Journal of CO_2 Utilization 18 (2017) 189–197

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

High pressure supercritical carbon dioxide adsorption in coal: Adsorption model and thermodynamic characteristics

Xu Tang[a,*], Nino Ripepi[a,b]

[a] Virginia Center for Coal and Energy Research (0411), Virginia Polytechnic Institute and State University, Blacksburg, VA, 24060, United States
[b] Department of Mining and Minerals Engineering, Virginia Polytechnic Institute and State University, Blacksburg, VA, 24060, United States

ARTICLE INFO

Article history:
Received 25 October 2016
Received in revised form 18 December 2016
Accepted 13 January 2017
Available online 13 February 2017

Keywords:
Carbon dioxide
Adsorption
Coal
Langmuir
Isosteric heat of adsorption

ABSTRACT

This work uses a dual-site Langmuir adsorption model to describe supercritical carbon dioxide ($scCO_2$) adsorption in coal up to 20 MPa and 253 K. The isosteric heat of adsorption for $scCO_2$ in coal is calculated analytically by considering both the real gas behavior and the adsorbed phase, which are ignored in the classic Clausius-Clapeyron approximation. It was found that the proposed model can not only reasonably interpret observed test phenomena but also has the intrinsic ability to extrapolate adsorption isotherms under different temperatures beyond test data. The crossovers of the observed adsorption isotherms under different temperatures can be simply attributed to the pressure-volume-temperature (PVT) behavior of the bulk gas during the adsorption process. Both the temperature dependence and adsorption uptake dependence of isosteric heat of adsorption are revealed; the higher the temperature and the adsorption uptake, the lower the isosteric heat of adsorption. The ideal gas law overestimates the isosteric heat of adsorption for $scCO_2$ in coal. The application of the dual-site Langmuir model allows for estimating the CO_2 storage capacity of deep unmineable coal seams, modeling CO_2 transport behavior via differentiating the true ratio between bulk phase and adsorbed phase, and investigating the true thermodynamic characteristics of CO_2 in coal under high pressures.

1. Introduction

Because of global warming and climate change concerns, global efforts have been made to decrease the concentration of carbon dioxide in the atmosphere [1–4]. Carbon dioxide capture, utilization and storage are considered crucial ways to meet the carbon dioxide emission reduction targets. Onshore geological sequestration of carbon dioxide typically involves capturing, transporting and injecting carbon dioxide into suitable underground formations for storage such as depleted oil and conventional gas reservoirs, unconventional natural gas reservoirs (unminable coal seams and shale formations), deep saline formations r, and basalt formations [5–10]. Among these geological formations, unminable coal seams are one of the promising options because of their potential for enhancing coalbed methane (ECBM) recovery while simultaneously sequestering carbon dioxide [11–14]. The enhanced natural gas will help to offset the cost of carbon dioxide sequestration. However, there are still some concerns about the long-term effect of sequestration of CO_2 in coal seams and potential environmental consequences [11,15]. Carbon dioxide injection issues arise during the field injection process because of the permeability decrease induced by coal swelling [16–21]. The existing phases of the injected carbon dioxide in the subsurface are crucial for the carbon dioxide storage capacity estimation. Therefore, field tests of ECBM with carbon sequestration were and are being conducted around the world, which are helpful to understand the potential benefits and practical issues [11,22–31].

It is well known that the affinity of carbon dioxide in coal is higher than methane, and the amount of carbon dioxide adsorbed in coal is always higher than methane at the same pressure. In order to evaluate the carbon dioxide storage potential of unmineable coal seams, the first step is to evaluate the adsorption capacity of carbon dioxide in coal via isothermal sorption tests. However, because of the heterogenous properties of coal, $scCO_2$ adsorption behavior in coal has not garnered research attention like it has for manmade materials. There are inconsistent test phenomena reported regarding $scCO_2$ adsorption in coal. Some researchers show peculiar test phenomena for $scCO_2$ in coal such as the bimodal Gibbs excess adsorption isotherms [32–34]. Other

---

* Corresponding author at: Virginia Center for Coal and Energy Research (0411), 133 Randolph Hall, Virginia Polytechnic Institute and State University,, Blacksburg, VA, 24060, United States.
E-mail addresses: xutang@vt.edu, xutangcbm@gmail.com (X. Tang).

http://dx.doi.org/10.1016/j.jcou.2017.01.011
2212-9820/

researchers exhibit smooth CO_2 excess adsorption isotherms in coal when the pressure rises up to 20 MPa [20,21,35–43]. Since the latter test phenomena can be reproduced and the former cannot, the peculiar test phenomenon is attributed to artificial test errors [38,40]. Even though the smooth CO_2 excess adsorption isotherms have been observed, an optimized model for modeling both the Gibbs excess and absolute adsorption uptake is still needed. Despite extensive research for $scCO_2$ adsorption in manmade materials, a number of semi-empirical models have been adopted by revising the classic Dubinin-Astakhov (D-A), Dubinin-Radushkevich (D-R), Langmuir and Toth equations to describe the sorption behavior of $scCO_2$ in coal by fitting each isothermal adsorption curves independently [20,21,35–45]. However, all these models are based on either the empirical density of adsorbed carbon dioxide (density of liquid carbon dioxide) in coal or the assumed constant volume of adsorbed carbon dioxide in coal. Even though good fitting results are obtained by each researcher, the physical meaning of the obtained parameters from these revised classical equations still needs to be confirmed. Furthermore, even though the coal swelling phenomena has been observed, few models include coal swelling to obtain absolute isotherms from Gibbs excess isotherms [40,46,47]. Considering both the adsorption and penetration (absorption) CO_2 in coal may explain the coal swelling effect during the sorption process. The penetration CO_2 can not only compensate the elastic energy change associated with volume change but also can change the macromolecular structure of coal [40,48,49]. In addition, these models cannot be used to extrapolate isotherms beyond test temperatures. The prediction of adsorption isotherms under high pressure and high temperature geological conditions are critical for carbon dioxide storage capacity estimations in the deep subsurface. Therefore, to reasonably interpret the adsorption behavior of $scCO_2$ in coal and predict adsorption isotherms under high temperature and high pressure in-situ conditions, a more concise and robust adsorption model is needed.

