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### Influence of supercritical CO<sub>2</sub> on pore structure and functional groups of coal: Implications for CO<sub>2</sub> sequestration



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#### ABSTRACT

To better understand the effects of  $CO_2$  sequestration and long-term storage, it is worth studying the interactions between supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>) and coal, and its influence on coal properties or, more specifically, the changes in coal pore structure and functional groups caused by SC-CO<sub>2</sub>. In this study, three different metamorphic grades of coal were sampled and exposed to SC-CO<sub>2</sub> (~40 °C and 10 MPa) for 120 h through a geochemical reactor, simulating CO<sub>2</sub> storage in deep coal seams. The functional groups and pore structure of different coal ranks before and after SC-CO<sub>2</sub> treatment were measured by Fourier Transform Infrared Spectroscopy (FTIR), Mercury Intrusion Porosimetry (MIP) and physical adsorption method. The results show that the absorption peak intensity of -OH groups, with intramolecular association and C-H stretching vibrations, clearly changed for anthracite compared to others. Compounds with weakly polar functional groups, such as hydrocarbons, epoxy and lipid compounds (ether or ester), decreased significantly, whereas strongly polar functional groups exhibited only a slight change. Pore structure and distribution of each pore phase showed the diversity present in different coal ranks. The development of seepage-flow pores (mesopore and macropore) was promoted by SC-CO<sub>2</sub>. For high rank and medium rank coals, the degree of pore development was significantly altered by SC-CO<sub>2</sub>, while pore development in low rank coal was largely unaltered. The results of this study contribute to the understanding of coal structure evolution and its effects on coal reservoir during long-term geological sequestration.

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#### 1. Introduction

Carbon dioxide (CO<sub>2</sub>), a greenhouse gas primarily derived from burning of fossil fuels, contributes to the global climate warming and has gained worldwide attention in recent decades. However, for developing countries such as China, maintaining economic development makes fossil fuel consumption indispensable (Edenhofer, 2014). According to the BP Statistical Review of World Energy (BP, 2015), China's CO<sub>2</sub> emissions grew by 0.9% in 2014, which was just above the global growth rate of 0.5% in the same year. Because fossil fuels are the most abundant energy resource in China, it is foreseeable that the fossil fuels will continue to be the dominant energy supply for a long time. Therefore, the development and deployment of clean coal technologies are crucial to promoting sustainable development in China and globally.

Despite the limitations and high expense in researching renewable energy, clean coal technology has developed rapidly in recent years, with an emphasis on Carbon Capture and Storage (CCS) technologies for reducing greenhouse gas emissions (Chen and Xu, 2010). Along with the possibility of enhanced coal bed methane recovery development, unmineable coal seams are a promising option for CO<sub>2</sub> storage (Arri et al., 1992; Seidle et al., 1996). The process includes capturing CO<sub>2</sub> from large industrial sources before it is emitted into the atmosphere and transporting it to a safe and permanent long-term storage site, usually in unmineable coal seams (Bachu, 2003).

The macromolecular structure of the coal can be affected by its pore structure (Karacan, 2007). Also, chemical interactions between the coal polymer (e.g., types of functional groups) and fluids

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within the coal matrix produce non-covalent bonding and electron transfer (Kolak and Burruss, 2006; Mirzaeian and Hall, 2006; Suuberg et al., 1994), which can, in turn, affect the overall molecular structure of coal. Based on these characteristics, the pore structure reflects the coal's physical structure and the types of functional groups determine its chemical (molecular) structure: both will reveal changes after exposure to SC-CO<sub>2</sub>. Therefore, research on this topic may provide a better understanding of coal-CO<sub>2</sub> interactions and predictions for long-term storage of CO<sub>2</sub> in deep coal seams. Recently, pore structure characteristics have been studied using Brunauer-Emmett-Teller (BET) analysis (Maphala and Wagner, 2012), adsorption experiments, small-angle neutron scattering (SANS) (Mirzaeian et al., 2010) and MIP. Meanwhile, changes in coal molecular structure were studied via X-ray diffraction (XRD) (Maphala and Wagner, 2012), FTIR (Mastalerz et al., 2012) and nuclear magnetic resonance (NMR) spectroscopy (Cao et al., 2011).

However, these studies were mainly conducted at low temperatures (subcritical) and CO<sub>2</sub> pressures (<5 MPa), different than SC-CO<sub>2</sub> conditions (>8 MPa). When CO<sub>2</sub> is injected into deep coal seams (>800 m depth), it will be immediately compressed to a supercritical state (critical temperature and pressure of 31.05 °C and 7.3 MPa, respectively) (Span and Wagner, 1996). The physical properties of CO<sub>2</sub>, such as density, viscosity and diffusivity, change significantly near this critical point. Preliminary work has been undertaken to better understand the effects of CO<sub>2</sub> sequestration and long-term storage, the interaction between SC-CO<sub>2</sub> and coal, as well as the influence of coal structure on CO<sub>2</sub> long-term storage. Generally, coal is a glassy, rigid and brittle solid. In this state, the diffusion of gas into coal is slow (Larsen et al., 1997). However, when coal comes into contact with certain organic solvents (SC-CO<sub>2</sub>) or is subject to higher temperatures, it can be plasticized and gas diffusion rates through pore structure increase. As a result, the coal structure is rearranged (Giri and Sharma, 2000; Painter et al., 2012). As an organic solvent, SC-CO<sub>2</sub> can alter the coal structure, properties and behavior (Day et al., 2008; Gathitu et al., 2009). In addition, a comprehensive literature search reveals that SC-CO<sub>2</sub> may change coal structure by mobilizing organic and inorganic constituents from the coal matrices (Burant et al., 2012; Kolak and Burruss, 2006; Monin et al., 1988). Several studies have shown that mineral matter in the coal can be dissolved and extracted with SCCO<sub>2</sub>-H<sub>2</sub>O treatment, leading to pore structure changes (Hayashi et al., 1991; Kumar and Shankar, 2000; Liu et al., 2010). Other work (Sakanishi et al., 2001) has suggested that injected CO<sub>2</sub> into coal seams can decrease the pH associated with water, altering the adsorption capacity for different coals. Overall, it has been proven that changes in coal structure under long-term storage of CO<sub>2</sub> will decrease CO<sub>2</sub> solubility (Karacan, 2007), improve pore connectivity and permeability of the coal reservoir, which may affect the storage capacity and stability of the coal seam (Ozdemir, 2016).

