

# Numerical investigation into CO<sub>2</sub> sequestration as hydrates and its long-term stability in submarine sediments<sup>#</sup>

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## ABSTRACT

Under suitable temperature and pressure conditions, CO<sub>2</sub> can combine with water to form solid CO<sub>2</sub> hydrates. Hydrate-based CO<sub>2</sub> sequestration in subsea sediments is an alternative option to mitigate global warming. In this work, we developed novel simulation codes and simulated CO<sub>2</sub> sequestration processes in subsea sediments based on site W19 in the Shenhu area. The results show that CO<sub>2</sub> hydrate massively forms after the end of injection and gradually expands into low-permeability cap that can stably exist for 100 years. The hydrate cap greatly restricts upward migration of liquid CO<sub>2</sub>, forcing it to gradually transform into dissolved phase and hydrate phase, which makes hydrate-based CO<sub>2</sub> sequestration feasible. Permeability, salinity, thermal conductivity of the formation and CO<sub>2</sub> injection rate all have significant impacts on the sequestration performance, which provides guidance for site selection and optimization of injection scheme.

**Keywords:** CO<sub>2</sub> sequestration, CO<sub>2</sub> hydrate, feasibility analysis, long-term stability, numerical code, CCUS

## NONMENCLATURE

### Abbreviations

CHSZ CO<sub>2</sub> hydrate-stability zone

### Symbols

$k$	Permeability (mD)
$M_{CO_2-D}$	Mass of dissolved CO <sub>2</sub> (kg)
$M_{CO_2-H}$	Mass of CO <sub>2</sub> in hydrate phase (kg)
$M_{CO_2-L}$	Mass of liquid CO <sub>2</sub> (kg)
$P$	Pressure (MPa)
$Q_i$	Mass injection rate of CO <sub>2</sub> (kg/s)
$R_{CO_2-D}$	Mass ratio of dissolved CO <sub>2</sub>
$R_{CO_2-H}$	Mass ratio of CO <sub>2</sub> in hydrate phase
$R_{CO_2-L}$	Mass ratio of liquid CO <sub>2</sub>
$S_{CO_2-L}$	Liquid CO <sub>2</sub> phase saturation
$S_H$	Hydrate phase saturation

$T$	Temperature (°C)
$t_i$	Injection time (y)
$X_s$	Salinity (wt%)
$\lambda_{wet}$	Wet thermal conductivity (W·m <sup>-1</sup> ·K <sup>-1</sup> )

## 1. INTRODUCTION

CO<sub>2</sub> sequestration refers to injecting CO<sub>2</sub> to geological reservoirs to achieve long-term isolation of CO<sub>2</sub> from the atmosphere [1]. At present, a variety of CO<sub>2</sub> sequestration methods have been proposed, including injecting and sequestration CO<sub>2</sub> into deep depleted oil and gas reservoirs, coal seams and deep saline aquifers [2] or directly injecting CO<sub>2</sub> into deep ocean [3]. Terrestrial CO<sub>2</sub> geological sequestration has higher requirements on reservoir sealing and caprock stability, while CO<sub>2</sub> sequestration in ocean is easily disturbed by ocean currents and will destroy the marine ecological environment [4]. Another feasible solution is to sequester CO<sub>2</sub> in subsea sediments, which combines the advantages of large marine storage reserves and reduces the dependence on reservoir conditions and negative impact on the environment [5]. In subsea sediments with low temperature and high pressure, part of CO<sub>2</sub> will combine with pore water to form solid hydrate with poor fluidity and reduce permeability of the formation.

The entire cycle time span of CO<sub>2</sub> injection, migration and sequestration in subsea sediments is so large that direct in-situ test takes a long and high investment. Using numerical simulation techniques to explore the relevant process is effective and economical. At present, the research on hydrate-based CO<sub>2</sub> sequestration in subsea sediments is still in its infancy, and available field data are limited. Little is known about the process of CO<sub>2</sub> transport and CO<sub>2</sub> hydrate formation in subsea sediments and there is a lack of numerical codes that can comprehensively consider the above processes [5].

