

1 **Flue Gas Injection into Gas Hydrate Reservoirs for Methane Recovery and Carbon**
2 **Dioxide Sequestration**

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9
10 **Abstract**

11 Flue gas injection into methane hydrate-bearing sediments was experimentally investigated to
12 explore the potential both for methane recovery from gas hydrate reservoirs and for direct
13 capture and sequestration of carbon dioxide from flue gas as carbon dioxide hydrate. A
14 simulated flue gas from coal-fired power plants composed of 14.6 mole% carbon dioxide and
15 85.4 mole% nitrogen was injected into a silica sand pack containing different saturations of
16 methane hydrate. The experiments were conducted at typical gas hydrate reservoir conditions
17 from 273.3 to 284.2 K and from 4.2 to 13.8 MPa. Results of the experiments show that injection
18 of the flue gas leads to significant dissociation of the methane hydrate by shifting the methane
19 hydrate stability zone, resulting in around 50 mole% methane in the vapour phase at the
20 experimental conditions. Further depressurisation of the system to pressures well above the
21 methane hydrate dissociation pressure generated methane-rich gas mixtures with up to 80
22 mole% methane. Meanwhile, carbon dioxide hydrate and carbon dioxide -mixed hydrates were
23 formed while the methane hydrate was dissociating. Up to 70% of the carbon dioxide in the
24 flue gas was converted into hydrates and retained in the silica sand pack.

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2 *sequestration*

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4 **1 Introduction**

5 An abundance of methane (CH₄) is trapped in gas hydrates in subsea sediments [1] and
6 permafrost regions [2], although the actual volumes of gas hydrate deposits worldwide are still
7 arguable [3]. Gas hydrates, a type of ice-like clathrate compounds, can be decomposed if the
8 temperature and pressure are outside their hydrate stability zone (HSZ), or the chemical
9 equilibrium between the hydrate phase and the adjacent environment is disturbed [4]. Based on
10 this principle, several methods were suggested for methane recovery from gas hydrates in
11 sediments, such as depressurisation, thermal stimulation, inhibitor injection [5], and carbon
12 dioxide (CO₂) replacement [6], or combinations of the above.

13 Thermal stimulation brings heat into gas hydrate deposit layers by a variety of methods such as
14 hot brine injection, steam injection, in-situ combustion, and electromagnetic heating.
15 Laboratory experimental results showed that about 50% of the recovered energy would be
16 consumed to generate the required heat for heating up the gas hydrate-bearing sediment [7].
17 Reservoir simulation indicated that thermal stimulation appears ineffective because of huge
18 quantity of heat loss to porous media in the hydrate layer or the geologic formations in the
19 vicinity [8], particularly for disperse low-saturation of gas hydrate deposits [9]. The Mallik
20 2002 gas hydrate research well programme tested the thermal stimulation technique at in situ
21 conditions (907-920 m below surface, 8 °C and 10 MPa) [10]. It was found that, unless the
22 hydrate layers exhibit sufficient thickness, hydrate saturation, and permeability, it is not
23 economically viable to heat a large mass of a hydrate-containing formation by the thermal
24 stimulation alone [11].

1 Inhibitor injection shifts the gas hydrate deposit conditions out of the hydrate stability zone
2 (HSZ) by injecting alcohol such as methanol, monoethylene glycol, and diethylene glycol. A
3 very large volume of methanol will be needed to treat the water in the hydrate layers and to
4 deal with the dilution by the water from hydrate dissociation as well. Moreover, injected
5 inhibitors could pose serious risk to damage the environment for the marine ecosystem. As a
6 result, it is believed that inhibitor injection technique on its own will not be viable for any type
7 of gas hydrate deposits [8].

8 Depressurisation method moves the hydrate reservoir conditions outside the HSZ by reducing
9 the pressure in the gas hydrate reservoir. By comparison to the thermal stimulation technique
10 and the inhibitor injection technique, it does not need to input additional energy or chemicals
11 into the hydrate reservoir, therefore, is technically simple, effective, and prompt inducement to
12 gas hydrate decomposition [12]. The depressurisation technique was successfully applied to
13 produce methane from gas hydrate reservoirs in both onshore and offshore field tests.
14 Messoyakha gas field in the West Siberian basin (Russia) is the only commercial production
15 reservoirs of gas hydrates in the world, where natural gas has been produced from gas hydrate
16 deposits since 1970s [13]. A series of scientific and engineering field trials were conducted in
17 the Mackenzie Delta of Canadian Arctic. The Mallik 2002 gas hydrate production research
18 well programme investigated the feasibility of gas hydrate production by thermal stimulation
19 and depressurisation in short-term production experiments [14], while the results of the Mallik
20 2007/2008 programme demonstrated that natural gas can be produced from gas hydrate
21 reservoirs by depressurisation alone [15]. Depressurisation method was also tested in the world
22 first offshore methane recovery field trial in Nankai Trough, Japan [16]. All these hydrate sites
23 are sandstone or marine sand reservoirs with high porosity, high permeability, and high hydrate
24 saturation. However, Boswell and Collett estimated that such sandstone-bedded gas hydrates
25 are only a small fraction of the total gas hydrate resources worldwide [17]. For the

1 overwhelming majority in low-permeability sediments or disperse distribution [18] of gas
2 hydrates, depressurisation becomes ineffective. Additionally, for the hydrate reservoirs well
3 inside the HSZ, the reservoir pressure has to be reduced very low to be able to dissociate the
4 gas hydrates. As a consequence, depressurisation results in huge volume of water production,
5 sediment instability, and sand production challenges [8]. Yamamoto et al. reported that sand
6 produced during depressurisation blocked the downhole production device and terminated the
7 gas production of the world's first offshore trial of gas production from marine hydrate
8 reservoirs after six days of gas flow in the Eastern Nankai Trough, Japan [19].

