

Study the Dissolution and Consumption of CO₂ Cushion Gas in UGS through Numerical Simulation[#]

Yun Chen¹, Zongran Li², Yuan Zhu¹, Dejun Liu^{1*}

1 School of Information Science and Engineering, China University of Petroleum – Beijing, Beijing, 102499, China

2 LNG Receiving Terminal Management Branch, National Oil and Gas Pipeline Network Group Co., Ltd., Dalian 116600, Liaoning, China

(Corresponding Author: liudj65@163.com)

ABSTRACT

As investment in the construction of UGS increases around the world, the operational efficiency and safety of UGS have attracted attention, which includes some problems that need to be faced. Currently, the dissolution of cushion gas in reservoir fluids has been little discussed. However, with the promotion of the use of CO₂ cushion gas, the impact of dissolution is one of the problems that has to be faced. We aim to show with this study that the dissolved consumption of cushion gas is critical as this affects the total gas volume. We considered two different scenario models, with and without chemical capture reactions. Through simulation, it was found that the increase in pressure increased the solubility of CO₂, but the total dissolved amount decreased. The increase in reservoir temperature reduces the solubility of CO₂ and also leads to a decrease in the total dissolved amount. In addition, chemical capture will affect the solubility of CO₂ to a certain extent, and its extent is related to pressure. A reduction in dissolved gas means an increase in free gas, potentially making the reservoir more sensitive to gas injection pressure. Therefore, chemical capture and hydration dissolution factors become key considerations in cushion gas design and UGS operation. This research helps promote efficient operation of UGS.

Keywords: underground gas storage, carbon dioxide, dissolve, pressure, temperature, reservoir

NONMENCLATURE

Abbreviations

UGS	Underground Gas Storage
CO ₂	Carbon Dioxide
NG	Natural gas

1. INTRODUCTION

1.1 The effect of buffer gas CO₂ on UGS performance

Cushion gas is indispensable in UGS. It has a dual role in improving safety and efficiency. As shown in Fig 1 different types of UGS have different cushion gas proportions. Firstly, the cushion gas plays a pressure buffering role in UGS^[2]. It helps maintain stable pressure during NG injection and production operations. This buffering role helps UGS adapt to changes in NG demand. And it prevents significant pressure fluctuations that could jeopardize the structural integrity of the reservoir. Secondly, the cushion gas will form a protective layer, minimizing the possibility of NG escaping into the environment. This can effectively prevent safety hazards and environmental issues related to NG leaks. Thirdly, the input of cushion gas replaces the working gas permanently trapped in the UGS. Its existence can effectively reduce the retention loss of working gas and improve the extraction efficiency of working gas.

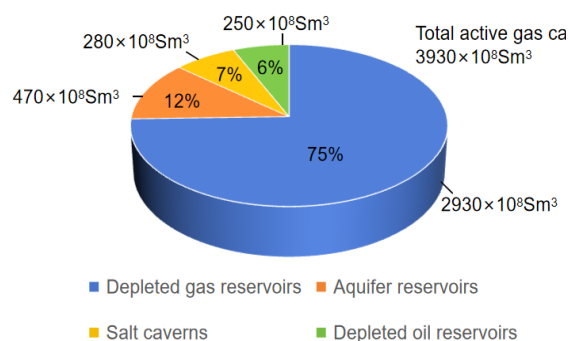


Fig. 1 Different UGS cushion gas setting ratios^[1]

[#] This is a paper for the 16th International Conference on Applied Energy (ICAE2024), Sep. 1-5, 2024, Niigata, Japan.

Curtis M. Oldenburg^[3] completed the simulation of NG injection into a UGS reservoir containing CO₂ cushion gas in 2003. Through analysis, it was found that compared with without CO₂ cushion gas, CO₂ cushion gas can allow the same UGS to store 30% more NG or even more. Sharif found that CO₂ cushion gas has better performance than N₂ cushion gas. However, part of the cushion air will dissolve in the water. This water is trapped in the porous bedrock of UGS. Compared to N₂, CO₂ has higher solubility^[4]. A portion of the cushion gas dissolved in the water will react with the bedrock. This reaction is irreversible and will cause the loss of cushion gas (mineral sequestration). It is indispensable to understand the dissolution rules of CO₂ cushion gas in UGS water. It is the prerequisite for implementing the design of UGS operation plan.

