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Petrophysical and Geo-mechanical Study of CO_2-Enhanced Gas Recovery and CO_2 Storage in Shales: A Critical Review

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Abstract

This paper comprehensively reviews the role of geomechanical and petrophysical studies in CO_2-enhanced gas recovery and/or CO_2 storage following CO_2 injection in shale gas reservoirs. In order to achieve CO_2-enhanced gas recovery (CO_2-EGR) from shale reservoirs and/or CO_2 storage in shale reservoirs, numerical models and designs rely on an effective appraisal of the target reservoir. This paper analysed the geomechanical and petrophysical characteristics that were taken into account while constructing models for a successful CO_2-EGR, in addition to examining assessments of shale reservoirs undertaken in diverse fields of research. The factors were weighted based on their importance in distinct shale reservoir settings. Natural fracture system, fracture conductivity, hydraulic fracture half-length, unconfined compressive strength (UCS), Young's modulus, Poisson's ratio, and other geo-mechanical and petro-physical parameters are important throughout the entire process, which also includes CO_2 injection, residual hydrocarbon mobilisation, variations in stress and strain during hydrocarbon production, and the subsequent impact on fracture network conductivity. This research will also give recommendations on how to improve the previously described geomechanical and petrophysical characteristics in order to achieve effective CO_2-enhanced gas recovery and/or CO_2 storage in shale gas reservoirs. The energy sector's goal is to continue employing unconventional resources to provide sustainable energy. As a result, this review study will contribute significantly to our understanding of how to reduce subsurface failure in CO_2-EGR fracturing and injection, as well as refracturing and CO_2 injection in depleted shale gas reservoirs for CO_2 storage.

Keywords: CO_2, EGR, Shale gas, adsorption.

1. Introduction

The concept of geological CO_2 storage has piqued the curiosity of many people since it presents a novel method for mitigating climate change [1-2]. CO_2 injection is one of the storage mechanisms in unconventional sources, such as shale gas reservoirs, where rapid expansion is expected due to the dynamism of shale gas plays [3-5]. This mechanism provides a two-pronged approach to CO_2 management by constructing a physical infrastructure for storing CO_2 absorbed from the atmosphere and providing an enhanced gas recovery option in shale gas production [4-8]. Due to the depletion of existing reservoirs, shale gas deposits are being widely explored and characterised as a prospective substitute for the provision of cleaner energy sources [9-12]. Despite the unconventional source's potential for global supply, studies have indicated that estimated ultimate recovery of shale gases is only realistic in the early life of the well [13]. The drop in output, which could be attributed to changes in the bulk matrix of

shale gas reservoirs, has necessitated the development of more effective and long-lasting gas recovery methods [11].

Methane (CH_4) is retained on the surfaces of gas shale as well as inside the micro- and mega-pores of the shale matrix, according to molecular research [5,14,16-17]. The poor permeability of shale reservoirs, however, limits the effectiveness of standard gas flooding approaches to boost recovery [18-19]. Carbon dioxide (CO_2) is preferentially adsorbed onto organic materials, dislodging methane at a ratio of up to 5:1 per molecule, according to experimental and theoretical studies. According to Cipolla *et al.* [14], this study provides a novel technique to carbon capture, utilisation, and storage (CCUS). CO_2 can potentially be held in gas shales, perhaps enhancing gas recovery (EGR). CO_2 is trapped in the shale gas reservoir through a series of mechanisms, including gas adsorption (CO_2 is adsorbed by organic matter and clay minerals in the shale matrix), residual trapping (CO_2 is trapped in pore spaces by capillary forces), and solubility trapping (CO_2 is dissolved into the brine). These three CO_2 trapping methods interact and compete with one another depending on the circumstances, while each makes a specific contribution to CO_2 storage.

Many researchers have looked into CO_2 storage and enhanced gas recovery (EGR) in shale gas deposits. The essential idea of CO_2-EGR is based on the selective adsorption of injected gas and the release of native natural gas from the organic matrix of the formation. Eshkalak *et al.* [20] investigated CO_2 flooding and the puff and puff approach in order to establish the most practical CO_2-EGR injection method. They came to the conclusion that the huff and puff injection scenario could not be used to achieve CO_2-EGR. The viability of the huff and puff injection scenario, according to Kim *et al.* [13]], is dependent on fracture conductivity and well spacing. To comprehend the dynamics of CO_2-EGR, they investigated geomechanical mechanisms and multi-component transport. They created a simulation model based on Barnett shale data and compared it to models from the Marcellus and New Albany shale formations, which have different reservoir features. Their findings show that CO_2 flooding and huff and puff injection increase CH_4 generation by 24% and 6%, respectively, as compared to no injection. The injected CO_2 was stored as follows at the end of the simulation time: 42% as free gas, 55% as adsorbed gas, and 3% as dissolved gas. They also highlighted that fracture permeability, hydraulic fracture half-length, well spacing, and Langmuir constants all had an impact on EGR and CO_2 storage. Liu *et al.* [12] used reservoir models of the Devonian and Mississippian New Albany Shale gas play to investigate CO_2 storage with EGR. According to their findings, gas adsorption, as the major method of storage, efficiently sequesters around 95% of the CO_2 introduced. Fathi and Akkutlu [21] simulated multi-component transport of CO_2 and CH_4 in shale reservoirs under huff and puff circumstances, accounting for the impacts of adsorption and competitive transport in the organic micropores of the shale during CO_2 injection. While several physical processes connected with CO_2 injection have been studied, the primary focus of this research will be on multicomponent transport and geomechanics during primary recovery and CO_2 injection. We will also address the repercussions of other physical processes, such as stress-dependent compaction, dissolution, multicomponent adsorption, and molecular diffusion.

2. Numerical simulations and theoretical concepts

Several research have evaluated the effectiveness of CO_2 EGR processes using compositional simulations and numerical modelling with the CMG-GEM software [12-13, 20]. Furthermore, CMG-CMOST has been applied to model development's history-matching needs [22]. The Computer Modelling Group (CMG) has developed a sophisticated general equation-of-state compositional simulator that may be used to simulate flows, chemical equilibria of aqueous processes, and mineral dissolution and precipitation kinetics [22-23]. According to Nghiem *et al.* [23], the modelling approach can also be used to mimic CO_2 sequestration processes at the field scale. It also discusses CO_2 migration (both gaseous and aqueous), dissociation, and solid mineralization.

2.1. Competitive multi-component adsorption

Multi-component adsorption has been recognised as the basic method of CO_2 storage and plays an important role in the CO_2 EGR process because CO_2 adsorbs more readily than CH_4 in shale gas reserves [3,24].