9 CO₂ replacement method is based on the fact that chemical potential of methane hydrate is
10 higher than that of CO₂ hydrate [20]. Theoretically, CO₂ molecules have relatively high
11 tendency to replace the methane molecules from the methane hydrate cages, which was initially
12 proposed by Ohgaki et al. [6]. Under ideal conditions such as high specific surface areas, high
13 permeability, good heat and mass transfer the process of CO₂ displacement process could be
14 fast and efficient. For example, nearly all methane in methane hydrate was replaced by CO₂ in
15 two half cylindrical sandstone cores separated with a purpose-made spacer [21]. Shin et al.
16 found that methane-isopentane hydrates almost completely disappeared after CO₂ replacement
17 using high-power decoupling ¹³C NMR and Raman spectra, in a mechanically stirred reactor
18 [22]. It was also observed that CO₂ replacement occurred quickly in fine hydrate particles that
19 were converted from ice powers in contact with methane [23]. In practice, for example, in
20 sediments or in-situ hydrate reservoirs, the process is constrained by a number of geologic
21 factors such as permeability, porosity, heat and mass transfer, and secondary hydrate formation.
22 Experimental study showed that the presence of excess water and clays resulted in slow CO₂-
23 CH₄ exchange rate [24]. It was also reported that high saturation of gas hydrates could lead to
24 lower percentage of CO₂ replacement [25]. The undesired CO₂ hydrate or CO₂-CH₄ mixed
25 hydrate could clog the pores in the sediments or isolate the methane hydrate from CO₂ by

1 forming CO₂ hydrate shells that coat on the methane hydrate crystals [26]. Recent results
2 showed that the efficiency of CO₂ replacement technique could be improved by introduction
3 of other gases. Masuda et al. experimentally investigated injection of a mixture of 60 mo% CO₂
4 and 40 mol% nitrogen (N₂) to improve the CO₂-CH₄ exchange rate and found that CO₂-CH₄
5 exchange ratios were about 30% for low hydrate-saturation and only 5% for high hydrate-
6 saturation in the sand cores [27]. The experimental results from Kang et al. showed that
7 injection of a simulated flue gas with 20 mol% CO₂ and 80 mol% N₂ increased the methane
8 recovery ratio from 64 to 85% [28]. Kang et al. experimentally demonstrated that injection of
9 CO₂ with air together can enhance CO₂-replacement process by decomposition-driven guest
10 exchange mechanism [29]. Lee et al. reported the latest results showing that flue gas can be
11 used to replace methane from structure H hydrates that was formed with methane and
12 neohexane [30]. The first field trial of the CO₂ replacement technique was successfully
13 conducted in the North Slope of Alaska [31]. 77% N₂ was added to the CO₂ stream to prevent
14 secondary hydrate formation and have a high CO₂-CH₄ exchange rate [32]. Garapati, et al.
15 conducted reservoir simulation to demonstrate how addition of N₂ affect the dynamic process
16 of gas production after injection of the CO₂-N₂ mixture [33]. In about 6 weeks of gas production,
17 in total, 23.2 mscm (million standard cubic meters) CH₄ was produced at the well head; about
18 54% of the injected CO₂ was stored underground; and more than 50% of the produced methane
19 was retained in the well until the well was further depressurised to below the methane hydrate
20 dissociation pressure [34].

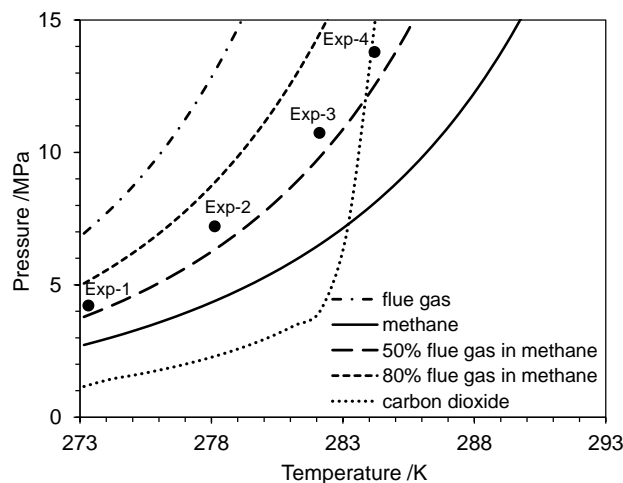
21 All the techniques reviewed above face challenges to be able to produce methane at an
22 economically viable rate, although they appear technically feasible [35]. Development of novel
23 techniques has therefore become crucial for the commercial viability of methane recovery from
24 gas hydrate reservoirs. This work proposes direct injection of flue gas into gas hydrate
25 reservoirs to decompose methane hydrates and recover methane from gas hydrates and

1 simultaneously sequester the CO₂ component of the flue gas as CO₂ hydrate or CO₂ mixed
2 hydrates in the hydrate reservoir formations. Application of the flue gas injection method could
3 substantially enhance the feasibility of depressurisation method for severe hydrate reservoir
4 conditions and avoid CO₂ capture burden of geologic storage of CO₂.

