Fuel 223 (2018) 32–43

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Full Length Article

The effects of supercritical CO_2 on mesopore and macropore structure in bituminous and anthracite coal

Shiqi Liu[a], Jingsheng Ma[b], Shuxun Sang[c,*], Tian Wang[c], Yi Du[c], Huihuang Fang[c]

[a] The Key Laboratory of Coal-based CO2 Capture and Geological Storage, Jiangsu Province, Low Carbon Energy Institute, China University of Mining and Technology, Xuzhou 221116, China
[b] Institute of Petroleum Engineering, Heriot-Watt University, EH14 4AS, United Kingdom
[c] Key Laboratory of Coalbed Methane Resources and Reservoir Formation Process, Ministry of Education, School of Mineral Resource and Geoscience, China University of Mining and Technology, Xuzhou 221116, China

ARTICLE INFO

Keywords:
Pore structure
Pore volume
Specific surface area
Connectivity
Coal rank

ABSTRACT

The effects of supercritical CO_2 ($scCO_2$) on coal pores play a critical role in CO_2 geological storage-enhanced coalbed methane recovery (CO_2-ECBM). To investigate the effects of $scCO_2$ on the pore structure and connectivity in coals of different ranks, CO_2 sequestration processes were replicated using a $scCO_2$ geochemical reactor. Four coal samples with different ranks were exposed to $scCO_2$ and water for 240 h under 80 °C and 20 MPa. Mercury intrusion porosimetry, nitrogen adsorption tests, and scanning electron microscopy analysis were used to identify the pore volume, pore size distribution, pore connectivity, and pore morphology of the coal samples before and after $scCO_2$-H_2O treatment. The increase in the macropore volume caused by the $scCO_2$ is mainly controlled by the pores $> 30\,\mu m$, resulted from the dissolution of carbonate minerals with large grain size in organic matter. The coal rank has a positive influence on the volume and specific surface area of the pores $> 30\,\mu m$, whereas coal rank is more significant for macropore specific surface area in the high-volatile bituminous coal and macropore volume in the low-volatile bituminous, semi-anthracite, and anthracite coal. With an increase in the coal rank, the volume and specific surface area of the mesopores increase. The changes in the mesopore volume in the high-volatile bituminous coal are caused by changes in the pores 20–50 nm in diameter, while these changes in the low-volatile bituminous coal, semi-anthracite, and anthracite are caused by changes in the pores < 20 nm, due to the formation of dissolution-created pores in minerals; additionally, many pores < 3 nm are generated by the $scCO_2$. At the macropore scale, the $scCO_2$ increases the volume of the non-effectively interconnected pores more than that of the effectively interconnected pores, indicating that the $scCO_2$ has a weak effect on the increase in macropore connectivity. The volume of the effectively interconnected pores increases more at the mesopore scale than at the macropore scale, and the $scCO_2$ treatment increases the connectivity of the mesopores.

1. Introduction

CO_2 sequestration in a coal seam can effectively displace CH_4 and has become an important method for the improvement of coalbed methane (CBM) development and the reduction of CO_2 emissions [1]. CO_2 geological storage-enhanced coalbed methane recovery (CO_2-ECBM) is an attractive approach for reducing greenhouse gas emissions and exploiting energy resources and has attracted considerable attention from many researchers [2]. Coal pores are the primary storage sites of CO_2 and are considered important channels for CO_2 injection and CBM output [3,4]. The structure, pore size distribution, and pore connectivity of coal is of great significance for CO_2-ECBM [5–7]. At an in situ reservoir temperature and pressure (burial depth > 800 m), CO_2 is likely to be present in a supercritical state (i.e., $Tc = 31.06\,^{\circ}C$, $Pc = 7.38$ MPa) [8]. The effect of supercritical CO_2 ($scCO_2$) on the transformation of the organic composition and inorganic minerals of coal may lead to changes in pore structure and connectivity [9–11].

The effects of $scCO_2$ on pore structure are complex and are affected by coal rank, mineralogy, water content, temperature, and pressure [12,13]. It is generally agreed that $scCO_2$ can increase the volume percent of macropores and decrease the volume percent of micropores in lignite/brown coal; conversely, in bituminous coal, $scCO_2$ can decrease the volume percent of macropores and increase the volume percent of micropores [8,14,15]. $ScCO_2$ has minor impact on

---

* Corresponding author.
E-mail addresses: liushiqi19840920@163.com (S. Liu), shuxunsang@163.com (S. Sang).

https://doi.org/10.1016/j.fuel.2018.03.036
Received 15 January 2018; Received in revised form 21 February 2018; Accepted 6 March 2018

macropores and mesopores in anthracite but increases the pore volume of micropores [3,16,17]. It is suggested that $scCO_2$ can increase the volume and specific surface area of micropores in bituminous coal and anthracite, while the smooth inner surface of macropores and mesopores decrease their specific surface area [18,19]. Water plays an important role in the reactions between $scCO_2$ and minerals in coal. Without water, the macropores in bituminous coal undergo no significant change during a $scCO_2$ treatment, as observed under field emission scanning electron microscopy (FESEM) [20]. $ScCO_2$-H_2O also impacts the pore morphology by increasing the number of ink-bottle-shaped pores in low-rank coal and either damaging or breaking up the ink-bottle-shaped pores in anthracite [3,14]. In conclusion, the effects of $scCO_2$ on coal pore structure and connectivity have generally been recognized and considered to be important to the effectiveness of CO_2-ECBM. However, the changes in coal pore structure and connectivity caused by $scCO_2$ are still controversial.

