Study methane recovery and CO₂ storage of gas hydrate replaced by CO₂/N₂ mixture in marine sediments

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ABSTRACT

Under the strategic goal of "carbon peak, carbon neutral", CCUS technology has become an important means of reducing CO_2 emissions and sustainable energy development in China. The replacement of CH_4/CO_2 hydrate has the advantages of being environmentally friendly and maintaining the stability of geological reservoirs. At present, the laboratory has done quite a lot of experiments and simulations on the research of natural gas replacement and recovery, but it mainly focuses on the research in coarse sand such as glass sand, however, there is little research on the real marine environment. Some studies show that porous media has a great impact on the replacement effect. This study simulates the geological conditions of the South China Sea with real natural marine sediments of the South China Sea as porous media, systematically studies various factors affecting the replacement process, and explains the change of the replacement rate and CO_2 storage rate through the analysis of the driving force of the replacement process. Under different pressure (1.9-5.6MPa), temperatures (-1.82-3.87 ℃), and hydrate saturation (10% - 20%), the CO_2/N_2 mixture is used to replace natural gas hydrate in argillaceous silt. The results show that higher displacement temperature and lower displacement pressure have a positive effect on the recovery of CH_4, and lower displacement pressure and higher hydrate saturation are conducive to improving the storage capacity of CO_2. In marine soil sediments with low permeability, the pore size of the hydrate reservoir is small, and the contact area between N_2/CO_2 and methane hydrate is small, which leads to the inconspicuous replacement effect and low efficiency. According to the experimental results, we should optimize the pressure and temperature conditions, further enhance the heat and mass transfer effect, improve the permeability of the reservoir, and then improve the storage rate and replacement efficiency.

Keywords: CO_2 sequestration; CH_4 recovery; Natural gas hydrate; CH_4/CO_2 replacement

NONMENCLATURE

Abbreviations	
MH	Methane hydrate
Symbols	
ϕ	porosity
V_{cha}	internal volume of the reactor
V_{pore}	pore volume
M_m	mass of marine soil filled into reactor
ρ_m	density of marine soil
V_m	volume of marine soil
V_W	volume of deionized water
V_g	volume of gas
V_h	volume of hydrate filled into the reactor
S_W	water saturation
ρ_{MH}	density of CH_4 hydrate
$n_{CH_4}^1$	moles of CH_4 gas when injected
$n_{CH_4}^2$	moles of methane gas in the gas phase not involved in CH_4 hydrate generation
n_{MH}	moles of CH_4 hydrate generation
P	pressure

T	temperature
V	volume
Z	compression factor

1. INTRODUCTION

Natural gas hydrate, also known as "combustible ice", is a special ice-like envelope compound formed by the main molecule and the guest molecule under high-pressure and low-temperature conditions[1]. The main molecules of natural gas hydrate are water molecules and the guest molecules are CH_4, CO_2, N_2, etc.[2] the water molecules are bound to each other by a hydrogen bond to form a "cage", and the guest molecules are bound in a cage-like structure. In general, each cage can hold one gas molecule, and since the empty cage structure is unstable, encapsulated gas molecules are needed to stabilize the caged crystal. Five hydrate crystal configurations with cage cavities are available[3], and these five different cage cavities are combined to form three types of gas hydrate structures, type I, type II and type H. The degree of adaptation of the guest molecule to the cage structure determines the degree of hydrate stability.

Natural gas hydrates, whose main component is CH_4, are widely found in permafrost zones and deep-sea bottoms, and their wide distribution and abundant reserves are considered the most important energy resource in the 21st century. According to the China Mineral Resources Report 2018, the gas hydrate reserves contained in China's waters are as high as 80 billion tons of oil equivalent, and more than 70% of natural hydrates worldwide contain natural gas [4]. Despite the high potential of gas hydrate development, its unique reservoir conditions make the extraction process much more complicated than that of oil and gas reservoirs. Before the formation of natural gas hydrates, a special layer of rock - carbonate cement - is deposited around them. If the extraction method is inappropriate, the decomposition of hydrate will lead to the weakening of the original cementation in the sediment layer, which will lead to the decrease of the strength of the sediment and cause a series of potential geological disasters, such as submarine landslides, seabed collapse, and the destruction of engineering structures. As a greenhouse gas, the presence of CH_4 may not only aggravate global warming but also cause geological disasters such as tsunamis and earthquakes, so how to achieve safe and efficient extraction of natural gas hydrate has become a focus of discussion in both academic and engineering circles.

Several hydrate mining techniques are commonly used at home and abroad, including thermal stimulation:[5,6], pressure-reduction mining[7,8], chemical inhibitor injection[9], CO_2 replacement mining [10-13], and a combination of several mining methods[14,15]. The mining principles of conventional methods such as thermal stimulation, pressure reduction, and injection of inhibitors are all based on the disruption of hydrate stable phase equilibrium conditions, using different driving forces in terms of temperature, pressure, and chemical potential to cause damage to hydrate reservoir conditions. The advantages of the depressurization method are no energy dissipation, simplicity and economy, but as depressurization mining proceeds, the temperature inside the hydrate reservoir decreases significantly, while hydrate decomposition generates water, which may lead to ice formation and secondary hydrate formation, thus causing ice plugging and seriously affecting gas production efficiency. The core concept of gas hydrate extraction by heat injection is to warm up the hydrate reservoir to provide sufficient temperature and heat to promote hydrate decomposition, but it is less economical to use the heat injection method alone. Using the injection of inhibitor method, the injection of alcohol inhibitor method is costly in the actual extraction process, and the injection of a large amount of inhibitor can cause great damage to the marine environment and groundwater.