As a crucial evaluation index for the thermodynamic process in physical adsorption tests, the isosteric heat of adsorption for $scCO_2$ in coal has rarely been considered by researchers. There are still several issues that exist regarding the calculation of this index for $scCO_2$ adsorption in coal [50–55]. First, the absolute adsorption isotherms must be obtained from the observed adsorption isotherms in order to calculate the isosteric heat of adsorption, where a robust model is needed [37,56]. Under low pressure conditions, the observed adsorption isotherm approximates the absolute adsorption isotherm, and there is no need to obtain the absolute adsorption isotherm. However, when the Gibbs excess adsorption behavior becomes obvious under higher pressure conditions, a reliable adsorption model is necessary to obtain the absolute adsorption uptake from observed adsorption isotherms. Second, even though the absolute adsorption isotherms can be obtained, the classic Clausius-Clapeyron approach is not appropriate because it cannot take the real gas behavior of $scCO_2$ and the adsorbed gas phase into consideration [50,51,55]. Fig. 1 shows the deviation of CO_2 behavior compared with ideal gas under different temperatures and pressures. The usage of the Clausius-Clapeyron approach therefore will hide the true behavior of the isosteric heat of adsorption because the Clausius-Clapeyron approach uses the ideal gas assumption and neglects the adsorbed gas phase volume [51,55]. It has been found that both the gas behavior and the adsorbed gas phase volume can significantly influence the isosteric heat of adsorption [51,55,57]. Therefore, in order to obtain the true behavior of the isosteric heat of adsorption, the real gas behavior and the adsorbed gas phase volume must be reasonably considered.

To tentatively solve the above-mentioned issues, this work first uses a dual-site Langmuir model to describe $scCO_2$ adsorption behavior in coal by considering both the adsorbed phase and the absorbed (penetrated) phase. Then, the published data of high pressure $scCO_2$ adsorption in two different coals are obtained from literature in order to validate the proposed model. Last, isosteric heats of adsorption for $scCO_2$ are calculated analytically by considering the real gas behavior of $scCO_2$ and the contribution of the adsorbed phase.

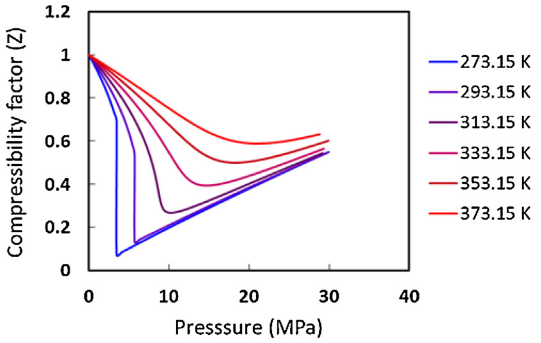

Fig. 1. Deviation behavior of the CO_2 under different temperatures and pressures (Data is obtained from the NIST Standard Reference Database 23 (REFPROP: Version 8.0.)).

2. Absolute adsorption model

Coal swelling is a pronounced phenomenon associated with CO_2 injection into coal seams, which can result in injectivity issues during field tests [11,26]. Researchers have used different approaches such as dilatometric method, optical or strain gages, and X-ray and small-angle scattering techniques to study the coal swelling effects in a laboratory scale, but have not reached an agreement on whether the coal swelling is universal or not. It was found that coal microstructures were unaffected by exposure to CO_2 over a period of days based on the SANS and USANS tests [58]. However, most other researchers agree that the uptake of CO_2 in coal results in the swelling monotonically with pressure which can be modeled by Langmuir-type curves based on laboratory evidence [19,40,59–62],

$$\varepsilon_s = \varepsilon_0 \cdot \frac{k_s P}{1 + k_s P} \tag{1}$$

where ε_s is the swelling strain under specific pressure, P, ε0 and ksare fitting coefficients.

Based on the assumption that coal swelling is induced by the CO_2 penetration (absorption) in the macrostructure of coal, the dual-site model is used for describing both the CO_2 adsorption and the CO_2 absorption in coal as shown in Eq. (2) [40,49]. Fig. 2 shows how the CO_2 phase changes before and after CO_2 sorption: the absolute adsorption is the sum of net adsorption and absorption uptake. The dual-site model therefore combines both the adsorption and absorption content of CO_2 in coal, represented by a Langmuir-type term. In addition, the absorption term

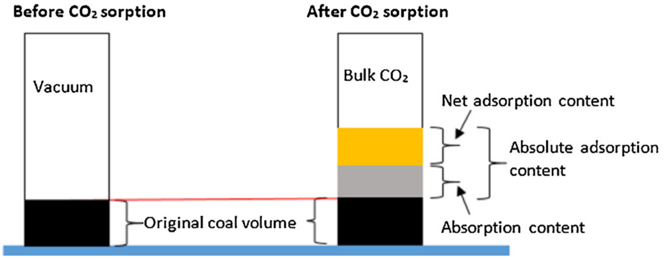

Fig. 2. The difference of CO_2-coal sorption system before and after CO_2 adsorption.