The pore structure and connectivity in coal are difficult to characterize. There are three main types of approaches that can be used for characterizing pores in coal: microscopy analysis, e.g., optical microscopy and electron microscopy; radiation, e.g., nuclear magnetic resonance (NMR), X-ray computed tomography (CT), small-angle scattering using X-rays and neutrons; gas adsorption and fluid intrusion methods, e.g., mercury intrusion porosimetry and nitrogen/CO_2 adsorption tests. Mercury intrusion porosimetry and nitrogen adsorption tests are the most widely used methods of measuring the pore structure and connectivity in coal because they are mature technologies and have high measurement speeds, low sample requirements, and low costs [21]. In this paper, an integrated approach combining mercury intrusion porosimetry and nitrogen adsorption testing was employed to describe the effects of $scCO_2$ on the pore structure and connectivity of bituminous coal and anthracite coal under 80 °C and 20 MPa, supported by scanning electron microscopy. This study aims to provide a better understanding of how $scCO_2$ affects the pore structure and connectivity, which can elucidate the theoretical effectiveness of CO_2-ECBM.

2. Samples and methodology

2.1. Samples

Four groups of coal samples with different ranks were collected in China: high-volatile bituminous coal from the Yangzhuang Mine, low-volatile bituminous coal from the Xinyuan Mine, semi-anthracite from the Yuwu Mine, and anthracite from the Sihe Mine. These samples were named Coal #1 to Coal #4, respectively (Table 1). Coal #1 was collected from coal seam #9 in the Taiyuan formation in the Bohaiwan basin (Fig. 1). Coals #2-#4 were collected from coal seam #3 of the Shanxi formation in the southern Qinshui basin (Fig. 1). The Bohaiwan basin and the southern Qinshui basin are not only the major regions for commercial development of CBM but also have the high potential for CO_2-ECBM in China. The collection, retention, and preparation of the coal samples were conducted according to the relevant Chinese standard GB/T 19222-2003 [22] and the international standard ISO 7404-2:1985. To prevent further oxidization, coal samples were wrapped in absorbent paper, hermetically sealed in plastic bags and stored at 5 °C after sample collection from the coal mine working faces. The key properties are shown in Table 1.

2.2. $ScCO_2$-H_2O treatment

(1) High-pressure reactor

$ScCO_2$-H_2O-coal interaction was investigated in a high-pressure reactor (Fig. 2). The reactor can simulate the conditions for CO_2 sequestration in a deep coal seam ($P < 35$ MPa; $T < 200$ °C). The key component of this apparatus is a high-pressure tubular stainless steel sample cell, which is 100 mm in diameter and 200 mm in height. A coal sample was held in a 60 to 80 mesh (0.20–0.25 mm) stainless steel tube in the sample cell, allowing the water and CO_2 to flow through the coal sample.

(2) Coal grain size

In principle, coal samples with a large average particle size are more favourable for experimentation because they more realistically reflect *in-situ* conditions. However, using coal with a large average particle size will result in an inconveniently long reaction time. Therefore, coal particles sieved into a 4–8 mm grain size range were chosen for the $scCO_2$-H_2O treatment. Because the volume of the sample cell was approximately 1500 ml, a 200 g coal sample was used for the $scCO_2$-H_2O treatment.

(3) Temperatures and pressures

The $scCO_2$-H_2O treatments were performed to replicate burial depth of 2000 m. The temperature and pressure of the burial depth were calculated from the temperature and depth of the subsurface constant temperature zone, average geothermal gradient, and average pressure gradient at the sampling location, corresponding to 80 °C and 20 MPa respectively.

(4) $ScCO_2$-H_2O treatment process

The basic $scCO_2$-H_2O treatment process is as follows.

A. After coal samples (about 200 g) were placed in the sample cell (Fig. 2), it was sealed and then preheated to the desired temperature.
B. After evacuation, 300 ml of deionized water was pumped into the sample cell. Deionized water was chosen to avoid the influences of ions in water on the results of the $scCO_2$-H_2O treatment.
C. Gas was pumped into the sample cell to reach a predetermined pressure. The temperature and pressure were monitored during the experiment to ensure system stability of ± 0.78 MPa and ± 0.8 °C.
D. According to the $scCO_2$-H_2O treatments carried out before, ion contents and element contents in reaction water were almost unchanged after 10 days, which means the experiments had already

Table 1
Properties of the coals used.

Samples	Sampling location	$R_{o,max}$ (%)	Proximate (wt.%)				Ultimate (wt.%)			
			M_{ad}	A_{ad}	V_{daf}	FC_{ad}	O_{daf}	C_{daf}	H_{daf}	N_{daf}
#1	Yangzhuang Mine	0.72	2.29	5.49	38.72	57.91	7.99	83.28	5.27	1.22
#2	Xinyuan Mine	1.81	0.81	5.35	15.26	80.20	9.30	80.32	4.43	1.14
#3	Yuwu Mine	2.19	1.10	11.98	13.44	76.19	2.44	91.73	4.12	2.44
#4	Sihe Mine	3.33	1.48	13.12	6.32	81.39	2.98	93.45	2.15	1.00

Note: $R_{o,max}$, the mean maximum reflectance values of vitrinite; wt.%, weight percent; M_{ad}, moisture; A_{ad}, ash yield; V_{daf}, volatile matter; FC_{ad}, fixed carbon content; O_{daf}, content of oxygen; C_{ad}, carbon content; H_{ad}, hydrogen content; N_{ad}, nitrogen content; "ad" means air-drying base; "daf" means dry ash-free basis.