

FORMATION AND DISSOCIATION OF CO₂ AND CO₂ – THF HYDRATES COMPARED TO CH₄ AND CH₄ - THF HYDRATES.

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ABSTRACT

This work is part of a research project sponsored by the Italian Electricity Agency for CO₂ disposal in form of hydrate. The dissociation behavior of CH₄ hydrate was taken as a reference for the study of the CO₂ hydrate preservation. The formation and dissociation of CO₂ and CO₂-THF mixed hydrates, compared to CH₄ and CH₄ – THF mixed hydrates, has been considered.

The experimental tests were performed in a 2 liter reaction calorimeter at pressures between 0.1 and 0.3 MPa. The dissociation has been followed at temperatures from -3 °C to 0 °C for CO₂ and CH₄ hydrates, and from -3 °C to 10 °C for THF mixed hydrates.

More than pressure, which is very important for methane hydrates, temperature affects the preservation of CO₂ and CO₂-THF mixed hydrates. Subcooling after formation is important for methane hydrate preservation, but it does not substantially affect CO₂ hydrate stability. In the studied P, T range, CO₂ hydrate does not present any anomalous self-preservation effect. The mixtures containing more ice show a slower dissociation rate. Methane hydrate requires less energy to dissociate than CO₂ hydrate and, therefore, is less stable. On the contrary, the mixed CO₂ – THF hydrates are less stable than the mixed methane hydrates. Modulated differential scanning calorimetry (MDSC) has been used for hydrate characterization: both CH₄ and CO₂ hydrates include two decomposition peaks, the first due to the melting of the ice and the second to the decomposition of the hydrate. The higher temperature of the decomposition peak of CO₂ hydrate confirms its higher stability respect to CH₄ hydrate.

Keywords Hydrate, CO₂, THF, CH₄, dissociation rate, MDSC

INTRODUCTION

Carbon sequestration is defined as the removal of greenhouse gases from industrial or utility plant

streams and their longterm storage in a way they cannot interact with the climate system. Various methods for selective CO₂ removal have been suggested, and some of them based on gas absorption, membrane process, cryogenic

fractionation, are in commercial use. Disposal of captured CO₂ in the ocean and in geological reservoirs has been proposed by many investigators[1–3].

Another challenge is to take advantage of the properties of CO₂ hydrates for carbon sequestration. The formation of CO₂ hydrates has been studied by a number of research groups.[4–12] A hydrate-based gas separation process has been proposed for CO₂ recovery from flue gases.[13]

Carbon dioxide and water form a stable system when pressure and temperature fall within the hydrate formation region ($P > 4.5$ MPa and $T < 283$ K); in the ocean, a long-lived system is formed (at higher P and lower T) only when seawater is saturated with respect to CO₂ [3,14]. The capacity and effectiveness of ocean sequestration can be increased by injecting CO₂ into deep sediments: a few hundred meters of sediments provide permanent geologic storage; additionally, CO₂ hydrate formation will impede the flow of liquid CO₂ [1].

The potential of CO₂ sequestration is also offered by disposal into caves or depleted natural gas reservoirs [15]. In this case a large amount of CO₂ could be potentially fixed by artificial rock weathering: the calcium silicate component of wollastonite reacts with carbonate ions and becomes CaCO₃ and silicate [16]. However, the reaction kinetics are very slow; therefore CO₂ should be released slowly from a storage system so that it could gradually react with the rock. The CO₂ hydrate should possibly provide such gradual release of the gas.

In the form of hydrate, CO₂ could have a number of uses (chemical production, greenhouse gas, etc.) or can be disposed in suitable geological environments. In any case it is important to understand the hydrate decomposition kinetics during storage, transportation, and disposal.

CO₂ hydrate crystallizes in the same structure (sI) of the methane hydrate, at relatively high pressure and low temperature.

The present work is part of a project aimed at the separation of carbon dioxide from the flue gases of powers plants, in the form of hydrate. The project also includes the storage, use, and disposal of the hydrate.

