Time-Dependence of Mechanical Property Alterations on Anthracite Coals Treated by Supercritical Carbon Dioxide

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1. Introduction

CO₂ sequestration in deep unmineable coal seams, commonly recognized as one of the most promising CO₂ mitigation methods [1–3], can also prominently promote CO₂-enhanced coalbed methane (CO₂-ECBM) recovery [4]. In particular, CO₂ reaches its supercritical state when its pressure and temperature exceed the critical point 7.38 MPa and 31.8°C, respectively. The critical point of CO₂ can be achieved at the depth of around 800 m under normal hydrostatic pressure. Physical properties such as density, diffusivity, and viscosity of supercritical carbon dioxide (Sc-CO₂) change dramatically near the critical point, thus affecting the interaction between rock (coal) and Sc-CO₂ [5, 6]. However, it is necessary to consider certain risks for achieving long-term safe storage of sequestered CO₂.

Unlike subcritical CO₂, Sc-CO₂ exhibits higher adsorption capacity [7] and unique physical properties. According to the extensive present measurements, functional groups and pore structure of each pore phase vary hugely in different coal ranks before and after Sc-CO₂ treatment [8–12]. However, the coal permeability decreases mostly after Sc-CO₂ injection due to the dominant role of sorption-induced swelling [13, 14]. Sc-CO₂ helps to develop seepage-flow pores (mesopores and macropores). In fact, Sc-CO₂ notably alters the development of pores in high-rank and medium-rank coals, whereas it scarcely affects that in low-rank coal. Besides, mineral matters in coal are dissolved and mobilized when they react with Sc-CO₂ [15]. This process of CO₂-ECBM recovery, which alters CO₂-adsorption-induced swelling of coal matrix, influences its hydromechanical properties in turn according to Griffith and Eng [16], and the adsorption effect is able to reduce the strength of materials.

The geomechanical properties of CO₂-treated coal are closely related to CO₂ storage volume and stability. A number of...
scholars have explored the influence of CO₂ adsorption on coal strength from subcritical state to supercritical state on both coal powder and tiny cubes. Studies [17, 18] revealed that the strength of low-rank coal decreased greatly with the increase of CO₂ adsorption. In many experiments, considerable reductions in uniaxial compressive strength and Young’s modulus were observed as a result of gaseous CO₂ saturation [17, 19, 20]. Sc-CO₂ adsorption can weaken all types of coals [21, 22]. Coal mass gets ductile as the coal becomes plasticized in the process of CO₂ adsorption, and this phenomenon is more notable under the condition of Sc-CO₂ adsorption. It has been put forward that physical and molecular microstructures of coal can be altered by the interaction between CO₂ and coal induced by sorption-induced swelling, pore size reset, hydrocarbon extraction, and macromolecular rearrangement [23–27]. However, the link between the weakening of coal strength and the microcosmic physical-chemical alterations of Sc-CO₂-treated coal is still rarely reported.

Currently, experiments on mechanical comparison before and after Sc-CO₂ did not take time effect into consideration. The time-dependent Sc-CO₂-treated coals provide a good proof for understanding the interaction between Sc-CO₂ and coal, which could also provide insights for coalbed CO₂ storage and Sc-CO₂-treated coal fracturing. Therefore, this study is aimed at investigating the time-dependent mechanical response of anthracite coal samples treated with Sc-CO₂. In addition to uniaxial compression, triaxial compression was applied to coals at different confining pressures to simulate the field stress environment. Then, coal cylinders were treated with Sc-CO₂ for 240 h and 960 h with nonconfining pressure to observe their damage levels. Finally, the time-dependent mechanical weakening effect was explained by introducing the coal cube model and combining the experimental results.

2. Materials and Experiments

2.1. Materials. Experimental coal samples were taken from Daning Coal Mine of Qinshui Basin Coalfield located in the south of Shanxi Province, China. The results of proximate analysis of the coal are presented in Table 1.

In order to conduct uniaxial and triaxial tests, a total of 14 coal samples perpendicular to the bedding were cored from large coal lumps. The samples were 50 mm in diameter and 100 mm in height. It is noteworthy that only homogeneous samples with no visible cleat were used for the mechanical property measurement, so that the effects of anisotropy and heterogeneity on experimental results could be minimized.