However, owing to the complex nature of coal, the interaction mechanisms between coal and CO<sub>2</sub> are not yet fully understood (Busch and Gensterblum, 2011; Goodman et al., 2005; Ozdemir, 2009; Van Heek, 2000; Zhang et al., 2013). As indicated earlier, SC-CO<sub>2</sub> conditions differ from subcritical CO<sub>2</sub> in the effect on structure, properties and behaviour of coal, which may cause different results from techniques used in previous studies. Additionally, special attention should be given to comprehensive changes in physical and chemical properties of SC-CO<sub>2</sub> treated coal instead of a single factor. In this study, changes in pore structure and functional groups of coal before and after exposure to CO<sub>2</sub> were investigated. Sufficient quantities of raw coal from three different metamorphic grades were sampled and treated in a high pressure SC-CO<sub>2</sub> geochemical reactor. Simultaneously, proximate analysis and vitrinite reflectance characterization were performed to test

essential coal parameters. Then, the absorption bands generated by the three different coal samples were measured by FTIR spectroscopy. The absorption bands were used to estimate functional group types and their abundance, which provided an overview of the composition and molecular structure of the coal samples. Finally, the key characteristics of pore structures, such as pore size distribution (PSD), pore volume and porosity, were analysed through MIP and a physical adsorption method. The purpose of the study is to provide a theoretical foundation for understanding the interaction mechanisms between SC-CO<sub>2</sub> and coal during long-term storage.

#### 2. Samples and experimental methods

#### 2.1. Sample collection

Three different metamorphic grade coal samples of anthracite, coking coal and long-flame coal, sampled from Wolonghu Coal Mine (Wanbei Coalfield), Haizi Coal Mine (Huaibei Coalfield) and Dalong Coal Mine (Tiefa Coalfield) respectively, were adopted in this study. The detailed sampling locations and basic parameters of these coal samples are listed in Table 1.

All of the coal samples were collected from fresh exposed mining face. Once a sample was obtained, it was sealed and immediately sent to the laboratory, in order to prevent oxidation. Then, coal samples were crushed and sieved to the appropriate quantities and particle sizes. For each test, the samples were divided into 2 portions evenly for comparative experiment, one was the untreated sample and the other was the sample which after the treatment of SC-CO<sub>2</sub>.

#### 2.2. Experimental methods

In this study, variations in physical parameters before and after SC-CO<sub>2</sub> treatment, proximate and coal petrology parameters, infrared spectrum analysis and pore structures of coal samples were comprehensively analysed.

The SC-CO<sub>2</sub> treatment of coal samples was conducted using a high pressure SC-CO<sub>2</sub> geochemical reactor developed by the National Engineering Research Center for Coal and Gas Control (NERC) (Fig. 1). The device consists of three major parts: a vacuum pump system, compression and gas injection system, and a constant temperature system. During the experiment, a coal sample was first degassed in the vacuum pump system (60 °C and 4 Pa for 8 h). Then, the ambient CO<sub>2</sub> in the cylinder was pressurized to a supercritical state and SC-CO<sub>2</sub> was injected into the sample tank through a booster pump. Subsequently, the pressure was maintained at 10 MPa for 120 h and the water bath temperature was held constant at 40 °C.

The proximate and petrographic analyses were determined using a 55E-MAG6600 automatic proximate analyser (Changsha Kaiyuan Instruments, China) and microscope photometer (Zeiss, Germany), respectively, following ISO recommendations (ISO 11722-1999 for moisture, ISO 1171–1997 for ash, ISO 562–1998 for volatile matter and fixed carbon, ISO 7404-5: 1994 for vitrinite reflectance).

The FTIR spectra of the coal samples were measured using a device that combined a VERTEX 80 fourier transform infrared spectrometer with a HYPERION 2000 infrared microscope (Bruker, Germany) at a resolution of 0.06 cm<sup>-1</sup> and spectral region of 8000-350 cm<sup>-1</sup>. For KBr pellet pressing, the steps were as follows: the coal samples (less than 200 mesh particle sizes) before and after SC-CO<sub>2</sub> treatment were mixed with pre-prepared KBr powder and were ground with mortar and pestle for 5–15 min. Then, the untreated and SC-CO<sub>2</sub> treated mixtures were put into a suitable mould

#### Table 1

Locations, depth, petrographic analyses and ranks of the sampled coals.