5 **2 Methods**

6 The major constituents of flue gas are nitrogen and CO₂. For example, coal-fired flue gas (post-
7 combustion) typically contains about 12-15% CO₂ and about 80% N₂ apart from water vapour
8 and oxygen [36]. As a concept-proof work, for simplicity, deionised water and a simulated flue
9 gas composed of 14.6 mol% CO₂ and 85.4 mol% N₂ were used. Injection of flue gas will move
10 the thermodynamic conditions of the gas hydrate reservoir toward lower temperature and higher
11 pressure. Figure 1 illustrates the HSZs of CO₂, methane, the simulated flue gas in the presence
12 of water, which was predicted using our in-house thermodynamic model HydraFLASH [37]. It
13 can be seen that 50 mol% of the flue gas can shift the methane hydrate phase boundary to the
14 left by 3.5 K.

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16

17 Figure 1 Predicted shifts in methane hydrate stability zone due to injection of flue gas and the
18 experiment conditions

19

1 Depending on the composition and concentration of the injected flue gas, injection of the flue
2 gas may result in shifting the hydrate reservoir conditions outside the methane HSZ hence
3 dissociation of the methane hydrate. Methane hydrate decomposes into water and methane gas
4 and the released methane gas will be mixed with the flue gas injected. The methane gas ratio
5 in the gas mixture will gradually increase as more methane is released from hydrate
6 dissociation. The hydrate decomposition will continue (though controlled by heat and mass
7 transfer) until the HSZ back to a region where the temperature and pressure conditions in the
8 hydrate-bearing sediments are located in the new HSZ of the mixed gas. In addition to the
9 immediate decomposition due to the HSZ shift, the methane molecules originally trapped in
10 the crystalline cages of the remaining methane hydrate could also be replaced by the CO₂
11 molecules in the injected flue gas, given that the tendency/driving force of CO₂-N₂ replacement
12 is much weaker than CO₂ only. Anderson predicted the enthalpy of dissociation and hydration
13 number of carbon dioxide hydrate and from the Clapeyron equation. His results showed that
14 CO₂ replacement is a relatively weak exothermic reaction [38] although methane hydrate
15 dissociation is also endothermic [39]. The overall consequence of the hydrate dissociation and
16 CO₂ replacement will cause a reduction in the local temperature, which hinders the methane
17 hydrate decomposition. Therefore, heat transfer also play an important role in methane recovery
18 by flue gas injection.

19 Meanwhile, some of the CO₂ presents in the injected flue gas could be stored in the sediments
20 through a variety of reactions. The CO₂ molecules could be combined with water in the pores
21 and form CO₂ hydrate, CO₂ mixed hydrates such as CO₂-CH₄ and N₂-CO₂-CH₄, given that the
22 typical gas hydrate reservoir conditions and limited CO₂ content of the flue gas do not favour
23 the formation of CO₂-N₂ hydrate, N₂-CH₄ hydrate, and N₂ hydrate. CO₂-CH₄ molecule
24 exchange may also occur and trap some CO₂ in a form of CO₂-CH₄ hydrate. Additionally, the
25 CO₂ in the flue gas may also dissolve in the surrounding water at a typical solubility several

1 times higher than that of methane at similar temperature and pressure conditions, depending on
2 the thermodynamic conditions and salinity. However, the amount of CO₂ dissolution in water
3 is constrained by CO₂ partial pressure. Finally, the dissolved CO₂ could be converted into other
4 solid minerals through mineralization reactions over geological time scale [40].

5 **3 Experimental**

6 Figure 2 shows the schematic diagram of the test set-up. The set-up comprises of a stainless
7 steel cylindrical cell with a movable piston. The cell is 75 mm in diameter and 300 mm in
8 length. Its effective volume is 800 cm³. The piston is used to change the cell volume and to
9 achieve the desired overburden pressure by applying hydraulic pressure behind the piston. A
10 linear variable differential transmitter (LVDT) is mounted on the piston rod to determine the
11 piston position hence the cell volume. A cooling jacket surrounding the cell is connected to a
12 thermostat to achieve the required temperature. The set-up is equipped with a hand pump to
13 initially adjust the overburden pressure and a Quizix pump to maintain the system pressure.
14 The working temperature range of the set-up normally is 253 K to 323 K, and working pressure
15 is up to 40 MPa. The system temperature is measured using a platinum resistance thermometer
16 (PRT) (accuracy 0.1 K) and the system pressure and the overburden pressure are measured
17 using two Druck pressure transducers (accuracy 0.05 MPa). A personal computer (PC) is used
18 to record the system pressures, temperature, and the piston movement through a data
19 acquisition device (DAD).

