Influences of supercritical carbon dioxide fluid on pore morphology of various rank coals: A review

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Abstract
Supercritical carbon dioxide is known to change the pore structure of coals and thus affect their carbon dioxide sequestration capacity. In this study, supercritical carbon dioxide dependence of pore morphology of coals was reviewed. Results indicated that the micropore surface area and volume of dry coals varied between –20% and 20% after exposure to supercritical carbon dioxide. Changes in the micropore size distribution of dry coals after supercritical carbon dioxide exposure were not found to be significant; however, the change in meso- and macropores with diameter of 2–8 nm was observed to be significant. Supercritical carbon dioxide and H₂O exposure mainly influenced pores with diameters of 0.4–0.7, 0.7–0.9 and 2–8 nm. The variation in the pore fractal dimensions of the coals ranged from –0.5% to 0.5% after supercritical carbon dioxide exposure. Furthermore, the dependence of supercritical carbon dioxide on the pore structure of coals relies on the coal rank. The change in the pore structure of the coals after supercritical carbon dioxide exposure was observed to be related to the following aspects. First, supercritical carbon dioxide induced swelling in coal matrix, thus reducing the pore surface area and volume of the coal matrix and compressing the cleat system. Next, the extraction of supercritical carbon dioxide mobilised the small organic molecules dispersed in the coal matrix; this increased the pore volume, particularly of micropores. Finally, the mineral dissolution/precipitation also changed the pore structure of the coals. To further examine supercritical carbon dioxide dependence of coal pore morphology, the following studies should be performed. The characterisation of the chemical and pore structure of coals should be combined with existing coal structure

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models to account for the mechanism of supercritical carbon dioxide changing the pore structure of coals. Combination of physical experiments and numerical simulations is recommended to predict the changes in porosity and permeability of coals due to long-term carbon dioxide sequestration.

Keywords
Coal, carbon dioxide, sequestration, supercritical fluid, pore structure

Introduction
Carbon dioxide (CO₂) capture and sequestration (CCS) has great potential for mitigating anthropogenic greenhouse CO₂ emissions. It has been estimated that globally, CCS can reduce 20% of CO₂ emitted from the energy industry (Haszeldine, 2009). Onshore geologic options for CO₂ sequestration mainly include depleted oil and gas reservoirs, oil reservoirs, salt aquifers and unmineable coal seams (Tao et al., 2019). Among these, CO₂ sequestration in coal seams (CO₂-ECBM) has been considered to not only mitigate CO₂ emissions, but also enhance coalbed methane (CH₄) recovery (Orr, 2009). The data published by the International Energy Agency indicate that worldwide, CO₂ storage capacity and amount of CH₄ recovered from coal seams could reach up to 4.88 × 10¹¹ billion tons and 5 × 10¹³ Nm³, respectively (Godec et al., 2014).

The CO₂-ECBM process incorporates complex interactions between multiple fluids, including CO₂, CH₄, H₂O and coals (Wang et al., 2015d; Zhang et al., 2019d); they have received a lot of interest (Li et al., 2017; Liu et al., 2018; Perra et al., 2011; Zhang et al., 2013a, 2017a, 2019c). The coal matrix has been found to have a good adsorption capability, which mainly accounts for CO₂ sequestration and CH₄ occurrence in the coal seams (Pillalamarry et al., 2011). Results have shown that the volume fractions of in-situ adsorbed CH₄ and CO₂ in the coal seams are 85% (Chang et al., 2015) and 95–98% (Busch and Gensterblum, 2011; De Silva and Ranjith, 2012; Topolnicki et al., 2013), respectively. The adsorption, diffusion and flow of CH₄ and CO₂ within coal reservoirs have mainly been determined by the pore structure of coals (Liu et al., 2010; Zhang et al., 2017b). The surface area, volume, pore size distribution and roughness of the pore surface have been observed to have a particularly significant effect on CO₂ storage and CH₄ production (Arami-Niya et al., 2016; Liu et al., 2015, 2017). The estimated optimum depth for CO₂ geologic storage is 800–1000 m (Orr, 2009), where coal reservoir temperature and pressure have been often higher than the critical temperature and pressure of CO₂, i.e. $T_c = 31.06°C$ and $P_c = 7.38$ MPa (Perry and Green, 1997). Therefore, CO₂ exists in a supercritical state that has a high diffusion and dissolution capability, and a low viscosity and surface tension (Nahar et al., 2018). Additionally, the three-dimensional network of coal comprises condensed aromatic and hydroaromatic compounds connected via short alkyl bridges, and ether and thioether linkages (Liu et al., 2019d). Organic compounds with a low molecular weight of <500 amu, including oxy-compounds and hydrocarbons, have been found to disperse in the macromolecular structure of coals. Furthermore, many types of inorganic minerals, such as calcite, dolomite and chlorite are found in coals. The injected supercritical carbon dioxide (ScCO₂) has the potential to extract organic compounds with a low molecular weight and dissolve
and precipitate some minerals within the coal matrix. In summary, the aforementioned characteristics of both ScCO₂ and coals have resulted in multiple interactions between the fluids and coals, i.e. ScCO₂-induced coal matrix swelling (Sampath et al., 2019), the extraction of small organic compounds (André et al., 2007; Kolak and Burruss, 2006), and mineral dissolution or precipitation (Li et al., 2017; Mavhengere et al., 2015; Zhang et al., 2016). These interactions have been found to be capable of changing the pore structure of coals (Liu et al., 2019a; Massarotto et al., 2010; Zhang et al., 2017b), thereby, affecting CO₂ storage and CH₄ production within target coal seams. Various studies have suggested that the effects of ScCO₂ on the pore structure of coals are associated with the physico-chemical property of coals, including coal rank (R_o,max), volatile matter and minerals, and coal reservoir conditions, such as temperature, pressure and moisture content (Arami-Niya et al., 2016; Radlinski et al., 2004). Although the ScCO₂ exposure dependence of coals has been studied extensively, the review on this area has scarcely been reported. Therefore, this study analysed the influences of ScCO₂ on the pore structure of various rank coals based on literature review. The potential mechanisms accounting for ScCO₂ exposure dependence of the pore structure of the coal were addressed. Future directions of study in this area are also given in this paper.

Table 1 shows that the studies on the effects of ScCO₂ fluid on the pore structure of coal began in 2000, and have since received significant interest. The coals tested in these studies included dry and moist samples. In addition, most studies were performed under static exposure conditions. Diverse characterisation methods including probe molecule adsorption, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM) were used.

