SUBSURFACE CARBON DIOXIDE STORAGE THROUGH CLATHRATE HYDRATE FORMATION

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Abstract: Rising atmospheric emissions as a result of fossil fuel consumption is a major concern for the developed and developing countries, considering the role it plays in the greenhouse effect and hence global climate change. Various schemes for underground CO_2 storage (viz. geologic disposal into coal seams, depleted oil/gas reservoirs, salt caverns, and deep oceans) have already been reported in the literature. Subsurface CO_2 storage through clathrate hydrate formation is a novel option for the reduction of atmospheric carbon content and permanent underground CO_2 disposal over geological periods. Depths of CO_2 injection, respective pressure-temperature conditions, water salinity etc. are all important factors for successful CO_2 sequestration. Furthermore if CO_2 is injected/stored in methane hydrate reservoirs it could be possible to produce low-carbon methane energy, thereby offsetting the cost of CO_2 transportation and disposal. In this communication, we present the results of experiments carried out to understand the mechanisms of CH_4 displacement in hydrate structure by injected CO_2 and the formation of simple CO_2 or mixed CH_4-CO_2 hydrates, thereby simulating the conditions of CO_2 injection into CH_4 hydrate reservoirs. We used two sets of experimental rigs specifically designed for studying gas hydrates in porous media. They are the Medium Pressure Glass Micromodel (80 bar) for visual observation of gas hydrate formation / dissociation and distribution in porous media, and the Ultrasonic Rig (400 bar) for studying CO_2 sequestration in CH_4 hydrates in synthetic porous media.

Key words: subsurface CO_2 sequestration, permafrost oil and gas reservoirs, CH_4 hydrate reservoirs, simple CH_4 / CO_2 hydrates or mixed CH_4 -CO_2 hydrates.

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1. INTRODUCTION

Gas hydrates were first identified in 1810 by Sir Humphrey Davy (Davy, 1811) and their compositions were later established by Faraday (Faraday 1823). Gas hydrates are naturally occurring crystalline inclusion compounds (clathrates) characterized by strictly determined structures for different gases (Makogon, 1997). Clathrates form when water establishes, due to hydrogen bonding, a cage-like structure around small guest molecules (e.g., light alkanes, carbon dioxide, hydrogen sulphide, nitrogen and oxygen) at low temperature and high-pressure conditions. Their formation, stable existence and decomposition depend upon the pressure, temperature and composition of the system. Gas hydrates can exist in one of the three most-common structures, I, II (Claussen, 1951; von Stackelberg and Müller, 1954; Jeffrey and McMullan, 1967) and H (Ripmeester et al., 1987) (Figure 1). Both CH_4 and CO_2 form structure I hydrate (Davidson, 1973), as do the mixtures of these gases (Adisasmito et al., 1991).

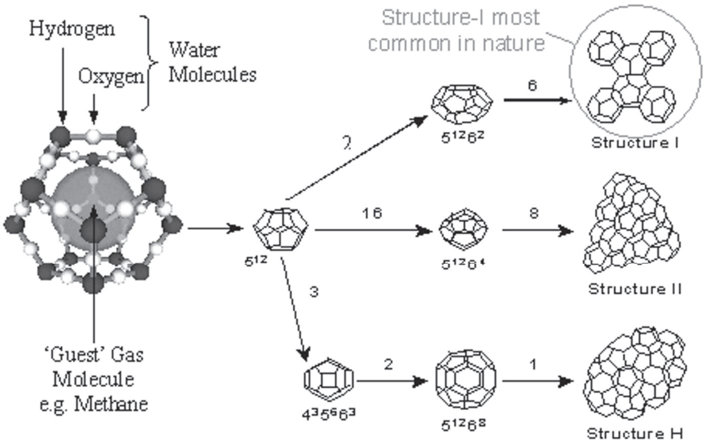

Figure 1. Different forms of clathrate hydrate structures. The numbers over the arrows indicate the number of cage types. (Modified from Sloan, 2003).

Very large sedimentary deposits of natural gas hydrates (14×10^{12} t.o.e.), whose existence was proven 30 years ago (Makogon, 1997), are inferred to occur in two types of geologic environments: permafrost regions (where cold temperatures dominate) and beneath the sea in sediments off the outer continental margins (where high subsurface pressures dominate). Both deposit types are regarded as potential energy storehouses. While methane, propane, and other gases are included in the hydrate structure, methane hydrates are the most common, and thus so are the structure-I hydrates. The methane source for clathrate hydrates formation may be either biogenic or thermogenic. Biogenic CH_4, resulting from the microbial breakdown of organic matter, form hydrates in shallow sediments. About 98% of all gas hydrate deposits come from biogenic methane sources, accumulated offshore in upper sedimentary layers. Thermogenic methane, coming from the thermal alteration of organic matter in sediment at depth, may form hydrates where deep gas migration pathways exist (Kvenvolden and Lorenson, 2001).

