CO_2-CH_4 exchange in the context of CO_2 injection and gas production from methane hydrates bearing sediments

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Abstract

In recent decades, scientists have made an amazing discovery: Methane hydrates in the ocean floor. These solid compounds could represent an important energy reserve. Today it is estimated that they contain equivalent carbon in the form of methane in a huge quantity, twice as much as all deposits of natural gas, oil and coal.

In the near future, we need evaluate the possibility to produce this new source of energy, particularly in replacement of oil and coal. The main question concerns the technology to be used because the methane hydrates are distributed in sediment, and they participate to their consolidation.

In this paper, we present a method which doesn't modify the structure of the sediment, by replacing the methane hydrate by CO_2 hydrate after injection of CO_2 gas.

1. Introduction

Gas hydrates are solid compounds. They are formed from the combinaition of gas (such as methane, ethane, propane...) and water under high pressure and low temperature. Clathrate hydrate has been first discovered in 1778 by Joseph Priestley as a laboratory curiosity. Nowadays, gas hydrates have the potential for numerous applications in the oil and gas industry and the energy sector, as for example through the use of clathrate hydrates as a means of gas storage, for the capture and sequestration of carbon dioxide, in air-conditioning systems in the form of hydrate slurries, in the water desalination and treatment, and the separation of different gases from flue gas streams to name but a few (Eslamimanesh et al, 2012). However, despite the potential applications of gas clathrate hydrates, like the ones mentioned above, there are also negative aspects to be mentioned in the discussion of these solid solutions. The uncontrolled decomposition of naturally occurring methane hydrates for example has been discussed as being capable of potentially contributing to the greenhouse gas effect (Englezos, 1993; Leggett, 1990), in particular if it is realised that the global warming potential (GWP) of methane within a period of 100 years is greater by a factor of 25 than the GWP value of carbon dioxide (Solomon et al, 2007). Moreover, gas clathrate hydrates have been identified as a source of problems in the oil and gas industry, for example. when being formed in drilling applications (Barker and Gomez, 1989) or in gas pipelines due to their ability of causing pipeline blockages (Eslamimanesh et al, 2012).

2. Context of the work

Methane is a natural component in sediments, originated from thermal degradation of fossil reservoirs or from bio-degradation of biological materials. Under pressure, in deep sea conditions, it forms methane hydrate reservoirs in many places of the world and in huge quantities. On ther other hand, carbon dioxide is a molecule which presents a better affinity to clathrate structure. The concept consists in injecting CO_2 in methane hydrate reservoirs in order to shift the equilibrium and form a CO_2 hydrate in the place of methane hydrate, and to recover methane.

The objective of our work is to study thermodynamic of CO_2-CH_4 methane hydrate, in presence of salts, and to understand the crystallization mechanism during the replacing of CH_4 by CO_2. In this work, we present a set of experimental results in order to validate a thermodynamic model which predicts the equilibrium conditions; pressure, temperature and composition of phases in presence of a mixture of CO_2 and CH_4.

3. Structure of gas hydrates

Gas clathrate hydrates are solid crystalline compounds which are built up by a network of hydrogen bonded water molecules comprising cage-like structural units, each of which can encapsulate one appropriately sized guest molecule. The guest species, which are generally molecules of low molecular weight gases and organic compounds (Sloan and Koh, 2008), stabilize the solid solvent, the thermodynamically metastable host lattice, by interacting with the water molecules of the cage through van der Waals forces (Ribeiro and Lage, 2008). Gas clathrate hydrates are thermodynamically stable in regions of ambient or lower temperatures (above or below the normal freezing point of water) and elevated pressures (typically more than 0.6MPa) (Englezos, 1993; Sloan, 2003) and crystallise in three different structures, the cubic structures I (sI) and II (sII), and the hexagonal structure H (sH). Structure I, which predominates in the earth's natural environments and contains small (0.4 - 0.55nm) guest species (Sloan, 2003), possesses a network of water molecules based on two different polyhedra as building units, which according to the nomenclature of Jeffrey (Jeffrey, 1984), are written as 5^{12} and $5^{12}6^2$. The cubic structure II hydrates, the lattice of which is composed of the polyhedra 5^{12} and $5^{12}6^4$, generally occur with larger (0.6 - 0.7nm) guests in mostly man-made environments (Jeffrey, 1984). Hydrates of hexagonal structure H, occurring in either environment, but only with mixtures containing both small and large (0.8-0.9 nm) guest species (Jeffrey, 1984), comprise three types of cavities, the polyhedra 5^{12}, $4^35^66^3$ and $5^{12}6^8$.