The main purpose of the work is the evaluation of the decomposition kinetics of CO₂ hydrate containing different quantities of ice, at low pressures (0.1–0.3 MPa) and temperatures between

-3 and 0 °C. The formation is studied at moderate pressures, more economical in the hypothesis of future industrial applications. A further purpose of the work is to compare the chemical species CH₄ and CO₂ during the hydrate formation and decomposition.

Moreover, in the present work the influence of THF on the formation and decomposition kinetics of mixed THF-CH₄ and THF-CO₂ hydrates has been studied in order to evaluate the THF stabilization effect. Preservation tests were carried out to determine the best pressure and temperature conditions for the mixed-hydrates conservation, with reference to the simple hydrates.

APPARATUS

The experimental apparatus for the formation and dissociation tests consists of a jacketed stainless steel reactor (RC1-Mettler Toledo) with an internal volume of about two liters, equipped with stirrer. A schematic view of the apparatus is shown in Figure 1. Pressure, temperature and stirrer revolutions are transmitted to a computer through a data acquisition board and are recorded at 3 second intervals; the instrument accuracy is $P \pm 0.001$ % MPa, $T \pm 0.1$ % °C. For hydrate formation, CO₂ gas (99.9%) is supplied from a cylinder bottle in the reactor containing the required amount of distilled water. An external oil circulation loop is attached to the chamber; the rate at which cold fluid flows through this loop is controlled by a plunger pump.

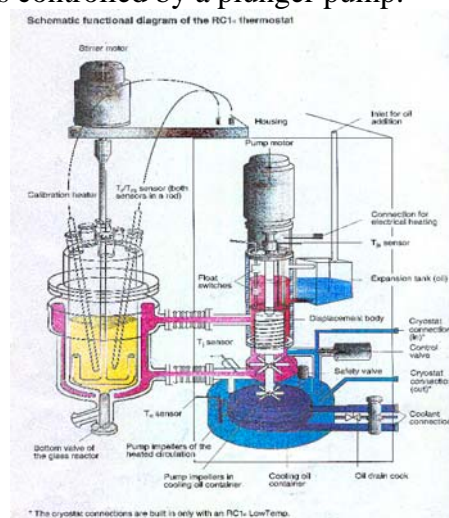


Figure 1. Schematic of the RC1 experimental apparatus.

HYDRATE FORMATION PROCEDURE

CO₂ hydrate formation.

Each experimental run starts by supplying about 570 g of water to the evacuated reactor chamber; the reactor is pressurized with carbon dioxide to 2 MPa, at 10°C. Stirring is then started at 100 rpm to dissolve CO₂ into water. The solubility is detected by a pressure decrease to about 1.8 MPa and a small temperature increase. After two repressurization steps to 2.0 MPa, the pressure remains stable and the water is saturated. CO₂ is a hydrophilic molecule more soluble into water than methane; this procedure is necessary to separate (during the following phases of the experimental run) the phenomena due to CO₂ solubilization and to hydrate formation, respectively. Moreover, the dissolved CO₂ provides the starting phase for the hydrate nucleation. The temperature is then lowered to 2°C to enter the hydrate stability zone in the equilibrium diagram, and stirring is increased to 400 rpm. Hydrate formation begins immediately and is detected by a pressure decrease, and a temperature increase from 2°C to 4°C (Fig. 2). To speed the formation rate, the reactor is repressurized to 20 MPa before reaching the equilibrium pressure at that temperature. The pressure curve in Figure 2 shows a series of repressurization steps whose amplitude (pressure drop) is correlated to the amount of CO₂ moles engaged by the hydrate lattice; the same amount can be calculated on the basis of the pressure decrease during the decomposition tests.

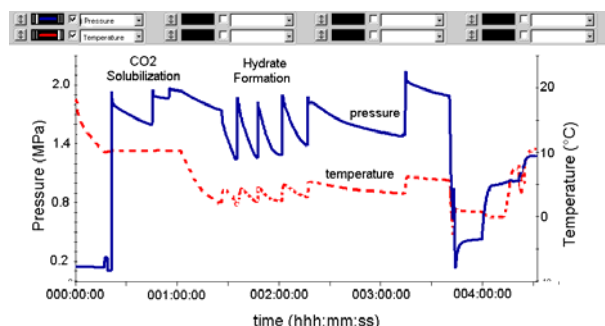


Figure 2. CO₂ hydrate formation from bulk water (570 ml). The upper curve refers to the pressure; the lower dotted curve refers to the temperature.

