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Quantitative measurement and mechanisms for CH_4 production from hydrates with the injection of liquid CO_2

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The recovery of gas from natural gas hydrates under the permafrost and in oceanic sediments is of particular interest in energy and environmental fields because of the attractive process to release methane gas through the injection of CO_2. The sequestration of CO_2, a notorious greenhouse gas, in hydrates has the potential to be used in enhanced gas recovery techniques, while simultaneously releasing CH_4 locked within the gas bearing hydrates. In this study, we present quantitative experiments to investigate results of possible CH_4-CO_2 exchange kinetics from injection of liquid CO_2 through CH_4 hydrates. The experiments performed use CH_4 hydrate formed from ice particles (75-90 or 125-150 microns in diameter) at approximately 10.34 MPa and 263 K. In order to reduce unexpected errors, nearly full conversion (> 95%) of ice particles to hydrates is achieved. Liquid CO_2 is injected into the pressure cell to sweep the residual CH_4 atmosphere, ensuring no free CH_4 is left in the gas phase. After soaking the hydrate for several hours, CH_4 is produced from the hydrates by injecting liquid CO_2. The final composition and analysis of the produced CH_4 is measured by using in-line gas chromatography. We also measure the CH_4 moles after hydrate dissociation to confirm the closure of the total mass balance of the experiment. From these data, we infer the mechanism for CH_4 production, identify the penetration depth of the dissociation/exchange on the hydrate particles, and propose physical models describing the mechanism for CH_4 production. These experiments are essential in the quantification of the production of CH_4 from CH_4 hydrates with the injection of CO_2.

1. Introduction

In energy and environmental sectors, the recovery of gas from natural gas hydrates, formed under the permafrost and in oceanic sediments, has been of particular interest. Naturally occurring gas hydrates, mostly containing CH_4, are regarded as a future energy resource.[1-3] On the other hand, the sequestration of CO_2, a global climate change gas, has the potential to be used in enhanced gas recovery techniques, as well as simultaneously releasing CH_4 locked within gas bearing hydrates.[4,5]

Many investigations suggest the possibility of exchanging CH_4 with CO_2 in natural gas hydrates in terms of kinetics,[6,7] thermodynamics[8-10] and molecular simulations,[11-13] which has the advantage of both CO_2 sequestration and CH_4 recovery. Compared with other technologies to produce gas from hydrates, such as depressurization[14-16] or heat injection methods,[17,18] this technology can reduce or eliminate water production, extend the recoverability to a wider range of geologic settings and potentially decrease near well bore stability and plugging.[19,20]

Recently, ConocoPhillips, in collaboration with the U.S. Department of Energy and the Japan Oil, Gas and Metals National Corporation (JOGMEC), drilled a gas hydrate test well in the Prudhoe Bay Unit, Alaska North Slope for feasibility tests at the field-scale. The test was designed to evaluate CH_4 gas production with the injection of CO_2 into gas hydrate bearing sandstone.[20] In those tests, a CO_2-N_2 gas mixture was injected into the test well, with subsequent demonstration of CH_4 liberation from the hydrate reservoir.[21] However, this technology of gas production from hydrate reservoirs remains unproven, as technical challenges remains due to the insufficient understanding of the mechanism for CH_4 production and CO_2 capture. Furthermore, most of the previous studies provide qualitative information on the CH_4 production rates during CH_4-CO_2 exchange in the hydrate.[6,22-25] Consequently, the rate of CH_4 production is not well quantified, and thus important information towards quantifying CH_4

release from various CH_4 hydrate saturations observed in natural settings is required.

In this study, we present quantitative experiments to investigate possible CH_4-CO_2 exchange kinetics from injection of liquid CO_2 through CH_4 hydrates. The experimental system uses a high-pressure pump for continuous injection of liquid CO_2, and an in-line gas chromatograph to quantify CH_4 released from the hydrates. CH_4 production kinetics from injecting liquid CO_2 into fine-grained CH_4 hydrates was measured, and from these data the mechanism for CH_4 production is inferred, such as identifying the penetration depth of the dissociation/exchange on the hydrate particles, and proposing physical models to describe the mechanism of CH_4 production. These experiments are essential in the quantification of the production of CH_4 from CH_4 hydrates with the injection of CO_2.

