

Article

Large-Scale Experimental Investigation of Hydrate-Based Carbon Dioxide Sequestration

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Abstract: Hydrate-based CO₂ sequestration is a novel approach that can not only realize permanent CO₂ sequestration but can also form an artificial cap to prevent its upward migration. In this work, a self-developed large-scale 3D apparatus was employed to investigate hydrate formation characteristics in hydrate-based CO₂ sequestration at a constant liquid CO₂ injection rate through a vertical well for the first time. Temperature and pressure evolutions in the sediment were analyzed in detail. Key indicators, including cumulative sequestered CO₂, CO₂ in hydrate and liquid phases, the instantaneous hydrate conversion, and liquid CO₂ retention rates, were calculated. The results show that hydrate continuously forms with increased CO₂ injection and exhibits strong heterogeneity due to the variation in hydrate formation rate and quantity. Severe liquid CO₂ heterogeneous fingering phenomena occur since hydrate deteriorates the effective pore structure and topology, resulting in relatively small cumulative sequestered CO₂ when a large amount of CO₂ is released from the outlet. Meanwhile, the instantaneous hydrate conversion and liquid CO₂ retention rates have large fluctuations owing to water consumption and variation in the effective contact area between liquid CO₂ and water. However, hydrate formation does not cause blockage of wellbore and formation nearby under given experimental conditions, which is beneficial for hydrate formation in deeper sediment. This study provides insights into hydrate formation and liquid CO₂ immigration regularity during hydrate-based CO₂ sequestration and demonstrates its feasibility at a field scale.

Keywords: hydrate-based CO₂ sequestration; CO₂ hydrate formation characteristics; cumulative sequestered CO₂; instantaneous hydrate conversion rate; liquid CO₂ retention rate



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1. Introduction

With the exacerbation of global warming, rising sea levels, and the intensification of extreme weather in recent years [1–4], CO₂ emission reduction has been gaining attention globally [5]. As one of the key approaches to achieving CO₂ reduction [6–9], CO₂ geological sequestration is estimated to contribute to a cumulative reduction ratio of over 15%. Currently, most field tests about CO₂ storage focus on saline aquifers [10–15] with sequestration mechanisms [16,17] involving structural trapping, capillary trapping, solubility trapping, and mineralization, with the latter being recognized as the most enduring and secure mode. However, the geochemical reaction rate is extremely slow [18,19] which aggregates CO₂ leakage risk [20]. As a novel CO₂ geological sequestration technology through the formation of hydrate in the sediment [21–23], hydrate-based CO₂ sequestration can not only enable stable CO₂ storage [24–26] but can also prevent its upward migration [27–30], reducing CO₂ leakage risk from the underlying layer. Current research on CO₂ regarding the replacement of natural gas hydrate [31–36] with the mechanical stability of the sediment

after the replacement is maintained by the generated CO₂ hydrate [37–39] has confirmed the feasibility of CO₂ sequestration in the form of solid hydrate [40–42]. Therefore, there is an urgent need to investigate CO₂ migration and hydrate formation characteristics during hydrate-based CO₂ sequestration.

In recent years, many investigations on hydrate-based CO₂ sequestration have been carried out [43–45]. Liu et al. (2018) [46] studied CO₂ hydrate dynamic formation regularity in depleted natural gas hydrate reservoirs through a series of sequential experiments, including natural gas hydrate formation and dissociation in the sediment as well as CO₂ injection and water replenishment combined with MRI. The results indicated that CO₂ hydrate and connate water saturation after hydrate formation was proportional to the initial water content, and subsequent water replenishment was beneficial for continuous CO₂ hydrate formation. Zheng et al. (2020) [47] summarized the research on hydrate-based CO₂ sequestration in various regions containing deep-sea and sub-seafloor saline formation, permafrost, and natural gas hydrate deposits. The technical feasibility, potential, challenges, and prospects of hydrate-based CO₂ sequestration were pointed out, while no effective analysis of the scale effects and economic aspects involved was conducted. In 2021, Zhang et al. [48] explored the feasibility of CO₂ sequestration in the sediment where the temperature and pressure for hydrate formation were satisfied with pressure-controlling methods through CO₂ injection and water production wells based on the CMG STARS simulator. The results showed that formed hydrate delayed CO₂ breakthrough to the water production well and inhibited the subsequent CO₂ injection by compressing the effective pore space to a certain extent. However, the simulation results were not validated with experimental data. In 2022, Kuang et al. [49] observed in situ CO₂ hydrate formation using pressure oscillations combined with low-field MRI techniques. The experimental results indicated that CO₂ hydrate preferentially formed in larger pores and hindered the CO₂–water contact area. In addition, it was beneficial for hydrate-based CO₂ sequestration at high initial water saturation when the displacement pressure was large. Zhao et al. (2023) [50] investigated CO₂ upward transport and the Plugging Law caused by hydrate formation in overlying layers at different injection rates by MRI and flow characteristic analysis. It was indicated that a low CO₂ injection rate and a high overburden pressure were beneficial for hydrate formation. Moreover, the strength of the hydrate cap increased with continuous hydrate formation. Meanwhile, Beatrice Castellani (2023) [51] analyzed the role of hydrate-based CO₂ sequestration in traditional CO₂ geological storage and discussed the knowledge required to pursue a stable, efficient, and environmentally friendly pathway for hydrate-based CO₂ sequestration.

Although many scholars have conducted foundational research on hydrate-based CO₂ sequestration [52–54], current conclusions drawn from small-scale experiments and numerical simulations need further validation due to the scale effects and complex mechanisms involved in hydrate formation and migration. To overcome the scale effects on CO₂ transport and hydrate formation in hydrate-based CO₂ sequestration, a self-developed large-scale 3D platform with a maximal volume of 1695 L, a maximal pressure of 30 MPa, and a temperature ranging from −20 to 200 °C was employed to investigate hydrate formation characteristics in the sediment where the temperature and pressure were satisfied for hydrate formation at a constant liquid CO₂ injection rate through a vertical well. The dynamic evolution of the pressure and temperature in the sediment was analyzed in detail, revealing CO₂ hydrate dynamic formation regularity. Afterward, the amount of cumulative sequestered CO₂, CO₂ percentage in hydrate and liquid phases, and the instantaneous hydrate conversion and liquid CO₂ retention rates were calculated. This work revealed liquid CO₂ transport and hydrate formation characteristics from a large-scale perspective for the first time, providing robust data support for hydrate-based CO₂ sequestration at a field scale.

2. Experimental Setup and Procedure

2.1. Experimental Setup

The self-developed large-scale 3D platform with a maximal volume of 1695 L, maximal pressure of 30 MPa, and temperature ranging from -20 to 200 °C was employed to carry out experiments on hydrate-based CO_2 sequestration. As shown in Figure 1, the whole system can be divided into eight parts, which are the main body module, liquid injection module, gas injection module, temperature control module, vacuum pump module, back pressure control module, ambient pressure control module, fluid production module, and data measurement and acquisition module. The main body module is the core of the entire system, which is used to reshape the sediment for CO_2 migration and hydrate formation. It consists of components such as a high-pressure reactor vessel, internal model, pipeline extraction system, load-bearing operating platform, hydraulic system, and so on. The liquid injection module is used for liquid CO_2 injection. The temperature control module is primarily composed of a stepwise low-temperature control chamber, a water jacket, and a refrigeration unit, which are used to adjust the temperature for hydrate formation. The ambient pressure control module is utilized to maintain the pressure difference between the internal model and the chamber in the reactor vessel. The back pressure module is employed to control pressure in the internal model to prevent an excessively high value caused by liquid CO_2 injection. The data measurement and acquisition module is used to quantify fluid production when the pressure in the internal module surpasses the back pressure at the outlet. The instruments or components involved in the experimental setup were sourced from Yongruida Technology Co., Ltd., Beijing, China.

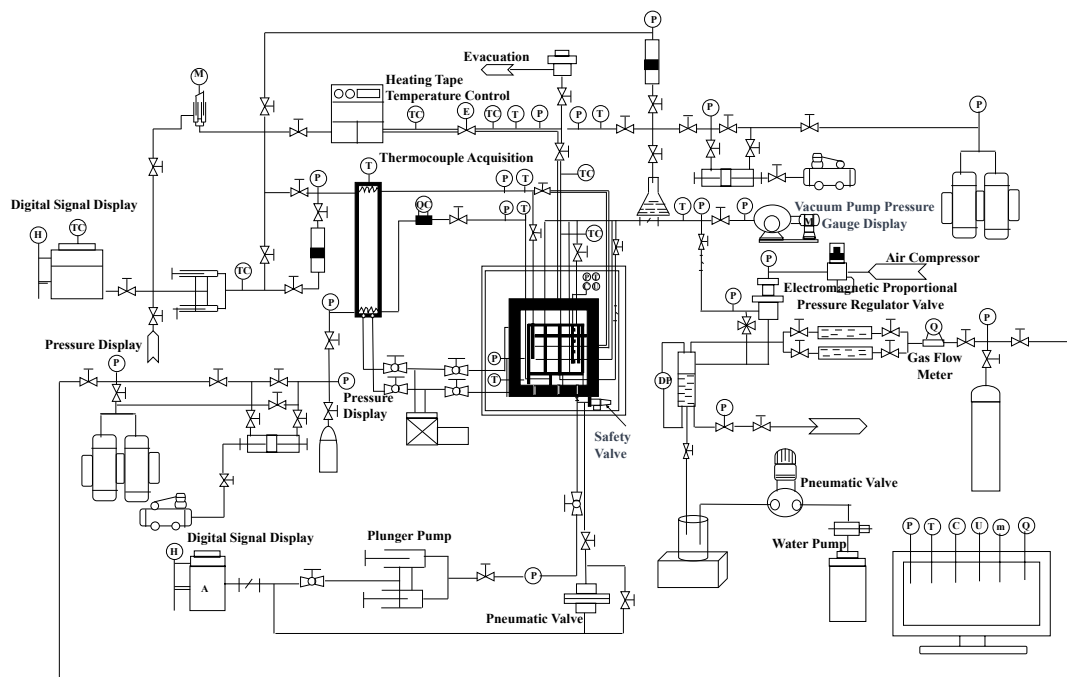


Figure 1. Schematic of the large-scale experimental setup.