The technology of CO_2 replacement of natural gas hydrate can be used to achieve efficient storage of CO_2 while natural gas extraction. The principle of replacement is that when the temperature drops below 283 K, the phase equilibrium of CH_4 hydrate and CO_2 hydrate will change, and the difference in thermodynamic properties between different components of the gas mixture can be used to achieve the purpose of replacement[16]. The advantage of the replacement method is that it does not destroy the stability of the original reservoir structure, minimizes the damage to the skeletal structure of the formation, and achieves the purpose of sequestering CO_2, which is a more environmentally friendly mining technology. Because of the complexity of the replacement process and the many influencing factors, the study of the replacement effect and the law has been the key topic of scholars' attention[17]. At present, relatively few studies have been conducted on the characteristics and mechanisms of CO_2 replacement extraction of gas

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hydrate in low-permeability muddy sands reservoirs in the South China Sea, mainly focusing on porous media composed of coarse-grained sands. In the study of CO_2 replacement of natural gas hydrate, we found that the replacement rate is slow, while the recovery rate of CH_4 is not satisfactory, and the replacement law for different types of hydrate is not clear. In this paper, we will use a CO_2/N_2 mixture for replacement experiments to explore the mechanism of gas hydrate extraction by gas mixture replacement, and the replacement characteristics are deeply investigated. Figure 1 shows the replacement phenomenon of CH_4-(N_2+CO_2) in the porous medium[18].

blockage of pores and throats, thus reducing permeability and flow properties and increasing the difficulty of mining[21,22]. The unconsolidated marine sediment sample particles used in this study have a median particle diameter of 5.482 μm, their specific gravity G_S=2.73 g/cm^3, specific surface area S_S=796.80 m^2/kg, and electrical conductivity of 2.32 mS/cm. The main components of the muddy silt sediments of the South China Sea sediments[23] are shown in the following table1, and their chemical composition is based on SiO_2, Al_2O_3, and Fe_2O_3 were dominant.

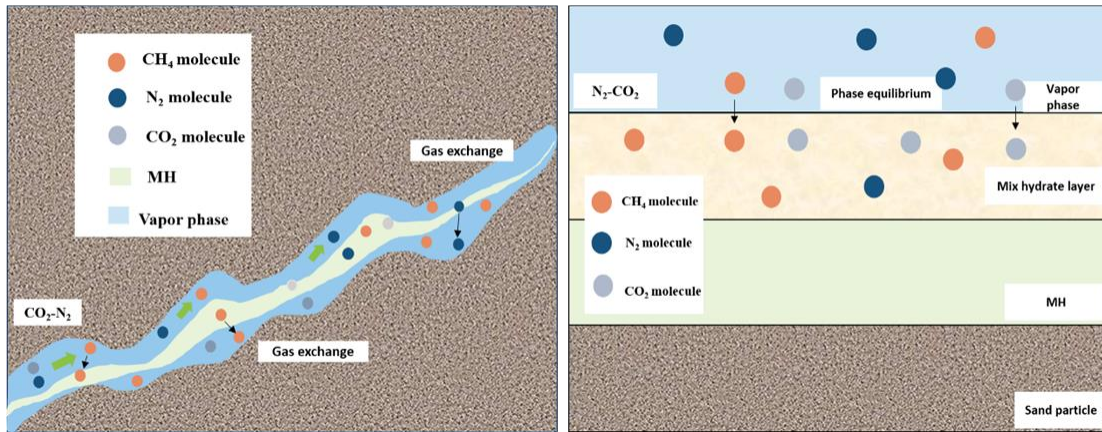Fig. 1. CO_2-N_2 gas exchange diagram of MH in the pore, the left diagram shows the gas exchange between N_2+CO_2 injected into the pore and MH, the right diagram shows the CH_4-(CO_2+N_2) gas exchange diagram at the interface

2. EXPERIMENTAL SECTION

2.1 Materials

The marine muddy silt sediments used in this paper were obtained from in situ hydrate mining in hydrate-bearing sediments decomposed in the Shenhu area of the South China Sea, China's South China Sea muddy sediments are non-fossiliferous rocks whose main mineral compositions are composed of quartz, clay minerals, and some feldspars[19,20]. The pore size distribution of the reservoir shows extensive spatial heterogeneity, in which the scale of both microbial fossil pores and clay pores are more significant. A computational analysis of the reservoir under different particle size compositions was carried out according to the percolation theory of porous media, and it was found that the smaller the particle size under the same conditions, the higher its permeability. In the mining process of muddy silt reservoirs in the South China Sea, the clay minerals will swell due to the influence of water generated by hydrate decomposition, which will cause

Tab. 1 Main components of marine clayey silt sediments in the South China Sea

Component	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MgO	K$_2$O
content%	69.50	19.89	5.68	2.45	2.45
	Na$_2$O	TiO$_2$	CaO	MnO	
	1.30	0.67	0.37	0.04	

The deionized water used in this experiment was produced by a laboratory water purification system (Aquapro2S, Aquapro International, USA) with a density of 1.00 g/cm^3 and a resistivity of 18.2 MΩ-cm at 298.15 K. Since deionized water does not have any electrons or charges, it can effectively avoid the interference of ion magazines with the experiment.

2.2 Experimental apparatus

Figure 2 shows the diagram of the experimental setup for marine clayey silt replacement mining, which