Shales containing kerogen, an organic-rich substance, can absorb and store a significant amount of gas (20-80%) [12,25]. However, some study suggests that CH_4 adsorption contributes for 5-30% of total gas production in shale reservoirs [14,26-27].

Estimation of gas adsorption in reservoir simulations has been previously and widely estimated using the Langmuir adsorption model (Eqn 1). This model, however, is only applicable to single component flow system [28]). Therefore, estimation of competitive multi-component adsorption/desorption in reservoir simulations can be done using the extended multi-component Langmuir isotherm as proposed by Yang [29]. The Langmuir adsorption model is given as;

$$n_a = \frac{n_0 P}{P_L + P} \qquad (1)$$

where, n_a is the adsorbed amount; n_o is the maximum adsorption amount; P is the pressure; P_L is the Langmuir pressure at which n_a is half of n_o.

For a competitive multi-component adsorption/desorption system, the adsorption amount of component i, is calculated using an Extended Langmuir model as presented in Eqn. 2. The thermo-dynamical correctness of this model is often uncertain [30] but seems to output a predicting result similar to those designed on a rigorous thermo-dynamical basis [31]. Pan [31] stated that the simplicity in the use of this model has made it the most ideal model for combination with other reservoir simulators in the estimation of the effects of multi-component adsorption. The extended Langmuir model is given as;

$$\omega_i = \frac{\omega_{i,max} B_i y_{ig} p}{1 + p \sum_j B_i y_{ig}} \qquad (2)$$

where, ω_i: the amount of adsorbed component i in the mixing gas, expressed in moles per unit mass of rock; $\omega_{i,max}$: the maximum amount of pure component i that can be adsorbed in the mixing gas, expressed in moles per unit mass of rock; y_{ig} :is the molar proportion of adsorbed component i in the gas phase; p is the pressure (specified as one-half of the Langmuir volume); and B_i is the parameter of the Langmuir isotherm relation.

The values of i,max, and Bi are taken from shale core samples and are considered to be functions of the shale's total organic content (TOC).

Aside the extended Langmuir model, other viable multi-component adsorption models exist. Fitzgerald et al. [32] reported the simplified local density model which has a characteristic prolonged computational period since numerical integration is required.

Instead of the well-known Langmuir isotherm, Wang et al. [33] suggested that some shale samples' adsorption behavior follows the BET [34] isotherm. The traditional BET isotherm depicts the adsorption process in three steps and assumes an unlimited number of adsorption layers: i. The adsorbate molecules first form a monolayer on the surface of the adsorbent due to attraction. ii. The adsorbate molecules continue to adhere to the surface while adsorption proceeds, but the rate of adsorption slows as the monolayer covers more surface area. iii. The monolayer eventually completely saturates the surface, prohibiting further adsorption of the adsorbate molecules.

When plotting the curve of the BET isotherm model, the x-axis represents the equilibrium concentration of the adsorbate in the gas phase and the y-axis represents the amount of adsorbate adsorbed per unit mass of adsorbent. The model is useful for estimating the surface area of porous materials and for characterizing the pore size distribution of these materials. Its limitation is stated below;

i. It assumes that the adsorbate forms a monolayer on the surface of the adsorbent, which may not be true in all cases.

ii. It does not account for the effect of multilayer adsorption or the formation of clusters of adsorbate molecules on the surface of the absorbent. Therefore, the BET isotherm model should be used with caution and its limitations should be considered when interpreting experimental data.

The BET isotherm model is given in equation 3 as;

$$G_a = \frac{V_L' C_{p_g^m}}{(p_g^m - p_o)[1 + (C-1)\frac{p_g^m}{p_0}]} \tag{3}$$

The Langmuir isotherm represents the gas content under reservoir conditions as Ga (m^3/kg) [26,35-36]. The BET equilibrium constant (C) determines the sorption-isotherm behaviour at lower pressure levels, and V'L is the BET maximum monolayer volume of adsorbed gas in m^3/kg; p_0 is the saturation pressure of the gas in Pa;

2.2. Dissolution

The dissolution of CO_2 in shale is a complex process that is influenced by several factors. For a component of gas, i, which dissolves in a formation water, the dissolution component is expressed as Henry's law (equation 4)

$$y_{iw} H_i = f_{iw} \tag{4}$$

where H_i denotes a component I denotes Henry's constant, f_{iw} the fugacity of component i in the aqueous phase, and y_{iw} the molar fraction of component i in the aqueous phase. Under the premise that the aqueous and gaseous phases are in thermodynamic equilibrium, f_{iw} equals the fugacity of component i in the gas phase. Equation 5 can be used to calculate h_i.

$$\ln H_i = \ln H_i^* + \frac{V_i(p - p^*)}{RT} \tag{5}$$

where V_i is the component i partial molar volume at infinite dilution, H_i is the Henry's constant at reference pressure p, R is the universal gas constant, and T is the temperature. To compute p and V_i, the Li and Nghiem [37] technique is utilised.

2.3. Molecular diffusion

The diffusion coefficient of a substance in a medium measure its rate of diffusion. In the context of shale, it specifies the rate at which ions or molecules permeate the rock's nanopores. Because of the extremely low permeability of the shale matrix, determining the diffusion coefficient of CO_2-CH_4 gas in saturated porous media is critical for the progress of CO_2 flooding technology and enhanced gas recovery.

Equation 6 can be used to calculate the binary coefficient for the gas component, i.e.

$$D_i = \frac{1 - y_i}{\sum_{j \neq i} D_{ij}^{-1}} \tag{6}$$

where Di is the diffusion coefficient of component i in the mixture, and y_i is the mole fraction of component i.

Competitive diffusion between CH_4 and CO_2 was modeled by means of this calculation. Fitted least square lines and developed a polynomial equation for the binary diffusion coefficient of some gases. Equation 7 represents the binary diffusion coefficients relationship.

$$D_{ij} = \frac{\rho^0 D_{ij}^0}{\rho} (0.99589 + 0.096016\rho_r - 0.22035\rho_r^2 + 0.032874\rho_r^3) \tag{7}$$

where p is the diffusing mixture's molar density, pr is the reduced density, $q^0 D_0{}^{ij}$ is the density-diffusivity product's zero-pressure limit, and D_{ij} is the binary diffusion coefficient between components i and j in the mixture. Equation 6 can be used to get the binary coefficient for gas component i, or D_i.