Sample	Sampling location	Depth (m)	Petrographic composition (vol. %)		Coal rank	
			V	Ι	М	
WLH	No. 8 coal seam, Wolonghu Coal Mine, Wanbei Coalfield, Anhui Province, China	530	73.01	22.12	4.87	Anthracite
HZ	No. 10 coal seam, Haizi Coal Mine, Huaibei Coalfield, Anhui Province, China	652	86.49	9.81	3.70	Coking coal
DL	No. 15 coal seam, Dalong Coal Mine, Tiefa Coalfield, Liaoning Province, China	555	92.19	3.25	4.56	Long-flame coal

V=Vitrinite; I=Inertinite; M = Mineral.



Fig. 1. Schematic of the high pressure SC-CO<sub>2</sub> geochemical reactor.

to be well distributed. By this step an equal quantity of sample powder can be exposed to the IR beam, which is essential for scrupulously comparing intensities of untreated and SC-CO<sub>2</sub> treated FTIR spectra. After vacuum pumping, the KBr pellets were exposed to the IR beam for the experiment. The FTIR spectra of the coal samples were determined by subtracting the KBr only reference spectra accurately calculate the FTIR spectra of the samples.

Pore structure analysis of the coal samples before and after SC-CO<sub>2</sub> treatment was performed using an Auto Pore IV 9500 mercury porosimeter (Micromeritic, USA), which can measure pore diameters of 0.003–180  $\mu$ m over a pressure range of 0.1–413 MPa. Before the test, samples were evacuated in the low-pressure station and when the vacuum pressure of the dilatometer was below 50  $\mu$ mHg, the low-pressure test was initiated. After completion of the low-pressure test, the dilatometer was operated until the end of the experiment. Equilibrium time at each data collection point was 10 s. The whole process was controlled by automatic computer data collection.

Micropore PSD in the coal samples before and after SC-CO<sub>2</sub> treatment were analysed using physical adsorption (N<sub>2</sub> as the probe molecule), employing an Autosorb iQ2 instrument (Quantachrome Instruments, USA). Prior to analysis, the untreated and SC-CO<sub>2</sub> treated samples were degassed under vacuum for 15 h at 150 °C to completely eliminate the gas impurities in coal. Then, a wide range of relative pressure (P/PO) is applied to determine the PSD in the micropore, minipore, mesopore range (approximately 0.6–300 nm). Additional methods and calculation models will be

discussed in subsequent sections.

#### 3. Results and analyses

#### 3.1. Proximate and petrographic analyses

The proximate and petrographic analysis results are listed in Table 2, the values of which are obtained from an average of three measurements, and experimental errors were controlled within  $\pm 2\%$ . As shown in Table 2, the moisture and ash content of SC-CO<sub>2</sub> treated coal were significantly less than that of the untreated coals. In addition, the volatile matter content decreased after SC-CO<sub>2</sub> treatment, in accord with Ro, max increases for the three coal samples. It is generally accepted that coal moisture and ash reflect the composition characteristics of inorganic substances, and volatile matter reflects compositional features of the organic matter. Therefore, compared to untreated samples, it should be a reduction of inorganic and organic matter for SC-CO<sub>2</sub> treated samples, which may be probably related to the mineral substances and organic compounds, respectively.

#### 3.2. FTIR analysis

Infrared spectrum analysis is a common method for identifying functional groups in complex mixtures because each group produces a unique molecular vibration spectrum. This information can then be compiled to derive molecular structure information (Xin et al., 2014). The position and intensity of absorption peaks in the infrared spectrogram confirms the different functional groups present in the overall molecular structure of coal (Li et al., 2013). Generally, some typical absorption peaks in the infrared spectrum before and after SC-CO<sub>2</sub> treatment can be analysed in detail on basis of changes in absorption peaks intensity. The macromolecular structure of coal is polymerized by the condensation of several aromatic rings and a small number of alicyclic or heterocyclic rings. The number of rings increases with degree of coalification. The other basic structural units in coal are primarily composed of alkyl side chains and a variety of functional groups, such as oxygencontaining, nitrogen-containing or sulphur-containing groups. To determine changes in characteristic absorption peaks in the infrared spectrum before and after SC-CO<sub>2</sub> treatment, the infrared spectrogram is divided into two parts: the functional group region (spectral peak range:  $4000-1500 \text{ cm}^{-1}$ ) and the fingerprint region (spectral peak range: 1500-400 cm<sup>-1</sup>). Fig. 2 shows the FTIR spectra of the functional group region for samples of three different metamorphic degrees of coal before and after SC-CO<sub>2</sub> treatment. The yellow circle represents the –OH groups with intramolecular association and the blue circle represents C-H stretching vibrations of aliphatic and naphthenic bonds.

The intensity of the -OH group absorption peak with intramolecular association for anthracite had no obvious changes after SC-CO<sub>2</sub> treatment, (Fig. 2, yellow circle). However, the intensity of this absorption peak clearly weakened in the coking and long-flame

Table	2
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Proximate analysis and vitrinite reflectance for anthracite, coking coal, long-flame coal before and after the treatment of SC-CO<sub>2</sub>.