2.2. Experimental Procedure. A customized high-pressure reactor that could provide a maximum saturation pressure of 32 MPa was adopted to ensure saturation conditions during the experiments. This reactor was equipped with an advanced temperature regulation system that could limit the fluctuation of set temperature to within 0.1°C. In this study, coal samples were saturated in CO₂ at a temperature of 35°C under a pressure of 8 MPa for 12 h or 48 h. Afterwards, the pressure chamber was gradually depressurized at a rate of 0.02 MPa/min, so that physical structure of the coal was not affected by pressure. Then, to avoid the effects of oxidation and humidity, the samples were immediately put into a small sealed bag filled with helium and sent for the mechanical test in the first time.

The mechanical tests were conducted by using an adsorption-permeation-mechanics coupled device whose maximum axial loading and maximum confining loading capacity could reach 600 KN. Axial and radial strain sensors, with maximum test ranges of 8 mm and 4 mm, respectively, were equipped for the sample deformation tests during stress loading, as exhibited in Figure 2. In this study, two main test scenarios were applied. First, the uniaxial and triaxial experiments were performed on raw coal samples under confining pressures of 0, 2, 4, and 6 MPa and under an axial loading rate of 0.3 MPa/min until the samples failed. During the experiments, the peak strength, axial strain, and radial strain were observed and recorded. Second, under the same confining pressure conditions, the procedures of uniaxial and triaxial tests were repeated on Sc-CO₂-treated samples for 12 h and 48 h.

3. Results

3.1. Strength Evolution of Time-Dependent Sc-CO₂ Treatment on Coal. After the uniaxial and triaxial experiments, the deviatoric stress- (σ₁-σ₃) strain behaviors for the raw and Sc-CO₂-treated samples under different confining pressures were obtained, as illustrated in Figure 3. The axial strain (ε₁), radial strain (ε₂), and volumetric strain (εᵥ)
Both cohesion and internal friction angle of coal samples undergo a decrease after Sc-CO$_2$ treatment. The cohesions of samples decrease by 8.9% and 27.4% after Sc-CO$_2$ treatment for 12 h and 48 h, respectively. The internal friction angles of samples drop by 8.36° and 13.71°, respectively, accounting for 17.53% and 28.75% of that of raw coal. Cohesion is the mutual attraction formed by molecular forces in the adjacent parts of coal, and frictional force and chain effect of coal matrix are expressed by internal frictional angle. A larger internal frictional angle implies higher mechanical strength. The Sc-CO$_2$ treatment obviously weakens the strength of coal samples, and the weakening effect is more obvious with a longer Sc-CO$_2$ treatment time.

3.2. Strain Evolution of Time-Dependent Sc-CO$_2$ Treatment on Coal. Coal deformation, which is reflected by Young’s modulus and Poisson’s ratio, could be calculated according to the deviatoric stress and strain obtained in the uniaxial and triaxial experiments (Table 3). The experimental results reveal that during SC-CO$_2$ treatment, SC-CO$_2$ saturation influences Young’s modulus and Poisson’s ratio in addition to the strength of anthracite coal. Young’s moduli drop by 25% and 40%, while Poisson’s ratios jump by 19.23% and 30.76% on average after Sc-CO$_2$ treatment for 12 h and 48 h (8 MPa), respectively. As the confining pressure increases from 0 to 6 MPa, the Young’s modulus grows from 2716 MPa to 3422 MPa during the test of 12 h Sc-CO$_2$ treatment. Meanwhile, Poisson’s ratio shows the same tendency, that is, it increases by a factor of 1.09-1.125 for the raw and treated coal samples. It can be concluded that the confining pressure and the Sc-CO$_2$ treatment share a competitive relationship in terms of Young’s modulus.

Coal is a highly brittle material that rarely moves due to its high-energy structure in a glassy state. The CO$_2$ adsorbed into coal matrix can improve its polymer structure and thus expand the free volume. As a result, the ductile properties of coal mass get promoted, which reduces Young’s modulus and raises Poisson’s ratio [28, 29].

