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## **A method to calculate the composition of clathrate hydrate of CO<sub>2</sub>-CH<sub>4</sub>, at equilibrium and during crystallization**

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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 energy reserve. Today it is estimated that they contain equivalent carbon under 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 evaluating 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 to study the thermodynamic of CO<sub>2</sub>-CH<sub>4</sub> clathrate hydrates, which is the prior step before testing and modeling the replacement of methane hydrate by CO<sub>2</sub> hydrate after injection of CO<sub>2</sub> gas.

**Keywords:** methane hydrate, dissociation, sediment core, heat and mass transfer.

### **1. Introduction**

Gas hydrates are solid compounds. They are formed from the combination 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 curiosity of laboratory. 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 of 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 green house 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 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, e.g. 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).

Methane is a natural component in sediments, originated from thermal degradation of fossil reservoirs, or originated 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 a other hand, carbon dioxide is a molecule which presents a better affinity to clathrate structure. The concept of CH<sub>4</sub>-CO<sub>2</sub> exchange consists in injecting CO<sub>2</sub> in methane hydrate reservoirs in order to shift the equilibrium and form a CO<sub>2</sub> hydrate in the place of methane hydrate, and to recover methane

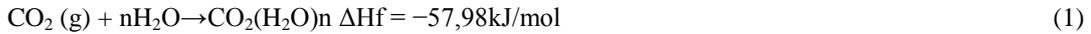
The objective of our work is to study thermodynamic of CO<sub>2</sub>-CH<sub>4</sub> methane hydrate, in presence of salts, and to understand the crystallization mechanism during the replacing of CH<sub>4</sub> by CO<sub>2</sub>. In this paper, we present a set of experimental results in order to validate a thermodynamic model which predicts the equilibrium conditions; Pressure, Temperature and composition of phases in presence of a mixture of CO<sub>2</sub> and CH<sub>4</sub>.

### **2. Advantages of using CO<sub>2</sub> gas for replacement of CH<sub>4</sub> hydrate in sediment**

Firstly, the method consisting to replace the methane in the methane hydrates reservoirs by CO<sub>2</sub> 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<sub>2</sub> hydrates formation (57,98 kJ / mol) is slightly higher than the heat of methane hydrates dissociation (54,49 kJ / mol) (Naval Goel 2006). Therefore, the transformation of methane hydrate into carbon dioxide hydrate is practically athermic:



Where n is hydration number (n about 6).

On Figure 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 to produce the 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<sub>2</sub>-CH<sub>4</sub> gas mixture, the concentration of carbon dioxide in hydrate phase will be more than 90%.

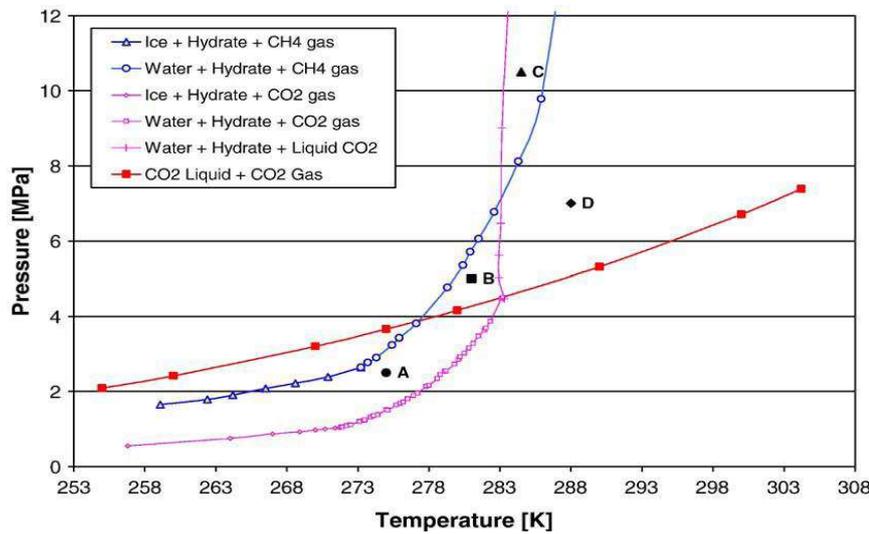


Figure 1. Equilibrium conditions of hydrate CO<sub>2</sub> and CH<sub>4</sub> (Naval Goel 2006)

