Supercritical CO₂ Interaction Induced Pore Morphology Alterations of Various Ranked Coals: A Comparative Analysis Using Corrected Mercury Intrusion Porosimetry and Low-Pressure N₂ Gas Adsorption

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ABSTRACT: Enhanced coal bed methane (ECBM) recovery via CO₂ geological storage (CGS) involves CO₂ adsorption and CH₄ desorption from coal pores, gas diffusion, and flow through coal matrix and cleats, which are closely related to coal pore morphology. To characterize and quantify the alterations of pore morphology of different ranked coals treated by supercritical CO₂ (ScCO₂), CGS was simulated with a custom-built high-pressure ScCO₂ geochemical reactor at 10 MPa and 35 °C for sub-bituminous coal, bituminous coal, and anthracite, respectively. The bituminous coal was collected from a ScCO₂-rich reservoir to examine the effect of second exposure to ScCO₂ on pore morphology. Mercury intrusion porosimetry (MIP) after data correction using the Tait equation (TE) and low-pressure N₂ gas adsorption (LPN₂GA) were employed. The decrease of coal matrix compressibility and increase of pore volume compressibility indicate that sub-bituminous coal becomes more resistant to microfracture closure and pore shrinkage after ScCO₂ treatment. Both the thermodynamics fractal model after MIP data correction and Frenkel–Halsey–Hill (FHH) model, which are strongly scale-dependent and meaningful from a geometric viewpoint, reveal a downward trend of the irregularity and heterogeneity of pore structures for sub-bituminous coal. The effects of hydrocarbon mobilization and inorganic matter dissolution by ScCO₂ play an important role in pore size distribution (PSD), pore volume (PV), and pore shape (PS) alterations, whereas these changes are quite small for bituminous coal. The above observed alterations of sub-bituminous coal are all positive, such as closed pore reopening, pore volume enlargement, pore roughness decline, pore connectivity enhancement, and gas desorption improvement, which makes sub-bituminous coal a desired option for CO₂-ECBM recovery.

1. INTRODUCTION

CO₂ sequestration has been identified as the most viable and effective option to mitigate the adverse effect of greenhouse gases on global warming.¹ Deeply depleted or unmineable coal seams could provide an approach for storing anthropogenic CO₂. The presence of matrix and cleat within coal structure creates favorable conditions for gas adsorption, desorption, diffusion, and flow.² The higher affinity of coal substance toward CO₂ than CH₄ and the denser state of CO₂ (supercritical state) guarantee the long-term isolation of CO₂.³,⁴ The injected CO₂ could displace the original adsorbed CH₄ and be sealed perpetually while enhancing the CH₄ recovery (referred to as CO₂-enhanced coal bed methane, ECBM), thereby offsetting the cost of CO₂ sequestration and providing additional clean energy for sustainable development of society.⁵,⁶ As the critical point of CO₂ is 30.97 °C and 7.38 MPa, in most cases, CO₂ is likely to be present in a supercritical state under the conditions of high reservoir temperature and pressure after being injected into deep coal seams.⁷,⁸ Compared with subcritical CO₂ (SubCO₂), many properties of supercritical CO₂ (ScCO₂), such as density, viscosity, diffusivity, and permittivity, change significantly. In addition, ScCO₂ exhibits higher adsorption capacity, greater dissolution, extraction, and expansion effect on coal than SubCO₂.⁹,¹⁰

The injected ScCO₂ will react with the organic and inorganic matters in coal; thus, considerable efforts have been devoted to the interaction between ScCO₂ and coal. Hitherto, researchers mainly focused on the following related aspects influenced by ScCO₂ injection: CO₂ adsorption,¹¹,¹² pore structure,¹³,¹⁴ permeability evolution,¹⁵ mechanical property,¹⁶,¹⁷,¹⁸,¹⁹ and soluble matter and elements in coal.²⁰,²¹ There are a number of techniques that could be used for characterizing coal pore morphology: field-emission scanning electron microscopy (FE-
SEM, NMR, small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS), γ-ray attenuation, X-ray computed tomography (CT), mercury intrusion porosimetry (MIP), low-pressure N₂ gas adsorption (LPN₂GA), etc. Among these methods, MIP and LPN₂GA are the most widely used methods and are often combined to depict pore morphology of coal. MIP is often considered as a conventional, relatively fast, and straightforward technique to interpret pore structure. However, sample compression during the mercury intrusion process might lead to misinterpretation of real pores. It is generally accepted that coal behaves like a viscoelastic gel rather than a rigid pore structure and the mechanical breaking of coal occurs at high mercury intrusion pressures. Therefore, prior to experimental data processing, the effect of coal matrix compression must be carefully considered and corrected. Plenty of investigations on the coal matrix compressibility and MIP data correction have emerged since the last few decades. Li et al. pointed out that coal compressibility has a significant effect on MIP data when the pressure is greater than 20 MPa. Song et al. discovered that coal matrix compressibility has a huge effect on the adsorption pore data and the matrix compression volumes basically equal to the pore volume of adsorption pores for tectonically deformed coals. Therefore, only the corrected MIP data should be used to unambiguously study the pore structure. To date, the impact of coal matrix compression on pore throat size distribution and pore volume during mercury intrusion process before and after ScCO₂ treatment has not been studied quantitatively in the literature.