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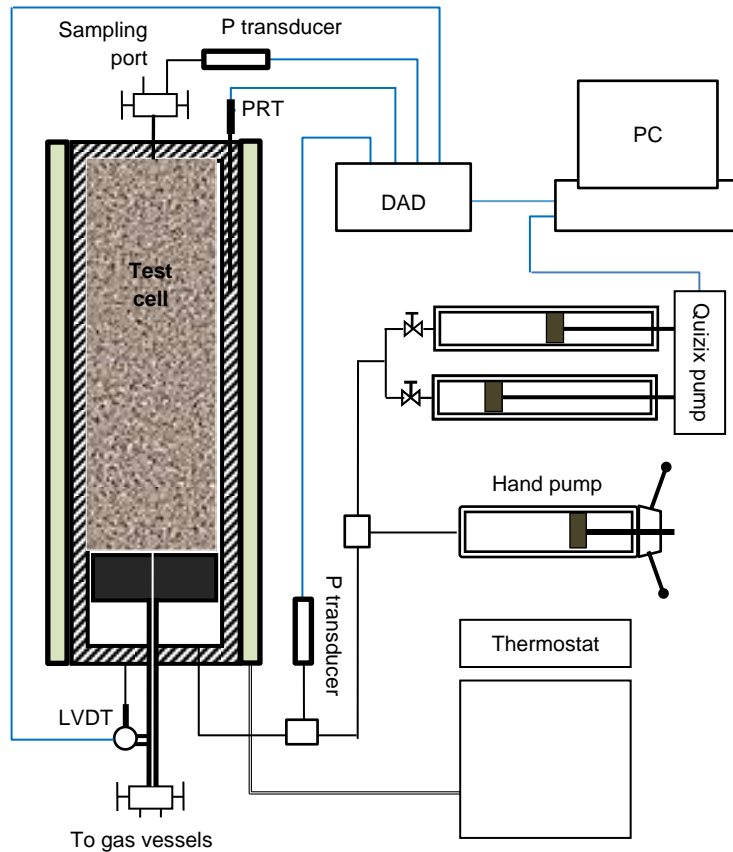


Figure 2 Schematic of the test set-up

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The methane recovery tests were conducted in two steps, i.e., hydrate formation and methane recovery. In the first step, silica sand with a mass-medium size 256.5 μm was partially saturated with deionised water and then loaded into the test cell. After applying vacuum to remove air, an overburden pressure of 3.5 MPa was applied to compact the water-wetted sediment. Methane was injected in the compacted sediment until the desired pressure and the cell was cooled to just above the freezing temperature of water to form methane hydrate. Next, after completion of methane hydrate formation, synthetic flue gas was injected to purge the remaining methane gas. To minimise methane hydrate dissociation, the purging pressure was about 0.7 MPa higher than the dissociation pressure of the flue gas hydrate. After purging, the cell pressure was quickly reduced to the desired point by returning the piston, which expanded

1 the cell volume thus reduced the system pressure without any need for withdrawing any fluids
 2 from the test cell. Methane recovery process started once the desired pressure was reached. The
 3 system temperature and pressure were maintained constant until depressurisation stage started.
 4 The methane recovery process was monitored by taking a series of gas samples at pre-
 5 determined time intervals, while the system pressure was maintained by a dual-cylinder pump
 6 (Quizix SP-5200, Chandler Engineering). The gas samples were analysed using a gas
 7 chromatograph (Varian 3600, Agilent Technologies). The average calibration errors of the gas
 8 chromatograph were $\pm 1.5\%$ for methane, $\pm 0.5\%$ for carbon dioxide, and $\pm 1.2\%$ for nitrogen.

9 **4 Experimental Results**

10 This work was set to experimentally investigate the feasibility of the flue gas injection
 11 approach, i.e., to understand three fundamental issues: how methane hydrate decomposes after
 12 exposing to a methane-flue gas mixture, how flue gas affects depressurisation process, and
 13 whether or not the CO₂ in flue gas could be sequestered while methane hydrate is decomposing
 14 due to the presence of the flue gas. To understand these issues, the experiments were conducted
 15 at different temperature-pressure conditions. As shown in Figure 1, Experiments 1 to 3 were
 16 set inside both methane and CO₂ HSZs, while Experiment 4 was set outside CO₂ HSZ but
 17 inside methane HSZ. The experimental temperature covered the typical temperature conditions
 18 of naturally-occurring hydrate reservoirs from around 273.3 to 284.2 K, whilst the experiment
 19 pressures were set to allow the system to reach a new thermodynamic equilibrium with about
 20 50 mol% methane in the vapor phase after flue gas injection.

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Table 1 Methane recovery experiment conditions

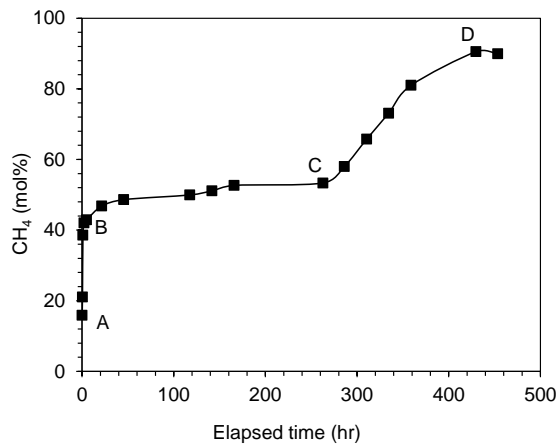
Experiment	T (K)	P (MPa)	ϕ (%)	S _h (vol%)	S _g (vol%)	S _w (vol%)
1	273.3	4.2	39.0	60.2	28.3	11.5
2	278.1	7.2	37.7	54.4	26.0	19.6
3	282.1	10.7	37.7	48.8	27.1	24.0
4	284.2	13.8	37.0	47.3	25.5	27.2

1
2 Silica sand was used to simulate marine sediments. The sand was mixed with water to have
3 around 55 pore volume% of water saturation. After vacuuming and compacting, methane was
4 injected to pressurise the system to around 20 MPa at a room temperature of around 293 K.
5 Methane hydrate was then formed by cooling the system directly to 273.3 K. After methane
6 hydrate formation, the system was heated to the desired temperature and depressurised to the
7 desired pressure. Finally, the saturation of methane hydrate, remaining water, and remaining
8 methane gas was determined based on PVT calculations. Table 1 shows the experimental
9 conditions before flue gas was introduced into the sand pack containing methane hydrate,
10 including experimental temperature (T) and pressure (P), porosity (ϕ), methane hydrate
11 saturation (S_h), remaining methane gas saturation (S_g), and remaining water saturation (S_w).