1.2 Solubility of cushion gas

The construction of UGS often makes secondary use of oil or gas reservoirs that have been deeply developed and depleted. The water in their bedrock pores comes from intruding bottom edge water. In order to ensure UGS storage capacity and recovery efficiency, its construction plan must consider the solubility of cushion gas in the reservoir water. Then, strategies are used to minimize the capture of cushion gas caused by mineral sequestration. In addition, the dissolution process of cushion gas in water will also significantly affect the diffusion state of the UGS working gas, which is often ignored in many studies.

Pressure changes during the working gas injection and production process will displace gas and water migration in the reservoir. Under the condition that dissolution is not considered, the gas-water phase interface is independent, and the physical description form under this condition is not hard. But things can start to get tricky when considering the contribution of solubility, there are three main capture methods for dissolution, which are physical dissolution, chemical dissolution and capillary force capture. In addition, when considering CO₂ as cushion gas, changes in CO₂ will also be affected by ambient pressure and temperature factors^[6]. It means that the loss of CO₂ in these factors is also different. Peters showed that only for reservoirs with very high permeability and a thin CO₂ layer, the pressure reduction due to CO₂ dissolution enhanced by convective mixing is important^[7]. Ahmadi measured the solubility of deionized water and mixed saltwater by designing physical experiments, and compared the experimental results with sCPA EoS and Duan models^[8]. Gasda proposed an alternative modeling option that

combines vertically integrated governing equations with an upscaled representation of the dissolution-convection process, and demonstrated the impact of different modeling choices on typical large-scale geological systems^[9]. Jay studied the changes in mineralogy and solute load of formation water caused by temperature, pressure, and dissolved CO₂ in a geochemical model of CO₂ sequestration^[10]. Rory's research found that solubility capture is the main storage mechanism after structural capture, which can remove 10-50% of CO₂ throughout the entire reservoir^[11].

It is important to note that solubility characteristics also vary depending on the type of reservoir (depleted hydrocarbon reservoirs and salt caverns) and the nature of the water involved. Other factors that affect solubility include geological conditions, time fluctuations, chemical processes, operation plans, etc. Intuitively, the factors affecting cushion gas migration are complex but worth facing. Efforts in this area not only help engineers understand and estimate gas conditions within UGS. It can also provide effective reference value for the research on UGS facilities for other gases (CO₂ storage, hydrogen storage, etc.).

There are many factors that affect the cushion gas in UGS. This study focuses on the changes in CO₂ cushion gas during the gas injection process of abandoned reservoir type UGS.. Its dissolution behavior caused by physical and chemical processes will be Consider it. In addition, temperature and pressure factors will be discussed as major influencing factors. In view of the current limitations of monitoring methods and experimental environments, this research will be implemented through numerical calculation and simulation. It can effectively eliminate interference from uncontrollable factors. Previous studies have investigated many reasons for the changes in CO₂ solubility in reservoirs, but there is little research on the amount of CO₂ cushion gas dissolution in UGS. We set up two scenarios to understand the changes in the dissolution of cushion gas in models with and without chemical capture, which is crucial for the operation of UGS.

2. CONSTRUCTION OF UGS SIMULATION MODEL INCLUDING CO₂ CUSHION GAS

2.1 Porous media model of abandoned reservoir type UGS

UGS transformed from abandoned reservoirs consists of three main parts: caprock , reservoir rock and surrounding rock. The caprock and surrounding rock