Fick's law can also be used to calculate the molecular diffusion of gas components [38]. The following hypothesis guided the development of Equation 8, which reflects this model:

i. During the diffusion process, there is very little liquid expansion.
ii. The diffusion process is carried out under constant isothermal conditions.
iii. The diffusion coefficient is constant and independent of liquid phase concentration and pressure at all beginning pressures.
iv. Because it is assumed that there is just gas diffusion and no flow in the liquid phase, liquid phase evaporation is ignored [39].

$$\frac{\partial c}{\partial t} + v \frac{\partial c}{\partial z} = D \frac{\partial^2 c}{\partial x^2} \tag{8}$$

Ignoring the mobile phase, since there is only diffusion, equation 8 becomes,

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{9}$$

Equation 10-12 represents the initial boundary conditions

$$h = 0, t_0 < t < t_{eq}, C_{(t,h)} = C_{eq} \tag{10}$$

$$0 < h < H, t = 0, C_{(t,h)} = 0 \tag{11}$$

$$h = H, t_0 < t < t_{eq}, \frac{dC_{(t,h)}}{dh} = 0 \tag{12}$$

2.4. Stress-dependent compaction

When external stress is applied on a rock unit, pore spaces are reduced. CO_2 is squeezed into the tiny pore spaces in the shale matrix under high pressure, leading to a reduction in the volume of the shale formation and an increase in its density. This condition can be described as stress-dependent compaction, and is a key mechanism of CO_2 storage in shale. Continuous injection of CO_2 (in gaseous state) into a shale matrix often increases the formation pressure as dissolution of the gas in the pore fluids are initiated. Further injection tends to increase pressure which compacts the shale matrix and pore volume. CO_2 storage mechanism by trapping sets in, as CO_2-containing pores close up. This technique can efficiently store CO_2 in a shale gas reservoir. As a result of the stress-dependent compaction process, the pore spaces contract and the cracks close, lowering the permeability of the shale formation and preventing CO_2 from escaping. Despite its potential effectiveness, stress-dependent compaction has the potential to be a dangerous technology for storing CO_2 in shale formations. An increase in pressure inside the formation, for example, could cause the shale matrix to fracture or trigger seismic activity, resulting in CO_2 leakage or other environmental problems. Additionally, there is a risk that the stored CO_2 could eventually migrate to the surface over long periods of time, making long-term monitoring and maintenance of storage sites necessary.

In other to model possible geo-mechanical deformations, stress-dependent correlations models alongside linear-elastic model are recommended. This can help account for the decline in production due to porosity and permeability variations [13].

Using exponential correlations, stress-dependent properties can be estimated as follows:

$$\emptyset = \emptyset_o e^{-A(\sigma' - \sigma_o)} \tag{13}$$

$$k_o = k_o e^{-B(\sigma' - \sigma_o)} \tag{14}$$

where A and B are the experimental coefficients and σ' is the effective stress.

The initial state is denoted by the subscript "o." Cho *et al.* [40]'s experimental coefficients were employed. The total stress for generic reservoirs is defined as follows, assuming a Biot's constant of 1.

$$\sigma = \sigma' + p \tag{15}$$

where equation (5) was used to replace the effective stresses in equations (13) and (14) and these equations were utilised to generate pressure multipliers for porosity and permeability.

3. Critical parameters for CO_2-CH_4 adsorption and desorption processes in shale gas

3.1. Temperature and pressure

Adsorption is the process by which gas molecules cling to the surface of a solid object. Several elements, including temperature and pressure, can influence this process. Temperature and pressure, according to Sang *et al.* [41], play a crucial impact in determining the total amount of gas that may be collected from shale formations. Higher injection pressures are said to cause more adsorption and desorption of gas components in shale [42]. This could be explained by the fact that higher pressure causes CH_4 and CO_2 molecules to be more concentrated in the gas phase, increasing the likelihood of adsorption on shale surfaces. Furthermore, increased pressure may cause the pore spaces in the shale to compress, so increasing the surface area available for adsorption. Experimental studies show that CH_4 molecules are typically adsorbed in the ring's core, whereas CO_2 molecules typically occupy the location of the oxygen atom in the six-membered oxygen ring [43-44]. When CO_2 is introduced into shale gas, a condition known as competitive sorption occurs; CO_2 adsorbs to the pore walls of the shale

gas more quickly than CH_4 and is more difficult to desorb. Incoming CO_2 might then occupy the adsorption sites of the CH_4 molecules, encouraging desorption and increasing CH_4 recovery.

Although the proportion of CH_4-free gas production declines progressively during the steady production stage, desorbed CH_4 compensates for this loss and maintains a consistent pace of shale gas production.

Importantly, after varying pressures of CO_2 injection, the CH_4 gas recovery rate rises rapidly, stabilises, and eventually falls to zero. In contrast to depletion production, the rate of CH_4 generation does not decline fast in the medium-term stage; rather, it remains constant for some time.

Rising temperatures, in general, reduce gases' ability to adsorb onto shale surfaces, reducing the adsorption capacity of shale that includes a lot of organic material. Marc *et al.* [42] showed that increasing the temperature lowered the adsorption capacity by around half. Higher temperatures can induce gas molecules to become more active and move faster, decreasing the possibility of them clinging to the surface of the shale. However, the specific effect of temperature on adsorption may vary depending on parameters such as shale properties and pressure levels. Understanding the temperature-pressure connection is essential for CO_2 adsorption in shale. Higher temperatures can reduce adsorption at high pressures while increasing adsorption at low pressures. As a result, it is critical to thoroughly examine the pressure and temperature properties in the surrounding environment for effective CO_2 storage in shale.

Persistent CH_4 production lowers pore pressure in shale gas, which closes pore gaps and reduces permeability. However, adding CO_2 to the shale raises the pore pressure, reopening the pore gaps and increasing permeability. These techniques promote increased CH_4 gas recovery as well as better CO_2 adsorption and storage in shale.

Finally, temperature and pressure can influence CO_2 and CH_4 adsorption and desorption in shale in the following ways:

The relative effects of temperature and pressure on adsorption and desorption processes in shale gas are possible.

1. In shale gas deposits, CO_2 adsorption is preferred above CH_4 adsorption.
2. Injecting CO_2 into shale hastens CH_4 desorption.
3. Increasing the pressure and rate of CO_2 injection is a realistic strategy to improve recovery efficiency and shale gas production rate. When the injection rate of CO_2 is more than 5 mL/min, it has a more evident effect on samples with lower porosity. The effect of increasing CO_2 injection pressure is more obvious in samples with lower permeability.