3.3. Pore and Fracture Distribution of Sc-CO$_2$-Treated Coal. The cumulative pore volume curves of raw and Sc-CO$_2$-treated coal samples were analyzed by means of mercury intrusion porosimetry (MIP), as displayed in Figure 5(a). The pore characteristics of coal samples can be explored according to the widths of hysteresis loops and the volumetric difference between mercury injection and extrusion curves. As can be seen from Figure 5, the cumulative mercury intrusion volume rises slowly when the pressure is lower than 20 MPa, while it increases sharply after the pressure exceeds 20 MPa. Compared with the raw coal samples, the mercury intrusion curves of Sc-CO$_2$-treated coal samples increase slower, indicating that Sc-CO$_2$-treated coal samples boast more uniform pore size distribution. Moreover, the cumulative mercury intrusion (0.302 cm$^3$/g) of Sc-CO$_2$-treated coal samples is 10.22% higher than that (0.274 cm$^3$/g) of raw coal samples. The pore size in the Sc-CO$_2$-treated samples alters, and the total pore volume expands. Besides, the hysteresis loop of Sc-CO$_2$-treated samples increases from 0.0028 cm$^3$/g to 0.0043 cm$^3$/g, which may result from

\[ \sigma_1 = \frac{1 + \sin \phi}{1 - \sin \phi} \sigma_3 + 2C \frac{\cos \phi}{1 - \sin \phi}, \]  

where $C$ is the cohesion and $\phi$ is the internal friction angle. The cohesion and internal friction angle could be obtained in light of the criterion, as shown in Table 2.
the decrease in semiclosed pores, the formation of more open pores, and the development of pore network. This is probably because Sc-CO$_2$ dissolves and mobilizes hydrocarbons, leading to adsorption-induced deformation and physical constriction [31, 32].

Figure 3: Deviatoric stress-strain relation curve of raw and Sc-CO$_2$-treated coal samples (black line = raw sample, red line = 12 h treated, and blue line = 48 h treated) under different confining pressures ((a) confining pressure 0 MPa, (b) confining pressure 2 MPa, (c) confining pressure 4 MPa, (d) confining pressure 6 MPa).

Figure 4: Relationship between maximum and minimum principal stresses of coal under the same treatment conditions.

Table 2: Cohesion and internal friction angle of coal samples under different conditions.

<table>
<thead>
<tr>
<th>Coal samples</th>
<th>Cohesion (MPa)</th>
<th>Internal friction angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw coal samples</td>
<td>3.79</td>
<td>47.69</td>
</tr>
<tr>
<td>Samples treated with Sc-CO$_2$ for 12 h</td>
<td>3.45</td>
<td>39.33</td>
</tr>
<tr>
<td>Samples treated with Sc-CO$_2$ for 48 h</td>
<td>2.75</td>
<td>33.98</td>
</tr>
</tbody>
</table>

Pore size distribution can be seen more intuitively from Figure 5(b). The mercury intrusion volume of mesopores and macropores in coal samples increases significantly by 0.0037 cm$^3$/g after Sc-CO$_2$ treatment, while that of transition pores and micropores decreases slightly by 0.0009 cm$^3$/g. Firstly, the CO$_2$ molecules were injected into the coal seam flow through the mesopores and macropores in the form of laminar flow or turbulent flow. The channel of gas flow expands when the volume of mesopores and macropores increases. Previous studies [29] also revealed that Sc-CO$_2$ treatment could result in smoother pore surface of coal samples and better connectivity of pores, which conduces to the diffusion and seepage of gas molecules. Eventually, after the Sc-CO$_2$ treatment, mesopores and macropores develop faster and better in coal, which may help gas to desorb and diffuse from coal matrix and transport in coal fracture.
3.4. Time-Dependent Sc-CO\textsubscript{2} Treatment on Coal Damage.

Two sets of coal cylinders were treated with Sc-CO\textsubscript{2} (9.65 MPa, 35°C) without stress constraint for 240 h and 960 h, respectively. Sc-CO\textsubscript{2} was released at the rate of 0.015 MPa/min to prevent the rapid decrease in gas pressure. Figure 6 displays the damage modes of Sc-CO\textsubscript{2}-treated samples in different time periods.