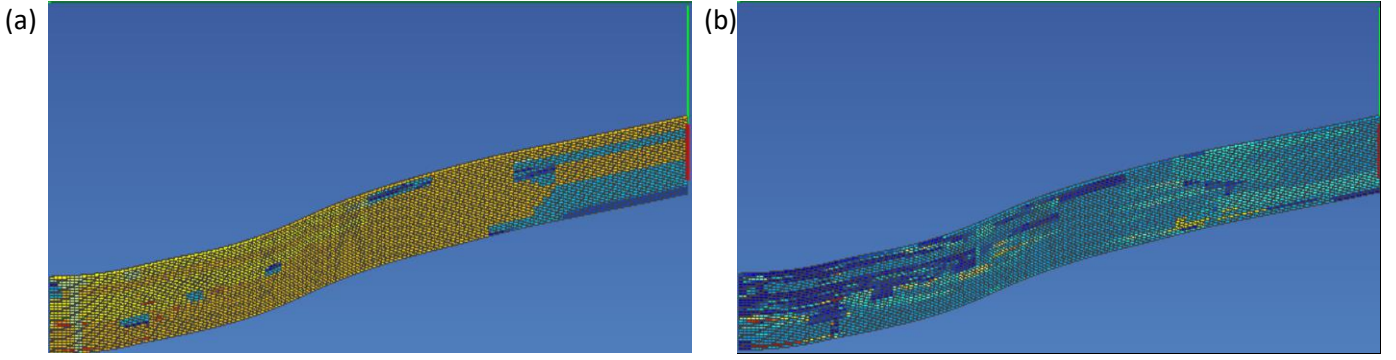


Fig. 2 (a) Reservoir porosity distribution; (b) Reservoir permeability distribution

have very poor permeability, which ensures the existence of a fixed boundary of UGS. And the reservoir rock is porous and has good connectivity between pores, which provides storage space for UGS. We selected a 2D geological slice containing an abandoned reservoir as the target model for our discussion. Its thickness and width are 434m and 1535m respectively. The UGS reservoir contained in it is irregular. It is located between a vertical depth of 1134.64 to 700.425 meters underground, with an average thickness of approximately 148 meters. As shown in Fig 2, the porosity and permeability distribution of the reservoir rock are respectively, and their numerical ranges are (0-0.283) mD and (0.00001-85) mD respectively. Then, based on the Van Genuchten model, the gas phase relative permeability K_{rg} and liquid phase relative permeability K_{rl} can be calculated using equations (1-4) respectively.

$$K_{rg} = (1 - \hat{S})^2 (1 - \hat{S}^2) \quad (1)$$

$$\hat{S} = (S_l - S_{rl}) / (S_l - S_{rl} - S_{rg}) \quad (2)$$

$$K_{rl} = \sqrt{S^*} \left\{ 1 - [S^*]^{\frac{1}{m}} \right\}^2 \quad (3)$$

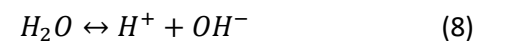
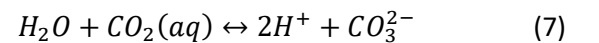
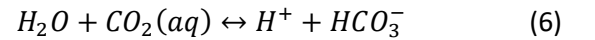
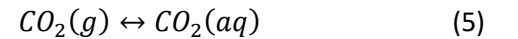
$$S^* = (S_l - S_{rl}) / (1 - S_{rl}) \quad (4)$$

The initial pressure conditions of the model are determined based on the depth and pressure gradient of the geological slice. Injection wells at a constant flow rate. If the flow resistance in the well is ignored and there is no casing in the well, then the injection well can be equivalent to the flow boundary. The caprock and surrounding rock of the reservoir are both low-permeability mudstone, so the upper and lower boundaries of the reservoir can be regarded as fluxless boundaries. The lateral boundary is set to infinite as the continuation of the reservoir.

2.2 CO₂ buffer gas dissolution model

Consider the dissolution reaction of CO₂ and water. due to the presence of intrusive bottom edge water in abandoned reservoirs. This results in a certain amount of cushion gas no longer existing as free molecules. The CO₂ cushion gas simultaneously undergoes mass transfer and other exchange behaviors such as dissolution, escape, and diffusion at the air-water interface. The amount of CO₂ consumed when the exchange process reaches equilibrium is called solubility. Solubility is affected by several factors. As the temperature increases, the solubility of CO₂ cushion gas will decrease^[12]. At constant temperature, the solubility of CO₂ per unit volume of water is proportional to ambient pressure.