**Effects of ScCO₂ on the pore morphology of coals**

In this study, the pore classification standard proposed by the International Union of Pure and Applied Chemistry was adopted. It classifies micro-, meso- and macropores as those with a diameter <2 nm, with a diameter ranging between 2 and 50 nm and with a diameter larger than 50 nm, respectively (Sing, 1985).

**Micropores**

The micropores of porous materials have been often found to accommodate the main adsorption space for the adsorbates (Do, 1998; Liu et al., 2019a, 2019c). Thus, micropores mainly determine the adsorption capacity of the adsorbates. With respect to CO₂-ECBM, it has been widely accepted that the micropore structure of the coal matrix determined the CO₂ storage capacity and in-situ CH₄ reserve of the target coal seams (White et al., 2005). Hence, the alterations in the micropores in the coals, after ScCO₂ exposure, are critical to actual CO₂-ECBM process. Many options can be used to estimate the micropore structure parameters of coals, including CO₂ adsorption, small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS). Among these, CO₂ adsorption at 273.15 or 298.15 K has been widely adopted to estimate the micropore parameters of coals as CO₂ can easily access micropores and ultramicropores (Amarasekera et al., 1995). Based on the CO₂ adsorption data, the Dubinin–Radushkevic and the Dubinin–Astakhov models have been used to calculate the micropore surface area (S_mic) and volume (V_mic), respectively (Wang et al., 2015c; Zhang et al., 2016).
| Year | Temperature (°C) | Pressure (MPa) | Exposure time (h) | Static or dynamic exposure | Coal rank (Ro,max, %) | Sample state | Characterisation methods | References |
|------|-----------------|----------------|------------------|---------------------------|---------------------|--------------|------------------------|------------|
| 2000 | 35              | 9.8, 14.7      | 20               | Dynamic                   | –                   | Dry basis, particle size of 0.5–0.85 mm | N₂ adsorption and FTIR | Iwai et al., 2000 |
| 2005 | 55              | 0.35           | –                | Static                    | –                   | –            | ATR-FTIR               | Goodman et al., 2005 |
| 2006 | 40              | 10             | 1 h static exposure and 0.25 h dynamic exposure | Static and dynamic | –                   | Air-dried basis, particle size of 0.25 mm | GCMS | Kolak and Burruss, 2006 |
| 2009 | 80, 130         | 13.8, 17.9, 21.2, 22.7, 55.8 | 48               | Static                    | –                   | Dry basis and as-received basis, particle size of 0.075–0.106 mm | CO₂/N₂ adsorption and SEM | Gathitu et al., 2009 |
| 2010 | 40              | 9.8            | 72               | Dynamic                   | –                   | As-received basis, particle size of 1–2, 2–4 and 4–8 mm | MIP and helium density | Liu et al., 2010 |
| 2010 | 20              | 2.67           | –                | Static                    | 0.63                | Moisture-equilibrated at 20°C, particle size of 0.25 mm | CO₂/N₂ adsorption and FTIR | Mastalerz et al., 2010 |
| 2010 | 38              | 9              | 120              | Static                    | 0.85, 0.90          | Coal samples blended with 19.5 mL ScCO₂ and 45.5 mL deionized water, particle size of 0.18–0.22 mm | CO₂ adsorption, MIP, SEM and XRD | Massarotto et al., 2010 |
| Year | Temperature (°C) | Pressure (MPa) | Exposure time (h) | Static or dynamic exposure | Coal rank (Ro,max, %) | Sample state | Characterisation methods | References |
|------|------------------|----------------|-------------------|-----------------------------|-----------------------|--------------|-------------------------|------------|
| 2011 | 55               | 16             | 24                | Static – Dry basis, block size of 30 × 9 × 9 mm (nominal dimension) | –                     | Dry basis, block size of 30 × 9 × 9 mm (nominal dimension) | CO₂ adsorption | Day et al., 2011 |
| 2012 | 55               | 15             | 48–72             | Dynamic                     | –                     | Dry basis, block size of 30 × 9 × 9 mm (nominal dimension) | CO₂ adsorption | Day et al., 2012 |
| 2013 | 35, 50, 65       | 10             | 24                | Static                      | 0.47, 0.87, 1.35, 4.06 | Dry basis, particle size of 0.18–0.25 mm | N₂ adsorption | Zhang et al., 2013a |
| 2013 | 55               | 15.3           | 2496              | Static – As-received basis, block size of 25.4 × 25.4 × 25.4 mm | –                     | Dry basis, particle size of 0.125–0.15 mm | CO₂/N₂ adsorption and SEM | Kutchko et al., 2013 |
| 2015 | 45               | 12             | 12                | Dynamic                      | 0.77, 0.88, 0.93, 2.62 | Dry basis, particle size of 0.125–0.15 mm | CO₂/N₂ adsorption and FTIR | Wang et al., 2015c |
| 2015 | 35               | 12.5           | 4320              | Static – As-received basis, block size of 0.5–1 mm | –                     | Dry basis, particle size of 0.5–1 mm | CO₂/N₂ adsorption and FTIR | Mavhengere et al., 2015 |
| 2015 | 40               | 10             | 0.25 h static exposure and 1 h dynamic exposure | Static and dynamic | 0.34, 0.37, 0.46, 0.68 | Dry basis, particle size of 0.841 mm | CO₂ adsorption | Kolak et al., 2015 |
| 2016 | 45               | 12             | 12                | Dynamic                      | 0.77, 0.88, 0.93, 2.62 | Air-dried basis, particle size of 0.125–0.15 mm | CO₂/N₂ adsorption | Zhang et al., 2016 |
| 2017 | 45               | 10             | 240               | Static                      | 2.92, 1.53, 0.62     | Dry basis, particle size of 0.18–0.25 mm | CO₂ adsorption | Zhang et al., 2017a |