mainly includes the reaction system, gas supply system and collection system. The reactor of the reaction system is customized from 316 stainless steel with a body size of $\Phi 100 \times 150$ mm, an effective volume of 1177.5 mL, a maximum pressure of 20 MPa, and a temperature requirement of -10 ℃ to 30 ℃. The kettle body is equipped with four temperature sensors with an accuracy range of ± 0.1 K. The kettle lid is equipped with four quick plug interfaces for air inlet and exhaust and for connecting the required pressure sensors with an accuracy range of ±25 kPa. The piping, valves, and interfaces attached to the kettle are from Swagelok, USA and Kumagawa, China. The temperature of the reaction system is controlled by a yulabo F38-EH water bath with a bath depth of 27 cm, heating power of 2 kW, temperature control range of -35 to 150 °C, display resolution of 0.1 °C, and stability of ±0.05 °C. The cooling fluid used in this water bath is ethylene glycol, and its dilution ratio is water: ethylene glycol=1:1. The reaction system is mainly used for the in situ generation of natural gas hydrate and the replacement reaction.
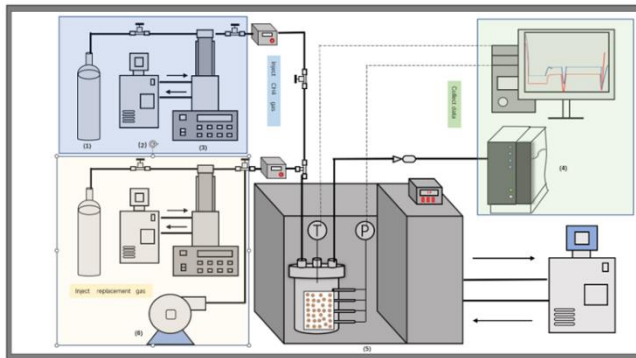

Fig. 2　Experimental setup of N_2/CO_2 replacement mining system for marine hydrate

The gas supply system consists of a high-precision ISCO high-pressure plunger pump, high-pressure piping system and various gas cylinders, etc. The ISCO pump is equipped with a heated refrigeration circulating water bath, using ethylene glycol as the refrigerant, which is used to control the gas temperature inside the pump with a temperature control accuracy of ±0.05 °C. The ISCO-500D high-pressure plunger pump is responsible for controlling the constant pressure of CH_4 gas in the in situ hydrate generation and recording the gas consumption. The ISCO-500D plunger pump is also responsible for injecting replacement gas to react with the produced in-situ hydrate.

The acquisition system consists of a computer, temperature, pressure sensors and a chromatograph. A pressure sensor (Nagano Company, Japan) with a range of 0-25 MPa and an accuracy of ±0.1% was placed on top of the reactor to monitor the pressure changes inside the reactor. Four equivalent temperature sensors (Yamari Industries, Japan) with a range of -30 °C to 100 °C and an accuracy of ±0.1 °C were placed on the side of the reactor to monitor the temperature changes in the reactor reservoir in real-time. The data collector is connected to the temperature and pressure sensors and sets to collect the temperature and pressure readings in the reactor every 30 s. The data is also fed back to the temperature and pressure curve drawn by the Excel sheet at the computer software end. The experimental chromatographic analyzer is Agilent 490 Micro GC, whose carrier gas is helium or hydrogen, which is used to measure the composition and proportion of the collected gas. When the sample of the gas mixture to be measured is vaporized at high temperature through the vaporization chamber, it will be pushed into the column by the inert gas (He), and due to the difference in boiling point and adsorption of the sampled sample, a dynamic equilibrium will be formed between the mobile phase and the solid phase. The gases are retained in the column for different times, thus allowing for multi-component separation and detection.

2.3 Experimental procedures

2.3.1 MH formation

To ensure the smooth operation of the experiment, the gas tightness of the reaction device was checked first, especially since the high-pressure reactor should be subjected to leak detection operation. First of all, the experiment was carried out by high-pressure leak testing of the empty kettle. High-purity N_2 was injected into the empty kettle until the pressure reached 10 MPa, and the temperature of the water bath was set to 293.15 K. The kettle was kept stable for 12 h. The tightness of the kettle was judged by the changes in temperature and pressure curves on the computer connected to the data collector, and at the same time, whether there were bubbles visible to the naked eye around the kettle was checked by the leak testing solution. If the pressure change of the reactor is less than 0.005 MPa within 10 h and there are no small bubbles around the reactor, the reactor can be considered to be well sealed. Otherwise, the leak should be checked and repaired. After the leak check of the empty kettle is completed, the reactor

is washed with gas to eliminate the influence of residual air in the pore space on the generation of CH_4 hydrate, and the experimental operation is to inject a small amount of CH_4 gas several times. Inject CH_4 gas into the washed kettle until the pressure in the kettle reaches the set pressure, and set the water bath temperature to 20 ℃, leak test the kettle filled with marine clayey powder sand, observe the pressure and temperature curve, if the pressure change is less than 0.005 MPa in 10 h, it means the kettle is well gas-tight and ready for the experiment. After the temperature and pressure stabilized, the temperature and pressure values were recorded; the temperature of the reactor was lowered to the preset temperature by the temperature control system to simulate the high-pressure and low-temperature hydrate generation environment; the temperature and pressure in the reactor were monitored, and when the temperature and pressure values remained unchanged within 5 h, the CH_4 hydrate generation was considered to be finished, and the sample preparation of natural gas hydrate sediment in the laboratory simulating the conditions of the muddy sands reservoir in the South China Sea was completed. Completion.

2.3.2 CH_4-(CO_2+N_2)replacement

After evacuating the air inside the reactor completely in the whole reaction system, CH_4 hydrate samples with different saturations were obtained by injecting different amounts of CH_4 gas, and the temperature of the water bath at the periphery of the reactor was set to 273.65 K. When the pressure and temperature inside the reactor decreased until they no longer changed, the CH_4 hydrate sample preparation was considered to be completed, and the saturation of CH_4 hydrate was finally calculated. The whole process of replacement reaction can be divided into three stages in this experiment, the first stage is the replacement stage. After the preparation of the hydrate sediment samples, since type I hydrates are self-protected at 242-271K and do not decompose when the pressure decreases[24], the temperature of ethylene glycol in the water bath was adjusted so that the autoclave was at 268.15 K. The self-protection effect of CH_4 hydrate is strong at this time, which can effectively reduce the decomposition of CH_4 hydrate. Quickly evacuate the CH_4 gas not involved in the reaction in the pores of the sediment by the vacuum pump and quickly inject the pre-cooled CO_2+N_2 gas mixture.