The dissolved amount of CO₂ cushion gas increases with the pressure of the reservoir until the three-phase pressure interval^[13]. Dissolved CO₂ will cause two behaviors in the water body. First, due to the concentration difference, CO₂ will diffuse from near the water body interface to the interior of the low-concentration water body. Secondly, the dissolution of CO₂ will cause the density of the aqueous solution to change, and the uneven dissolution distribution will be affected by gravity, which will lead to convection. The occurrence of natural convection will affect the rate of dissolution. If the exchange reaction at the interface is considered, the dissolution of CO₂ mainly involves the process shown in the formula (5-8).



Based on the above dissolution process, the solubility of buffer gas in water is determined by balancing its fugacity in water^[14]. Henry studied the fugacity of buffer gas in water and gave a standard calculation theory^[15]. Solubility can be calculated using

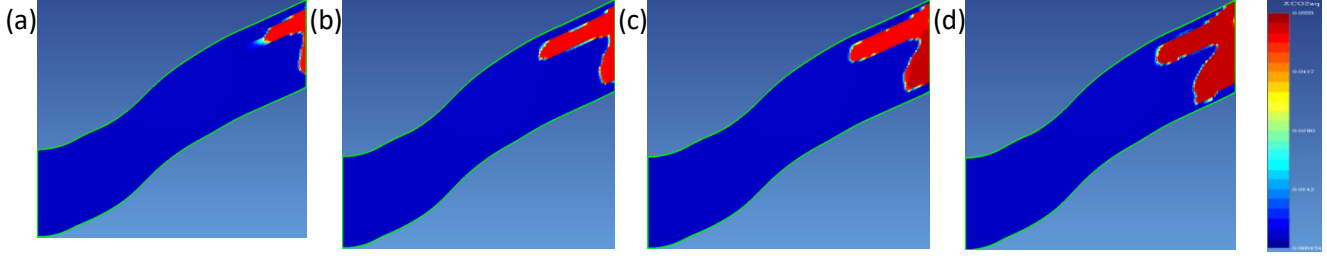


Fig. 3 Reservoir CO2 distribution at different periods of time((a)0.25 years; (b)0.5 years; (c)0.75 years; (d)1 years).

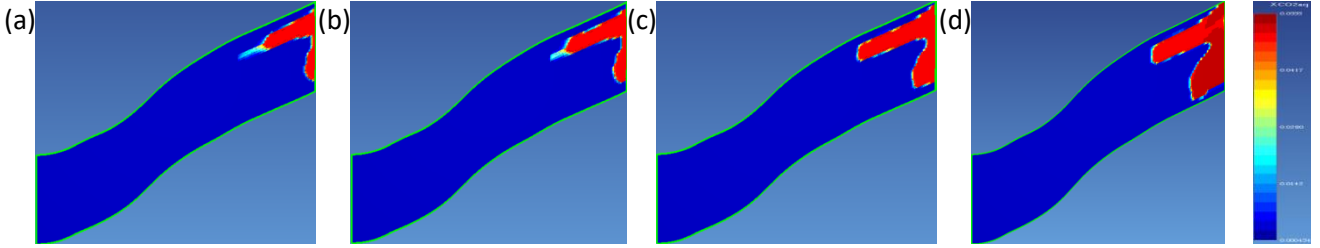


Fig. 4 Consider reservoir CO2 distribution at different time periods under chemical capture conditions((a)0.25 years; (b)0.5 years; (c)0.75 years; (d)1 years).

the standard Henry constant and the fractional molar volumes of different components at standard pressure, as shown in the formula (9-10). It also considers the effects of both temperature and pressure [16].

$$H_i = H_i^* \exp\left[\frac{V_i^\infty (P_i - P_{ref})}{RT}\right] \quad (9)$$

$$P_i = C_i H_i \quad (10)$$

where H_i is Henry's coefficient, H_i^* is Henry's constant, V_i^∞ represents the partial molar volume, P_i is pressure, P_{ref} is the reference pressure, R is the universal gas constant, T is temperature and C_i is the concentration of the component in the aqueous phase. The result of the above dissolution process is that the concentration of ions in the water will increase significantly. What needs to be considered next is the further reaction of these CO2 dissolved in water.

