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A Review of Carbon Dioxide Adsorption to Unconventional Shale Rocks Methodology, Measurement, and Calculation

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Review Paper

A review of carbon dioxide adsorption to unconventional shale rocks methodology, measurement, and calculation



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Abstract

Carbon dioxide (CO₂) injection has been applied extensively in hydrocarbon reservoirs for both increasing oil recovery and CO₂ storage purposes. Recently, CO₂ injection has been proposed to increase oil recovery and for CO₂ storage in shale reservoirs. During CO₂ injection in shale reservoirs, adsorption will take place on the surface of the rock, which will impact both the oil recovery and the storage capacity. This research provides a roadmap to the different types of adsorption and the adsorption measurements and calculations with emphasis on the ones most applicable during CO₂ injection in shale reservoirs. The main two types of adsorption are initially explained including physisorption and chemisorption, and the major applicable adsorption isotherms are explained and their limitations are listed. The research then focusses on physisorption and its types, and hysteresis trends since chemisorption does not occur in shale reservoirs during CO₂ injection. The different methods used to measure adsorption are then illustrated and explained including volumetric, gravimetric, volumetric-gravimetric, oscillometry, and impedance spectroscopy. The different calculation methods for volumetric adsorption are then explained. Finally, the most common errors that have been observed during measurement and calculation of adsorption are listed and explained, while mentioning the method to avoid each error. This research provides a guideline to the proper and accurate measurement of CO₂ adsorption on shale rock during enhanced oil recovery applications and CO₂ storage operations in unconventional shale reservoirs to improve the productivity and applicability of this application.

Keywords CO₂ adsorption · Unconventional shale rocks · Review

1 Introduction

Carbon dioxide (CO₂) injection is currently one of the most applied enhanced oil recovery techniques in the oil industry due to several important reasons [1, 2]. Firstly, CO₂ injection, either through flooding of cyclic huff-n-puff, can increase oil recovery significantly [3, 4]. Secondly, CO₂ can be stored in several types of hydrocarbon reservoirs as part of the carbon storage initiative to reduce greenhouse emissions [5–8]. Recently, CO₂ injection in unconventional low permeability shale reservoirs has been investigated for both enhanced oil recovery from these reservoirs, and CO₂ storage Jin and Firoozabadi [9]. In both applications,

the CO₂ will adsorb to the shale rock surface, which will have an effect of oil recovery, and also CO₂ storage capacity [10–12].

The adsorption of CO₂ on the surface of shales, along with other rock, has been investigated using both computer simulation and modelling, and experimental work. Mohammad, S. [13] aimed to identify the most common sources of error associated with undergoing adsorption experiments. The errors investigated included the amount adsorbed through calculations, the void volume measured using helium, and the density of the injected gas which will affect the compressibility factor. Bahadori and Vuthaluru [14] developed a new correlation that can

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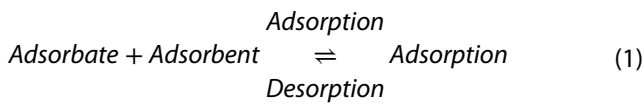
predict CO₂ adsorption isotherms for pressures up to 17.5 psi, and 196 °C. The correlation was based on previously reported data, correlated as a function of CO₂ partial pressure for different temperatures. Clarkson and Haghsheenas [15] used several models and tested their applicability in modeling CO₂ adsorption. They found that the simple Langmuir and Dubinin–Radushkevich models were the most adequate for modeling supercritical single component adsorption on coal and shale as long as the density value is adjusted on the simulator for the CO₂ since it has a direct effect on the compressibility value. Yu [16] used BET Isotherm rather than Langmuir Isotherm to model gas adsorption in Marcellus Shale. They observed that the Langmuir isotherm does not accurately model adsorption in all cases in the Marcellus shale, and hence a combination of BET and Langmuir isotherm should be applied. They also compared the results from both isotherms and evaluated long term adsorption. Psarras [17] investigated CO₂ adsorption capacity in shale cores from the Eagle Ford basin using Molecular Simulation. The impact of increasing pressure and temperature, and also change in organic content and material was investigated. Le [18] developed a new computational model to model flow of methane in fractured shale matrix based on averaging mass conservation equations. The model accounted for methane adsorption which had a strong effect on the flow of the gas and its relative permeability. They study did not use CO₂ however. Sudibandriyo [19] illustrated the difference between the absolute adsorption, and Gibbs adsorption by measuring both values for the shale. They also showed that the helium compressibility can be obtained using correlation to measure the void space, whereas the CO₂ values should be obtained using other methods. Lafortune [20] measured CO₂ adsorption on Mesozoic Marine Basin shale samples from France using magnetic suspension balance. The samples were crushed to powder size, and used for the adsorption experiments. As the temperature increased, the adsorption decreased, while increasing the pressure resulted in an increase in adsorption. The mineral composition of the shale also affect the adsorption capacity of CO₂. Luo [21] investigated adsorption of several gases including methane, CO₂, and binary mixtures with different mole percentages of each gas using powdered shale samples of less than 0.5 mm particle size. They measured adsorption based on a volumetric adsorption setup, and integrated a filter disk to prevent the particles from entering into the valves. Yuan [22] attempted to use helium porosimeter to measure the volumetric adsorption capacity of Argillite rick shales. Since the volumetric based adsorption operates in the same manner as the helium porosimeter, the values they obtained were representative of the adsorption values on the shale. Lu [23] developed a novel model fully based on a numerical producer combined with

Artificial Neural-Network Technique to evaluate the lost gas volume, which includes the gas volume adsorbed to the surface of the coal, which occurs during production of coal. Perez and Devegowda [24] applied Monte Carlo Simulation to model methane and CO₂ adsorption. According to their results, having the rocks confined increased the adsorption capacity on the shale due to the increase in the attraction of the gas molecules which results in the density of the adsorbed phase being higher than that of the free phase.

Based on the previous work conducted on CO₂ adsorption to shales, it is clear that there are several methods present to measure adsorption experimentally and using computer simulation, and also, there are more than one methods to calculate the adsorption value after conducting experiments. This research provides a detailed explanation of the different types of adsorption, and the one mostly related to CO₂ adsorption to shale rock. The research also mentions the most commonly used adsorption isotherms to model CO₂ adsorption to shale, and the advantages and disadvantages of each method. The research then explains the different types of physisorption, and then indicates the type that is most observed during CO₂ injection in shale reservoirs. The different types of experimental methods to measure adsorption are also explained in details, and the advantages and disadvantages of each method is mentioned. The two most common methods used to quantify CO₂ adsorption to shales are also shown, and the method by which they are applied is explained. By providing a comprehensive guideline to CO₂ adsorption on shale rocks, this research aims to function as a roadmap to the application of experimental studies on CO₂ adsorption in unconventional shale reservoirs for enhanced oil recovery and CO₂ storage purposes.

2 Types of adsorption

Adsorption is defined as the adhesion of atoms, ions, gas molecules, or liquids to the surface of an adsorbent [25]. There are two main constituents during any adsorption; these include the adsorbent, and the adsorbate [26, 27]. The adsorbent is the surface on which adsorption will take place. The adsorbate is the substance which will adsorb on to the adsorbent's surface [28]. Adsorption occurs due to the adsorbent experiencing bond deficiency, which makes it thermodynamically favorable for the adsorbent to adsorb the adsorbate [29]. Desorption will occur once the adsorbate has enough energy to overcome the force holding it to the surface of the adsorbent and free itself from the surface. The general equation for adsorption is shown [30].