One of the key processes that affect CO₂-ECBM recovery is the flow of gases through altered dimensions of cleats, which largely depends on cleat compressibility. There is a dynamic response of coal during CO₂ sequestration, and the volumetric changes can be estimated by coal matrix compressibility. For a given pore pressure variation, compressibility introduces the contribution of coal deformation to reservoir permeability and CBM production. It is well known that a coal bulk body consists of matrix volume and pore volume, which correspond to confining pressure and pore pressure. Thus, two different kinds of compressibilities (coal matrix compressibility and pore volume compressibility) have extensively been studied and they will keep attracting significant attention as CBM production continues to increase. Pore compressibility denotes the excess fluid volume that can be stored in or flow through the pore space as a result of pore pressure increase; therefore, pore compressibility has been considered as an important parameter that could influence the overall gas transportation system. The commonly experimental methods for determining compressibility include MIP, NMR, and uniaxial or triaxial stress experiments. Hitherto, considerable experiments on compressibility of oil, gas, and coal reservoirs have been conducted but there are quite few research works regarding the variation of compressibility before and after ScCO₂ treatment.

The influences of ScCO₂ on coal are not only in physical and chemical aspects but also in pore irregularity and heterogeneity. Fractal theory has been extensively used to characterize fragmented objects with no characteristic length. It is an important parameter to quantitatively study gas flow properties and gas storage capacity. It could provide an intrinsic, quantitative measurement to uncover the textural evolution during the process of ScCO₂ treatment.

Using MIP data, many scholars employed the Menger sponge model to obtain three fractal dimensions (D₀, D₂, and D₃) of coal before and after ScCO₂ treatment under different pressure ranges, which could be categorized as three different stages of mercury intrusion (interparticle filling, intrapore filling, and matrix compression). This has been accompanied by much debate, as most calculation results of D₂ from the above literature were in the range of 2.9—3.1. These fractal dimension values are quite suspicious from the perspective of Euclidean geometry. In addition, to the best of our knowledge, there is simply no way of separating the effects of intraparticle filling and coal compression using only MIP data. Therefore, more reliable models based on corrected MIP data are required to calculate fractal dimension so that the roughness of coal before and after ScCO₂ treatment can be presented clearly and precisely.

In this study, we carefully examined the effect of ScCO₂ on coal matrix compressibility and pore compressibility using original MIP data. Then, we replotted the MIP curves to obtain true mercury intrusion volumes for all samples on the basis of the Tait equation. Afterward, combined with the LPN₂GA method, we provided a richer picture of the changes of fractal dimension, pore volume, pore size distribution (PSD), and pore shape before and after ScCO₂ treatment comprehensively and systematically. Uniquely, the influence of a second exposure to ScCO₂ on coal was also examined by selecting a sample from ScCO₂-rich reservoirs. This study aims to provide a more precise and rational approach to understand the interactions between ScCO₂ and coal, which could illuminate the theoretical effectiveness of CO₂-ECBM.

2. RESULTS AND DISCUSSION

2.1. Coal Matrix Compressibility and Pore Volume Compressibility. To calculate the coal matrix compressibility (kₘ) with eq 4, the first step is to determine the coal compression interval. It was investigated that BJH method will underestimate the pore size by ~20—30% for pore diameter ~<10 nm. After comparing different density functional theory (DFT) models, we selected the N₃ adsorption branch data using the quenched solid density functional theory (QSDFT) model and assumed the pore shape to be slit and cylindrical. This model has the smallest fitting error (<0.5%) among other DFT models. Therefore, d₁ and d₂ were determined to be 6 and 33 nm, with mercury pressure ranging from 41 to 226 MPa. Although data from the whole matrix compression range is required to calculate kₘ, since the fitting results of ΔVₘ/ΔP of this range are excellent (greater than 0.99), a portion of data (41—226 MPa) could represent the overall situation. Table 1 gives the calculation parameters of kₘ and kₚ. Figure 1 displays the tendency of pore volume compressibility with pressure.

It is found that kₘ of coal DL and HSW (Rₘ,max = 0.69—0.93%) is between (1.884—2.699) × 10⁻⁴ MPa⁻¹, which is consistent with the results of Guo et al. ((2.01—2.74) × 10⁻⁴ MPa⁻¹, Rₘ,max = 0.65—0.88%) and Cai et al. ((1.55—2.37) × 10⁻⁴ MPa⁻¹, Rₘ,max = 0.54—1.19%). However, kₘ of coal WLH ((1.108—1.507) × 10⁻⁴ MPa⁻¹, Rₘ,max = 2.74%) is slightly lower than that of coal DL and HSW. The reason is that the metamorphic grade of coal WLH is generally high and it undergoes higher geotemperature, higher geostress, and longer burial time. Thus, the compaction effect is relatively strong, which makes coal WLH harder to compress. Comparing the three sets of coal before and after ScCO₂ treatment, it can be seen that kₘ of coal HSW and WLH after ScCO₂ treatment increases by 36.9 and 36.0%, respectively, whereas kₘ of coal DL after ScCO₂ treatment decreases by 6.8%. By determining the coal matrix
compressibility of different coal ranks, Cai et al. have found that micropores can effectively resist coal matrix compressibility and this conclusion is consistent with ours, as shown in Figure 2. Moreover, we have also noticed that mesopores are also acting in the same role in effecting \( k_c \) as micropores. Therefore, it is concluded that the volumes of micropores and mesopores are inversely proportional to \( k_c \). The decrease of \( k_c \) indicates that the sub-bituminous coal becomes more difficult to compress after ScCO\(_2\) treatment, whereas the opposite trend is observed for bituminous coal and anthracite.