When the pressure in the reactor reaches the set value, close the valve and set the temperature of the water bath controlling the reactor to the preset replacement temperature, record the temperature and pressure of the injected replacement gas to the average temperature in the reactor measured by the thermocouple, at which time the replacement reaction can be regarded as starting to proceed. The temperature and pressure values after 2 h of gas exchange were recorded because the gas diffusion process occurred after the gas exchange was injected and the temperature and pressure were not stable enough.
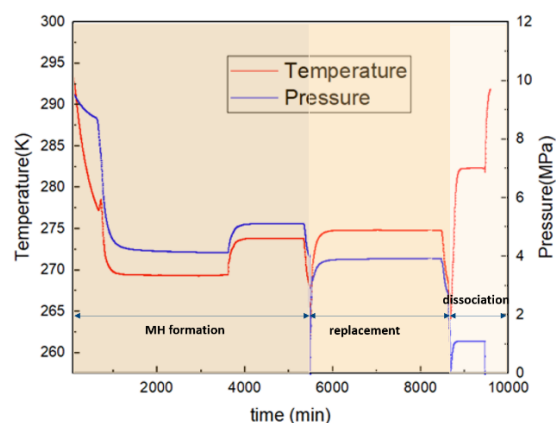

Fig. 3. Methane hydrate generation, CO_2/N_2 replacement, mixed hydrate decomposition temperature and pressure history

After 50 h of replacement, the sampling tube and bag are evacuated and the residual gas in the reactor is sampled. The temperature and pressure values of the data collector were used uniformly due to slight differences in the data collector temperature, water bath temperature, and mercury thermometer during this replacement process. The second stage is hydrate decomposition. After the replacement of CH_4 hydrate by CO_2/N_2 mixture, the temperature of the water bath is lowered to 268.15 K. The purpose of lowering the temperature is to prevent the decomposition of hydrate during the evacuation of residual gas. After venting, the temperature was increased to 293.15 K, the mixed hydrate dissociation occurred, and sampling was performed with a sampling bag. The third stage is the test analysis, where the multi-component gases (N_2, CO_2, CH_4) in the gas phase are quantified in situ

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using calibrated gas chromatography and the molar amounts of the corresponding multi-component gases are calculated. The amount of CH_4 in the gas phase from which CH_4 hydrate was replaced and the amount of CO_2 in the mixture to form CO_2 hydrate were obtained. Fig.3. shows Methane hydrate generation, CO_2/N_2 replacement, mixed hydrate decomposition temperature and pressure history.

2.4 Calculation method

There is no unified method for calculating the saturation of natural gas hydrate, so this experiment was conducted by calculating the consumption of CH_4 gas to obtain the saturation of hydrate, First, the amount of sediment required in the process of remodeling the marine muddy sands sediment was calculated, and the volume of the reactor was 1177.5 mL, and the density of marine muddy sands was 2.73 g/mL. The deionized water taken in the laboratory is taken as ideal, i.e., the mass of 1 mL of water is 1 g. Porosity is an important characteristic of soil, which is the ratio of the pore volume of soil to the volume of soil particles, and is closely related to the degree of compactness in this experiment. The mass of the sample required for the experiment is calculated as shown in the following equation:

$$\phi = \frac{V_{pore}}{V_{cha}} \qquad (1)$$

$$V_m = V_{cha} - V_{pore} \qquad (2)$$

$$M_m = \rho_m V_m \qquad (3)$$

$$S_W = \frac{V_W}{V_{pore}} \qquad (4)$$

$$V_{pore} = V_W + V_g + V_h \qquad (5)$$

Where ϕ represents the porosity, V_{cha} represents the internal volume of the reactor, V_{pore} represents the pore volume, M_m represents the mass of marine soil filled into the reactor, ρ_m represents the density of marine soil, 、 V_m represents the volume of marine soil, V_W 、 V_g and V_h represents the volume of deionized water, the volume of gas and the volume of hydrate filled

into the reactor, S_W represents the water saturation.

CH_4 hydrate is a type I hydrate, its molecular formula is $CH_4 \bullet 6H_2O$, M_{MH} =124.14 g/mol, ρ_{MH} representing the density of CH_4 hydrate, its value is taken as 0.92 g/cm3 because the solubility of CH_4 gas in deionized water is low, so the loss of CH_4 in water is not considered in this study, so it can be calculated by the following equation Saturation of CH_4 hydrate:

$$n_{CH_4}^1 = \frac{P_{CH_4}^1 \times V_{CH_4}^1}{Z_{CH_4}^1 \times T_{CH_4}^1 \times R} \qquad （6）$$

$$n_{CH_4}^2 = \frac{P_{CH_4}^2 \times V_{CH_4}^2}{Z_{CH_4}^2 \times T_{CH_4}^2 \times R} \qquad （7）$$

$$n_{MH} = n_{CH_4}^1 - n_{CH_4}^2 \qquad （8）$$

$$V_{MH} = \frac{M_{MH} \times n_{MH}}{\rho_{MH}} \qquad （9）$$

$$S_{MH} = \frac{V_{MH}}{V_{pore}} \qquad （10）$$

$$S_{MH} = \frac{V_{MH}}{V_{pore}} \qquad （11）$$

$$V_W^2 = V_W - V_{MH}^W \qquad （12）$$

$n_{CH_4}^1$ 、 $n_{CH_4}^2$ 、 n_{MH}, represent the moles of CH_4 gas when injected, the moles of methane gas in the gas phase not involved in CH_4 hydrate generation, and the moles of CH_4 hydrate generation, respectively; P, T, V, and Z represent the pressure, temperature, volume, and compression factor of gas-phase CH_4 before and after CH_4 hydrate generation. Where superscript '1' represents the state parameters of gas-phase CH_4 before participating in the reaction, superscript '2' represents the state parameters of gas-phase CH_4 after the generation of CH_4 hydrate, and the compression factor is calculated by the PR equation. The molar constant of gas R=8.314 J/(mol-K), represents the saturation of CH_4 hydrate.

$$P_3 V_3 = n_3 Z_3 T_3 R \qquad (13)$$

$$N_{r1} = n_3 [CH_4]\% \qquad (14)$$

$$\eta = \frac{N_{r1}}{n} \tag{15}$$

$$\eta` = 1 - \frac{N_{r2}}{n_3[CO_2]\%} \tag{16}$$

where P_3、V_3、n_3、T_3, represent the pressure, volume, quantity, temperature and other parameters when injecting the gas mixture, N_{r1}, N_{r2} represent the CH$_4$ gas replaced and the CO$_2$ gas involved in the replacement, respectively; η, $\eta`$ represent the CH$_4$ replacement rate and CO$_2$ sequestration rate, respectively; $[CH_4]\%$ $[CO_2]\%$ represent the proportion of CH$_4$ and CO$_2$ in the gas mixture measured by the chromatography analyzer, respectively.