3.2. Moisture, total organic content (TOC), and pore structure

Researchers have been investigating how moisture affects the adsorption and desorption processes during CO_2 injection because shale gas reserves are known to include considerable amounts of organic matter and moisture [45]. The adsorption and desorption isotherms show that the amount of adsorption increases with moisture content (Figure 1). Water is a polar molecule that easily attaches to mineral surfaces, which explains why. Furthermore, water may enter macropores more easily than CO_2 due to its smaller diameter. Fan *et al.* [45] discovered that moisture significantly lowered CO_2 and CH_4 adsorption capabilities. They discovered that in a kerogen matrix with a moisture content of 1.8 weight percent, the CO_2 and CH_4 adsorption capabilities fell from 1.547 mmol/g and 0.089 mmol/g in dry kerogen to 0.096 mmol/g and 0.001 mmol/g, respectively.

Organic elements, particularly complex macromolecules generated from plant and animal remains, are abundant in shale gas. The influence of TOC on CO_2 storage in shale is critical to consider. This organic substance's porous structure contributes in its ability to absorb and retain CO_2. As a result, it could act as a CO_2 sink. In terms of CO_2 storage, TOC can provide larger surface area for CO_2 adsorption. Organic matter has a vast surface area that can function as an adsorbent for CO_2 molecules due to its porous structure. Shale with a higher organic matter concentration may have a higher potential to store CO_2. Second, when organic matter and CO_2 mix, stable mineral carbonates are formed, which can be used to store carbon in

shale gas reservoirs over time. In summary, when different gas shale samples exhibit varied levels of adsorption and desorption at the same temperature and pressure, the TOC can be responsible for an influence under an isothermal condition. In shale gas samples with high TOC, adsorption capacity and TOC will be substantially positively associated. When the TOC level of shale gas is high, it might impact the porosity and permeability of the shale. This can reduce CO_2 adsorption capability and shale gas reservoir storage efficiency.

The pore structure of shale greatly influences how CO_2 is adsorbed. The pore structure of shale can be divided into two categories: post-depositional secondary pores (which form as a result of tectonic activity or diagenesis) and sync-depositional primary pores (which form as a result of tectonic activity and include intergranular, intragranular, and organic matter pores) [46]. Although they have a significant impact on shale flow behaviour and CO_2 adsorption capacity, the size and distribution of these holes can be exceedingly complex [47-48].

The occurrence of illite-smectite clays in natural shales has been linked to the production of micropores, which are required for adsorption [49-50]. Chalmers and Bustin [51] found that vitrinite, a component of shales, has a higher methane adsorption capacity than inertinite and liptinite due to its larger micropore volume. According to research Chalmers and Bustin, [51] and Levy et al. [52], increasing shale thermal maturity and microporosity enhances the capacity of CH4 sorption.

According to Rexer et al. [53], supercritical CO_2 adsorption studies at 273 K and 195 K for Posidonia shales and kerogen demonstrated a significant linear relationship between pore volume and maximal CH4 sorption uptake. According to the sorption mass balances of the kerogen and shale isotherms, organic matter accounted for almost half of the CO_2 sorption in dry shales, with clay minerals accounting for the other half.

Because of their high surface area to volume ratios, micropores smaller than 2 nm have excellent adsorption capacities. However, because of their small size, these micropores may make it difficult for CO_2 molecules to penetrate, resulting in delayed adsorption kinetics. Because of their lower surface area-to-volume ratios, mesopores (2-50 nm) and macropores (>50 nm) usually have lower adsorption capabilities [45]. However, the kinetics of adsorption are accelerated because CO_2 molecules can enter these bigger holes more quickly. The tortuosity and pore connectivity of the shale matrix can affect CO_2 diffusion rates. The total adsorption capacity can be reduced by a porous network with high connectivity and tortuosity [54].
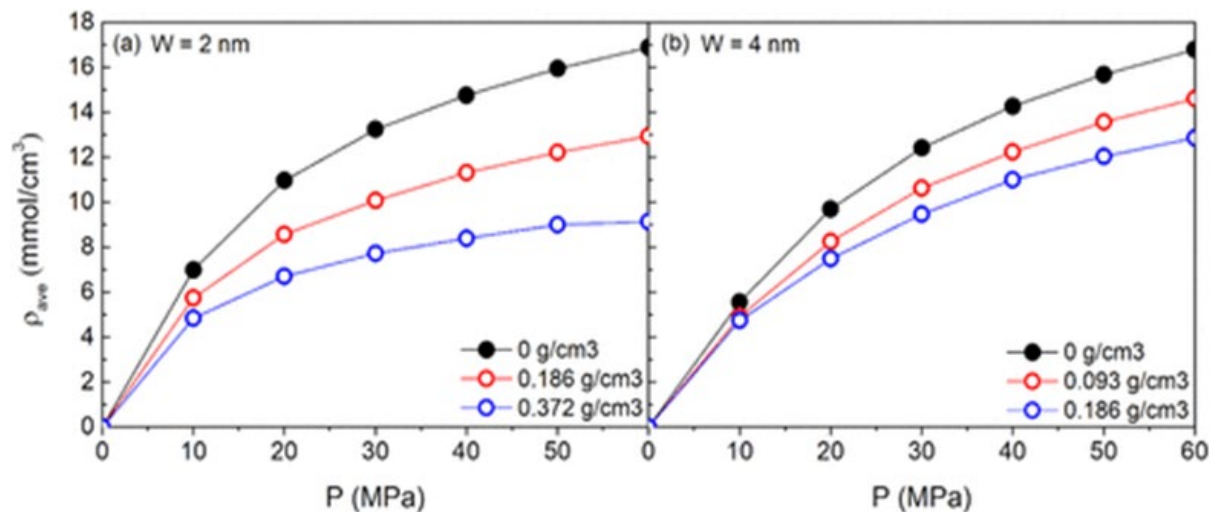

Figure 1. Average density of methane trapped in kerogen slit pores with various pore diameters.

The findings for a pore width of 2 nm are shown in panel (a), whereas the results for a pore width of 4 nm are shown in panel (b). The lines in black, red, and blue represent CH4 adsorption under various circumstances, notably the dry circumstance and the moist circumstance with various contents.

4. Critical parameters for CO_2-CH_4 dissolution processes in shale gas

The factors below are crucial for evaluating the potential of shale formations for CO_2 storage and CH_4-EGR via dissolution mechanism.

4.1. Porosity and permeability

The porosity and permeability of shale formations are critical factors that affect the dissolution of CO_2. Permeability refers to the ability of fluids to travel through rock, whereas porosity refers to the volume of open space within the rock. Shale formations with low porosity and permeability can limit the quantity of dissolved CO_2 that can diffuse and advect through the pore network. Some shale formations, however, may have higher porosity and permeability due to natural fissures or other geological features, which might improve CO_2 dissolution and transport.