During the various repressurization steps (clearly visible in both curves), the pressure drop is progressively decreased due to the solid hydrate

formation. Figure 2 shows that after 5 steps and about 20 minutes from the starting of the experiment, the pressure decrease tends to be much slower, and from a practical point of view the reaction can be considered quite complete: the corresponding experimental pressure and temperature values are respectively 1.95 MPa and 4.8 °C, that is slightly outside the stability region of the equilibrium diagram.

CH₄ hydrate formation.

Each experimental run starts by supplying about 570 g of water to the evacuated reactor chamber; the reactor is then pressurized with methane to 4.5-5.5 MPa and the temperature lowered to the desired level (1 °C). Stirring is then started at 500-600 rpm.

Hydrate formation begins immediately after stirring is started and is shown by a pressure decrease and a small temperature increase due to reaction exothermicity [17] (Figure 3). The amount of formed hydrate can be calculated from the pressure drop. Small variations of pressure and stirring rate produce different hydrate concentrations, in the range 30-70% (hydrate conversion respect to water).

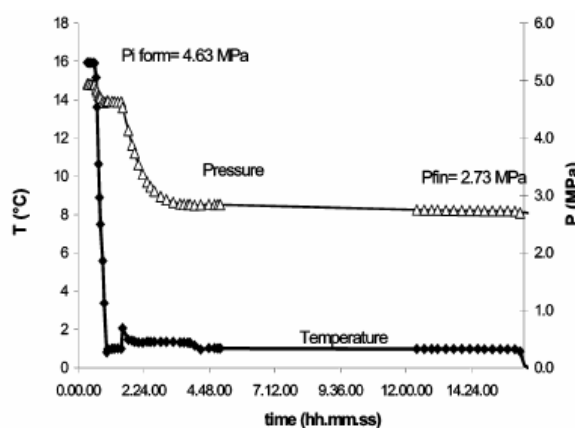


Figure 3. Methane hydrate formation from bulk water. The start of stirring is indicated by a sharp pressure drop, corresponding to the hydrate formation at 4.63 MPa.

CO₂ - THF hydrate formation..

CO₂-THF hydrates are formed by filling the reactor with about 750 g of THF solution (19% THF by weight) and pressurizing the reactor to about 2.0 – 2.2 MPa, with carbon dioxide.

CO₂-THF hydrate formation is shown in Figure 4

with a conversion of about 30%. The conversion is calculated on the basis of the amount of water fed into the reactor. By applying similar pressure conditions during the formation of both simple and mixed clathrates, the amount of entrapped gas in simple CO₂ hydrate is higher with respect to CO₂-THF hydrates.

The temperature increase in the simple hydrate is higher: 6°C against 2°C for mixed hydrate.

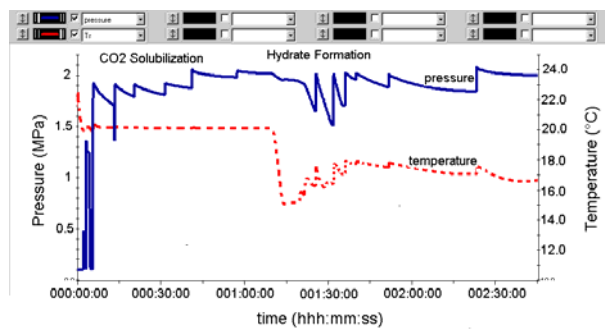


Figure 4. CO₂ - THF hydrate formation from bulk water (570 ml). The upper curve refers to the pressure; the lower dotted curve refers to the temperature.

CH₄ - THF hydrate formation.

CH₄-THF hydrates are formed by filling the reactor with about 750 g of THF solution (19% THF by weight) and pressurizing the reactor to about 4.5 - 4.8 MPa, with methane.

CH₄-THF hydrate formation is shown in Fig. 5, (conversion 30%). The conversion was calculated with the same method of CO₂ - THF hydrate procedure.

Also in this case the amount of entrapped gas in simple CH₄ hydrate is higher with respect to mixed hydrates.