2.3 Chemical dissolution model considering the participation of minerals in bedrock

As CO2 dissolution occurs, the anion concentration in the water body increases significantly. It drives minerals in the bedrock to react with it and consumes anions in the water. This reaction is irreversible and consumes dissolved CO2. It is called 'chemical capture'. The existence of micropores makes the contact area between bedrock and CO2-containing solution larger. In addition, high-concentration solutions accelerate diffusion into micropores under the action of concentration gradient and hydrodynamic force. This behavior makes it easier for CO2 to be chemically captured in bedrock. Consider the chemical capture of

CO2 by minerals. The chemical formulas of the dissolution and precipitation processes of different types of minerals can be known from Sun^[17]. Based on the statistical results, the dissolution formula derived by Spycher is shown in (11)^[18].

$$x_{CO_2} = \frac{\Phi_{CO_2} (1 - y_{H_2O}) P_{tot}}{55.508 \gamma'_x K_{CO_2(g)}^0} \exp\left(-\frac{(P - P^0) \bar{V}_{CO_2}}{RT}\right) \quad (11)$$

P is total pressure, \bar{V} is the average partial molar volume of each pure condensed phase over the pressure range $P - P^0$, Φ is the fugacity coefficient of each component in the CO2-rich (compressed gas) phase, and R is the gas constant. The γ'_x is an activity coefficient for aqueous CO2.

3. RESULTS COMPARISON AND ANALYSIS

In the previous section, we gave the construction method of underground gas storage model. Let's discuss the effects of temperature and pressure on gas injection implementation in terms of years. Here, we stipulate that the reservoir is filled with water. The gas injection flow rate is stabilized at 0.0115Kg/s, which ensures that there will be no interference caused by rock mass rupture. The initial formation pressure is 16MPa. The temperature is fixed at 42°C, and the interference of other factors is not considered. It should be noted that water not only dissolves CO2, but also water can be displaced by CO2.

The changes in CO2 dissolved mass fraction of the model considering only dissolution and including

chemical capture conditions were observed respectively. Comparing Fig 3 with Fig 4, we can intuitively see that the CO₂ migration range is smaller and the dissolved mass fraction is lower under chemical capture conditions. But in general, the CO₂ dispersion of the two types of calculation models is similar. This means that under the same pressure and temperature conditions, the presence of chemical capture reduces a certain amount of CO₂. More CO₂ tends to be absorbed by the reservoir water in dissolved form, and this process is reversible. But it cannot be denied that chemical capture cannot be ignored, especially in the long-term operation of UGS, in which injection and extraction are far more than once.

It is well known that pressure and temperature change the physical properties of matter, and it applies to this problem as well. First, we analyze the effect of pressure on the dissolution changes of CO₂ in UGS. We set the initial formation pressures of the model to be 11MPa, 21MPa, 31MPa, and 41MPa respectively. And calculate the effect of formation pressure on the dissolved mass fraction of the UGS model. The result is shown in Fig 5. It can be found that when the initial pressure of the formation increases from 11MPa to 21MPa, the dissolved mass fraction of the two types of

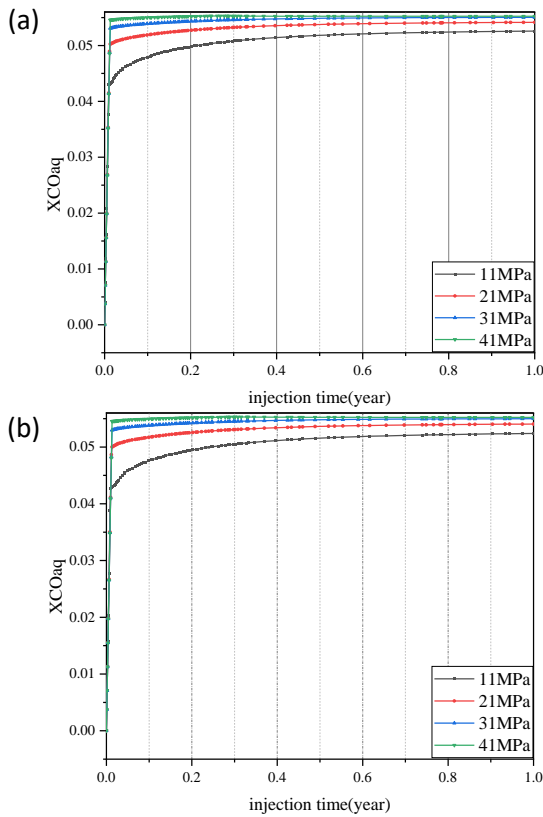


Fig. 5 (a) the relationship between CO₂ dissolved mass fraction and injection time; (b) The relationship between CO₂ dissolved mass fraction and injection time considering chemical capture conditions