Compared to other large-scale 3D experimental systems, this platform has an internal reaction vessel with a size of $760 \times 760 \times 700$ mm³ (Figure 2a), which can be used to apply confining pressure and better reshape the real sediment. The components of the square internal module include a lifting lug, top endcap, sintered filter cartridge, cylinder, porous plate, bottom endcap, and bottom pipeline. Nine vertical and nine horizontal wells are placed in the internal module, with their distribution shown in Figure 2b. Three vertical wells labeled V3, V5, and V7 are distributed in the lower region, which has a distance of 90 mm to the bottom. Two vertical wells named V1 and V9 are located in the first layer

from the top of the internal model, while another two vertical wells, namely, V2 and V8, are situated in the second layer. The V4 and V6 wells are positioned in the third layer. Three horizontal wells, namely, H1, H2, and H3, are penetrated to a depth of 150 mm into the internal model, while the horizontal wells H4, H5, and H6 are extended to a depth of 350 mm. The H7, H8, and H9 wells are extended to a depth of 500 mm into the internal model. The horizontal and vertical wells exhibit interleaved arrangements, allowing for liquid CO₂ injection under different well types or well patterns. In the experiment, the internal module is used to reshape the marine sediment with sieved sand to investigate CO₂ immigration and hydrate formation during CO₂ injection, and the vertical well labeled as V5 is employed as the injection well.

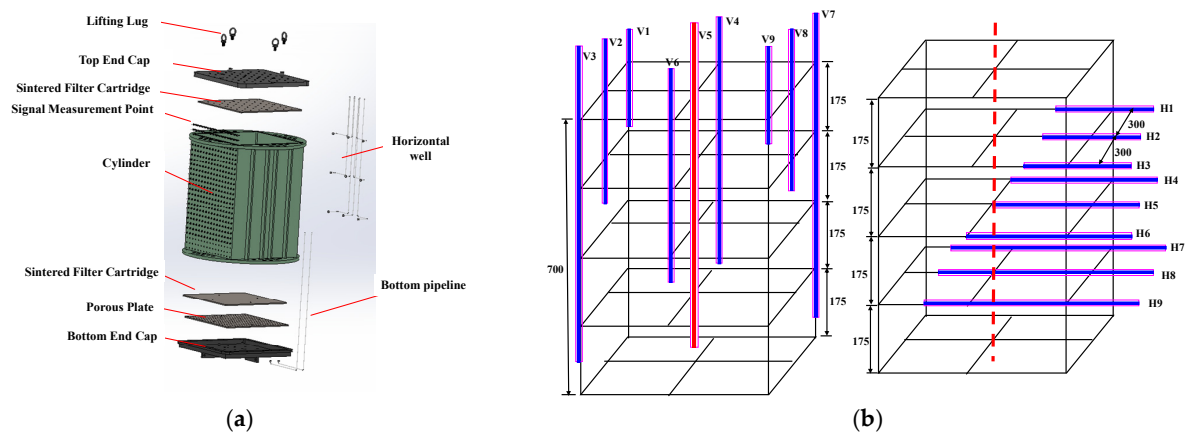


Figure 2. (a) Internal model. (b) Well patterns (Dashed lines mean central axis of the internal reaction vessel).

In addition, eighty temperature and eighty pressure detection points are distributed at five layers in the internal model, with sixteen of them arranged in each layer, as shown in Figure 3. The temperature detection points exhibit a square-shaped distribution in each detected cell, while the pressure detection points show a diamond-shaped arrangement. The temperature and pressure detection points are arranged in an interleaved distribution, which can be used for real-time monitoring during liquid CO₂ injection. The temperature and pressure signals collected by the detection points are transferred to a computer in another room to be recorded.

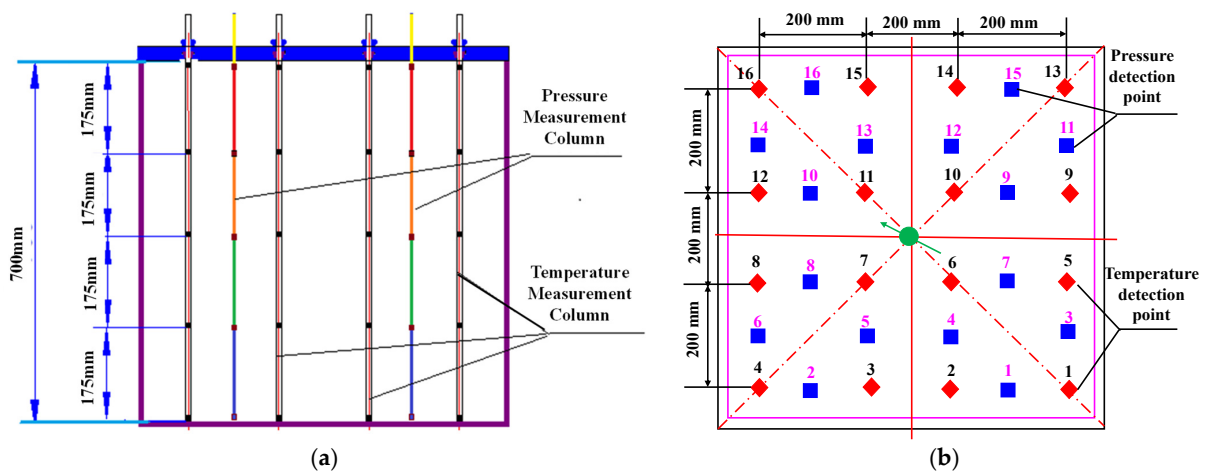


Figure 3. Distribution of the temperature and pressure detection points in the internal model: (a) side view and (b) top view (Color labels of red and blue dots respectively represent temperature and pressure detection points with the numbers indicating their index identifiers, green arrow indicates injection well).

2.2. Experimental Procedure

The detailed experimental procedure of hydrate-based CO₂ sequestration is shown as follows:

- (1) A certain amount of sand with a particle size of 120 mesh was first prepared and mixed with water for sand washing. Afterward, the sand was placed into the incubator for drying and was selected a second time to ensure the consistency of the sand particle mesh.
- (2) The sieved sand and water were mixed again in the stainless steel to make all the sand wet, and the water between the sand particles was discharged. The sand with the remaining water was then evenly stirred to ensure that the water on the sand surface was as uniform as possible.
- (3) The wet sand was filled into the internal model and compacted evenly layer by layer. After sealing, the internal model was turned over and kept standing to ensure the uniform distribution of water between the sand particles. The internal model was then placed into the large reactor vessel with a volume of 1695 L.
- (4) Nitrogen was then injected into the internal model from the bottom until the pressure reached 13.5 MPa, which was maintained for 7 h to test the seal of the system.
- (5) After the seal check, water was injected into the internal model from the bottom to displace the nitrogen. The top valve was then closed, and water injection continued until the pressure in the internal model reached 11 MPa.
- (6) The chiller and cold-water jacket were then opened to adjust the temperature of the internal model to 7 °C. It can be seen from Figure 4 that the reshaped sediment satisfied the condition for hydrate-based CO₂ sequestration.
- (7) Afterward, liquid CO₂ was injected into the internal model at a constant flux of 10 mL/min through an intermediate vertical well labeled as V5. To avoid an exceedingly high pressure in the inlet model, an outlet was set at the bottom with a back pressure of 12 MPa.
- (8) The water and CO₂ produced were recorded once the outlet was opened due to a pressure difference. When one tank of liquid CO₂ injection was completed, another tank was opened until a large amount of CO₂ was released from the outlet.
- (9) The cumulative sequestered CO₂ and proportion of CO₂ in the hydrate and the fluid were calculated.

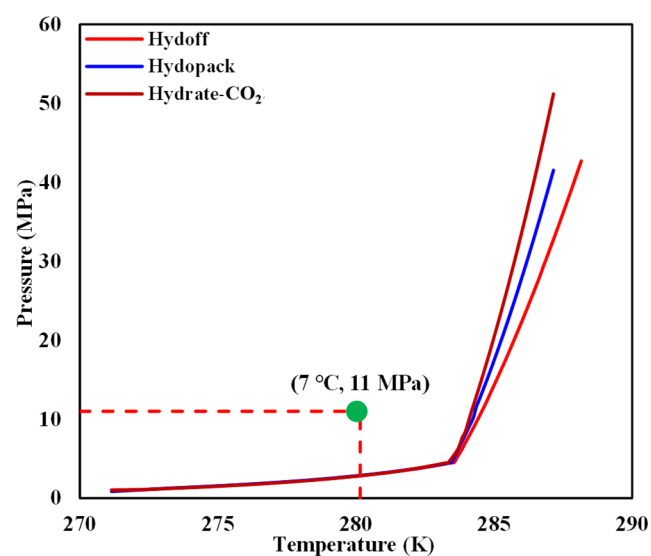


Figure 4. Comparison of the initial temperature and pressure in the internal model with a CO₂ hydrate-phase equilibrium curve.