2. Experimental methodology

2.1 Apparatus description

Figure 1 shows the experimental set-up for the quantitative studies of CH_4-CO_2 exchange, with CO_2 flooding and composition analysis with an in-line gas chromatograph (HP-5890). Gaseous CO_2 is pressurized with a gas booster to 8.963 MPa (1,300 psig) in the Ruska pump (500 ml in volume), thus generating liquid CO_2, which is subsequently injected into the cell at a controlled flow rate. For some of the experiments, a small supply vessel (23 ml, item F in Figure 1) immersed in the water bath was used to cool the liquid CO_2 prior to its injection into the cell. The pressure cell (170 ml) was made of stainless steel and its pressure controlled through several backpressure regulators. A gas purifier filled with silica gel and sodium chloride is placed downstream from the cell to absorb any moisture in the effluent stream of the cell.

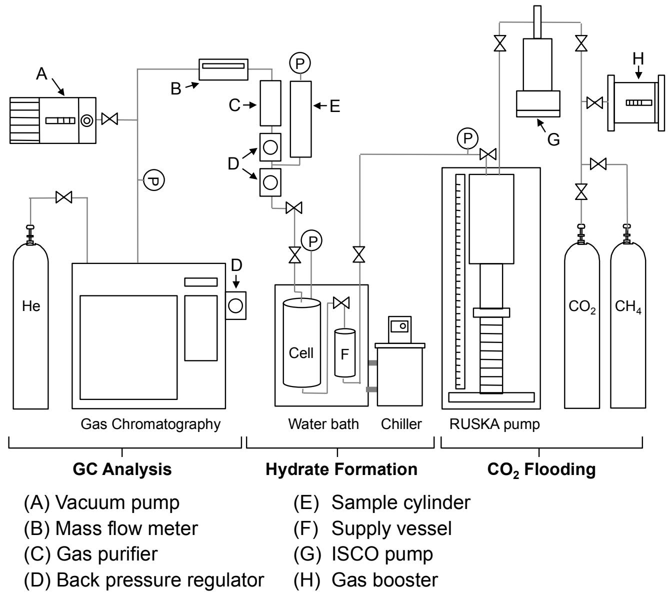

Fig. 1 Experimental apparatus for quantitative CH_4-CO_2 exchange studies.

2.2 Experimental procedure

CH_4 hydrates are prepared from approximately 33 grams of powdered hexagonal ice grains sieved to obtain size-controlled particles (e.g., diameter of 75-90 or 125-150 μm). The ice particles are loaded into the pressure cell maintained at 263 K, the cell is sealed, and CH_4 gas is subsequently pressurized until the system pressure reaches approximately 10.34 MPa (1,500 psig) through a supply vessel immersed in the water bath (cooling the gas prior to entering the cell). Hydrate formation is allowed to continue to near 100% conversion of the ice, resulting eventually in no further change in system pressure (typically after 10-14 days). The amount of hydrate formed is determined from the difference between the initial and final pressures in the cell. The conversion to hydrates is then estimated by an equation-of-state assuming a hydration number of 6. To obtain high conversion, a temperature ramping method between 263 K and 272 K is used, resulting in a final conversion generally corresponding to over 95%. This step is done to i) to minimize the sintering between the particles and ii) to intentionally promote expansion of the particles from the temperature increase so to facilitate gas diffusion to core of the particle. Experiments were performed at 263 K and 275 K, temperatures chosen to ensure no free water below the ice melting point and to study the temperature effect above the ice melting point, respectively.

