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Evaluation of CO₂ Storage in a Shale Gas Reservoir Compared to a Deep Saline Aquifer in the Ordos Basin of China

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Abstract: As a new “sink” of CO₂ permanent storage, the depleted shale reservoir is very promising compared to the deep saline aquifer. To provide a greater understanding of the benefits of CO₂ storage in a shale reservoir, a comparative study is conducted by establishing the full-mechanism model, including the hydrodynamic trapping, adsorption trapping, residual trapping, solubility trapping as well as the mineral trapping corresponding to the typical shale and deep saline aquifer parameters from the Ordos basin in China. The results show that CO₂ storage in the depleted shale reservoir has merits in storage safety by trapping more CO₂ in stable immobile phase due to adsorption and having gentler and ephemeral pressure perturbation responding to CO₂ injection. The effect of various CO₂ injection schemes, namely the high-speed continuous injection, low-speed continuous injection, huff-n-puff injection and water alternative injection, on the phase transformation of CO₂ in a shale reservoir and CO₂-injection-induced perturbations in formation pressure are also examined. With the aim of increasing the fraction of immobile CO₂ while maintaining a safe pressure-perturbation, it is shown that an intermittent injection procedure with multiple slugs of huff-n-puff injection can be employed and within the allowable range of pressure increase, and the CO₂ injection rate can be maximized to increase the CO₂ storage capacity and security in shale reservoir.

Keywords: CO₂ geological storage; shale; phase transformation; pressure perturbation; injection schemes

1. Introduction

The capture of anthropogenic carbon dioxide (CO₂) from industrial or other emission sources and its long-term storage in geological formations to limit its emission into the atmosphere is referred to as geological carbon storage (GCS) [1]. GCS is regarded as one of the most effective technologies to reduce the greenhouse gas emissions from the combustion of fossil fuels. Besides the conventional CO₂ storage sites in the deep saline aquifers, depleted oil and gas reservoirs, and un-minable coal [2,3], the depleted shale reservoir is also rapidly becoming a new and potentially promising CO₂ storage option because of the booming production of the unconventional shale gas [4,5].

Interest in CO₂ storage in shale reservoirs has grown recently because shale is widely reported to possess higher affinity to CO₂ than CH₄ and has huge potential for CO₂ adsorption trapping. For example, Heller and Zoback [6], Kang et al. [7], and Zhang [8] all tested the CO₂/CH₄ adsorption capacity of shale from different places in the world and demonstrated that the CO₂ adsorption capacity to shale was greater than that of CH₄ under surface condition. Several feasibility studies for CO₂ storage in shale reservoirs have demonstrated that CO₂ can be trapped in the shale matrix and at the same time can significantly enhance the methane recovery by CO₂/CH₄ competitive adsorption [9].

Liu et al. [10] indicated that 95% of injected CO₂ can be permanently sequestered in the Devonian and Mississippian New Albany shale with gas adsorption being the dominant storage mechanism. A large storage capacity of CO₂ in shale reservoirs has also been evaluated and it was estimated that the CO₂ storage capacity of the Marcellus shale in the eastern United States alone could store between 10.4 and 18.4 Gt of CO₂ between now and 2030 [11].

In GCS, it is very important to study the CO₂ plume evolution and migration as well as different phase transformations due to various trapping mechanisms for the sake of security. In a shale reservoir, there is one more trapping mechanism for CO₂ compared to those in the deep saline aquifers, and that is the adsorption trapping of CO₂ to the surface of the host rock simultaneously promoting the desorption of the in-place CH₄ [12]. It is important to recall here the other well-known trapping mechanisms, namely the hydrodynamic trapping, solution trapping, mineral trapping and residual or capillary trapping. Furthermore, although all these trapping mechanisms may take effect within a given reservoir, they occur at different time scales. Moreover, only a few of these mechanisms contribute significantly to plume immobilization in time scales comparable to the injection times or arguably even over the duration of the site stewardship. On shorter time scales, hydrodynamic trapping, residual, and adsorption trapping are the dominant mechanisms that play an important role in plume immobilization and reservoir [13–16]. In the long-term, a significant amount of CO₂ will be trapped through dissolving into the formation water (solubility trapping) and finally being permanently stored in mineral phase by reacting with the host rock (mineral trapping), which gradually begins to contribute to CO₂ plume immobilization in shale reservoirs [12].

The physical understanding of CO₂ storage mechanisms in shale reservoirs is still in very preliminary stage; not all of the above listed trapping mechanisms have been considered in the previous studies [10,12,17,18]. Furthermore, CO₂ plume evolution and spatial and time scales of phase transformations also depend on the CO₂ injection strategy to some extent. Juanes et al. [15] have explored the impact of relative permeability hysteresis on CO₂ storage in deep saline aquifers and found that the injection of water slugs alternating with CO₂ injection can increase the effectiveness of storage by increasing the CO₂ trapped in the residual phase and reducing the CO₂ leakage risk caused by the free and mobile phase. Kim et al. [17] also suggested the huff-n-puff injection scheme as a good viable option for CO₂ storage and shale gas recovery in the Barnett shale. The huff-n-puff injection is also called the cyclic injection, in which the CO₂ is not continuously injected but is divided into several stages, and each stage includes gas injection and a soaking process. However, the effect of different CO₂ injection strategies on CO₂ storage in a shale reservoir and shale gas recovery has not been thoroughly investigated; it is the goal of this paper to address this problem in detail.