There are two main types of adsorption, including physisorption, and chemisorption. Several adsorption isotherms are also present to quantify adsorption for different adsorbents and adsorbates. The main types of adsorption, along with the adsorption isotherms and a subdivision of physisorption types are shown in Fig. 1 below. Each of the parameters mentioned in the figure will be explained in details later on. The main types that can be applied effectively and accurately to CO₂ adsorption on shale rocks will be pointed out as well.

2.1 Physisorption

Physisorption, also referred to as physical adsorption, is the type of adsorption that takes place between CO₂ and shale during CO₂ injection in unconventional shale reservoirs [31–34]. It occurs at very low heats of adsorption, usually ranging between 20 and 40 kJ/mol. This is one of two main reasons why physisorption is a reversible or partially reversible process, meaning that desorption can occur after physisorption has taken place [35]. The second reason is that physisorption does not require any activation energy. It usually forms at low temperatures, and decreases significantly with increasing temperature. During physisorption, the adsorbate will form multi-molecular

layers on the adsorbent [30, 36]. The gas molecules of the CO₂ are held on the surface of the shale via Van Der Waals forces, which are considered weak forces [5, 37]. The main characteristics of physisorption during CO₂ injection in shale reservoirs is shown in Fig. 2.

2.2 Chemisorption

Chemisorption, also referred to as chemical adsorption, does not occur during CO₂ injection in shale reservoirs. It occurs at a high heat of adsorption, usually ranging from 30 to 400 kJ/mol. It requires a high activation energy to sever the bonds holding the adsorbate to the adsorbent. The adsorbate is held to the adsorbent via chemical bonds, which makes the process irreversible, unless extremely high energy is input into the system. Another main difference between physisorption and chemisorption is that during chemisorption, the adsorbate forms mono-molecular layers on the surface of the adsorbent, as opposed to the multi layers formed during physisorption [30, 38]. This is extremely advantageous for physisorption especially during CO₂ storage processes in shale reservoirs since the formation of multi-layers of the CO₂ on the shale surface will result in a higher volume of CO₂ adsorbed, and hence, a high CO₂ storage volume [39]. Figure 3 shows the main characteristics of chemisorption. The shale in Fig. 3 is for explanation purposes only, since chemisorption will not form during CO₂ injection in unconventional shale reservoirs.

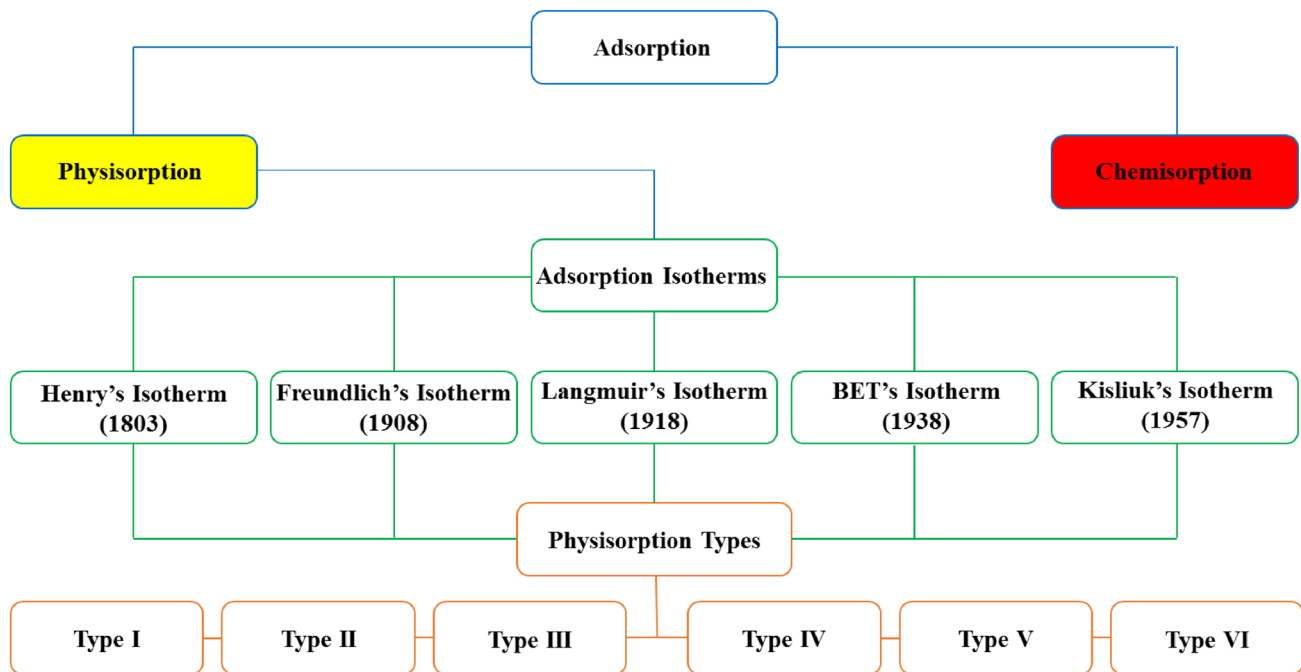


Fig. 1 Flowchart of main types of adsorption and adsorption isotherms

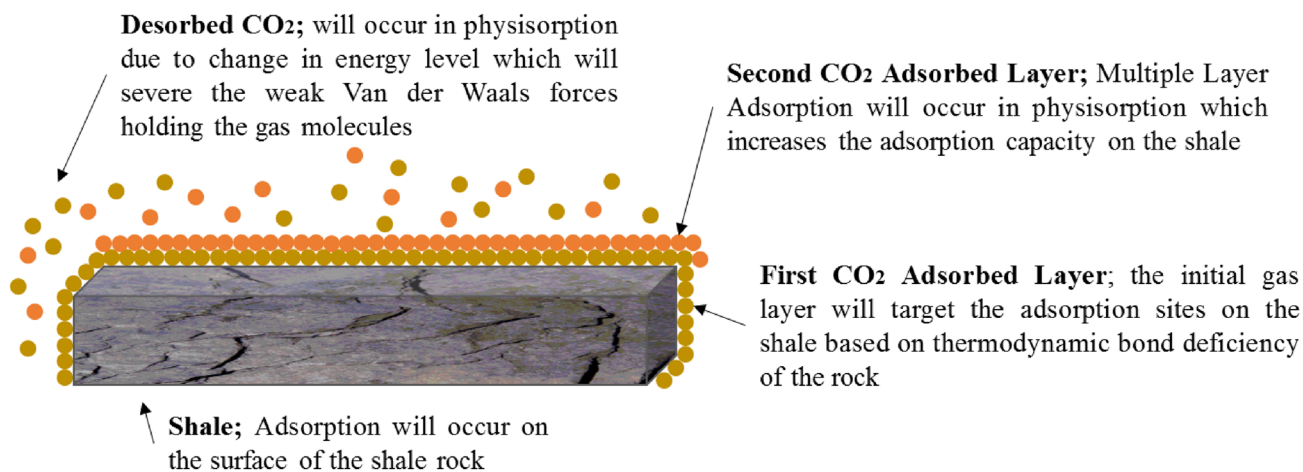
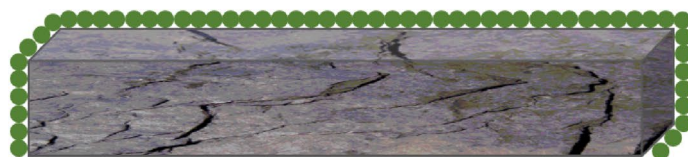


Fig. 2 Main characteristics of physisorption

Desorbed CO₂; desorption will not occur in chemisorption unless tremendous energy is input to desorb the gas since the molecules are held via chemical bonds.