After CH_4 hydrate formation, liquid CO_2 is injected (123 ml/hour) into the pressure cell to sweep the residual CH_4 gas, ensuring no free CH_4 is left in the gas phase. During the liquid CO_2 flood, the cell pressure is kept constant at ~9.00 MPa via a preset backpressure regulator. The gas passing through the backpressure regulator is collected into a sample cylinder (550 ml in volume), and the gas composition is analyzed using an in-line gas chromatograph. The final mole fraction of CH_4 in the sweep stage generally reaches below 0.2%.

After soaking hydrates in liquid CO_2 for several hours, any CH_4 produced from the hydrates and dissolved in liquid CO_2 is moved into a sample cylinder by further injection of liquid CO_2. The composition of the fluid collected in the sample cylinder is measured by gas chromatography.

We also measure the amount of CH_4 remaining in the hydrates by complete dissociation of the sample; this provides a quantitative measure to confirm the closure of the total CH_4 mass balance in the experiment. To dissociate the hydrates completely, first the cell temperature is increased up to room temperature at a constant pressure (~9.00 MPa), then liquid CO_2 is injected to sweep all CH_4 from the cell, and finally the cell pressure is decreased to atmospheric pressure. The gas composition is analyzed continuously via gas chromatography so that the amount of CH_4 determined can be used to close the CH_4 mass balance in the experiment.

Table 1. Summary of all experimental runs performed. The reported error was calculated in terms of mass balance of CH_4, that is, the initial n_{CH4} trapped in the hydrate phase (a), should equal the sum of total n_{CH4} produced from hydrates during all soaks (b), and n_{CH4} dissociated (c). The experiments of group A and B were performed with 75-90 µm diameter ice particles at 263 K and 275 K, respectively, without a supply vessel. Group C and D are for experiments performed with 75-90 µm and 125-150 µm diameter particles respectively, at 275 K with a supply vessel immersed in the water bath.

Group	Expt.	(a) Initial n_{CH4} occupied in hyd	(b) Total n_{CH4} produced from hyd during soaks	(c) n_{CH4} dissociated from hyd	(d) Error (b+c) / (a)
A	Run1	0.2517	0.0232	0.2237	1.9%
	Run2	0.2290	0.0334	0.1846	4.9%
B	Run3	0.2467	0.0685	0.1745	1.5%
	Run4	0.2618	0.0945	0.1535	5.3%
	Run5	0.2546	0.1026	0.1482	1.5%
C	Run6	0.2924	0.0653	0.2214	1.9%
	Run8	0.2873	0.0967	0.1828	2.7%
D	Run7	0.2921	0.0513	0.2514	3.5%

3. Results & Discussion

3.1 n_{CH4} produced from hydrates

Table 1 shows a summary of all the experiments performed for this study. Note that each set of conditions was repeated to verify the reproducibility and demonstrate the deviation among independent runs. As explained in the experimental procedure, CH_4 hydrates were soaked in the liquid CO_2 for a number of hours for each of the different soaks. The production of CH_4 from the hydrates resulted from the chemical potential difference of the species (CH_4 and CO_2) between the fluid and hydrate phases. We used the pressure, temperature, and volume conditions (with an equation of state) to determine the number of moles of CH_4 produced from hydrates. All the details of these results, including mole fraction of CH_4 during each soak, are presented in the Supporting Information.

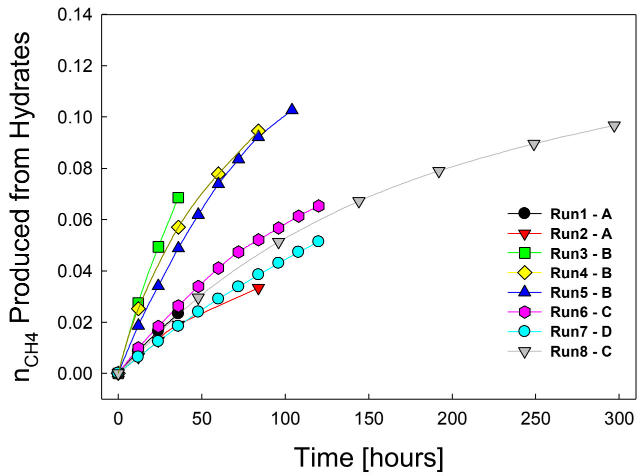

Fig. 2 Summary of the moles of CH_4 produced from hydrates over time for all tests performed.