12 **4.1 Decomposition kinetics at constant pressure**

13 Methane recovery immediately started once the system was depressurised to the desired point
14 after purging out most of the remaining methane gas. As a typical example, in Experiment 1,
15 Figure 3 illustrates the kinetic process of methane decomposition after the flue gas was injected.
16 In the first few hours from A to B, the methane hydrate is dissociated very fast, leading to a
17 sudden increase in methane concentration from the initial value to above 40 mol% in the vapour
18 phase. This is called quick dissociation stage (Stage 1). Masuda et al. showed very similar
19 dissociation process for nitrogen-induced methane hydrate dissociation using their hydrate
20 reservoir simulator [41]. The fast dissociation stage was also experimentally observed for air-
21 induced hydrate dissociation by Haneda et al. [42]. From B to C in Stage 2, the methane was
22 kept slow dissociation over about 160 hours and the methane concentration became constant
23 after about 270 hours. Finally, from C to D in Stage 3, the system was depressurised in steps
24 at the same temperature and more methane was produced from methane hydrate
25 decomposition, which will be discussed in Section 4.2.

1 Such kinetic characteristics was observed in all four experiments, as shown in Figure 4. In
 2 Stage 1, the injected flue gas diluted/reduced methane concentration around methane hydrate
 3 crystals, therefore, shifted the gas hydrate stability zone. The methane hydrate quickly
 4 dissociated and released more methane to the vapor phase. The increase of the methane
 5 concentration made the system to approach a new thermodynamic equilibrium. In Stage 2, the
 6 methane concentration gradually rose to such a level that the system became very close to
 7 equilibrium. As a result, the methane hydrate decomposition was quickly slowed down. In fact,
 8 in the following discussion, it will be seen that mixed hydrates (e.g., CO₂-CH₄) formation was
 9 also occurring, which reduced the increasing rate of the methane in the vapor. Table 2 presents
 10 the experimentally determined methane concentrations and release rates at the end of the
 11 methane decomposition Stages 1 and 2. Most of the methane was recovered very quickly in
 12 Stage 1. In Stage 1 the methane recovery rate was more than 100 times higher than in Stage 2.
 13



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 Figure 3 Methane recovery process was divided into three stages (Experiment 1)

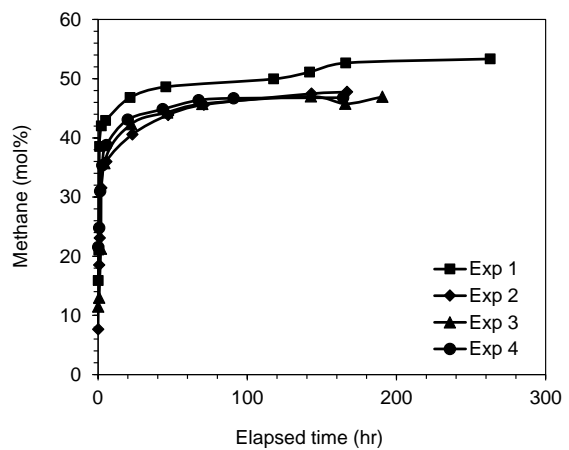


Figure 4 Changes in methane content after the flue gas was injected

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1 Table 2 Determined methane concentration and CO₂ ratio in methane recovery by flue gas
 2 injection (Stages 1 and 2)

Experiment	T K	P MPa	Stage	CH ₄ (mol%)			CO ₂ /(CO ₂ +N ₂) (%)	
				Initial	Final	Rate (mol/hr)	Initial	Final
1	273.3	4.2	1	15.9	42.9	0.0544	8.8	9.6
			2	42.9	53.3	0.00018	9.6	4.3
2	278.1	7.2	1	7.6	36.0	0.0565	11.4	14.6
			2	36.0	47.8	0.00049	14.6	6.0
3	282.1	10.7	1	11.5	35.7	0.0894	11.8	15.4
			2	35.7	46.9	0.00061	15.4	9.6
4	284.2	13.8	1	21.5	38.8	0.101	10.5	11.7
			2	38.8	46.7	0.00102	11.7	11.1

3

4 **4.2 Depressurisation**

5 Depressurisation was performed at a series of pressure steps after the new thermodynamic
 6 equilibrium was reached at the set pressure. The system was maintained at each pressure step
 7 over 24 hours to ensure equilibrium was achieved. Figure 5 illustrates how the methane was
 8 recovered during depressurisation. In Figure 5 the vertical dotted lines indicate the methane
 9 hydrate dissociation pressures at the corresponding experimental temperatures. The presence
 10 of the flue gas made it possible to produce methane from the methane hydrate by
 11 depressurisation well above the methane hydrate dissociation pressure. For example,
 12 depressurisation can produce the gas with more than 65 mol% methane at a pressure about 0.7
 13 MPa above the methane hydrate dissociation pressure at 273.3 K (Experiment 1), with about
 14 60 mol% methane at a pressure about 0.8 MPa above the methane hydrate dissociation pressure
 15 at 278.1 K (Experiment 2), and with 55 mol% methane at a pressure about 1.4 MPa above the
 16 methane hydrate dissociation pressure at 282.1 K (Experiment 3). In Experiment 4 the methane
 17 hydrate was almost fully decomposed before depressurisation so that no much more methane
 18 was released during depressurisation before the system pressure became lower than the
 19 methane hydrate dissociation pressure, i.e., 8.1 MPa at 284.2 K.