Second CO₂ Adsorbed Layer; Chemisorption is characterized by being mono-layered adsorption and hence only a single layer will be present on the adsorption sites



First CO₂ Adsorbed Layer; the initial gas layer will have a heat of adsorption ranging from 40-400 kJ/mol, which is considered very high compared to physisorption.

Shale; Gas adsorption on shales occurs as physisorption and not chemisorption

Fig. 3 Main characteristics of chemisorption

3 Adsorption isotherms

Several adsorption isotherms have been developed along the years to model adsorption. Each of these isotherms has its own assumptions and limitations, which makes only a few of them applicable for accurate quantification of CO₂ adsorption on shale reservoirs. An adsorption isotherm predicts adsorption capacity of the adsorbate on the adsorbent at a specific temperature, hence the name isotherm, which comes from isothermal, measuring constant temperature. The main adsorption isotherms will be explained, with a main focus on those applicable to CO₂ adsorption in shale reservoirs.

3.1 Henry's isotherm

Henry's Adsorption Isotherm was developed in 1803. It is the simplest form of adsorption isotherm and is usually referred to as the linear adsorption isotherm. The surface area of the adsorbate adsorbed onto the surface of the adsorbent is assumed to be proportional to the partial pressure of the injected gas. It is modeled using the equation [40].

$$X = K_H P_p \tag{2}$$

where X is the fraction of the surface of the adsorbent covered, P_p is the partial pressure, and K_H is Henry's adsorption constant, which is equal to:

$$K_H = \lim_{\delta \rightarrow 0} \frac{\delta_s}{\delta(z)} \quad (3)$$

where δ_s is the surface number density, which is the concentration of adsorbate molecules on the surface of the adsorbent, and $\delta(z)$ is the number density at free phase of adsorbate.

Henry's Isotherm is best used to describe the initial stage of the adsorption. It is not fully applicable however in complex adsorption processes, and thus is not the most suitable isotherm to use when modelling CO_2 , or any other gas, adsorption to shale rock surface [41].

3.2 Freundlich isotherm

Freundlich and Kuster developed the first non-linear adsorption isotherm in 1906. It was an empirical formula developed for gas adsorbates. The formula is presented [41].

$$\frac{x}{m} = KP^n \quad (4)$$

where x is the mass of the adsorbate that is adsorbed, m is the total mass of the adsorbent, P is the pressure of the adsorbate, in this case CO_2 gas, and K and n are constants unique to each adsorbate at a specific temperature.

The Freundlich Isotherm has several drawbacks including that it is only applicable for gases, it is an empirical formula, and it does not function properly at high pressures. It can be used to model CO_2 adsorption on shales at very low pressures, but deviates from the true value as the pressure increases, and thus it is not applicable in modeling real field applications since most of them are at relatively high pressures.

3.3 Langmuir isotherm

Langmuir developed the first scientifically based adsorption formula. The formula was developed in 1918 to model gas adsorption on solid surfaces. It was derived based on statistical thermodynamics. The formula is shown [42].

$$K_{ads} = \frac{[AS]}{[A][S]} \quad (5)$$

where K_{ads} is the adsorption equilibrium constant, $[AS]$ represents the adsorbate molecules that have adsorbed to the surface of the adsorbent, $[A]$ represents the adsorbate concentration, and $[S]$ represents the surface of the adsorbent.

Langmuir defined the fraction of adsorption sites on the adsorbent that have been occupied by the adsorbate as θ . The sites that are not occupied can be represented as $[1 - \theta]$. By using these definitions, the following formula is reached [42].

$$\frac{[AS]}{[S]} = \frac{\theta}{1 - \theta} \quad (6)$$

Using the above formula, and the definition of K_{ads} , mentioned previously, the final form of the Langmuir Adsorption Isotherm can be reached. This is shown.

$$\theta = \frac{K_{ads}[A]}{1 + K_{ads}[A]} \quad (7)$$

The Langmuir Adsorption Isotherm has a wide range of applicability, especially that it can be used to model both physisorption and chemisorption. It is one of the most applied isotherms to model CO_2 adsorption to shale rocks. The isotherm does have some drawbacks however, which are manifested in the assumptions made during its development. These assumptions include that the adsorbent has a specific number of sites where the adsorbate can get adsorbed, the adsorption will occur in only one layer, hence the isotherm can only model monolayer adsorption, and the adsorption sites are energetically equivalent and the adsorbed molecules do not interact [43].

3.4 Brunauer–Emmett–Teller isotherm

The Langmuir isotherm assumes monolayer adsorption, which maybe applicable in chemisorption, however, it will deviate from the true solution in physisorption, which takes place between CO_2 and shale, since physisorption involves multi-layer adsorption. The BET Adsorption Isotherm was developed in 1938, and is an improved version of the Langmuir Adsorption Isotherm. BET can account for multi-layer adsorption, which in turn can properly model physisorption. It has been applied by many researchers to model CO_2 adsorption in shale reservoirs, and has proven to be superior to the Langmuir isotherm in many cases. The BET isotherm formula is shown [44].

$$\frac{P_e}{v(P_o - P_e)} = \frac{1}{v_m c} + \frac{c - 1}{v_m c} \frac{P_e}{P_o} \quad (8)$$

where P_e and P_o are the equilibrium and saturation pressures of the adsorbate at the temperature of adsorption, v is the adsorbed gas quantity, v_m is the monolayer adsorbed gas quantity, c is the BET constant equal to:

$$c = \exp\left(\frac{E_1 - E_2}{RT}\right) \quad (9)$$

where E_1 is the heat of adsorption for the first layer, E_2 is the heat of adsorption for the second and higher layers, and is equal to the heat of liquefaction.

The BET isotherm essentially applies the Langmuir isotherm to multiple layers while taking into consideration the difference in adsorption between each layer. The BET is one of the most suited isotherms that can model physisorption, and thus can accurately model CO_2 adsorption to shale. It has two drawbacks however, which include that it assumes that the gas molecules only interact with the adjacent layers, above and beneath it, and it is considered complex to use, compared to the other isotherms [44].

4 Physisorption types

Since physisorption is more complex than chemisorption in terms of forming multi-layers of adsorbate on the adsorbent, several physisorption types have been observed. These types can be grouped into six major divisions based on the behavior of the adsorption quantity at different partial pressures. Relative pressure is defined as the sample pressure divided by the saturation vapor pressure [45]. Using relative pressure allows for the removal of the effect of temperature on the sample change in pressure and thus allows for the creation of an isotherm [46]. Different isotherms will depend on the saturation vapor pressure. The relative pressure ranges from 0 to 1, where a relative pressure of 1 represents a complete saturation, meaning that all adsorption sites available have been occupied by the CO_2 [47, 48]. Based on the properties of the fluid and the rock, the relation between the relative pressure and the adsorption will change. The six main types of physisorption isotherms are shown in Table 1.

5 Adsorption hysteresis

Adsorption hysteresis is the process of adsorption then desorption of the adsorbate on the adsorbent, usually during multi-layer physisorption, due to the capillary condensation in mesopores structures [49]. The four most commonly observed hysteresis loops are shown in Fig. 4. The four loops are usually observed as a sequence of extremity, beginning from H1, which is considered the least extreme, up to H4, which is the most extreme. H2 and H3 are considered intermediates. The desorption branch of the hysteresis loop will take one of the four shales seen in Fig. 4 and is a strong function of the adsorbate rather than the adsorbent, and so in CO_2 adsorption on shale, the desorption will be a strong function of the CO_2 conditions such as temperature, and partial pressure rather than the shale adsorption sites. Type H4 is the most commonly seen

in shale since it is associated with narrow slit-like pores, indicated by micro-porosity [50].