The coal samples saturated with Sc-CO\textsubscript{2} for 240 h present limited fractures and cracks compared with raw coal samples. However, after Sc-CO\textsubscript{2} treatment for 960 h, the coal samples, which have a more complicated fracture network, lose the main mechanical strength and become looser with poor cohesion. In fact, it can be easily stripped by hand. Judging by the crack shapes, the failure belongs to tensile failure due to compression that may be caused by coal matrix swelling. This is consistent with Zhang et al.’s observation [33]. From the appearance, there are some assumptions that the coal damage is attributed to the time-dependent Sc-CO\textsubscript{2} transport and adsorption-induced swelling, and it has been recently observed that the unswelling phase is due to the induced swelling stresses [34]. These stress fields are highly anisotropic; the maximum effective stresses concentrate on the mineral surface in most cases; the Von Mises stresses continuously rise with the increase of coal matrix swelling until the coal fails [33]. CO\textsubscript{2} saturation alters the unswelling phase of the shear-dominant failure mechanism in the raw coal into the failure along the cleat, the tensile failure plane, and the splitting failure plane system [22, 29, 35]. This is mainly because of the generation of secondary cracks resulted from CO\textsubscript{2} adsorption-induced heterogeneous swelling and local swelling stress.

4. Discussion

4.1. Time-Dependence of Mechanical Weakening Effect on Sc-CO\textsubscript{2} Treatment. The coal cube model, which is widely used to
describe gas transport and permeability evolution from coal matrix to fractures [36, 37], also matches well with Sc-CO$_2$ injection and coal strength evolution with time. Hence, the model is introduced to reveal the time-dependence of coal mechanical property variation after Sc-CO$_2$ injection (Figure 7). The two parts of fracture and matrix strength weakening effects are attributed to stress-strain evolution with time.

Based on the above observations, the Sc-CO$_2$ treatment not only causes a decrease in the mechanical properties (peak strength, elastic modulus, cohesion, and internal frictional angle) of coal in triaxial or uniaxial stress environments but also modifies the properties of coal mass, leading to a transition from brittle failure to ductile failure. The coal treated with Sc-CO$_2$ for 48 h undergoes a more obvious decrease in mechanical properties than the coal treated for 12 h. Other experiments suggest that the mechanical properties of Sc-CO$_2$-treated coal will not decrease continuously over time and can be presented using a simple Langmuir type equation [38]. Flow of Sc-CO$_2$ through the cleats is driven by pressure and can be described using Darcy’s law at first. The adsorption-induced swelling and the reduction in fracture surface energy opens the fractures, hence reducing tensile strength and facilitating crack formation. As the Sc-CO$_2$ treatment leads to the dissolution of minerals, fractures become smoother and apertures expand. When the stress of adsorption-induced swelling exceeds the matrix cohesion, a new crack surface is formed [16]. Sc-CO$_2$ can enhance the

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**Figure 6:** Damage appearance of Sc-CO$_2$-treated coal samples under different saturated times: (a) and (b) are a comparison before and after treatments for 240 h and 960 h, respectively.

**Figure 7:** Time-dependence of mechanical weakening on Sc-CO$_2$ treatment with coal cube model.
coal permeability by promoting the development of micro pores, mesopores, and macropores in coal. In this way, fracture morphology is transformed through mineral dissolution, desorption shrinkage, and new minor crack generation, which all contributes to raising the coal porosity and lowering the coal strength.

