Numerical Study of CO$_2$ Geological Storage in Saline Aquifers without the Risk of Leakage

Yuan-Heng Li, Chien-Hao Shen, Cheng-Yueh Wu and Bieng-Zih Hsieh *

Department of Resources Engineering, National Cheng Kung University, Tainan 701, Taiwan;
henry.lee619@gmail.com (Y.-H.L.); shenha0206@gmail.com (C.-H.S.); cocoleeeric@gmail.com (C.-Y.W.)

Received: 31 August 2020; Accepted: 8 October 2020; Published: 10 October 2020

Abstract: The purpose of this study is to reduce the risk of leakage of CO$_2$ geological storage by injecting the dissolved CO$_2$ solution instead of the supercritical CO$_2$ injection. The reservoir simulation method is used in this study to evaluate the contributions of the different trapping mechanisms, and the safety index method is used to evaluate the risk of CO$_2$ leakage. The function of the dissolved CO$_2$ solution injection is performed by a case study of a deep saline aquifer. Two scenarios are designed in this study: the traditional supercritical CO$_2$ injection and the dissolved CO$_2$ solution injection. The contributions of different trapping mechanisms, plume migrations, and the risk of leakage are evaluated and compared. The simulation results show that the risk of leakage via a natural pathway can be decreased by the approach of injecting dissolved CO$_2$ solution instead of supercritical CO$_2$. The amount of the CO$_2$ retained by the safe trapping mechanisms in the dissolved CO$_2$ solution injection scenario is greater than that in the supercritical CO$_2$ scenario. The process of CO$_2$ mineralization in the dissolved CO$_2$ solution injection scenario is also much faster than that in the supercritical CO$_2$ scenario. Changing the injection fluid from supercritical CO$_2$ to a dissolved CO$_2$ solution can significantly increase the safety of the CO$_2$ geological storage. The risk of CO$_2$ leakage from a reservoir can be eliminated because the injected CO$_2$ can be trapped totally by safe trapping mechanisms.

Keywords: mineralization mechanisms; dissolved CO$_2$ injection; storage safety

1. Introduction

Since the Industrial Revolution, the consumption of fossil fuels in transportation, industrial, electrical, and other sectors has resulted in a large increase in greenhouse gas emissions, thereby promoting environmental disasters, such as global warming. To promote environmental protection and to halt the consequences of climate change, remediation techniques are required to reduce anthropogenic CO$_2$ emissions to keep the rise in global temperatures below 2 °C above pre-industrial temperatures in the 21st century. Carbon capture and storage (CCS) is one of the solutions. CCS is a practical approach to cut down CO$_2$ emissions by means of a series of technologies, including the capture, transportation, and storage of CO$_2$. Deep saline aquifers have the largest CO$_2$ storage capacity in the geological storage options.

The most important issue for the CO$_2$ geological storage is the risk of leakage. For the storage to be, the risk of any leakage should be controlled to as low as possible. The evaluation of the risk of leakage is essential for public acceptance and public policy [1,2]. The risk of leakage can be reduced by a safe injection strategy with understanding the functions of different trapping mechanisms.

The traditional injection strategy is the supercritical CO$_2$ injection, i.e., CO$_2$ is injected into a reservoir as a mobile supercritical phase. The injected supercritical CO$_2$ is trapped below a non-permeable cap-rock in the beginning; this is structural trapping. The injected supercritical CO$_2$
plume migrates upward due to its buoyancy. The mobility of the supercritical CO\(_2\) creates a higher risk of leakage for the CO\(_2\) storage because, in this mechanism, it relies on the containment of the storage system. However, in the post-injection period, the residual gas, solubility, and mineralization trapping mechanisms will work to improve the safety of the storage since these trappings make the stored CO\(_2\) as an immobile phase to effectively lower the risk of leakage [3–5].

An alternative method of CO\(_2\) storage to the traditional supercritical CO\(_2\) injection has been discussed in recent years. A novel method of CO\(_2\) storage based on injecting a dissolved CO\(_2\) solution has been proposed. CO\(_2\) is dissolved in water, which is extracted from an aquifer at a surface facility before injection [6]. However, the CO\(_2\) dissolution procedure at the surface facility requires compressing the water at high pressure and may cause unaffordable energy and costs. An alternative strategy of dissolving CO\(_2\) involves the production of brine from the reservoir, followed by a re-injection where the brine mixes with the CO\(_2\) in the wellbore of the injection well at a certain depth [7]. Significant advantages are attained by injecting CO\(_2\) as a saturated solution with the brine [8].

When the CO\(_2\) is dissolved in water, the density of the CO\(_2\) solution is greater than that of the formation water. The CO\(_2\) solution naturally sinks in the aquifer due to the gravity effect, and this can reduce the risk of leakage because the plume is moving away from the top of the reservoir (moving downward). Recently, research has been conducted concerning the injection of dissolved CO\(_2\) solution into igneous rock (e.g., basalt). Instead of supercritical CO\(_2\), CO\(_2\) the dissolved in geothermal wastewater was injected into and stored in the formation. Because basaltic rocks are rich in calcium, magnesium, and iron (while also being more reactive in formation water than sedimentary rock), the bulk of the CO\(_2\) is trapped by mineral trapping within a few years instead of thousands of years [9–11]. After the stored CO\(_2\) transforms into carbonate minerals, the risk of CO\(_2\) leakage can be eliminated, thereby enhancing the storage safety and public acceptance of this solution.

The whole process of transforming the CO\(_2\) phase through a different trapping mechanism plays an essential role in evaluating the risk of CO\(_2\) leakage, no matter whether it is in the traditional supercritical CO\(_2\) injection or the dissolved CO\(_2\) solution injection. This is the first paper to discuss the differences in the trapping mechanisms between injecting the dissolved CO\(_2\) and injecting supercritical CO\(_2\) into a reservoir in sedimentary basins. Because the difference in the process of trapping mechanisms would affect the mobility of stored CO\(_2\) and the leakage risk, the differences in injecting different fluid should be discussed. Sedimentary rock is less rich in calcium, magnesium, and iron than igneous rock, but the transformation of the injected dissolved CO\(_2\) into carbonate minerals can still be faster than that achieved by the traditional supercritical CO\(_2\) injection because the solubility trapping mechanism can occur immediately in the reservoir.