3. RESULTS AND DISCUSSION

3.1 Experimental conditions

Figure 4 contains the phase equilibrium curve of CO$_2$/N$_2$(79.35%CO$_2$+20.65%N$_2$) mixture hydrate, CH$_4$ hydrate phase diagram, CO$_2$ hydrate phase diagram, N$_2$/CO$_2$(79.35%CO$_2$+20.65%N$_2$) mixture phase equilibrium curve with CO$_2$ gas-liquid diagram calculated by CSMGem software, as well as the CH$_4$ gas injection into the muddy silt reservoir at the state point, the state point when the N$_2$/CO$_2$ (79.35%CO$_2$+20.65%N$_2$) mixture is injected into the muddy silt sediment reservoir, the state point at the end of CH$_4$ hydrate generation, and the state point when the replacement is stable.
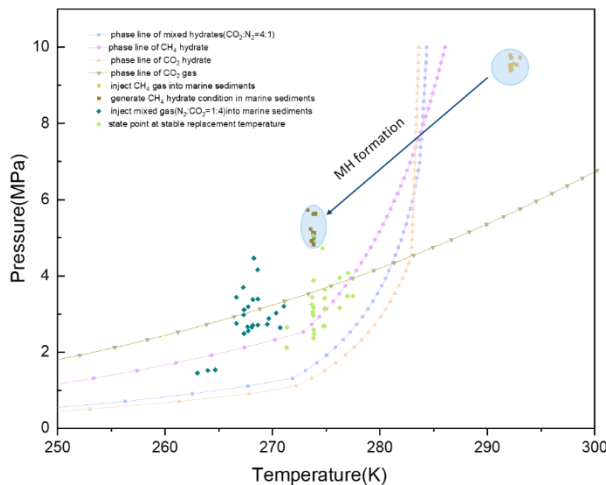

Fig. 4 Experimentally relevant phase equilibrium conditions of CH$_4$ hydrate、CO$_2$/N$_2$ hydrate and various gases with their working conditions

The phase diagram is divided into three parts, area A, area B, and area C. In area A, both CH$_4$ hydrate and mixed hydrate can exist stably, and in area C, mixed hydrate can exist stably but CH$_4$ hydrate cannot exist stably. area B and area C are gaseous CO$_2$, and area A is liquid CO$_2$.

3.2 Effects of replacement pressure on CH4-(CO2+N2) replacement

Table 2 shows the conditions of CH$_4$-(CO$_2$+N$_2$) replacement of muddy silt gas hydrate in natural gas hydrate, the replacement gas used is N$_2$/CO$_2$ (79.35%CO$_2$+20.65%N$_2$), the experiments from S1 to S5 are at the replacement temperature of 273.65 K (near zero point), S6 to S11 are at the replacement temperature The experiments at 274.85 K for each gas parameter under muddy silt reservoir conditions are as follows:

Tab. 2 CH$_4$-(CO$_2$+N$_2$) replacement conditions

Group	Specimen Parameters			Replacement Conditions（CO$_2$ injection→Completed 50 h Replacement）	
	φ/ %	Sw/ %	Sh/ %	P/MPa	T/K
S$_1$	59.99	40.09	19.09	1.81→3.23	263.0·1→273.83
S$_2$	59.99	40.11	18.92	1.90→3.10	263.98→273.85
S$_3$	59.99	40.07	18.08	3.30→3.82	265.70→273.80
S$_4$	59.99	39.93	19.35	4.62→4.85	267.27→273.82
S$_5$	59.99	39.93	19.23	5.58→6.32	268.26→273.81
S$_6$	59.99	40.11	18.56	1.92→3.36	264.67→274.73

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S7	59.99	39.93	20.02	2.75→3.35	268.56→274.85
S8	59.99	40.11	18.60	3.31→3.95	268.06→274.85
S9	59.99	40.07	17.31	3.43→4.27	267.25→274.85
S10	59.99	40.07	17.11	3.72→4.55	267.33→274.86
S11	59.99	39.93	19.61	5.20→5.91	268.62→274.65

The muddy silt reservoir conditions were kept consistent in experimental groups S1 to S5, i.e., the CH_4 hydrate saturation was between 18% and 19%, the initial water saturation was 40%, and the replacement temperature was uniformly set at 278.83 K, which is slightly above the freezing point. The effect of CO_2/N_2 (79.35%CO_2+20.65%N_2) on the hydrate replacement effect was studied in the range of 1.81-5.58 MPa for the replacement pressure, and Figure 5 (a)(b) summarizes the variation pattern of CO_2 sequestration rate and CH_4 hydrate extraction rate under different replacement pressure conditions.
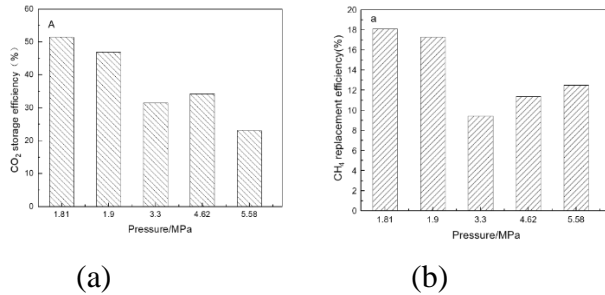