Due to the complexity of the underground environment and very slow reaction rate of aluminosilicate minerals with ambient CO₂ under storage conditions, numerical models and simulations are of great significance in the assessment of CO₂ migration in a shale reservoir for long-term storage. In this study, CO₂ storage in Yanchang shale in the Ordos basin of China is investigated by numerical simulation. The dual-porosity, dual-permeability modeling approach is employed to establish the one-stage hydraulic fractures in a shale reservoir. It includes Darcy and diffusive flow, hysteresis effects, CO₂ dissolution, CO₂–water–shale reactions as well as CO₂/CH₄ sorption and desorption. The CO₂ storage performance in a shale reservoir is compared to that in a deep saline aquifer from the Shenhua CO₂ Capture and Storage project in the northern part of the Ordos Basin. The effect of various CO₂ injection schemes, namely the high-speed continuous injection, low-speed continuous injection, huff-n-puff injection and water/gas alternating injection, on the phase transformation of CO₂ in the shale reservoir and CO₂-injection-induced pressure perturbations in the reservoir formation are analyzed.

The complexity of the underground environment mainly shows in the heterogeneity and anisotropy of the porous and fractured reservoirs, which are also important factors impacting the evolution of CO₂ in different phases [19–21]. Considering the calculation efficiency, the geological and hydrological properties are reasonably homogenized and simplified. We believe that this study can not only obtain

some generic findings about the effectiveness of CO₂ storage and the CO₂ plume migration in a shale reservoir, but can also provide guidance for the risk assessment for CO₂ storage in shale reservoir.

2. Geological Background

The Ordos basin, with an area of 370,000 km², is the second largest sedimentary basin containing abundant oil and gas resources in the Northern China. It is a typical cratonic basin with low porosity and permeability, which developed into a large stable basin during the Paleozoic period. The tectonic movement during the basin development was dominated by regional uplift and subsidence leading to the uplifts and depressions type terrain in the basin. The basin is divided into six substructures, the Shanbei Slope characterized by a huge monoclonal structure located in the middle of the basin and surrounded by the Yimeng Uplift in the north, the Jinxi Flecture Belt in the east, the Weibei Uplift in the south, the Tianhuan depression and the western margin thrust belt in the west. Most of the gas and oil resources are distributed in the Shanbei Slope, not only for the conventional oil and natural gas but also for the shale gas. Three sets of black shale in the Ordos basin are the Ordovician Pingliang shale, the carboniferous-permain shale and the Triassic Yanchang shale. However, the Yanchang shale has been demonstrated to have the most potential for shale gas exploitation because of its high TOC (Total Organic Carbon) content (an important indicator of a shale gas reservoir) and the actual drilling of 1000~3000 m³ of gas and 2~5 tonnes of oil per day with hydraulic fracturing.

In addition to the huge amount of oil/gas reserves in the Shannbei slope, it is also a favorable structural unit for the geological storage of CO₂ in China due to its relatively stable tectonic environment with rare regional faults. In 2010, the first Chinese full-chain CO₂ capture and geological storage demonstration project—the Shenhua Project—was launched in the northeast of the Shannbei Slope and 0.302 million tonnes (Mt) of CO₂ was injected at the end of 2015 [22]. Five sets of reservoir-caprock assemblages exist in the Shenhua saline aquifer. From top to bottom, they are the Liujiagou, Shiqianfeng, Shihezi, Shanxi and Majiagou assemblage, respectively (Figure 1). The main target formations for CO₂ storage are saline aquifers with low porosity, low permeability and high heterogeneity. The average porosity of the target reservoir is 9.3%, which varies in the range of 7~20%, while the average permeability is 5.615 mD with the range 0.5~10 mD.

Figure 1. Geological map and oil/gas resources distribution in the Shanbei slope of the Ordos basin, China (Modified from [23,24]).

3. Material and Methods

3.1. Governing Equations for Different Trapping Mechanisms

3.1.1. Multi-Component Adsorption

It has been widely reported that CO₂ is preferentially adsorbed to organic shale by a factor 2~5 times greater than that for CH₄. Adsorption trapping is a dominant mechanism for CO₂ storage in a shale reservoir. To calculate the competitive adsorption and desorption of CO₂ and CH₄, the extended Langmuir isotherm described by Equation (1), which has been shown to give a reasonable correlation with binary gas sorption of CH₄ and CO₂ in the Yanchang shale, is applied in the present model.

$$C_i = \frac{C_{i,max} \times B_i \times y_{ig} \times P}{1 + P \times \sum_i B_i \times y_{ig}} \quad (1)$$

where C_i is the adsorbed moles amount of component i per unit mass of rock, $C_{i,max}$ is the maximum adsorbed moles amount of component i per unit mass of rock, B_i is the constant parameter in Langmuir isotherm, y_{ig} is the adsorbed molar fraction of component i in the gas phase, and P is the pressure.