The temperature increase in the CH₄-THF hydrate is higher: 8°C against 2°C for simple CH₄ hydrate (see Fig. 3 and 5).

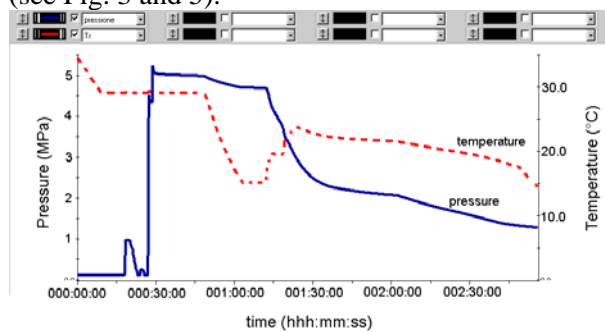


Figure 5. CH₄ - THF hydrate formation from bulk water. The solid curve refers to the

pressure; the dotted curve refers to the temperature.

HYDRATE CHARACTERIZATION.

When the amount of added water is known, the percentage of hydrate in the sample can be calculated from the pressure drop during the hydrate formation (and/or from the pressure increase during decomposition). Modulated differential scanning calorimetry (MDSC) can be used for hydrate characterization [17, 18]. With respect to conventional DSC, one of the major contributions of this technique is that the total heat flow rate can be separated into two additional signals [19]. The first one is directly correlated to the heat capacity of the material, while the second one is a function of temperature and time characteristics of the tests. These terms can be plotted separately in two curves. In the present work, MDSC tests were performed at atmospheric pressure following the procedure described in previous papers [17, 18].

The reactor temperature was lowered to -20 °C; the reactor was then depressurized and opened. A sample was then quickly transferred to the MDSC pan kept in a container at -20 °C. For the test, the pan was again transferred to the MDSC apparatus and kept at -20 °C.

A typical MDSC reversing (heat capacity) curve of a sample containing about 40% of CO₂ hydrate (respect to the near ideal stoichiometry) is shown in Figure 6 and can be compared to the methane hydrate curve in Figure 7. The curve in Figure 6 includes two peaks with apexes at -0.56 and 10.20 °C, respectively. The first peak is due to the melting of the ice and the second to the decomposition of the hydrate. The corresponding peaks of the CH₄ hydrate (Figure 7) are at -0.23 and 4.47 °C, respectively. The higher temperature of the decomposition peak of CO₂ hydrate confirms its higher stability with respect to CH₄ hydrate.

Methane hydrate requires less energy (about 54 kJ/mol) than CO₂ hydrate to dissociate and, therefore, is less stable [20]. Two chemically different molecules such as carbon dioxide and ethane (polar and not polar, respectively) show similar heats of dissociation (ΔH 73 and 72 kJ/mol, respectively [21, 22]).

The activation energies for the decomposition of CH₄, C₂H₆, and CO₂ hydrates decomposition are respectively 81, 104, and about 103 kJ/mol [23];

these values confirm the higher stability of CO_2 and C_2H_6 hydrates with respect to CH_4 hydrate. Kuhs et al. have found differences in the degree of perfection of ice produced from decomposing CH_4 and CO_2 hydrates, with the latter showing less imperfection and, therefore, better preservation below 0°C [24, 25]. At temperatures higher than 0°C , the solubility of carbon dioxide in liquid water probably influences the decomposition rate.

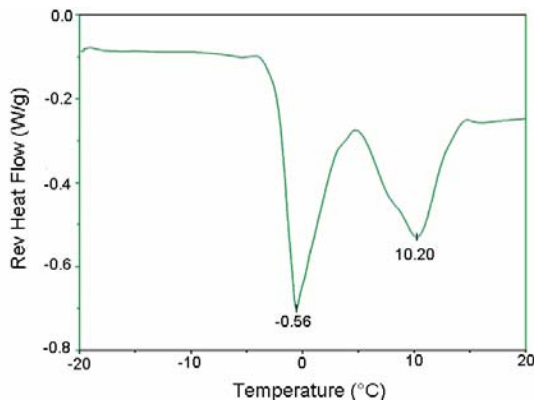


Figure 6. Typical MDSC curve (reversing heat flow) of CO_2 hydrate containing about 40% CO_2 . The first peak is due to ice melting while the second peak is referred to hydrate dissociation.