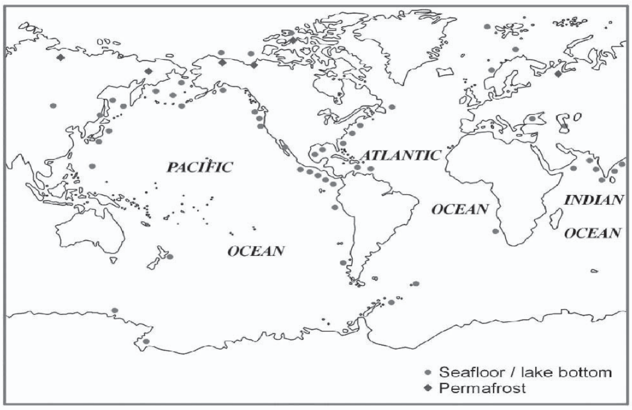

Figure 2. Worldwide occurrences of natural gas hydrate deposits (Modified from Kvenvolden and Lorenson, 2001).

The formation and distribution of gas hydrates in subsurface sediments is controlled by two opposing factors: temperature increases associated with increasing depth (the geothermal gradient) and pressure gradients. Since hydrates are generally stable under relatively low temperatures, the geothermal gradient (2-3°C/100m) limits hydrate formation and existence to relatively shallow, cooler regions of the Earth's crust. Considering seabed temperature and water salinity, hydrates are generally stable at water depths greater than 300 m in continental areas and 500 m in offshore areas. These two factors restrict the existence of clathrate hydrates in subsurface sediments to a region called the Hydrate Stability Zone (Figure 3).

1.1 Gas hydrate production and related issues

Methane gas, a low carbon energy source, can provide an energy supply for many years if produced from naturally occurring CH_4 hydrate reservoirs. The various CH_4 recovery methods (e.g. depressurisation, thermal stimulation, inhibitor injection or a combination of these methods: Sloan, 1998) have already been investigated and are reported in the literature.

These production methods may induce instability in the hydrate rich sediments. The likely mechanism is that hydrate decomposition at the base of the hydrate stability zone convert consolidated sediments into loose gas-charged sediments. This causes a decrease in the shear strength and facilitates the occurrence of landslides, tsunamis or other natural disasters, such as the 1986 Lake Nyos disaster (Rogers, 1996). After massive landslides on the continental slopes, mud volcano eruptions could cause massive hydrate dissociation and the release of CH_4 into the atmosphere, which would contribute to climate change. Natural gas pipelines laid from production platforms to shore may warm sea floor sediments and decompose surrounding hydrates. A concern of the oil and gas industry is also the fact that drilling through hydrate zones might destabilize supporting foundations for platforms and production wells. Disruptions to the ocean floor from hydrate decomposition could also result in surface slumping or faulting, endangering work crews and the environment. Loss of seawater buoyancy because of hydrate-released gas could endanger floating structures (Hovland and Gudmestad, 2001).

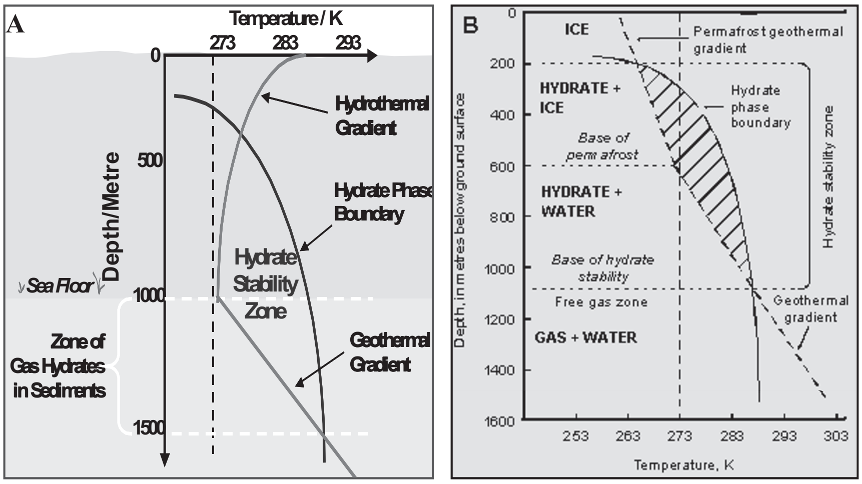

Figure 3. A. Seafloor CH_4 hydrate stability zone. B. Permafrost CH_4 hydrate stability zone.

1.2 Greenhouse gases and their mitigation

Rising levels of the greenhouse gases (mainly CO_2) in the atmosphere have been a great concern for most of the developed and developing nations because of the major climate changes that have been observed in recent decades. One of the options for mitigating the rising greenhouse gas concentrations is their sequestration and storage in subsurface formations.

The petroleum industry has been practicing the methods of sequestering CO_2 in oil and gas reservoirs for Enhanced Oil and Gas Recovery over the last few decades, with an economic incentive to partially offset the sequestration cost. Based on the same ideology, options for CO_2 disposal are being extended for Enhanced CBM recovery, Enhanced gas recovery from CH_4 hydrate reservoirs etc. We propose the option of CO_2 injection into suitably chosen geologic formations and its permanent storage through clathrate hydrate formation.