(a)　　　　　　　　(b)

Fig. 5　The effect of replacement pressure on the extraction of replacement at a temperature of 0.65°C above zero point

As shown in Figure 5(a), the replacement pressure has a significant effect on the CH_4 extraction rate, which is highest at a replacement pressure of 1.81 MPa, while the CO_2 sequestration rate is also highest; the CH_4 extraction rate reaches 18.10% and the CO_2 sequestration rate is 51.42%. This is mainly because the decomposition drive of hydrate is stronger under the lower replacement pressure conditions, so the CH_4 hydrate is decomposing while the replacement reaction is going on, which not only improves the gas production

rate but also opens the hydrate reservoir channel for the replacement reaction and promotes the diffusion of CO_2/N_2 replacement gas in the CH_4 hydrate, thus increasing the mixed hydrate production and also improving the CO_2 sequestration rate. When the pressure increases to 1.9 MPa, the pressure does not change much, and the CH_4 extraction rate and CO_2 sequestration rate show a small decrease accordingly, and the replacement efficiency is 17.25% and the CO_2 sequestration rate is 46.95% at this time, meanwhile, the state points on the phase equilibrium diagram show that the mixed gas pressure is 1.81 MPa and 1.90 MPa when CH_4 hydrate is in the non-stationary zone, and CH_4 hydrate cannot exist stably, which accelerates the decomposition of CH_4 hydrate. When the pressure increases to 3.3 MPa, the CH_4 extraction rate and CO_2 sequestration rate of the replacement reaction are both low, and the CH_4 extraction rate is 9.44%, which is mainly because the decomposition driving force of CH_4 hydrate is obviously lower than the above two groups. At this time, the injected CO_2 was in the liquid state. It has been found[25,26] that compared with gaseous CO_2, liquid CO_2, CO_2 emulsion, and supercritical CO_2 have good diffusivity and conductivity, and the interface between the replacement gas and CH_4 hydrate is larger, so it can effectively enhance the replacement efficiency of CH_4 and the sequestration rate of CO_2 during replacement mining. This is consistent with the conclusion obtained from this experiment that when the mixture pressure is 4.62 MPa, the extraction and sequestration rates of CH_4 are higher than those at 3.3 MPa replacement pressure and the CO_2 sequestration rate is higher, but still lower than those at 1.81 MPa and 1.9 MPa replacement pressure conditions.
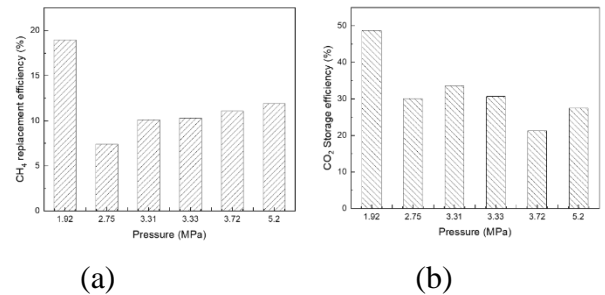

(a)　　　　　　　　(b)

Fig. 6　Effect of pressure on displacement effect at 1.70 ℃

However, when the replacement pressure continues to increase to 5.58 MPa, the driving force of the replacement reaction is stronger, so the CH_4 extraction rate in the replacement reaction is further improved, and the extraction rate of CH_4 hydrate increases to 12.48% at this time, but the CO_2 diffusion is

limited because the mixed hydrate formed by liquid CO_2 in the reservoir covers the surface of CH_4 hydrate and because the fine-grained reservoir has low. The CO_2 sequestration rate appears to be reduced due to factors such as low permeability and capillary action. From Fig. 5 (a) and (b), it can be seen that the CO_2 sequestration rate and CH_4 extraction rate do not increase in equal proportion, and the effect of liquid water and residual gas with replacement pressure is not significant, which plays a positive role in controlling water volume and maintaining reservoir stability in the experiment, and liquid CO_2 has a positive effect on hydrate replacement.

The experimental curves of the CH_4 replacement rate and CO_2 sequestration rate for experimental groups S6 to S11 are shown in Fig.6 (a)(b) for the same reservoir conditions with a replacement pressure range of 1.92-5.20 MPa and replacement temperature set at 274.85 K. The experimental curves are shown in Fig. 6(a)(b). From Fig. 6(a)(b), it is found that the CH_4 extraction rate and CO_2 sequestration rate are the highest under the mixed gas pressure of 1.92 MPa, which is mainly because CH_4 hydrate is in the non-stationary zone at this moment, CH_4 hydrate cannot exist stably, and CH_4 hydrate decomposition releases CH_4 gas and free water faster, so the CH_4 extraction rate is higher; meanwhile, the CH_4 hydrate decomposition water and the pore The residual water content increases, which is conducive to the combination with CO_2/N_2 mixture to form a mixed hydrate, so the CO_2 sequestration rate is higher. However, as the mixture pressure increases to 2.75 MPa, the extraction rate of CH_4 and the sequestration rate of CO_2 are significantly lower than in the previous group of experiments, which is mainly caused by the weaker driving force of CH_4 hydrate decomposition, so the CO_2 sequestration rate is stronger than that at low pressure. As the pressure increases from 2.75 MPa to 3.31 MPa, the CH_4 extraction rate and CO_2 sequestration rate at this time are experimentally good at higher pressure, which is mainly due to the high replacement pressure and strong replacement driving force, which is conducive to the direct replacement reaction of CO_2 molecules in the gas mixture with CH_4 molecules in the CH_4 hydrate. As the pressure increased to 3.33, 3.72 MPa, the CH_4 extraction rate continued to increase, but the CO_2 sequestration rate did not show a clear pattern. When the mixture pressure was increased to 5.20 MPa, the CO_2 was liquid at this time, so the CO_2 replacement rate was enhanced due to the strong permeability of liquid CO_2 and its strong diffusion ability, and the enhanced replacement of liquid CO_2 had a positive effect on the CO_2 sequestration rate, and the CH_4 extraction rate

increased to 11.92%. In terms of replacement pressure, the CO_2 sequestration rate in CO_2/N_2 mixture replacement gas hydrate did not show a clear pattern.