### 3. Experimental approach

#### 3.1 Materials of experiment

In this work we used two bottle gas of CO<sub>2</sub> and CH<sub>4</sub> (4, 5 in the Figure 2) are provided by Air liquide under high pressure cylinder. The water for experiment is distilled water was obtained from the MILLI-Q 185 PLUS system. In the liquid phase contains LiNO<sub>3</sub> as a tracer (10ppm weight fraction). In this experimental the quantities of materials are:

Table 1 The quantities of material Experiment

Volume Reactor ( liter)	CO2 (mol)	CH4 (mol)	Li <sub>0</sub> <sup>+</sup> (mg/ml)	Water (ml)
2,36	3,026	0,9927	10,4	800,15

#### 3.2 Experimental set-up

The experimental apparatus (Figure 2) is designed to measure the thermodynamic equilibrium points in 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 100 bars. The reactor is equipped with a vertical stirrer with four blades. The stirring rate can vary between 0 and 600

rpm. The temperature is 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 Lithium 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 and pressure is measured with an accuracy of 0.01 MPa in the range 0-10MPa. A ROLSI sampler is mounted on the reactor. It allows to sampling online the gas and to sending the sample into a gas chromatograph (GC Varian model 38002) equipped with a TCD detector and two columns PoraBOND Q and CP-Molsieve. 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.

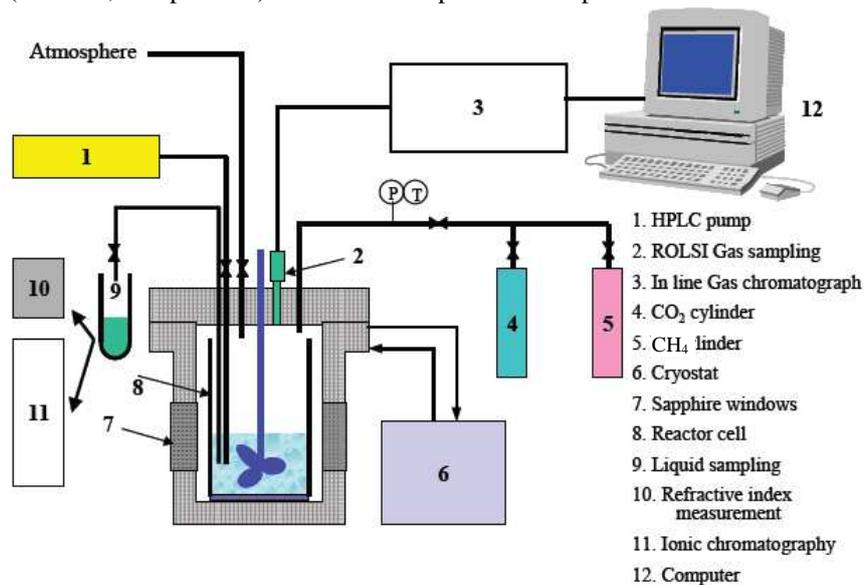


Figure2: Experimental device

### 3.3 Procedure of our experiences

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.

The experiments are realized following 4 steps

Step 1: Injection of pure methane gas.

Step 2: Injection of CO<sub>2</sub> gas.

After the pressure is stable, 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 400 rpm.

Step 3: Injection of water for crystallization of mixed CO<sub>2</sub>-CH<sub>4</sub> hydrates

The stirrer is stopped. Water containing 10ppm of a lithium tracer is added. The volume of the injected solution is controlled, (in this experiment 800,15 ml). Pressure, temperature and gas compositions are monitored. 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.

Step 4: Dissociation of hydrates.

When the system is in equilibrium (temperature and pressure), heating the reactor by the temperature is increased by steps of 1°K until full dissociation of hydrates (Figure 3). During each step, the pressure in the reactor increases due to the dissociation of hydrates and reaches to a constant value which represents the thermodynamic equilibrium, in this time the gas and the liquid phase are sampled to determine the compositions of the phase at equilibrium. 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.