Sample	Moist (%)	Ash (%)	Volatile matter (%)	Ro, max (%)
Anthracite (untreated)	4.815	28.05	11.145	2.9246
Anthracite (SCCO <sub>2</sub> -treated)	2.95	25.52	10.6	2.9693
Coking coal (untreated)	0.665	16.115	21.725	1.8608
Coking coal (SCCO <sub>2</sub> -treated)	0.43	12.865	21.17	1.8613
Long-flame coal (untreated)	6.565	18.43	42.215	0.6207
Long-flame coal (SCCO <sub>2</sub> -treated)	4.29	17.635	41.165	0.6211

coal samples after SC-CO<sub>2</sub> treatment. Generally, this absorption peak gradually decreases in intensity with increases in carbon content, and it is well known that carbon content increases with metamorphic grade. Anthracite, which is the highest rank coal, has high carbon and low oxygen content. As a result of its original composition, the intensity of the –OH group absorption peak in anthracite would have been expected to show almost no changes with SC-CO<sub>2</sub> treatment compared with coking coal and long-flame coal. These results are consistent with the research of Iwai et al. (2000).

The intensity of the C-H stretching vibration changes with the degree of coalification (Fig. 2, blue circle). Generally, the higher the degree of condensation in the aromatic rings, fewer, shorter side chains and functional groups will be present (Iwai et al., 1998). Thus, C–H stretching vibrations of aliphatic and naphthenic bonds weakened and even disappeared. The C-H absorption peak intensity of anthracite decreased significantly after SC-CO<sub>2</sub> treatment with the aliphatic and naphthenic adsorptions dropping to 2.141% and 1.882% transmittance, respectively. Moreover, the C-H absorption peak intensity of the other two coal samples decreased slightly after SC-CO<sub>2</sub> treatment, with the transmittance of aliphatic and naphthenic adsorption bands dropping to 0.996% and 0.716% (coking coal), and 0.934% and 0.734% (long-flame coal). These results show that the C-H stretching vibration of aliphatic and naphthenic bonds essentially depends on the degree of coalification, clearly represented in the infrared spectrogram and is obviously weakened in high rank coal after SC-CO<sub>2</sub> treatment.

In addition, if the characteristic absorption peaks of the functional group region are combined with the fingerprint region, the full range of changes in the majority of characteristic absorption peak intensities after SC-CO<sub>2</sub> treatment is visible (Fig. 2). Those peaks with major changes correspond to strongly polar functional groups (Fig. 2, purple circles), such as carboxyl ( $2780-2350 \text{ cm}^{-1}$ ), free –OH (3697–3625 cm<sup>-1</sup>) and –S–H (2525 cm<sup>-1</sup>) stretching vibrations. In contrast, other characteristic absorption peak intensities only changed slightly after SC-CO<sub>2</sub> treatment, corresponding to weakly polar or non-polar functional groups (Fig. 2, green circles), such as -CH, -CH<sub>2</sub>, -CH<sub>3</sub> symmetrical stretching vibrations in naphthenic or aliphatic bonds (2900, 2858-2847, 2882–2862 cm<sup>-1</sup>), C=C stretching vibrations of aromatic or fused rings (1635–1595 cm<sup>-1</sup>), carbonyl in aldehydes, ketones and esters (1750-1700 cm<sup>-1</sup>) and C-O in epoxy compounds or ethers (1040–910, 950–750 cm<sup>-1</sup>).

As mentioned above, the compounds containing the weakly polar or non-polar functional groups are more easily extracted by SC-CO<sub>2</sub>; however, the extraction effect for strongly polar functional groups are not obvious. To be specific, polyaromatic hydrocarbons, aliphatic and aromatic hydrocarbons, which contain weakly polar or non-polar functional groups, may be mobilized from coal matrices with SC-CO<sub>2</sub> treatment (Kolak et al., 2015). It is well known that coal has a dual pore structure that includes both matrix pores and fractures. Because CO<sub>2</sub> is a non-polar molecule, SC-CO<sub>2</sub> was used in the experiment to extract coal with the result that some compounds in the matrix pores or fractures can be extracted by SC-CO<sub>2</sub> and flow from the seepage channel along with air (Zhang et al., 2013). In this process, emphases should be given to compounds extracted by SC-CO<sub>2</sub>, which may cause environmental issues needing special attention on practical enhanced coal bed methane (ECBM) projects (Wang et al., 2015). Moreover, it has been proven that major components of volatile constituents that contain types of hydrocarbons, existing in the pore mouths or necks, cause a negative effect on the connectivity of pore structure (Bae et al., 2009; Nguyen and Bhatia, 2007). The details will be discussed in section 4.1.

#### 3.3. Pore structures

#### 3.3.1. Macropore and mesopore

With a simple principle and short-time test, MIP has been widely accepted to measure a wide range of pore radii on different materials, such as coal samples (Rouquerol et al., 1994). At present, MIP is still regarded as the standard method to measure PSD and pore volume of macropore and mesopore.

Using the pore classification method proposed by B. B. Hodot (Cai et al., 2013; Yang et al., 2012; Zhao et al., 2014; Zhou et al., 2016), which is widely used in China, the PSD was generated (Fig. 3).

Changes in incremental intrusion as a function of pore diameter are displayed in Fig. 3. All curves show multiple peaks in each phase and an increasing speed of mercury intrusion is zero. The results suggest that pore volume distribution is discontinuous. Mercury can intrude into macropores and from there into micropores by increasing the intrusive pressure, which happens inside macropores. When the intrusive pressure exceeds a certain value, multiple peaks occur frequently with increasing mercury intrusion due to development of subsequent mesopores, minipores and micropores in the coal.