6 Adsorption measurement

Several methods have been applied to measure the adsorption value [51, 52]. The main methods applied include volumetric, gravimetric, volumetric-gravimetric, oscillometry, and impedance spectroscopy. Each of these methods will be explained, and the main advantages and disadvantages of each will be pointed out.

6.1 Volumetric measurement

The volumetric method of measuring adsorption is considered one of the simplest, yet effective methods of measuring adsorption in terms of the mechanism [53]. The mechanism is based on Boyles Volumetric Gas Expansion law [54]. An illustration of the setup for volumetric adsorption measurement is shown in Fig. 5.

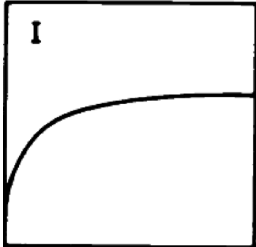
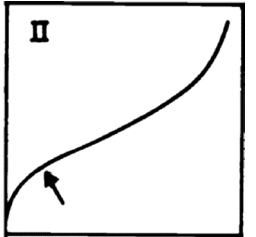
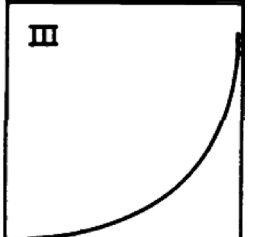
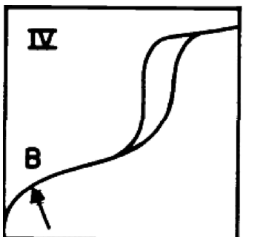
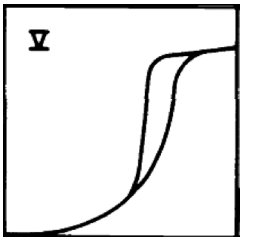
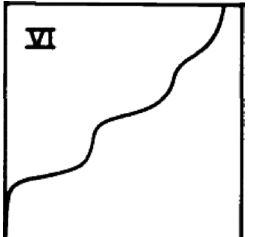
The volumetric adsorption apparatus is composed of a reference cell, where the adsorbate, CO_2 , is initially pressurized, and heated to the design conditions. The sample cell contains the adsorbate sample, shale, and is connected to the reference cell and separated via a high pressure valve. The reference cell should be smaller in volume than the sample cell to allow sufficient gas expansion to be observed; this will help reduce the difficulty in observing the equilibrium pressure. Once both cells are ready, and the CO_2 in the reference cell is pressurized and heated, the valve is opened and the gas is allowed to expand. Once the equilibrium pressure is reached, the adsorption value can be calculated. The volumetric method has several advantages that make it a widely used method, however, it also has some major disadvantages that must be noted and accounted for when using this method to avoid error in the adsorption value. The main advantages and disadvantages of the volumetric method are presented in Table 2.

6.2 Gravimetric measurement

The gravimetric method to measure adsorption is based on mass rather than pressure. Using the microbalance, the difference in mass can indicate the amount of gas that has adsorbed to the shale [55]. The setup is nearly identical to the volumetric setup, with the only difference being that the pressure transducers are replaced with the microbalance. An illustration of the gravimetric adsorption measurement setup is shown in Fig. 6.

The gravimetric adsorption measurement method has many advantages [56, 57], and also has some major drawbacks both of which should be known before conducting

Table 1 Physisorption isotherm types [49]

| Physisorption isotherm type | Description | Chart |
|-----------------------------|--|---|
| Type I | Type I isotherms are usually observed in solids with micro-pores, with relatively small external surfaces, activated carbons, and zeolites. The main adsorption limiting factor is the accessibility of the micro-pores rather than the surface area |  |
| Type II | Type II isotherm represents both mono and multi-layer adsorption. The arrow in the plot points to the pressure at which multi-layer adsorption will commence. It is the normal isotherm obtained for both micro and macro porous adsorbents |  |
| Type III | Type III is most noticeable for its convex shape which makes it difficult to determine the transition between mono and multi-layer adsorption. It is not very common, especially for shale reservoirs |  |
| Type IV | Type IV is mostly characterized by its hysteresis loop which occurs due to the adsorbate condensation in mesopores. It is not very common in shale reservoirs, and is only noticeable for a limited number of adsorbates |  |
| Type V | Type V is another form of Type III which is only observed for a very limited number of adsorbents. It is considered the least observed type |  |
| Type VI | Type VI represents stepwise multi-layer adsorption, where the steepness of the steps depends on the temperature of the experiment. This is usually observed for noble gases such as krypton and argon |  |

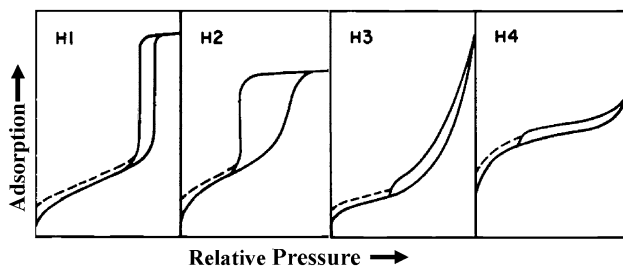


Fig. 4 Types of physisorption hysteresis behavior [49]

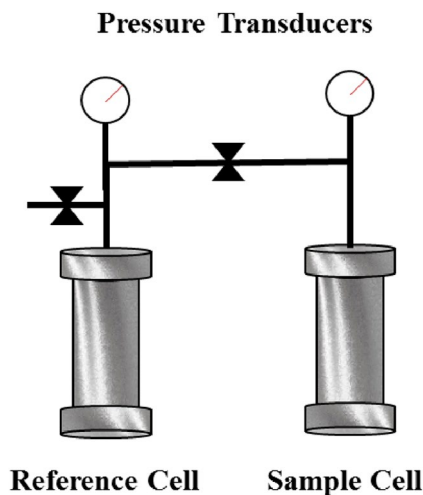


Fig. 5 Illustration of volumetric adsorption apparatus

the experiment to avoid errors. The advantages and disadvantages of the gravimetric adsorption method are presented in Table 3.

6.3 Volumetric–gravimetric measurement

Since both the volumetric and the gravimetric adsorption measurement methods have some advantages and

disadvantages, combining both to measure adsorption was performed in order to overcome some of the disadvantages. This was referred to as the volumetric-gravimetric method [56]. An illustration of the setup used to conduct the volumetric-gravimetric adsorption measurements is shown in Fig. 7.

The setup is a combination of both the volumetric and the gravimetric adsorption setups, explained previously. The volumetric adsorption setup is connected to a microbalance, and hence both the pressure difference and the weight change can be recorded. The main advantage of this setup is the extremely high accuracy since both the pressure change and weight change results can be compared. The disadvantages of the setup are the high complexity of the new setup due to the presence of both the pressure transducers and the microbalance, and the large volume of adsorbent, shale, needed since the volumetric measurement of the setup will be inaccurate without a large volume [56].