Therefore, the purpose of this research is to study the elimination of the risk of leakage of CO\(_2\) geological storage by injecting the dissolved CO\(_2\) solution instead of the supercritical CO\(_2\) injection. Specifically, the transformation process of trapping mechanisms of the different injected phase CO\(_2\) in a sedimentary basin is discussed in this study. The contributions of the different trapping mechanisms are evaluated by the reservoir simulation, and the risk of CO\(_2\) leakage is estimated from the safety index method. This study uses a case study to perform the function of the dissolved CO\(_2\) solution injection in a deep saline aquifer. The traditional supercritical CO\(_2\) injection and the dissolved CO\(_2\) solution injection scenarios are designed in this study, and the contributions of different trapping mechanisms, plume migrations, and the risk of leakage are evaluated and compared.

2. Methodology

To effectively assess the leakage risk of CO\(_2\) storage, the safety index (SFI) was used in this study. The SFI was estimated by the dynamic number of moles of CO\(_2\) retained by the trapping mechanisms after CO\(_2\) had been injected into the target reservoir. The safety index was defined as [12]:

\[
SFI = \frac{(n_{CO_2(aq)} + n_{CO_2(gas)} + n_{CO_2(sol)} + n_{CO_2(min)})}{n_{CO_2(inj)}}
\]
where $n_{\text{CO}_2(\text{res})}$ is the number of moles of the CO$_2$ retained by the residual gas mechanism as immobile supercritical phase; $n_{\text{CO}_2(\text{aq})}$ is the number of moles of the CO$_2$ retained by the solubility trapping mechanism; $n_{\text{CO}_2(\text{ion})}$ is the moles of the CO$_2$ retained by the ionic trapping mechanism; $n_{\text{CO}_2(\text{min})}$ is the number of moles of the CO$_2$ retained by the mineral trapping mechanism, and $n_{\text{CO}_2(\text{inj})}$ is the number of moles of injected CO$_2$.

The residual gas trapping mechanism plays an essential role in trapping supercritical CO$_2$ in a saline aquifer. In the porous media, supercritical CO$_2$ can be trapped by capillary and wettability effects as an immobile phase [13,14]. When the imbibition curve is different from the drainage curve for the relative permeability of the gas ($k_{rg}$), the residual gas exists. In this study, the imbibition and drainage curves of the relative permeability of the gas were designed using Land’s model [15].

For the solubility trapping mechanism, the solubility of gas in the water is important because a large amount of CO$_2$ is able to be dissolved in the saline. Because the dissolution rate of the gas phase in the aqueous phase is rapid, the aqueous and gas phase are able to be assumed to be in thermodynamic equilibrium. The solubility trapping mechanism in a saline aquifer can be modeled by the phase equilibrium controlled by the equivalent fugacities between the aqueous ($f_{\text{maq}}$) and gas phases ($f_{\text{mg}}$):

$$f_{\text{mg}} = f_{\text{maq}}, m = 1, \ldots, N_c$$ (2)

The Peng–Robinson equation of state (PR-EOS) was adopted to compute the gas fugacity, $f_{\text{mg}}$, of component $m$ [16]. The fugacity of component $m$ in the aqueous phase, $f_{\text{maq}}$, can be computed by Henry’s law:

$$f_{\text{maq}} = y_{\text{maq}} \cdot H_m$$ (3)

where $H_m$ is Henry’s law constant (atm·L/mol) for component $m$ at a given $p$ and $T$.

Henry’s constant, which is affected by the temperature, pressure, and salinity of the saline, can be normally expressed as follows at a constant temperature:

$$\ln H_m = \ln H_m^* + \frac{v_m (p - p^*)}{RT}$$ (4)

where $H_m^*$ is the Henry’s law constant (atm·L/mol) of component $m$ at $p^*$ and $T$; $R$ is the gas constant; and $v_m$ is the partial molar volume of component $m$ in solution.

The chemical reactions that take place between components in the aqueous phase and between carbonate minerals and aqueous CO$_2$ are crucial in this study. The components in the aqueous phase were composed of soluble gas components, $N_c$, and components that only exist in the aqueous phase, $N_a$. It may be assumed that $N_m$ is the number of mineral components, $N_{\text{aq}}$ is the number of components in the aqueous phase ($N_{\text{aq}} = N_c + N_a$), and $N_{\text{ct}}$ is the total number of components ($N_{\text{ct}} = N_{\text{aq}} + N_m$). The chemical reaction in the aqueous phase between species has the stoichiometry of [14]:

$$\sum_{k=1}^{N_{\text{aq}}} v_{k,\alpha} A_k = 0, \alpha = 1, \ldots, R_{\text{aq}}$$ (5)

where $R_{\text{aq}}$ is defined as the number of chemical reactions between aqueous components, $v_k$ is the stoichiometric coefficient of component $k$ in the chemical reaction, and $A_k$ is the chemical symbol for the $k$ aqueous species.

The precipitation/dissolution chemical reactions for minerals have the stoichiometry [14]:

$$\sum_{k=1}^{N_{\text{ct}}} v_{k,\beta} A_k = 0, \beta = 1, \ldots, R_{\text{mn}}$$ (6)

where $R_{\text{mn}}$ is the number of reactions between the minerals and aqueous components.
The chemical reactions in the aqueous phase would be expressed by chemical equilibrium reactions because the chemical reactions that occurred in the components in the aqueous phase are usually relatively faster than the mineral precipitation/dissolution reactions. The dissolution or precipitation chemical reactions for minerals can then be described as rate-dependent reactions.