3. Results and Analysis

3.1. Evolution of the Temperature and Pressure during Liquid CO₂ Injection

3.1.1. Evolution of the Temperature

The dynamic evolution of the temperature in each layer is shown in Figure 5. It can be seen that the temperature does not remain constant, while an irregular variation occurs in the local position during liquid CO₂ injection. Since the injected liquid CO₂ will not transform to dry ice or gas to cause heat variation under the given temperature and pressure conditions, the fluctuation in the temperature at local positions indicates the localized formation of CO₂ hydrate with different formation rates and formation times and heterogeneous distribution. The increase in the local temperature grows more pronounced at the position where hydrate is generated at a faster rate and in larger quantities. Since the temperature control module is always in operation during liquid CO₂ injection and water has large thermal conductivity, the temperature at which CO₂ hydrate forms gradually decreases after the formation rate slows down.

It is worth noting that the generated CO₂ hydrate does not cause plugging near the injection well at a liquid CO₂ injection rate of 10 mL/min. This is mainly because the amount of hydrate generated near the wellbore is less and not as dense as imagined at the given injection rate. The formed CO₂ hydrate may either be displaced or disrupted with continuous CO₂ injection, preventing hydrated-induced plugging. However, CO₂ hydrate-induced plugging with different liquid CO₂ injection rates and well types cannot be ruled out.

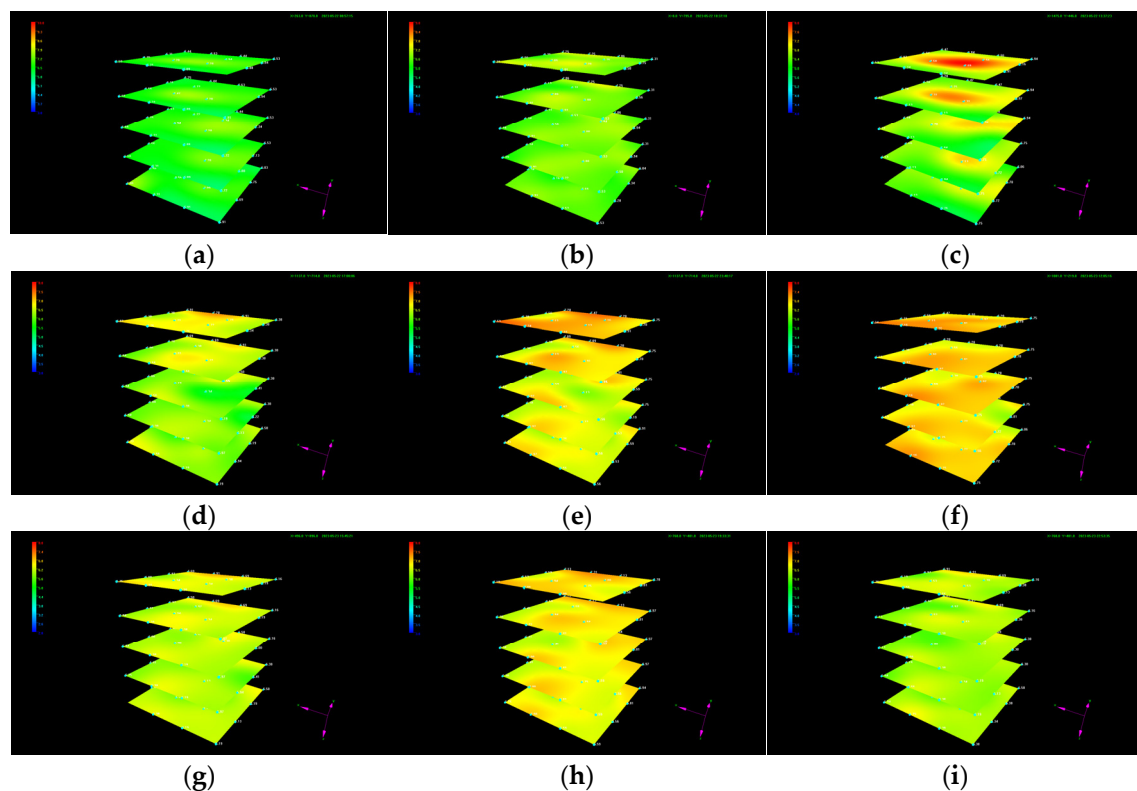


Figure 5. Evolution of the temperature during liquid CO₂ injection. (a) $t = 0.2$ h; (b) $t = 1.87$ h; (c) $t = 4.87$ h; (d) $t = 8.25$ h; (e) $t = 14.92$ h; (f) $t = 27.33$ h; (g) $t = 31$ h; (h) $t = 34.8$ h; and (i) $t = 38.13$ h.

To better analyze the dynamic temperature evolution during liquid CO₂ injection, variations in the temperature at detection point 11 in each layer near the injection well as well as the average temperature in the sediment are summarized in Figure 6a,b. It can be seen from Figure 6a that the temperature at detection point 11 in each layer exhibits a sawtooth variation pattern with the evolution regularity among different layers showing

a relatively consistent trend. The temperature evolution regularity is mainly induced by the combined effect of three factors, including hydrate formation, the large thermal conductivity of formation water, and a low-temperature control module that is always in operation during liquid CO₂ injection. When the heat release induced by CO₂ hydrate formation at point 11 in each layer is dominant, the temperature increases. As the hydrate formation rate slows down, the impact of hydrate formation on temperature rise gradually weakens. When the effect of large water thermal conductivity and a low-temperature control module on the prevention of a temperature rise exceeds the heat release from hydrate formation, the temperature decreases, which results in sawtooth fluctuations in the temperature. It is also noted that the magnitude of temperature fluctuations at detection point 11 in each layer varies at different liquid CO₂ injection stages and among different layers. The degree of the increase in temperature in the first layer at the first tank of liquid CO₂ injection is larger than that at other injection stages and layers. This is primarily because the CO₂ density is smaller than that of water under the experimental temperature and pressure conditions. The injected liquid CO₂ gradually moves upward to the first layer, resulting in a much larger contact area between liquid CO₂ and water at point 11 than that at the same position in other layers. The CO₂ hydrate formation rate and quantity grow much larger, leading to an instantaneous release of large amounts of heat and a sharp increase in temperature at point 11 in the first layer. When CO₂ hydrate formation is stable, the effect of water thermal conductivity and the low-temperature control module dominates, causing a significant decrease in temperature. Since the generated hydrate at detection point 11 hinders the effective contact between water and subsequently injected liquid CO₂ to some degree, the hydrate formation rate and quantity decrease, resulting in a small magnitude of temperature fluctuations with continuous CO₂ injection at this point. Hydrate formation at different positions in the sediment also results in similar fluctuations in the average temperature at different magnitudes of CO₂ injection (Figure 6b), while the smoothness of temperature fluctuations is more gradual than the variation in temperature at a certain detection point.

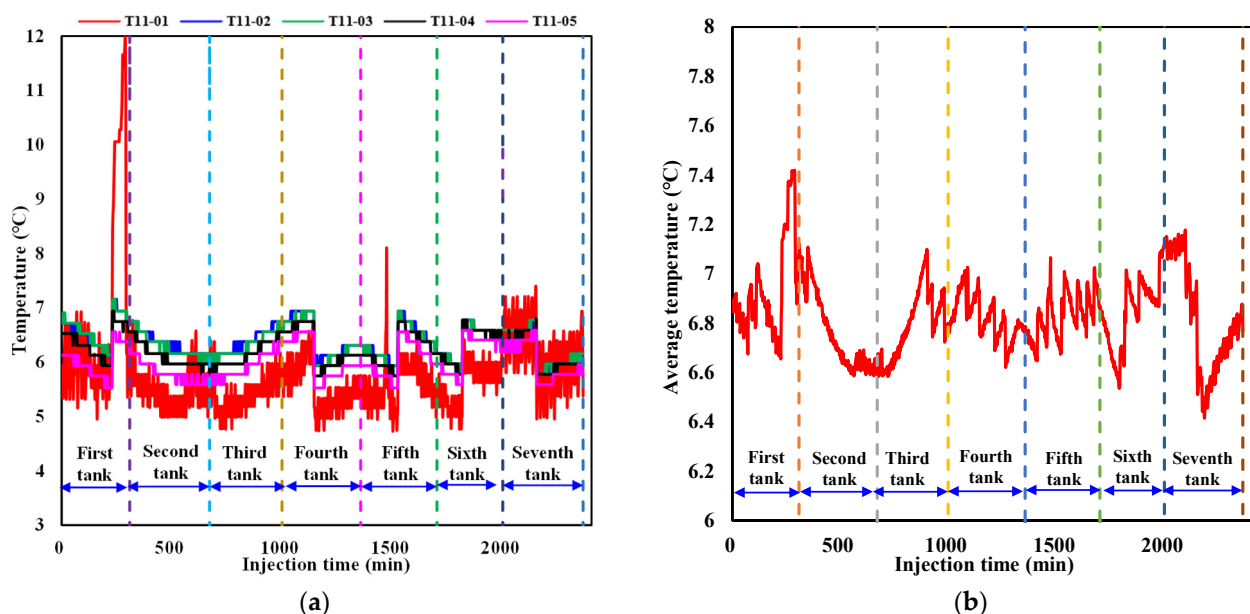


Figure 6. Variation in the temperature during liquid CO₂ injection. (a) Temperature variation at point 11 in each layer near the injection well. (b) Variation in the average temperature in the sediment.