The combination of the gas molecules with the water can be described by the equation:

$$G.n\_hydH_2O \leftrightarrow G\ (gaz) + n\_hydH_2O$$

Where n_hyd is the hydration number. In the structure I, hydrate crystallize as 5.77 £ n_hyd £ 7.4 (Sloan and Koh 2008).

The concept of exchanging carbon dioxide with methane in deposits of natural gas hydrates is regarded as a possible way of producing methane and sequestrating CO_2 (Ohgaki et al, 1996; Hirohama et al, 1996). This concept is considered as a rupture technology, to be added in the portfolio of technologies, alongside to concepts such as thermal stimulation, depressurization or chemical shifting.

4. Advantages of using CO_2 gas for replacement of CH_4 hydrate in sediment

Firstly, the method consisting to replace the methane in the methane hydrates reservoirs by CO_2 will contribute to drop the emissions of greenhouse gases.

Secondly, the hydrate structure still remains in place in the sediment, only the gas content being shifted. So, it can be assumed that the mechanical stability of the reservoir is not modified.

Lastly, the heat of CO_2 hydrates dissociation (57.98kJ/mol) is slightly higher than the heat of methane hydrates dissociation (54.49kJ/mol) (Naval Goel 2006). Therefore, the transformation of methane hydrate into carbon dioxide hydrate is practically athermic:

$$CO_2\ (g) + nH_2O \rightarrow CO_2(H_2O)n\ \Delta H_f = -57{,}98kJ/mol$$

$$CH_4\ (H_2O)n \rightarrow CH_4(g) + nH_2O\ \Delta H_f = 54{,}49kJ/mol$$

Where n is hydrate number (n about 6) for methane and carbon dioxide

On Fig.1, we can determine the (pressure - temperature) area where carbon dioxide can be injected for dissociation of methane hydrate. It is the region A or B in which the methane hydrate is not longer stable, but the carbon dioxide still remains stable.

Ohgaki et al. (1996) have demonstrated experimentally the possibility of producing methane gas from the hydrate by injecting carbon dioxide. They found that the mole fraction of carbon dioxide in the hydrate phase becomes higher than in the gas phase, at the equilibrium. Furthermore, Hirohama et al (1996) showed that the pressure in reservoir after methane hydrate dissociation remains approximately the same as before dissociation.

Seo et al. (2001) suggest that if the mole fraction of carbon dioxide is kept above 40% in the CO_2-CH_4 gas mixture, the concentration of carbon dioxide in the hydrate phase will be more than 90%.

5. Experimental approach

5.1. Experimental set-up

The experimental apparatus (Fig.2) is designed to measure the thermodynamic equilibrium points in the presence of gas mixture and to determine the composition of all phases (gas, liquid and hydrate). The reactor consists of a 2.5 liter autoclave reactor in which the pressure can reach up to 10MPa. The autoclave is provided with two sapphire windows (12 x 2cm) on both sides of the reactor to see inside the reactor. The reactor is equipped with a vertical stirrer with four blades. The stirring rate can vary between 0 and 600rpm. The reactor is temperature controlled by a double jacket in which is circulated a fluid at constant temperature from a cryostat HUBERT CC-250. A Pyrex cell is laid inside the reactor and filled with water containing Li+ as an anion tracer. The concentration of the anion is controlled in the range 0 - 10ppm by using a HPLC pump (JASCO). Temperature is monitored by 2 Pt100, at the bottom and the top of the reactor. Pressure is measured with an accuracy of 0.01MPa in the range 0 - 10MPa. A ROLSI sampler is mounted on the reactor. It allows sampling the gas online sending the sample into a gas chromatograph (GC Varian model 38002) equipped with a TCD detector and two columns PoraBOND Q and CP-Molsieve. This system allows two columns in parallel to separate a wide range of gases. The peak integration is possible with software provided by Varian Galaxie. A sampling system can retain the liquid phase through a valve. It is analyzed off-line by ion chromatography and refractometry. The data acquisition (pressure, temperature) is saved on the personal computer.