The chemical equilibrium reactions can be computed using chemical equilibrium constants [14,17], and the governing equations are

\[ Q_\alpha - K_{eq,\alpha} = 0, \alpha = 1, \ldots, Raq \]  

(7)

\[ Q_\alpha = \prod_{k=1}^{n_{Aq}} a_k^{v_{k\alpha}} \]  

(8)

where \( Q_\alpha \) is the activity product, \( K_{eq,\alpha} \) is the chemical equilibrium constant for the aqueous reaction \( \alpha \), \( a_k \) is the activity of component \( k \), and \( v_{k\alpha} \) are the stoichiometry coefficients.

The activities \( a_k \) are associated with the molality \( m_k \) (moles per kg of \( H_2O \)):

\[ a_k = \gamma_k m_k, k = 1, \ldots, N_{aq} \]  

(9)

where \( \gamma_k \) is the activity coefficient and equals 1 for an ideal solution.

Nevertheless, for most cases, the B-dot model is used to describe the non-ideal and preferred model for ionic activity coefficients [14,17]:

\[ \log \gamma_i = -\frac{A_\gamma z_i^2 \sqrt{I}}{1 + \hat{a}_i B_\gamma \sqrt{I}} + \hat{B} I \]  

(10)

where \( A_\gamma, B_\gamma \) and \( \hat{B} \) are temperature dependent parameters, \( \hat{a}_i \) is the ion size parameter, and \( I \) is the ionic strength, which can be expressed by:

\[ I = \frac{1}{2} \sum_{k=1}^{n_{aq}} m_k z_k^2 \]  

(11)

where \( z_k \) is the charge of the \( k \)-th ion.

As for the dissolution/precipitation reaction of mineral, the rate law is as follows [14,17]:

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

(12)

where \( r_\beta \) is the rate of the mineral reaction, \( \hat{A}_\beta \) is the reactive surface area for mineral \( \beta \), \( k_\beta \) is the rate constant of the mineral reaction, and the activity product, \( Q_\beta \), is analogous to the activity product for the aqueous chemical equilibrium reactions:

\[ Q_\beta = \prod_{k=1}^{n_{Aq}} a_k^{v_{k\beta}} \]  

(13)

The rate of formation/consumption of the different aqueous species is expressed by:

\[ r_{k\beta} = v_{k\beta} \cdot r_\beta \]  

(14)

The rate constant of the mineral reaction can be calculated at a different temperature, \( T \), using the reference temperature, \( T_0 \):

\[ k_\beta = k_{0\beta} \exp \left[ -\frac{E_{0\beta}}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right] \]  

(15)
where $E_{\beta\beta}$ is the activation energy for reaction $\beta$ (J/mol) and $k_{0\beta}$ is the reaction rate constant for reaction $\beta$ at $T_0$ (mol/m$^2$s).

To compute the reactive surface area of the mineral reaction, the change in the moles of minerals via dissolution/precipitation is involved:

$$\dot{A}_\beta = \dot{A}^\circ_\beta \cdot \frac{N_\beta}{N^\circ_\beta}$$

(16)

where $\dot{A}^\circ_\beta$ is the initial reactive surface, $N_\beta$ is the number of mineral $\beta$ moles per unit gridblock of the volume at a given time, and $N^\circ_\beta$ is the number of mineral $\beta$ moles per unit gridblock of the initial bulk volume.

3. Geological Description

The case study was based on a potential target site, the Y-field in Northwestern Taiwan, for CO$_2$ geological storage. The target formation for this study is the Yutengping (YTP) sandstone formation, which is a deep saline aquifer in the Y-field. The YTP sandstone formation is overlain by the Chinshiu (CS) Shale, which is a thick shale formation regionally distributed in Northwestern Taiwan. The thickness of the CS Shale is about 200 m. Due to the thickness and the extremely low permeability, the CS Shale is considered to be a caprock with great integrity that can prevent the leakage of the injected CO$_2$ stored in the reservoir. The Shihliufen (SLF) Shale, which is the formation under the YTP sandstone, is the impermeable underburden for the CO$_2$ geological storage in the storage system.

The structural map of the YTP sandstone formation is shown in Figure 1. The YTP sandstone formation in the Y-field is an anticline structure sealed by two faults. The strike of the anticline axis is NE to SW. The formation top of the YTP sandstone is about 1240–1500 m. There are 11 pre-existing wells that were used to produce gas from the deeper formation, and they were the geological investigation wells for the CO$_2$ storage in the Y-field.

![Figure 1. Structural map of the Yutengping (YTP) formation in the Y-field.](image-url)
was calculated by the Ordinary Kriging method from the results of the well logging interpretation of each pre-existing well. The top view of the three-dimensional model of the YTP sandstone formation is shown in Figure 3.

Figure 2. The analyzed results of the lithology of the sublayers in the YTP formation at well Y-15.

Figure 3. Top view of the three-dimensional model of the YTP sandstone formation.

4. Simulation Model Design

The General Equation of state Model simulator (GEM simulator) (GEM 2015.10, Computer Modelling Group LTD., Calgary, AB, Canada) developed by the Computer Modelling Group (CMG) was used in this study to simulate the complex processes of CO₂ storage by coupling the multiphase fluid flow and geochemical mechanisms. The GEM simulator is a commercial compositional simulator based on the Equation of State (EOS). The greenhouse gas module (GHG module) of the GEM simulator, which was used to simulate the complex process of trapping mechanism, included the convective and dispersive transportations of the components, the thermodynamic equilibrium between the gas/aqueous phases, the chemical reactions that occurred in the formation water, and the mineral reactions reacted with the mineral in the porous media [13,14,18].