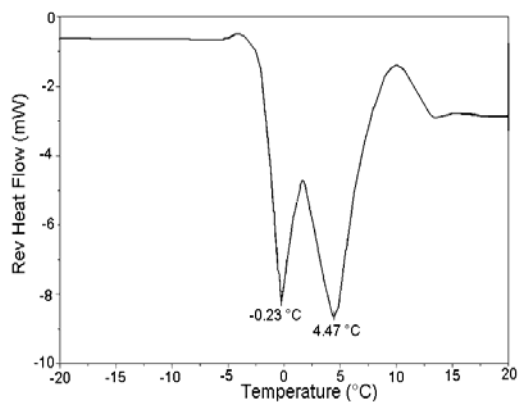


Figure 7. Typical MDSC curve (reversing heat flow) of CH_4 hydrate containing about 40% CH_4 . The first peak is due to ice melting while the second peak is referred to hydrate dissociation.

Figure 8 shows the reversing curve of CO_2 -THF hydrate; the curve includes different peaks with apexes at -1.9°C , 6.1°C and 14.8°C , respectively. The first peak is due to the melting of the solid ice + THF hydrate eutectic, the second to the decomposition of CO_2 -THF hydrate; the third peak is due to the partial vaporization of THF.

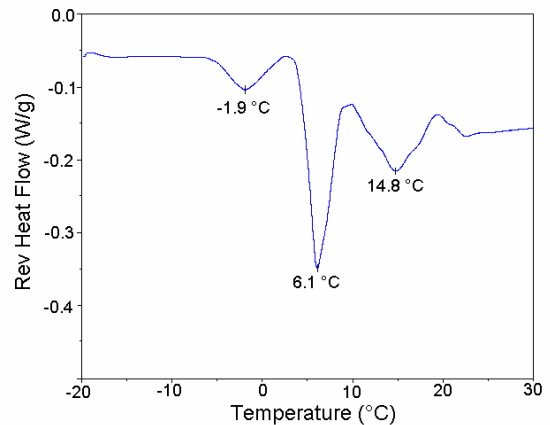


Figure 8. Typical MDSC curve (reversing heat flow) of CO_2 -THF hydrate. The first peak is due to solid eutectic melting, the second peak is referred to CO_2 -THF hydrate dissociation and the following peaks are due to the partial vaporization of THF.

Figure 9 shows the reversing curve of CH_4 -THF hydrate. The curve includes three peaks with apexes at -1.76°C , 8.47°C and 17.89°C respectively. The first peak is due to the melting of the ice+THF hydrate eutectic, the second to the decomposition of the CH_4 -THF hydrate; the following peaks are due to the partial vaporization of THF.

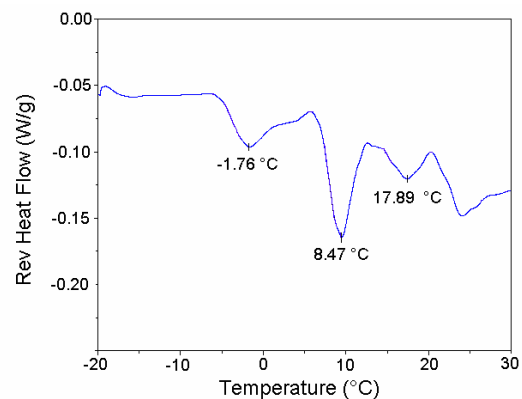


Figure 9. Typical MDSC curve (reversing heat flow) of CH_4 -THF hydrate. The first peak is due to solid eutectic melting, the second peak is referred to CH_4 -THF hydrate dissociation, and the following peaks are due to the partial vaporization of THF.

HYDRATE DISSOCIATION TESTS.