Figure 2 shows the summary for all tests listed in Table 1, with plots of the number of moles of CH_4 produced from hydrates as a function of time during the soaks with liquid CO_2. Each data set in Figure 2 corresponds to the amount of CH_4 produced during each soak. One can see that the kinetic trend of the same group was similar (e.g., B: Run3, Run4, Run5), and all of them showed a gradual decrease in rate of CH_4 production with time.

Figure 3 compares the amount of CH_4 produced in each group at the same soak time (at 80 hours). Based on these results, the following observations can be made.

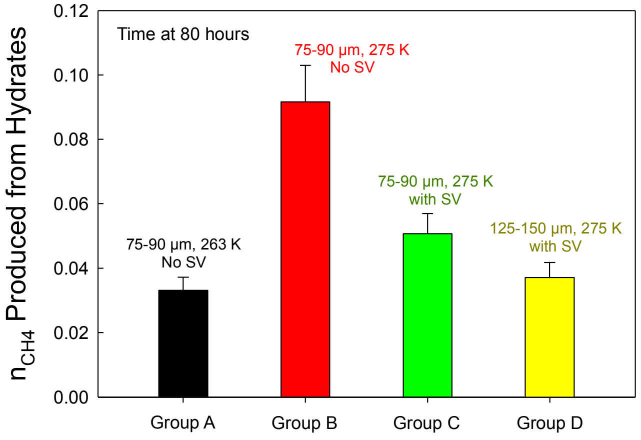

Fig. 3 Comparison of the moles of CH_4 produced from hydrates for each group at 80 hours of soak time. SV in the figure means supply vessel immersed in the water bath. All error bars were calculated from several experiments performed under the same conditions, with the exception of group D, where the error corresponds to 95% confidence.

a) Group A vs. Group B
The experimental temperature was different for these two groups of tests: 263 K (A) vs. 275 K (B). A significantly larger amount of CH_4 (2.8 times more) was produced from group B compared to group A. As the temperature for group A was below the ice point, the mobility of the gas and water was likely highly restricted. This result clearly demonstrates that the temperature is an important factor for CH_4 production from hydrates.

b) Group B vs. Group C
To better understand the temperature effect on the amount of CH_4 produced, we performed experiments with and without a supply vessel immersed in a water bath (pre-cooling the injected liquid CO_2 before contact with the CH_4 hydrates in the pressure cell; without supply vessel, liquid CO_2 is introduced directly from the Ruska pump kept at room temperature). Experiments in group C are well controlled and all the CH_4 produced could be attributed to CH_4 released from the hydrates due to chemical potential difference. Whereas some of the CH_4 produced in group B is likely due to the partial dissociation of the hydrates as warm liquid CO_2 is introduced into the pressure cell. As shown in Figure 3, the amount of CH_4 in group B is about 1.8 times greater than that in group C.

c) Group C vs. Group D
The surface area of contact between the fluid phase and hydrate particles can be an important factor for the amount of CH_4 produced. Experiments in group D are performed with ice particles of 125-150 μm in diameter, compared to those of 75-90 μm in group C (larger particles, smaller surface area). As expected, experiments in group C produce more CH_4 (about 1.4 times) than that of group D.

3.2 Demonstration of CO_2-CH_4 exchange

While temperature and pressure also affect the stability of the hydrates, we expect the chemical potential difference of the species in the difference phases as the main driving force for the CH_4 hydrate dissociation at the surface. At the start of each soak period, there is no free CH_4 gas in bulk liquid CO_2.

Over the course of each experiment and soak time, the cell pressure always increased. During each soak, the system is closed, so there are only two possible reasons for the increase in pressure: change in the hydration number due to the different hydrates of CH_4, CO_2 or CO_2/CH_4 mixture, or release of CH_4 from CH_4 hydrate dissociation.