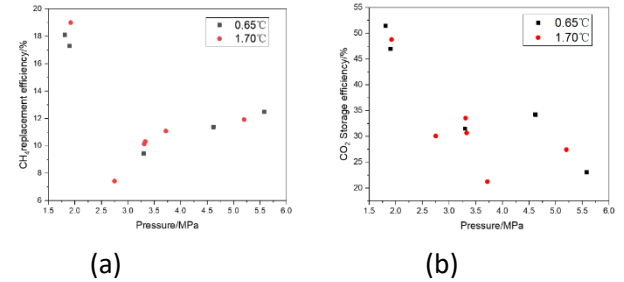(a)   (b)

Fig. 7   Effect of pressure on replacement extraction under different temperature conditions

Comparing the effect of pressure on muddy silt natural gas hydrate at replacement temperature 0.65 ℃ (slightly above freezing point) and 1.70 ℃, the experimental reservoir conditions remain basically the same, and its CH_4 replacement rate and CO_2 sequestration rate are shown in Figure 7. The trends of their CH_4 recovery rates are found to be basically consistent, with the highest CH_4 hydrate recovery rate under the condition of low replacement pressure, and the CH_4 hydrate recovery rate shows a precipitous decrease when the pressure increases all a certain point, after which the CH_4 recovery rate increases as the pressure increases. This may be because the pressure increases, the driving force of the replacement reaction is greater, so the CH_4 extraction rate increases, and the effect of pressure on the CH_4 extraction rate are greater when the replacement temperature is higher than the low-temperature case as can be seen from the left side of Figure 7. From the right side of Figure 7, it can be seen that the CO_2 sequestration rate does not show complete consistency between the high and low-temperature cases. The common point is that the CO_2 sequestration rate is larger under the conditions of lower pressure, which is mainly related to the driving force of CH_4 hydrate decomposition, and the high content of free water makes it easier to form CO_2 hydrate, but as the pressure increases, the CO_2 sequestration rate does not show a consistent pattern under different temperature conditions, which may be because the temperature slightly higher than the temperature near the freezing point, with the increase of pressure CO_2 hydrate is less stable, and the capillary force is stronger in the muddy sands, and the gas permeability is weak, which is not conducive to gas exchange.

3.3 Influences of the temperature on CH_4/CO_2 replacement

To study the effect of temperature on CH_4 hydrate replacement, the same reservoir conditions were set, i.e., water saturation of 40% and hydrate saturation kept between 17-19%, where S_{12} was below the freezing point and S_{13} was slightly above the freezing point for the experimental condition, and the temperature range of the experimental setup was 271.33-276.96 K. Five sets of S12-S16 were conducted in this chapter experiments, the experimental parameters are shown in Table 3, and the experimental results are shown in Figure 8. In order to reduce the experimental error, the unified system pressure was equal to 0 MPa after the discharge of CH_4 gas, and the CO_2/N_2 mixture was immediately injected into the autoclave at a low-temperature until the pressure reached 3.3 MPa, and the gas injection was stopped, and the temperature and pressure indications at this moment were recorded.

Tab. 3   Experimental conditions of CH_4-(CO_2+N_2) replacement

Group	Specimen Parameters			Replacement Conditions （CO_2 injection→Completed 50 h Replacement）	
	ϕ/%	Sw/%	Sh/%	P/MPa	T/K
S_{12}	59.99	40.36	18.20	3.21→2.65	267.35→271.33
S_{13}	59.99	40.34	17.84	3.39→2.96	267.63→273.80
S_{14}	59.99	40.36	16.89	3.29→3.95	267.74→276.25
S_{15}	59.99	40.34	19.76	3.38→4.07	268.17→277.02
S_{16}	59.99	40.56	19.52	3.44→4.34	266.64→276.96

As can be seen from Figure 8(a), the replacement rate of CH_4 increases from 14.27% to 35.29% as the replacement temperature increases from 271.33 K to 276.96 K. Under the higher replacement temperature conditions, the hydrogen bonding force becomes weaker and the kinetic energy of molecules increases, accelerating the molecular motion, thus increasing the contact interface and frequency between CO_2 and CH_4 hydrate[27], and the escaping CH_4 molecules are not only generated by CO_2 replacement but are also associated with thermal stimulation. It was found that when the temperature is below the freezing point, the CH_4 hydrate replacement efficiency is low and the CO_2 sequestration rate is relatively low, but still better than the sequestration effect in the high-temperature case. When the temperature is below the freezing point, the driving force of CH_4 hydrate decomposition is weak, and at the same time, in the lower state, the rate of CH_4 gas release from CH_4 hydrate decomposition is slower and the diffusion of CO_2 molecules is not strong due to the existence of self-protection effect and the obstructive effect of ice particles on the diffusion and transport of gas in the pore channels, which seriously affects the replacement process and makes the extraction rate of CH_4 and CO_2 sequestration rate is not high. When the temperature rises to 273.80 K, the temperature is slightly higher than the freezing point, which weakens the self-protection effect; under the influence of reaction heat, the surface of ice particles melts and a liquid film appears, and the reaction changes from the original gas-solid contact to liquid-gas contact, the melting of ice weakens the obstruction of ice in the pore channel and expands the pore channel; the high-temperature provides a certain thermal driving force to the system, which strengthens the replacement process and improves. The high-temperature provides a certain thermal driving force to the system, which strengthens the replacement process and increases the extraction rate of CH_4 and promotes the further diffusion and transport of CO_2.
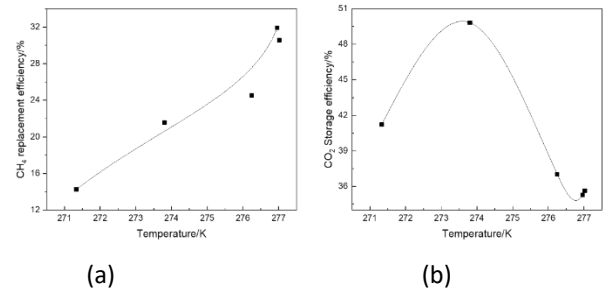