The formation in the study area was discretized into 45 × 29 × 7 grid blocks. The x and y dimensions of each grid block were 580 × 570 ft. The reservoir parameters, such as porosity and
The sand and shaly sand layers act as a reservoir in the YTP sandstone formation, while the sandy shale and shale layers act as a barrier inter-layer in the YTP sandstone formation. For the relative permeability curves this study used, the irreducible water saturation was set at 0.2, and the maximum residual gas saturation was assigned to be 0.4 for the residual gas trapping mechanism modeling. The formation temperature of the YTP sandstone formation was 162 °F, and the initial pressure was 2445 psi at a reference depth of 5400 ft. In this study, the Luchukeng (LCK), Touhuanping (THP), and Lungkang (LK) faults were designed as no-flow boundaries, and there is an open boundary at the west of the study area.

Table 1. Reservoir parameters and initial conditions.

| Parameter          | Unit | Value |
|--------------------|------|-------|
| Porosity           |      |       |
| Sand               | frac.| 0.25  |
| Shaly Sand         | frac.| 0.23  |
| Sandy Shale        | frac.| 0.05  |
| Shale              | frac.| 0.025 |
| Permeability       |      |       |
| Sand               | mD   | 530   |
| Shaly Sand         | mD   | 200   |
| Sandy Shale        | mD   | 0.001 |
| Shale              | mD   | 0.0001|
| Formation Pressure | psi  | 2445  |
| Formation Temperature| °F  | 162   |
Table 2. Chemical reactions of the aqueous phase and mineral reactions used in this study. (The reaction rate constant was adopted from the Thibeau et al. (2007) [22]).

| Intra-Aqueous Chemical Reactions                  | $K_{eq}$ at 33 °C |
|--------------------------------------------------|--------------------|
| $\text{Al(OH)}_2^{2+} + 2\text{H}^+ \leftrightarrow \text{Al}^{3+} + 2\text{H}_2\text{O}$ | 4.75               |
| $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^-$ | –6.35              |
| $\text{CO}_3^{2-} + \text{H}^+ \leftrightarrow \text{HCO}_3^-$               | 10.31              |
| $\text{KOH} + \text{H}^+ \leftrightarrow \text{K}^+ + \text{H}_2\text{O}$            | 15.43              |
| $\text{OH}^- + \text{H}^+ \leftrightarrow \text{H}_2\text{O}$             | 13.74              |

| Geochemical Mineral Reactions                    | $k_{0\beta}$ at $T_0$ |
|--------------------------------------------------|----------------------|
| $\text{Anorthite} + 8\text{H}^+ \leftrightarrow 4\text{H}_2\text{O} + \text{Ca}^{2+} + 2\text{Al}^{3+} + 2\text{SiO}_2(\text{aq})$ | 25.72 at 33 °C |
| $\text{Calcite} + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$ | 1.6 at 33 °C |
| $\text{Kaolinite} + 6\text{H}^+ \leftrightarrow 5\text{H}_2\text{O} + 2\text{Al}^{3+} + 2\text{SiO}_2(\text{aq})$ | 6.77 at 33 °C |
| $\text{Muscovite} + 6\text{H}^+ \leftrightarrow 6\text{H}_2\text{O} + \text{K}^+ + 3\text{Al}^{3+} + 3\text{SiO}_2(\text{aq})$ | 12 at 25 °C |

Table 3. Initial molality of the primary aqueous components of the saline at the reservoir conditions and the volume percentages of the minerals in the rock used in the simulation model.

| Primary Species | Molality (mole/kg) | Mineral         | Volume Percentage (%) |
|-----------------|-------------------|-----------------|-----------------------|
| $\text{H}^+$   | $8.90 \times 10^{-9}$ | Anorthite       | 13.15%                |
| $\text{Ca}^{2+}$ | $8.75 \times 10^{-5}$ | Kaolinite       | 3.77%                 |
| $\text{K}^+$   | $6.68 \times 10^{-5}$ | Calcite         | 0%                    |
| $\text{Al}^{3+}$ | $7.24 \times 10^{-11}$ | Muscovite      | 6.43%                 |
| $\text{SiO}_2$ | $2.35 \times 10^{-8}$ | Quartz         | 73.65%                |

A schematic diagram of the injection process used in this study is shown in Figure 4. Using the up-dip of the anticline in the Y-formation, an up-dip injection well was designed to prevent the injected free-moved supercritical CO$_2$ splitting from the target anticline. The perforated intervals of the injection well were assumed to be the sandstone layer and the three shaly sand layers. A scenario analysis was performed for two injection fluids: traditional supercritical CO$_2$ and dissolved CO$_2$ solution. This case study was designed by injecting 0.2 million tons of CO$_2$ per year for 10 years via the one injection well. The simulation period was designed for 1000 years to observe the transformation process of trapping mechanisms after the injection period. For the dissolved CO$_2$ injection scenario, the CO$_2$ concentration of the injected solution was 1.005 (mole/kg-H$_2$O), considering the CO$_2$ solubility at the initial static bottom-hole pressure (1980 psi) and formation temperature (162 °F). The injection rate of the injected solution was 68,460 bbl/day. Because a large volume of water was required in the dissolved CO$_2$ injection scenario, one pre-existing well was assigned as the production well from which water in the YTP formation was produced at the rate required for the water supply.

Figure 4. The injection scenario used in this study (a) Schematic diagram of the injection interval in the YTP formation; (b) schematic diagram of the supercritical CO$_2$ scenario; (c) schematic diagram of the dissolved CO$_2$ solution scenario.
5. Results and Discussion

5.1. Supercritical CO\(_2\) Scenario

The injection profile of the supercritical CO\(_2\) scenario is shown in Figure 5. The initial bottom-hole pressure was about 2000 psi. With the continuous injection of supercritical CO\(_2\), the bottom-hole pressure rose to about 2250 psi after 10 years of injection. Based on the evaluation result of the maximum sustainable pressure in the YTP formation in this target site, the smallest evaluated value of the maximum sustainable pressure was about 1100 psi [23]. In the supercritical CO\(_2\) scenario, the pressure increment induced by CO\(_2\) injection was just about 250 psi, so it would not lead to a geomechanical failure occurring in the target reservoir. After the well shut-in, since the supercritical CO\(_2\) is accumulated at the top of the anticline, the well bottom-hole pressure would decrease slowly. At the end of the simulation, the bottom-hole pressure was about 2120 psi, which was higher than the initial bottom-hole pressure. Because the increment of the bottom-hole pressure was not very great, the buildup of the bottom hole pressure was considered safe over this injection period and post-injection period.