(continued)
| Year | Temperature (°C) | Pressure (MPa) | Exposure time (h) | Static or dynamic exposure | Coal rank (Ro,max, %) | Sample state | Characterisation methods | References |
|------|------------------|----------------|------------------|---------------------------|------------------------|--------------|-------------------------|------------|
| 2017 | 40               | 10             | 120              | Static                    | 2.92, 1.86, 0.62       | Dry basis, particle size of 1–3 mm and 0.2–0.25 mm | CO₂/N₂ adsorption and MIP | Zhang et al., 2017b |
| 2017 | 45               | 12             | 16               | Dynamic                   | 0.47, 0.67, 2.86       | Dry basis, particle size ≤ 0.075 mm | N₂ adsorption, MIP and FTIR, CO₂/N₂ adsorption, FTIR, NMR and XRD | Li et al., 2017 |
| 2017 | 40               | 10             | 24               | Static                    | 0.79, 1.06, 1.33, 1.58, 1.80 | As-received basis, particle size of 0.0814–0.25 mm | N₂ adsorption, MIP and FTIR, N₂ adsorption, MIP and XRD | Chen et al., 2017 |
| 2018 | 80               | 20             | 240              | Static                    | 0.72, 1.81, 2.19, 3.33 | Coal samples blended with 300 mL deionized water, particle size of 4–8 mm | N₂ adsorption, MIP and SEM | Liu et al., 2018 |
| 2018 | 80               | 20             | 240              | Static                    | 3.64, 3.33, 2.83       | Coal samples blended with 600 mL deionized water, particle size of 4–8 mm, block size of 10 × 10 × 10 mm | N₂ adsorption, MIP, SEM, and XRD | Du et al., 2018 |
| 2018 | 62, 82, 102      | 15             | 0.2, 1, 3        | Static                    | –                      | Particle size of 0.18–0.25 mm | N₂/CO₂ adsorption and TGA | Li et al., 2018 |
| 2018 | 45               | 12             | 480              | Static                    | 2.69                   | Dry basis, moisture equilibrated coal; particle | N₂ adsorption, MIP and SEM | Zhang et al., 2018 |
### Table 1. Continued.

| Year | Temperature ($^\circ$C) | Pressure (MPa) | Exposure time (h) | Static or dynamic exposure | Coal rank (Ro,max, %) | Sample state | Characterisation methods | References |
|------|-------------------------|-----------------|-------------------|---------------------------|-----------------------|--------------|--------------------------|------------|
| 2018 | 50                      | 20              | 24                | Dynamic                   | –                     | Block size of 100 (H) × 100 (W) × 200 (L) mm | N$_2$ adsorption and FTIR | Zhang et al., 2019a |
| 2019 | 62.5                    | 15              | 240               | Static                    | 0.72, 1.89, 2.19, 3.33 | Coal samples blended with 300 mL deionized water, particle size of 4–8 mm | CO$_2$ adsorption, FTIR, and XRD | Liu et al., 2019b |
| 2019 | 40                      | 10              | 720               | Static                    | –                     | Dry basis, air dried basis and moist coal samples containing 10% water, particle size of 0.075 mm | N$_2$ adsorption and XRD | Jiang and Yu, 2019 |

FTIR: Fourier transform infrared spectrometer; ATR-FTIR: attenuated total reflection Fourier transform infrared spectroscopy; GCMS: gas chromatography–mass spectrometry; SEM: scanning electron microscope; MIP: mercury intrusion porosimetry; XRD: X-ray diffraction; NMR: nuclear magnetic resonance; TGA: thermogravimetric analyser.
Surface area and volume of the micropore. Previous studies reported that $S_{\text{mic}}$ of dry coals decreases after ScCO$_2$ exposure (Mavhengere et al., 2015; Zhang et al., 2016, 2017b), and ScCO$_2$-induced matrix swelling was considered the primary reason for that. Studies on as-received coals also reported the same trend as that of the dry coals after ScCO$_2$ exposure (Kutchko et al., 2013; Mastalerz et al., 2008). Furthermore, H$_2$O has been considered to play a critical role in the interactions between ScCO$_2$ and coals. H$_2$O has been verified to enhance the effects of ScCO$_2$ on coal pores, to produce complex interactions in the ScCO$_2$–H$_2$O–coals system (Jiang and Yu, 2019; Li et al., 2017). Furthermore, Daning coal ($R_{o,\text{max}}=2.86\%$) collected from Qinshui coal field and Xiegou coal ($R_{o,\text{max}}=0.67\%$) collected from Hedong coal field were observed to exhibit the smallest ($-1.1\%$) and the highest ($-8.27\%$) change in $S_{\text{mic}}$, respectively, after ScCO$_2$ and H$_2$O exposure (Li et al., 2017). However, some studies also reported that ScCO$_2$ exposure could increase $S_{\text{mic}}$ of coals (Jiang and Yu, 2019; Mastalerz et al., 2010). Therefore, to better evaluate the influence of ScCO$_2$ exposure on the micropores of coals, the parameters $f_{S_{\text{mic}}}$ and $f_{V_{\text{mic}}}$ were calculated using equations (1) and (2), respectively, and selected to determine the variation in $S_{\text{mic}}$ and $V_{\text{mic}}$ of coals after ScCO$_2$ exposure.

\[
    f_{S_x} = \frac{S_{x,f} - S_{x,i}}{S_{x,i}} \times 100\% 
\]

\[
    f_{V_x} = \frac{V_{x,f} - V_{x,i}}{V_{x,i}} \times 100\% 
\]

where $S_{x,i}$ and $S_{x,f}$ are the pore surface areas of coals, before and after ScCO$_2$ exposure, respectively; $V_{x,i}$ and $V_{x,f}$ are the pore volumes of coals, before and after ScCO$_2$ exposure, respectively; and $x$ represents the micropores or meso- and macropores of coals.

As shown in Figure 1, both $f_{S_{\text{mic}}}$ and $f_{V_{\text{mic}}}$ varied between $-20\%$ and $20\%$. Interestingly, $f_{S_{\text{mic}}}$ of coals, after ScCO$_2$ exposure, exhibited the same pattern as that of $f_{V_{\text{mic}}}$.