4.2. Pore fluid composition

The composition of pore fluids in shale formations can also influence CO_2 solubility. The chemical equilibrium of the system may vary as a result of chemical reactions between dissolved CO_2, minerals, and salts in pore fluids. The formation of solid carbonates as a result of CO_2 interaction with minerals such as dolomite or calcite may result in a reduction in the quantity of dissolved CO_2 in pore fluids. The pH of pore fluid is essential because it influences carbonic acid dissociation and the speciation of dissolved CO_2.

4.3. Pressure and temperature

Temperature and pressure variables in shale formations can have a significant impact on how CO_2 dissolves. Rising pressure and decreasing temperature enhance the solubility of CO_2 in water, which promotes CO_2 dissolution in pore fluids. However, in order to avoid the production of solid carbonates or the release of dissolved CO_2, pressure and temperature levels must be kept within a specified range. Temperature and pressure can also influence dissolved CO_2 advection and diffusion via the network of shale pores.

4.4. CO_2 injection rate and concentration

The rate and volume of CO_2 injected into shale formations can both influence how rapidly CO_2 dissolves. Higher injection rates and concentrations may increase the partial pressure differential between the injected CO_2 and the pore fluids, hastening CO_2 dissolution. Larger injection rates, on the other hand, may cause fractures or other geological changes that affect the porosity and permeability of the shale formation. Furthermore, if the CO_2 infusion exceeds the pore fluids' solubility limit, solid carbonates or dissolved CO_2 may be ejected.

4.5. Total organic content

The amount of organic material present can have a significant influence on CO_2 solubility in shale formations. Organic compounds in shale can change the chemical balance and reduce the concentration of dissolved CO_2 in pore fluids via mechanisms like as adsorption or chemical reactions. In contrast, the organic material may serve as a carbon source for CO_2 infusion, resulting in further processes that form solid carbonates. As a result, the shale deposit might store CO_2 for a very long time.

The CO_2 disintegration process in shale is a complex phenomenon impacted by a variety of causes. Among the variables to consider are the porosity and permeability characteristics of the shale formation, the composition of the pore fluids, the current temperature and pressure, the volume and rate of CO_2 injection, and the amount of organic material in the shale. Analyzing these factors in depth is critical for establishing whether or not shale formations may be used for dissolution-based CO_2 storage.

5. Effects of stress-dependent properties on CO_2-EGR

5.1. Natural fracture permeability, hydraulic fracture half length and well spacing

When carbon dioxide is introduced to shale formations, fissures spontaneously occur, which considerably facilitate in the transportation of gas toward the extraction well. When developing models for CO_2-enhanced gas recovery (CO_2-EGR) in shale reservoirs, a dual porosity and dual permeability model is an efficient technique to show the intrinsic fracture structure. According to Kim *et al.* [13], the New Albany Shale had significant matrix porosity and permeability, but this did not prevent CO_2 from flowing into the production well. While the natural fracture porosity and permeability of the New Albany Shale are lower, the matrix porosity and permeability are higher. This was attributed to the incredibly low permeability of the natural fissures. Additionally, if there is a large well spacing between the injection and production wells, there might not be any CH_4 recovery from shale gas. CO_2 cannot adequately flow towards the production well because of the reservoir's dense packing and the excessive distance between the injector and producer. In these conditions, further drilling to apply the CO_2 flooding technique may be considered. In conclusion, the most crucial factor to consider when considering CO_2 injection in shale reservoirs is the characteristics of the fractures that are present in the formation.
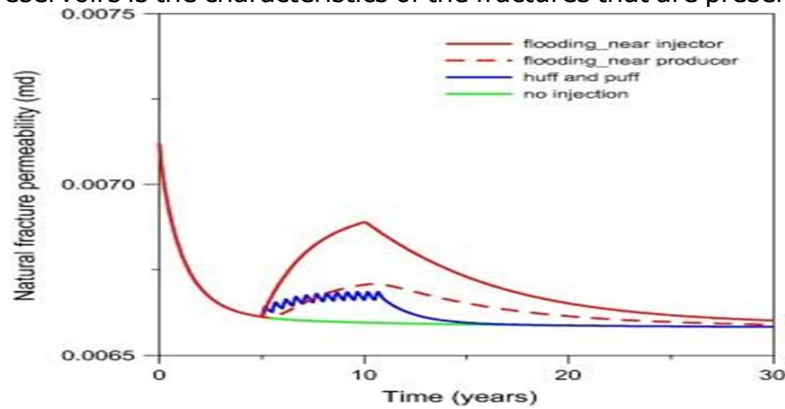

Figure 2. Average fracture permeability under pulsed injection conditions [13].

Longer hydraulic half-length shale gas reservoirs are better suited to CH_4 generation, particularly when injected using the huff and puff approach (figure 3). The creation of CH_4 tends to rise as the fracture half-length increases. However, keep in mind that the chance of CO_2 breakout increases with fracture half-length. In other words, a hydraulic fracture has a predetermined half-length. The hydraulic fracture half-length should be the major concern for field application of CO_2 injection in shale gas reservoirs.
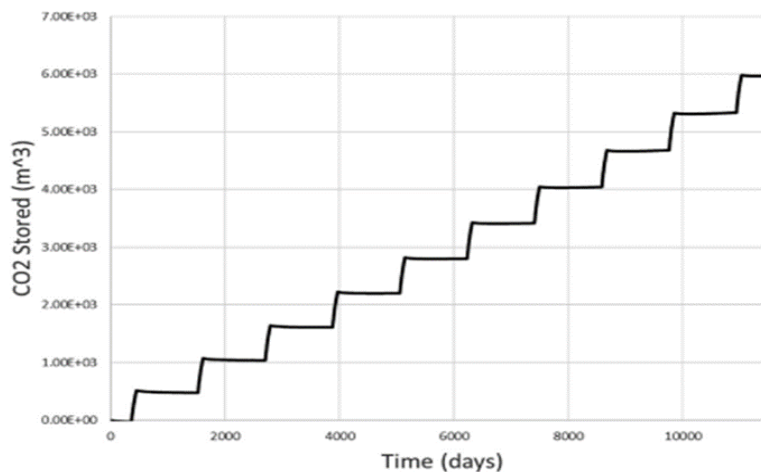

Figure 3. CO_2 storage efficiency under optimal pulsed injection [70].