However, the flow through the coal matrix, which is modeled by Fick’s law of diffusion, is assumed to be driven by the concentration difference and needs a long time to reach full Sc-CO$_2$ saturation. The coal strength further declines as the Sc-CO$_2$ diffuses into coal matrix after long-term treatment. A covalently cross-linked, three-dimensional macromolecular model, together with an intra- and intermolecular model [39, 40], has been widely recognized to describe the organic matrix. Former research of the authors suggested that the injection of Sc-CO$_2$ into coal can lead to the swelling effect, namely, the viscoelastic relaxation of its highly cross-linked macromolecular structure. Sc-CO$_2$ is capable of mobilizing small hydrocarbon molecules from the coal matrix [41] (Figure 7). That is, Sc-CO$_2$ can reduce the intermolecular force in coal atoms. From a macro perspective, the effect is manifested by the decreases in cohesion and internal friction angle with the decrease in coal strength and deformation. The time-dependent model of coal mechanical property weakening contributes to the time-dependent Sc-CO$_2$ transport through coal mass fracture and matrix and physical-chemical reactions in the corresponding position.

4.2. Implication for In Situ Sc-CO$_2$ Coalbed Injection and Storage. The preferable coal seams for CO$_2$ sequestration exist at depths of greater than 800 m. The interaction between coal and Sc-CO$_2$ and the mechanical strength evolution have been widely studied in recent years [22, 29, 38]. The time-dependent triaxial experiments (up to 6 MPa) indicate that the longer the treatment time is, the more significantly the peak strength decreases. The failure mode of coal transits from brittle failure to ductile failure with the rise of confining pressure. In addition, the stress magnitude is much higher than the value obtained in in situ experiments at depths of over 800 m, implying that the further decrease in coal permeability is dominantly controlled by the swelling induced by Sc-CO$_2$ sorption [42]. The ductile deformation of Sc-CO$_2$-treated coal causes the fractures to close and the CO$_2$ to desorb under high effective stress, which also lowers coal permeability to hinder further transport of CO$_2$. It is also found that the CO$_2$ injection volume drops in a short period of time due to the sorption-induced swelling as well as high stress in the field [43, 44]. According to above findings, the coal seam might not be a suitable layer for long-term CO$_2$ storage despite its great adsorption affinity. Nowadays, Sc-CO$_2$ fracturing is applied to enhancing CBM/shale or increasing permeability to improve gas recovery [45]. The injected Sc-CO$_2$ should cracks the coal seam as quickly as possible to prevent plastic deformation of fully saturated coal. The fractures generated during hydrofracturing heal with the release of pressure because of the plastic deformation nature of CO$_2$-saturated coal, creating unfavorable formation properties. These observations imply that the ductile behavior of Sc-CO$_2$-adsorbed coal is significantly enhanced with the plasticization of coal, and the surface energy reduces critically at the beginning of CO$_2$ sequestration. However, the effect of Sc-CO$_2$ is reduced over time. This laboratory tests provide a better vision for the effects of CO$_2$ sequestration or ECBM in coal seams in a controlled environment.

5. Conclusion

Sc-CO$_2$ treatment significantly alters time-dependent mechanical properties of anthracite coal. Greater decreases in peak strength were observed after Sc-CO$_2$ treatment for 12 h and 48 h. Higher confining pressure corresponds to greater compressive strength when the coal samples fail. Besides, the strain of coal experiences a transition from brittle to ductile as the confining pressure rises and Sc-CO$_2$ treatment time prolongs. As the treatment time passes, Sc-CO$_2$ saturation reduces cohesion, internal friction angle, and Young’s modulus and raises Poisson’s ratio, which also controls the evolution of coal strain and failure. Sc-CO$_2$ treatment facilitates the development of mesopores and macropores in coal by dissolving and mobilizing hydrocarbons. The coal samples treated with Sc-CO$_2$ for 240 h and 960 h show a different damage appearance, as it alters from limited fractures to a complicated fracture network. A time-dependent Sc-CO$_2$ flow through the coal matrix and the physical-chemical reaction model was proposed to build the link between coal fracture and matrix mechanical weakening effect from experiments. Sc-CO$_2$ interacts with coal in a complicated way after CO$_2$ flows and diffuses from particle coal to massive coal through fractures and coal matrix. Moreover, the saturation of CO$_2$ can lead to the swelling, dissolution, and surface energy reduction of coal with the passage of time, which in turn has a large influence on coal strength and fracture development. The time-dependence of Sc-CO$_2$ transport and interaction with coal may have profound meanings for coalbed CO$_2$ storage and Sc-CO$_2$ organic rock fracturing.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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