3.1.2. Evolution of the Pressure

The dynamic evolution of the pressure distribution in each layer during liquid CO₂ injection is shown in Figure 7, indicating that the pressure in the sediment gradually increases before the outlet valve opens. Since the sand particle size used for sediment

reformation is uniform and the sediment is compacted uniformly layer by layer during reconstruction, the reshaped sediment is relatively homogeneous. If there was no hydrate formation, the overall pressure should have had high values near the injection well and gradually decreased with increasing distance from the vertical liquid CO₂ injection well at a constant rate. However, it is evident that the dynamic evolution of pressure in the sediment indicates an irregular variation with locally low pressure at some positions, which is attributed to localized hydrate formation under the experimental temperature and pressure conditions. The generated hydrate alters the heterogeneity and anisotropy in the sediment to some degree, causing the pressure distribution to exhibit irregular variations during liquid CO₂ injection. When the pressure in the sediment exceeds the back pressure at the outlet, the outlet valve opens and the overall pressure gradually decreases, accompanied with fluid production from the outlet. The outlet valve automatically closes when the pressure in the sediment is smaller than the outlet back pressure. With the continuous CO₂ injection, the average pressure in the sediment gradually increases again. Liquid CO₂ injection continues until a large amount of CO₂ is produced at the outlet.

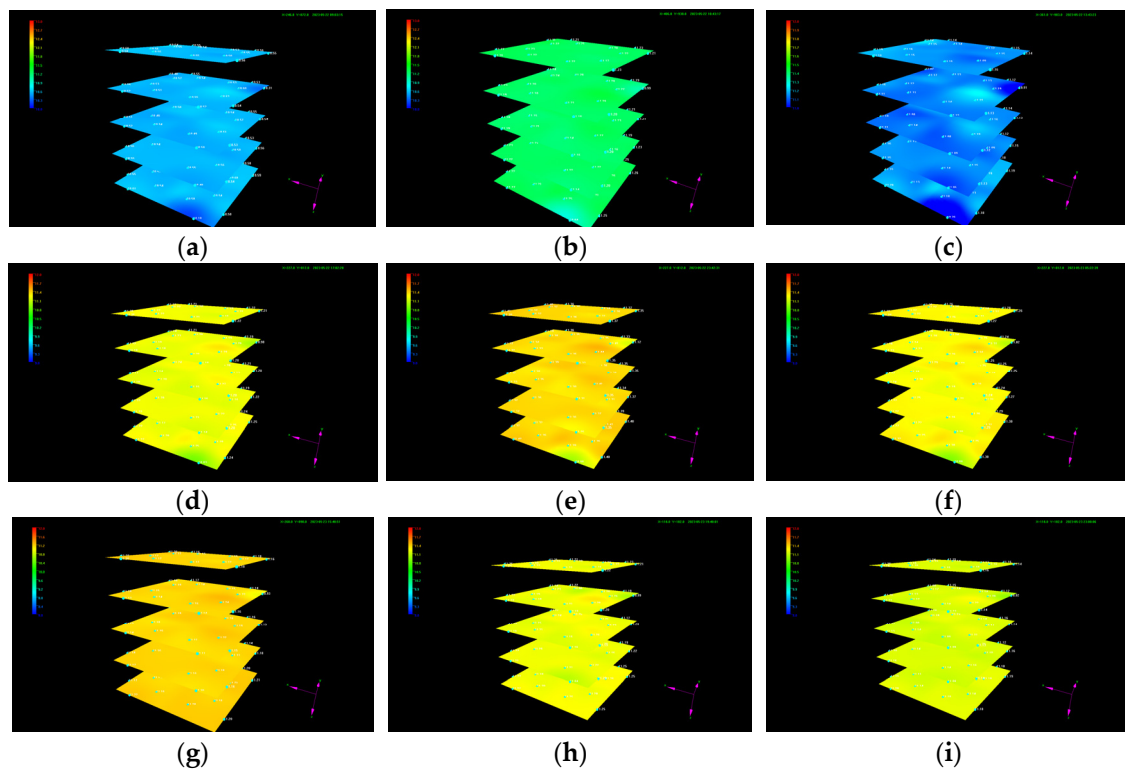


Figure 7. Variation in the pressure distribution during liquid CO₂ injection. (a) $t = 0.3$ h; (b) $t = 1.97$ h; (c) $t = 4.97$ h; (d) $t = 8.28$ h; (e) $t = 14.95$ h; (f) $t = 20.62$ h; (g) $t = 31.05$ h; (h) $t = 34.92$ h; and (i) $t = 38.25$ h.

To better characterize the pressure evolution during liquid CO₂ injection, variations in the pressure at detection point 10 in each layer near the injection well as well as the average pressure in the sediment are respectively illustrated in Figure 8a,b. It can be seen from Figure 8a that the pressure at point 10 in each layer exhibits a certain degree of fluctuation, with the amplitude in the fifth layer generally being higher than that in other layers during liquid CO₂ injection. The irregular fluctuation in pressure at the interval of the outlet valve from closing to opening can be attributed to a change in the volume of liquid CO₂ and a variation in the effective pore structure caused by hydrate formation. Since the density of CO₂ hydrate is slightly higher than that of liquid CO₂, hydrate formation results in a slight reduction in fluid volume, leading to a small decrease in pore pressure. Meanwhile, the formed hydrate aggravates the heterogeneity of the sediment, resulting in an increase in the disorderliness of pressure propagation and heterogeneous pressure distribution.

Therefore, the pressure at detection point 10 in each layer exhibits irregular fluctuations. When the pressure in the sediment surpasses the back pressure at the outlet, the outlet valve automatically opens and the pressure rapidly decreases as the fluid flows out from the outlet. The pressure evolution at detection point 10 in each layer in the whole process of liquid CO₂ injection can be attributed to the joint effects of CO₂ hydrate formation, fluid expelled from the outlet, and continuous liquid CO₂ injection. Since the outlet valve is located at the bottom of the internal model, the magnitude of the pressure fluctuation caused by the fluid released from the outlet has a greater impact on the fifth layer than the other four layers. It is observed from Figure 8b that the localized pressure fluctuation also results in irregular variations in the average pressure of the sediment, while the magnitude and smoothness of the evolution have some differences in local pressure fluctuations at a certain point.

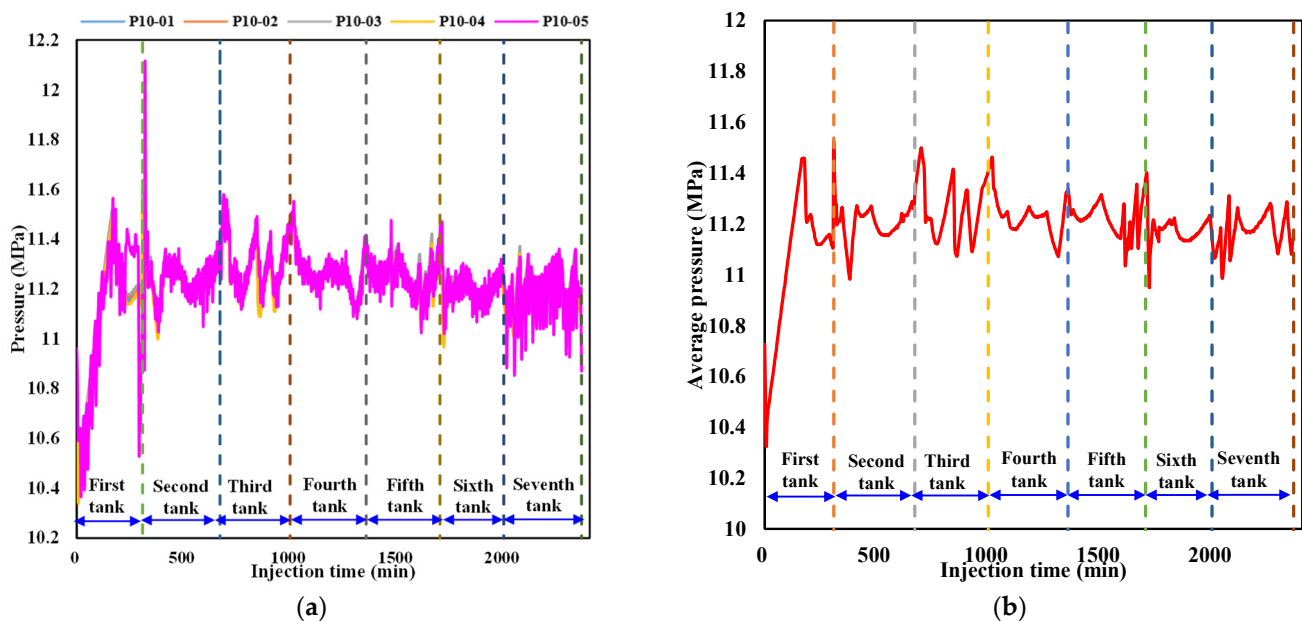


Figure 8. Variation in the pressure during liquid CO₂ injection. (a) Pressure variation at detection point 10 in each layer near the injection well. (b) Variation in the average pressure in the sediment.