models increases by 2.99% and 3.15%. However, when the formation pressure increases from 31MPa to 41MPa, their dissolved mass fractions only increase by 0.36% and 0.42% respectively. When the reservoir pressure decreases, CO₂ leaching occurs due to the decrease in solubility. This is similar to the conclusion obtained by Xu^[19].

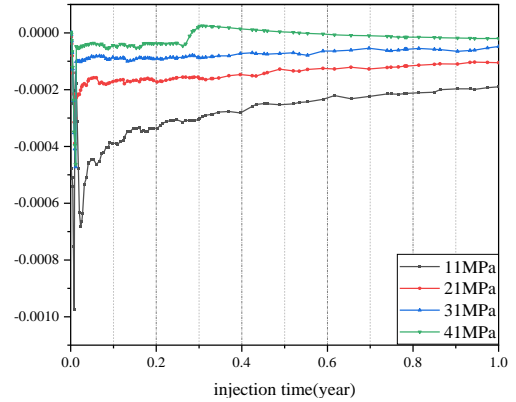


Fig. 6 Contribution of chemical capture as a function of time

Table 1 Total dissolved gas

Reservoir Pressure	Total Dissolved Amount (kg)	Total Dissolved Amount (kg) (Chemical Capture)
11MPa	8.5069E+04	5.9923E+04
21MPa	8.3536E+04	5.8080E+04
31MPa	8.2107E+04	5.6409E+04
41MPa	8.0275E+04	5.5133E+04

In addition, one third of a year after injection, the dissolved mass fraction of CO₂ tends to be stable. Fig 6 shows the difference between the two models, which represents the contribution of chemical capture. A noteworthy phenomenon is that the smaller the pressure, the greater the difference in dissolved mass fractions between the two models. As the pressure increases, the difference in dissolved mass fraction between the two models is almost 0. This indicates that increasing pressure reduces the effect of chemical capture behavior on the dissolved mass fraction.

We calculated the total amount of dissolution in the entire reservoir for one year of gas injection for both types of models. It can be clearly seen from Table 1 that the total amount of gas dissolved in the model including chemical capture is significantly lower than the case without it. Furthermore, although as the pressure increases, the dissolved mass fraction increases in the

physical model. However, the final total amount of dissolution is reduced, which may be due to the restrictive effect of pressure on dissolution transport. As the reservoir pressure increases from 11MPa to 41MPa, the total dissolved amount of the two models decreases by 4794kg and 4790kg respectively.

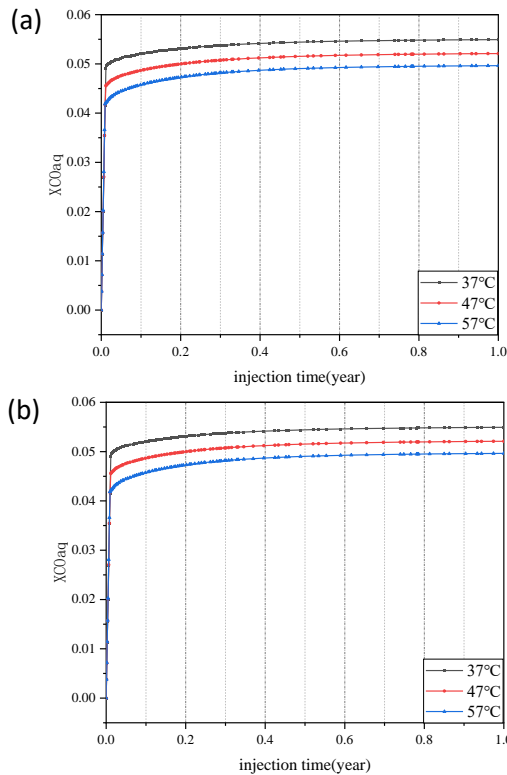


Fig. 7 (a) the relationship between CO2 dissolved mass fraction and injection time; (b) The relationship between CO2 dissolved mass fraction and injection time considering chemical capture conditions