#### 4. Results

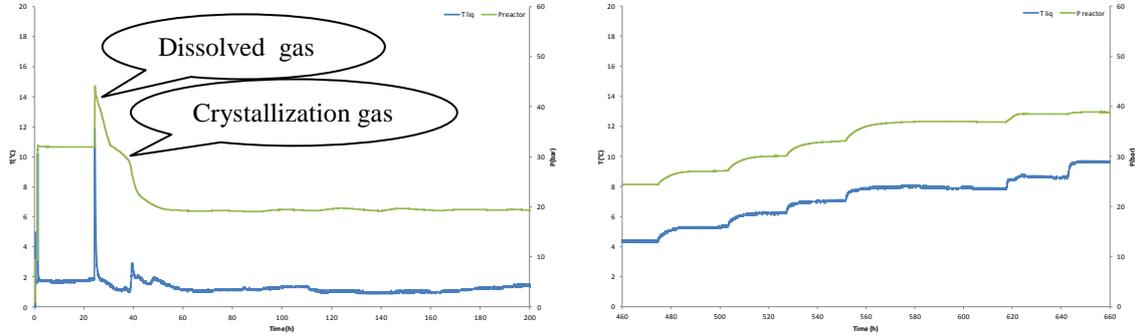


Figure 3 Evolution of pressure and temperature during crystallization and dissociation

According to mass balance of each component, the quantity of CH<sub>4</sub> and CO<sub>2</sub> in different phases can be calculated by the following equations:

$${}^n[\text{CH}_4]^{\text{H}} = {}^n[\text{CH}_4]^{\text{initial}} - {}^n[\text{CH}_4]^{\text{G}} - {}^n[\text{CH}_4]^{\text{L}} \quad (3)$$

$${}^n[\text{CO}_2]^{\text{H}} = {}^n[\text{CO}_2]^{\text{initial}} - {}^n[\text{CO}_2]^{\text{G}} - {}^n[\text{CO}_2]^{\text{L}} \quad (4)$$

$${}^n[\text{CH}_4]^{\text{G}} = {}^n\text{G} \cdot \text{XCH}_4 \text{ in reactor} \quad (5)$$

$${}^n[\text{CO}_2]^{\text{G}} = {}^n\text{G} \cdot \text{XCO}_2 \text{ in reactor} \quad (6)$$

$${}^n\text{G} = \frac{P_{\text{eq}} V^{\text{G}}}{Z_{\text{mixte}} RT} \quad (7)$$

Where: XCO<sub>2</sub> and XCH<sub>4</sub> are the concentration of CO<sub>2</sub> and CH<sub>4</sub> in phase gas

${}^n[\text{CH}_4]^{\text{L}}$ ,  ${}^n[\text{CO}_2]^{\text{L}}$  are calculated by equation from Henry following the correlation of Holder (1980),  ${}^n[\text{CH}_4]^{\text{H}}$ ; and  ${}^n[\text{CO}_2]^{\text{H}}$  are the moles fractions of CH<sub>4</sub> and CO<sub>2</sub> in hydrate phase, respectively;  ${}^n[\text{CH}_4]^{\text{G}}$ ; and  ${}^n[\text{CO}_2]^{\text{G}}$  are the moles fractions of CH<sub>4</sub> and CO<sub>2</sub> in gas phase in the reactor;  ${}^n\text{CH}_4$ ; released and  ${}^n\text{CO}_2$ ;  ${}^n\text{G}$  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.

$$H_i = H_{i,Psat} \exp\left(\frac{v_i^{\infty}(P - P_i^{\text{sat}})}{RT}\right) \quad (8)$$

$$H_{i,Psat} = \exp\left(A + \frac{B}{T}\right) \quad (9)$$

Where  $H_i$  is the Henry coefficient, A and B are constants in table 2

Table 2 Constant for Henry law with correction with Holder (1980)

Gas	A	B	$v_i^{\infty}$ (cm <sup>3</sup> /mol)
CH <sub>4</sub>	15,826277	-559,0631	32
CO <sub>2</sub>	14,283146	-050,3269	32

The volume of liquid in equilibrium is determined by following the concentration of a tracer (Li<sup>+</sup>) in the liquid phase.

$$V_{\text{eq}}^{\text{L}} = \frac{[\text{Li}^+]_{\text{mi}} V_w^0}{[\text{Li}^+]_{\text{eq}}} \quad (10)$$

And

$$V_w^H = V_w^0 - V_w^L = V_w^0 - V_w^0 \frac{[Li^+]_{ini}}{[Li^+]_{eq}} = V_w^0 \left( 1 - \frac{[Li^+]_{ini}}{[Li^+]_{eq}} \right) \quad (11)$$