![Figure 1](image.png)
Changes in the micropores of coals are known to mainly stem from the coal matrix swelling, extraction and mineral dissolution and precipitation because of the exposure to ScCO₂. Among these, coal matrix swelling has been found to be closely related to $R_{o,max}$, i.e. the swelling ratio of the coal matrix decreases with increasing $R_{o,max}$ (Majewska et al., 2010; Yu et al., 2003). Furthermore, the extraction effect and mineral dissolution and precipitation effects have been found to depend upon the volatile matter yield and ash content, respectively (Zhang et al., 2013a, 2019a). Based on this, the changing amplitude of the micropore surface area ($f_{S_{mic}}$) and micropore volume ($f_{V_{mic}}$) were plotted against $R_{o,max}$. The normalised pore structure parameters, i.e. $|f_{V_{xy}}|$ (equation (3)) and $|f_{A_{xy}}|$ (equation (4)) were plotted against volatile matter yield and ash content, respectively.

$$|f_{V_{xy}}| = \frac{|f_{xy}|}{V} \times 100\%$$  \hspace{1cm} (3)

$$|f_{A_{xy}}| = \frac{|f_{xy}|}{A} \times 100\%$$  \hspace{1cm} (4)

where $V$ is the volatile matter yield, wt%; $A$ is the ash content, wt%; $|f_{V_{xy}}|$ and $|f_{A_{xy}}|$ are the volatile matter yield and ash content normalised pore structure parameter changing amplitude, %, respectively; $x$ represents the pore surface areas or volumes of coals; and $y$ represents the micropores or meso- and macropores of coals.

Figure 2(a) and (b) show the U-shaped trend between $|f_{S_{mic}}|$ and $|f_{V_{mic}}|$ of the dry coals and $R_{o,max}$. It can be observed that $|f_{S_{mic}}|$ and $|f_{V_{mic}}|$ decreased as $R_{o,max}$ increased from 0.5% to 2.0%. As $R_{o,max}$ increased further, $|f_{S_{mic}}|$ and $|f_{V_{mic}}|$ showed an inverse increase. Furthermore, the swelling ratio of the coal matrix was observed to decrease with increasing $R_{o,max}$. Thus, both the $|f_{S_{mic}}|$ and $|f_{V_{mic}}|$ of low-rank coals decreased as $R_{o,max}$ increased to approximately 2.0%. However, high-rank coals have developed micropore structure that was expected to enhance the extraction strength of ScCO₂ to promote the extraction of some small organic compounds from the micropores of coals. Therefore, $|f_{S_{mic}}|$ and $|f_{V_{mic}}|$ were observed to increase with the increasing $R_{o,max}$. Both $|f_{S_{mic}}|$ and $|f_{V_{mic}}|$ also increased significantly as the volatile matter yield and ash content increased (Figure 2(c) to (f)). In general, the effects of small organic compound extraction and mineral dissolution and precipitation increased the microporosity of coals after ScCO₂ exposure (Du et al., 2018; Zhang et al., 2013a). The above-mentioned effects depend highly upon the volatile matter yield and ash content of coals, which can account for the increasing trend shown in Figure 2(c) to (f).

**Micropore size distribution.** Apart from $S_{mic}$ and $V_{mic}$, the micropore size distribution (PSD) of coals has also been found to be influenced by ScCO₂ exposure (Kowalczyk et al., 2008; Li, 2018; Li et al., 2017; Liu et al., 2019b; Mastalerz et al., 2010; Wang et al., 2015c; Zhang et al., 2017a). The PSD of coal is usually determined from the non-local density functional theory model using CO₂ adsorption data.

The influences of ScCO₂ on the PSD of micropores of coals have been contested. Specifically, for coals, after exposure to ScCO₂ and H₂O, ScCO₂ exposure has been observed to mainly affect the micropores of coals, with the pore diameter range of 0.4–0.7 nm and 0.7–0.9 nm (Figure 3), which has been attributed to the heterogeneity of physicochemical
properties of coals (Balan and Gumrah, 2009; Gensterblum et al., 2014). It is important to note that ScCO₂ can only break the substructure in coals but has been found to be unable to break the spatial structure of coals formed by chemical cross-links (Kutchko et al., 2013; Mastalerz et al., 2010). Generally, the micropore volume has exhibited a decreasing trend after ScCO₂ exposure, when the intensity of the matrix swelling has been observed to be stronger than the other effects. Instead, the micropore volume has been found to increase

Figure 2. Relationship between $|f_{\text{Smic}}|$ ((a), (c) and (e)) and $|f_{\text{Vmic}}|$ ((b), (d) and (f)) and $R_{0,\text{max}}$ (%) ((a) and (b)), volatile matter yield ((c) and (d)) and ash content of coals ((e) and (f)).
Source: reproduced with permission from Kutchko et al., 2013; Mavhengere et al., 2015; Wang et al., 2015c; Zhang et al., 2016, 2017a.
However, for the dry coals, numerous studies have shown that ScCO₂ exposure cannot significantly change the PSD of the micropores of coals (Figure 4). Therefore, the change in the PSD of the micropores of coals has been mainly attributed to H₂O. Based on previous studies, the influences of H₂O on the physicochemical properties of coal samples have mainly included the following aspects: (1) H₂O occupies the adsorption space of CO₂ in the coal matrix, thereby weakening the CO₂ storage capacity (Ozdemir and Schroeder, 2009); (2) oxygen-containing functional groups on coal surface act as adsorption sites of CO₂ and H₂O, thus, creating competitive adsorption exists between CO₂ and H₂O (Day et al., 2008b, 2011); (3) mineral dissolution and precipitation effects increase the pore surface areas and volumes of coals; and (4) H₂O adsorbed on the coal matrix enhances the swelling ratio, thus, degrading the pore morphology of coals (Krooss et al., 2002; Zhang et al., 2014).
**Meso- and macropores**

The meso- and macropores of coals are known to often accommodate storage space for free gas and are also known to act as a seepage channel (Wang et al., 2015a). Thus, the meso- and macropores often partially determine the storage capacity and adsorption and diffusion rate of CO₂ (White et al., 2005). N₂ adsorption and desorption method has been widely adopted to determine the meso- and macropores of coals. The meso- and macropore surface areas ($S_{\text{meso/mac}}$) of coals have been calculated using the Brunauer–Emmet–Teller equation, based on the N₂ adsorption branch falling in the $P/P_0$ range of 0.05–0.30 (Brunauer et al., 1940). The total pore volume has been estimated using the Barrett–Joyner–Halenda (BJH) model, based on the desorption branch of the isotherm. Furthermore, the meso- and macro-pore PSD profiles of coals have also been estimated using the BJH model, based on the desorption isotherm (Barrett et al., 1951).

