minerals (Dai and Chou, 2007; Dai et al., 2008; Wang et al., 2012; Liu et al., 2014). Although numerous studies have investigated mineral occurrence and composition, little is known regarding their relationships with gas sorption capacity. Instead, mineral occurrence has been directly correlated to the microstructure of coal. Additionally, the interpretation that mineral material has minimal surface area implicates the microstructure in the relationship between mineral and gas sorption capacity, and this requires further study.

In this study, we primarily analyze the features of mineral material (including mineral content, mineral occurrence, and mineral composition) to elucidate their influence on gas sorption capacity. Qualitative and quantitative analyses are used to reveal the characteristics of mineral occurrence and composition. Attributes of microstructure and gas sorption capacity also are evaluated including surface area, pore structure, Langmuir volume, and Langmuir pressure. Then, we use statistical methods to clarify the relationships among minerals, microstructure, and gas sorption capacity. Finally, we try to explain the contradicting results in the literature regarding the influence of minerals on the gas sorption capacity of coal. This study will lead to a better understanding of the way minerals effects gas sorption capacity, and hence it can act as a foundation for the prediction of gas accumulation and production.

2. Experimental work

2.1. Sample collection and description

A total of 22 coal samples were chosen from five different basins in north China. The samples consisted of large cubic blocks, $30 \times 30 \times 30$ cm^3 in size, were cut from fresh coal faces in active coal mines. Each coal block was carefully sealed with plastic wrap to prevent weathering and oxidation. All the samples were then shipped to the laboratory for experimental tests.

The geographical locations for all 22 samples are shown in Fig. 1 and the detailed information for each sample including location, burial depth, thickness, bearing formations, and rank is shown in Table 1. One sample (A1) was collected from the No. 4 coal seam in the Tuha basin. Three samples (B2, B3, and B4) were obtained from the No. 9 coal seam in the Junggar basin. One sample (C5) was collected from the No. 11 coal seam of the Hailar basin. Two samples (D6 and D7) were selected from the No. 6 and No. 3 coal seam in the northern Ordos basin. Seven samples (D8 to D14) were collected from different coal seams in the western and southern parts of the Ordos basin. Two samples (D15 and D16) were from the No. 11 coal seam of the southeast part of the Ordos basin. The last six samples (E17 to E22) were obtained from the No. 3 coal seam in the southern portion of the Qinshui basin. More details on this five basins, including geological background, CBM exploration status, and the range of coal rank, were investigated from different literature (Liu et al., 2013; Xu et al., 2012; Meng et al., 2014; Li et al., 2014; Su et al., 2005; Cai et al., 2011; Tao et al., 2012; Lv et al., 2012).

2.2. Sample characterization

Proximate analysis was initially performed to set up a baseline for further investigations. The SEM and XRD analyses were then applied to identify, observe, and quantify the mineral matter. Based on prior results, fourteen samples were selected for low-temperature nitrogen (N_2) adsorption to characterize the surface area and pore structure. Finally, sorption isotherms were estimated to quantify the gas sorption capacity. To minimize oxidation, all the crushed samples were stored in environmental chambers and maintained at temperatures less than 10 °C.

2.2.1. Proximate analysis

A 5E-MAC III infrared fast coal analyzer was used to determine the moisture, volatile matter, ash yield, and fixed carbon content of 22 coal samples. The tests were performed in accordance with standard procedures (ASTM, 2006) at the National Engineering Research Center of CBM Development & Utilization at the China University of Geosciences, Beijing.

2.2.2. SEM and XRD tests

Two or three small pieces were cut from each of the 22 coal samples so that each piece had one face with an area of approximately 1×1 cm^2. These subsamples were used for SEM and EDX analyses at the laboratory of the National CBM Engineering Research Center in China. The accelerating voltage was 20 KV and the beam current was 10^{-10} A.

The remaining material of the 22 coal samples were pulverized down below 200 mesh for XRD analysis with a LabX XRD-6000 at the laboratory in National CBM Engineering Research Center in China. Samples were scanned from 5 to 45° 2θ, with a step interval of 0.04 s and a 2 s counting time for each step. The X-ray diffractograms of 22 samples were subjected to quantitative mineralogical analysis using Siroquant™. This commercial interpretation software was developed by Taylor (1991) using the principles of diffractogram profiling explained by Rietveld (1969). Further details demonstrating the use of this technique for coal-related materials are given by Ward et al. (1999, 2001) and Ward (2002).

2.2.3. Low temperature N_2 isotherm measurements

The 14 samples chosen for further testing were pulverized to 100 mesh. The N_2 low-temperature (77 K) adsorption/desorption tests were performed following the Chinese National Standard (GB/T19587, 2004) via a Quadrasorb SI analyzer. The Brunauer, Emmett, and Teller (BET) method was used to indicate the specific surface area from the nitrogen isotherm data (Brunauer et al., 1938). The BET equation is expressed as:

$$\frac{1}{W\left(\frac{P_o}{P}-1\right)} = \frac{1}{W_m C} + \frac{(C-1)}{W_m C}\left(\frac{P}{P_o}\right) \quad (1)$$

where, W is the weight of gas adsorbed at pressure P, W_m is the