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Analysis of carbon dioxide sequestration in shale gas reservoirs by using experimental adsorption data and adsorption models

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ABSTRACT

For carbon dioxide (CO_2) sequestration in depleted shale gas reservoirs or CO_2 injection as an enhanced shale gas recovery technique, it is important to understand the adsorption mechanism in these reservoirs. In this study, experimental adsorption measurements for Dadas shale samples were conducted at 25 °C, 50 °C, and 75 °C up to approximately 2000 psia by using pure CO_2 (maximum adsorption capacity 0.211 mmol/g at 25 °C) and pure methane (CH_4) (maximum adsorption capacity 0.0447 mmol/g at 25 °C). By using Langmuir isotherm and Ono-Kondo lattice models (three-layer and monolayer), experimental adsorption results were evaluated and adsorption isotherms were constructed. It was concluded that Ono-Kondo monolayer model is really capable of fitting adsorption isotherms, especially at high pressures for CO_2 adsorption. For initial gas-in place calculations, the equations used by the help of Langmuir isotherm were modified with Ono-Kondo monolayer model and proposed to calculate the amount of CO_2 that might be stored as adsorbed and free gas in depleted shale gas reservoirs. For the case in this study, it was calculated that adsorbed gas concentration changes from 39.2% to 71.8% between 5000 psia and 500 psia. Moreover, binary mixture Ono-Kondo monolayer model was used to evaluate the adsorption isotherm of CO_2–CH_4 mixtures by using their pure adsorption experimental data. This data is useful if there is a purpose to inject CO_2 as an enhanced shale gas recovery technique because of the adsorption capacity difference between CH_4 and CO_2.

1. Introduction

Due to high consumptions of fossil fuels, global atmospheric CO_2 concentration and other greenhouse gases have been increasing. It is known that high concentration of CO_2 in the atmosphere causes global climate change. By 2030, CO_2 emissions will have increased by 63% from 2004 level, which is almost 90% higher than 1990 levels (IEA, 2004). Although the main source of CO_2 is the consumption of fossil fuels, currently it is impossible to change energy sources from fossil fuels to other renewable energy sources such wind, solar, nuclear power, etc. This is because currently alternative energy sources are not able to supply the world energy demand. Therefore, researchers have mainly focused on various CO_2 capture and sequestration techniques. There are many studies about the injection of CO_2 into depleted oil and gas reservoirs (Taber et al., 1997), deep saline aquifers (Ennis-King and Paterson, 2003), unmineable coalbeds (Gray, 1995), gas hydrates (Abbasov, 2014; Dashti et al., 2015) and depleted shale gas reservoirs (Zatsepina and Darvish, 2010; Sun et al., 2013; Merey, 2013).

If CO_2 storage and sequestration technologies are developed and applied efficiently, it is estimated that there will be 45% CO_2 emission reduction from the total 32 Gt of carbon dioxide emission (IEA, 2006). For this purpose, Zendehboudi et al. (2012) investigated a newly developed large scale geological CO_2 sequestration process known as the Ex Situ Dissolution Approach (ESDA) numerically and analytically. Moreover, Zendehboudi et al. (2013) discussed various aspects such as CO_2 displacement, geochemical reactions, CO_2 leakage, pressure build-up, well spacing, and dissolution efficiency for the ESDA and proposed a systematic way for this approach. In order to check any CO_2 leakage in CO_2 storage areas, it is vital to monitor CO_2 leakage. Monitoring technologies can only cost 4–6 cents per ton sequestered or 6–9 cents per ton sequestered for enhanced monitoring for an effective early warning system (Benson, 2004, 2005). Gislason et al. (2010) studied the CO_2 storage optimization in basaltic rocks and investigated CO_2 storage feasibility for the Carbix project. In these investigations, modeling and simulation studies are also important. Hassanzadeh et al.

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(2008) proposed a simple and accurate fluid model (predicting CO_2–brine density, solubility, and formation volume factor) which is necessary for black-oil flow simulations of CO_2 storage in geological formations. Deep saline aquifers are also potential places for CO_2 storage. Emami-Meybodi et al., 2015 studied this potential and also the dissolution of CO_2 in deep saline aquifer. Recently, many scientists have focused on CO_2 storage in unconventional reservoirs such as gas hydrates and shale gas reservoirs (Wang et al., 2015). CO_2 injection into natural gas hydrates is considered as a production method because of CO_2–CH_4 swabbing in the cages of hydrates (Merey and Sinayuc, 2016). Therefore, CO_2 injection into pure CH_4 hydrates was studied by Ors and Sinayuc (2014). Abbasov (2014) investigated CO_2 injection into natural gas mixture (CH_4, propane (C_3H_8) and CO_2) hydrates and good replacement percentages were obtained. Although there is no almost commercial production in gas hydrates, feasible gas production from shale gas reservoirs is possible. CO_2 storage in depleted shale gas reservoirs are considered because CO_2 might be stored both as adsorbed phase and free gas in pores. Moreover, CO_2 injection into shale gas reservoirs might be used as an enhanced gas recovery due to adsorption difference between CO_2 and CH_4 (Schaef et al., 2014; Li and Elsworth, 2014).

In recent years, unconventional reserves such as shale gas reservoirs have become a major alternative source of energy in the world. Scientists have conducted many studies about shale gas production mechanism, hydraulic fracturing and horizontal drilling (Kok and Merey, 2014). Moreover, shales are considered as possible CO_2 sequestration places (Kang, 2011; Sun et al., 2013). Shales are defined as organic-rich and very fine grained sedimentary rocks and they have natural fractures and matrix systems (Crain, 2011). In shale gas reservoirs, significant amounts of natural gas exist as conventional “free” gas in porous spaces as well as “adsorbed” gas on shale matrix (Lancaster et al., 1993). When a gas and a solid interact, there are intermolecular attractive forces between them. If these intermolecular attractive forces are greater than those existing between molecules of gas itself, gas accumulates on the surface of solid. This phenomenon is called adsorption of gas on solid (Velanki, 1995). Adsorption capacities of shale gas reservoirs range from 20% to 85% depending on total organic carbon content (TOC) and clay content (Lancaster et al., 1993).