![Figure 5](image-url)

**Figure 5.** Injection profile of the supercritical CO\(_2\) scenario (a) During the injection period, (b) During the total simulation period.

![Figure 6](image-url)

**Figure 6.** Spatial distribution of the CO\(_2\) saturation in the supercritical CO\(_2\) scenario.
Based on the simulation results of the spatial distribution of CO$_2$ saturation (Figure 6), the CO$_2$ plume expanded to its largest size when the injection well was shut-in (10 years). After that, the plume gradually shrank due to the contribution of the solubility trapping mechanism. At the end of the simulation period (1000 years), the CO$_2$ plume area was smaller than the largest size due to the contributions of the solubility, ionic, and mineral trapping mechanisms. Since the density of supercritical CO$_2$ was smaller than that of the formation water and the trapping mechanisms associated with geochemical reactions occur slowly, the CO$_2$ plume was still located at the top of the anticline in the YTP formation at the end of the simulation.

The spatial distribution of the CO$_2$ molality is shown in Figure 7. The plume of the CO$_2$ dissolved in the saline of the formation was similar to that of the supercritical CO$_2$. The plume of the CO$_2$ molality expanded slightly in the early stages after the injection well was shut-in because of the downward migration of the CO$_2$-saturated water with a high density caused by CO$_2$ dissolution. In the later stages, the plume of the CO$_2$ molality shrank due to the contributions of the ionic and mineral trapping mechanism. However, the plume of the CO$_2$ molality was still located at the top of the anticline in the YTP formation at the end of the simulation.

Figure 7. Spatial distribution of the CO$_2$ molality in the supercritical CO$_2$ scenario.

The spatial distribution of the change in the moles of calcite is shown in Figure 8. At the end of the injection, there was no significant mineral precipitation. The contribution of the mineral trapping mechanism becomes significant after hundreds of years. CO$_2$ in the HCO$_3^-$ and CO$_3^{2-}$ forms achieved via ionization and dissociation results in the precipitation of calcite. At the end of the simulation, the calcite precipitated in the region near the plume of the CO$_2$ molality.

The evolution profiles of kaolinite, calcite, muscovite, and anorthite are shown in Figure 9. Anorthite, which is a calcium-rich mineral which is non-carbonate in the formation, dissolves to provide calcium to the formation water caused by formed carbonic acid in the formation water. Calcite and kaolinite precipitate resulting from the calcium ions, which are from the dissolution of anorthite. In regions with a decrease in pH due to CO$_2$ dissolution, the dissociation of muscovite releases potassium ions into the formation water and leads to the precipitation of kaolinite. The geochemical reactions of the minerals did not achieve a balance between dissolution and precipitation at the end of the simulation.
of the simulation. The trend of the dissolution of anorthite and trend of the precipitation of calcite and kaolinite showed that the amount of CO\textsubscript{2} trapped by the mineral trapping mechanism would be greater if the simulation time were increased.

### Supercritical CO\textsubscript{2}

![Graph showing the spatial distribution of the CO\textsubscript{2} molality in the supercritical CO\textsubscript{2} scenario.](image)

**Figure 7.** Spatial distribution of the CO\textsubscript{2} molality in the supercritical CO\textsubscript{2} scenario.

**Figure 8.** Spatial distribution of the change in moles of calcite in the supercritical CO\textsubscript{2} scenario.

5.2. **Dissolved CO\textsubscript{2} Scenario**

The injection profile of the dissolved CO\textsubscript{2} scenario is shown in Figure 10. With the continuous injection of the CO\textsubscript{2} solution, the bottom-hole pressure rose to about 2350 psi after the 10-year injection period. In the dissolved CO\textsubscript{2} scenario, the pressure increment induced by injecting the CO\textsubscript{2} solution was about 350 psi. Although the pressure increment in the dissolved CO\textsubscript{2} scenario was higher than that in the supercritical CO\textsubscript{2} scenario, it was still less than the sustainable pressure constraint of

![Graph showing evolutions of kaolinite, calcite, muscovite, and anorthite in the supercritical CO\textsubscript{2} scenario.](image)

**Figure 9.** Evolutions of kaolinite, calcite, muscovite, and anorthite in the supercritical CO\textsubscript{2} scenario.

The injection profile of the dissolved CO\textsubscript{2} scenario is shown in Figure 10. With the continuous injection of the CO\textsubscript{2} solution, the bottom-hole pressure rose to about 2350 psi after the 10-year injection period. In the dissolved CO\textsubscript{2} scenario, the pressure increment induced by injecting the CO\textsubscript{2} solution was about 350 psi. Although the pressure increment in the dissolved CO\textsubscript{2} scenario was higher than that in the supercritical CO\textsubscript{2} scenario, it was still less than the sustainable pressure constraint of
1100 psi, and geomechanical failure will not happen in the target reservoir. After the well shut-in, the pressure decreased quickly because of the balance of the formation pressure in the aquifer is fast due to the convection. At the end of the simulation, the bottom-hole pressure was close to the initial bottom-hole pressure.

**Figure 10.** Injection profile of the dissolved CO$_2$ scenario: (a) During the injection period, (b) During the total simulation period.