The \( k_c \) calculated by eq 5 ranges from 0.00247 to 0.02502 MPa\(^{-1}\), corresponding to the pressure range from 5.4 to 223.8 MPa. Similar results were also obtained by Li et al.\(^{46}\) who calculated \( k_c \) ranging from 0.00025 to 0.03779 MPa\(^{-1}\) with a pressure range of 10–200 MPa and a temperature range of 25–600 °C, respectively. Figure 1 shows that \( k_c \) decreases with the pressure increasing, and \( k_c \) of coal DL is higher than that of other samples. The reason lies in the fact that the onset pressure of coal DL, which denotes the dominance of coal compression over pore filling, is lower than that of other samples; thus, the structure of the lower rank sub-bituminous coal is more susceptible to being modified during MIP. Comparing Figure 1 with Figure 2, we have noticed that the pore compressibility tendency is very contrary to that of pore volume, which is easy to understand from the definition of \( k_c \). As coal DL before ScCO\(_2\),

| Sample     | \( V_P \) (cm\(^3\)/g) | \( k_c \times 10^{-4} \) MPa\(^{-1}\) | \( \Delta V_P \times 10^{-4} \) cm\(^3\)/g/MPa | \( \Delta V_P \times 10^{-2} \) cm\(^3\)/g/MPa\(^{-1}\) |
|------------|------------------------|---------------------------------------|---------------------------------------------|---------------------------------------------|
| coal DL    | untreated              | 1.764 (\( R^2 = 0.999 \))             | 0.035                                       | 1.729                                       |
|            | treated                | 1.479 (\( R^2 = 0.998 \))             | 0.055                                       | 1.424                                       |
| coal HSW   | untreated              | 1.775 (\( R^2 = 0.998 \))             | 0.233                                       | 1.542                                       |
|            | treated                | 1.816 (\( R^2 = 0.997 \))             | 0.229                                       | 1.587                                       |
| coal WLH   | untreated              | 0.929 (\( R^2 = 0.997 \))             | 0.071                                       | 0.853                                       |
|            | treated                | 0.921 (\( R^2 = 0.995 \))             | 0.066                                       | 0.855                                       |

Figure 1. Relationship between pore volume compressibility and pressure.

Figure 2. Micro-, meso-, and macropore volumes of the six samples.
treatment contains hydrocarbons and inorganic matter, the compositions after ScCO₂ treatment change to a great extent, which results in the huge difference of $k_\text{p}$ at pressure ranges of 0–50 MPa. However, for anthracite coal WLH and coal HSW that has been exposed to ScCO₂ more than once, the coal composition remains unchanged. Therefore, only a slight difference of $k_\text{p}$ is observed.

To support this deduction, further characterization of both untreated and ScCO₂-treated DL coal samples was conducted by means of an infrared spectrum analysis using the Nicolet 6700 Fourier-transform infrared (FT-IR) spectrometer (Thermo Fisher Scientific, United States) at a resolution of 2 cm⁻¹ and the spectral region of 4000–650 cm⁻¹. As shown in Figure 3, peaks with major changes, such as −OH stretching vibration, aliphatic CH₃ asymmetric stretching vibration, aliphatic CH₃ symmetric stretching vibration, aromatic nucleus (C=C), aliphatic CH₂ and CH₃ bending vibration, and phenolic deformation C−O−C (stretching) weaken significantly. Heek proposed a three-dimensional macromolecular structure network of coal, which is composed of condensed aromatic and hydroaromatic compounds.⁶⁷ Therefore, ScCO₂ has the potential to extract and mobilize the aliphatic, aromatic, and naphthenic hydrocarbons or oxy-compounds. Moreover, Liu et al. discovered that the concentration of some carbonate minerals decreased in a treated coal sample compared with the untreated one and confirmed that many isolated pores blocked by minerals became continuous.³⁰

2.2. MIP Data Correction. To obtain reliable MIP data, we used Tait equation (TE) to correct the original mercury intrusion volume overestimated by coal compression, as shown in Figure 4. Obviously, the corrected data for the ScCO₂-treated and untreated coals are much lower than the original data, validating the compressible nature of coal. This result agrees well with previous findings.⁵⁵,³⁶,⁴⁸ The original intrusion volume gradually deviates from the true pore volume with the decrease of pore diameter.  