Where  $V_w^H$ ,  $V_w^0$ ,  $V_w^L$  are the volume of water in hydrate phase, initial and liquid phase at equilibrium.  
 A summary of steps of calculation is presented in the figure 4:

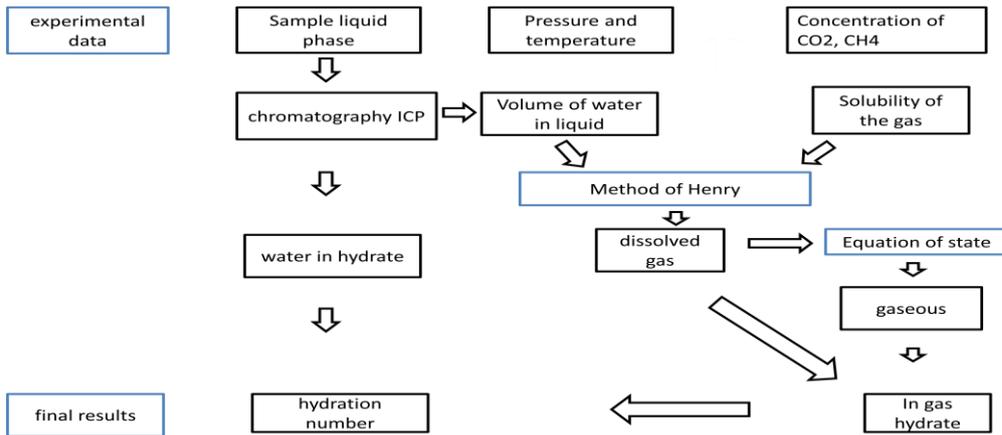


Figure 4 Treatment of data

*Determination of the hydration number of the hydrates at equilibrium:*

Experimentally, we can determine the volume of water (and the number of moles of water) which has reacted to form hydrate. This volume is determined from the difference of the tracer concentration of  $LiNO_3$  being present in the liquid phase between the beginning and equilibrium (Eq. (10)). The number molar of gases ( $n_G$ ) which have been incorporated into the lattice structure of the hydrate are calculated by equation of state (Soave-redlich-kwong). According to this way we can calculate the hydration number of these respective hydrate equilibrium. Table 3 shows Synthetic table the calculation in one experiment, assuming that structure I is formed.

Table 3 Synthetic table the calculation in one experiment

T°K	P <sub>eq</sub> (MPa)	X <sub>CO2</sub>	X <sub>CH4</sub>	M <sub>w</sub> <sup>H</sup>	n <sub>CO2</sub> <sup>LID</sup>	n <sub>CH4</sub> <sup>LID</sup>	n <sub>CO2</sub> <sup>G</sup>	n <sub>CH4</sub> <sup>G</sup>	Li <sup>+</sup> (mg/l)	Z <sub>GAS</sub>	X <sub>CO2</sub> <sup>H</sup>	X <sub>CH4</sub> <sup>H</sup>	N° HYD
275,350	1,920	0,655	0,345	210,387	0,444	0,022	0,944	0,497	14,110	0,908	0,776	0,224	5,536
276,050	2,050	0,776	0,224	224,662	0,537	0,015	1,219	0,352	14,460	0,887	0,670	0,330	6,586
277,150	2,260	0,659	0,341	193,180	0,515	0,025	1,130	0,585	13,710	0,892	0,783	0,217	6,085
277,650	2,440	0,665	0,335	167,332	0,578	0,026	1,242	0,626	13,150	0,883	0,780	0,220	6,007
278,650	2,710	0,670	0,330	134,957	0,662	0,028	1,406	0,692	12,510	0,870	0,779	0,221	6,089
279,650	3,010	0,678	0,322	95,530	0,767	0,030	1,602	0,761	11,810	0,854	0,765	0,235	6,183
280,450	3,310	0,682	0,318	54,491	0,879	0,032	1,799	0,839	11,160	0,839	0,740	0,260	6,455

After perform some experimental with composition difference we have compared these results are with the model from the GasHyDyn software, in the figure 5 shows the phase diagram of hydrate of  $CO_2 - CH_4$  mixture at temperature of 2,2°C. The experimental results are closed to the simulated values and new experiments are still under testing.