(a)   (b)

Fig. 8   Effect of temperature on replacement experiments

3.4 Replacement behaviors in fine sediments with different hydrate saturations

In this experiment, under the same replacement conditions and the same porosity conditions, the water saturation in the reservoir was changed to cause different saturation of CH_4 hydrate, and three sets of experiments from S_{17} to S_{19} were done for hydrate saturation of 9.37%, 13.05%, and 17.08%, respectively. The experimental parameters are shown in Table 4, and the conclusion is shown in Figure 9. At this time, all CH_4 hydrates are in the stable zone and the state of CO_2 is liquid. It is found that the hydrate saturation has little

effect on the CH₄ extraction rate when the hydrate saturation is between 9.37% and 17.08%, which are 10.77%, 9.56% and 9.44% respectively. This is basically similar to the conclusion made by Wang Tian that there is no obvious linear relationship between CH_4 replacement rate and hydrate saturation. The effect of hydrate saturation on replacement is mainly manifested as affecting the rate of replacement reaction and the extraction rate of CH_4. With high saturation of CH_4 hydrate, the extraction rate of CH_4 mainly comes from the decomposition of hydrate in the initial stage of the replacement reaction, but when the experiment proceeds to the later stage, the replacement rate is mainly due to the degree of diffusion of CO_2/N_2 mixture into the hydrate sediment reservoir for the replacement reaction with CH_4 hydrate. When the hydrate saturation increases from 9.37% to 13.05%, the CO_2 sequestration rate decreases from 20.28% to 16.41%, but the CH4 extraction rate does not differ significantly. This indicates that in the initial stage of the replacement reaction, CH4 hydrate saturation is higher, so the hydrate decomposition area is also larger, and the gas production is correspondingly higher, but as the reaction proceeds, in the later stage of the replacement, hydrate saturation is higher, pore space is less, and CO_2 diffusion barrier increases, so the replacement volume is relatively less.

Tab. 4　Internal state parameters of reservoirs under different hydrate saturation conditions

Group	Specimen Parameters			Replacement Conditions （CO_2 injection→Completed 50 h Replacement）	
	ϕ/%	Sw/ %	Sh/%	P/MPa	T/K
S₁₇	59.99	32.59	9.37	3.60→4.06	269.65→273.65
S₁₈	59.99	36.34	13.05	3.41→3.96	269.52→273.85
S₁₉	59.99	40.07	17.08	3.30→3.82	270.70→273.75

When the hydrate saturation is further increased to about 17%, the CO_2 sequestration rate is found to be significantly higher, with a sequestration rate of 31.52%, and the residual water content in the reservoir is significantly lower, indicating that more CO_2/N_2 gas mixture combines with free water to form CO_2 hydrate. Although the pattern exhibited in this CH_4 hydrate saturation interval range with CH_4 extraction rate and CO_2 sequestration rate is not obvious, when the initial

hydrate content in the sediment is larger[28,29], the free water content is more favorable for CO_2 sequestration.
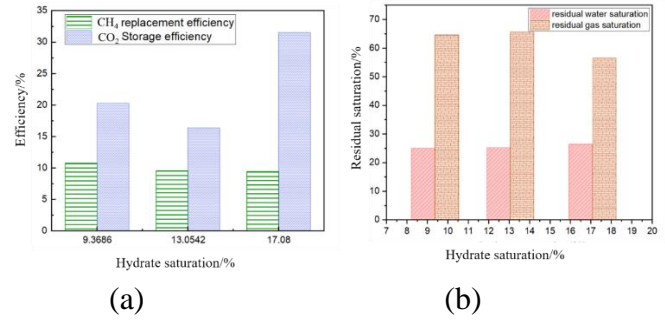

(a)　　　　　　　　(b)

Fig. 9　Effect of different hydrate saturation on replacement experiments

4. CONCLUSIONS

In this paper, we systematically studied the influencing factors of CO_2/N_2 replacement mining in sediment hydrates under a simulated real reservoir environment of marine soil in the South China Sea. The study found that temperature, pressure, hydrate saturation, and the strength of the effect of pressure on hydrate replacement under different temperature cases, and the following conclusions can be drawn:

(1) Lower replacement pressure is favorable to CH_4 hydrate mining, with lower pressure, CH_4 hydrate decomposition is strong; with the increase of pressure, high-pressure liquid CO_2/N_2 mining is larger, but under the condition of muddy silt reservoir, facilitating the effect is limited when the pressure reaches a certain degree.

(2) Under high-temperature conditions, the gas is subject to strong heat and mass transfer, which is favorable to the extraction of CH_4 gas, but the temperature is higher, but the sequestration of CO_2 is poor. This indicates that the extraction of gas relies mainly on the decomposition of CH_4 hydrate rather than CH_4-(CO_2+N_2) substitution;

(3) The effect of hydrate saturation on CO_2 sequestration is more significant, and the higher hydrate saturation is more favorable to CO_2 sequestration, and its effect on CH_4 extraction is not significant;

(4) The conditions required for hydrate generation in marine clayey silt conditions are more demanding, and its replacement of natural gas hydrate is much lower than the theoretical limit of replacement under ideal conditions (75%), and it is found that the effects of temperature and pressure on the replacement of CH_4 hydrate in muddy silt reservoir conditions are more obvious and more worthy of further study.

DECLARATION OF INTEREST STATEMENT

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.

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