3.1.2. Dissolution

Henry's law is preferred to calculate the dissolution of CO₂ in the formation water as follows (Equation (2)):

$$x_{CO_2} = \frac{f_{CO_2}}{H_{CO_2}^* \times \exp\left[V_{CO_2}^\infty \times \frac{P - P_{ref}}{RT}\right]} \quad (2)$$

where x_{CO_2} is the aqueous molar fraction of CO₂; f_{CO_2} is the fugacity of CO₂ in the aqueous phase, which can be calculated from Peng and Robinson's equation-of-state; $H_{CO_2}^*$ is the Henry's constant at reference pressure P_{ref} ; $V_{CO_2}^\infty$ is the partial molar volume of CO₂ at infinite dilution; and R and T are the universal gas constant and temperature, respectively.

3.1.3. Trapping and Relative Permeability Hysteresis

To characterize the trapped saturation and relative permeabilities of the non-wetting phase after a flow reversal, several empirical models of hysteresis have been developed [25–27] among which Land's model has been demonstrated to reliably predict the residual CO₂ saturation in consolidated porous media [28]. As a result, the Land's model is used in this paper to calculate the residual trapping. During CO₂ storage in the subsurface, the reservoir goes through a process from drainage to imbibition, as shown in Figure 2. Once the injection started, the drainage process begins with gas saturation increasing. The imbibition process follows when the injection stops and gas saturation decreases, resulting in the residually trapped gas saturation, S_{gr} , which is computed from Equation (3). The relative permeability of gas on the drainage to imbibition scanning curve can be found in the reference [29].

$$S_{gr} = S_{gcrit} + \frac{S_{g,max} - S_{gcrit}}{1 + C * (S_{g,max} - S_{gcrit})} \quad (3)$$

where S_{gcrit} is the critical gas saturation and is assumed as 0.05, C is Land's parameter calculated by the simulator so as to be internally consistent with the inputs S_{gcrit} , $S_{g,max}$ (maximum gas saturation, assumed 0.9) and $S_{gr,max}$ (maximum residual gas saturation, assumed as 0.4).

Corey's model is employed to simulate the relative permeability variation with saturation, as given in Equations (4)–(6):

$$k_{rl}^d = \hat{S}^4 \quad (4)$$

$$k_{rg}^d = (1 - \hat{S})^2 (1 - \hat{S}^2) \quad (5)$$

$$\hat{S} = (S_l - S_{li}) / (1 - S_{li} - S_{gi}) \quad (6)$$

where k_{rl}^d and k_{rg}^d are the relative liquid and gas permeability on the drainage curve, while S_{li} and S_{gi} stand for the irreducible liquid and gas saturation and are assumed as 0.1 and 0.0, respectively.

Figure 2. (a) Corey's model and (b) Land's trapping model.

3.1.4. CO₂-Water-Rock Reactions

The mineral dissolution and precipitation reactions are described by a kinetic rate law as given in Equation (7), where r_β is the rate, $\hat{A}_\beta$ is the reactive surface area for mineral β and Q_β is the activity product of mineral reactions β , and the $K_{eq,\beta}$ is the chemical equilibrium constant. $\hat{A}_\beta$ and $K_{eq,\beta}$ for different minerals are available in the literature [30,31]. The data presented in Liu et al. [12] has been adopted in this study.

$$r_\beta = \hat{A}_\beta k_\beta \left(1 - \frac{Q_\beta}{K_{eq,\beta}} \right) \quad (7)$$

The B-dot model [32] was employed to calculate ionic activity coefficients (Equation (8)), where A_γ , B_γ and $\dot{B}$ are temperature dependent parameters, $\dot{a}_i$ is the ion size parameter, I is the ionic strength, C_i and z_i are concentration (mol/kg H₂O) and electrical charge of species i . I can be calculated using Equation (9).