According to Energy Information Administration (EIA, 2013)'s report, the amount of technically recoverable shale gas in the world is approximately 7795 trillion cubic feet (tcf). This amount is very important to supply the world energy demand. However, in order to produce gas from shale gas reservoirs, hydraulic fracturing is necessary to increase the permeability of shale gas reservoirs from nanodarcy values to darcy values (Kok and Merey, 2014). After successful hydraulic fracturing operations, gas is produced from free pores and then, with the decrease of pressure, adsorbed gas is desorbed and flows though the pores (Song et al., 2011). CO_2 injection is considered as an enhanced recovery method in shale gas reservoirs or as CO_2 sequestration in the depleted shale gas reservoirs because shale gas reservoirs have high permeability values after fracturing and CO_2 can be both stored in free spaces and also as adsorbed phase on the surface of shale matrix (Wang et al., 2011; Khosrokhavar et al., 2014). Therefore, many studies have been conducted to investigate CO_2 sequestration in shale gas reservoirs. Tayari et al. (2015) investigated a preliminary assessment of the economic feasibility of storing CO_2 in depleted unconventional natural gas-bearing shale formations. Similarly, Eshkalak and Aybar (2015) proposed that CO_2 sequestration in shale gas reservoirs might be feasible because the capacity of CO_2 storage changes from 5 to 10 kg/ton per shale formation. For CO_2 sequestration in shale gas reservoirs, the adsorption capacity of CO_2 at different pressures should be evaluated. Chareonsuppanimit et al. (2012) conducted adsorption experiments on New Albany shale samples at 328.2 K and high pressures (up to 1798 psia) for CO_2, N_2 and CH_4 by using the volumetric experimental set-up and results were evaluated by using a simplified local-density (SLD) adsorption model. According to the results, the adsorption capacity of CO_2 is very high compared to CH_4 and N_2. The lowest adsorption capacities were obtained for N_2. Because of higher adsorption capacity of CO_2, Heller and Zoback (2014) proposed that their experimental results are quite favorable for CO_2 injection as an enhanced recovery or the CO_2 storage perspective. Similarly, Kang et al. (2010) conducted experimental, SEM and numerical analysis on shale samples of Forth Worth basin and it was found that up to 97% of the uptaken gas (CO_2) is stored in adsorbed state inside the organic pores depending on the shale-gas-reservoir pressure. As well as experimental studies, Fathi and Akkutlu (2014) evaluated shale gas reservoirs numerically to increase the gas production from shale gas reservoirs by injecting CO_2 and using the adsorption difference between CO_2 and CH_4. This enhanced recovery method was also suggested by Rogala et al. (2014).

After conducting adsorption experiments, the results are evaluated by different adsorption models. These model parameters are especially used during modeling and numerical studies in shale gas reservoirs (Bacon et al., 2015). Adsorption capacities are measured at several pressure values and the graph of adsorption capacity versus pressure is called “adsorption isotherm” (Matott, 2007). By using adsorption models, these data are evaluated and formulated. Then, the adsorption value at any pressure is easily calculated by using the formula. There are many adsorption models such as Langmuir isotherm, BET isotherm, Freundlich Isotherm, Ono-Kondo model, etc. However, Langmuir isotherm is commonly used for the evaluation of adsorption data because it is easy to use and practical for engineering purposes (Ruthven, 1984). Moreover, for the evaluation of CO_2 adsorption experimental results, Langmuir model cannot fit to the adsorption isotherm because of unusual behavior of CO_2 adsorption isotherm especially at high pressures compared to those of CH_4 and N_2. Therefore, Chareonsuppanimit et al. (2012) used simplified local-density (SLD) adsorption model for the evaluation CO_2 adsorption data instead of Langmuir isotherm. Similarly, Sudibandriyo et al. (2010) used Ono-Kondo models for the evaluation of CO_2 adsorption data on coal samples at high pressures. Another advantage of Ono-Kondo adsorption model is its ability to predict the volume of adsorbed layer. While the evaluation of experimental results, equations of states are used to calculate the amount of unadsorbed (free) gas and adsorbed gas at different pressures. However, most of adsorption experimental studies ignore the volume of adsorbed gas on the surfaces of samples. Different than Langmuir isotherm, Ono-Kondo model can be used to calculate the volume of adsorbed gas by using the experimental data (Sudibandriyo et al., 2010; Sudibandriyo, 2010; Merey, 2013).

In this study, pure CH_4 adsorption experiments and pure CO_2 adsorption experiments on shale samples (Dadas Formation, Turkey, TOC ~ 4.0% and medium clay content) were conducted at 25 °C, 50 °C and 75 °C by using volumetric adsorption experimental set-up to understand the effect of CO_2 on adsorption behaviors of shale samples. The aim of CO_2 adsorption experiments is to investigate possible storage of CO_2 in depleted shale gas reservoirs after depletion or as a recovery technique in shale gas reservoirs. It is also aimed to evaluate raw experimental adsorption data by using Langmuir model and Ono-Kondo models. Layered structures of adsorption on shale samples were investigated with Ono-Kondo monolayer model and three-layer model. Moreover, by using Ono-Kondo monolayer model data of the experiments of pure CH_4 and pure CO_2, a theoretical approach to binary mixtures of adsorption of CH_4 and CO_2 was investigated for possible CO_2 injection as an enhanced recovery method. In this study, a formula was proposed