1.3 CO_2 storage through clathrate hydrate formation

Subsurface CO_2 sequestration and its permanent storage through clathrate hydrates formation is a novel method for reducing the concentration of carbon dioxide in the atmosphere. CO_2 forms stable hydrate compounds at lower temperature and pressure conditions compared to other hydrate formers, especially CH_4 hydrates (Figure 4). Since methane hydrates have been inferred to be present in permafrost and outer continental rises and slopes, and are known to have existed over many centuries, it should be possible to store atmospheric carbon dioxide as solid hydrate compounds in subsurface rock pores over many geological periods. This method is volumetrically efficient as each volume of hydrate can accommodate about 175 volumes of gas.

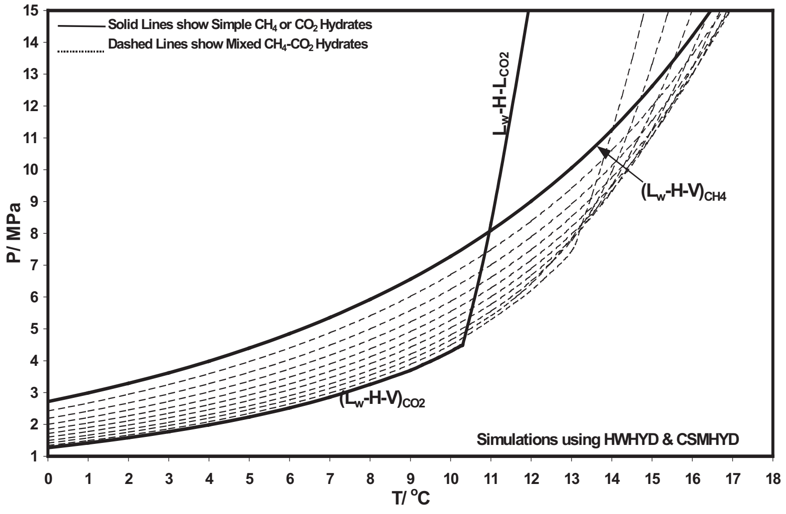

Figure 4. Phase diagram for simple CH_4, CO_2 and mixed CH_4-CO_2 hydrates.

Low temperatures, high pressures and the availability of adequate amounts of hydrate-forming gas are the necessary conditions for hydrate formation that are known to be prevalent in natural permafrost sediments in oil and gas reservoir provinces. Drilling, exploration and production activities for the exploitation of these oil and gas reservoirs have been taking place over many decades. Carbon dioxide sequestration in the sedimentary sections, which have been depleted of oil and gas volumes, would not only re-pressurize these reservoirs and consequently produce oil and gas, but would also safely store the injected carbon dioxide as clathrate hydrates in the later stages. In-place infrastructure can be used to inject the carbon dioxide into subsurface permafrost sedimentary sections (including formations other than oil and gas provinces), which would diminish the cost of CO_2 disposal. Injected CO_2 would be converted into hydrates and occupy the pore spaces of the host rock. The possibility of their atmospheric seepage would be very little as the overlying permafrost layers would act as an impermeable barrier in the form of a cap rock, thus preventing diffusion or upward migration of CO_2 through pores (Duxbury and Romanovsky, 2004; Clarke, 2001). Even in offshore sediments where oil and gas reservoirs exist, there is an increased chance of hydrate accumulations associated with them (e.g. North Sea, Indian Ocean, Taiwan).

Our experimental investigations were aimed at better understanding the processes affecting CO_2 injection into CH_4 hydrate reservoirs, thereby allowing permanent storage of CO_2 in the form of clathrate hydrates.

2. EXPERIMENTAL INVESTIGATIONS OF CO_2 INJECTION INTO CH_4 HYDRATE RESERVOIRS

Injecting CO_2 into subsurface CH_4 hydrate reservoirs would displace some of the CH_4 in the hydrate crystal lattice, converting simple CH_4 hydrates into either simple CO_2 hydrates or double CH_4-CO_2 hydrates. This process could be of particular interest for many reasons. It enables low carbon energy recovery in the form of CH_4 gas, while offsetting the cost of CO_2 transportation and storage. In addition sediment pore spaces potentially re-occupied by the CO_2 hydrate would maintain the mechanical stability of the gas-producing formations, thus preventing the possible hazard of slope failures. The most important part of this production process is that the injected greenhouse gas, carbon dioxide, is permanently and safely stored as clathrate hydrates in subsurface geologic formations over geologic times.

Oghaki et al. (1996) investigated the possibility of methane production from hydrate reservoirs in conjunction with CO_2 injection. Later, Hirohama et al. (1996), Komai et al.(1999, 2003) and Ota et al. (2004) investigated these processes. All of these studies were conducted under bulk conditions (i.e. absence of porous media). The kinetics of replacement was investigated on the micro-scale by Uchida et al. (2001) and Lee et al. (2003). Sivaraman (2003) studied the effect of CO_2 on methane recovery in the presence of porous media, with the test pressure below the CO_2 saturation pressure. McGrail et al. (2004) used micro-emulsions along with CO_2 to investigate similar processes.