The mercury intrusion volume of all coal samples after SC-CO<sub>2</sub> treatment clearly increased in the macropore phase (Fig. 3A and B), indicating that coal samples may develop more visible pores and macropores after SC-CO<sub>2</sub> treatment. In the long-flame coal, when the mercury intrusion reached ~100 nm of the pore diameter, the incremental intrusion volume started to increase. When the pore diameter was approximately 6 nm, the incremental intrusion reached its peak value, about four times higher than that in anthracite and coking coal. This indicated that compared with anthracite and coking coal, long-flame coal contained more minipores and micropores than visible pores and macropores (Fig. 3C). The pore volume distribution in the minipore and micropore phases accounted for ~90% of the cumulative pore volume, showing that minipores and micropores remained the primary pore component in long-flame coal. However, the peak value after SC-CO<sub>2</sub> treatment reduced this by ~40%, which indicates that SC-CO<sub>2</sub> changed the minipore and micropore distribution. Moreover, in the micropore phase, all pore distribution curves appeared relatively smooth after SC-CO<sub>2</sub> treatment with fewer multiple peaks. For long-flame coal, the two pore distribution curves (before and after SC-CO<sub>2</sub> treatment) show similar trends in the minipore, mesopore



**Fig. 2.** Infrared spectrogram of functional group region 4000–1500 cm<sup>-1</sup> for anthracite (A), coking coal (B) and long-flame coal (C), and the fingerprint region (1500–400 cm<sup>-1</sup>) for anthracite (D), coking coal (E), long-flame coal (F) before and after SC-CO<sub>2</sub> treatment. The yellow circle represents the –OH groups with intramolecular association and the blue circle represents C–H stretching vibrations of aliphatic and naphthenic bonds. Moreover, purple circles represent the transmittance of the characteristic absorption peaks that changed greatly, whereas the green circles highlight absorptions that did not show much change. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Changes of incremental intrusion as a function of pore diameter for anthracite (A), coking coal (B) and long-flame coal (C) before and after SC-CO<sub>2</sub> treatment by applying MIP.

and macropore phases, but not the micropore phase. For anthracite, differences were only apparent in the micropore and macropore phases. Coking coal was more complicated than the other two coal ranks because different phases presented different cases with very little consistency. These results indicate that different pore structures and distributions for various coal ranks produce different

#### effects in each phase.

#### 3.3.2. Micropore and minipore

To accurately and systematically analyse micropore and minipore, gas adsorption techniques were applied for assessing a wide range of pore sizes, including the complete range of micropore and minipore. Pore size analysis of micropore and minipore can be performed with methods based on the Barett-Joyner-Halenda (BJH approach) and the application of QSDFT, which leads to major improvements in pore size analysis of nanoporous carbon materials (Landers et al., 2013). The BJH method was chosen on account of the accuracy in measuring pore sizes greater than 10 nm (Thommes, 2010). Meanwhile, DFT method is suitable for the PSD from micropore to mesopore.

In Fig. 4A1, B1 and C1, the fitting errors for PSD using DFT were scattered widely, from a low of 0.4% for untreated anthracite coal to a high of 3% for the SC-CO<sub>2</sub> treated long-flame coal. The DFT calculation model was chosen as slit/cylindrical pores and QSDFT adsorption branch model was chosen as uniform. All untreated curves presented similar trends with two or three obvious peaks in the micropore (<10 nm) stage. There is a decrease in the SC-CO<sub>2</sub> treated curves, especially in the micropore stage. Notably, these clear peaks mentioned above declined similarly after SC-CO<sub>2</sub> treatment. In addition, compared to the untreated coal curves, the SC-CO<sub>2</sub> treated coal curves from 0.8 nm to 2 nm vanished. As illustrated in Fig. 4A-1, B1 and C1, interaction of anthracite, coking coal and long-flame coal with SC-CO<sub>2</sub> may result in a decrease in micropore (<10 nm). A previous study by Gathitu et al. (2009) demonstrated that SC-CO<sub>2</sub> may cause micropore collapse, which may result in a micropore stage reduction. While the PSD of MIP is not highly accurate for high pressure (micropore and minipore stage), as mentioned in Fig. 3, it presents trends in accordance with the PSD using DFT curves. However, DFT curves in the minipore (10 nm-32 nm) stage may not be evident before and after SC-CO<sub>2</sub> treatment because of unreliable data.

As a consequence, the BIH method was more reliable and accurate for minipore (10 nm-100 nm) analysis. As shown in Fig. 4A2, B2 and C2, the PSD using BJH reveals a similar profile for the three different metamorphic grade coals. The degree of difference between untreated and SC-CO<sub>2</sub> treated curves is relatively significant for anthracite and coking coal while it is relatively non-significant for long-flame coal, which corresponds with the MIP results in Fig. 3. Furthermore, it is apparent that the untreated coal curves exceed the SC-CO<sub>2</sub> treated coal curves in the minipore (10 nm-100 nm) stage, whereas in the mesopore stage (100 nm-300 nm) the SC-CO<sub>2</sub> treated coal curves are higher than the untreated coal curves. Thus 100 nm may be a key diameter, providing a clear distinction in the distribution before and after SC-CO<sub>2</sub> treatment. In addition, a trend for mesopore volume (100 nm-300 nm) shows the difference between untreated and SC-CO<sub>2</sub> treated coals increases gradually. By chosing the closest and farthest point to 100 nm as marked in Fig. 4, the changes in the difference between the two points for the SC-CO<sub>2</sub> treated curves show an increasing trend with long-flame coal rising by 2.123 cc/ nm/g, anthracite rising by 3.37 cc/nm/g and coking coal rising by 4.022 cc/nm/g, compared with the untreated curves. Combined with the MIP result in Fig. 3, it can be speculated that  $SC-CO_2$  may alter the pore structure of anthracite and coking coal significantly, while it may not significantly change long-flame coal, especially in the minipore, mesopore and macropore stage.