To this end, based on the well-established simulation code TOUGH+HYDRATE, we developed a novel thermo-

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hydro-mechanical multi-field coupled numerical code CO<sub>2</sub>\_HYD to simulate CO<sub>2</sub> injection and sequestration processes in subsea sediments. Simulation results showed that long-term effective sequestration of CO<sub>2</sub> in subsea sediments can be realized through the combined hydrate capture and hydrate self-sealing effect.

## 2. NUMERICAL METHOD

### 2.1 Numerical codes

Hydrate-based CO<sub>2</sub> sequestration in subsea sediments is a complex multiphysics process, involving multiphase flow, heat transfer and hydrate formation and dissociation. To accurately characterize this process, we develop a novel thermo-hydro-mechanical multi-field coupled simulator CO<sub>2</sub>\_HYD based on the state-of-art TOUGH+HYDRATE code. The framework of TOUGH+HYDRATE is maintained while we modify the primary variable switch method (PVSM) for possible phase changes in liquid CO<sub>2</sub>-CO<sub>2</sub> hydrate system during sequestration. We adopt Peng-Robinson equation to calculate the density of liquid CO<sub>2</sub> at varying pressure and temperature. We introduce calculation method of Spycher et al. [6] to consider the solubility of liquid CO<sub>2</sub> in H<sub>2</sub>O and incorporate the friction theory [7] for viscosity modeling of liquid CO<sub>2</sub>. As for thermophysical properties of CO<sub>2</sub> hydrate, we replace the original methane hydrate phase equilibrium with the CO<sub>2</sub> hydrate phase equilibrium curve derived from CSMGem, and consider the effect of NaCl on phase equilibrium using the equation of Dickens and Quinby-Hunt [8]. In addition, we modify a series of properties associated with CO<sub>2</sub> hydrate, including enthalpy of formation, density, thermal conductivity, and heat capacity.

### 2.2 Numerical model

#### 2.2.1 Geological background

The sequestration target area is selected in the Shenhu area, South China Sea, where the subseafloor formation is silty sediment with a median radius of about 8.0 μm and natural gas hydrates are rich here at a burial depth of 100~200 m [9]. According to geological survey of site W19 in the Shenhu area, the water depth is 1273.9 m and the seafloor temperature and pressure are 3.75 °C and 12.86 MPa, respectively, with a geothermal gradient of 45 °C/km. This temperature and pressure condition here is highly suitable for CO<sub>2</sub> hydrate formation, which is why we select this area as the target site. The average porosity of the formation is 0.40 and the absolute permeability ranges from 1 mD to 10 mD [10, 11].

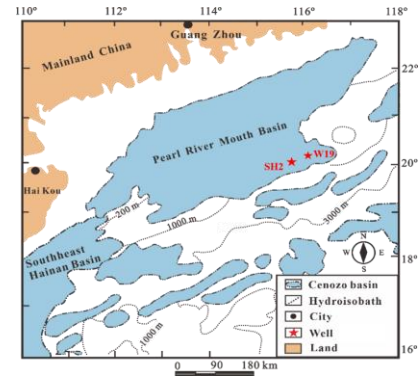


Fig. 1 Location of site W19 in the Shenhu area, South China Sea

#### 2.2.2 CO<sub>2</sub> injection and sequestration as hydrate process

Fig. 2 shows schematic of CO<sub>2</sub> injection and sequestration as hydrate. According to the prior calculation by the CO<sub>2</sub>\_HYD code, the bottom boundary of the CO<sub>2</sub> hydrate-stability zone (CHSZ) is located approximately at Z = -121.5 m. To facilitate faster hydrate formation, the CO<sub>2</sub> injection interval is designed from Z = -90 m to Z = -120 m, with a total length of 30 m, located within the CHSZ. The top of injection section is set to 90 m below the seafloor in order to prevent potential CO<sub>2</sub> leakage into the ocean. For preliminary exploratory purposes, we design a relatively low constant CO<sub>2</sub> injection rate ( $Q_i = 4.5 \times 10^{-3}$  kg/s = 141.9 t/y) and short injection duration ( $t_i = 5$  y) to prevent mechanical destabilization of unconsolidated sediments as much as possible. The injection is stopped after 5 years, then we observe and verify the long-term stability of CO<sub>2</sub> sequestration as hydrate.