$$\log \gamma_i = -\frac{A_\gamma z_i^2 \sqrt{I}}{1 + \dot{a}_i B_\gamma \sqrt{I}} + \dot{B}I \quad (8)$$

$$I = \frac{1}{2} \sum_i^n z_i^2 C_i \quad (9)$$

3.2. Model Description

To evaluate the effect of CO₂ storage in shale reservoirs by comparing with a realistic CCS storage site in the deep saline aquifer, the YC shale (short for Yanchang shale) from the southern part of the Shannbei slope and the LJG sand (short for the Liujiagou sand) in the Shenhua CCS project were chosen as the target reservoir in this study. For numerical simulation, the advanced general equation-of-state compositional simulator GEM [33] was employed. For comparison and simplification, simplified 2-D homogeneous models with a burial depth of 925 m and thickness of 30 m vertically were established both for the shale and sand reservoir. Besides, a one-stage hydraulic fracturing horizontal well with a half-length of 165 m was located in the middle of the model for the shale (Figure 3a) and a vertical well without fracturing for the sand reservoir. The classical dual porosity dual permeability method was adopted to describe the fractured shale reservoir, the conductivity of the hydraulic fracture was discretized into 16 mD·m according to the actual hydraulic fracture width in the Yanchang shale gas exploitation site [34], while the conventional single porosity-permeability system was employed for the sand. The 2-D model was discretized into 19 × 25 grids in a horizontal plane with a volume of 30 m

$\times 30 \text{ m} \times 30 \text{ m}$ in total. The grids for the hydraulic fracture were refined to accurately describe the fluid flow between matrix and fracture for the shale reservoir. During the calculation, the dynamic time step adjusting method was employed.

Figure 3. (a) Schematic of the computational model and (b) the mineral composition of the Yanchang (YC) shale and Liujiagou (LJG) sand.

There are also several geological and geochemical property differences for the sand and shale, which are summarized in Table 1. Typical rock compressibility values at depths of interest for CO_2 storage range from 10^{-11} to $5 \times 10^{-9} \text{ Pa}^{-1}$ ($10^{-8} \sim 5 \times 10^{-6} \text{ kPa}^{-1}$), but always increase with rock permeability [35]. As a result, the compressibility was assumed to be higher for the sand than the shale reservoir in this study.

Table 1. Properties of Yanchang shale and the Shenhua saline aquifer used in the simulation.

Properties	YC Shale		LJG Sand
	Matrix	Fracture	
Pressure			
Temperature/(°C)		34.15 ^a	56 ^c
Porosity/(%)		10 ^a	9.3 ^c
Gas Diffusivity/(m ² /s)		1.00 × 10 ^{−9} ^b	1.00 × 10 ^{−9} ^b
Rock density/(kg/m ³)		2249 ^a	2249 ^a
Permeability/(mD)	2.53 × 10 ^{−4} ^a	3.300 × 10 ^{−3} ^a	5.615 ^c
Salinity(%)		3	
TOC/(%)		5 ^a	/
Compressibility/(1/Pa)	4.5 × 10 ^{−10} ^c	4.5 × 10 ^{−9} ^c	2.5 × 10 ^{−9} ^d
Maximal adsorbed gas(CO ₂)/(cm ³ /g)	1.258 ^a	/	/
Langmuir adsorption constant(CO ₂)/(1/Pa)	1.295 × 10 ^{−7} ^a	/	/
Maximal adsorbed gas(CH ₄)/(cm ³ /g)	0.224 ^a	/	/
Langmuir adsorption constant(CH ₄)/(1/Pa)	6.702 × 10 ^{−8} ^a	/	/

Source: ^a [8]; ^b [10]; ^c [24]; ^d [35].

Figure 3b shows the mineral composition of the Yanchang shale. As indicated by Zhang [8], the shale in the Yanchang area is mainly composed of clay, quartz, feldspar, calcite and pyrite. Clay minerals are the major mineral constituent with a content of 43.54–55.38%. The major clay minerals are chlorite, kaolinite, illite and mixed-layer illite and smectite (illite/smectite). Quartz occupying a content of 21.34–25.2% ranks in second place. The topmost Liujiagou sand was chosen for comparison, the mineral composition of which was employed in the model [36]. Quite different from shale, sand is rich in quartz and feldspar mineral, and Figure 3b shows a different mineral composition of sand and shale used in this study. Based on the available previous research and other empirical information [37–39], ankerite, dawsonite, magnesite and dolomite were chosen as the secondary minerals. The initial volume fraction of all the secondary minerals is assumed to be zero and a threshold mineral volume fraction of 10^{-6} is also assigned.

The precipitation begins when the non-existing minerals' volume fraction exceeds the threshold value; the volume fraction is updated at each time step according to user-defined specific surface area.

The density and viscosity of CO₂ are calculated from the Peng and Robinson equation [40] and Jossi, Stiel, and Thodos correlations [41], respectively. A validation of the geochemical modeling of water–rock interactions with mineral compositions listed in Figure 3b was performed with TOUGHREACT [42] prior to the final reactive transport simulation. TOUGHREACT is a widely used non-isothermal multiphase reactive transport simulator for geochemical reactions modeling during CO₂ storage in subsurface to obtain the initial chemical composition of formation water.