#### 3.3.3. Further analysis on pore structures

To improve the reliability of experiment data, further analysis on MIP was performed and is shown in Fig. 5 and Table 3.

Under the same pressure, all cumulative pore volumes after SC-



**Fig. 4.** DFT PSD curves for anthracite (A1), coking coal (B1) and long-flame coal (C1) before and after SC-CO<sub>2</sub> treatment. Experimental data for samples are calculated with slit/ cylindrical pores and QSDFT adsorption branch model. BJH PSD curves measured using N2 at 77 K for anthracite (A2), coking coal (B2) and long-flame coal (C2) before and after SC-CO<sub>2</sub> treatment.



**Fig. 5.** Changes in cumulative pore volume as a function of pressure for anthracite (A), coking coal (B) and long-flame coal (C) before and after SC-CO<sub>2</sub> treatment by applying MIP.

CO<sub>2</sub> treatment were significantly higher than the untreated groups (Fig. 5). Similarly, further quantitative comparison of untreated and SC-CO<sub>2</sub> treatment groups (Table 3) indicate that porosity and total pore volume for anthracite, coking coal, long-flame coal increased slightly after exposure to CO<sub>2</sub>. The porosity and total pore volume for anthracite showed an obvious increase, with respective growth rates of 0.2336% and 6.4% because SC-CO<sub>2</sub> changed the size and shape of the pore structures. Thus, more mercury could be held in the pores of SC-CO<sub>2</sub> treated coal samples than in untreated samples. Moreover, the mercury intrusion curves of all coal samples were not coincident with the mercury extrusion curves, which is interpreted using the so-called "Ink Bottle theory" as reported in open literature (Suuberg et al., 1995). However, the curves of each coal sample after SC-CO<sub>2</sub> treatment indicated a different hysteresis compared with untreated, which was primarily related to the metamorphic degree of the coals. For high rank coal (anthracite) and medium rank coal (coking coal), mercury intrusion/extrusion curves after SC-CO<sub>2</sub> treatment were almost all higher. For low rank coal (long-flame coal), the cumulative pore volume was significantly higher than the other two samples. The curve of the longflame coal after SC-CO<sub>2</sub> treatment was very close to the before treatment curve even though the former was slightly above the latter. However, hysteresis was obvious, which may result from the large proportion of minipores and micropores in the long-flame coal. A majority of mercury remained in the minipores and micropores as a result of the "Ink Bottle" effect in the mercury extrusion process.

Generally, the gas (CO<sub>2</sub>) flow is mainly laminar, whereas turbulent flow is common in mesopores and macropores, diffusion and adsorption are present in minipores, and adsorption dominates in micropores. Thus, seepage-flow pores are classified as >100 nm, while adsorption pores are classified as <100 nm. The insets in Fig. 5 highlight the changing percentage of different pore types with and without SC-CO<sub>2</sub> treatment. Seepage-flow pores (>100 nm, mesopore and macropore) of coking coal and adsorption pores (<100 nm, minipore and micropore) of long-flame coal were the most developed. The proportion of seepage-flow pores for all coal samples after SC-CO<sub>2</sub> treatment increased, with anthracite rising by 5.48%, coking coal rising by 4.59% and long-flame coal rising by 1.26%. Thus, the overall proportion of adsorption pores decreased. Combined with the results of the DFT, BJH and MIP methods, it can be deduced that SC-CO<sub>2</sub> treatment may promote the development of mesopores and macropores, and restrain the minipores and micropores development in the three metamorphic grade coal samples, especially in the micropore range of 0.8 nm-2 nm. The decrease of micropores after SC-CO<sub>2</sub> treatment can be explained by the effect of adsorption-induced deformation in pores, which may lead to the expansion of micropores with increasing CO<sub>2</sub> pressure (Yang et al., 2011). Previous studies have shown that the extraction effect of SC-CO<sub>2</sub> causes a decline in the roughness degree of coal surface, and the effect is to transform smaller pores into larger pores (Gathitu et al., 2009; Wang et al., 2015; Zhang et al., 2013). The total pore volume and porosity of coal, as shown in Table 3, increased moderately after SC-CO<sub>2</sub> treatment. A previous study noted that some substances may prevent adsorbing molecules from passing through pores, but SC-CO<sub>2</sub> extraction can promote more

Table 3	
Analysis results of mercury intrusion method on porosity and total pore vol	ume.