5.2. Procedure of our experiences

The experiments are realized following 4 steps:

Step 1: Injection of pure methane gas:

Initially, the reactor is evacuated by a vacuum pump. The methane or carbon dioxide gas is injected and purged three times to ensure that air is totally evacuated. Then, the reactor is loaded with the first gas (the same that has just been used for purges).

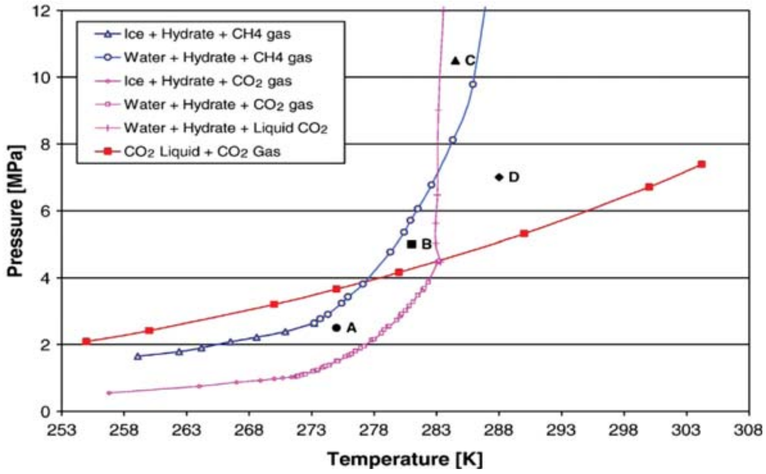

Fig.1. *Equilibrium conditions of hydrate CO_2 and CH_4 (Naval Goel 2006)*

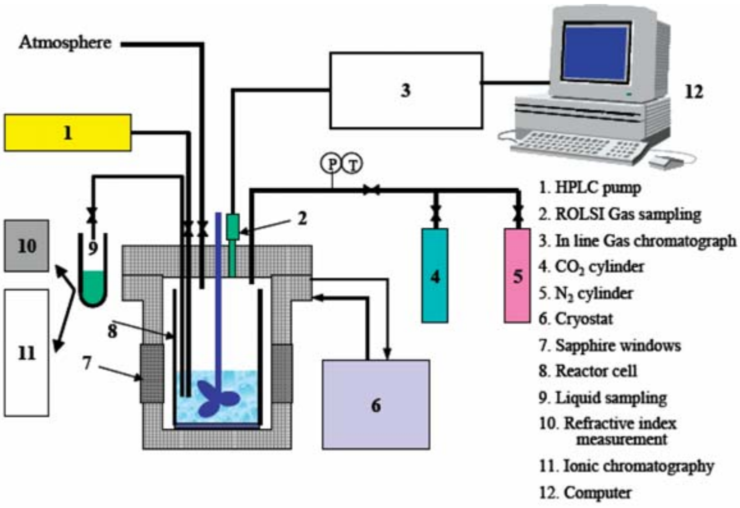

Fig.2. *Experimental device*

Step 2: Injection of CO_2 gas:

After the pressure is stable (to calculate the quantity of gas), another gas is added up to the required total pressure. The gas mixture is cooled and maintained at the operating temperature with the cryostat. It is stirred at a rate of approximately 400rpm.

Step 3: Injection of water for crystallization of mixed CO_2-CH_4 hydrates:

The stirrer is stopped. Water containing 10ppm of a lithium tracer is added by an HPLC pump (high pressure). The mass of the injected solution is controlled, about 800g. Pressure, temperature and gas composition are monitored. Then, the stirrer is run again. After a delay corresponding to the induction time, the crystallization starts, gas is consumed and the pressure is dropped down to the equilibrium. The crystallization is occurring during hours and days and the gas phase is sampled. The liquid phase is also sampled and analyzed later by ion exchange chromatography.