3.3. Simulation Cases and Validation

For comparison, the burial depth of the shale and the sand were both assumed at 925 m corresponding to the initial temperature of 34.15 °C and pressure of 9250 kPa with the thermal and pressure ingredient of 0.016 °C/m and 10 MPa/km [24], respectively. However, the CO₂ storage in shale is initialized after the depletion of shale gas production when the reservoir pressure is reduced due to the gas exploitation, which was assumed to be 7500 KPa at the beginning of CO₂ storage. Similarly, there remain only brine and CH₄ in the reservoir before CO₂ injection at the end of the shale gas production, while the initial CH₄ saturation in the matrix and fracture was 40% and 10%, respectively. CO₂ should be displayed as in supercritical phase; however, both GEM and TOUGHREACT are unable to distinguish CO₂ to be either in the supercritical or in subcritical phase from the gas phase. As a result, all the supercritical CO₂ is considered as a single non-wetting phase, that will henceforth be referred to as “gas” CO₂. CO₂ is continually injected at a maximum bottom-hole pressure of 22 MPa for 30 years, which means that the bottom-hole pressure of the injector shown in Figure 3a should be kept stable at 22 MPa during the whole period of CO₂ injection. The entire simulation duration is set at 500 years for both scenarios.

The effect of CO₂ storage in a shale reservoir and a deep saline aquifer was first compared. For the sand case (case 1 shown in Table 2), the gas diffusion, dissolution, drainage and imbibition, and CO₂–water–rock reactions are modeled. However in the shale case (case 2), the gas adsorption effect is also included in the simulation. To validate the ability of geochemical reactions modeling in GEM, the sand case was also built using TOUGHREACT. As shown in Figure 4, the obtained gas saturation and pH curve variation with the time at the injection cell are in good agreement for both simulators. The slight difference in gas saturation at the early and late stage of the simulation for TOUGHREACT and GEM may be due to differences in the geochemical reaction model. The different choice of the geochemical reaction model can significantly influence the CO₂ mineral trapping efficiency both in capacity and velocity. To explore the effect of different CO₂ injection schemes on CO₂ plume migration and phase transformation, three additional cases are considered, as shown in Table 2. Case 2 and case 3 are used to analyze the impact of CO₂ injection rate by maintaining the same injected CO₂ volume but changing the injection period. Case 2, case 3 and case 4 are considered to analyze the influence of continuous injection (case 2), huff-n-puff injection (case 4) and water alternating gas injection (case 5) on the CO₂ storage in shale reservoirs. The boundary of the simulation domain was assumed to be open in all simulations.

Table 2. Simulation cases.

Case Description	Description				Lithology
	Gas Adsorption	CO ₂ Injection Rate/(m ³ /day) *	CO ₂ Injection Period /(year)	CO ₂ Injection Scheme	
Case1	/	4000	30	Continuous injection	LJG sand
Case2		4000	30	Continuous injection	YC shale
Case3		2000	60	Continuous injection	YC shale
Case4		4000	30	Huff-n-puff injection	YC shale
Case5		4000	30	Water alternating gas injection	YC shale

* 4000 m³/day ≈ 0.09 kg/s.

Figure 4. Comparison of the gas saturation and pH change with time in the injection cell using the two numerical programs—GEM and TOUGHREACT.

4. Results and Discussion

4.1. Comparison of CO₂ Storage in Shale and Deep Saline Aquifer

The cumulative levels of CO₂ trapped with different mechanisms for the YC shale and LJG sand at the same CO₂ injection rate are compared and plotted in Figure 5. It can be observed that with a total amount of 1861.55 Mmoles (1861.55×10^6 moles) of CO₂ injected in 30 years, 656.59 Mmoles was in the free phase, 474.66 Mmoles was adsorbed, 102.03 Mmoles was trapped in residual phase, 179.12 Mmoles was dissolved in the formation water, and the remaining 458.06 Mmoles was trapped as mineralized CO₂ in shale at 500 years. For sand, 1075.36 Mmoles was in the free phase, 279.44 Mmoles was trapped through hysteresis, 155.88 Mmoles was in dissolution phase, and the rest 353.82 Mmoles was stored through CO₂–water–shale reactions. Within a timescale of <200 years, sand reservoir possesses priority in trapping CO₂ not only in the free gas phase and residual phase but also in the dissolution phase as well as the mineral phase. As time goes on, the superiority of sand trapping of CO₂ in the stable chemical phase is overwhelmed by shale.

Figure 5 also displays the CO₂ plume distribution at 30 years and 500 years for the sand and shale reservoir. Due to the high permeability of LJG sand compared to the YC shale, both CO₂ and pressure migrate faster along the horizontal plane, and this phenomenon is discussed in detail later. However, the pressure perturbation induced by CO₂ injection in the shale reservoir was constrained close to the stimulation zone. Once injection stopped, the in-place groundwater invaded the gas in the pores and micro-fractures and created the accumulation of CO₂ in residual phase. The larger CO₂ plume in the sand reservoir increases the interfacial area for subsequent residual trapping, dissolution and even the reaction with minerals (Figure 5a,b).