To discuss the effect of temperature on the dissolution of CO2 cushion gas, we show the model calculation results under the conditions of 37°C, 47°C and 57°C. Similarly, we give the change curves of the dissolved mass fraction of the two models. As shown in Fig 7, we found that when the reservoir temperature increased from 37°C to 47°C, the dissolved mass fraction of the two models decreased by 5.15% and 4.03%. When the reservoir temperature increased from 47°C to 57°C, the dissolved mass fraction decreased by 4.72% and 3.15%. The increase in temperature leads to a decrease in the dissolved mass fraction of CO2. After half a year, the dissolved mass fraction of CO2 tends to a constant value. We can see that the dissolution process is more sensitive to temperature. Fig 8 shows the difference in dissolved mass fraction under the two models. It can be seen that compared to pressure, temperature has little effect on the rate and total amount of chemical capture.

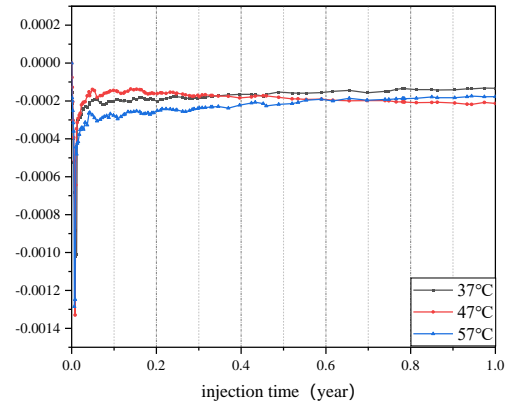


Fig. 8 Contribution of chemical capture as a function of time

Table 2 Total dissolved gas

Reservoir Temperature	Total Dissolved Amount (kg)	Total Dissolved Amount (kg) (Chemical Capture)
37°C	8.5242E+04	5.8428E+04
47°C	8.3465E+04	5.8047E+04
57°C	8.2095E+04	5.6172E+04

We counted the total dissolution volume for each year of the two models. It can be clearly seen from Table 2 that the total dissolved amount when chemical capture is considered will be lower than the case where it is not considered. This conclusion is consistent with the previous one. As the temperature increases, the dissolved mass fraction decreases, and the final total dissolved amount decreases. As the reservoir temperature increases from 37°C to 57°C, the total dissolved amount of the two models decreases by 3147kg and 2256kg respectively. It is not difficult to find that temperature has a negative correlation with solubility and has little correlation with chemical capture.

4. CONCLUSIONS

This study mainly discusses the effects of temperature and pressure on the diffusion and dissolution of CO2 cushion gas in UGS. Here we also include the presence of chemical capture. We found that as the reservoir pressure increases (11-41)MPa, the dissolved mass fraction of CO2 cushion gas in the model with and without chemical capture increases by 5.06% and 5.40% respectively. However, the negative effect of pressure on diffusion causes their total dissolved CO2 to decrease by 5.64% and 7.99% respectively. As the temperature increases (37-57) °C, the dissolved mass fraction of CO2 decreases by 9.63% and 9.73%

respectively under the two types of models, and the total dissolved amount also decreases by 3.69% and 3.86% respectively. These findings highlight the importance of considering chemical capture of cushion gas when conducting feasibility studies or designing and operating underground gas storage. The total amount of gas dissolved cannot be seen solely by solubility. It also needs to consider the movement and diffusion conditions of the gas. Less dissolved gas means more free gas in the pore space, leading to a more rapid increase in reservoir pressure, which may more easily lead to reservoir deformation and gas leakage. This study lays the foundation for cushion gas design of underground gas storage. Future research work will continue to explore the impact of changes in pH, ion concentration, permeability, etc. on the dissolution and diffusion of cushion gas under the two types of dissolution models. And study appropriate injection and production strategies to mitigate the impact of dissolved gas in the cushion.

ACKNOWLEDGEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

REFERENCE

- [1] Al-Shafi M, Massarweh O, Abushaikha A S, et al. A review on underground gas storage systems: Natural gas, hydrogen and carbon sequestration. *Energy Reports*, 2023; 9: 6251-6266.
- [2] Mu L, Liao X, Yu Q, et al. Study on operation strategy of aquifer underground gas storage using CO₂ as cushion gas. *Carbon Management Technology Conference. CMTC*, 2019: CMTC-552947-MS.
- [3] Oldenburg C M. Carbon dioxide as cushion gas for natural gas storage. *Energy & Fuels*, 2003; 17(1): 240-246.
- [4] Shoushtari S, Namdar H, Jafari A. Utilization of CO₂ and N₂ as cushion gas in underground gas storage process: A review. *Journal of Energy Storage*, 2023; 67: 107596.
- [5] Amiri I I, Zivar D, Ayatollahi S, et al. The effect of gas solubility on the selection of cushion gas for underground hydrogen storage in aquifers. *Journal of Energy Storage*, 2024; 80: 110264.
- [6] Teng H, Masutani S M, Kinoshita C M, et al. Solubility of CO₂ in the ocean and its effect on CO₂ dissolution. *Energy conversion and management*, 1996; 37(6-8): 1029-1038.
- [7] Peters E, Egberts P J P, Loeve D, et al. CO₂ dissolution and its impact on reservoir pressure behavior. *International Journal of Greenhouse Gas Control*, 2015; 43: 115-123.
- [8] Ahmadi P, Chapoy A. CO₂ solubility in formation water under sequestration conditions. *Fluid Phase Equilibria*, 2018; 463: 80-90.
- [9] Gasda S E, Nordbotten J M, Celia M A. Vertically averaged approaches for CO₂ migration with solubility trapping. *Water Resources Research*, 2011; 47(5).
- [10] Black J R, Carroll S A, Haese R R. Rates of mineral dissolution under CO₂ storage conditions. *Chemical Geology*, 2015; 399: 134-144.
- [11] Leslie R, Cavanagh A J, Haszeldine R S, et al. Quantification of solubility trapping in natural and engineered CO₂ reservoirs. *Petroleum Geoscience*, 2021, 27(4): petgeo2020-120.
- [12] WU Shuangliang. Study on mass transfer of carbon dioxide buried in deep brine. Qingdao: China University of Petroleum (East China); 2015, p. 35-56.
- [13] Spycher N, Pruess K, Ennis-King J. CO₂-H₂O mixtures in the geological sequestration of CO₂. I. Assessment and calculation of mutual solubilities from 12 to 100 C and up to 600 bar. *Geochimica et cosmochimica acta*, 2003; 67(16): 3015-3031.
- [14] Amiri I I, Zivar D, Ayatollahi S, et al. The effect of gas solubility on the selection of cushion gas for underground hydrogen storage in aquifers. *Journal of Energy Storage*, 2024; 80: 110264.
- [15] Li Y K, Nghiem L X. Phase equilibria of oil, gas and water/brine mixtures from a cubic equation of state and Henry's law. *The Canadian Journal of Chemical Engineering*, 1986; 64(3): 486-496.
- [16] Sander R. Compilation of Henry's law constants (version 4.0) for water as solvent. *Atmospheric Chemistry and Physics*, 2015; 15(8): 4399-4981.
- [17] Sun L, Liu Y, Cheng Z, et al. Review on Multiscale CO₂ Mineralization and Geological Storage: Mechanisms, Characterization, Modeling, Applications and Perspectives. *Energy & Fuels*, 2023; 37(19): 14512-14537.
- [18] Spycher N, Pruess K. CO₂-H₂O mixtures in the geological sequestration of CO₂. II. Partitioning in chloride brines at 12-100 C and up to 600 bar. *Geochimica et Cosmochimica Acta*, 2005; 69(13): 3309-3320.
- [19] Xu R, Li R, Ma J, et al. Effect of mineral dissolution/precipitation and CO₂ exsolution on CO₂

transport in geological carbon storage. *Accounts of chemical research*, 2017; 50(9): 2056-2066.