The spatial distribution of the CO$_2$ molality is shown in Figure 11. The plume of the CO$_2$ dissolved in the saline in the formation was located at the top of the anticline in the YTP formation at the end of the injection process. Because of the effect of the production well, during the injection period, the direction of the migration of the CO$_2$ plume was slightly toward the production well. After the shut-in of the injection well, the area of the plume of the CO$_2$ molarity expanded because of the downward migration of the higher-density CO$_2$ solution in comparison to the formation water. The shape of the plume of the CO$_2$ molarity changed due to the structure of the YTP formation in the Y-field. After 500 years, the majority of the plume of high CO$_2$ concentration had disappeared as the result of the contributions of the geochemical reactions (i.e., ionic and mineral trapping mechanisms).

**Figure 11.** Spatial distribution of the CO$_2$ molality in the dissolved CO$_2$ scenario.
The spatial distribution of the change in moles of calcite is shown in Figure 12. At the end of the injection, there was no significant mineral precipitation. The contribution of the mineral trapping mechanism appeared after 100 years. In the early stages, the calcite precipitated near the top of the anticline, where the plume of the CO$_2$ molarity was. Because the plume of the CO$_2$ molarity migrated downward, the calcite precipitated at the bottom of the YTP formation in the later stages. The calcite precipitated both at the top of the anticline and the bottom of the YTP formation in the Y-field at the end of the simulation period (1000 years).

![Figure 12](image-url)

**Figure 12.** Spatial distribution of the change in moles of calcite in the dissolved CO$_2$ scenario.

The evolution profiles of kaolinite, calcite, muscovite, and anorthite are shown in Figure 13. The geochemical reactions of the minerals occurred at a fast rate in the dissolved-CO$_2$ injection scenario. The majority of the injected CO$_2$ was transformed into carbonate minerals after 400 years. The rate of the geochemical reactions thereby decreased. The balance between the dissolution and precipitation geochemical reactions of the minerals was achieved after about 600 years.

![Figure 13](image-url)

**Figure 13.** Evolutions of kaolinite, calcite, muscovite, and anorthite in the dissolved CO$_2$ scenario.
5.3. Comparison of the Supercritical CO$_2$ and Dissolved CO$_2$ Scenarios

Based on the simulation results of the spatial distribution of the CO$_2$ molality in these two scenarios described above (Figure 14), the plume area of the supercritical CO$_2$ scenario was smaller than that of the dissolved CO$_2$ scenario when the injection well was shut-in (10 years). In the supercritical CO$_2$ scenario, the highest molality of CO$_2$ in the aqueous phase was located near the wellbore. At the end of the simulation period (1000 years), the plume area of the supercritical CO$_2$ scenario decreased due to the contributions of the ionic and mineral trapping mechanisms. However, the plume area of the dissolved CO$_2$ scenario disappeared because of the fast rate at which the geochemical reaction occurred to form carbonate.

![Figure 14. Comparison of the spatial distribution of CO$_2$ molality between scenarios.](image)

The spatial distributions of the change in moles of calcite in these two scenarios are shown in Figure 15. When the injection well was shut-in (10 years), in both scenarios, there was no significant mineral precipitation. The contribution of the mineral trapping mechanism became significant after hundreds of years. At the end of the simulation period, the calcite precipitated at the top of the anticline in the supercritical CO$_2$ scenario. This occurred because the majority of the injected CO$_2$ was still located at the top of the anticline in the YTP formation as a result of the low density of supercritical CO$_2$. In the dissolved CO$_2$ scenario, at the end of the simulation period (1000 years), the calcite mostly precipitated at the bottom of the YTP formation because the plume of the CO$_2$ solution moved downward. The area of the calcite distribution in the dissolved CO$_2$ scenario was much larger than that of the supercritical CO$_2$ scenario. This occurred because the process of transforming the CO$_2$ in an aqueous phase into a mineral phase is shorter than the process of transforming CO$_2$ in a supercritical phase into a mineral phase.

The evolution profiles of kaolinite, calcite, muscovite, and anorthite in these two scenarios are shown in Figure 16. Calcite, kaolinite, and muscovite are precipitation-phase minerals that occur when CO$_2$ was injected into the YTP formation. Anorthite is a dissolution-phase mineral that provides a source of calcium in the formation water. The rate of the geochemical reactions of the minerals was much faster in the dissolved CO$_2$ scenario than that in the supercritical CO$_2$ scenario. In the dissolved CO$_2$ scenario, the majority of the injected CO$_2$ was transformed into the carbonate minerals after 400 years, and the balance between dissolution and precipitation reactions of the minerals was
achieved after about 600 years. Compared to the dissolved CO$_2$ scenario, the geochemical reactions of the minerals did not achieve such a balance after 1000 years in the supercritical CO$_2$ scenario in the YTP formation.

![Figure 15. Comparison of the spatial distribution of the change in moles of calcite between scenarios.](image)

![Figure 16. Comparison of evolutions of kaolinite, calcite, muscovite, and anorthite between scenarios.](image)

The contributions of the different trapping mechanisms in these two scenarios are shown in Figure 17. In the supercritical CO$_2$ scenario, when the injection well was shut-in (10 years), 71.93% of the total 2-million tons of injected CO$_2$ was trapped by structural trapping, and 9.88%, 17.70%, 0.48%, and 0.01% of the injected CO$_2$ was stored by residual gas, solubility, ionic, and mineral trapping, respectively. Ten years after the injection well was shut-in (i.e., 20 years of simulation time), 56.81%, 24.41%, 17.67%, 1.03%, and 0.08% of injected CO$_2$ was stored by structural, residual gas, solubility, ionic, and mineral trapping, respectively. One-hundred years after the injection well was shut-in (110 years of simulation time), 47.68%, 31.58%, 16.63%, 1.69%, and 2.42% of the injected CO$_2$ was stored by structural, residual gas, solubility, ionic, and mineral trapping, respectively. At the end of the simulation (1000 years of simulation time), 32.26%, 30.16%, 13.89%, 1.54%, and 22.15% of the injected CO$_2$ was stored by structural, residual gas, solubility, ionic, and mineral trapping, respectively.
If the risk of CO₂ leakage is defined by the amount of CO₂ stored by secure trapping mechanisms, the safety index (SFI) can be evaluated by the number of the moles of CO₂ retained by the safe trapping mechanisms (i.e., residual gas, solubility, ionic, and mineral trapping) [12]. The SFI for the supercritical CO₂ scenario was 0.2807 at the end of injection (10 years). In the post-injection period, the SFIs were 0.4319, 0.5232, 0.6774 at the simulation times of 20, 110, and 1000 years (Figure 18).