3.2. Water and Gas Production Behavior during Liquid CO₂ Injection

The production characteristics of water and CO₂ from the outlet during liquid CO₂ injection are respectively shown in Figure 9a,b. As is indicated in Figure 9a, water production exhibits intermittent behavior due to the pressure difference between the sediment and the outlet. When the pressure in the sediment exceeds the back pressure, the outlet valve opens and water is expelled. Otherwise, the outlet valve closes, and no water is produced. It is noticed that the amount of water produced is almost the same every time the outlet valve opens. Combined with Figure 9b, it can be seen that the fluid released from the outlet does not contain CO₂ each time the outlet valve opens during the first six tanks of liquid CO₂ injection since the injected CO₂ in the sediment has not arrived at the outlet. In the process of injecting the seventh tank of liquid CO₂, CO₂ breaks through the outlet and the production rate rapidly increases. The cumulative CO₂ produced reaches 108.44 L in a short period before liquid CO₂ injection is terminated. In the next part, the cumulative sequestered CO₂ and its quantity in hydrate and liquid phases are calculated.

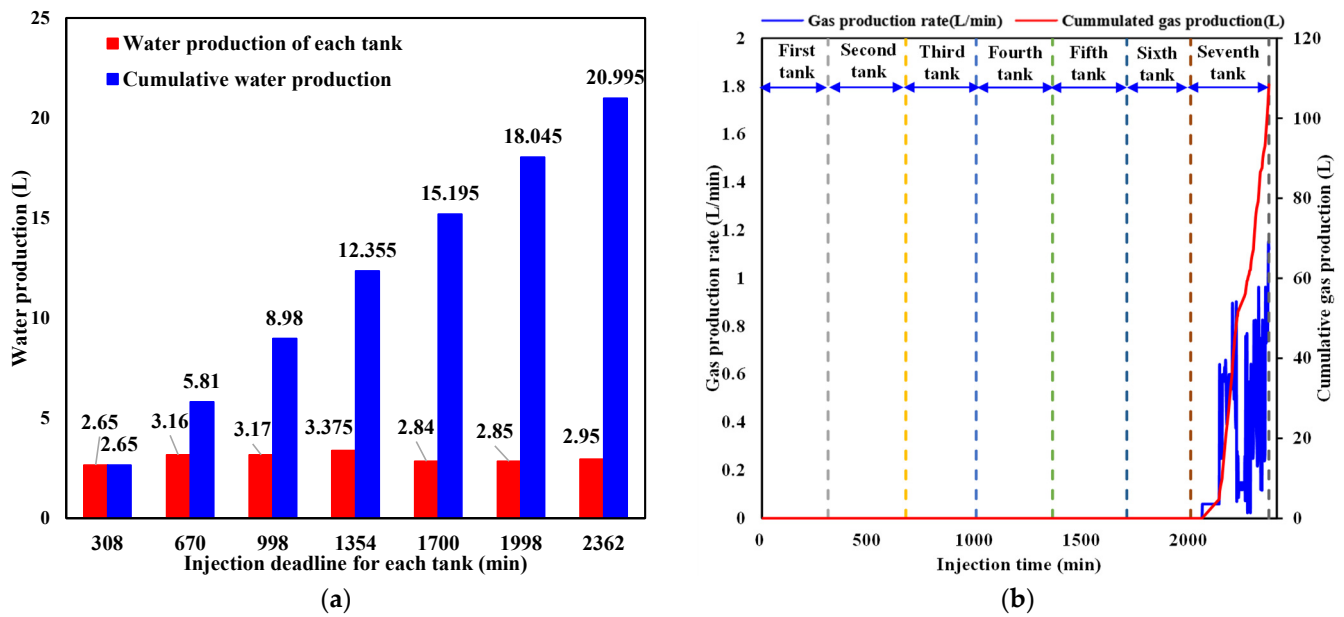


Figure 9. Water and CO₂ production behavior during liquid CO₂ injection. (a) Water production behavior. (b) CO₂ production behavior.

3.3. Sequestration Calculation in Hydrate-Based CO₂ Storage

3.3.1. Cumulative CO₂ Sequestration

The expression of cumulative sequestered CO₂ at different times can be obtained using the mass conservation law, as follows:

$$m_{sco2i} = m_{injco2i} - m_{outco2i} = \rho_{injco2i} V_{injCO2i} - \rho_{outco2i} V_{outCO2i} = \rho_{injco2i} Q_{injCO2} t - \rho_{outco2i} V_{outCO2i} \quad (1)$$

where m_{sco2i} , $m_{injCO2i}$, and $m_{outCO2i}$ are, respectively, the amount of cumulative sequestered, injected, and produced CO₂ at different times, in Kg; $\rho_{injCO2i}$ and $\rho_{outCO2i}$ are, respectively, the densities of injected and produced CO₂ under the corresponding condition, in Kg/m³; $V_{injCO2i}$ and $V_{outCO2i}$ are, respectively, the injected and produced CO₂ volumes under the corresponding condition, in m³; Q_{injCO2} is the liquid CO₂ injection rate, in L/min; and t represents the injection time, in min.

The CO₂ density at different temperatures and pressures during injection can be obtained by referring to Figure 10 [55] or the manual [56].

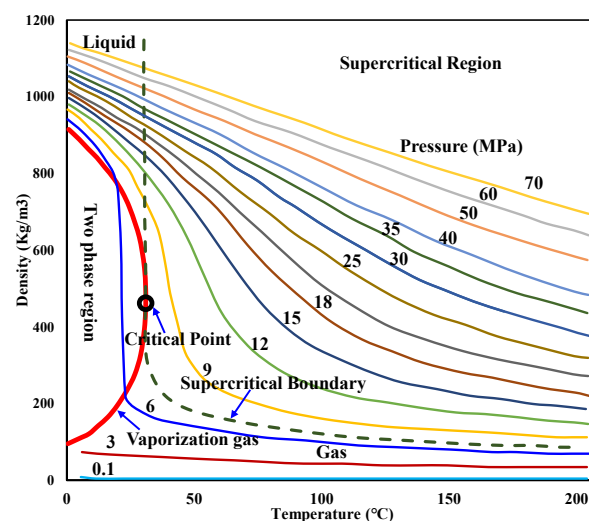


Figure 10. CO₂ density at different temperatures and pressures.

The cumulative sequestered CO₂ with time during liquid CO₂ injection is calculated and illustrated in Figure 11. It can be seen that the cumulative sequestered CO₂ in the sediment increases almost linearly with an increase in CO₂ injection at a constant rate before large amounts of CO₂ are released from the outlet. When liquid CO₂ injection is terminated, the cumulative sequestered CO₂ reaches 22.098 Kg.

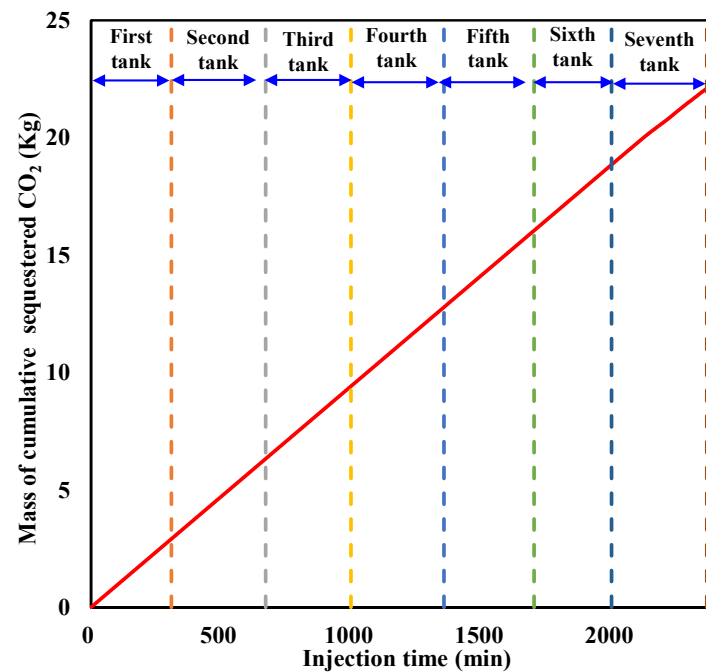


Figure 11. Cumulative sequestered CO₂ in the sediment during injection.

For comparison with CO₂ sequestration in saline aquifers, a novel cumulative sequestration factor in hydrate-based CO₂ storage is defined as the ratio of the equivalent volume of the cumulative sequestered CO₂ to the effective pore volume in the sediment. It is calculated by taking into consideration that the cumulative sequestration factor reaches 0.1353 PV when liquid CO₂ injection is stopped, indicating a relatively low sequestered amount.

This can be mainly attributed to three reasons. One is that viscous fingering occurs due to a low viscosity ratio of liquid CO₂ to formation water, resulting in low sweep efficiency. Another is that the formed hydrate aggravates the heterogeneity and anisotropy of the sediment, causing severe heterogeneous fingering phenomena. The third is that the effective pore space for subsequent CO₂ injection is compressed due to hydrate formation.

3.3.2. CO₂ Sequestration in Hydrate and Liquid Phases

Since the dissolved CO₂ in water is much easier to form hydrate, the quantity of dissolved CO₂ is extremely low in hydrate-based CO₂ sequestration, which can be ignored. In addition, the generated hydrate at the CO₂–water interface will prevent the effective contact between remaining CO₂ and water from the further formation of hydrate. As a result, we assume that the sequestered CO₂ in the sediment co-exists in hydrate and liquid phases in the large-scale 3D experiment on hydrate-based CO₂ sequestration.