**Meso- and macropore surface area and volume.** Previous studies have reported the influences of ScCO₂ exposure on meso- and macropores of coals. Results have indicated that ScCO₂ exposure always decreased $S_{\text{meso/mac}}$ of many dry coals; however, in some cases, it increased $S_{\text{meso/mac}}$ of some of the dry coals having certain metamorphism (Zhang et al., 2013a). Contrarily, $S_{\text{meso/mac}}$ of coals has been found to significantly increase with regard to ScCO₂–H₂O–coal system (Du et al., 2018; Liu et al., 2018). Based on these studies, it has been considered that H₂O also plays an essential role in changing the meso- and macropores of coals. Particularly, H₂O can significantly enhance the mineral dissolution and precipitation ability exerted by ScCO₂, thus, increase the pore volumes and surface areas of coals. Besides, the effects of ScCO₂ on meso- and macropore structure of coals have also been associated with ScCO₂-induced matrix swelling and small organic compounds extraction (Du et al., 2018; Gathitu et al., 2009; Li et al., 2017; Liu et al., 2018; Zhang et al., 2013a).

Thus, the changing amplitude of meso- and macropore surface areas ($|f_{S_{\text{meso/mac}}}|$) and volumes ($|f_{V_{\text{meso/mac}}}|$) of coals, after ScCO₂ exposure, has been related to $R_{O,max}$, volatile matter yield and ash content, respectively. However, a discrete correlation has been found between $|f_{S_{\text{meso/mac}}}|$ and $|f_{V_{\text{meso/mac}}}|$ and $R_{O,max}$ (Figure 5(a) and (b)), indicating that the extraction and mineral dissolution and precipitation, besides the coal matrix swelling, also affect the meso- and macropore structure of coals. In general, matrix swelling has been considered to decrease the meso- and macropore space of coals. Furthermore, the extraction of small organic compound by ScCO₂ has been considered to increase the quantity of meso- and macropores of coals. However, the occurrence rule of minerals within coals is extremely complicated. Thus, effect of mineral dissolution and precipitation of ScCO₂ on meso- and macropores of various ranks of coals is complex. To summarise, the aforementioned effects of ScCO₂ exposure on meso- and macropores of coals can account for the discrete relationship shown in Figure 5(a) and (b).

Figure 5(c) to (f) indicates that both $|f_{S_{\text{meso/mac}}}|$ and $|f_{V_{\text{meso/mac}}}|$ significantly increased with increasing volatile matter yield and ash content of coals, which was identical to the trend of $|f_{S_{\text{mic}}}|$ and $|f_{V_{\text{mic}}}|$, as shown in Figure 2(c) to (f). However, both $|f_{S_{\text{meso/mac}}}|$ and $|f_{V_{\text{meso/mac}}}|$ of coals were larger than $|f_{S_{\text{mic}}}|$ and $|f_{V_{\text{mic}}}|$, which was associated with following aspects. While the meso- and macropores of coals are abundantly found in the minerals (White et al., 2005), the throat diameters of meso- and macropores have been found to be larger than that of the micropores (White et al., 2005). These two factors enhance the strength of extraction and mineral dissolution and precipitation effects of
ScCO$_2$ on the meso- and macropores of coals, thereby enlarging the changing amplitude of the meso- and macropores of coals after ScCO$_2$ exposure.

**Meso- and macropore size distribution.** As displayed in Figure 6, many studies have found that ScCO$_2$ exposure significantly changes the pores with diameters of 2–8 nm (Gathitu et al., 2009; Li et al., 2017; Zhang et al., 2017a, 2016). The micropores of coals have been found to...
determine the adsorption capacity of CH\textsubscript{4} and CO\textsubscript{2} (Cai et al., 2013; Do, 1998; Liu et al., 2019c), whereas, some studies have also shown that the initial uptake of CO\textsubscript{2} is dominated by the mesopores of coals, particularly, the pores with diameters of 4–10 nm (Li et al., 2017; Mastalerz et al., 2008). Moreover, the bonded and adsorbed water has been found to be mainly present in pores with diameters of 2–10 nm of the low-rank coals, thereby, inducing

Figure 6. Meso- and macropore size distribution of coals before and after ScCO\textsubscript{2} exposure; (a) to (c) are the coals from ScCO\textsubscript{2}–H\textsubscript{2}O–coal system and (d) to (f) are the dry coals. Source: reproduced with permission from Li, 2018; Zhang et al., 2017a.
stronger swelling effect. For high-rank coals, the mesopore walls consist of molecular orientation domains (Prinz and Littke, 2005), which contain some functional groups, such as C=O groups (Zhang et al., 2016). When CO₂ and H₂O are adsorbed on these functional groups on the coal surface, they alter the mesopores. Therefore, a noticeable change is found in the PSD of meso- and macropores with diameters of 2–8 nm of coals, after ScCO₂ exposure.

Roughness of the pore structure

The pore structure of coals is highly complex and heterogeneous, making its quantitative analysis more difficult. Fractal theory has been widely acknowledged as a useful tool to estimate the complexity of the pore structure of coals. The key parameter regarding fractal theory is the fractal dimension (D), which indicates the roughness of the pore structure. Experimental methods, including physical adsorption, SAXS and SANS can generate D of coals. Among these, physical adsorption using N₂ as a probe molecule is considered simply to study the fractal property of the coal pore surface. Based on the N₂ adsorption data, various mathematical models such as Avnir model (Avnir and Jaroniec, 1989), Frenkel–Halsey–Hill (FHH) (Li et al., 2015; Zhu et al., 2016), modified FHH (Yao et al., 2008), Neimark (Neimark et al., 1993), Sierpinski (Jiang et al., 2013) and Menger (Song et al., 2018) summarised in Table 2 can be used to calculate the D of coals.

By combining the low-temperature N₂ adsorption data with the Avnir model, D of coals, before and after ScCO₂ exposure, can be estimated, as summarised in Figure 7. It has been found that D of all the coal samples varied from 2.4 to 2.7, proving that the pore morphology of coals was irregular and fractal. D of coals was observed to vary between –0.5% and 0.5%, due to ScCO₂ exposure. Generally, with increasing D, the pore surface of coals was observed to get rougher. Instead, the pore surface of coals becomes smoother (Gathitu et al., 2009; Wang et al., 2015c; Zhang et al., 2013a, 2016, 2017a).