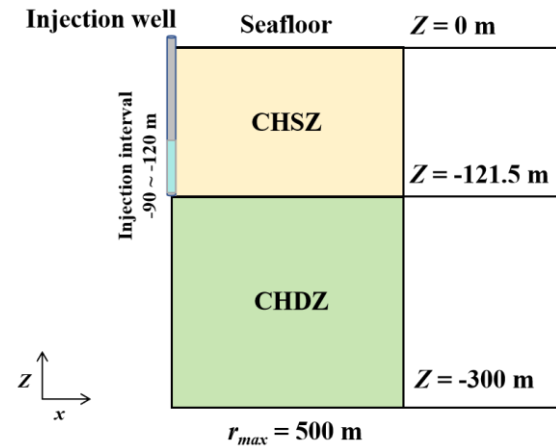


Fig. 2 Schematic of CO<sub>2</sub> injection and sequestration as hydrate

#### 2.2.3 Design of simulation cases

To elucidate the geological controlling factors of the CO<sub>2</sub> sequestration via hydrate technology and provide

guidance for sequestration site selection, sensitivity analyses are respectively performed on absolute permeability  $k$ , wet thermal conductivity  $\lambda_{\text{wet}}$ , and salinity  $X_s$ , which are three key geological factors in terms of mass transfer, heat transfer, and CO<sub>2</sub> phase equilibria. The absolute permeability of sediments in the Shenhu area ranges from 1 mD to 10 mD [10, 11] and salinity ranges from 3.05 wt% to 3.50 wt% [11]. For sand-rich shallow subsea sediments, the wet thermal conductivity is 3.1 W·m<sup>-1</sup>·K<sup>-1</sup>, and it is 1.7 W·m<sup>-1</sup>·K<sup>-1</sup> for silty sediments [12]. During the simulation case design, the upper and lower limits of the parameters are the above-mentioned values, and the middle value of salinity and wet thermal conductivity is the average of the above-mentioned values while middle value of absolute permeability is 5 mD. In addition, we design a 3-level 3-factor full factorial study based on these parameter values using statistical software Minitab, to further understand the controlling mechanism, the interactions between the three key geological parameters, and their relative importance.

### 3. RESULTS AND DISCUSSION

#### 3.1 Evolution of $P$ , $T$ and spatial distribution of various phases and components

Fig. 3 shows spatial distributions of  $P$ ,  $T$ ,  $S_H$ ,  $S_{\text{CO}_2\text{-L}}$ ,  $X_{\text{CO}_2}^A$  and  $X_i$  at different time points during sequestration stage. Since CO<sub>2</sub> injection is stopped, the  $P$  and  $T$  around the well decrease rapidly. As observed in Fig. X2(c), the decreased  $T$  provides the prerequisite condition for the massive generation of CO<sub>2</sub> hydrate during the sequestration stage. Under suitable  $P$  and  $T$  conditions, CO<sub>2</sub> hydrate gradually forms downward and  $S_H$  greatly increases. The CO<sub>2</sub> hydrate with high  $S_H$  stably present at  $t = 100$  y verifies the long-term stability of hydrate-based CO<sub>2</sub> sequestration.