Step 4: Dissociation of hydrates:

When the system is in equilibrium (temperature and pressure), the temperature is increased by steps of 1°C until full dissociation of hydrates (Fig.3). During each step, the pressure in the reactor increases due to the dissociation of hydrates. After complete dissociation of hydrate, the pressure in the reactor continues to increase but only in respect to the dilatation of gases and decrease of the solubility of gases. At each stage of dissociation, the gas and liquid phases are sampled and respectively analyzed by gas chromatography and ion exchange chromatography to determine the gas compositions in gas phase and the lithium concentration in the liquid phase.

5.3. Results

5.4. Calculations for gas composition in the different phases

According to mass balance of each component, the quantity of CH_4 and CO_2 in different phases can be calculated by the following equations:

$n[CH_4]^H = [nCH_4]\text{initial} - n[CH_4]^G - n[CH_4]^L$ (1)

$n[CO_2]^H = [nCO_2]\text{initial} - n[CO_2]^G - n[CO_2]^L$ (2)

$n[CH_4]^G = nG.XCH_4$ in reactor (3)

$n[CO_2]^G = nG.XCO_2$ in reactor (4)

$n[CH_4]^L$, $n[CO_2]^L$ are calculated by equation from Henry following the correlation of Holder (1980) where $n[CH_4]^H$; and $n[CO_2]^H$ are the moles fractions of CH_4 and CO_2 respectively in the hydrate phase; $n[CH_4]^G$; and $n[CO_2]^G$ are the moles fractions of CH_4 and CO_2 in gas phase in the reactor; n CH_4; released and nCO_2; nG is the number of moles of gas in the reactor, which is determined by equation of state; n released is the number of moles of the released gas from the reactor.

$$H_i = H_{i,Psat} \exp\left(\frac{v_i^{\infty}(P - P_i^{sat})}{RT}\right) \qquad (5)$$

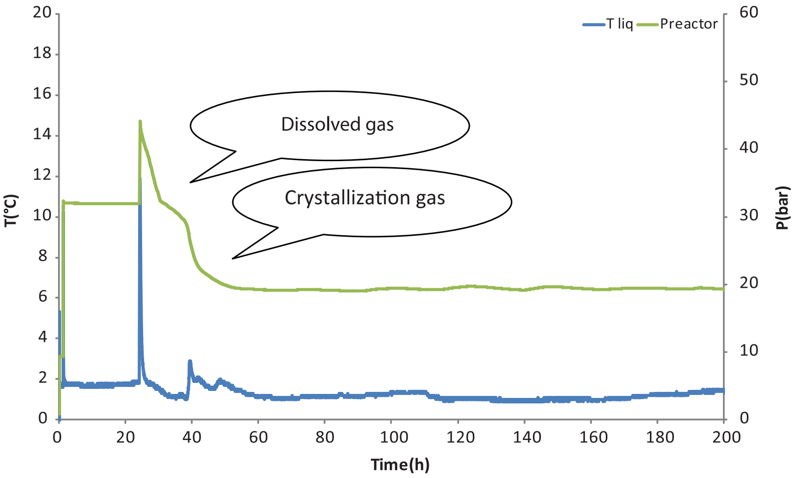

Fig.3. *Evolution of pressure and temperature during the step of crystallization*