6.4 Oscillometry measurement

Oscillometry adsorption measurement is based on the oscillation of the sample cell, which results in a beam distortion which can be used to measure adsorption. An illustration of the setup is shown in Fig. 8. The setup consists of an oscillating disk filled with the adsorbent, shale. The disk is fixed to a torsional wire and is stabilized by a steam beneath it. At the bottom of the stem, a small mirror is fixed. A laser beam is directed to the mirror as the oscillating disk is rotating. The beam is reflected via the mirror, and based on the angle of the oscillating disk, the reflection of the laser beam will create two angles, referred to as α_1 and α_2 . The reflected beams are received by the diodes which produce electric signals of opposite signs, and hence the time when the reflected beam is crossing the area between the two diodes can be detected very accurately. The oscillation of the pendulum will produce several time signals which will be used to calculate angular

Table 2 Volumetric adsorption method advantages and disadvantages

| Advantages | Disadvantages |
|--|--|
| Simple concept: Volumetric gas adsorption setups are very simple compared to the other methods and do not require complex equipment to give accurate results | Volume of adsorbent: The volume of shale needed to conduct the adsorption experiments using the volumetric method is much larger than that needed in the other measurement methods. At least several grams are needed for accurate measurements to be obtained |
| Apparatus and measurement: As long as the pressure transducers are calibrated accurately, the measurements become very simple to conduct | Equilibrium indication: CO ₂ adsorption can last for seconds, minutes, hours, or even days in some cases. The pressure equilibrium can sometimes be very difficult to observe and can sometimes be misleading which may lead to erroneous results |
| | Cell wall adsorption: The CO ₂ may adsorb to the wall of the reference cell or the sample cell which may result in some errors in the adsorption value. This may be overcome however during the adsorption calculation; this will be explained in the calculation section |

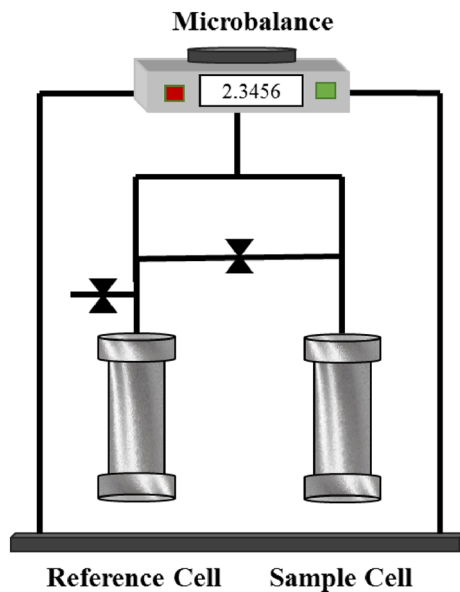


Fig. 6 Illustration of gravimetric adsorption apparatus

frequency and logarithmic decrement, using a Gaussian Minimization procedure. This can then be used to measure the adsorption value [56].

The main advantage of using the oscillometry method to measure adsorption is the measuring apparatus since it allows for the determination of both the total mass of the adsorbent and the adsorbate without using helium method. The oscillometry does have some disadvantages as well. The advantages and disadvantages of the oscillometry adsorption method are summarized in Table 4.

6.5 Impedance spectroscopy

When a weakly electric material, such as shale, is exposed to a static or alternating electric field, the molecular state of the material is changed. The nuclei of the atoms or the

molecules are shifted in the direction of the electric field, whereas the electrons are moved in the opposite direction, hence dipole moments are created. The sum of the dipole moments in the material are referred to as the dielectric polarization of the material and can be measured using impedance [56]. By applying oscillating electric field, specific impedance curves can be obtained, which are unique to different materials. A molecular interpretation of the curves can be used to quantify the adsorption value. An illustration of the setup is shown in Fig. 9.

The main advantages of using the impedance spectroscopy adsorption measurements and the main disadvantages of using this method are presented in Table 5 in order to avoid error when measuring adsorption using this method.

7 Volumetric adsorption calculations

Calculation of the adsorption value takes place after the experiment has been conducted. Since there are several methods to conduct the adsorption experiments as shown above, there are multiple equations that are applied based on the results obtained using the experimental method. For example, if the volumetric method is used, the equilibrium value obtained will be a pressure reading and so the input to the equations must be a pressure reading in order to obtain the adsorption value, however, if the impedance spectroscopy experimental method is used, an impedance value will be input to a different equation to obtain the adsorption value. Since this research is focused on CO₂ adsorption to shale rocks, the equations explained will be related to the volumetric method, since this is the most widely used adsorption measurement technique for CO₂ adsorption to shale [58–60]. There are two main methods used to perform the adsorption calculation for the volumetric experimental method including the absolute

Table 3 Gravimetric adsorption method advantages and disadvantages

| Advantages | Disadvantages |
|---|---|
| Accuracy: The microbalances used for the gravimetric adsorption measurements are usually extremely accurate | Complexity: Microbalances are much more complex in terms of usage compared to the volumetric setup |
| Volume of Adsorbent: A few milligrams of shale can be used to obtain extremely accurate results using the gravimetric method | |
| Cell Wall Adsorption: Wall adsorption does not pose a problem during gravimetric adsorption measurement since mass balance of the gas is not part of the calculation. It will be a problem however during multicomponent adsorption | Measurement: The setup requires recording of many parameters such as pressure, temperature, concentration, and also several calibrations are needed which adds to the complexity of the measurement |
| Adsorption Kinetics: Modern microbalances can record the kinetics of adsorption even if they are very fast or slow since they can record every tenth of a second in some cases | |

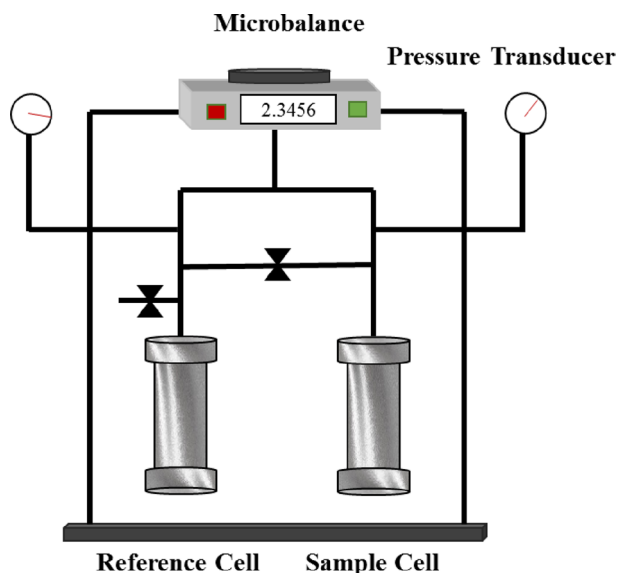


Fig. 7 Illustration of volumetric-gravimetric adsorption apparatus

adsorption calculation, and the Gibbs adsorption calculation, both of which will be explained [61].

Generally, adsorption is a function of the adsorbent, which is the shale, the adsorbate, which is the CO₂, and the volume of the CO₂ adsorbed. The general adsorption equation is shown.

$$V_{total} = V_{solid} + V_{gas} + V_{ads} \tag{10}$$

where V_{total} is the total volume of the system, V_{solid} is the volume of the shale in the sample cell, V_{gas} is the volume of the CO₂ injected, and V_{ads} is the volume of the CO₂ adsorbed.