To determine the mechanism for CH_4 production, we utilize the pressure increase data along with the proposed mechanism for "exchange" and "no exchange" shown in Figure 4. For the "no exchange" case, CH_4 is released from the hydrates, but no CO_2 hydrates are formed (CO_2 only causes the CH_4 hydrate to dissociate).

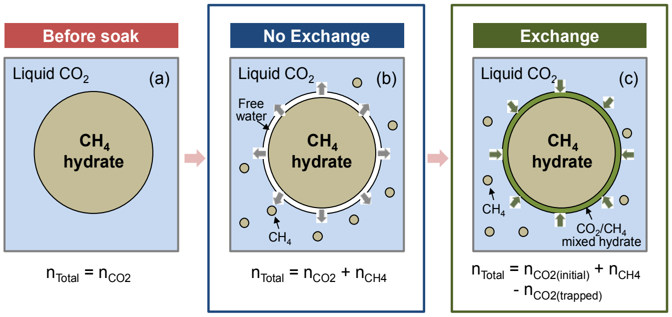

Fig. 4 Illustration of the potential mechanisms for CH_4 production based on "exchange" and "no exchange" between CO_2 and CH_4 hydrates. (a) Initial state before soaking: no residual CH_4 in the fluid phase. (b) "No exchange" case: CH_4 hydrate is dissociated and no CO_2 is incorporated into the hydrate. (c) "Exchange" case: CH_4 is produced from hydrate and a mixed CO_2/CH_4 hydrate is re-formed.

In the "exchange" case, CH_4 hydrates are dissociated and a mixed CO_2/CH_4 hydrate is immediately re-formed. As such, the total number of moles of CO_2 in the "no exchange" case would be slightly larger than in the "exchange" case, as all the CO_2 molecules would be in the free fluid phase. Based on these two scenarios, the experimentally measured pressure traces can be compared with the system response based on the proposed mechanisms to infer their validity. Details of the calculations for the pressure traces are provided in the Supporting Information.

Figure 5 shows the pressure data (points) during soaks with the calculated lines for the "exchange" and "no exchange" cases. As shown in Figure 5(b), the pressure data fit well with the calculated line simulating exchange until the 4th soak, approximately 48 hours accumulated after soaking, while after that time, larger deviations are seen between the data and calculated lines. Similar comparisons and agreement are also observed for other experimental data. As shown in Figure 5(d), pressure data for the 1st soak, up to 48 hours, matched well with calculated line based on the "exchange" mechanism; however, the data for the subsequent soaks have trends in between the two calculated lines simulating the "exchange" and "no exchange" cases. Based on the results shown in Figure 5, we conclude that CO_2/CH_4 exchange did occur during the initial 48 hours, but subsequently, the exchange ratio gradually decreases as the soak time progresses.