At the same time, since hydrate formation is an exothermic and pressure-reducing reaction, significant  $T$  increase and  $P$  decrease can be observed in the hydrate formation area. Subsequently, due to the heat exchange with the surroundings, the high-temperature zone caused by the heat release of hydrate formation gradually disappears ( $t = 50$  y), and the temperature eventually tends to the initial temperature of the formation ( $t = 100$  y). The upward migration of liquid CO<sub>2</sub> is completely restricted by the upper dense hydrate cap, and is gradually converted into CO<sub>2</sub> hydrate and dissolved CO<sub>2</sub> as the sequestration progresses. The increase of salinity results from CO<sub>2</sub> hydrate formation that extracts water from the pore fluid, which will in turn inhibit the continuous formation of CO<sub>2</sub> hydrate.

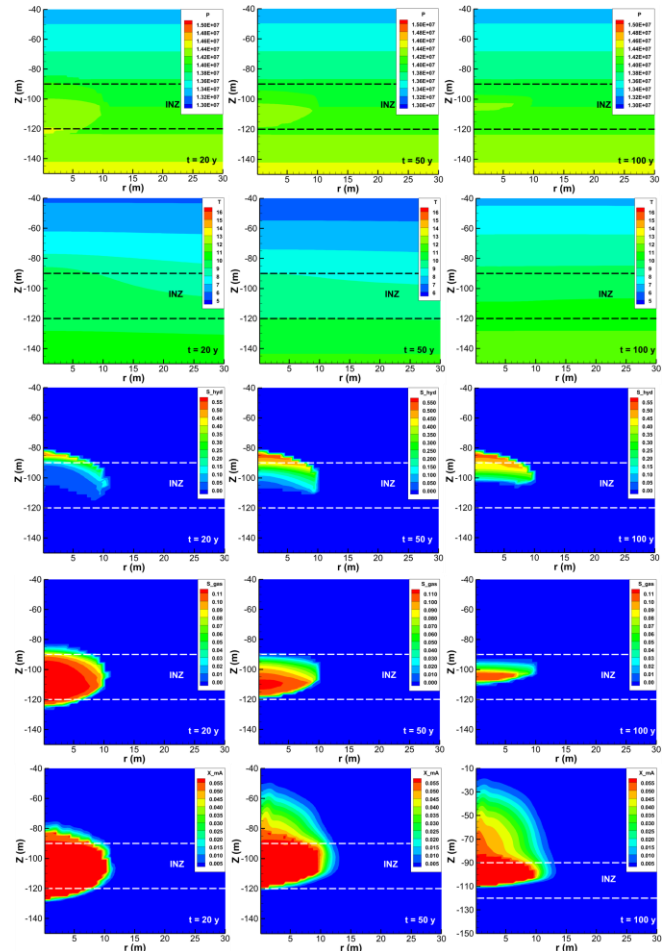


Fig. 3 Spatial distributions of  $P$ ,  $T$ ,  $S_H$ ,  $S_{\text{CO}_2\text{-L}}$ ,  $X_{\text{CO}_2}^A$  and  $X_i$  at different time points during sequestration stage ( $t = 5 \sim 100$  y)

#### 3.2 Evolution of CO<sub>2</sub> mass among various phases

During CO<sub>2</sub> injection and sequestration as hydrate process, the CO<sub>2</sub> component exists in the liquid CO<sub>2</sub> phase (CO<sub>2</sub>-L), the hydrate phase (CO<sub>2</sub>-H) and aqueous phase (CO<sub>2</sub>-D). Fig. 4 shows the time evolution of mass distribution of CO<sub>2</sub> component among above various phases during CO<sub>2</sub> injection stage (S1) and sequestration stage (S2). As seen in Fig. 4,  $M_{\text{CO}_2\text{-L}}$  and  $M_{\text{CO}_2\text{-D}}$  increase linearly over time in S1, implying that the CO<sub>2</sub> dissolution rate remains nearly constant.