When the shale sample is placed in the sample cell, the shale grains will not fill up the whole cell since some voids will remain between the grains. It is crucial that these void spaces are measured since the total volume of the adsorbent and the adsorbate will be incorrect if the void space is not measured. The general definition of the void space is given as:

$$V_{void} = V_{gas} + V_{ads} = V_{total} - V_{solid} \tag{11}$$

where V_{void} is the void space volume. The void space is usually measured before the adsorption experiment and a gas with very low adsorption potential is used, usually helium. The void space is calculated based on the pressure, temperature, compressibility, and volume of the gas in the pump and the cell. The equation for the void space is shown [61].

$$V_{void} = \frac{\left(\frac{P_h \Delta V}{zT}\right)_{pump}}{\left(\frac{P_2}{z_2 T} - \frac{P_1}{z_1 T}\right)_{cell}} \tag{12}$$

where P_h is the pressure of the helium in the pump, ΔV is the change in volume of the helium between the pump and the cells, P_2 and P_1 are the pressure of the helium after and before expansion respectively, z_1 and z_2 are the

Fig. 8 Illustration of oscillometry adsorption apparatus

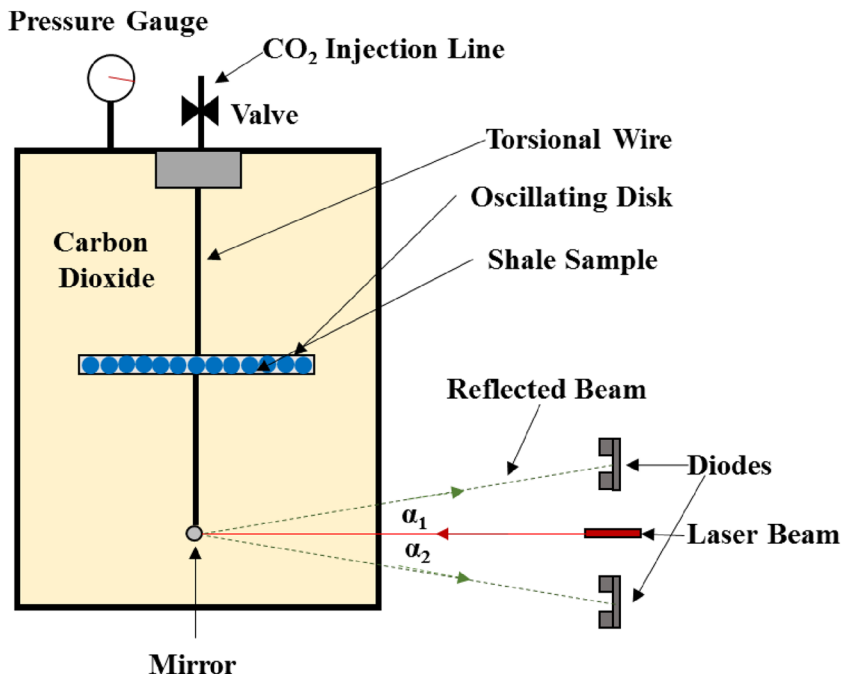


Table 4 Oscillometry adsorption method advantages and disadvantages

| Advantages | Disadvantages |
|---|--|
| Measuring apparatus: Allows for accurate the determination of both the total mass of the adsorbent and the adsorbate without using helium method. | Calibration: The torsional wire is severely affected by temperature and thus should be calibrated constantly to avoid errors in the reading, or the material should be heat resistant. Pendulum material: The pendulum must be made of high durability material that will not be affected or affect the laser beam Pressure limitation: The oscillometry method is not accurate at low pressures and thus should not be used at these conditions Duration of experiment: The experiment will sometimes take a few weeks to undergo, which makes it extremely time consuming compared to the few hours, or at most few days needed using the volumetric or gravimetric methods |

Fig. 9 Illustration of impedance adsorption apparatus

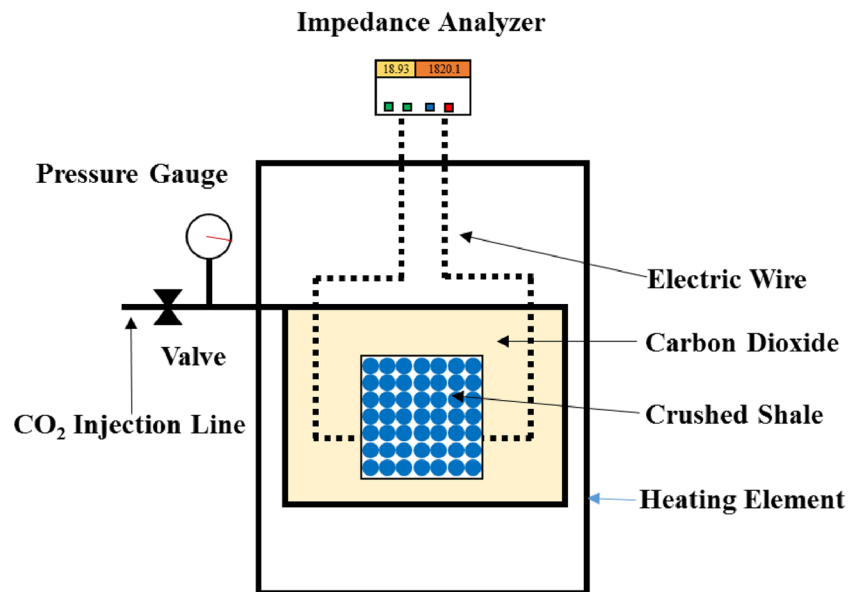


Table 5 Impedance spectroscopy adsorption method advantages and disadvantages

| Advantages | Disadvantages |
|--|---|
| Measuring Apparatus: Dielectric impedance measurements are very easily performed and can yield accurate results even under extreme pressure and temperature conditions Kinetics Observation: Impedance measurements can detect internal changes and chemical processes which cannot be observed using volumetric or gravimetric methods Versatility: In addition to measuring adsorption, impedance can be used to characterize the adsorbent material | Adsorbent Material: Only dielectric or weakly electric conducting material can be used since materials that can conduct electricity easily will heat up, which may cause problems Frequency Spectrum: A broad range of frequency is needed, which results in longer durations and more complex measurements Molecular Interpretation: Interpretation of the impedance measurements and curves can be extremely tedious and thus the other methods are usually preferred over it |

compressibility of the helium before and after expansion, and T is the temperature of the cells.

After calculating the void space, the CO₂ adsorption can be calculated based on the total volume injected

and the total volume unadsorbed based on the number of moles using the following equation.

Table 6 Main sources of error in volumetric adsorption determination

| Source of error | Explanation |
|----------------------|---|
| Volume adsorbed | Some calculations assume no helium adsorption, which could result in an error if the application requires accounting for this adsorption, and thus, if helium adsorption will impact the application, the Gibbs adsorption should be used |
| Volume injected | The volume of CO ₂ injected should be calculated based on the volumes of the cells and the compressibility values, rather than depending on the injected volume on the pump, since it does not always reflect the correct value of injected CO ₂ |
| Density of adsorbate | The density of the adsorbate is affected by many conditions including temperature, pressure, and compressibility. Although it is easy to obtain the density even with change in pressure and temperature, the compressibility factor is somewhat confusing and is usually assumed or obtained using correlation, which results in an error in the adsorption value. Caution should be taken when using a specific adsorption value and when calculating the value. Also, specific correlations will work for some gasses but not others |
| Temperature change | Changing the temperature will affect both the overall adsorption, and the gas itself. The gas will begin to expand which will make it extremely difficult to observe the equilibrium value, since the pressure will increase with time. To avoid this, the CO ₂ should be preheated to the required temperature along with the whole setup to avoid gas expansion after the experiment has commenced |
| Cell's volume | Both the reference cell and the sample cell volumes must be known since they are imperative in the calculations. Any dead volume must be accounted for in the calculations, including the connections, extra volume in the sample cell, and the volume within the fittings and valves |

$$n_{ads} = n_{inj} - n_{unads} \quad (13)$$

where n_{ads} is the number of moles of CO₂ adsorbed to the shale, n_{inj} is the total number of moles of CO₂ injected, and n_{unads} is the number of moles of CO₂ that were not adsorbed.

For both the absolute and the Gibbs calculation methods, the number of moles of CO₂ injected is agreed upon, and is calculated as follows.

$$n_{inj} = \left(\frac{P\Delta V}{zRT} \right)_{pump} \quad (14)$$

Where R is the universal gas constant, equal to 8.314 J/mol·K.