Although both reservoirs experience a pressure reduction response to injection stoppage, the pressure variation is neglected within the CO₂ plume for the sand reservoir and the fluid flow is dominated by diffusion in horizontal plane. However, there is nearly a 17-MPa pressure difference between the injection site and the margin of the CO₂ plume in shale; both advection and diffusion control the CO₂ migration. As a result, the CO₂ plume still expands outward for the shale but remains nearly unchanged for the saline aquifer after injection stops. It leads to wider CO₂ plume at 500 years for shale than for the sand reservoir. The pressure perturbation caused by CO₂ plume evolution combined with the transformation of the adsorbed phase into the dissolved phase causes the phenomenon of shale having more chemical trapping of CO₂ in the longer term.

The various CO₂ storage mechanisms have different operating time frames, among which the hydrodynamic and adsorption trapping take effect immediately after the CO₂ injection, while the residual gas, dissolution and particularly the mineral trapping mechanisms are a slow process, and can occur over a time scale of centuries to millennia. Instead, these three mechanisms play an essential role in increasing the security and safety of CO₂ geological storage [3]. In addition, different trapping mechanisms are strongly coupled and are competitive with each other, and different phases of CO₂ in the reservoir inter-convert dynamically. To improve CO₂ storage security as well as efficiency, the CO₂ injection strategy should be optimized based on the idea of expanding CO₂ plume and decrease in the percentage of CO₂ in the free gaseous phase.

Figure 5. (a,b) Cumulative CO₂ storage under different mechanisms in shale and sand; (c,e) free CO₂ distribution for case 1 (YC shale) at 30 years and 500 years; (d,f) free CO₂ distribution for case 2 (LJG sand) at 30 years and 500 years.

4.2. Effect of CO₂ Injection Rate on CO₂ Storage in Shale

As stated previously, to enhance the CO₂ storage security in a shale reservoir by constraining the capacity of free and mobile-phase CO₂ and to maintain a relatively gentle pressure perturbation, the CO₂ injection strategy should be precisely designed and optimized. The effects of the CO₂ injection rate on the overall performance of the sequestration project are investigated firstly. We do so by comparing case 2 and case 3. The same amount of CO₂ is injected in both cases, but over a period of 30 years in case 2 and over a period of 60 years in case 3.

The cumulative CO₂ in different phases for both cases (case 2 and case 3) is shown in Figure 6a,b. By comparing the deviation of the cumulative CO₂ stored in different phases for case 2 and case 3 at 500 years shown in Table 3, the change in residual trapping is most dramatic with the change in the injection rate. It can be seen from Table 3 that there was a 19.52% reduction in the residual trapping of CO₂ due to a decrease in the CO₂ injection rate. In addition, case 3 also has more CO₂ in the mobile free phase than case 2; the deviation is 38.56 Mmoles at 500 years. More CO₂ exists in the free phase to promote its horizontal migration. This result is also supported by the profile of the gas saturation in the fractures of the shale reservoir as shown in Figure 6c–h. This profile clearly shows that the

free-phase CO₂ migrates further horizontally at higher CO₂ injection rate especially during the period of CO₂ injection.

Figure 6. (a,b) Cumulative CO₂ storage under different mechanisms at different CO₂ injection rates; (c,e,g) free CO₂ distribution for case 2 at 30 years, 100 years and 500 years; and (d,f,h) free CO₂ distribution for case 3 at 30 years, 100 years and 500 years.

Table 3. Comparison of CO₂ amount in different phases for case 2 and case 3.

Cumulative CO ₂ Trapped under Different Mechanisms/(10 ⁶ moles)					
Case	Hydrodynamic Trapping	Adsorbed Trapping	Residual Trapping	Dissolution Trapping	Mineral Trapping
Case2	656.59	474.66	102.03	179.12	458.06
Case3	695.15	472.18	82.11	177.39	443.53
Deviation	5.87%	−0.52%	−19.52%	−0.97%	3.17%

4.3. Effect of Huff-N-Puff Injection and Water Alternating Gas Injection

Finally, we investigate the performance of the CO₂ sequestration project using the huff-n-puff injection scheme and the injection of alternating slugs of water and CO₂ scheme, which are widely used in the oil/gas industry to enhance oil and gas production. We compare the results of case 2, case 4 and case 5. In all the three cases, CO₂ is injected at a rate of 4000 m³/day over a period of 30 years. In case 2, the injection of CO₂ is continuous. In case 4, CO₂ is first injected for 15 years, then the well is shut-down and soaked for five years, and, finally, the well is opened again and injected for another 15 years. In case 5, the injection scheme is as follows: CO₂ is first injected at a rate of 4000 m³/day for 15 years, water is then injected at a rate of 50 m³/day for 5 years, and finally the CO₂ is injected at the rate of 4000 m³/day for another 15 years.