The hydrate dissociation tests are conducted immediately after hydrate formation in the reactor. In order to check how such a procedure affects the preservation, some samples are subcooled to $-20\text{ }^{\circ}\text{C}$ before the dissociation tests. During the tests, temperature and pressure are set at non equilibrium conditions, i.e. at pressures between 0.1 and 0.3 MPa and temperatures between $-4\text{ }^{\circ}\text{C}$ and $0\text{ }^{\circ}\text{C}$ for the simple hydrates, and between $-4\text{ }^{\circ}\text{C}$ and $10\text{ }^{\circ}\text{C}$ for the hydrates with THF. The experimental apparatus permits a rapid control of the temperature and pressure. After the desired temperature is reached, the reactor is depressurized to the required pressure; the rate of dissociation is then measured following the pressure increase. After one hour, the temperature is increased again and the step is repeated. The dissociation rate can be calculated from the various step of the pressure curve.

Results and Discussion

Previous experiments have shown that methane hydrate dissociation depends, besides on storage temperature and pressure, on the gas saturation and on the previous thermal history (subcooling) of the samples [26]. Methane hydrate can be preserved metastably in bulk at 0.1 MPa (or better at 0.3 MPa) at temperatures slightly below $0\text{ }^{\circ}\text{C}$. The present experiments have confirmed that, at the conditions (P , T) of this work, the dissociation of CO_2 hydrate does not show any anomalous self preservation effect. In the following discussion, the dissociation rate is expressed as percent of gas moles lost with respect to the gas moles in the hydrate, over a time of 1 s.

Correlation between hydrate dissociation and P/T Parameters.

Table 1 reports, as an example, the dissociation rates of CO_2 hydrate (30%) at different temperatures and pressures. For a more immediate comprehension, the table also reports the time necessary to fully dissociate the samples. As expected, the dissociation rates increase with the temperature and decrease at higher pressures.

Pressure	Dissociation rate (%mol/sec)				Days to complete dissociation			
	Temperature				Temperature			
	$-3\text{ }^{\circ}\text{C}$	$-2\text{ }^{\circ}\text{C}$	$-1\text{ }^{\circ}\text{C}$	$0\text{ }^{\circ}\text{C}$	$-3\text{ }^{\circ}\text{C}$	$-2\text{ }^{\circ}\text{C}$	$-1\text{ }^{\circ}\text{C}$	$0\text{ }^{\circ}\text{C}$
1 bar	4.37E-05	1.70E-04	5.15E-04	1.12E-03	26	7	2	1
2 bar	4.37E-05	9.46E-05	4.12E-04	6.39E-04	26	12	3	2
3 bar	4.E-05	7.92E-05	2.56E-04	3.81E-04	29	15	5	3

Table 1. Dissociation Rates and days required for complete dissociation of CO_2 hydrate samples.

Comparison between dissociation of CO_2 hydrate and CH_4 hydrate.

In the case of methane, both subcooled (to $-8\text{ }^{\circ}\text{C}$) and not-subcooled samples are considered; this is not necessary for CO_2 because the behavior of subcooled and not-subcooled samples is similar. The CH_4 hydrate decomposition at $0\text{ }^{\circ}\text{C}$ is too fast to be detected and is not reported. In the considered temperature range, CO_2 hydrate is more stable than CH_4 hydrate at both 0.1 and 0.2 MPa (not reported), and its decomposition can be detected up to $0\text{ }^{\circ}\text{C}$ (Figure 10).

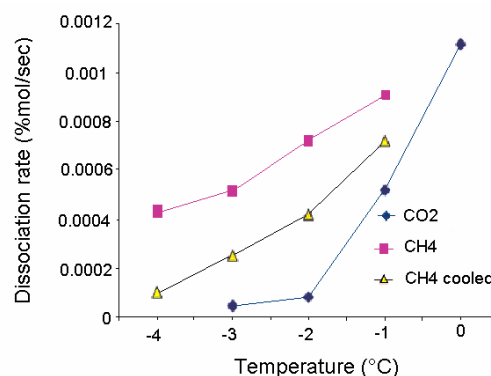


Figure 10. Comparison between dissociation rate of CO_2 and CH_4 hydrates stored at 0.1 MPa in the temperature range -4 to $0\text{ }^{\circ}\text{C}$.