For pores >350 μm, the differences of pores’ proportion in the total pore volume between the uncorrected and corrected data are quite small. For pores <350 μm, the cumulative mercury intrusion curves begin to separate and the differences get larger as the pressure increases, indicating that coal matrix compressibility correction has a significant effect on pore data (<350 μm). The pore throat size distribution before and after data correction shows an identical variation trend, and the only difference is the pore volume of each corresponding pore diameter. As shown in Figure S, compared with the uncorrected data, the corrected pore volume in the range of 10–300 nm decreased by 79.31 and 78.35% for untreated and treated coal DL, followed by coal HSW (61.86 and 72.60%) and coal WLH (66.44 and 74.53%), respectively, indicating that matrix compression volumes contributed more than half of the recorded mercury intrusion volumes. Also, it could be concluded that pore volume from MIP after TE correction is much closer to that of the BJH model from N₂ adsorption despite the discrepancy existing. The differences are due to the fact that real pore systems have sophisticated arrangements of varying sized pores and connecting channels and methods of MIP and N₂ adsorption are conceptually different in the first place. Mercury intrusion yields information about the largest entrance to a pore rather than the actual “pore size”: a large pore body to which access from the surface could be gained only through a narrow pore throat will be counted as many small pores, whereas N₂ adsorption method explores the pore body.²⁹ This conclusion could provide enlightenment to the joint use of MIP and N₂ adsorption methods to depict pore structure in the full pore diameter range.

2.3. Surface Fractal Dimensions Analyses. 2.3.1. Thermodynamics Model. The surface fractal dimension evolution in the process of ScCO₂ treatment from the perspective of thermodynamics is shown in Figures 6 and 7. The relevant fractal theories based on Neimark and Zhang’s methods could be found elsewhere.⁶⁰,⁵¹ The first observation of the curves is the necessity of correcting MIP data. Using Neimark’s method, all D values calculated by the uncorrected MIP data correction exceed 3, which was meaningless from a geometric point of view and is attributed to coal matrix compression or pore wall collapse under high mercury pressure. Zhang’s method also exhibits a higher D value for uncorrected data than the corrected ones, some of which are bigger than 3 (coal DL). Although the results of coal HSW and WLH before data correction are within the range of fractal geometry, the D values were very close to 3 and doubtful.

The second observation of the regressed fractal dimension is that D values calculated from corrected data using both methods are strongly scale-dependent. The average D values in the whole pore diameter range are not reasonable and dependable, and they cannot characterize the real pore structure. For pore diameters less than 10 nm, the fractal features do not exist on any coal samples ($D > 3$) whether the data are corrected or not, which indicates that mesopore structures could hardly be detected accurately by MIP. In fact, regardless of the scaling relationship adopted, all bold D values in Figures 6 and 7, which are reasonable and dependable, exhibit a declining trend after the ScCO₂ treatment in the same pore diameter range (except coal DL using Neimark’s method).

2.3.2. Frenkel–Halsey–Hill (FHH) Fractal Analysis. The results from the LPN₆GA FHH fractal analysis are displayed in Figure 8 and Table 2.⁵² It was revealed that there are two to three linear segments from low to high relative pressure on the plots of $\log(V/V_m) - \log(\log(P_0/P))$ for both adsorption and desorption branches. The regression analysis uncovers the good linear relation where the average $R^2$ is greater than 0.99 for all samples. Theoretically, the calculation of $D$ from low relative pressure should be “$3(1 + A)$.” However, the calculated $D$ is smaller than 2 for most of the samples, which makes $D$ unreasonable and meaningless. Although the Van der Waals and capillary force are co-instantaneous during the N₂ adsorption...
experiment, the capillary condensation effect might be dominant over the entire pressure range. The real surface fractal dimension is between $3(1 + A)$ and $3 + A$, indicating that the calculated $D$ in Table 2 that is based on the pure capillary condensation effect might be overestimated. This study focused on a comparative analysis; thus, the overestimation effect could be ignored.

Comparing Figure 8a,c,e with b,d,f, there is a transition region 3 ($0.4 < P/P_0 < 0.5$) connecting region 1 and region 2 for the desorption branch data, the $D$ of which is smaller than 2, whereas for the adsorption branch, the calculated $D$ is illogical when $P/P_0 < 0.01$ (region 3 for coal DL, region 2 for coal HSW and WLH); thus, these meaningless $D$ values are not be listed in Table 2. The linear fitting regime and $D$ are different by adsorption and desorption isotherm. The variation could be interpreted as the hysteresis effect of N$_2$ sorption, as will be discussed in detail in section 3.5. In the literature, it is generally accepted that fractal dimension calculated from two segments ($D_1$: $0.5 < P/P_0 < 1.0$, $D_2$: $0 < P/P_0 < 0.5$) denotes the surface fractal dimension and pore structure fractal dimension, respectively. $D_1$ implies the complexity of the pore structure, and higher $D_1$ represents higher gas-liquid surface tension that reduces gas adsorption capacity, while $D_2$ indicates the fractal characteristics induced by
Both processes could effectively reopen the closed pores, thus enlarging the pore numbers and total pore volumes of coal DL. However, in the range of 35–223 nm, pore transformation to larger pores due to ScCO₂ is observed. This transformation is verified by the following: (1) In the range of 274–2062 nm, the pore volume increases from 0.001084 to 0.00232 cm³ g⁻¹ (by 114.02%). (2) As shown in Figures 6 and 7, in the pore range of 0.06–4 μm, the obvious drops of D values using methods of Neimark (from 2.787 to 2.593) and Zhang (from 2.746 to 2.565) after the ScCO₂ treatment elucidate that pores have become smoother and more regular in the process of pore transformation.