In S1, CO<sub>2</sub> component exists mainly in liquid phase, followed by dissolved phase, with very little CO<sub>2</sub> hydrate generation. This is caused by the compression heat during CO<sub>2</sub> injection analyzed previously. At the end of S1,  $R_{\text{CO}_2\text{-L}}$  is 69.93%,  $R_{\text{CO}_2\text{-D}}$  is 29.24%, while  $R_{\text{CO}_2\text{-H}}$  only accounts for 0.8%, which suggests CO<sub>2</sub> hydrate act only as a cap to ensure sequestration security rather than as the primary storage medium. In S2, CO<sub>2</sub> hydrate massively forms under suitable  $T$  condition and  $R_{\text{CO}_2\text{-H}}$  improves rapidly from initial 0.83% to final 45.94% ( $t = 100$  y). Meanwhile,  $R_{\text{CO}_2\text{-D}}$  slightly increases from initial

29.24% to final 38.42%. As a consequence,  $R_{CO_2-L}$  is only 15.64% at  $t = 100$  y. In S2,  $CO_2$  hydrate progressively became the main medium for sequestering  $CO_2$  and continues to be a cap, sealing off the underlying liquid  $CO_2$ .

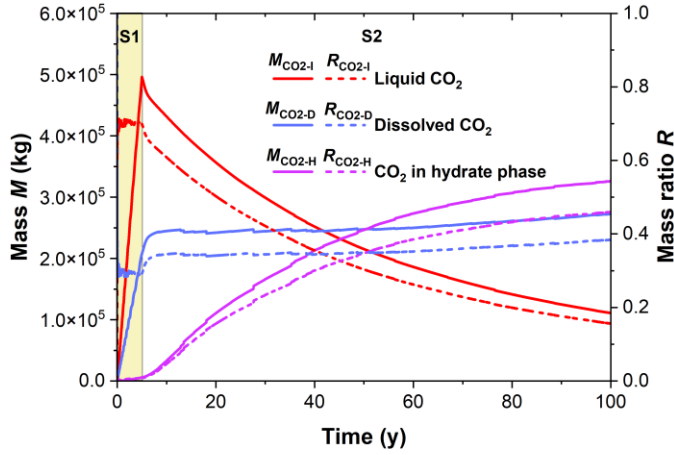


Fig. 4 Evolution of mass distribution of  $CO_2$  component among various phases during  $CO_2$  injection and sequestration as hydrate (S1: injection stage,  $t = 0-5$  y; S2: sequestration stage,  $t = 5-100$  y).

### 3.3 Sensitivity analysis on key geological and engineering parameters

In this section, we conducted a systematic sensitivity analysis on key geological engineering factors that may affect the sequestration performance, including permeability, salinity, thermal conductivity, and injection rate.

Fig. 5 shows evolution of mass and mass ratio of  $CO_2$  hydrate phase under different conditions. Permeability, salinity, thermal conductivity of the formation and  $CO_2$  injection rate all have significant impacts on the sequestration performance. To be specific, lower permeability, higher thermal conductivity, lower salinity, and lower injection rate are more favorable for the conversion of liquid  $CO_2$  to  $CO_2$  hydrate. Above results will provide guidance for site selection and optimization of sequestration scheme.