In the dissolved CO₂ scenario, when the injection well was shut-in (10 years), 0.15% of a total of 2 million tons of the injected CO₂ was stored by residual gas trapping, and 84.95%, 14.86%, and 0.04% of the injected CO₂ was stored by solubility, ionic, and mineral trapping, respectively. It is worth noting that there was a very small amount of CO₂ trapped by the residual gas trapping mechanism indicating that there was a small amount of supercritical CO₂ released from the CO₂ solution during the injection period because of the slightly high molarity of CO₂ in the aqueous phase near the wellbore of the injection well. The released supercritical CO₂ would be restricted by the hysteresis effect as the residual gas that is immobilized and trapped in the pore spaces of the rock. Therefore, all of the injected CO₂ was trapped by safe and low-risk trapping mechanisms, and the SFI for the dissolved CO₂ scenario was 1 at the end of injection (10 years).

Ten years after the injection well was shut-in (20 years of simulation time), 0.14%, 82.10%, 17.41%, and 0.35% of the injected CO₂ was stored by residual gas, solubility, ionic, and mineral trapping, respectively. One hundred years after the injection well was shut-in (110 years of simulation time), 0.05%, 66.15%, 18.51%, and 15.29% of the injected CO₂ was stored by residual gas, solubility, ionic, and mineral trapping, respectively. At the end of the simulation (1000 years of simulation time), 3.70%, 14.81%, and 81.49% of the injected CO₂ were stored by solubility, ionic, and mineral, respectively.
Compared to the supercritical CO\(_2\) scenario, the SFI during both the injection period and during the total simulation period remained at 1, indicating that all the injected CO\(_2\) was trapped by safe trapping mechanisms (Figure 18). The solubility trapping mechanism can occur immediately after CO\(_2\) is injected into the reservoir. The transformation of CO\(_2\) into solid carbonate is, therefore, faster. The majority of the injected CO\(_2\) can be transformed into solid carbonate within hundreds of years. The rest of the injected CO\(_2\) was trapped by the ionic trapping mechanism because a balance between the dissolution and precipitation of the minerals was reached, and the transformations from ionic phases into mineral phases stopped after about 600 years.

In conclusion, changing the injection fluid from supercritical CO\(_2\) to dissolved CO\(_2\) can increase the safety of the CO\(_2\) storage significantly and eliminate the risk of CO\(_2\) leakage from the reservoir due to the injected CO\(_2\) being stored by secure trapping mechanisms. The simulation results showed that the geochemical reactions occurred more rapidly, consequently accelerating the rate of mineralization by means of the dissolved CO\(_2\) injection. The plume of the CO\(_2\) molarity was observed to disappear by the end of the simulation. The majority of the injected CO\(_2\) was transformed into solid carbonate, which is chemically stable and environmentally benign.

6. Conclusions

The risk of leakage and the plume migration between the scenarios involving the injection of supercritical CO\(_2\) and dissolved CO\(_2\) into a reservoir were studied and discussed in this study. In the supercritical CO\(_2\) injection scenario, the majority of the injected CO\(_2\) was retained by the structural trapping. The supercritical CO\(_2\) plume was still located at the top of the anticline after 1000 years. At this point, the contribution of the mineral trapping mechanism was about 22%, and the contribution of the structural trapping mechanism, which indicated the presence of mobile supercritical CO\(_2\) that might migrate upward in the reservoir, was about 32%.

In the dissolved CO\(_2\) solution injection scenario, the plume of the injected CO\(_2\) migrated downward because of the higher density of the CO\(_2\) solution than that of the formation water. The majority of the plume of CO\(_2\) in the aqueous phase had disappeared after a few hundred years caused by the contributions of the ionic and mineral trapping mechanisms. The majority of the injected CO\(_2\) was transformed into solid carbonate within hundreds of years.

The risk of acute CO\(_2\) leakage related to mechanical or geomechanical failures can be controlled and reduced through well-regulated management of the injection rate and injection pressure. The risk of chronic leakage via a natural pathway can be decreased by the approach of injecting CO\(_2\) solution instead of supercritical CO\(_2\). The amount of the CO\(_2\) retained by the safe trapping mechanisms in the dissolved CO\(_2\) scenario was greater than that in the supercritical CO\(_2\) scenario. In addition, the process of CO\(_2\) mineralization was much faster than that in the supercritical CO\(_2\) scenario. Changing the injection fluid from supercritical CO\(_2\) to a dissolved CO\(_2\) solution can significantly increase the safety of the CO\(_2\) geological storage. It can also eliminate the risk of CO\(_2\) leakage from the reservoir because the injected CO\(_2\) can be trapped totally by safe trapping mechanisms. Therefore, the potential environmental impact of CO\(_2\) storage can be reduced.

Author Contributions: Data curation, Y.-H.L.; Funding acquisition, B.-Z.H.; Supervision, B.-Z.H.; Validation, C.-H.S.; Writing—original draft, Y.-H.L.; Writing—review and editing, C.-Y.W. and B.-Z.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Science and Technology, Taiwan (R.O.C.): MOST 106-2221-E-006-186.

Acknowledgments: The work presented in this paper was supported by the Ministry of Science and Technology, Taiwan (R.O.C.). We thank the CPC Corporation, Taiwan, for offering practical suggestions of the setting of the geological and reservoir properties.