2.1 CO_2 sequestration experiments on ultrasonic Rig-1

In the present work experiments into the replacement of CH_4 in hydrates by injected CO_2 were carried out under isothermal conditions (2 ^{0}C) within operating pressures just above the methane hydrate dissociation pressures, in the range of 50 psia. This test mimics reservoir conditions where replacement is observed under excess gas conditions (i.e. very little or no free water). The compositions of coexisting phases have been measured via the gas chromatography (GC) method.

2.1.1 Materials

CH_4 and CO_2 gases used in the evaluation of CH_4 replacement were purchased from Air Products PLC, with a certified purity of 99.995 vol. %. Glass beads were purchased from BioSpec Products Inc. Distilled water was used in all experiments.

2.1.2 Apparatus

The experimental set up shown in Figure 5 was used to investigate the replacement of CH_4 in the hydrate structure by the injected CO_2. It consists of a high-pressure stainless steel cell, a feed system for CH_4, CO_2 and water, and instrumentation for measuring temperature and pressure. The high-pressure cell is constructed of stainless steel with an internal pressure rating of 6,000 psia and an internal volume of 630 cc. The cell is surrounded by a coolant jacket with circulating fluids controlled by a programmable cryostat (-20 ^oC to 80 ^oC) that can be kept stable to within ± 0.05 ^oC. Sediments can be compacted to any given overburden pressure by means of a piston system. In this work half of the experimental cell, as shown in Figure 5, was filled with glass beads. Pore fluid pressure was controlled independently. Temperatures and pressures were monitored by means of a PRT and *Quartzdyne* pressure transducers (accuracy of ± 1.16 psia for 0-20000 psia), respectively. In addition, the pressure could be held constant for long periods of time with a high-pressure Quizix pump.

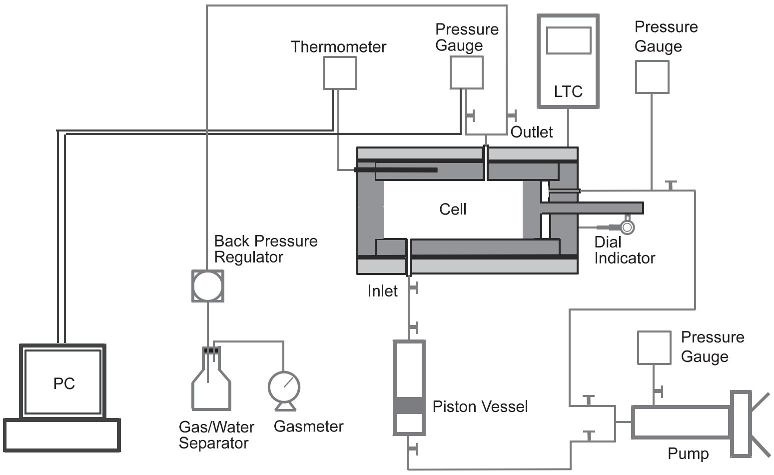

Figure 5. Experimental set-up for the CO_2 sequestration tests.

The analytical work was carried out using a Varian 3600 Gas Chromatograph configured with two thermal conductivity detectors (TCD): one is dedicated for 'parts-per-million' moisture analysis of hydrocarbon gases, while the other conducts conventional gas analysis. Composition measurement of the C_1-CO_2 binary gas samples fall into the conventional gas analysis category, and the separations were performed on a 3m x 1/8" x 2mm i.d. column, using an oven temperature program of 20 ºC to 250 ºC, ramped at 15 ºC per minute, with no isothermal periods. Detector temperature was 300 ºC, and the 6-port 'Valco' injection valve was maintained at laboratory temperature, with no heating applied. For calibration purposes several CH_4-CO_2 gravimetric standards were prepared in-house to cover the range of concentrations encountered; this was done using a small, stainless steel pressure vessel of around $15cm^3$ and weighing with a 'Mettler' "Mass Comparator" balance (accurate to ± 0.001g). From these the appropriate relative molar response factors for the CO_2 were calculated across the required range of concentrations, with the CH_4 and CO_2 mole fractions then calculated using the derived response factors.

2.1.3 Experimental procedure

These preliminary tests were carried out under excess gas conditions for their simplicity, though most methane hydrate reservoirs are believed to be under excess water conditions. The test consisted of the following three steps: i) methane hydrate formation; ii) injection of CO_2 in the methane hydrate-vapour system; and finally, iii) measurement of methane recovery through replacement in hydrates by CO_2 over gas chromatograph. Most of the water and methane was utilized for the methane hydrate formation. The test was conducted in a synthetic porous media (glass beads) under thermodynamic conditions where both CO_2 and CH_4 hydrate are stable. Also the system pressure was kept below the saturation pressure of CO_2.