Sample	Anthracite Anthracite		Coking coal	Coking coal	Long-flame coal	Long-flame coal
	(untreated)	(SCCO <sub>2</sub> -treated)	(untreated)	(SCCO <sub>2</sub> -treated)	(untreated)	(SCCO <sub>2</sub> -treated)
Porosity (%)	4.3648	4.5984	4.6205	4.8092	7.0968	7.1290
Total pore volume (mL/g)	0.0328	0.0349	0.0372	0.0388	0.0619	0.0639

gas adsorption on the coal surface (Bae et al., 2009); Therefore, the extraction effect may be the primary factor for increasing total pore volume. For high rank coal (anthracite) and medium rank coal (coking coal), adsorption pores and seepage-flow pores clearly changed. However, for low-rank coal (long-flame coal) no change was evident, which may be related to the pore space formation due to coal metamorphism. The changes in all of pore types caused by SC-CO<sub>2</sub> treatment may be connected to characteristic pore properties. The development of seepage-flow pores determined seepage characteristics of coal structure to some degree; the interconnection of adjacent seepage-flow pores may form a cleat and fracture system under the constant influence of SC-CO<sub>2</sub> treatment.

## 4. Discussion of coal structure evolution during CO<sub>2</sub> geological storage and its effects on the coal reservoir

In this paper, the coal structure evolution can be discussed from the microscopic and macroscopic perspectives. Generally, pore structure in a coal matrix can be regarded as the microscopic perspective of coal structures, which was analysed in detail through the above experiments. The macroscopic perspective typically indicates the fracture system, such as permeability and fracture aperture, in the coal structures.

#### 4.1. Microscopic perspective

FTIR analysis indicates that the weakly polar or non-polar functional groups, corresponding to the polyaromatic hydrocarbons, aliphatic and aromatic hydrocarbons, were extracted from the coal matrices by SC-CO<sub>2</sub>. It has been proven that energy barriers, caused by volatile hydrocarbons, which exist in pore mouths, or necks of coal matrix, may prevent gas molecules from passing through physical constrictions (Bae et al., 2009; Nguyen and Bhatia, 2007). With SC-CO<sub>2</sub> treatment, volatile hydrocarbons were removed from coal matrix and barriers to adsorbing molecules disappeared. Moreover, higher pressure and temperature under SC-CO<sub>2</sub> conditions can provide sufficient energy to molecules for passing through the pores. Consequently, the physically constricted pore spaces will be opened and connectivity in pores improved. The pore structure analysis results after SC-CO<sub>2</sub> treatment confirmed that SC-CO<sub>2</sub> contributes to the increase in total pore volume and development of seepage-flow pores, which may have positive effects on the accessibility of meso- and macropore spaces, improving the seepage capacity of coal and facilitating gas desorption.

#### 4.2. Macroscopic perspective

As a key parameter impacting seepage characteristics of a coal reservoir, permeability is mainly controlled by aperture and magnitude degree of the fracture system (Liu et al., 2016). The influencing factors on fracture aperture (W) can be related to external stress (W<sub>1</sub>), CO<sub>2</sub> injection pressure (W<sub>2</sub>), adsorption swelling effect (W<sub>3</sub>), and SC-CO<sub>2</sub> extraction (W<sub>4</sub>). Therefore, the fracture aperture (W) can be described as Eq. (1):

$$W = -W_1 + W_2 - W_3 + W_4 \tag{1}$$

The coal structure evolution of the macroscopic perspective, occurring in the fracture system of the coal reservoir during  $CO_2$  storage, is a dynamic process. This process can be divided into four stages (namely Decreasing Stage, Stable Stage I, Increasing Stage and Stable Stage II), which are illustrated in Fig. 6. In the earlier stage, during  $CO_2$  injection (Decreasing Stage), fracture aperture in the coal narrowed and the permeability of the coal reservoir

decreased due to the predominance of the external stress (W<sub>1</sub>). With plenty of CO<sub>2</sub> injected into the system, the adsorption swelling effect began to take effect, and coupled with external stress, the permeability of the reservoir decreased to a minimum. Then Stable Stage I was gradually reached during the middle period of CO<sub>2</sub> injection. During this period,  $W_2+W_4-(W_1+W_3) = constant$ , namely, fracture aperture under the injecting SC-CO<sub>2</sub> pressure. remained in balance. Subsequently, with an increase of injection pressure, dissolved substances filled the fractures, and some organic and inorganic constituents extracted by SC-CO<sub>2</sub> in the pore may have caused expansion of the original fracture system and formed more secondary small-scale fractures. With higher injection pressure and SC-CO<sub>2</sub> extraction, the permeability of coal reservoir increased steadily, which happened in the later stage during CO<sub>2</sub> injection. Eventually, the system pressure balanced again and the fracture aperture reach stablity once again.

For this experiment, the temperature and pressure conditions (40 °C and 10 MPa for 120 h, respectively) were above the critical point, which simulated the practical condition in a coal reservoir. Generally, the maximum adsorption swelling of the coal appears at a condition where temperature between 25 and 55 °C and pressure between 8 and 10 MPa. After this point, the adsorption swelling effect will not make sense (Day et al., 2008). Thus, the adsorption swelling effect (W<sub>3</sub>) could be ignored in these experimental conditions. However, the injection pressure of CO<sub>2</sub> (W<sub>2</sub>) and SC-CO<sub>2</sub> extraction (W<sub>4</sub>) were still regarded as the main factors controlling fracture aperture (W). However, the external stress (W<sub>1</sub>) could be ignored under high SC-CO<sub>2</sub> pressure as well (Massarotto et al., 2010). Therefore, it can be concluded that the condition in this study was located in the Increasing Stage, as shown in Fig. 6. The injection under high SC-CO<sub>2</sub> pressure experienced a pressure increase in the cleat system, leading to fracture expansion. Meanwhile, SC-CO<sub>2</sub> extraction and dissolution effects on some substances create significant improvements to connectivity and seepage characteristics of the fracture system through the whole coal reservoir (Massarotto et al., 2010). Therefore, the channel for gas diffusion and seepage may suffer irreversible modifications, which could increase the permeability of coal reservoir.