To calculate the proportion of sequestered CO₂ in hydrate and liquid phases, the mass conservation law of CO₂, including the injected, sequestered, and produced CO₂, is first applied using Equation (2):

$$\rho_{co2i} V_{co2i} + \rho_{scco2} V_{hi} R_{co2} = m_{injco2i} - m_{outco2i} \quad (2)$$

where ρ_{CO2i} and ρ_{SCCO2} are CO₂ densities, respectively, at the corresponding temperature and pressure in the internal model and under atmospheric conditions, in Kg/m³; V_{CO2i} and V_{hi} represent the volumes of liquid CO₂ and hydrate sequestered in the sediment, in

m^3 ; and R_{CO_2} is CO_2 volume under standard conditions released from per-volume hydrate dissociation, in $175 \text{ m}^3/\text{m}^3$.

The mass of the initial, retained, and effluent water in the internal model at a certain stage of liquid CO_2 injection also satisfies the mass conservation law with the expression indicated in Equation (3):

$$\rho_w(V_p - V_{hi} - V_{co2i}) + \rho_w V_{hi} R_w = \rho_w V_p - \rho_w V_{wouti} \quad (3)$$

where ρ_w is the water density, in Kg/m^3 ; V_p represents the effective pore volume in the sediment, in m^3 ; R_w is the water volume released from per-volume CO_2 hydrate dissociation, in $0.75 \text{ m}^3/\text{m}^3$; and V_{wouti} represents the water volume released from the outlet at different liquid CO_2 injection stages, in m^3 .

The volume of sequestered CO_2 in hydrate and liquid phases can be determined by combining Equations (2) and (3) with their expressions shown in Equations (4) and (5):

$$V_{hi} = \frac{m_{inco2i} - m_{outco2i} - \rho_{co2} V_{wouti}}{\rho_{co2}(R_w - 1) + \rho_{sco2} R_{co2}} \quad (4)$$

$$V_{co2i} = \frac{m_{inco2i} - m_{outco2i}}{\rho_{co2}} - \frac{\rho_{sco2} R_{co2}}{\rho_{co2}} \left(\frac{m_{inco2i} - m_{outco2i} - \rho_{co2} V_{wouti}}{\rho_{co2}(R_w - 1) + \rho_{sco2} R_{co2}} \right) \quad (5)$$

The saturation of CO_2 hydrate and liquid CO_2 at different injection stages is calculated based on Equations (4) and (5), respectively, with the result illustrated in Figure 12, which indicates that a portion of injected liquid CO_2 transforms to hydrate, resulting in hydrate saturation increasing with time. Since hydrate preferentially forms at the interface of CO_2 and water with small Gibbs free energy and hinders their effective contact to some degree, which is not beneficial for further hydrate formation, not all liquid CO_2 can transform into hydrate, with its saturation showing a nonlinear increasing trend with continuous CO_2 injection, while hydrate saturation is always larger than that of liquid CO_2 . It can also be seen that both the final liquid CO_2 and hydrate saturation were small with values of 8.98% and 12.63%, respectively, when the CO_2 injection was stopped. This is mainly because the formed hydrate aggravates the heterogeneity and anisotropy in the sediment, resulting in severe heterogeneous figuring phenomena. As a result, the sweep efficiency of injected CO_2 is small, with a substantial portion of the water being retained in the sediment, which cannot be effectively displaced by CO_2 when a large amount of CO_2 is released from the outlet.

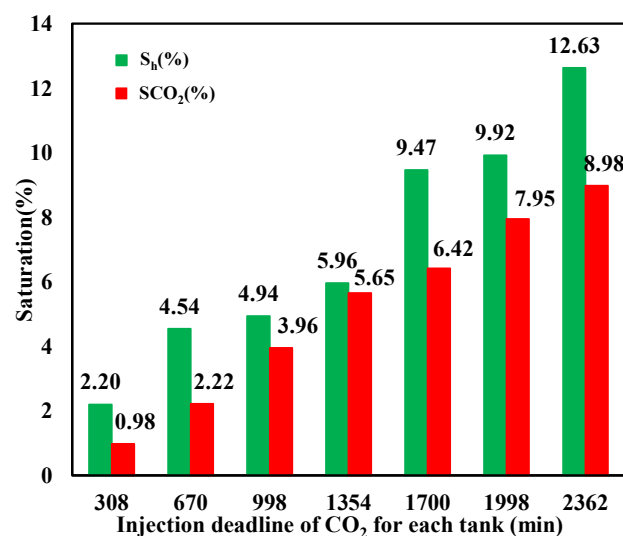


Figure 12. Hydrate- and liquid-based CO_2 saturation during injection.

The mass percentage of CO₂ in hydrate and liquid phases relative to the cumulative sequestered CO₂ at different injection stages is depicted in Figure 13, which shows that the CO₂ percentage in the hydrate phase is always smaller than that in the liquid phase, although hydrate saturation is higher than liquid CO₂ in the sediment. This is primarily because CO₂ hydrate contains a significant proportion of water, with approximately 0.75 volume of water released from per-volume hydrate dissociation. The challenge of further enhancing hydrate saturation and CO₂ fraction in the hydrate phase still remains.

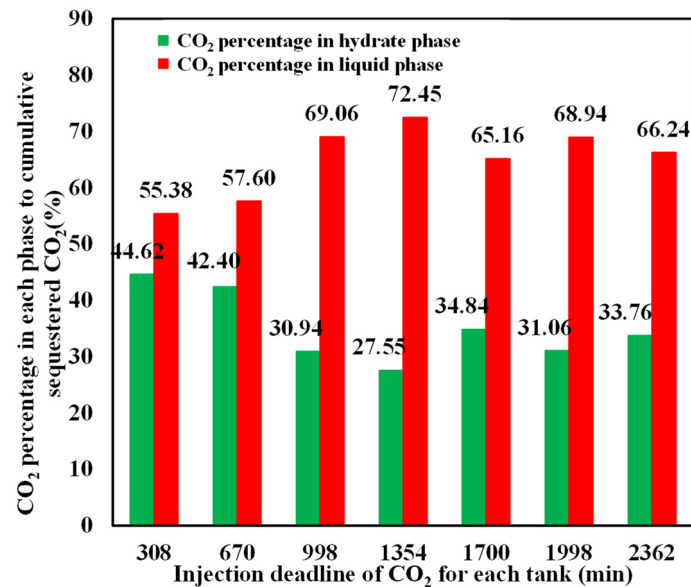


Figure 13. Percentage of sequestered CO₂ in hydrate and liquid phases.

3.3.3. Instantaneous Hydrate Conversion and Liquid CO₂ Retention Rates

In order to further investigate the dynamic formation characteristics of CO₂ hydrate during liquid CO₂ injection, the instantaneous hydrate conversion rate is proposed, which is defined as the ratio of the mass difference of CO₂ converted to hydrate at different injection stages to the cumulative sequestered CO₂. The detailed expression is indicated in Equation (6):

$$\alpha_{hi} = \frac{\rho_{SCCO_2}(V_{hi} - V_{hi-1})R_{hCO_2}}{m_{CO_2t}} \times 100\% \quad (6)$$

Similarly, the liquid CO₂ instantaneous retention rate is defined as the ratio of the mass difference of liquid CO₂ sequestered in the sediment at different injection stages to the cumulative sequestered CO₂, with the expression shown in Equation (7):

$$\alpha_{li} = \frac{\rho_{CO_2i}V_{CO_2i} - \rho_{CO_2i-1}V_{CO_2i-1}}{m_{CO_2t}} \times 100\% \quad (7)$$

Equations (6) and (7) were utilized to calculate the instantaneous hydrate conversion rate and the liquid CO₂ instantaneous retention rate, respectively, during injection, with the result shown in Figure 14. It can be seen that both rates exhibit significant fluctuations with increasing CO₂ injection. At the initial stage of liquid CO₂ injection, the sediment has a large amount of formation water. The injected CO₂ immigrates uniformly in the initially homogeneous sediment. The injected CO₂ has thorough contact with the formation water, resulting in a large CO₂–water contact area. Therefore, the instantaneous conversion rate of hydrate increases with increasing CO₂ injection. However, a proportion of water in the sediment is consumed as a result of hydrate formation with continuous CO₂ injection. The generated hydrate impedes the direct contact between subsequently injected CO₂ and formation water, reducing their effective contact area. As a result, the instantaneous hydrate conversion rate changes to a decreasing mode. The quantity of the generated

hydrate gradually increases as the amount of CO₂ injection continues to increase, which causes a more pronounced degradation of the effective pore structure and aggravation of heterogeneity in the sediment. The injected CO₂ then shifts toward high-permeability zones with large pore throat radii and good connectivity. Consequently, the contact area between liquid CO₂ and formation water increases, resulting in a gradual increase in the instantaneous hydrate conversion rate. With the ongoing injection of liquid CO₂, the effective contact area between liquid CO₂ and water decreases a second time, leading to a reduction in the instantaneous hydrate conversion rate. The superimposition of the aforementioned factors results in irregular fluctuations in the instantaneous hydrate conversion rate and liquid CO₂ instantaneous retention rate. There is an overall opposite evolutionary trend between the instantaneous liquid CO₂ retention and hydrate conversion rate during CO₂ injection. However, it can be found that the two rates exhibit the same increasing trend for the second tank of liquid CO₂ injection. This is mainly because hydrate formation lags behind liquid CO₂ injection. In the process of injecting the second tank of liquid CO₂ injection, the injected CO₂ from the first one continues to generate hydrate, resulting in an instantaneous hydrate conversion rate and instantaneous liquid CO₂ retention rate, both evolving in the same increasing trend.