A reduction in CH_4 recovery might result from a rise in the Langmuir volume constants, which can be calculated using density logs or total organic carbon (TOC) logs in shale gas reservoirs. This occurs as a result of the CO_2 flow being disturbed by the high CO_2 adsorption rate close to the injection well. While there is substantial CO_2 adsorption and CH_4 desorption at the injection well, there is less CO_2 adsorption and CH_4 desorption owing to the lower flow of CO_2 near the production well.
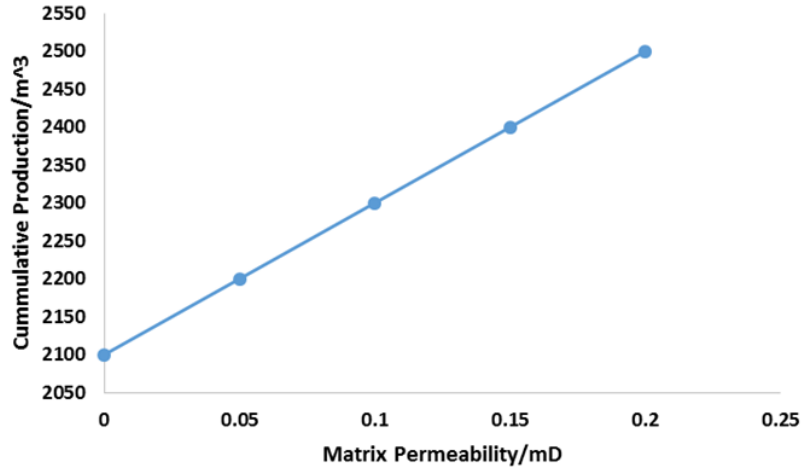

Figure 4. CH_4 production under optimal pulsed condition [45].

5.2. Matrix and fracture permeability evolution

Permeability changes are common in the shale matrix and fracture under diverse CO_2 injection scenarios. The desorption of gas from shale causes the matrix of the shale reservoir to shrink and cracks to spread due to the rise in net stress caused by the decrease in reservoir pressure. Furthermore, as a result of CO_2 absorption, the shale matrix contracts, reducing its permeability. A decrease in permeability could be induced by a number of causes, including changes in fracture geometry, the Langmuir swelling coefficient, and void stiffening. When larger injection pressures are used (overpressure injection), matrix permeability decreases in comparison to when lower injection pressures are used. This is due to the injection increasing CO_2 injectivity and, hence, gas generation by partially compensating for the pressure decrease caused by mechanical factors. The evolution of permeability during pulsed injection shows a decrease in matrix permeability and a rise in fracture permeability, which is similar to continuous injection scenarios.

5.3. CO_2-EGR and shale reservoir geo-mechanics

In addition to enhancing CH_4 gas recovery, injecting gaseous or supercritical CO_2 into shale gas reservoirs mechanically alters the geo-mechanical properties of the shale materials [54-55]. When saturated with supercritical CO_2, shale minerals lose some of their Uniaxial Compressive Strength (UCS) and Young's Modulus value. Heller and Zoback, [56], Lyu et al., [57], Luo et al., [55]. CO_2-water-rock interactions are responsible for the obvious decrease in strength and Young's Modulus in CO_2-saturated shale samples [58]. The preference of the shale matrix for adsorbing CO_2 over CH_4 causes swelling, which reduces the material's strength and Young's modulus [54,56,59]. In terms of dissolving, CO_2 dissolves in water, causing mineral dissolution and carbonate mineral precipitation. Zhang [54] established through experimentation that pore development in shale material is induced by dissolution and precipitation mechanisms, resulting in a drop in both UCS and Young's Modulus. He demonstrated this by adding CO_2 to shale samples until the UCS and Young's Modulus declined from 58.82 MPa and 5.22 GPa, respectively, to 40.42 MPa and 3.79 GPa. Yin et al. [60] used an experiment to show how, with CO_2 saturation, a shale's UCS and elastic modulus (E) might decline to 22.9% and 23.1%, respectively.

Furthermore, brittle qualities may be demonstrated by shale minerals following CO_2 injection. This mechanical feature of shale can be expressed using the Brittleness Index (BI), which is the ratio of reversible strain to total strain [61-62]. According to mineral composition studies, shale material that is stiff and unsaturated has a greater BI value than shale material that is saturated with supercritical CO_2 [54,61]. This phenomenon is caused by the dissolution reactions and CO_2/H_2O adsorption mechanisms prevalent in shale reservoirs, which tend to make shale more flexible and durable. According to Zhang [54] and Hou *et al.* [61], as saturation or injection duration increases, the value of BI decreases even more.

Shale materials may deform as a result of CO_2 injection into shale reservoirs, resulting in swollen strains. At lower pressures, the CO_2 adsorption process may be the cause of the deformation of shale, but at higher pressures, the injection pressure may be the cause of the deformation [63]. In research by Ao *et al.* [63], studies showed that as the saturation duration rose, the tensile strength, triaxial compressive strength, and elastic modulus of CO_2-treated shale dropped. These variations are due to CO_2 dissolving in shale reservoirs, as well as pressure and adsorption-related stresses. The strength of shale reduced as treatment times increased. According to Griffith *et al.* [64], Gibbs *et al.* [65], Scherer [66], and Pan *et al.* [67], gas adsorption impacts shale via sorption and dissolving mechanisms. These findings are consistent with the findings of this inquiry.

5.4. Shale properties

The efficiency of stress-dependent compaction as a CO_2 storage technology is highly reliant on the shale formation features. Shale formations with a higher clay concentration have a bigger specific surface area and lower permeability, making them better at absorbing CO_2 [68-69]. However, a high clay concentration might increase brittleness and susceptibility to cracking under pressure, causing CO_2 to seep out of storage.

5.5. CO_2 properties

The properties of the CO_2 poured into the shale formation also have a substantial impact on stress-dependent compaction. CO_2 can exist in a supercritical state at depths of more than 800 metres, acting as a viscous fluid that can seep into the smallest pore spaces in shale. If the CO_2 is not compressed sufficiently to fill all of the pore spaces, the storage mechanism's efficiency suffers.

5.6. Temperature

The temperature of the shale formation can also affect stress-dependent compaction. Elevated temperatures may render the shale more susceptible to stress-induced deformation, reducing its ability to store carbon dioxide. High temperatures might also hasten the chemical reactions that occur between the shale and CO_2, potentially resulting in the breakdown of the stored CO_2.