### Table 2. Various fractal models.

| Model       | Form                                                                 | Description                                                                 | References         |
|-------------|----------------------------------------------------------------------|----------------------------------------------------------------------------|--------------------|
| Avnir       | \[\frac{V}{V_m} = K[\ln(P_0/P)]^{-r}\] \[D = 3 - r\]               | Good linearity only with relative pressure \(P/P_0\) < 0.5                  | Avnir and Jaroniec, 1989 |
| FHH         | \[\ln V = K\ln(\ln(P_0/P)) + C\] \[D = K + 3\]                     | Applicable to describe heterogeneous pore with 8–217 nm in-situ coal       | Zhu et al., 2016   |
| Modified FHH| \[\frac{V}{V_m} = K[\ln(P_0/ P)]A\] \[D = 3 + A\]                 | Applicable to \(P/P_0\) between 0 and 0.5                                  | Yao et al., 2008   |
| Neimark     | \[\lg S_{p/p_0} = A\lg r + \text{const}\] \[D = 2 - A\]           | Applicable to \(P/P_0\) between 0 and 0.5                                  | Zhang et al., 2016 |
| Menger      | \[D = \{\ln[\frac{dV(r)}{dr}] - \ln x\}/\ln P(r) + 4\]              | Not applicable to describe heterogeneities of pores                       | Song et al., 2018  |
| Sierpinski  | \[V = \alpha(P - P_c)3D\]                                          | Applicable to study fractal characteristics of coal nanopores              | Clarkson et al., 2013 |
The fractal theoretic system consists of single-fractal theory and multi-fractal theory. The single-fractal model is known to only generate apparent information of the pore structure of coals (Wang et al., 2015d). However, multi-fractal theory can be used to divide a fractal material into many sub-regions with different degrees of singularity. The analysis of the fractal features of different sub-regions can reveal more fractal information about the pore structure of coals, including capacity dimension ($D_0$), information dimension (Shannon entropy) ($D_1$), correlation dimension ($D_2$) and correlation parameters of the pore unit, within different pore sizes ($H$). Thus, future investigation on multi-fractal can gain more information regarding the effects of ScCO$_2$ on the pore morphology of coals.

Long-term ScCO$_2$ exposure dependence of the pore morphology of coals

CO$_2$ geologic sequestration in the coal seams is a long-term process. It can be observed from Table 1 that very few studies have investigated the ScCO$_2$ exposure dependence of the pore morphology of coals under relatively longer time scale (120–4320 h). However, numerous studies have carried out investigations under short time scale (≤72 h). Therefore, the change in the pore morphology of coals, due to ScCO$_2$ exposure, during longer time scale has gained interest in recent years. Guo et al. (2018) examined the interaction between ScCO$_2$, H$_2$O and coals for 5–6 months and found that the average pore diameter, porosity and microfracture of coals increased due to dissolution of calcite and dolomite. Particularly, $S_{\text{meso/mac}}$ and $V_{\text{meso/mac}}$ of all the coal samples were observed to increase by approximately 30–73% and 40–54%, respectively. In addition, Xiao et al. (2009) also demonstrated the positive effect of mineral dissolution on the porosity of the reservoirs. They adopted the reactive transport modelling to study the spatial and temporal evolution of the injected CO$_2$ and associated gas–fluid–rock interactions, and predicted that calcite dissolution can increase the porosity of carbonate reservoirs containing the formation water from 30% to 41% in 10,000 years.
It should be noted that H₂O also plays an essential role in long-term interaction between ScCO₂ and coals. Kutchko et al. (2013) exposed two dry unconfined cores (L × W × H: 25.4 × 25.4 × 25.4 mm) of the bituminous coals to ScCO₂ (15.3 MPa and 55°C) for 104 days. Results from both field-emission SEM and N₂/CO₂ adsorption indicated that no significant changes were observed in the pore morphology of all the coal samples. Furthermore, Mavhengere et al. (2015) studied the pore structure characteristics of a vitrinite-rich dry coal after exposure to ScCO₂ (12.5 MPa and 35°C) for six months and found that ScCO₂ significantly decreased the surface area and number of micropores of the coal sample. They attributed the decreasing pore structure parameters to vitrinite swelling induced by CO₂. In conclusion, the existing studies show that long-term ScCO₂ exposure can enhance the porosity of coals via mineral dissolution with the aid of H₂O. Under other conditions, long-term exposure can decrease or barely change the porosity of coals.

It is worth noting that the coal matrix swelling, extraction and mineral dissolution and precipitation associated with ScCO₂ exposure are very slow. Thus, the sole experimental method cannot reveal the real impact of long-term ScCO₂ exposure on the porosity of coals. Instead, the combination of physical experiments and numerical simulations is recommended to address this issue. Specifically, the numerical simulations, such as Reactive Transport Modelling (Pruess et al., 2001; Xiao et al., 2009), are a promising way to predict the changes in porosity and permeability of coals due to mineral dissolution and precipitation associated with long-term CO₂ sequestration, as well as the influence of mineral heterogeneity of coal reservoirs on CO₂ injectivity and storage security.

Mechanism of ScCO₂ on the pore morphology of coals

Change in the pore structure of coals, after ScCO₂ exposure, mainly arises due to multiple effects, including matrix swelling (Figure 8(a)) (Wang et al., 2015c), small organic compounds extraction (Figure 8(b)) and mineral dissolution and precipitation (Figure 8(c)).

Matrix swelling

Coal matrix has been found to not only adsorb the injected ScCO₂, but also dissolve it, thus, inducing coal matrix swelling (Cai et al., 2018). It has been reported that coal matrix swelling can compress the cleat space of the coal seams, thereby, reducing the permeability of the coal seams. Thus, coal matrix swelling adversely affects the migration of CO₂ and CH₄ within the target coal seams.

Studies have shown that coal matrix swelling induced by ScCO₂ reduces the pore surface area and volume of coals (Day et al., 2011; Karacan, 2003; Li et al., 2012). Coal matrix swelling has been found to be associated with the fluid type and metamorphic degree of coals (Wang et al., 2015b). Under same operating temperature and pressure, the ratio of coal matrix swelling has been found to decrease in the order of CO₂ > CH₄ > N₂ (Mazzotti et al., 2009; Pini et al., 2009; Van Bergen et al., 2011), which was found to be consistent with the order of adsorption strength among these fluids. Helium is a non-adsorbing gas (Mohammad et al., 2009), thus, the coal matrix swelling induced by He is almost negligible. These information suggests that injecting mixed gas, such as CO₂ and N₂, instead of pure CO₂, can mitigate the significant decreasing permeability of the coals seams due to coal matrix swelling induced by pure CO₂. Furthermore, many studies have confirmed that the swelling ratio of the coal matrix increases with decreasing Rₜo,max (Day et al., 2012; Ferreiro
et al., 2010). Thus, a change in the pore structure of low-rank coals is more pronounced than that of high-rank coals.