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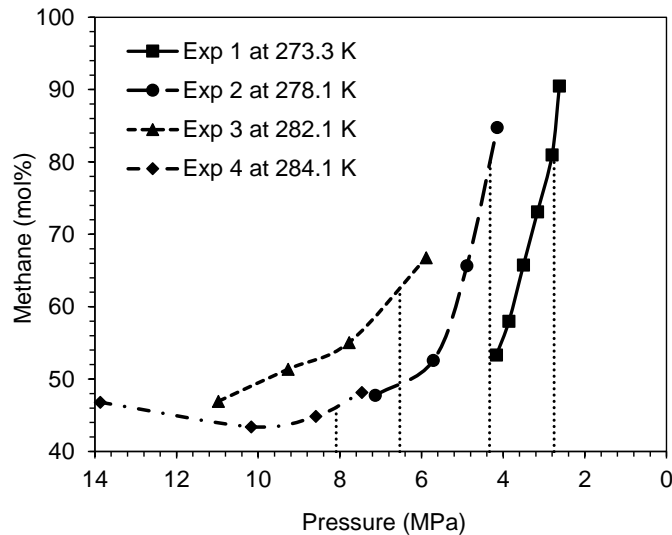


Figure 5 Methane hydrate starts decomposition well inside the methane HSZ

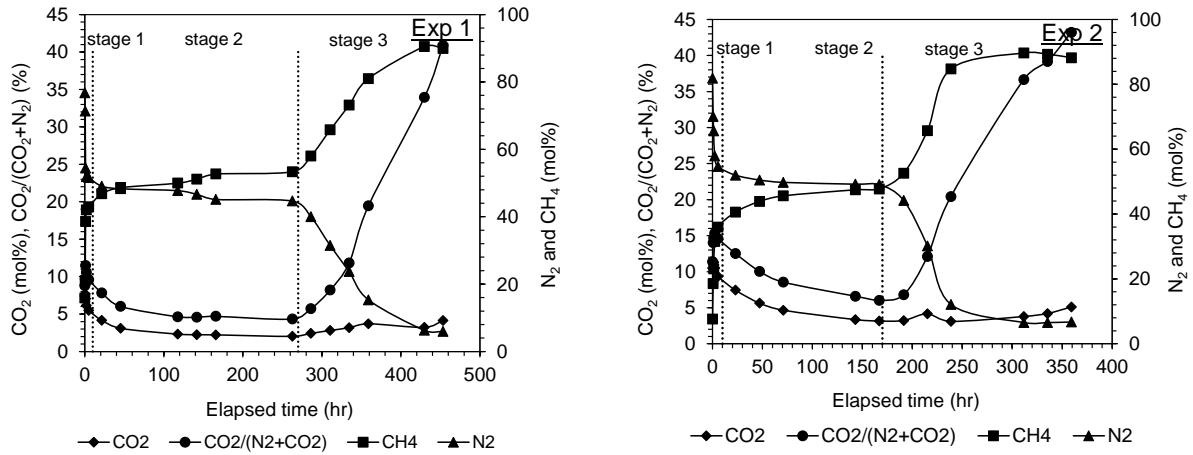
Injection of flue gas leads to methane hydrate decomposition at a pressure well above the methane hydrate dissociation pressure. This may make it possible to minimize the required depressurization degree of a hydrate reservoir to be able to produce methane gas from the hydrate. Minimized depressurization means limited pressure difference between the hydrate reservoir and the production well, hence less driving force for water flow and sand migration. Furthermore, the remaining reservoir pressure will also eliminate or reduce the requirement of external pumps to lift the produced water to allow the gas flow [8]. This could substantially improve the feasibility of the depressurization method for severe gas hydrate reservoir conditions such as low permeable Class 1 hydrate deposits with low permeability, Classes 2 and 3 that are deep inside the HSZ, and dispersive distributed hydrate deposits [12].

4.3 CO₂ sequestration

The potential of the flue gas injection method was also examined for CO₂ capture and storage in hydrate reservoirs. In Figure 6 the ratio of CO₂/(CO₂ + N₂) is used as an indicator of the reduction of the absolute CO₂ content due to formation of CO₂ hydrate or CO₂-involved mixed hydrates, given that N₂-CH₄ and N₂-CO₂ hydrates cannot form at the experimental conditions