As shown in Figure 7, for the huff-n-puff injection scheme, the addition of CO₂ soaking time has a limited impact on the performance of CO₂ storage in a shale reservoir compared to the continuous injection, especially for long-term CO₂ storage. However, at the beginning, the amount of free CO₂ increases while the immobile CO₂ in residual as well as the dissolved phase decreases for the huff-n-puff injection scheme, which is not beneficial for the storage safety of CO₂. On the other hand, the water alternating gas injection scheme can somehow reduce the free-phase CO₂ as well as the adsorbed-phase CO₂ by enhancing the CO₂ dissolution into the formation water and trapping it in the micro-pores in

the residual phase within the timescale of 300 years. However, with the continual ex-solution of CO₂ from formation water in the longer term, the CO₂ reaction with the host rock is also prohibited.

Figure 7. Cumulative CO₂ storage in different storage mechanisms using various CO₂ injection schemes. (a): gas phase; (b): adsorbed phase; (c): dissolved and residual phase; (d): mineral phase

Figure 8 shows the free-phase CO₂ distributions for case 2, case 4 and case 5 at 30 years, 100 years and 500 years. It can be observed that, for case 2 and case 4, although the addition of soaking time for CO₂ injection can hinder the gaseous CO₂ migration in the horizontal direction, once injection stops, the migration rate is accelerated and the mobile CO₂ can even move faster than in the case of the continuous injection scheme. The gaseous CO₂ front in Y direction at 500 years arrives at 600 m for the huff-n-puff scenario but only at nearly 580 m for the continuous injection scenario. On the other hand, the water alternating gas injection scheme (case 5) can apparently decrease the capacity of mobile CO₂ during the whole period of CO₂ storage.

4.4. Pressure Perturbation Induced by CO₂ Injection

The performance of CO₂ storage in the subsurface is highly dependent on the pressure evolution in the formation. The adsorptive behavior of gas onto an organic substrate is largely dependent on pressure. Although there are different types of adsorption models that can be used to describe the CO₂ adsorptive behavior to shale, for example the Langmuir model used for the New Albany shale [43] and the Devonian shale from the Kentucky [5], and the BET-type adsorption of CO₂ onto Barnett shale [44], they all show that the CO₂ adsorption capacity is a function of ambient pressure. The CO₂ dissolution into the formation water is also largely impacted by pressure. Xu et al. [45] indicate that the pressure variation in the reservoir can affect the dissolution of CO₂ into the formation brine. As the volume of dissolved CO₂ changes, the original chemical equilibrium between CO₂ (aq.), H₂CO₃, and HCO₃[−] can be re-established and the mineral reactions will also change accordingly.

Figure 8. Free CO₂ distributions for case 2, case 4 and case 5 at 30, 100 and 500 years. (a,b,c) compares the gas phase CO₂ distribution of continuous injection scenario at 30 yrs, 100 yrs and 500 yrs, respectively; (d,e,f) shows the gas phase CO₂ distribution of huff-n-puff injection scenario at 30 yrs, 100 yrs and 500 yrs; (g,h,i) gives gas phase CO₂ distribution of water alternative injection scenario at 30 yrs, 100 yrs and 500 yrs.).

Furthermore, pressure variation is also a cause for the change in residual trapping. The non-wetting gas to invade the smaller pores is driven by the higher formation pressure, and the snap-off also results in the increase in macroscopic trapping that occurs readily in smaller pores during imbibition. On the other hand, the gravity effect impacts the displacement pattern of water by CO₂ for low capillary entry pressure. Compared with high-viscosity fluid, the low-viscosity gas can form more stable paths when penetrating the high permeability regions of the porous medium, and only the largest pores can be invaded to lead to reduced snap-off during an eventual imbibition process [15].

Figure 9 shows the pressure variation at observation point #1 ($X = 275$ m, $Y = 375$ m), which is located at the injection site for case 1, case 2, case 3, case 4 and case 5. The drastic pressure build-up induced by CO₂ injection in the LJG sand is larger and more lasting compared with the YC shale, which displayed with a rapid speed of pressure up and down (Figure 9a). The higher permeability not only enhances the fluid penetration into the rock pores and fractures, but also increases the pressure transmission through the reservoir. The pressure perturbation was constrained within the stimulation zone for the shale reservoir; however, the pressure variation was extended to the whole simulation domain for the sand cases and decreased very slowly responding to the injection well shut-in. The significant pressure deviation between the injecting site and the surrounding area was the cause of CO₂ plume expansion within the shale reservoir and also increased the interfacial area for subsequent CO₂ dissolution and mineral trapping.

Figure 9. Pressure evolution at observation point # 1 ($X = 275$ m, $Y = 375$ m) for different cases. (a) compares the pressure perturbation of continuous injection scenario of shale and sand and also the influence of injection rate; (b) shows the pressure build-up of continuous injection scenario, huff-n-puff injection scenario and water alternate injection scenario of shale reservoir).