#### 4.3. How SC-CO<sub>2</sub> affects long-term sequestration

The experimental results of different coal samples under a similar condition of SC-CO<sub>2</sub> storage in this study demonstrate various features depending on the coal ranks. Also, with an explanation for coal structure evolution from the macroscopic perspective, the injection time, volume and temperature have important influences on fracture aperture and permeability within a coal reservoir, which may affect CO<sub>2</sub> sequestration (Massarotto et al., 2010). Therefore, the sequestration conditions of the target coal seams should be fully evaluated based on the properties of coal samples and CO<sub>2</sub>, in order to choose an appropriate solution.

The positive effects of SC-CO<sub>2</sub> on coal reservoirs, as mentioned above, contribute to the accessibility of seepage-flow pores and the connectivity of fracture system. These changes may improve the permeability of target coal seams and CO<sub>2</sub>-ECBM. The negative effects are mainly environmental safety and health (ES & H) issues and CO<sub>2</sub> security storage. On one hand, SC-CO<sub>2</sub> injection for geological sequestration has the potential to remove some substances, i.e., polyaromatic hydrocarbons, aliphatic and aromatic hydrocarbons, from the coal matrix (Kolak et al., 2015). These substances may be related to biological toxicity and can be accompanied by the flow of gas or water (Zhang et al., 2013). Once achieving to the adequate amount, these substances can be brought into the surrounding geological coal seams and groundwater, which may be detrimental to ES & H for humans (White et al.,



#### SC-CO<sub>2</sub> Injecting Time

Fig. 6. Evolution of the fractures and permeability of coal reservoir during the SC-CO<sub>2</sub> injection.

2005). On the other hand, under the condition of  $CO_2$  geologic sequestration, SC- $CO_2$  fluids may tend to migrate around the target reservoir, leading to accumulation under the cap rock (Wang et al., 2016). It is well known that the sealing ability of the cap rock is the key to safety storage of  $CO_2$  (Zhang et al., 2009). However, dissolved  $CO_2$  in formation water may decrease the pH of the reservoir, breaking the chemical equilibrium of the original mineral substances and cause the mineral dissolution (Lin et al., 2008; Liu et al., 2010). Eventually, SC- $CO_2$  may reduce the sealing ability of the cap rock. Thus, the connectivity and seepage characteristics of fracture system through the reservoir can be improved, and the main effect is  $CO_2$  leakage and release from the faults or fractures, which can result in a significant safety risk (Aydin et al., 2010; Bildstein et al., 2010).

#### 5. Conclusions

Experiments in this study showed that the absorption peak intensity of -OH groups with intramolecular association in the highest rank coal (anthracite) weakened slightly compared with coking coal and long-flame coal after SC-CO<sub>2</sub> treatment. However, the C–H absorption peak intensity of anthracite was clearly weakened after SC-CO<sub>2</sub> treatment. The SC-CO<sub>2</sub> may also have the ability to extract organic matter in coal. Compounds (such as some hydrocarbons or other compounds) with weakly polar functional groups significantly decreased after SC-CO<sub>2</sub> treatment, whereas strongly polar functional groups showed only a slight change.

The mercury intrusion results illustrate that pore structure and distribution change was dependent on the coal rank. After SC-CO<sub>2</sub> treatment, long-flame coal showed significant differences only in the micropore phase, whereas the differences on anthracite were mainly in the micropore and macropore phase. The effects on coking coal were disordered and complicated for each pore phase before and after SC-CO<sub>2</sub> treatment, but the pore distribution curve in the micropore phase exhibited fewer multiple peaks after SC-CO<sub>2</sub> treatment. The physical adsorption method indicated that the micropore (<10 nm) results using the DFT method and minipore (10 nm-100 nm) results using the BJH calculation model largely agreed with the MIP method results. The obvious peaks in the DFT

PSD decreased similarly after SC-CO<sub>2</sub> treatment, especially in the micropore (<10 nm) stage, accompanied by the disappearance of peaks between 0.8 nm and 2 nm. The BJH PSD of the three coals had similar changes from 10 nm to 300 nm, and the changes after SC-CO<sub>2</sub> treatment indicated that mesopore volume (100 nm-300 nm) increased gradually. Furthermore, the total pore volume and porosity for all coal samples after SC-CO<sub>2</sub> treatment increased slightly with the largest increase in anthracite with 0.2336% (pore volume) and 6.4% (porosity). After SC-CO<sub>2</sub> treatment, there was a clear change in pore development in the high rank and medium rank coals, but only a slight change occurred in low rank coal.

During long-term storage of CO<sub>2</sub>, the evolution of pore structure in the coal matrix and fracture system contribute to the accessibility of seepage-flow pore spaces and connectivity of fracture system, which may improve the permeability of the target coal seams and CO<sub>2</sub>-ECBM. However, ES & H issues and the security storage of CO<sub>2</sub> should be considered as guidelines for CO<sub>2</sub> geologic sequestration.

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