The reversibility of the coal matrix swelling has been a pending subject of analysis. Based on the pore structure analysis or ATR-FTIR, some studies have considered that ScCO$_2$-induced swelling of coal matrix is an irreversible process (Goodman et al., 2005; Zhang et al., 2013a). Contrarily, other studies have used the optical method or tensometric measurement to find that the process of coal matrix swelling is completely reversible (Cegielska-Stefańska and Czapliński, 1993; Day et al., 2008a). In addition, there has never been a consensus among the researchers about the mechanism of coal matrix swelling. It has been reported that ScCO$_2$ dissolved in the coal matrix can work as a plasticiser, thereby, creating additional free volume of coals, inducing molecular motion and rearranging the

Figure 8. Schematic diagram of effects of ScCO$_2$ on coals: (a) matrix swelling, (b) extraction effect and (c) mineral dissolution.
coal physical structure (Goodman et al., 2005; Larsen et al., 1997). However, the coal matrix swelling has also been explained by the chemical interactions between ScCO₂ and coals through hydrogen bond and/or electron transfer, thus, reducing the crosslink degree of macromolecular structure of coals (Walker et al., 1988). The disagreement regarding the reversibility and mechanism of coal matrix swelling induced by ScCO₂ is significantly close due to the complexity and heterogeneity of the coal structure. Hence, a deep resolution of the coal structure can help in clarifying the mechanism of coal matrix swelling induced by ScCO₂. First, various methods such as nuclear magnetic resonance, laser Raman spectroscopy, FTIR, XRD, high-resolution transmission electron microscopy, are recommended to determine the aromaticity, aliphaticity, functional groups and species of the main elements of coals. Furthermore, due to the complex and heterogeneous structure of coals, the experimental methods cannot fully elucidate the coal structure. Thus, it is necessary to apply the tools based on quantum chemistry theory, such as VASP, Gaussian, DMol and PWSCF to calculate and optimise the coal macromolecule structure. Next, the experimental and theoretical results need to be combined with the exiting coal models such as Heredy and Wender, Given, Wiser, Shinn and Hirsch to accurately study the coal structure for efficient examination of the coal matrix swelling process. Finally, advanced imaging technology, such as atomic force microscope, can be used since it provides the visual information of the intermolecular hydrogen bond (Zhang et al., 2013b). Usage of these methods can also help in further studying the mechanism of ScCO₂-induced coal matrix swelling.

**Extraction effect**

Small organic compounds with molecular weight < 500 amu, have been found to disperse within the macromolecular structure of coals (Mathews and Chaffee, 2012). The injected CO₂ has been observed to always exist as a supercritical fluid in the coal reservoirs (Orr, 2009). It is known to have excellent dissolution and mass transfer ability, which can aid in the extraction and mobilisation of small organic compounds from the coal matrix. Thus, the extraction effect of CO₂ exposure can change the pore structure of coals.

For \( R_{o,\text{max}} \geq 1.5\% \), the amplitude of the micropore parameter of coals has been observed to change due to the extraction effect of ScCO₂; they have been observed to increase with increasing \( R_{o,\text{max}} \) (Figure 2(b)). This was typically attributed to the developed pore structure of high-rank coals, which promoted the migration of ScCO₂ within coals and finally enhanced the extraction process (Liu et al., 2010). In addition, H₂O prefers oxygen-containing functional groups on coal surfaces as adsorption sites, thereby preventing CO₂ from entering coal pores. Hence, H₂O can weaken the extraction effect of ScCO₂, particularly in low-rank coals (Kolak et al., 2015). Furthermore, ScCO₂ can only extract trace amounts of small organic compounds. Thus, ScCO₂ has a minor impact on meso- and macropores (Kutchko et al., 2013). ScCO₂ extraction via extraction A and B has been reported to have two adverse effects on the pore structure of coals, as illustrated in Figure 8(b) (Zhang et al., 2019b). On the one hand, if ScCO₂ exhibits only slight extractability to some organic compounds in coals, small organic compounds may block the pores and further reduce coal pore space. On the other hand, the pore space of coals will be enlarged if some organic compounds are extracted and escape from the pore throat.

The small organic compounds extracted by ScCO₂ have been found to comprise biologically toxic aliphatic and polycyclic aromatic hydrocarbons (Kolak and Burruss, 2006; Kolak et al., 2015; Zhang et al., 2013a) that can be mobilised by ScCO₂ and enter the
groundwater system. Thus, actual CO₂-ECBM should focus on environmental safety and health issues related to CO₂ sequestration. Furthermore, the temperature and pressure dependencies of the composition of organic compounds extracted from the coal matrix by ScCO₂ and their effects on changing pore structure of coals after ScCO₂ exposure needs to be studied further.

**Mineral dissolution and precipitation effects**

The actual coal seams have been always found to contain water (Massarotto et al., 2010; Tong et al., 2019), which has been considered to likely react with ScCO₂ and form carbonic acid (H₂CO₃). Thus, the multiple complex chemical reactions summarised in Table 3 have been found to occur between some types of minerals contained in coals and H₂CO₃. The minerals of coals typically undergo the following three types of interactions, after CO₂ is injected into the target coal seams, i.e. dissolution of minerals (Credoz et al., 2011; Hedges et al., 2007), transformation of clay minerals (Farquhar et al., 2015) and formation of new minerals (Liu et al., 2015). H₂CO₃ has been found to leach out and dissolve some minerals in coals, especially, minerals filled in the pores and fractures, such as carbonate and aluminosilicate minerals (Black et al., 2015; Dawson et al., 2015). The dissolution of minerals has been observed to increase the pores and fractures of coals and generate pores in the minerals, which can increase the volume and connectivity of meso- and macropores (Chen et al., 2017; Liu et al., 2018). Thus, the dissolution of minerals helps in increasing the CO₂ adsorption capacity of the target coal seams. Under the conditions of temperature being 60°C and pH being 4, the reaction rates of calcite and dolomite have been found to be 10⁻⁵–10⁻³ and 10⁻⁷–10⁻⁵ mol·m⁻²·s⁻¹, respectively (Sonnenthale and Spyoher, 2001). ScCO₂–H₂O has been found to exhibit strongest reactivity to calcite, followed by dolomite, chlorite and albite, respectively. However, such reactions have not been found to be significant for illite, quartz and kaolinite (Du et al., 2018). Figure 9 shows that calcite on the coal surface dissolved and almost disappeared (Figure 9(b)) after ScCO₂ exposure. The inner calcite then generated some cone pores (Figure 9(d)) and newly dissolved crystal faces (Figure 9(f)). However, the dissolution of dolomite only generated some rhomboid pores (Figure 9(d)). It has been confirmed that dolomite is more difficult to dissolve in ScCO₂ than calcite. Inorganic compounds, such as silicate and carbonate, have been observed to have high polarity of metal ions (Iwai et al., 2000), which prevent the inorganic compounds of dry coals from being dissolved in ScCO₂ (Iwai et al., 2000; Wang et al., 2015c). However, inorganic minerals have been found to dissolve in ScCO₂–H₂O–coal system due to exchange of inorganic minerals with H⁺ (Du et al., 2018). Thus, the pore structure of coals has been considered to get further enhanced (Li, 2018; Liu et al., 2018). Therefore, injecting CO₂, H₂S