The pressure build-up in case 3 at the injection point is smaller than in case 2, which significantly weakens the residual trapping, as shown in Table 3. The pressure decrease also leads to the release of CO_2 from the formation water, which, combined with gas desorption causing more CO_2 , exists in the free phase. Considering pressure perturbation induced by the three CO_2 injection schemes (as shown in Figure 9b), although the water alternating gas injection scheme can increase the CO_2 storage security in a shale reservoir by trapping more CO_2 in the immobile phase, it induces large pressure build-up during water injection.

4.5. Implication to CO_2 Storage Safety and Stability

Due to the high diffusivity of gaseous or supercritical CO_2 , the free-phase CO_2 is generally believed to be in the unstable phase, which can easily migrate into the preferential pathways, such as natural or artificial fracture, unfolded fault and abandoned wells and leak from the storage site. Bachu et al. [3] state that the residual-gas trapping, dissolution, and mineralization of CO_2 are essential mechanisms in increasing the security and safety of geological storage of CO_2 in a saline aquifer after cessation of injection as less and less CO_2 remains in the free, mobile phase over time. It is similar for CO_2 storage in a shale reservoir. Figure 10 compares the CO_2 storage security evolution with time for LJG sand and YC shale. It can be seen that the CO_2 storage security increases with time both for shale and sand because more and more CO_2 gets stored as a trapped phase over time. Although LJG sand possesses the advantage in trapping more CO_2 in the residual, dissolution as well as mineral phase in the short term, this merit is overwhelmed by YC shale as time goes on. Besides, more than 20% of gaseous CO_2 is trapped in the adsorbed phase; the overall unstable mobile-phase CO_2 in the YC shale reservoir is significantly less than the LJG sand, which indicates that shale shows superiority in security of CO_2 storage over saline aquifer.

In addition, the pressure perturbation induced by CO_2 injection is also a very important indicator of storage security. The storage of industrial-scale CO_2 into a deep saline aquifer can cause large and lasting pressure perturbations that can potentially increase the risk of the leakage of CO_2 through a fracture in caprock through the overlying aquifer and cause pollution. It can also result in fault activation inducing seismicity [46,47]. As stated previously, the pressure build-up in a saline aquifer is more severe than in a shale reservoir and is longer lasting with time. However, the pressure perturbation in a shale reservoir is also highly dependent on the CO_2 injection rate and stimulation of the fractured zone.

Economically, CO_2 storage in a deep saline aquifer is a relatively non-profitable project since it requires heavy investment in well drilling, manufacturing, maintenance and monitoring etc. In case of

the low-porosity and low-permeability Shenhua saline aquifer considered in this paper, the extra hydraulic fracturing is also needed to stimulate the reservoir. The high drilling costs primarily contribute to the huge economic cost of a GCS projects. It is estimated that the drilling cost for a vertical well at depth of 2200 m can be as high as USD 4.86 million according to the International Oil Drilling Investment Estimate method and related drilling costs classification. However, the storage of CO₂ in the depleted shale reservoir can avoid the costs in constructing drilling wells.

Figure 10. Storage security of CO₂ in (a) a deep saline aquifer and (b) in a depleted shale reservoir.

5. Conclusions

This study presents a comprehensive analysis of the potential of CO₂ storage in a shale reservoir based on the geological parameters of Yang Chang (YC) shale in the Ordos basin of China by taking into account the Darcy and diffusive flow, gas sorption/desorption, hysteresis effects, CO₂ dissolution, and CO₂–water–shale reactions. The advantage and disadvantage of CO₂ storage in YC shale are analyzed by comparing them with the CO₂ storage in LJG sand (saline aquifer) from the Shenhua GCS project in China. To enhance CO₂ storage security in shale by constraining the capacity of free and mobile-phase CO₂ and to maintain a relatively gentle pressure perturbation, different injection strategies, including the low rate continuous injection, high rate continuous injection, huff-n-puff injection and the water alternate injection are compared. The results can be summarized as follows:

1. From the point of view of CO₂ phase transformation, CO₂ storage in shale can be safer than in saline aquifer by trapping more CO₂ in immobile phases, including adsorbed, residual, dissolution and mineral phase with lesser percentage remaining in free mobile phase in longer-term. Although, the saline aquifer has the advantage in trapping more CO₂ in the residual, dissolution and mineral phase in the short term.
2. The pressure perturbation induced by CO₂ injection in the saline aquifer is longer lasting and generally larger than in the shale reservoir. The pressure build-up in shale can be rapidly released when CO₂ injection is stopped.
3. Although the water alternating injection scheme can significantly increase the dissolution and residual phase of CO₂ in short to middle term, the pressure build-up caused by water injection is more drastic than other schemes. For the aim of increasing the fraction of immobile CO₂ while maintaining a safe pressure-perturbation, the intermittent injection procedure with multiple slugs of huff-n-puff injection can be employed to replace the continuous CO₂ injection. Within the allowable range of pressure increase, the CO₂ injection rate can be maximized to increase the CO₂ storage capacity and security in a shale reservoir.

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