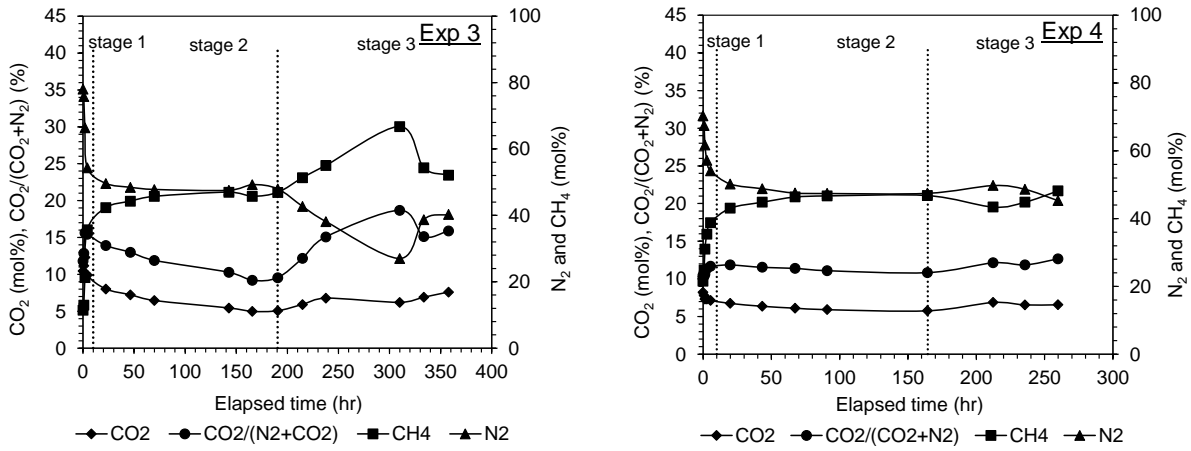
1 according to thermodynamic modelling. The concentrations of CO₂, nitrogen, and methane are
 2 also plotted in Figure 6 to enable analysis of the kinetic process of CO₂-involved hydrate
 3 formation.

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8 Figure 6 Changes in CO₂ content in vapour phase after flue gas injection and during
 9 depressurisation

10

11 In Stages 1 and 2, methane hydrate continuously dissociated as its phase equilibrium was
 12 broken by the injected flue gas, which leads to reduction in the concentration of CO₂ and
 13 nitrogen. Most importantly, the CO₂ ratio also continuously decreased. The reduction in the
 14 CO₂ ratio suggests that the CO₂ molecules in the vapour phase were converted into hydrates.

1 Thermodynamically, the CO₂ could be trapped in any types of a simple CO₂ hydrate, CO₂-CH₄
2 hydrate, and N₂-CO₂-CH₄ hydrate. The CO₂ content decreased to the minimum value at the
3 end of Stage 2, where a new thermodynamic equilibrium was reached. In Experiments 1 to 3,
4 the CO₂ ratio kept rising during depressurisation, indicating CO₂ was being released from
5 decomposition of those mixed CO₂ hydrates. According to thermodynamic modelling, the N₂-
6 CO₂-CH₄ hydrate was dissociated before the system was depressurised out of the methane
7 HSZ, while the CO₂-CH₄ hydrate could not fully dissociate until the system was depressurised
8 out of the CO₂ HSZ. However, the appearance of the maximum methane concentration implies
9 that the methane hydrate and CO₂-CH₄ mixed hydrate were fully dissociated at the second last
10 point at (273.3 K, 2.80 MPa) in Experiment 1, at the third last point (278.1 K, 2.99 MPa) in
11 Experiment 2, at the third last point (281.1 K, 5.88 MPa) in Experiment 3, and at the fourth last
12 point (284.2 K, 13.87 MPa) in Experiment 4. In Figure 6 more CO₂ was released from CO₂
13 hydrate at the last point at (273.3 K, 0.85 MPa) in the Experiment 1 plot, the last point at (278.1
14 K, 1.72 MPa) in the Experiment 2 plot, and the last point at (281.1 K, 3.79 MPa) in the
15 Experiment 3 plot, where these points were outside the CO₂ HSZ. There was no such a rise in
16 the CO₂ content observed, as Experiment 4 was conducted just outside the CO₂ HSZ, as shown
17 in Figure 1.

18

19 Table 3 The amount of CO₂ in the vapour phase captured in hydrates*

Experiment	Temperature (K)	CO ₂ in vapour (mole)		CO ₂ in hydrates	
		Initial	Final	(mole)	(%)
1	273.3	0.0358	0.0106	0.0252	70.4
2	278.1	0.0561	0.0177	0.0384	68.5
3	282.1	0.1369	0.0710	0.0659	48.1
4	284.2	0.1287	0.1096	0.0191	14.8

20 * CO₂ dissolution in water is small and negligible compared to inclusion in gas hydrates.

21

1 Table 3 shows the amount of CO₂ in the vapour phase captured in hydrates. The initial CO₂
2 content was measured in the vapour phase after completion of purging the remaining methane
3 and the final CO₂ content was measured at the end of Stage 2 prior to depressurisation. 70.4%,
4 68.5%, 48.1%, and 14.8% of CO₂ initially in the vapour phase were captured and retained in
5 the hydrates in the porous media in Experiments 1 to 4, respectively. This demonstrates two
6 advantages over the conventional hydrate-based CO₂ capture (HBCC) method. A multi-stage
7 HBCC process with 1 mol% tetra-n-butyl ammonium bromide has to be applied to achieve the
8 CO₂ split fractions similar to those that was gained in Experiments 1 and 2 [43]. The CO₂
9 hydrate formation not only directly capture CO₂ from the flue gas and store it in the hydrate
10 reservoir formation, but also could reduce the impact of methane hydrate decomposition on the
11 wellbore and seafloor stability. Furthermore, the results suggest that deepness inside the CO₂
12 hydrate HSZ plays a substantial role in the CO₂ sequestration from the flue gas, given that the
13 four experiments were conducted in a similar deepness inside the methane hydrate phase
14 boundary (Figure 1). This is understandable because the conditions deeply inside the CO₂ HSZ
15 would provide stronger driving force to promote formation of more CO₂ hydrate, CO₂-CH₄
16 hydrate, and N₂-CO₂-CH₄ hydrate. If taking into account the sharp slope change in CO₂ hydrate
17 phase boundary at about 282 K, it would be generally suggest that the hydrate reservoirs at low
18 temperatures could be better choices for CO₂ capture and storage by flue gas injection.