At the temperature of $0\text{ }^{\circ}\text{C}$ the hydrate dissociation gives CO_2 and liquid water, instead of ice: the formation of liquid water is the key permitting rapid and complete breakdown of the hydrate [10]. The dissociation rate of the hydrate is influenced by the CO_2 concentration in bulk water [27], which is much higher than the methane concentration. Therefore, the CH_4 hydrate dissociation is faster than CO_2 hydrate.

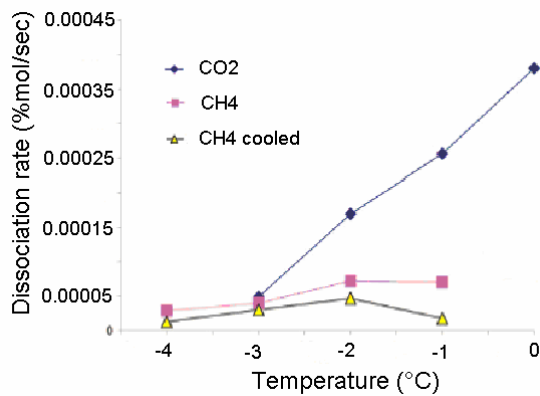


Figure 11. Comparison between dissociation rate of CO₂ and CH₄ hydrates stored at 0.3 MPa in the temperature range from -4° C to 0 °C.

With respect to methane, molecules such as CO₂ form more stable hydrates structures due to the different cavity occupation [20] and to their higher activation energies of decomposition [23]. The preservation of CO₂ hydrates is less influenced by pressure, which is more important in “keeping” the methane molecules inside the cages. Subcooling introduces “perfection” in the ice cages and contributes to stabilize the CH₄ hydrate more than the CO₂ hydrate [23, 24].

Differences between methane hydrates and THF - methane hydrates.

Figure 12 compares the dissociation rates of CH₄-THF hydrates and the dissociation rates of CH₄ hydrate at 0.1 and 0.3 MPa, also considering the temperatures below zero degrees.

The dissociation of methane hydrate sharply increases with temperatures up to -1°C; over this temperature the rate is so fast that can not be measured. It is interesting to notice that in the low temperature ranges (below -3°C) the influence of THF is negligible. At a pressure of 0.1 MPa, methane hydrate decomposes very rapidly while is quite stable at 0.3 MPa and at temperatures below -3°C.

At 0.3 MPa and -3°C the rates are similar, while at higher temperatures (e.g. -1°C) the decomposition of THF/CH₄ hydrate is about five times lower.

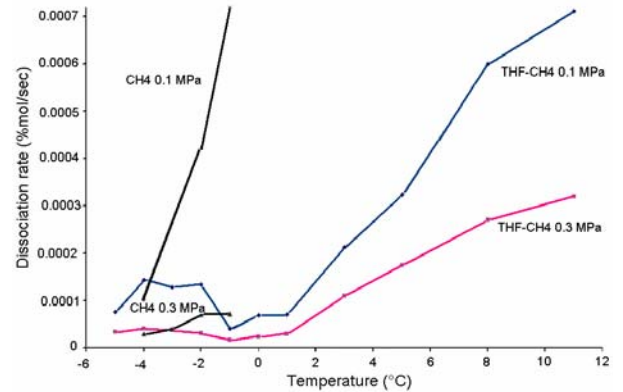


Figure 12. Comparison between the dissociation rates of CH₄ hydrate and THF-CH₄ mixed hydrates at 0.1 and 0.3 MPa.

The minimum value reached at -1°C by the mixed hydrates corresponds to the melting of the THF hydrate/ice eutectic [28]. The energy necessary for the endothermic melting of the eutectic is taken from the heat necessary for mixed hydrate decomposition and that probably helps their preservation; in fact, the corresponding decomposition rate is the lowest.

To give a more immediate and practical idea of these data, Table 2 shows how many days are necessary to fully dissociate the simple and mixed methane hydrates at 0.3 MPa and at various temperatures.