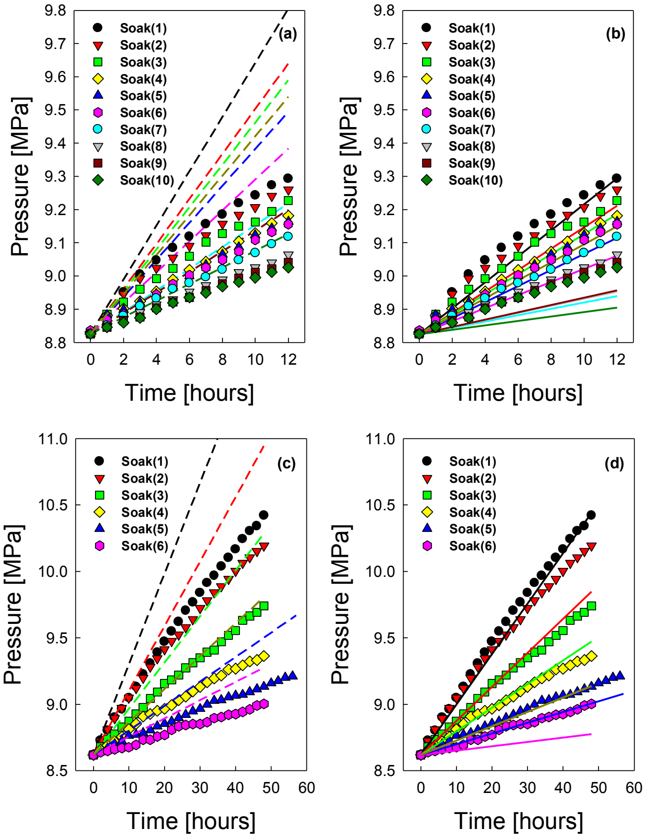

Fig. 5 Results of calculations to demonstrate possible CO_2 and CH_4 exchange. Data from Run 6 (a and b) and Run 8 (c and d) are used. Symbols and lines correspond to experimental data and calculated cases, respectively. Plots a and c are for the "no exchange" case (dashed lines), and plots b and d are for the "exchange" case (solid lines).

We can also infer the mechanism for CH_4 production by calculating the penetration depth for dissociation/exchange on the hydrate particles. Figure 6 shows the penetration depth profile of a hydrate particle accumulated after each soak in Run 6. The penetration depth was calculated with several assumptions: 1) the particle diameter is 80 μm for the experiment with particles of 75-90 μm in diameter, 2) there is no volume change of the particle during exchange, 3) hydrate cage occupancy is obtained via CSMGem[26] at the experimental temperature and pressure, and 4) the calculation is based on the moles of CH_4 produced from hydrates in the experiment. The number of hydrate particles is calculated by the volume of hydrates in the cell and the assumed diameter for the particles. As CO_2 or CO_2/CH_4 mixed hydrates both form structure I, the volume of CH_4 produced from hydrates is calculated using the volume of the unit cell (lattice constant a = 12 Å). As shown in Figure 6, the final penetration depth for CO_2/CH_4 mixed hydrates is determined to be about 4.85 μm after 120 hours (10th soak).

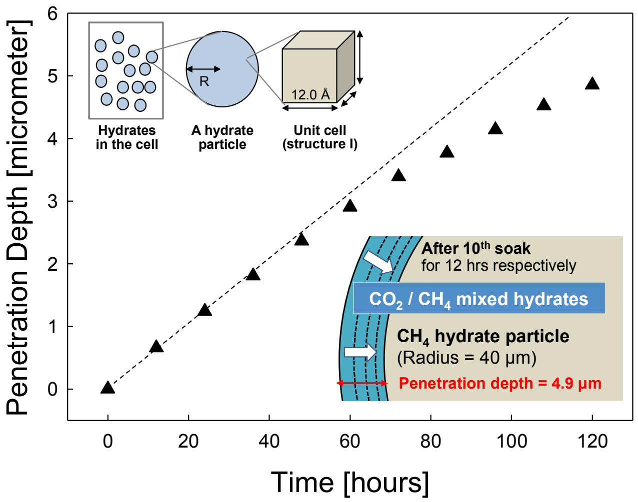

Fig. 6 Penetration depth accumulated after each soak in Run 6. Dashed line only serves to guide the eye.

We also see that the penetration depth gradually decreases after each soak as each new layer of CO_2/CH_4 mixed hydrates formed provides additional resistance for CO_2 to diffuse and reach the inner core of pure CH_4 hydrate.