5.7. Outcome of stress-dependent compaction on CO_2 storage

i. The compression of pore spaces inside shale increases the density of the rock. Because of its increased density, shale has less porosity and is less susceptible to CO_2 leakage.

ii. Immobilization: The compression of pore spaces in shale may cause CO_2 to become immobile, making gas escape more difficult. Long-term storage can be improved by efficiently storing carbon dioxide (CO_2) inside rock formations and making use of the narrower pore spaces formed during stress-induced compaction.

iii. The shale's restricted pore spaces may make CO_2 escape even more difficult. The contraction of the pore pores pulls carbon dioxide (CO_2) into ever-smaller spaces, limiting the gas's freedom of movement inside the rock. It is probable that the restricted mobility in this condition will boost the long-term storage capabilities of carbon dioxide (CO_2).

iv. Enhanced Capillary Forces: As the pore spaces in shale are squeezed, capillary forces rise, which enhances CO_2 retention. Because of its enhanced capillary force, which keeps CO_2 from escaping, shale has a better capability for long-term storage. It is critical to remember

that when pore space is reduced, the amount of carbon dioxide (CO_2) that may be caught is limited. The quantity of pore space available for CO_2 storage is restricted, and storage capacity will not be attained until the pore spaces inside the shale are entirely constricted. Furthermore, pore spaces may compress to the point where trapped carbon dioxide is released if the shale formation is unable to sustain the higher stress induced by the carbon dioxide injection.

5.8. Mechanisms of CO_2 storage in shale via stress-dependent compaction

5.8.1. Reduction in pore space

Stress-dependent compaction reduces pore space, facilitating CO_2 storage in shale deposits. When CO_2 is introduced into shale, it fills the rock's pore spaces. As the pressure of the CO_2 injection grows, so does the tension on the shale. This force compresses the pore spaces, increasing shale density while limiting the volume of CO_2 storage available. One of the key mechanisms that allows for longer-term CO_2 storage in shale formations is pore volume decrease.

5.8.2. Chemical trapping

Chemical sequestration, also known as stress-induced compaction, is an alternative method for storing CO_2 inside shale formations. When shale is exposed to CO_2, a chemical reaction occurs between the shale and CO_2, essentially storing CO_2 inside the rock. Stress-dependent compaction compresses shale, increasing the exposed surface area for CO_2 input and thereby improving chemical trapping effectiveness. Compression also increases the concentration of dissolved minerals in pore fluids, which increases the number of reactants accessible for chemical reactions. Chemical trapping improves the efficiency of CO_2 storage in shale deposits through a variety of means, including:

i. Mineral precipitation occurs when CO_2 is introduced, and the minerals in the shale transform into stable mineral compounds. These minerals are found in the shale matrix due to their high ability to absorb and sequester CO_2, keeping it from escaping into the atmosphere.

ii. Carbonate Formation: Carbonate is formed when CO_2 reacts with calcium and magnesium ions found in pore fluids. This chemical process produces dolomite and calcite, two stable carbonate minerals. These minerals can effectively retain CO_2 for an extended period of time.

iii. As a result of a reaction between CO_2 and silicate minerals present in shale, the geological process of carbonation forms stable carbonate minerals. Carbonation allows CO_2 to be stored for a longer period of time.

iv. Mineral Dissolution: When CO_2 is injected into a shale formation, the minerals may dissolve under certain conditions. There are more dissolved minerals in the pore fluids as a result of the dissolving process, which adds more reactants to the mix for chemical trapping reactions.

The existence of dissolved minerals in pore fluids, as well as the specific CO_2 injection parameters (pH, temperature, and pressure), all determine whether or not shale formations are suited for chemical trapping. A detailed site assessment and the implementation of a strong monitoring system are required to assess a shale formation's ability to successfully store chemicals in the context of CO_2 storage projects.

5.8.3. Mechanical trapping

Mechanical trapping, which is performed through stress-dependent compaction, is another method for capturing CO_2 within shale formations. The proposed technique comprises erecting impermeable barriers that successfully hold carbon dioxide within the shale formation and prevent it from escaping into the surrounding area. As CO_2 is added into the shale formation, it fills the pore spaces in the rock. The shale is stressed further as the pressure of the injected CO_2 grows, causing the pore spaces to compress. Impermeable barriers may form during the

compression process, reducing the amount of carbon dioxide that may be stored in the shale reservoir. Mechanical trapping has the potential to improve CO2 storage efficiency in shale formations in a variety of ways.

i. Shale pore spaces compress to form impermeable barriers, keeping CO_2 out of the system. By trapping CO2 within the shale formation, these barriers may prevent CO_2 from entering the atmosphere.

ii. Fracture-based Sequestration: If the shale formation has fissures naturally, stress-dependent compaction-induced compression may cause these fissures to shut, trapping carbon dioxide within the shale.

iii. Improved Reservoir Stability: The stress-dependent compaction process that compresses shale has the potential to improve the stability of CO_2 reservoirs by reducing the likelihood of fissures and leaking.

iv. The narrow pore apertures of the shale may make CO_2 escape more challenging. In the long run, the restricted likelihood of escape and limited movement can help to increase CO_2 storage capacity. It is crucial to recognize that a range of factors can influence how well mechanical trapping increases the long-term capacity of CO_2 storage in shale formations. Special geological conditions, such as the presence of specific minerals in clay that can hinder fluid movement, are required for impermeable barriers. Furthermore, extensive site characterization and monitoring are essential to verify that this mechanism works properly.

5.8.4. Enhanced capillary forces

Because of the effects of stress-dependent compaction, capillary forces are particularly essential in the trapping of CO_2 inside shale strata. Pressure added to the shale matrix increases the capillary forces that hold CO_2 in situ. When CO_2 is introduced into a shale formation, the pore spaces inside the rock become occupied. Capillary forces in shale are amplified by stress-dependent compaction, which aids in CO_2 retention. Because of the combined effects of surface tension and fluid adhesion to solid surfaces, capillary forces are primarily responsible for the retention of fluids inside the pore structure of a porous material.

i. A variety of techniques might be utilized to boost capillary forces and improve CO_2 storage in shale layers.

ii. By enhancing CO_2 retention in the shale reservoir, increased capillary forces can limit CO_2 leakage.

iii. Improved CO_2 retention may boost long-term storage capacity by minimizing the chance of re-release.

iv. By limiting CO_2 movement within the shale reservoir, better CO_2 retention can significantly reduce the risk of leakage.

v. Using a process called as stress-dependent compaction, shale can be compressed to promote reservoir stability. This method dramatically reduces the likelihood of a fracture and consequent CO_2 leakage in reservoirs. It is critical to remember that the effectiveness of this process is reliant on a number of elements when contemplating the prospect of gradually increasing CO_2 storage capacity in shale formations due to increased capillary forces. Numerous shale formation properties, such as mineralogy, wettability, and pore size distribution, influence how effective increased capillary forces are. A thorough examination of the site, as well as ongoing inspection, are essential to assure the effective operation of this device.