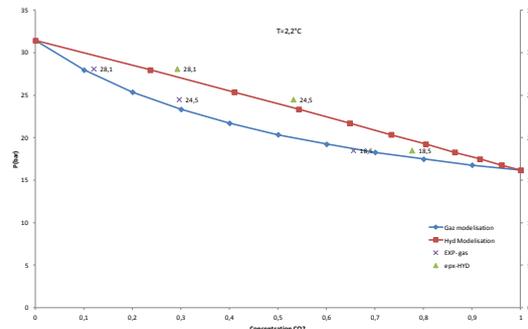


Figure 5 Phase diagram of hydrate CO2 - CH4 mixture at 2.2°C

## **Conclusion**

This work participates to the long term issue to produce methane from methane hydrate bearing sediments. The method consists in injecting CO<sub>2</sub> in sediments and shifting the chemical equilibrium of methane hydrate, to form carbon dioxide clathrate hydrates. So, this thematic belongs to the topic of gas production, but also to CO<sub>2</sub> mitigation

In the work, we presented experimental results about the equilibrium of CO<sub>2</sub>-CH<sub>4</sub> gas mixture. Our experiments indicate that we form a solid in thermodynamic equilibrium with the gas mixture.

The next step is to study the kinetic 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>-CH<sub>4</sub> hydrate following the equilibrium given in (figure 3). It will allow us, after developing a suitable model to quantify the kinetics of conversion of a solid phase to another solid phase.

After, we want to build a new device which will crystallize methane hydrates in porous media, following the procedure that we have experimented in Tonnet and Herri (2009). These hydrates are then subjected to a flow of CO<sub>2</sub> 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 participates to the development of new technologies taking profit of the physical properties of gas hydrates.

Among the new technologies we are developing, we can also cite the CO<sub>2</sub> 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, 1999a, 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 is also specialised on the determination of physical properties of gas hydrates, such as Hamaker constant with application to the evaluation of agglomeration (Bonney et al, 2005a) or determination of refractive index (Herri and gruy, 1996; Bonney et al, 2005) with application to the conception of particle sizes (Herri et al, 1999a).

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## Une méthode de calculer la composition d'un hydrate mixte CO<sub>2</sub>-CH<sub>4</sub>, à l'équilibre et au cours de la cristallisation

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### Résumé

Le concept de remplacement de méthane par le dioxyde de carbone dans les gisements d'hydrates de gaz naturel est considéré comme une façon possible de produire du méthane et de piéger le CO<sub>2</sub> (Ohgaki et al 1996; 1996 Hirohama et al.). Il peut être considéré comme une nouvelle technologie de production du méthane à côté des autres technologies possibles de stimulation thermique, injection chimique ou dépressurisation.

Le méthane des clathrates d'hydrates sont des solides dans lesquels l'eau se structure en un réseau de 3 dimensions créant des cavités libres pouvant piégées des molécules de gaz. Le méthane est un composant naturel dans les sédiments dont l'origine est la dégradation thermique des réservoirs fossiles ou de biodégradation des matériaux biologiques. Sous la pression et dans des conditions de mer profonde, des gisements d'hydrates de méthane se sont formés dans de nombreux endroits du monde en très grandes quantités. Le concept de production de méthane, présenté dans cette étude, consiste à injecter du CO<sub>2</sub> dans les gisements d'hydrates de méthane déplaçant ainsi les équilibres. Un hydrate de CO<sub>2</sub> (ou mixte CO<sub>2</sub>-CH<sub>4</sub>) sera alors formé à la place de l'hydrate de méthane, et le méthane pourra être ainsi récupéré. Ce travail a comme objectif d'étudier, dans un premier temps, la thermodynamique des hydrates mixtes CO<sub>2</sub>-CH<sub>4</sub>, en présence de sels. Cela va permettre de connaître les mécanismes de cristallisation pendant le remplacement du CH<sub>4</sub> par le CO<sub>2</sub>. Nous présentons ici, un ensemble de résultats expérimentaux qui nous a permis de valider un modèle thermodynamique qui prédit les conditions d'équilibre (pression, température) et les compositions des phases (gaz, liquide, hydrate) dans les cas des hydrates mixtes CO<sub>2</sub>-CH<sub>4</sub>.

**Mots-clés:** Hydrates de méthane, cristallisation, gaz, CH<sub>4</sub>-CO<sub>2</sub>

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