As a bituminous coal that experienced a second exposure to ScCO₂, the results of PSD and CPV from the N₂ adsorption (DFT) method of coal HSW emerge with quite small differences before and after the ScCO₂ treatment. As mentioned in section 4.1, coal HSW was collected at a geo environment with water + CO₂ systems that might trigger numerous dissolution chemical reactions or hydrocarbon extraction. Therefore, the second treatment of coal HSW in the laboratory will not bring about evident changes to the pore structures.

For coal WLH with a high rank, we do not observe any obvious changes of CPV and PSD from the MIP method. Just like the other two samples, the multimodal phenomenon of PSD using the DFT model is also observed for coal WLH, which indicates the discontinuous feature of pore structure. As can be seen from Figure 9 a2,b2,c2, the peak number did not change apparently after the ScCO₂ treatment of coal DL and HSW. However, for coal WLH, all peaks marked 1, 2, and 3, located at 0.926–1.682, 3.317–4.678, and 4.842–5.952 nm, disappear after the ScCO₂ treatment. It is believed that the coal pore morphology change induced by ScCO₂ interaction will transform smaller pores (micropore and mesopore) into larger pores (macropore).

2.5. Physisorption Isotherm Analysis. Figure 10 exhibits the N₂ adsorption–desorption isotherms of the three sets of samples before and after the ScCO₂ treatment. According to the IUPAC technical report on the updated classification of physisorption isotherms and hysteresis loops, all curves are identified as type II isotherms and H3 type hysteresis loops, with unlimited monolayer-multilayer adsorption up to high saturation pressure P/P₀. The sharp inflection point B that corresponds to the completion of monolayer coverage and the onset of multilayer adsorption is also observed for all curves. There are two major contributing factors for generating hysteresis loops: (a) existence of certain well-defined metastable states and associated capillary condensation delay, (e.g., in a cylindrical pore, the adsorbed multilayer metastability may lead to delayed condensation); (b) condensate entrapment through network effects (e.g., for ink-bottle pore shape, the wide bodies are filled as before and remain filled during desorption until the narrow throats empty at lower pressures). The feature of the H3 loop is the sharp step-down of the desorption isotherm, which is located at P/P₀ ~ 0.4–0.5 for N₂ at 77 K, as shown in Figure 10. The isotherms types of all samples remain unchanged after the ScCO₂ treatment, which indicates that no new pore shape categories emerge. The variation trend of the amount of adsorbed N₂ is basically consistent with CPV and PSD calculated from the QSDFT model, as discussed in section 2.4. Compared with coal DL and WLH, coal HSW has narrow and inconspicuous hysteresis loops, which implies that coal HSW has more slit-shaped pores and less cylindrical and ink-bottle pores. The smaller loops of coal HSW indicate more open
pores and better connectivity, whereas the sudden descent of the desorption branch between 0.4 and 0.5 (\(P/P_0\)) of coal DL and WLH illustrates the existence of ink-bottle shaped pores. Normally, in the case of N\(_2\) adsorption at 77 K, the lower closure point is often located at \(P/P_0 \sim 0.4\). Any observed hysteresis recorded below this point and extending to the lowest attainable pressure (referred to as low-pressure hysteresis (LPH)) is mainly due to: (a) faulty experimental technique, (b) insufficient equilibrium time, (c) presence of impurities either on the surface or in the gas phase, and (d) expansion and contraction of adsorbents. For coal DL and WLH, the hysteresis loops exhibit in the entire range of the desorption isotherm branch. Generally, the deformation of coal caused by physisorption is very small and reversible and the effect has been ignored. In addition, as the isotherms of coal HSW show no obvious LPH below 0.42 and all samples are pretreated and operated under the same experimental conditions, we excluded the influencing factors (a), (b), and (d). As illustrated in section 4.1, coal HSW had been treated by a natural Sc\(\text{CO}_2\) geochemical reactor for millions of years; the impurities on coal had been...

Figure 6. Logarithm plots of intrusion surface versus intrusion pressure for the six samples before and after data correction: (a) untreated coal DL; (b) Sc\(\text{CO}_2\)-treated coal DL; (c) untreated coal HSW; (d) Sc\(\text{CO}_2\)-treated coal HSW; (e) untreated coal WLH; (f) Sc\(\text{CO}_2\)-treated coal WLH. (NU: Neimark’s method using uncorrected data; NC: Neimark’s method using corrected data).
extracted and dissolved by ScCO₂ fluid completely, which could explain the absence of LPH on the isotherms. Coal treatment in laboratory conditions is far less complicated than in situ reservoirs; thus, a second exposure to ScCO₂ has little effect on the pore structures. For $P/P₀ < 0.4$, the LPH of coal DL and WLH after ScCO₂ treatment gets narrower and smaller, indicating the decrease of hydrocarbons and inorganic matter and the pore structure complexity, which coincides with the conclusions in sections 2.1, 2.3.2, and 2.4.