6. Critical parameters for CO_2-CH_4 diffusion processes in shale gas

The dispersion of injected CO_2 into the shale reservoir's porous matrix is a significant component of the CO_2 flooding technique. The calculation of shale diffusion coefficients is critical for the transport of ions and molecules via shale nanopores. Diffusion coefficients in shale can be affected by mineralogy, porosity, and organic matter content. The following presentation discusses a number of significant factors impacting shale expansion.

6.1. Pore size distribution

The size of the holes has a significant impact on how materials flow through the shale nanopores. Shale deposit pore structure is complex, with a wide range of pore sizes and shapes. The diffusion rate falls when the pores narrow and molecules or ions must take a more circuitous path. As a result, as pore size shrinks, so does the rate of diffusion.

6.2. Chemical composition of the pore fluid

The chemical composition of the pore fluid can significantly influence the diffusion process in shale formations. The diffusion coefficient of a chemical might alter based on how it interacts with the pore fluid and minerals in the shale. When comparing the rates of ion diffusion via nanopores, it is revealed that ions with higher ionic radii exhibit slower diffusion than ions with lower radii.

6.3. Temperature

Diffusion rates in shale might vary due to temperature changes. Raising the temperature leads molecules to be in a higher energy state, increasing the rate of diffusion. However, if exceptionally high temperatures are present, the pore structure of the shale may alter, affecting the dispersion rates.

6.4. Pressure

Pore fluid pressure can also influence diffusion rates. Diffusion rates may decrease as a result of high pressure squeezing and narrowing the pores.

6.5. Organic matter content

The significant volumes of organic compounds present in shale may influence diffusion rates. Organic materials' ability to act as a diffusion barrier can limit the movement of ions and molecules through nanopores. This is because organic stuff has a higher hydrophobicity than surrounding minerals, which narrows the pore space.

6.6. Mineralogy

Diffusion rates can also be impacted by the shale's mineralogy. The interaction of molecules or ions with mineral surfaces can be altered by the surface properties of different minerals. Diffusion rates, for instance, can be slowed down by the adsorption of molecules or ions by high surface area minerals like clays.

7. Conclusion

The purpose of this study was to examine the petrophysical and geomechanical effects of CO_2-EGR in a shale gas reservoir. Temperature, pressure, TOC, natural fracture system, fracture conductivity, hydraulic fracture half-length, unconfined compressive strength (UCS), Young's modulus, Poisson's ratio, and other variables have been found to be important in the enhanced gas recovery process of injecting CO_2 into shale reservoirs. The primary outcomes of this review work are as follows:

i. Multicomponent adsorption, dissolution, molecular diffusion, and stress-dependent compaction are significant characteristics in CO_2-EGR multicomponent transport processes. When designing a competitive multi-component adsorption/desorption system for efficient CO_2-EGR research, the extended Langmuir Constant's thermodynamical correctness is the ideal model to utilise.

ii. Because CO_2 adsorbs more readily than CH_4 in a shale gas reservoir, raising injection pressure increases gas component adsorption and desorption in shale because higher pressure creates a larger concentration of CO_2 and CH_4 molecules in the gas phase. As a result of this process, the possibility of their being adsorbed to the shale surfaces increases. Adsorption capacity, on the other hand, decreases by a factor of two when temperature is doubled.

iii. An increase in moisture content correlates to an increase in adsorption. Furthermore, when the TOC of a shale gas sample is high, adsorption capacity and TOC will have a very positive relationship.

iv. Improved capillary forces, chemical trapping, mechanical trapping, and pore space reduction are the primary processes for stress-dependent CO_2 storage in shale gas reservoirs. As a result, there is a significant linear relationship between the pore volume acquired by supercritical CO_2 adsorption and the maximum CH_4 sorption uptake. Mesopores (2-50 nm) and macropores (>50 nm) may have lower adsorption capacities than micropores. This is due to their lower surface area to volume ratio. Furthermore, a densely connected and convoluted pore network might slow down CO_2 diffusion, lowering total adsorption capacity.

v. Improved isobaric and isothermal conditions make CO_2 transport and dissolution easier. Rising pressure and decreasing temperature enhance the solubility of CO_2 in water, which can promote CO_2 dissolution in pore fluids.

vi. Higher injection rates and concentrations can enhance the partial pressure gradient between the injected CO_2 and the pore fluids, assisting in CO_2 dissolution. Higher injection rates, on the other hand, may cause fractures or other geological changes that affect the porosity and permeability of the shale formation. Larger CO_2-injectivity rates produce more gas just by virtue of the mechanical action. When compared to the no injection situation, an ideal pulsed injection schedule can enhance CH_4 gas output by 9.34%.

vii. Increased porosity and permeability of natural fractures promote CO_2 flow to the producing well (after injection). In addition to relatively poor natural fracture permeability, recovery of CH_4 from shale gas can be minimal if well spacing is high. Longer hydraulic half-length shale gas reservoirs are better for CH_4 generation, especially when injected using the huff and puff approach. An increase in the Langmuir volume constants (derived from a density log or TOC log) of shale gas reservoirs may result in a decrease in CH_4 recovery.

viii. The preferential adsorption of CO_2 over CH_4 in the shale matrix causes swelling, which reduces strength and Young's modulus. Shale that is stiff and unsaturated has a higher BI value, but shale that is saturated with supercritical CO_2 has a lower BI value. Shale deformation can be attributable to the CO_2 adsorption process at lower pressures; at higher pressures, injection pressure is responsible for shale deformation. The tensile strength, triaxial compressive strength, and elastic modulus of CO_2-treated shale all decreased as saturation time rose. These changes could be caused by both adsorption/pressure-induced strain and the dissolving influence of CO_2 in shale reservoirs.

8. Recommendations

i. The extended Langmiur constant is recommended in modelling multicomponent transport in CO_2-EGR, since it has an advantage of being thermodynamically correct.

ii. Competitive multicomponent transport models and field-scale CO_2-EGR should be designed to accommodate high CO_2 injection pressures since it favors the adsorption and desorption of gas components in the system, hence, enhancing gas recovery.

iii. Since enhanced CO_2 adsorption is favored under increased moisture content, it is advised that CO_2 should be injected in a water-charged or supercritical condition. This will also promote enhanced CH_4 recovery.

iv. For effective dissolution of CO_2 in pore fluids, the CO_2-EGR system should be designed to allow for increased isobaric and decreased isothermal conditions, as this will enable increased CO_2 solubility.

v. Enhanced gas recovery is favored if CO_2 injection rate is high and balanced and also, if it is carried out under huff and puff method. It is recommended that injection condition should be pulsed.

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