In this experiment, glass beads of 0.5 mm diameter were used to act as the reservoir sediments. Glass beads were placed into the cell to occupy 50% of the total cell volume, and then saturated with distilled water. CH_4 was introduced in the cell at room temperature so as to have the system pressure at a value higher than the three-phase equilibrium pressure of methane hydrate at that temperature. After gas injection, the test system was left at about 20 °C and 2000 psia overnight to stabilize and reach phase equilibrium. The following day, normally, the test system was directly cooled down to the target temperature by a cooling bath to form hydrates. During the initial stages of cooling the system pressure continues to decrease for a number of hours. However, as the methane hydrate begins to form a sharp decrease in cell pressure is observed, indicating that CH_4 is being absorbed from the headspace into the hydrate structure. Growth of methane hydrates was continued even before the injection of CO_2 into the cell. The results of CH_4 hydrate formation tests are presented in Table 1.

Table 1. Test conditions and details of methane hydrate formation.

Test	**$T /^0C$**	**P / psia**	**n_1**	**n_h**	**n_2**	**n_w**
1	2	520 to 485	1.815	0.524	1.291	0.395

In Table 1 n_1 is the moles of methane injected into the vapour phase before hydrate formation while n_2 represents the moles of methane remaining after hydrate formation, n_h shows the amount of the methane (moles) enclathrated in the hydrates, and n_w are the moles of free water remaining after CH_4 hydrate formation and before CO_2 injection in the cell.

The cell temperature was then increased to a value within the CH_4 hydrate stability region so that the cell system could be monitored for changes in vapour phase composition. Methane in the vapour phase was subsequently partially replaced by carbon dioxide in two to three injection cycles while keeping the internal pressure higher than the three-phase (liquid-vapour-hydrate) equilibrium pressure for methane hydrates. On completion of the CO_2 injection step, the pressure of the system was adjusted to the target conditions for the investigation of methane replacement by CO_2 in hydrates. CH_4 hydrates, along with 2% free water, were allowed to soak with the CO_2-CH_4 gas mixture for a certain period. For each equilibrium condition, samples were withdrawn once every 24 to 72 hours, and analyzed with the GC for the possible rise in methane content.

2.1.4 Results and discussions

Initial composition of the gas phase was 30.33% CH_4 and 69.67% CO_2 at the beginning of replacement step. Pressure and temperature conditions were such that CO_2 would remain in gaseous state. During the initial 20 hours of the process the methane recovery rate was high, which may be attributed to the simultaneous enclathratisation of both CH_4 and CO_2. Carbon dioxide has a higher affinity towards occupying cavities in the hydrate structure than does CH_4, and thus most of the free water could be utilised for CO_2 hydrate formation. It is more likely that the rate of CO_2 going into the hydrate state would be higher than CH_4. A small decrease in system pressure was observed during this period, and no rise in temperature was observed (which could be due to large heat capacity of the system). Headspace CO_2 started replacing CH_4 in the hydrate lattice from this point onwards. It is expected that the methane hydrates in the immediate vicinity of the CO_2-CH_4 headspace would be initially converted into CO_2 hydrates. Slow diffusive mass transfer of CO_2 through the porous sediments drove further methane replacement and continued to rise over the next 80 hours. Most likely mixed CH_4-CO_2 hydrates were formed at this stage, which slowed down the exchange during the latter stage. For replacing methane in hydrates, CO_2 took 206 hours to recover 8.3 mole% of methane. This replacement rate in porous media was high compared to the results published by Hirohama et al. (1996). These authors recovered 6.9 mole% of methane in the gas phase over 800 hours when CO_2 was used to replace methane in hydrates in the presence of a methane hydrate - water system (i.e. bulk conditions). The possible reason for the higher replacement rate could be due to the high gas-solid interface available in the porous media.

The replacement reaction is started when the cell pressure is controlled under isothermal conditions. CO_2 probably starts to replace methane in the hydrates within the first layer near the methane hydrate – gas mixture interface. Later replacement of CH_4 in the host hydrate lattice by CO_2 remains a diffusion-limited process. Replacement processes were continued until termination of the tests.

2.2 CO_2 storage investigation with a visual glass micromodel

A Visual Micromodel was used to study the potential for the underground sequestration of carbon dioxide in methane hydrate reservoirs. Phase behaviour of reservoir fluids in porous media have been extensively studied earlier using micromodels (Sohrabi et al., 2000), while its potential application in gas hydrate studies has been demonstrated by Tohidi et al.

(2001). Pore scale studies were aimed towards providing insight into gas hydrate growth from dissolved gas (CO_2-water) and gas hydrate distribution / cementing characteristics of grains in THF-, CO_2- and CH_4-water systems. Later Anderson et al. (2001) produced visual information on phase distribution in porous media, and hydrate-grain cementation for CH_4-water and CH_4-CO_2-water systems. Here we present the results of experiments conducted using the Medium Pressure Micromodel for studying the effect of CO_2 injection on already-existing methane hydrates in porous media.

2.2.1 Experimental investigation

Two micromodel rigs are currently in operation: a medium pressure set-up (1204 psia) and a high-pressure set-up (5947 psia). The central glass micromodels consist of an etched glass base-plate topped with a sealed glass cover plate (Figure 6). Either a geometrically designed network of pores, tubes or reproductions of actual thin sections of real sediments can be used to construct the micromodels by etching with hydrofluoric acid. The cover plate has an inlet and an outlet, which allows fluids to be pumped through the enclosed pore network using small-volume piston vessels or a precision *Quizix* pump (Figure 7).