The difference between the absolute and the Gibbs adsorption value is mainly in the number of moles of CO₂ that are unadsorbed. This difference will be indicated when explaining each calculation method and its principles.

7.1 Gibbs adsorption

Gibbs adsorption calculation neglects the volume occupied by the adsorbed phase when calculating the volume of unadsorbed gas. The adsorbed CO₂ on the shale rock will occupy some volume in the sample cell, and thus will affect the value of the unadsorbed CO₂ volume calculated. The Gibbs calculation assumes that the volume occupied by the adsorbed CO₂ is not occupied. This will result in some error in the adsorption capacity calculation. The equation for the Gibbs adsorption is shown [19].

$$n_{ads}^{Gibbs} = n_{total} - V_{void}\rho_{gas} \quad (15)$$

7.2 Absolute adsorption

Absolute adsorption takes into consideration the volume occupied by the adsorbed phase when the unadsorbed volume is calculated. The volume occupied by the adsorbed CO₂ on the shale surface will affect the remaining volume that can be occupied by the unadsorbed CO₂, which shows that the absolute adsorption will yield much more realistic results compared to the Gibbs volume [61]. The number of moles of CO₂ adsorbed therefore becomes as follows.

$$n_{ads}^{abs} = n_{total} - V_{gas}\rho_{gas} \quad (16)$$

8 Main sources of error in volumetric adsorption determination

When measuring and calculating the adsorption value, several common errors have been made which will affect the adsorption quantity severely. These errors are extremely commonplace and have been noticed amongst many researchers. In this section, this research summarizes the main errors that are associated with the adsorption calculation using the volumetric adsorption method, especially for CO₂ adsorption, and explains the error and how to avoid it. The main errors are presented in Table 6 [13, 56, 62, 63].

9 Conclusions

During the application of CO₂ injection in unconventional shale reservoirs, CO₂ adsorption is an imperative factor that will impact enhanced oil recovery potential, and CO₂ storage capacity. This research provides a roadmap to the different types of adsorption and adsorption isotherms and measurement techniques to function as a guideline for the accurate application of experimental CO₂ adsorption in shale reservoirs. The main conclusions obtained from this research are summarized below.

- Adsorption is a function of both the adsorbate and the adsorbent. This shows that in order to properly study CO₂ adsorption to shale, both the CO₂ and shale properties should be considered.
- The most applicable isotherm to model CO₂ adsorption to shale is the BET since it overcomes the limitations of the Langmuir isotherm.
- Adsorption hysteresis is extremely important since it can give an indication of the adsorption–desorption cycle and thus can hint to the actual capacity of CO₂ that can be stored.
- The most common experimental methods used to measure adsorption are the volumetric and the gravimetric methods due to their simplicity and high accuracy as long as they are conducted properly.
- Different adsorption methods will have different sources of error. Each method must therefore be studied thoroughly in order to avoid conducting errors that may impact the accuracy of the results.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

References

1. Al Ismail MI et al (2014) The effect of CO₂ adsorption on permeability anisotropy in the eagle ford shale. Unconv Resour Technol Conf. <https://doi.org/10.15530/URTEC-2014-1921520>
2. Liu Q et al (2018) Macroscale mechanical and microscale structural changes in chinese wufeng shale with supercritical carbon dioxide fracturing. Soc Pet Eng. <https://doi.org/10.2118/181369-PA>
3. Meng X et al (2017) Experimental and numerical study of enhanced condensate recovery by gas injection in shale gas-condensate reservoirs. Soc Pet Eng. <https://doi.org/10.2118/183645-PA>
4. Reynolds MM, Buendia J (2017) Permanently sequester anthropogenic carbon dioxide—through hydraulic fracturing. Soc Pet Eng. <https://doi.org/10.2118/185033-MS>
5. Kang SM et al (2011) Carbon dioxide storage capacity of organic-rich shales. Soc Pet Eng. <https://doi.org/10.2118/134583-PA>
6. Ibrahim AF, Nasr-El-Din HA (2015) Carbon dioxide sequestration in coal formations. Int Pet Technol Conf. <https://doi.org/10.2523/IPTC-18278-MS>
7. Khaleel, M. et al., 2018. Amine-functionalized hierarchical zeolites for carbon dioxide capture. Society of Exploration Geophysicists
8. Golshahi N et al (2019) Asphaltene structural changes induced by carbon dioxide injection. Offshore Technol Conf. <https://doi.org/10.4043/29730-MS>
9. Jin Z, Firoozabadi A (2016) Thermodynamic modeling of phase behavior in shale media. Soc Pet Eng. <https://doi.org/10.2118/176015-PA>
10. Orr FM (2004) Storage of carbon dioxide in geologic formations. Soc Pet Eng. <https://doi.org/10.2118/88842-JPT>
11. Hall FE et al (1994) Adsorption of pure methane, nitrogen, and carbon dioxide and their binary mixtures on wet fruitland coal. Soc Pet Eng. <https://doi.org/10.2118/29194-MS>
12. Kazemi M, Takbiri-Borujeni A (2016) Molecular dynamics study of carbon dioxide storage in carbon-based organic nanopores. Soc Pet Eng. <https://doi.org/10.2118/181705-MS>
13. Mohammad S et al (2009) Experimental uncertainties in volumetric methods for measuring equilibrium adsorption. Energy Fuels 23:2810–2820. <https://doi.org/10.1021/ef8011257>
14. Bahadori A, Vuthaluru H (2010) Rapid prediction of carbon dioxide adsorption isotherms for molecular sieves using simple correlation. Soc Pet Eng. <https://doi.org/10.2118/122882-PA>
15. Clarkson CR, Haghshenas B (2013) Modeling of supercritical fluid adsorption on organic-rich shales and coal. Soc Pet Eng. <https://doi.org/10.2118/164532-MS>
16. Yu W et al (2016) Modeling gas adsorption in marcellus shale with langmuir and BET isotherms. Soc Pet Eng. <https://doi.org/10.2118/170801-PA>
17. Psarras P et al (2017) Methane and CO₂ adsorption capacities of kerogen in the eagle ford shale from molecular simulation. Acc Chem Res. <https://doi.org/10.1021/acs.accounts.7b00003>
18. Le TD et al (2017) A new matrix/fracture multiscale coupled model for flow in shale-gas reservoirs. Soc Pet Eng. <https://doi.org/10.2118/181750-PA>
19. Sudibandriyo M et al (2003) Adsorption of methane, nitrogen, carbon dioxide, and their binary mixtures on dry activated carbon at 318.2 K and pressures up to 13.6 MPa. Langmuir 19(13):5323–5331. <https://doi.org/10.1021/la020976k>
20. Lafortune S et al (2014) Assessing CO₂ adsorption capacities onto shales through gravimetric experiments: a first step in the feasibility study of coupling “Fracking” with carbon storage. Energy Proc 63(5933–5937):1876–6102. <https://doi.org/10.1016/j.egypro.2014.11.629>
21. Luo X et al (2015) Adsorption of methane, carbon dioxide and their binary mixtures on Jurassic shale from the Qaidam Basin in China. Int J Coal Geol 150–151:210–223. <https://doi.org/10.1016/j.coal.2015.09.004>
22. Yuan H et al. (2017) Investigation on gas-adsorption-induced swelling and permeability evolutions of cox argillite. In: 23ème Congrès Français de Mécanique, France
23. Lu M et al (2017) A new method for the estimation of lost gas during the measurement of the gas content of coal. Soc Pet Eng. <https://doi.org/10.2118/176976-PA>