3. CONCLUSIONS

The decrease of coal matrix compressibility indicates that sub-bituminous coal becomes harder to compress after ScCO₂ treatment, which might prevent microfracture closure, pore shrinkage, or connectivity loss due to bond breakage between interconnected pores. The increase of pore volume compressibility of sub-bituminous coal manifests that more gas could be stored in or flow through the pore space with the increase of pore pressure.
MIP data correction using TE is vital especially when pore diameter is smaller than 350 μm. A good match of pore volume between the corrected MIP method and BJH method of LPN2GA could be achieved. Fractal dimensions calculated by the thermodynamics model using corrected MIP data are strongly scale-dependent and are meaningful only in a limited pore size range. The results of thermodynamics and FHH methods both reveal that the irregularity of pore surfaces and heterogeneity of pore structures of sub-bituminous coal and anthracite after the ScCO2 treatment decrease, which signifies the improvement of gas desorption, flow, and diffusion properties.

The major changes of PSD and PV in sub-bituminous coal are the increase of micro-, meso-, and macropore volumes, whereas a decline of the micromesopore volume and peak numbers is observed for anthracite after ScCO2 treatment. The narrower and smaller LPH of sub-bituminous coal and anthracite after ScCO2 treatment demonstrates the decrease of impurities and...
pore structure complexity, which facilitates the development of connected pores. In addition, more slit-shaped pores exist in the original bituminous coal and the ScCO\(_2\)-treated one, which is very helpful for the CO\(_2\)-ECBM recovery.

In summary, ScCO\(_2\), which has strong extraction ability, dissolves the impurities, reopens the closed pores, enlarges pore volumes, and enhances the pore connectivity, thus enabling sub-bituminous coal to be more suitable for CO\(_2\)-ECBM recovery, while for anthracite, both positive and negative effects exist simultaneously, which makes it challenging to determine the dominant factors affecting CO\(_2\) storage. A series of evidences verify that coals from the Haishiwan coal mine in the Yaojie coal field are experiencing interaction with ScCO\(_2\), which could be regarded as a natural analogue for future CO\(_2\) storage projects.

### 4. MATERIALS, METHODS, AND THEORIES

#### 4.1. Sample Collection.

Coal samples used in this study were collected from the Dalong coal mine in the Tiefa coal field, Haishiwan coal mine in the Yaojie coal field, and Wolonghu coal mine in the Huabei coal field in China, which represent sub-bituminous coal, bituminous coal, and anthracite, respectively.\textsuperscript{59−61} Once the samples were collected from freshly exposed mining faces, they were wrapped in absorbent paper, sealed hermetically in polyethylene plastic ziplock bags, sent back to the laboratory, and preserved in containers full of helium to prevent further oxidation and humidity. The collected coal samples were code-named coal DL, coal HSW, and coal WLH, respectively. Proximate analyses (moisture, ash, volatile matter, and fixed carbon) of the samples were performed according to the China National Standard GB/T 212-2008 using a SEMAG6600 proximate analyzer (Changsha Kaiyuan Instruments, China). The maximum vitrinite reflectance coefficient (R\(_{\text{vm}}\)) was determined according to international standard (ISO 7404-5, 1984) using a microscope photometer (Zeiss, Germany). The physical properties of the coal samples are listed in Table 3.

It is worth noting that during the late Jurassic to the early Cretaceous period, dynamic thermal metamorphism of the F19 fault ductile-brittle shear zone of the Haishiwan coal mine resulted in CO\(_2\) release from basement carbonate regions and the geological evolution and multiperiodical F19 fault controls the formation, migration, and entrapment of CO\(_2\) in the coal reservoir.\textsuperscript{62} Therefore, large volumes of CO\(_2\) have been observed in the Yaojie coal field, with the CO\(_2\) concentration ranging from 34.10 to 98.64%\textsuperscript{68} Moreover, the practical CO\(_2\) extraction amount is much larger than the predicted Langmuir volume. The depth of the sampling location of coal HSW is approximately 800 m, where the temperature and pressure of coal seam gas exceed the critical points (30.97 °C, 7.38 MPa) of CO\(_2\).\textsuperscript{64} All of these indirect evidences suggest that coal HSW is likely to have been exposed to ScCO\(_2\) and the physical and chemical structures of the samples have already been altered to some extent. This group of selection is to validate the presence of ScCO\(_2\) in the Haishiwan coal mine and observe the effect of second exposure to ScCO\(_2\) on the pore morphology of coal.