### Table 3. Chemical reactions of various minerals in carbonic acid.

| Reaction | Mineral | Equation |
|----------|---------|----------|
| Dissolution | Calcite | CO₂+H₂O+CaCO₃=Ca(HCO₃)₂ |
| Dolomite | CaMg(CO₃)₂+2CO₂+2H₂O=Ca(HCO₃)₂+Mg(HCO₃)₂ |
| Precipitation | Chlorite | [Fe/Mg]₅Al₂Si₃O₁₀(OH)₈+5CaCO₃+5CO₂=5Ca[Fe/Mg](CO₃)₂+Al₂Si₂O₅(OH)₄+SiO₂+2H₂O |
| | Potassium Feldspar | 2KAlSi₃O₈+2CO₂+3H₂O=2KHCO₃+4SiO₂+Al₂Si₂H₄O₉ |

Source: reproduced with permission from Guo et al., 2018.
and SO$_2$ fluid is considered to enhance the intensity of dissolution effect, thereby increasing the pore volume of coals and to mitigate the hazardous gaseous pollutants emitted into the atmosphere.

With respect to secondary minerals, they are not considered to be precipitated, when the saturation index (SI), is less than zero. SI of aluminium hydroxide mineral ($\text{Al(OH)}_3$) has been found to be the highest among the minerals contained in coals (Hayashi et al., 1991; Tarkowski et al., 2011), indicating that $\text{Al(OH)}_3$ is most likely to form secondary minerals in coals. In ScCO$_2$–H$_2$O–coal system, $\text{Al(OH)}_3$ has been found to readily react with H$^+$, resulting in the concentration of Al$^{3+}$ around the minerals, which subsequently combine.

**Figure 9.** Changes in carbonate before and after ScCO$_2$ exposure. Source: reproduced with permission from Du et al., 2018.
with the H₄SiO₄ and Fe ions. The new aluminium silicate minerals are generated due to the low solubility of aluminium silicate. Moreover, the newly formed aluminium silicate minerals comprise a large number of nanoscale pores with surface area greater than that of mineral Al(OH)₃. Thus, the newly formed aluminium silicate minerals can increase the storage capacity of CO₂ within the target coal seams.

The minerals in coals have been found to comprise primary and secondary minerals, with mass fractions of 1–2%, and < 10%, respectively (Xie, 2012). The type of identifiable inorganic minerals has been observed to reach up to 316 (Yu et al., 2015). Thus, the occurrence rule for the inorganic minerals in coals is extremely complex, which makes further exploration of the interaction mechanism between ScCO₂ exposure and the minerals in coals more difficult. Moreover, with regard to CO₂-ECBM, sealing of the roof and floor in the coal seams is critical for CO₂ storage in geologic time scale. However, very few the studies have examined the reactions between ScCO₂ and the minerals in the roof and floor, which should be studied in future.

Conclusions

CO₂-ECBM is a viable option for geological storage of CO₂. The stored CO₂ is known as a supercritical fluid (ScCO₂), with great potential to change the pore structure of coals. Thus, the influences of ScCO₂ on the pore morphology of various rank coals were examined in this study. The main conclusions derived from this study are summarised below.

For the dry coals, the Sₘic and Vₘic of coals, due to ScCO₂ exposure, varied between −20% and 20%. ScCO₂ exposure was not observed to significantly change the PSD of the dry coals. However, the meso- and macropores, with the diameters of 2–8 nm of the dry coals evidently changed. For ScCO₂–H₂O–coal system, ScCO₂ exposure mainly affected the pores of coals with diameter ranges of 0.4–0.7, 0.7–0.9 and 2–8 nm. The fractal dimension of the coal pore surface was observed to vary between −0.5% and 0.5%. Moreover, it was considered that long-term SCCO₂ exposure could enhance the porosity of coals via mineral dissolution, with the aid of H₂O. Otherwise, the long-term exposure could decrease or scarcely change the porosity of coals.

The changes in the pore surface of coals, after ScCO₂ exposure, were mainly associated with the coal matrix swelling, small organic compounds extraction and mineral dissolution and precipitation. It has been evidently found that the ScCO₂-induced matrix swelling decreased the pore surface area and volume of the coal matrix, and further compressed the cleat space of the coal seams. The extraction effect of ScCO₂ could extract or mobilise small organic compounds within the coal matrix, thus, increasing or decreasing the pore surface area and volume of coals. Generally, the extraction had a significant impact on the micropores than the meso- and macropores of coals. Finally, the dissolution and precipitation increased the pore surface area and volume of coals.

To clarify the influences of ScCO₂ on the pore structure of coals during the implementation of CO₂-ECBM, following studies should be carried out. First, multiple advanced characterisation methods, quantum chemistry simulation as well as existing coal models need to be combined to explore ScCO₂–induced coal matrix swelling. Furthermore, temperature and pressure dependence of the composition and concentration of the organic compounds extracted from the coal matrix should be studied, and their effects on changing pore structure of coals after ScCO₂ exposure should be examined. Finally, combination of physical experiments and numerical simulations are recommended to predict the changes in
porosity and permeability of coals due to mineral dissolution and precipitation associated with long-term CO\textsubscript{2} sequestration, as well as the influence of mineral heterogeneity of coal reservoirs on CO\textsubscript{2} injectivity and storage security.

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