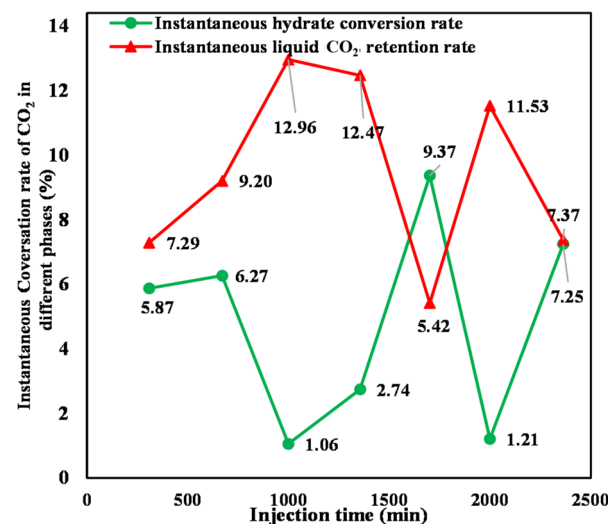


Figure 14. Instantaneous hydrate conversion and liquid phase retention rates of sequestered CO₂.

4. Conclusions

- (1) Irregular variations in the temperature and pressure at a certain point and in each layer during CO₂ injection confirm the generation of CO₂ hydrate as well as its heterogeneous spatial distribution.
- (2) When CO₂ is injected into the deposit at a constant rate and no large amount of gas is expelled from the outlet, the cumulative sequestered CO₂ increases approximately linearly with continuous CO₂ injection, while hydrate saturation is always larger than liquid CO₂.
- (3) CO₂ hydrate aggravates the heterogeneity and anisotropy of the sediment, resulting in low CO₂ sweep efficiency and small cumulative sequestration in the sediment when a large amount of CO₂ is released from the outlet.
- (4) The instantaneous hydrate conversion rate and liquid CO₂ retention rate both exhibit irregular fluctuations due to the consumption of formation water by CO₂, variation in the effective contact area between liquid CO₂ and water, and heterogeneity aggravation of the sediment.

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Conflicts of Interest: Authors Weixin Pang, Yang Ge, Mingqiang Chen, Xiaohan Zhang, Huiyun Wen, Qiang Fu and Xin Lei were employed by the company Research Institute of China National Offshore Oil Cooperation. Shouwei Zhou was employed by the company China National Offshore Oil Corporation. The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Markewitz, P.; Kuckshinrichs, W.; Leitner, W.; Linssen, J.; Zapp, P.; Bongartz, R.; Schreiber, A.; Müller, T.E. Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂. *Energy Environ. Sci.* **2012**, *5*, 7281–7305. [\[CrossRef\]](#)
2. Yoro, K.O.; Daramola, M.O. CO₂ emission sources, greenhouse gases, and the global warming effect. In *Advances in Carbon Capture*; Rahimpour, M.R., Farsi, M., Makarem, M.A., Eds.; Woodhead Publishing: Salztown, UK, 2020; pp. 3–28.
3. Lee, Z.H.; Sethupathi, S.; Lee, K.T.; Bhatia, S.; Mohamed, A.R. An overview on global warming in Southeast Asia: CO₂ emission status, efforts done, and barriers. *Renew. Sustain. Energy Rev.* **2013**, *28*, 71–81. [\[CrossRef\]](#)
4. Quadrelli, R.; Peterson, S. The energy–Climate challenge: Recent trends in CO₂ emissions from fuel combustion. *Energy Policy* **2007**, *35*, 5938–5952. [\[CrossRef\]](#)
5. Nejat, P.; Jomehzadeh, F.; Taheri, M.M.; Gohari, M.; Abd Majid, M.Z. A global review of energy consumption, CO₂ emissions and policy in the residential sector (with an overview of the top ten CO₂ emitting countries). *Renew. Sustain. Energy Rev.* **2015**, *43*, 843–862. [\[CrossRef\]](#)
6. Albertz, M.; Stewart, S.A.; Goteti, R. Perspectives on geologic carbon storage. *Front. Energy Res.* **2023**, *10*, 1–13. [\[CrossRef\]](#)
7. Yang, B.; Shao, C.; Hu, X.; Ngata, M.R.; Aminu, M.D. Advances in Carbon Dioxide Storage Projects: Assessment and Perspectives. *Energy Fuels* **2023**, *37*, 1757–1776.
8. Lin, Q.; Zhang, X.; Wang, T.; Zheng, C.; Gao, X. Technical Perspective of Carbon Capture, Utilization, and Storage. *Engineering* **2022**, *14*, 27–32. [\[CrossRef\]](#)
9. de Coninck, H.; Benson, S.M. Carbon Dioxide Capture and Storage: Issues and Prospects. *Annu. Rev. Environ. Resour.* **2014**, *39*, 243–270. [\[CrossRef\]](#)
10. Ringrose, P.S.; Furre, A.-K.; Gilfillan, S.M.V.; Krevor, S.; Landrø, M.; Leslie, R.; Meckel, T.; Nazarian, B.; Zahid, A. Storage of Carbon Dioxide in Saline Aquifers: Physicochemical Processes, Key Constraints, and Scale-Up Potential. *Annu. Rev. Chem. Biomol. Eng.* **2021**, *12*, 471–494. [\[CrossRef\]](#)
11. Wei, N.; Li, X.; Jiao, Z.; Stauffer, P.H.; Liu, S.; Ellett, K.; Middleton, R.S. A Hierarchical Framework for CO₂ Storage Capacity in Deep Saline Aquifer Formations. *Front. Earth Sci.* **2022**, *9*, 1–21. [\[CrossRef\]](#)
12. Ismail, I.; Gaganis, V. Carbon Capture, Utilization, and Storage in Saline Aquifers: Subsurface Policies, Development Plans, Well Control Strategies and Optimization Approaches—A Review. *Clean Technol.* **2023**, *5*, 609–637. [\[CrossRef\]](#)
13. Worden, R.H. Carbon Dioxide Capture and Storage (CCS) in Saline Aquifers versus Depleted Gas Fields. *Geosciences* **2024**, *14*, 146. [\[CrossRef\]](#)
14. Williams, G.A.; Chadwick, R.A. Influence of reservoir-scale heterogeneities on the growth, evolution and migration of a CO₂ plume at the Sleipner Field, Norwegian North Sea. *Int. J. Greenh. Gas Control* **2021**, *106*, 103260. [\[CrossRef\]](#)
15. Wen, G.; Li, Z.; Long, Q.; Azizzadenesheli, K.; Anandkumar, A.; Benson, S.M. Real-time high-resolution CO₂ geological storage prediction using nested Fourier neural operators. *Energy Environ. Sci.* **2023**, *16*, 1732–1741. [\[CrossRef\]](#)
16. Akai, T.; Kuriyama, T.; Kato, S.; Okabe, H. Numerical modelling of long-term CO₂ storage mechanisms in saline aquifers using the Sleipner benchmark dataset. *Int. J. Greenh. Gas Control* **2021**, *110*, 103405. [\[CrossRef\]](#)
17. Luo, A.; Li, Y.; Chen, X.; Zhu, Z.; Peng, Y. Review of CO₂ sequestration mechanism in saline aquifers. *Nat. Gas Ind. B* **2022**, *9*, 383–393. [\[CrossRef\]](#)
18. Bickle, M.J. Geological carbon storage. *Nat. Geosci.* **2009**, *2*, 815–818. [\[CrossRef\]](#)
19. Bradshaw, J.; Bachu, S.; Bonijoly, D.; Burruss, R.; Holloway, S.; Christensen, N.P.; Mathiassen, O.M. CO₂ storage capacity estimation: Issues and development of standards. *Int. J. Greenh. Gas Control* **2007**, *1*, 62–68. [\[CrossRef\]](#)