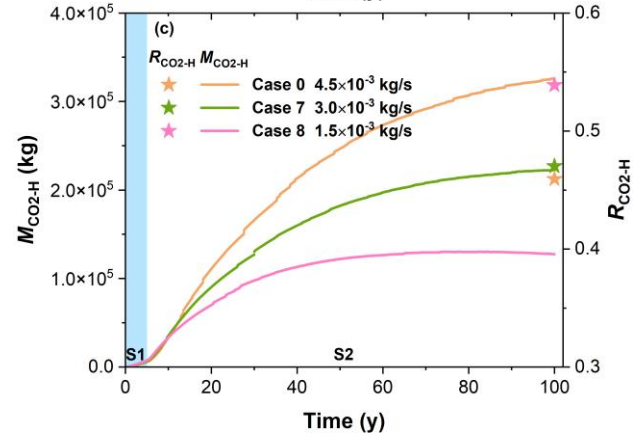
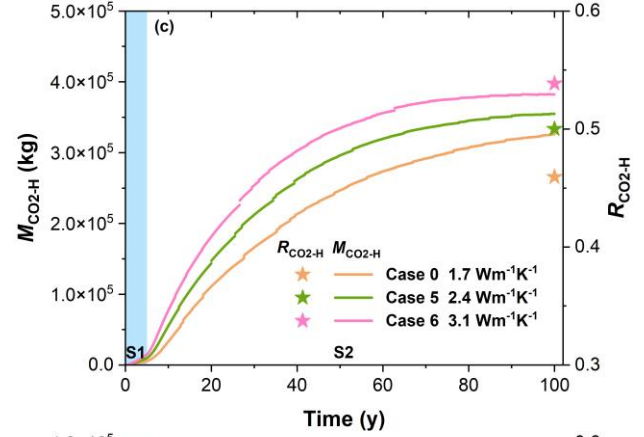
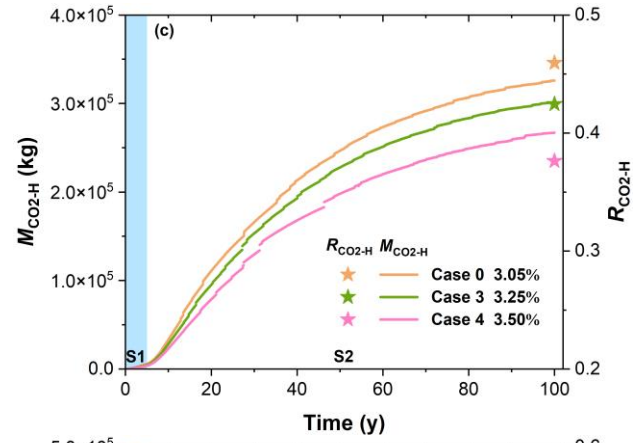
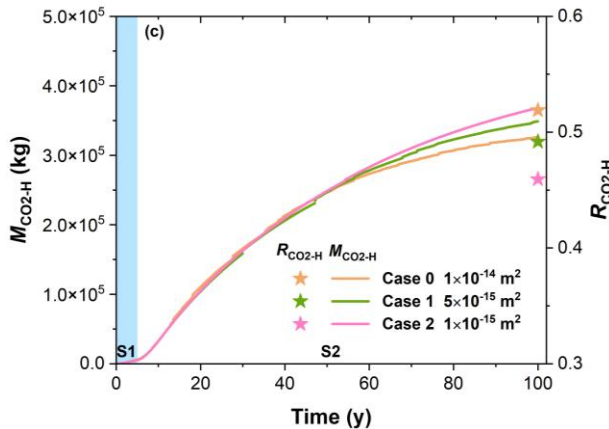


Fig. 5 Evolution of  $CO_2$  hydrate mass and mass ratio under different conditions.

## 4. CONCLUSIONS

The present work built novel multi-field coupled codes and numerically investigated the feasibility of carbon sequestration in subsea sediments by hydrate method at field scale for the first time. The following conclusions are drawn:

(1) It is feasible to sequester  $CO_2$  in subsea sediments in Shenhu area. Under suitable pressure and temperature,  $CO_2$  can combine with pore water to form  $CO_2$  hydrate, which is stored in sediments in the form of solid phase.

(2) CO<sub>2</sub> hydrate massively forms after the end of injection and gradually expands into low-permeability cap that can stably exist for 100 years. The hydrate cap greatly restricts upward migration of liquid CO<sub>2</sub>, forcing it to gradually transform into dissolved phase and hydrate phase, which makes hydrate-based CO<sub>2</sub> sequestration feasible.

(3) Permeability, salinity, thermal conductivity of the formation and CO<sub>2</sub> injection rate all have significant impacts on the sequestration performance, which provides guidance for site selection and optimization of injection scheme.

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