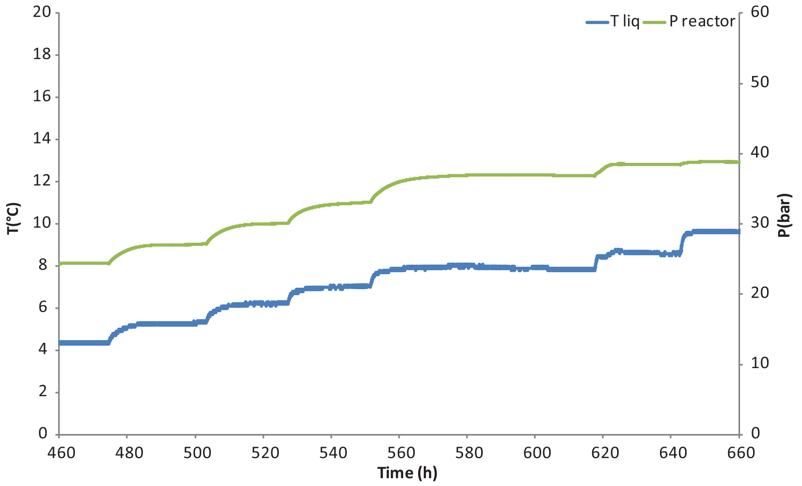

Fig.4. *Evolution of pressure and temperature during the step of dissociation*

Table 1. *Constant for Henry constant calculation with Holder (1980)*

Gas	A	B	v_i^{∞} (cm³/mol)
CH_4	15.826277	-1559.0631	32
CO_2	14.283146	-2050.3269	32

$$H_{i,Psat} = \exp\left(A + \frac{B}{T}\right) \qquad (6)$$

Where H_i is the Henry coefficient, A and B are constants in Table 1.

The volume of liquid in equilibrium is determined by following the concentration of a tracer (Li +) in the liquid phase

$$V_{eq}^L = \frac{[Li^+]_{ini} V_w^0}{[Li^+]_{eq}} \text{ and } V_w^H = V_w^0 - V_{eq}^L = V_w^0 - V_w^0 \frac{[Li^+]_{ini}}{[Li^+]_{eq}}$$

$$= V_w^0 \left(1 - \frac{[Li^+]_{ini}}{[Li^+]_{eq}}\right)$$

Where V_w^H, V_w^0, V_{eq}^L are the volume of water in hydrate phase, initial and liquid phase at equilibrium.

A summary of steps of calculation is presented in the Fig.5.

The Fig.6 shows the phase diagram of hydrate of CO_2-CH_4 mixture at temperature of 2.2°C. These results are compared with the model from the GasHyDyn software. The experimental results are close to the simulated values and new experiments are still under testing.

6. Conclusion

This work contributes to the long term issue to produce methane from methane hydrate bearing sediments. The method consists in injecting CO_2 in to sediments and shifting the chemical equilibrium of methane hydrate, to form carbon dioxide clathrate hydrates. So, this thematic theme relates the topic of gas production, but also to CO_2 mitigation.