19 **5 Discussions**

20 Methane recovery by flue gas injection involves complex reactions. Figures 3 and 4 show that
21 the methane hydrate quickly dissociated once the flue gas was introduced into the sand pack
22 containing methane hydrate, methane gas, and water. In an in-situ hydrate reservoir the rate of
23 the methane hydrate decomposition may be dominantly controlled by heat transfer in Stage 1
24 due to the fast heat absorption from the endothermic reaction of methane hydrate
25 decomposition [41]. In Stage 2 the methane hydrate decomposed very slowly as the methane-

1 carbon dioxide-nitrogen mixture was approaching the new phase equilibrium with the
2 remaining methane hydrate. Fresh flue gas-rich gas mixture is needed to continue dissociating
3 the methane hydrate. The permeability of the porous media will be important for the mass
4 transfer process. In other words, the methane recovery rate may be mainly constrained by mass
5 transfer in Stage 2. Moreover, in addition to methane hydrate decomposition, the kinetics of
6 the methane recovery by flue gas injection is rather more complex compared to conventional
7 depressurisation, thermal stimulation, and CO₂-CH₄ replacement. Flue gas injection results in
8 formation of various hydrates such as CO₂ hydrate, CO₂-CH₄ hydrate, N₂-CO₂-CH₄ hydrates,
9 and possible CO₂ replacement as well. The existing kinetic models [44] need to be coupled
10 with a thermodynamic model to be able to simulate the kinetic process of methane recovery by
11 flue gas injection.

12 In Figure 6 it can be seen that the CO₂ ratio to the sum of CO₂ and nitrogen kept increasing till
13 the system was depressurised out of the CO₂ HSZ. The ratio became much higher than its initial
14 value. This is attributed to the fact that some of the CO₂ hydrate, N₂-CO₂-CH₄ hydrate, and N₂-
15 CO₂ hydrate could be formed during the flue gas injection and the purge of the remaining
16 methane, which was not measured in the first gas sample. Thermodynamically, the N₂-CO₂-
17 CH₄ hydrate can stay as long as the system pressure is higher than the methane hydrate
18 dissociation pressure, while the formed CO₂ hydrate and CO₂-CH₄ hydrate can stay as long as
19 the system is not depressurised out of the CO₂ HSZ. This feature can enhance the security to
20 retain CO₂ in the hydrate reservoir formation when methane is recovered.

21 The amplitude of the shift in the required depressurization pressure depends on the methane
22 content in the produced gas. For example, in Experiment 2 at 278.1 K (Figure 5), about 66
23 mol% methane in the vapor phase needs to depressurize the system to 0.5 MPa above the
24 methane hydrate dissociation pressure, 53 mol% and 48 mol% methane need 1.3 MPa and 2.7
25 MPa above the methane hydrate dissociation pressure, respectively. Methane is recovered in a

1 CH₄-N₂-CO₂ mixture. Therefore, gas separation is required to separate the methane from the
2 produced methane-rich gas mixtures containing nitrogen and residual CO₂, which might
3 constrict the cost effectiveness of the flue gas injection method to some extent. Fortunately,
4 there are some gas separation technologies that have been used to separate methane from the
5 CH₄-N₂ and CH₄-N₂-CO₂ gas mixtures for the enhanced coalbed methane recovery (ECBM)
6 [45]. It was found that polyimide membranes could be used to separate N₂ or CO₂ from natural
7 gases [46]. White et al. indicated that removal of N₂ from ECBM gas mixtures is economically
8 feasible for N₂ content up to 30% [47].

9 **6 Conclusions**

10 Flue gas injection into gas hydrate-bearing sediments was experimentally investigated for
11 methane recovery and CO₂ sequestration. The results show that injection of the flue gas results
12 in fast dissociation of the methane hydrate by shifting the methane hydrate stability zone. The
13 methane concentration in the vapour phase reached over 50 mol% at the typical methane
14 hydrate reservoir conditions from 273.3 K and 4.2 MPa to 284.2 K and 13.8 MPa. Further
15 depressurisation of the system to pressures well above the methane hydrate dissociation
16 pressure produced methane in methane-rich gas mixtures and the methane concentration could
17 be up to 80 mol%, depending on the experimental temperature and pressure. It was also found
18 that CO₂ hydrate and some CO₂ mixed hydrates such as N₂-CO₂-CH₄ hydrate and CO₂-CH₄
19 hydrate were formed during the methane recovery after the flue gas was injected. About 70%
20 of the CO₂ in the flue gas was converted into hydrates and retained in the silica sand pack. As
21 a result, the flue gas injection method has considerable potentials to improve the economic
22 viability and feasibility of methane recovery from gas hydrate reservoirs and CO₂ capture and
23 storage in geological formations.

24

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