T	v (%mol/sec)		100% dissociation (days)	
	CH ₄ Hydrates	THF/CH ₄ Hydrates	CH ₄ Hydrates	THF/CH ₄ Hydrates
-4	2.90E-05	9.58E-05	40	12
-3	4.00E-05		29	
-2	7.00E-05	5.93E-06	17	195
-1	7.20E-05		16	
0		2.45E-05		47
3		1.10E-04		11
5		1.75E-04		7
8		2.70E-04		4
11		3.20E-04		4

Table 2. Dissociation rate and time required for the dissociation of CH₄ and mixed THF/CH₄ hydrates (30% conversion).

It appears that the best preservation conditions can be obtained slightly below zero °C (e.g. -1°C): in this case, 66 days are necessary for complete dissociation, against less than 16 days for methane hydrate.

Mixed hydrates could be stored for short periods at low pressures and at temperatures slightly over zero °C; this is not practically possible for methane hydrates.

Differences between carbon dioxide hydrates and THF – carbon dioxide hydrates.

Figure 13 compares the dissociation rates of CO₂ hydrates and CO₂-THF hydrates in a temperature range from -6°C to 4.5°C.

At temperatures below 0°C, the CO₂ hydrate is more stable than the CO₂-THF hydrate (e.g. at -4°C the CO₂ hydrate dissociation rate is one order of magnitude lower than CO₂-THF hydrate).

However, the dissociation rate of CO₂-THF hydrate shows a minimum at 0°C due to the eutectic (THF hydrate-ice) melting. At temperatures above the ice melting point, the dissociation rate gradually increases in a way similar to CH₄ mixed hydrates.

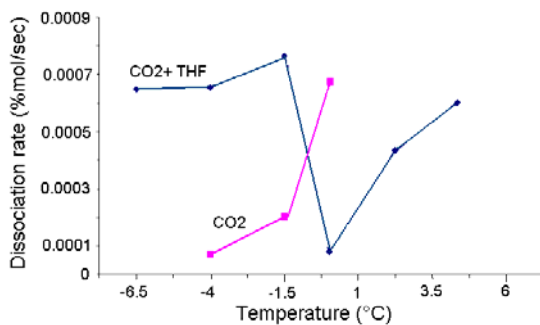


Figure 13. Comparison between the dissociation rates of CO₂ hydrate and THF-CO₂ mixed hydrates, at 0.1MPa.

Differences between THF – CO₂ hydrate and THF – CH₄ hydrate.

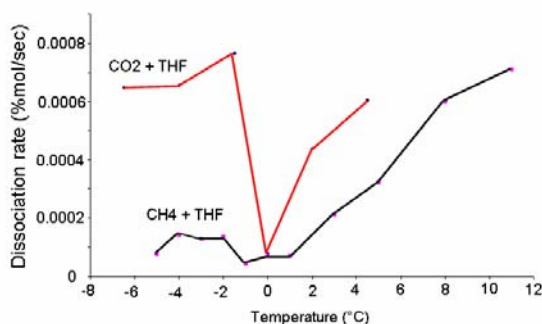


Figure 14. Comparison between the dissociation rates of THF-CH₄ hydrate and THF-CO₂ mixed hydrates at 0.1MPa.

Figure 14 compares the dissociation rates of THF-CH₄ hydrate and THF-CO₂ hydrates. The

dissociation rate of THF-CO₂ is normally higher respect to the THF-CH₄ hydrate. In this case a clathrate structure formed by two hydrophilic guest species is less stable respect to the hydrates formed by one hydrophobic and one hydrophilic specie. The minimum of both curves is given by the eutectic (THF hydrate-ice) melting.

Conclusion.

This work on CO₂ hydrate formation and dissociation was conducted to study its potential for the application in carbon sequestration at low pressures.

The THF-CH₄ and THF-CO₂ hydrates were also considered to study the potential of THF in natural gas and carbon dioxide storage and transportation. The hydrates containing THF can be stored at temperature higher than 0°C, even though for shorter periods. This is not possible for the simple hydrates. The presence of other solid components besides the hydrates (e.g. eutectic in the THF/water system and ice in the THF-CO₂ hydrates) probably plays a role in the conservation at low temperatures.

The hydrophilic and hydrophobic nature of the guest causes a different behavior during the dissociation: in fact, the CO₂ hydrate is more stable than CH₄ hydrate; however, this dissociation trend is inverted when CO₂ and CH₄ are transformed into hydrates in the presence of THF.

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