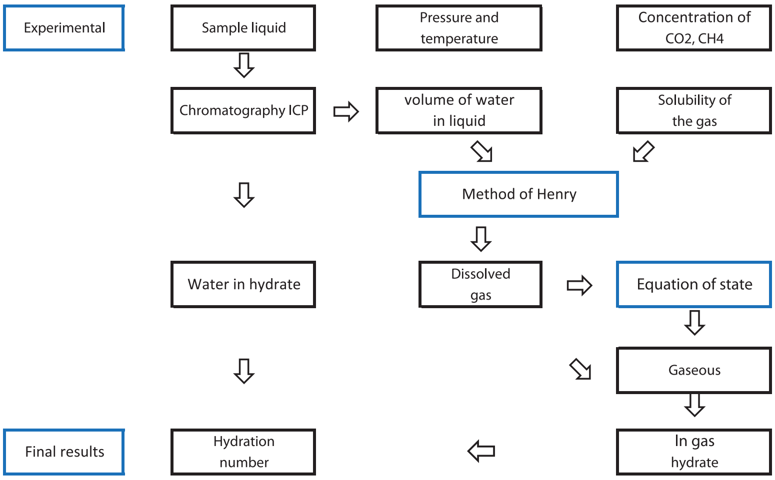

Fig.5. *Treatment of data*

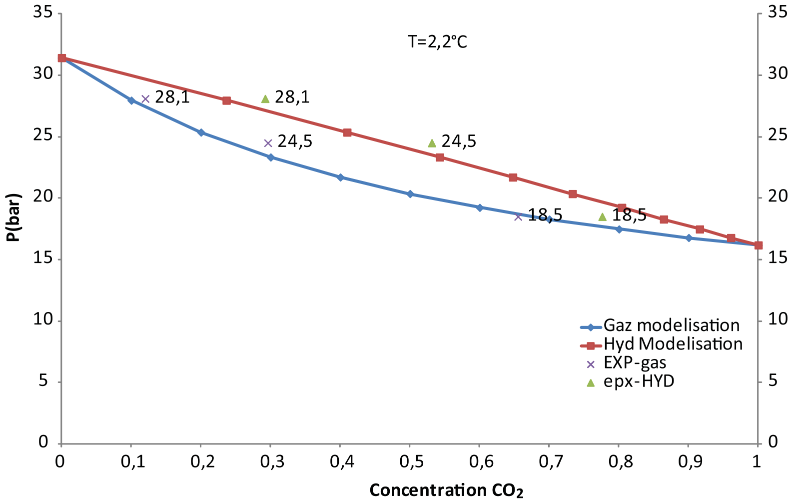

Fig.6. *Phase diagram of hydrate CO_2-CH_4 mixture at 2.2°C*

In the work, we presented experimental results about the equilibrium of CO_2-CH_4 gas mixture. Our experiments indicate that we can form a solid in thermodynamic equilibrium with the gas mixture.

The next step is to study the kinetics of replacement of methane by carbon dioxide in the hydrate structure. The work is undergoing (Herri and Kwaterski, 2012). Currently, we start looking to model the formation of methane hydrate and replace it with the CO_2 in the reactor, depending on conditions such as temperature and pressure of the tank.

We produce a dispersion of crystals of methane hydrate in a wetting medium, with an excess of liquid water. It forms slurry. Then, these crystals are destabilized by CO_2 injection and we monitor the composition of the gas that is enriched in methane because of the dissociation of methane hydrate and formation of CO_2-CH_4 hydrate following the equilibrium given in (Fig.6). It will allow us, after developing a suitable model to quantify the kinetics of conversion of a solid phase to another solid phase.

Subsequently, we want to build a new device which will crystallize methane hydrates in porous media, following the procedure that we have experimented (Tonnet and Herri, 2009). These hydrates are then subjected to a flow of CO_2 through the porous medium, and then we can observe the different limitations.

This technology is a new technology developed from the needs of gas industry. In our laboratory, it contributes to the development of new technologies taking advantaget of the physical properties of gas hydrates.

Among the new technologies we are developing, we can also cite the CO_2 capture to recover the carbon dioxide from gas power station (Herri et al, 2011; Herri and Kwaterski, 2012; Kwaterski and Herri, 2012) or other industries such a steel making plants (Duc et al, 2005).

We can cite also the technology consisting in storing energy under the form of a slurry of clathrate hydrate, for air condition applications (Darbouret et al, 2005; Douzet et al, 2012).

If clathrate hydrates can be used with a profitable objective, they still remain a problem in the oil industry because they can form crystals in the different facilities after extraction of the oil, especially in deep sea conditions. Our laboratory is also specialized in the flow assurance to prevent the nucleation, growth and agglomeration (Herri et al, 1999; Pic et al, 2000, 2001; Cournil and Herri, 2003, Fidel Dufour et al, 2005; Cameirao et al, 2012), and to propose solutions if a plug forms (Nguyen Hong Duc et al, 2005).

Our laboratory also specialises in the determination of physical properties of gas hydrates, such as Hamaker constant with application to the evaluation of agglomeration (Bonnefoy et al, 2005) or determination of refractive index (Herri and Gruy, 1996; Bonnefoy et al, 2005) with application to the conception of particle sizes (Herri et al, 1999).

Our competences can be applied to other domains, and we cite the extrapolation of our work concerning thermodynamics to the planet science, and the modelling of the atmospheric behavior on Mars, at very low pressure and temperature, both in the recent period (Herri and Chassefiere, 2012) or in the ancient time (Chassefière et al, 2012).

So, the applications of gas hydrates concerns a great number of industries (Gas production, CO_2 mitigation, Refrigeration, flow assurance) and a great number of scientific domains (Geosciences, Industrial crystallization, Chemical Engineering, Planetary sciences), and can be probably be fruitfully applied in Vietnam (Nguyen Hong and Herri, 2006).

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