In both set-ups the glass micromodels are mounted in a vessel that exerts an overburden pressure and are surrounded by coolant jackets controlled by temperature-controlled baths. Temperature is measured by a probe mounted in the overburden cell, and transducers measure pressure on the model inlet and outlet lines. Temperature can be kept stable to within ± 0.05 °C. Temperatures and pressures are monitored by means of a PRT and *Quartzdyne* pressure transducers (accuracy of ± 1.16 psia for 0-20000 psia), respectively.

Magnifying cameras are mounted above the models, with illumination being provided by cold light sources. Because the micromodel pore structure is only one pore thickness deep it is possible to clearly observe phase changes and fluid flow behaviour. Digital video footage is recorded during the experiment, and the pictures presented here are ones recorded either from video footage or camera clippings.

Existing equipment has been employed in the study of a wide variety of hydrate systems pertaining to various scenarios, from hydrates in sub-sea sediments to flow assurance. The technique provides novel visual information on the mechanisms of clathrate growth, micro-scale dissociation and phase distribution, with respect to pressure, temperature, wettability and fluid composition (presence of inhibitors, liquid hydrocarbons, free and dissolved gas).

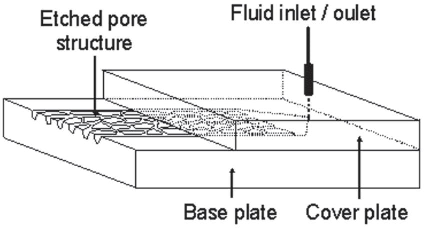

Figure 6. Glass micromodels: pore structure and operational scheme.

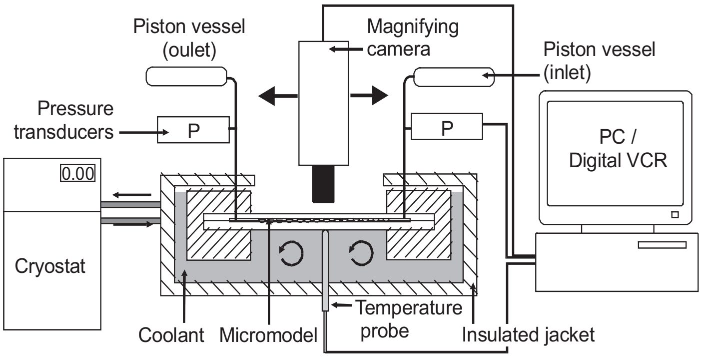

Figure 7. Glass micromodel: experimental set-up.

In all experiments the liquid (water) phase was dyed with methyl blue. Hydrates and gas exclude this dye, thus increasing the contrast between the phases, while it is not known to have any measurable effect on clathrate stability.

2.2.2 Results and discussion

Glass micromodels are used for the visual observation of the CO_2 trapping mechanism. The tests were conducted in the simple methane hydrate - water system, thereby mainly simulating reservoir conditions where excess free water exists in naturally-occurring hydrate-rich sediments.

Formation of small methane hydrate crystals occurs from free CH_4 gas, which is then followed by the injection of CO_2 into the methane hydrate-water system. Figures 8-A through D are representative micromodel images of the phase distribution prior to and after CO_2 injection. This experiment was conducted under temperature and pressure conditions where only simple CH_4 hydrates are stable, but not simple CO_2 hydrates, and CO_2 is in the liquid state. Temperature was kept constant throughout the experiment.

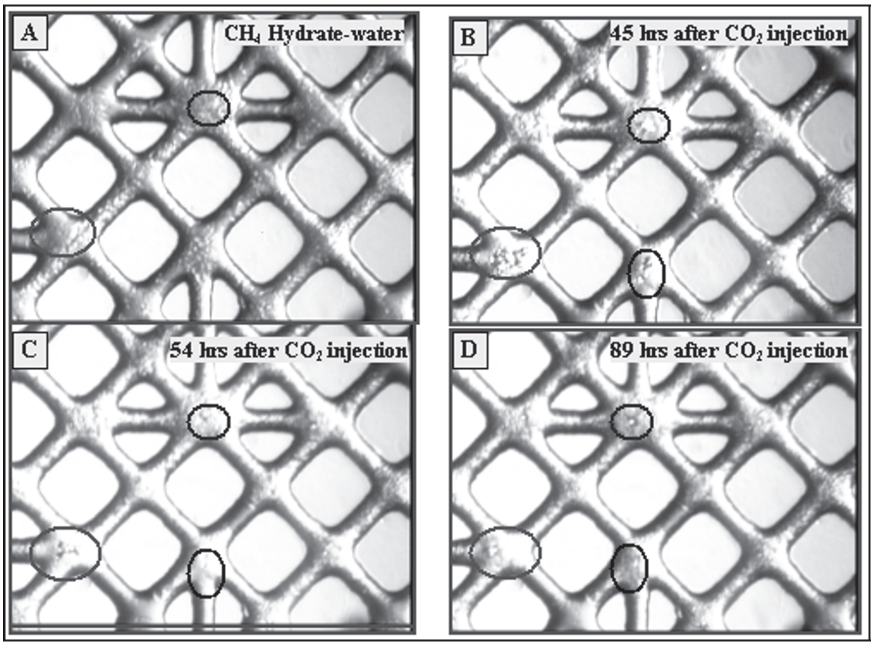

Figure 8. Micromodel images: CO_2 injection and the consequent changes in the already existing methane hydrates morphology.