Conflicts of Interest: The authors declare no conflict of interest.
References

1. Bachu, S. Legal and regulatory challenges in the implementation of CO$_2$ geological storage: An Alberta and Canadian perspective. *Int. J. Greenh. Gas Control* 2008, 2, 259–273. [CrossRef]

2. Yanagi, K.; Nakamura, A. Towards a low/zero carbon society for the Asia-Pacific Region: Policy and legal development for carbon capture and storage (CCS) in Japan. In *Sustainability and Law*; Springer: Cham, Switzerland, 2020; pp. 585–605.

3. Bachu, S.; Gunter, W.; Perkins, E. Aquifer disposal of CO$_2$: Hydrodynamic and mineral trapping. *Energy Convers. Manag.* 1994, 35, 269–279. [CrossRef]

4. Emami-Meybodi, H.; Hassanzadeh, H.; Green, C.P.; Ennis-King, J. Convective dissolution of CO$_2$ in saline aquifers: Progress in modeling and experiments. *Int. J. Greenh. Gas Control* 2015, 40, 238–266. [CrossRef]

5. IPCC. *IPCC Special Report on Carbon Dioxide Capture and Storage*. In *Prepared by Working Group III of the Intergovernmental Panel on Climate Change*; Metz, B., Davidson, H., de Coninck, C., Loos, M., Meyer, L.A., Eds.; Cambridge University Press: Cambridge, UK; New York, NY, USA, 2005; p. 442.

6. Burton, M.; Bryant, S.L. Surface dissolution: Minimizing groundwater impact and leakage risk simultaneously. *Energy Procedia* 2009, 1, 3707–3714. [CrossRef]

7. Pool, M.; Carrera, J.; Vilarrasa, V.; Silva, O.; Ayora, C. Dynamics and design of systems for geological storage of dissolved CO$_2$. *Adv. Water Resour.* 2013, 62, 533–542. [CrossRef]

8. Ganjdanesh, R.; Bryant, S.; Orbach, R.; Pope, G.; Sepehrnoori, K. Coupled carbon dioxide sequestration and energy production from geopressured/geothermal aquifers. *SPE J.* 2014, 19, 239–248. [CrossRef]

9. Matter, J.; Takahashi, T.; Goldberg, D. Experimental evaluation of in situ CO$_2$-water-rock reactions during CO$_2$ injection in basaltic rocks: Implications for geological CO$_2$ sequestration. *Geochem. Geophys. Geosystems* 2007, 8. [CrossRef]

10. Matter, J.; Stute, M.; Snæbjörnsdóttir, S.; Oelkers, E.; Gislason, S.; Aradóttir, E.; Gunnlaugsson, E. Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. *Science* 2016, 352, 1312–1314. [CrossRef] [PubMed]

11. Snæbjörnsdóttir, S.O.; Oelkers, E.H.; Mesfin, K.; Aradóttir, E.S.; Dideriksen, K.; Gunnarsson, I.; Gunnlaugsson, E.; Matter, J.M.; Stute, M.; Gislason, S.R. The chemistry and saturation states of subsurface fluids during the in situ mineralisation of CO$_2$ and H$_2$S at the CarbFix site in SW-Iceland. *Int. J. Greenh. Gas Control* 2017, 58, 87–102. [CrossRef]

12. Hsieh, B.Z.; Nghiem, L.; Shen, C.H.; Lin, Z.S. Effects of complex sandstone–shale sequences of a storage formation on the risk of CO$_2$ leakage: Case study from Taiwan. *Int. J. Greenh. Gas Control* 2013, 17, 376–387. [CrossRef]

13. Kumar, A.; Noh, M.H.; Ozah, R.C.; Pope, G.A.; Bryant, S.L.; Sepehrnoori, K.; Lake, L.W. Reservoir simulation of CO$_2$ storage in aquifers. *SPE J.* 2005, 10, 336–348. [CrossRef]

14. Nghiem, L.; Sammon, P.; Grabenstetter, J.; Ohkuma, H. Modeling CO$_2$ storage in aquifers with a fully-coupled geochemical EOS compositional simulator. In *SPE/DOE Symposium on Improved Oil Recovery*; Society of Petroleum Engineers: Tulsa, Oklahoma, 17–21 April 2004.

15. Land, C.S. Calculation of imbibition relative permeability for two-and three-phase flow from rock properties. *Soc. Pet. Eng. J.* 1968, 8, 149–156. [CrossRef]

16. Peng, D.Y.; Robinson, D.B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* 1976, 15, 59–64. [CrossRef]

17. Bethke, C. *Geochemical Reaction Modeling: Concepts and Applications*; Oxford University Press: Oxford, UK, 1996.

18. Nghiem, L.; Shrivastava, V.; Kohse, B.; Hassam, M.; Yang, C. Simulation and optimization of trapping processes for CO$_2$ storage in saline aquifers. *J. Can. Pet. Technol.* 2010, 49, 15–22. [CrossRef]

19. 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. *Can. J. Chem. Eng.* 1986, 64, 486–496. [CrossRef]

20. GAMS. *Solmineq.88 Geochemical Aqueous Equilibrium Models*; Geochemical Applications & Modelling Software Ltd.: Edmonton, AB, Canada, 2011.

21. GAMS *GAMSPath Geochemical Reaction Path Models*; Geochemical Applications & Modelling Software Ltd.: Edmonton, AB, Canada, 2011.
22. Thibeau, S.; Nghiem, L.X.; Ohkuma, H. A modelling study of the role of selected minerals in enhancing CO₂ mineralization during CO₂ aquifer storage. In SPE Annual Technical Conference and Exhibition; Society of Petroleum Engineers: Anaheim, CA, USA, 11–14 November 2007.

23. Lin, Q.-H. In-Situ Stress and Fault Reactivation Potential in Response to Fluid Injection in Yunghoshan Structure. Master’s Thesis, National Central University, Taoyuan, Taiwan, 2014.

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).