20. Wang, Z.; Li, H.; Liu, S.; Xu, J.; Liu, J.; Wang, X. Risk evaluation of CO₂ leakage through fracture zone in geological storage reservoir. *Fuel* **2023**, *342*, 127896. [\[CrossRef\]](#)
21. Katsuki, D.; Ohmura, R.; Ebinuma, T.; Narita, H. Formation, growth and ageing of clathrate hydrate crystals in a porous medium. *Philos. Mag.* **2006**, *86*, 1753–1761. [\[CrossRef\]](#)
22. Sadeq, D.; Iglaier, S.; Lebedev, M.; Rahman, T.; Zhang, Y.; Barifcani, A. Experimental pore-scale analysis of carbon dioxide hydrate in sandstone via X-Ray micro-computed tomography. *Int. J. Greenh. Gas Control* **2018**, *79*, 73–82. [\[CrossRef\]](#)
23. Circone, S.; Stern, L.A.; Kirby, S.H.; Durham, W.B.; Chakoumakos, B.C.; Rawn, C.J.; Rondinone, A.J.; Ishii, Y. CO₂ Hydrate: Synthesis, Composition, Structure, Dissociation Behavior, and a Comparison to Structure I CH₄ Hydrate. *J. Phys. Chem. B* **2003**, *107*, 5529–5539. [\[CrossRef\]](#)
24. Kim, H.-S.; Cho, G.-C. Experimental Simulation of the Self-Trapping Mechanism for CO₂ Sequestration into Marine Sediments. *Minerals* **2019**, *9*, 579. [\[CrossRef\]](#)
25. Almenningen, S.; Gauteplass, J.; Fotland, P.; Aastveit, G.; Barth, T.; Ersland, G. Visualization of hydrate formation during CO₂ storage in water-saturated sandstone. *Int. J. Greenh. Gas Control* **2018**, *79*, 272–278. [\[CrossRef\]](#)
26. House, K.Z.; Schrag, D.P.; Harvey, C.F.; Lackner, K.S. Permanent carbon dioxide storage in deep-sea sediments. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 12291–12295. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Tohidi, B.; Yang, J.; Salehabadi, M.; Anderson, R.; Chapoy, A. CO₂ Hydrates Could Provide Secondary Safety Factor in Subsurface Sequestration of CO₂. *Environ. Sci. Technol.* **2010**, *44*, 1509–1514. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Gauteplass, J.; Almenningen, S.; Ersland, G.; Barth, T.; Yang, J.; Chapoy, A. Multiscale investigation of CO₂ hydrate self-sealing potential for carbon geo-sequestration. *Chem. Eng. J.* **2020**, *381*, 122646. [\[CrossRef\]](#)
29. Sun, Z.; Li, N.; Jia, S.; Cui, J.; Yuan, Q.; Sun, C.; Chen, G. A novel method to enhance methane hydrate exploitation efficiency via forming impermeable overlying CO₂ hydrate cap. *Appl. Energy* **2019**, *240*, 842–850. [\[CrossRef\]](#)
30. Cui, J.; Sun, Z.; Kan, J.; Jia, S.; Sun, C.; Chen, G.; Wang, X.; Yuan, Q.; Li, N. Study on the factors affecting the sealing performance and mechanical stability of CO₂ hydrate cap during gas production from methane hydrate. *J. Nat. Gas Sci. Eng.* **2021**, *93*, 104050. [\[CrossRef\]](#)
31. Zhang, L.; Yang, L.; Wang, J.; Zhao, J.; Dong, H.; Yang, M.; Liu, Y.; Song, Y. Enhanced CH₄ recovery and CO₂ storage via thermal stimulation in the CH₄/CO₂ replacement of methane hydrate. *Chem. Eng. J.* **2017**, *308*, 40–49. [\[CrossRef\]](#)
32. Lee, S.; Lee, Y.; Lee, J.; Lee, H.; Seo, Y. Experimental Verification of Methane–Carbon Dioxide Replacement in Natural Gas Hydrates Using a Differential Scanning Calorimeter. *Environ. Sci. Technol.* **2013**, *47*, 13184–13190. [\[CrossRef\]](#)
33. Liu, T.; Wu, P.; Chen, Z.; Li, Y. Review on Carbon Dioxide Replacement of Natural Gas Hydrate: Research Progress and Perspectives. *Energy Fuels* **2022**, *36*, 7321–7336. [\[CrossRef\]](#)
34. Wei, W.; Li, B.; Gan, Q.; Li, Y. Research progress of natural gas hydrate exploitation with CO₂ replacement: A review. *Fuel* **2022**, *312*, 122873. [\[CrossRef\]](#)
35. Ndlovu, P.; Babaee, S.; Naidoo, P. Review on CH₄-CO₂ replacement for CO₂ sequestration and CH₄/CO₂ hydrate formation in porous media. *Fuel* **2022**, *320*, 123795. [\[CrossRef\]](#)
36. Jia, W.; Song, S.; Li, C.; Wu, X. Predictions on CH₄ recovery factors using the CO₂ replacement method to develop natural gas hydrate resources. *J. CO₂ Util.* **2020**, *41*, 101238. [\[CrossRef\]](#)
37. Hyodo, M.; Li, Y.; Yoneda, J.; Nakata, Y.; Yoshimoto, N.; Kajiyama, S.; Nishimura, A.; Song, Y. A comparative analysis of the mechanical behavior of carbon dioxide and methane hydrate-bearing sediments. *Am. Miner.* **2014**, *99*, 178–183. [\[CrossRef\]](#)
38. Ersland, G.; Husebø, J.; Graue, A.; Kvamme, B. Transport and storage of CO₂ in natural gas hydrate reservoirs. *Energy Procedia* **2009**, *1*, 3477–3484. [\[CrossRef\]](#)
39. Ren, L.; Jiang, M.; Wang, L.; Zhu, Y.; Li, Z.; Sun, C.; Chen, G. Gas hydrate exploitation and carbon dioxide sequestration under maintaining the stiffness of hydrate-bearing sediments. *Energy* **2020**, *194*, 116869. [\[CrossRef\]](#)
40. Kvamme, B.; Graue, A.; Buanes, T.; Kuznetsova, T.; Ersland, G. Storage of CO₂ in natural gas hydrate reservoirs and the effect of hydrate as an extra sealing in cold aquifers. *Int. J. Greenh. Gas Control* **2007**, *1*, 236–246. [\[CrossRef\]](#)
41. Castellani, B.; Rossetti, G.; Tupsakhare, S.; Rossi, F.; Nicolini, A.; Castaldi, M.J. Simulation of CO₂ storage and methane gas production from gas hydrates in a large scale laboratory reactor. *J. Pet. Sci. Eng.* **2016**, *147*, 515–527. [\[CrossRef\]](#)
42. Baldwin, B.A.; Stevens, J.; Howard, J.J.; Graue, A.; Kvamme, B.; Aspenes, E.; Ersland, G.; Husebø, J.; Zornes, D.R. Using magnetic resonance imaging to monitor CH₄ hydrate formation and spontaneous conversion of CH₄ hydrate to CO₂ hydrate in porous media. *Magn. Reson. Imaging* **2009**, *27*, 720–726. [\[CrossRef\]](#) [\[PubMed\]](#)
43. Sun, Y.; Jiang, S.; Li, S.; Wang, X.; Peng, S. Hydrate formation from clay bound water for CO₂ storage. *Chem. Eng. J.* **2021**, *406*, 126872. [\[CrossRef\]](#)
44. Cao, X.; Wang, H.; Yang, K.; Wu, S.; Chen, Q.; Bian, J. Hydrate-based CO₂ sequestration technology: Feasibilities, mechanisms, influencing factors, and applications. *J. Pet. Sci. Eng.* **2022**, *219*, 111121. [\[CrossRef\]](#)
45. Zhang, X.; Zhang, M.; Yang, H.; Li, J.; Li, Y.; Wu, Q. Experimental study on the formation characteristics of CO₂ hydrate in porous media below the freezing point: Influence of particle size and temperature on the formation process and storage capacity. *Energy Sci. Eng.* **2022**, *10*, 1164–1176. [\[CrossRef\]](#)
46. Liu, Y.; Wang, P.; Yang, M.; Zhao, Y.; Zhao, J.; Song, Y. CO₂ sequestration in depleted methane hydrate sandy reservoirs. *J. Nat. Gas Sci. Eng.* **2018**, *49*, 428–434. [\[CrossRef\]](#)

47. Zheng, J.; Chong, Z.R.; Qureshi, M.F.; Linga, P. Carbon Dioxide Sequestration via Gas Hydrates: A Potential Pathway toward Decarbonization. *Energy Fuels* **2020**, *34*, 10529–10546. [[CrossRef](#)]
48. Zhang, K.; Lau, H.C. Sequestering CO₂ as CO₂ hydrate in an offshore saline aquifer by reservoir pressure management. *Energy* **2022**, *239*, 122231. [[CrossRef](#)]
49. Kuang, Y.; Zhang, L.; Zheng, Y. Enhanced CO₂ sequestration based on hydrate technology with pressure oscillation in porous medium using NMR. *Energy* **2022**, *252*, 124082. [[CrossRef](#)]
50. Zhao, G.; Zheng, J.; Gong, G.; Chen, B.; Yang, M.; Song, Y. Formation characteristics and leakage termination effects of CO₂ hydrate cap in case of geological sequestration leakage. *Appl. Energy* **2023**, *351*, 121896. [[CrossRef](#)]
51. Castellani, B. Potential Pathway for Reliable Long-Term CO₂ Storage as Clathrate Hydrates in Marine Environments. *Energies* **2023**, *16*, 2856. [[CrossRef](#)]
52. Junji Yamaguchi, A.; Sato, T.; Tobase, T.; Wei, X.; Huang, L.; Zhang, J.; Bian, J.; Liu, T.-Y. Multiscale numerical simulation of CO₂ hydrate storage using machine learning. *Fuel* **2023**, *334*, 126678. [[CrossRef](#)]
53. Zatsepina, O.Y.; Pooladi-Darvish, M. Storage of CO₂ as Hydrate in Depleted Gas Reservoirs. *SPE Reserv. Eval. Eng.* **2012**, *15*, 98–108. [[CrossRef](#)]
54. De-Galda, V.; Rahmanian, N.; Batrshin, D. Assessment of CO₂ Storage as Hydrates in Saline Aquifers using Machine Learning Algorithms. *Chem. Eng. Trans.* **2021**, *86*, 517–522.
55. Nordbotten, J.M.; Celia, M.A.; Bachu, S. Injection and Storage of CO₂ in Deep Saline Aquifers: Analytical Solution for CO₂ Plume Evolution During Injection. *Transp. Porous Media* **2005**, *58*, 339–360. [[CrossRef](#)]
56. Anwar, S.; Carroll, J.J. Density (kg/m³) of Carbon Dioxide as a Function of Temperature and Pressure. In *Carbon Dioxide Thermodynamic Properties Handbook*; Scrivener Publishing LLC: Beverly, MA, USA, 2016; pp. 9–148.

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