Another important aspect of the subsurface storage of carbon dioxide is that favourable temperatures and pressures are not the only adequate conditions for the formation of gas hydrates in sub-sea sediments. In case of CO_2 subsurface injection, be it permafrost / seafloor storage or sequestration coupled with additional energy recovery (such as CO_2 injection into methane hydrate reservoirs), hydrate-forming gas concentration (carbon dioxide) should exceed its solubility in water in equilibrium with gas hydrates. This maximum concentration is designated by the solubility of CO_2 in the presence of gas hydrates at the given system pressure and temperature. If the CO_2 concentration in the water is higher than the solubility limit, excessive CO_2 will precipitate from solution producing gas hydrates, thereby forming new gas hydrate cells on the gas hydrate surface.

Methane hydrates were formed from dissolved gas in the region of the hydrate stability zone at 10.8 ^oC. Figure 8-A shows tiny methane hydrate crystals, whose morphology changes over the next 45 hours in the encircled areas. During this time, CO_2 surrounding the CH_4 hydrate crystals seems to have displaced methane in the hydrate lattice, however its release in the system is hindered by available dissolved/excess CO_2 and by the existing excess water. Once methane is released from the structure it immediately mixes with the dissolved CO_2. Since the thermodynamic conditions are favourable for clathrate hydrate formation the mixed CH_4-CO_2 gas hydrates forms. The time lapsed in this process is very small, about 8 to 9 hours, when we carefully analyze the morphology change in the encircled sections of Figure 8-C over Figure 8-B. Mixed hydrate formation occurred around the locations where methane hydrates were already present before CO_2 injection. CO_2 hydrates were formed from the gas dissolved in the water phase. The solubility of CO_2 played an important role in the formation of CO_2 hydrate from the water phase, which resulted in a concentration gradient and the subsequent diffusion across CO_2 hydrate-water interface. The re-formation of the mixed-gas hydrates was nearly complete after 89 hours (Figure D). However under real reservoir conditions the heat released from CO_2 and mixed CH_4-CO_2 hydrate formation could result in local temperature increases and the dissociation of methane hydrates. This possible phenomenon was not investigated in this phase of the work. Nevertheless, the glass micromodel proved to be an invaluable facility for generating micro-scale data to better understand gas hydrate formation and dissociation mechanisms.

3. CONCLUSIONS

The experimental results of CO_2 sequestration in CH_4 hydrate reservoirs and subsequent CH_4 recovery (under excess gas conditions) were obtained by using two types of experimental set ups. The experimental investigation using the Ultrasonic Rig imitated CO_2 injection in a methane hydrate reservoir under excess gas conditions. An increase in CH_4 composition in the headspace gas samples indicates that CH_4 enclathrated in the host hydrate lattice was partially replaced by the injected CO_2. Injection of CO_2 below its saturation pressure in this test produced 7.97-mole% methane in 206 hours. The experimental results show that the CH_4 recovery rate in porous media was higher than previous results obtained by Hirohama et al. (1996) under bulk conditions.

The tests in the Visual Glass Micromodel showed that CO_2 injection into sediments containing methane hydrates under excess water conditions was converted into either CO_2 hydrates or mixed CO_2-CH_4 hydrates. However, it should be noted that these tests were conducted under constant temperature conditions, which may not be the case in real reservoirs due to the release of heat as a result of CO_2 and/or mixed CH_4- CO_2 hydrate formation.

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REFERENCES

Adisasmito, S, Frank, RJ, and Sloan, ED Jr, 1991, Hydrates of Carbon-Dioxide and Methane Mixtures. *Journal of Chemical Engineering Data* **36**(1): 68-71.

Anderson, R, Biderkab, AB, Tohidi, B., and Clennell, MB., 2001, Visual Observation of Gas Hydrate Formation in Glass Micromodels. *EAGE 63rd Conference & Technical Exhibition* — Amsterdam, The Netherlands, 11 - 15 June, 2001.

Clarke, J, 2001, Gas Hydrate Deposits in Oil-Gas Provinces of Russia. *Internet Geology News Letter* No. **80**.

Claussen, WF, 1951, A second water structure for inert gas hydrates. *Journal of Chemical Physics* **19**:1425-1432.

Davidson, DW, 1973, Clathrate Hydrates, in: *Water: A Comprehensive Treatise,* F. Franks, ed., Plenum Press, New York, pp.115-163.

Davy, H, 1811, Phil. Trans. Roy. Soc. London **101**, 1 (Quoted in Sloan, 1998).

Duxbury, N, and Romanovsky, V, 2004, Permanent Sequestration of Emitted Gases in the form of Clathrate Hydrates. *NASA TechBriefs*.: NPO-30256, 55.