24. Perez F, Devegowda D (2017) Methane and carbon dioxide adsorption in kerogen models using molecular simulations, Mewbourne School of Petroleum and Geological Engineering, The University of Oklahoma, Norman
25. Bouzgarrou S et al (2015) Experimental adsorption and modelisation of CO₂ on adsorbents collected from Elborma field in South Tunisia. *J Surf Eng Mater Adv Technol* 5:52–63. <https://doi.org/10.4236/jsemat.2015.51006>
26. Kecheng Z et al (2019) Molecular simulation of carbon dioxide and methane adsorption in shale organic nanopores. *Energy Fuels* 33(3):1785–1796. <https://doi.org/10.1021/acs.energyfuels.8b02851>
27. Al-Mutarreb AM et al. (2018) The influence of shales characteristics on CO₂ adsorption behaviour under sub-critical conditions. IOP conference series: earth and environmental science. Doi: <https://doi.org/10.1088/1755-1315/164/1/012031>
28. Chareonsuppanimit P et al (2012) High-pressure adsorption of gases on shales: measurements and modeling. *Int J Coal Geol* 95:34–46. <https://doi.org/10.1016/j.coal.2012.02.005>
29. Heller R, Zoback M (2014) Adsorption of methane and carbon dioxide on gas shale and pure mineral samples. *J Unconv Oil Gas Resour* 8:14–24. <https://doi.org/10.1016/j.juogr.2014.06.001>
30. Zhang P (2016) Adsorption and desorption isotherms. Kere-Search Group, Portland
31. Eliebid M et al (2017) Adsorption role in shale gas recovery and the feasibility of CO₂ in shale enhanced gas recovery: a study on shale gas from Saudi Arabia. *Soc Pet Eng*. <https://doi.org/10.2118/187667-MS>
32. Manju M, Joewondo P (2014) CO₂ sorption capacity in clay-rich shales with moisture content. In: 14th Greenhouse gas control technologies conference Melbourne 21–26 October (GHGT-14). SSRN: <https://ssrn.com/abstract=3365692>
33. Ngo T (2015) Reservoir capacity estimates in shale plays based on experimental adsorption data. Masters Thesis
34. Lutynski M et al (2017) CO₂ sorption of Pomeranian gas bearing shales—the effect of clay minerals. *Energy Proc* 125:457–466. <https://doi.org/10.1016/j.egypro.2017.08.153>
35. Clarkson CR (2003) Application of a new multicomponent gas adsorption model to coal gas adsorption systems. *Soc Pet Eng*. <https://doi.org/10.2118/78146-PA>
36. Aljamaan H et al (2017) Multiscale imaging of gas adsorption in shales. *Soc Pet Eng*. <https://doi.org/10.2118/185054-MS>
37. Sathre R, Masanet E (2013) Prospective life-cycle modeling of a carbon capture and storage system using metal-organic frameworks for CO₂ capture. *RSC Adv* 3:4964–4975
38. Jedli H et al (2017) Carbon dioxide adsorption isotherm study on various cap rocks in a batch reactor for CO₂ sequestration processes. *Appl Clay Sci* 136(199–207):0169–1317. <https://doi.org/10.1016/j.clay.2016.11.022>
39. Chen G et al (2016) Research of CO₂ and N₂ adsorption behavior in K-illite slit pores by GCMC method. *J Sci Rep* 6:37579. <https://doi.org/10.1038/srep37579>
40. Henry W (1803) Experiments on the quantity of gases absorbed by water, at different temperature and under different pressures. *Philos Trans R Soc Lond* 93:29–42
41. Foo KY, Hameed BH (2010) Insights into the modeling of adsorption isotherm systems. *Chem Eng J* 156:2–10. <https://doi.org/10.1016/j.cej.2009.09.013>
42. Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica, and platinum. *J Am Chem Soc* 40(9):1361–1403. <https://doi.org/10.1021/ja02242a004>
43. Czepirski L et al (2000) Some generalization of langmuir adsorption isotherm. *Internet J Chem* 3:14
44. Brunauer S et al (1938) Adsorption of gases in multimolecular layer. *J Am Chem Soc* 60(2):309–319. <https://doi.org/10.1021/ja01269a023>
45. Ehrburger-Dolle F (1999) A new way to analyze adsorption isotherms. *Langmuir* 15(18):6004–6015. <https://doi.org/10.1021/la981349r>
46. Cook M, Douglas H (1949) Extrapolation of adsorption isotherms to high relative pressures and the determination of the surface pressure of adsorbed films on solids. *J Am Chem Soc* 71(3):791–797. <https://doi.org/10.1021/ja01171a009>
47. Van Dongen RH et al (1971) Physical adsorption at high relative pressures. *Surf Sci* 28(1):237–257. [https://doi.org/10.1016/0039-6028\(71\)90097-5](https://doi.org/10.1016/0039-6028(71)90097-5)
48. Brown T et al (2019) Pressure-varying Langmuir parameters and stepped nitrogen adsorption on alumina and silica. *Phys Chem J R Soc Chem* 21:2558–2566
49. Sing, K., 1984. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. International Union of Pure and Applied Chemistry, Physical Chemistry Division, Commission on Colloid and Surface Chemistry Including Catalysis
50. Thommes M et al (2015) Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC technical report). *J Pure Appl Chem* 87:1–19
51. Zhao H et al (2017) Sorption hysteresis of light hydrocarbons and carbon dioxide in shale and kerogen. *Sci Res*. <https://doi.org/10.1038/s41598-017-13123-7>
52. Shi J et al (2019) Competitive adsorption phenomenon in shale gas displacement processes. *RSC Adv* 2019(9):25326–25335. <https://doi.org/10.1039/C9RA04963K>
53. Santos JM, Akkutlu IY (2013) Laboratory measurement of sorption isotherm under confining stress with pore-volume effects. *Soc Pet Eng*. <https://doi.org/10.2118/162595-PA>
54. Rani S et al (2015) Comparison of void volume for volumetric adsorption studies on shale from India. *J Nat Gas Sci Eng* 26:725–729. <https://doi.org/10.1016/j.jngse.2015.07.012>
55. Fuji T et al (2015) Evaluation of CO₂ sorption capacity of rocks using a gravimetric method for CO₂ geological sequestration. *Energy Proc* 1(1):3723–3730. <https://doi.org/10.1016/j.egypro.2009.02>
56. Keller J, Staudt R (2005) Gas adsorption equilibria, experimental methods and adsorptive isotherms. Springer Science, Berlin
57. Yang S et al (2016) Effects of multicomponent adsorption on enhanced shale reservoir recovery by CO₂ injection coupled with reservoir geomechanics. *Soc Pet Eng*. <https://doi.org/10.2118/180208-MS>
58. Smit B et al (2014) Introduction to carbon capture and sequestration. Imperial College Press, London
59. Yanian Z et al (2015) Study on controlling factors of shale gas adsorption. *Acta Geol Sin* 89:300–301
60. Tajnik T et al (2013) Investigation of adsorption properties of geological materials for CO₂ storage. *Int J Energy Res* 37:952–958. <https://doi.org/10.1002/er.2901>
61. Charoensuppanimit P et al (2016) Measurement and modeling of gas adsorption on shales. *Energy Fuels* 30(3):2309–2319. <https://doi.org/10.1021/acs.energyfuels.5b02751>
62. Mohagheghian E et al (2015) Carbon dioxide compressibility factor determination using a robust intelligent method. *J Supercrit Fluids* 101(140–149):0896–8446. <https://doi.org/10.1016/j.supflu.2015.03.014>
63. Gasparik M et al (2015) High-pressure/high-temperature methane sorption measurements on carbonaceous shales by the manometric method: experimental and data-evaluation considerations for improved accuracy. *Soc Pet Eng*. <https://doi.org/10.2118/174543-PA>

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