#### 4.2. High-Pressure ScCO\(_2\) (HP-ScCO\(_2\)) Geochemical Reactor.

Theoretically, a larger bulk coal sample should be adopted to simulate the in situ conditions of deeply depleted or unminable coal seam for CO\(_2\) sequestration as it captures the real conditions and avoids particle size discrimination. However, using a large bulk coal sample requires an extremely long reaction time to reach CO\(_2\)–coal equilibrium. Therefore, particle sizes between 1 and 3 mm were chosen in this study for ScCO\(_2\) treatment to minimize the equilibrium time.
A custom-built HP-ScCO₂ geochemical reactor was used for the treatment experiment, as shown in the abstract graphic. The sample cell was placed in a water bath to sustain the temperature at a relative stable value, and the room temperature was also kept constant by an air conditioner. A displaying unit for monitoring any gas leakage or temperature fluctuation that might have occurred in the treatment process was used. Before being put into the sample cell of the reactor, all samples were placed in a vacuum drying oven at 110 °C for 12 h to remove moisture in the samples. Prior to CO₂ injection, coal samples were degassed at 40 °C for 12 h by a vacuum pump. After CO₂ was allowed into the sample cell, the air compressor began to work to increase the cell pressure to about 12 MPa. Soon afterward, CO₂ began to adsorb on the surface of coal and the system pressure decreased gradually until the final temperature and pressure were stabilized at 35 °C and 10 MPa, respectively, after 50 h. The ScCO₂ treatment experiment lasted for 200 h for a complete reaction between coal and ScCO₂. When the experiment ended, the sample cell was gradually depressurized at a rate of 0.015 MPa min⁻¹ to avoid possible damage to the physical structure of the coal samples as a result of sudden pressure drops.

4.3. Mercury Intrusion Porosimetry (MIP) and Low-Pressure N₂ Gas Adsorption (LPN₂GA). In this study, coal samples with particle size between 1 and 3 mm were examined by a PoreMaster 33 automated mercury intrusion porosimeter (Quantachrome Instruments) in a low-pressure station (1–30 psi) and a high-pressure station (30–33000 psi) consecutively, which permits to measure pore volume in the range of about 2 × 10⁻⁵ to 7 nm diameter calculated by the Washburn equation.⁶⁴ To eliminate the effect of interparticle filling, MIP data from the...
high-pressure station was used. The surface tension of 480 dynes/cm and a contact angle of 140° between coal and mercury were employed. The samples underwent a vacuum heating treatment to ensure that all in situ fluids were removed before mercury was introduced into the testing cell, hence enabling the assumption that the pore pressure is approximately zero and the system confining pressure equals to the effective pressure on the pores before any intrusion happens.

Micropores and mesopores were characterized by LPN$_2$GA, which was conducted on an autosorb iQ physical adsorption instrument (Quantachrome Instruments). About 2.0–3.0 g of the samples of 0.2–0.25 mm size were degassed to remove moisture and residual gases. ASiQwin software package (v 4.0) system was used to obtain low-pressure N$_2$ adsorption and desorption isotherm at relative pressures ($P/P_0$) ranging from 0.001 to 0.995 for determination of pore volume, pore size distribution, and fractal dimensions following Barrett–Joyner–Halenda (BJH), density functional theory (DFT), and Frenkel–Halsey–Hill (FHH) methods. To better facilitate the comparisons of our results with the literature on pore structure alterations treated by ScCO$_2$, we adopted the classification from International Union of Pure and Applied Chemistry (IUPAC) for pore size analysis in this work: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). Although N$_2$ cannot fully detect pore volumes smaller than 2 nm, we could still obtain the pore volume information in the range of 0.889–2 nm using the following calculation model by DFT method: N$_2$ at 77 K on carbon (slit/cylindr. pores, QSDFT adsorption branch). Therefore, the micropore volume referred in this study is the cumulative pore volume in the range of 0.889–2 nm.

### 4.4. Coal Compressibility and MIP Data Correction

#### 4.4.1. Compressibility of Coal Matrix and Coal Pore Volume

Coal matrix compressibility refers to the relative changes of coal matrix volume under external force, and compressibility is inversely proportional to the bulk modulus. A blank run that was carried before the experiment ascertained that the compressibility of the apparatus was negligible and contributed very little to the mercury volume uptake even at the highest pressure applied. Therefore, coal compressibility ($k_c$) can be defined as:

$$k_c = -\frac{1}{V_c} \frac{dV_c}{dP}$$

where $V_c$ is the coal matrix volume and $dV_c/dP$ represents the volume changes of coal matrix as a function of pressure.

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Table 3. Physical Properties of Coal Samples (wt %, ad)$^a$

| coal samples | moisture | ash | volatile matter | fixed carbon | $R_{max}$ |
|--------------|----------|-----|-----------------|--------------|-----------|
| coal DL      | 4.11     | 9.23| 47.49           | 45.71        | 0.6949    |
| coal HSW     | 6.17     | 4.12| 31.87           | 61.30        | 0.9323    |
| coal WLH     | 1.66     | 11.86| 12.57           | 75.79        | 2.7401    |

$^a$Air-dried basis.
As coal contains many micropores and mesopores, some pores, such as pores with diameter smaller than 7 nm or inaccessible pores (such as induced and naturally isolated pores), could not be penetrated by mercury even at the highest pressure (33 000 psi); we assumed that \( V' \) in eq 1 includes these small pores and inaccessible pores. Therefore, we can write the following equation for a compressible solid

\[
\Delta V_{\text{obs}} = \Delta V_p + \Delta V_c
\]

where \( \Delta V_{\text{obs}} \), \( \Delta V_p \), and \( \Delta V_c \) represent observed mercury intrusion volume, true pore volume, and matrix compression volume, respectively.