Faraday, M, 1823, Phil. Trans. Roy. Soc. London **113**, 160 (Quoted in Sloan, 1998).

Hirohama, S, Shimoyama, Y, Wakabayashi, A, Tatsuta, S, and Nishida, N, 1996, Conversion of CH_4-Hydrate to CO_2-Hydrate in liquid CO_2. *Journal of Chemical Engineering of Japan*; **29**(6):1014-1020.

Hovland, M, and Gudmestad, OT, 2001, Potential Influence of Gas Hydrates on Seabed Installations, in: *Natural Gas Hydrates- Occurrence, Distribution and Detection,* CK Paul and WP Dillon, eds., Geophysics Monograph 124, American Geophysical Union, Washington, pp. 307-315.

Jeffrey, GA, and McMullan, RK, 1967, The Clathrate Hydrates, in: *Progress in Inorganic Chemistry*. Cotton, F.A, ed., Interscience, New York, pp. 43-108.

Komai, T, Kawabe, Y, Kawamura, T, and Yoon, J, 2003, Extraction of Gas Hydrates using CO_2 sequestration. In: *International Offshore and Polar Engineering Conference*, Hawaii USA, 2003.

Komai, T, Yamamoto, Y, and Ogha, K, 1999, Dynamics of Reformation and Replacement of CO_2 and CH_4 gas hydrates. In: *Third International conference on Gas Hydrates*, Salt lake City, Utah, USA.

Kvenvolden, KA, and Lorenson, TD, 2001, The Global Occurrence of Natural Gas Hydrate, in: *Natural Gas Hydrates- Occurrence, Distribution and Detection,* Paul, CK and Dillon, WP, eds., Geophysics Monograph 124, American Geophysical Union, Washington: pp. 3-18.

Lee, H, Seo, Y, Seo, YT, Moudrakovski, IL, and Ripmeester, JA, 2003, Recovering methane from solid methane hydrate with carbon dioxide. *Angewandte Chemie-International Edition* **42**(41):5048-5051.

Makogon, YF, 1997, *Hydrates of Hydrocarbons*. PennWell Books, Oklahoma.

McGrail, BP, Zhu, T, Hunter, RB, White, MD, Patil, SL, and Kulkarni, AS, 2004, A New Method for Enhanced Production of Gas hydrates with CO_2. In: *Gas Hydrates: Energy Resource Potential and Associated Geologic Hazards*, AAPG Hedberg conference, Vancouver, Canada, 2004.

Oghaki, K, Takano, K, Sangawa, H, Matsubara, T, and Nakano, S, 1996, Methane Exploitation by Carbon Dioxide from Gas Hydrates- Phase Equilibria for CO_2 - CH_4 mixed hydrate system. *Journal of Chemical Engineering of Japan* **29**(3): 478-483.

Ota, M, Abe, Y, Watanabe, M, Smith, RL, and Inomata, H, 2005, Methane Recovery from Methane Hydrate using pressurized CO_2. *Fluid Phase Equilibria*, Vol 228-229: 553-559, PPEPPD proceedings, Available online Nov 2004. .

Ripmeester, J.A., Tse, J.S., Ratcliffe, C.I., and Powell, B.M., 1987, A new clathrate hydrate structure. *Nature*: 325, 135.

Rogers, RE, Yevi, 1996, Gas hydrate theory explains lake Nyos disaster. In: *Proceedings of The 2nd International Conference on Natural Gas Hydrates*, Toulouse, France, 1996.

Sivaraman, R, 2003, The potential role of hydrate technology in sequestering carbon dioxide. *Gas TIPS*. Fall 2003 . http://www.gastechnology.org/

Sloan, ED Jr, 1998, *Clathrate Hydrates of Natural Gases*. Marcel Dekker Inc., New York.

Sloan, ED Jr, 2003, Fundamental Principles and Applications of Natural Gas Hydrates. *Nature* **426**:353-359.

Sohrabi, M, Henderson, GD, Tehrani, DH, and Danesh, A, 2000, Visualization of Oil recovery by Water Alternating Gas (WAG) injection using High Pressure Injection Using High Pressure Micromodels-Water-Wet System. *Proceedings of the 2000 SPE Annual Technical Conference and Exhibition,* Dallas, Texas, 1-4 October, SPE 63000.

Tohidi, B, Anderson, R, Clennell, B, Burgass, RW, and Biderkab, AB, 2001, Visual Observation of Gas Hydrate Formation and Dissociation in Synthetic Porous Media by Means of Glass Micromodels. *Geology* **29**(9): 867–870.

Uchida, T, Takeya, S, Ebinuma, T, and Narita, H, 2001, Replacing Methane with CO_2 in clathrate hydrate: Observations using Raman Spectroscopy. In: *Proceedings of Greenhouse Gas Control Technologies,* East Melbourne..523-527.

von Stackelberg, M, and Müller, HR, 1954, Feste Gas Hydrate II., *Zeitschrift fuer Elektrochem* **58**:25-31 (Quoted in Sloan, 1998).