3.3 Kinetic trends of CO2-CH4 exchange process

Another approach to test the physical mechanism for the exchange process is to compare the data to possible physical models for diffusion/reaction. The Avrami equation[27,28] and shrinking core model[28-30] are well known physical models for crystallization kinetics. The Avrami model is applicable in the initial reaction stage of the hydrate film, while the shrinking core model is for diffusion through the hydrate film. The general CO_2-CH_4 exchange reaction has a similar physical phenomenon, as it must occur at the surface first and then be diffusion limited as interior layers of the hydrate particles are further exposed to CO_2. The relevant equations are:

Avrami model: $\alpha = 1 - \exp\left(-k_1 t^n\right)$

Shrinking core model: $(1-\alpha)^{1/3} = -\frac{\sqrt{2k_2\left(t-t^*\right)}}{r} + \left(1-\alpha^*\right)^{1/3}$

where, α is the hydrate conversion ratio at time t, α^* is the hydrate conversion ratio when diffusion through hydrate film starts at time t^*, k is the rate constant with the subscript indicating the growth stage, n is the Avrami exponent, and r is the radius of particle. The hydrate conversion ratio as a function of time is regressed with both equations to obtain the rate constant k_1, k_2 and the Avrami exponent n.

Table 2. Parameters regressed for Avrami and shrinking core models.

System	Avrami model		Shrinking core model		
	k_1	n	t^*	α^*	$c\left(=-\sqrt{2}\,k_2/r\right)$
75-90 μm	0.003	0.922	60 hrs	0.107	-0.0055
125-150 μm	0.002	0.982	48 hrs	0.040	-0.0056

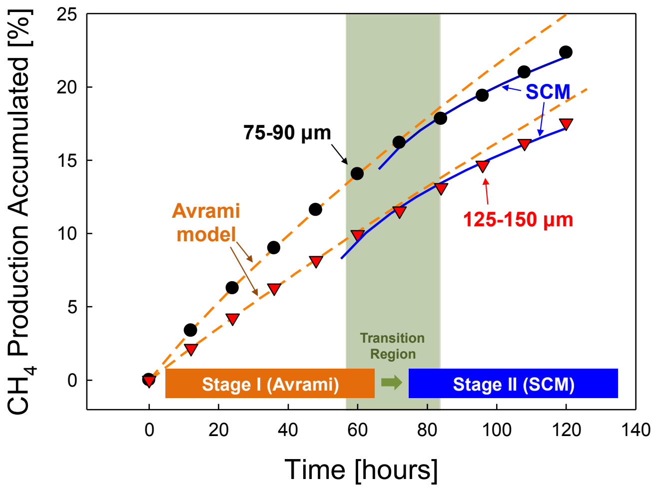

Fig. 7 Avrami (dashed line) and shrinking core model (SCM, solid line) comparison for % CH_4 production accumulated in Run 6 and Run 7.

Figure 7 plots the accumulated production ratio data for Run 6 and Run 7 and comparisons with the two kinetic models. Generally, in the exchange process, we assume there are two stages: i) fast surface reaction, and ii) gradual slow process due to resistance to diffusion through the formed mixed hydrate layer. The experimental data matched well with the Avrami model in stage I, while the shrinking core model fitted well in stage II. The parameters for the models are listed in Table 2. Note that the transition region is not well defined from the selected number of experiments, but it is expected to differ for different systems under different conditions.

4. Conclusion

A well-controlled experimental system has been developed for obtaining quantitative information, which was previously poorly characterized, in the CO_2-CH_4 exchange process for hydrates. The experiments reported are essential in the quantification of the production of CH_4 from CH_4 hydrates with the injection of CO_2. Several experiments were performed to understand the effect on temperature in the CH_4 production from hydrates. From these data, we conclude that temperature is an important variable influencing the production of CH_4 from hydrates. To demonstrate the mechanism for CH_4 production, in particular whether CO_2 and CH_4 are exchanged in the hydrate, a quantitative assessment is made by calculating the pressure response of the system for the cases of "exchange" and "no exchange". We find that CO_2 and CH_4 are initially exchanged, however, as time progresses (soak time) the exchange rate is gradually decreased. This exchange process can be also explained from estimates of the penetration depth for exchange of a hydrate particle and kinetic models describing the physical process of diffusion/reaction. The analysis of the results suggests two stages for hydrate exchange: a fast surface reaction which is only reaction limited for exchange, and a diffusion limited process at the hydrate core which considers the decreased diffusivity of the gas through the pre-formed hydrate layer.

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Notes and References

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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