In the high-pressure regime, we can assume that \( \Delta V_{\text{obs}}/\Delta P \) is the constant \( \beta \) from the significance of the regression coefficient between pressure and mercury intrusion volume \((R^2 > 0.99)\). Therefore, \( \Delta V_c/\Delta P \) could be approximated by

\[
\frac{\Delta V_c}{\Delta P} \approx \beta - \frac{\sum_i \Delta V_{p_i}}{\Delta P}
\]

where \( d_i \) and \( d_j \) are the lower and upper pore diameter limit of the coal compression interval that could be determined from fractal dimensions by the Menger sponge model,\(^{66,67} \) which will be discussed in detail in section 2.1. The sum of the pore volume in the range of \( d_i - d_j \) is obtained from N\(_2\) adsorption data. In the high-pressure regime, we assume that \( \Delta V_c/\Delta P \) is independent of pressure in the condition that pores included in the sample remain unchanged during compression; then, \( dV_c/dP \) equates with \( \Delta V_c/\Delta P \); then, coal matrix compressibility could be calculated through eq 4 where \( V_c' \) is the matrix volume per unit mass, which was the reciprocal of skeletal density calculated from the MIP test.

\[
k_p = -\frac{1}{V_c'} \frac{dV_c}{dP}
\]

Friesen calculated the fractal dimension of the porous medium from the following relation\(^{66} \)

\[
\log \left( \frac{dV_c(P)}{dP} \right) \propto (D - 4) \log P
\]

In most instances, we could assume that cumulative pore volume could be replaced by cumulative intruded mercury volume.\(^{57,58,64,66} \) Then, integrating eq 6 and substituting \( V_c' \) with \( V_{\text{obs}} \) gives

\[
V_{\text{obs}}(P) = a + bP^{D-3}
\]

where \( a \) and \( b \) are fitting parameters. It is well known that the increase of the pore volume is resulted from coal matrix compression when mercury pressure exceeds a certain value.\(^{55,58} \) thus, the \( D \) value in eq 7 that represents the coal matrix compression process is fitted from the curve \( \log (dV/dP) \) versus \( \log (P) \), where \( dV/dP \) is independent of pressure. Combining eqs 5 and 7, the coal pore volume compressibility could be deduced as\(^{68} \)

\[
k_p = \frac{b(D - 3)P^{D-4}}{a + bP^{D-3}}
\]

### 4.4.2. MIP Data Correction Based on the Tait Equation

Most researchers adopted coal matrix compressibility to correct MIP data.\(^{33,34,69} \) However, there are some drawbacks of this method. The first disadvantage lies in the fact that we can observe some decreasing intervals of the cumulative intrusion curves and this is impossible as the intruding mercury volume could only increase monotonically into the sample cell without withdrawals.\(^{69} \) The second defect of this method is that the deformation process caused by mercury compression is assumed to be elastic; thus, \( \Delta V_{\text{obs}}/\Delta P \) is considered to be constant in the high-pressure regime but in the intermediate and low-pressure regions, this might not be the case. Therefore, applying the calculated compressibility derived from the linear region of the intrusion curve to correct the data of the whole pore range is obviously questionable. The third deficiency of this method is the neglected mercury compression, which could affect the readings of the MIP data, especially in high-pressure regions. For all of the above reasons, we proposed the semiempirical Tait equation (abbreviated TE) method to correct MIP data.

The semiempirical TE has been widely used to fit volume data of a material under hydrostatic compression over broad pressure ranges in past decades. The simplicity and accuracy in producing high-pressure volume data for dense gases, liquids, and liquid mixtures have stimulated the interest of many researchers.\(^{70–72} \) Although TE was originally proposed and applied to a variety of liquids, it is now being put forward to describe volume changes due to compression of solids.

\[
\frac{V - V_0}{V_0} = C \log \left( \frac{B + P}{B + P_0} \right)
\]

In eq 9, \( V \) is the volume summation of unfilled pores and solid matrix and it equals to the apparent volume per unit mass. The subscript 0 refers to the pressure point where mercury begins to compress the sample. \( C \) and \( B \) are Tait parameters derived from the fit.

Smithwick generalized the equation of liquid samples for the case of a porous, compressible solid, and the total volume of pores could be expressed as\(^ {72} \)

\[
V_p(P) = \frac{R(P) - C \log \left( \frac{B + P}{B + P_0} \right)}{1 - C \log \left( \frac{B + P}{B + P_0} \right)}
\]

where \( R(P) \) is defined as

\[
R(P) = \frac{V_{\text{obs}}(P)}{V_0} + C_{\text{Hg}} \log \left( \frac{B_{\text{Hg}} + P}{B_{\text{Hg}} + P_0} \right)
\]

In eq 11, \( C_{\text{Hg}} = 0.1754 \) and \( B_{\text{Hg}} = 1815 \) MPa are Tait parameters from mercury compression data of Bridgman.\(^ {74} \) As implied in other MIP data processing, the pore walls are assumed to be rigid enough to retain their original shapes during mercury intrusion.

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Notes
The authors declare no competing financial interest.

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