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## **CO<sub>2</sub> REMOVAL FROM A CO<sub>2</sub> – CH<sub>4</sub> GAS MIXTURE BY HYDRATE FORMATION: EVALUATION OF ADDITIVES AND OPERATING CONDITIONS**

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### **ABSTRACT**

This paper presents an experimental study of CO<sub>2</sub> capture by means of gas hydrate crystallization, which seems to be a promising alternative to conventional processes for removal of CO<sub>2</sub> from natural gas streams, especially when the CO<sub>2</sub> is to be reinjected in a geological formation. The gas phase used here is a mixture of 25 mol% CH<sub>4</sub> and 75 mol% CO<sub>2</sub>. Different mixtures of kinetic and thermodynamic additives (sodium dodecyl sulfate, SDS, and tetrahydrofuran, THF) dissolved in water are used with the aim to accelerate the hydrate formation and to enhance CO<sub>2</sub> capture selectivity. The experiments are performed in a batch reactor under quiescent conditions. The composition of the gas phase is monitored by gas chromatography in the course of the experiments. The influence of THF concentration and operating conditions (particularly the load pressure) has been evaluated on the gas mixture solubility, the hydrate formation kinetics and the CO<sub>2</sub> capture selectivity. The results show that THF (used in combination with SDS) plays a key role in the hydrate formation process and does not influence the CO<sub>2</sub> capture selectivity, at least in the range of concentrations studied. It is also shown that decreasing the gas loading pressure improves the selectivity of CO<sub>2</sub> capture.

*Keywords:* gas hydrates, CO<sub>2</sub> capture, gas separation, additives, THF, SDS, natural gas

### **INTRODUCTION**

In 2009, the consumption of natural gas in the world was close to three trillions cubic meters [1]. Carbon dioxide (CO<sub>2</sub>) is encountered in an increasing number of natural gas fields and it must be removed to improve the heating value of the gas or meet pipeline specifications.

There are many ways to remove CO<sub>2</sub> from natural gas, such as absorption, adsorption, cryogenic fractionation and membrane separation. These processes have been proven successful for the selective removal of CO<sub>2</sub>, but their major drawback is their large energy costs [2].

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The capture of CO<sub>2</sub> by means of gas hydrate crystallization appears to be a cost-effective technological alternative for CO<sub>2</sub> removal from natural gas streams, especially when the CO<sub>2</sub> is to be reinjected in a geological formation. In fact, the costs needed for the reinjection are considerably reduced, since the capture process is carried out at high pressure.

Clathrate hydrates are non-stoichiometric crystalline inclusion compounds consisting of a network of hydrogen – bonded water molecules, in which different types of low molecular weight compounds can be enclathrated when the appropriate conditions of moderately low temperature (a few degrees above 0 °C) and high pressure (in the range of a few MPa) are met [3,4]. When hydrate crystals are formed from a gas mixture, the composition of the hydrate is different from that of the original mixture, i.e., the hydrate phase is enriched with one of the gas components. For this reason, gas hydrate crystallization can potentially be used as a separation process for CO<sub>2</sub> capture [5].

In the case of CO<sub>2</sub> – CH<sub>4</sub> gas mixtures, the hydrate phase boundaries for these pure components are relatively close which render difficult their separation by means of hydrate crystallization [6,7]. The slow kinetics of hydrate formation is another bottleneck. However, previous studies have reported that under appropriate pressure and temperature conditions hydrates formed from a CO<sub>2</sub>-CH<sub>4</sub> mixture contain more than 90 mol% CO<sub>2</sub> when the equilibrium vapor phase composition is in the range of 40 mol% CO<sub>2</sub> [8,9]. On the other hand, CO<sub>2</sub> uptake by gas hydrate formation proceeds more quickly than the methane uptake [6,10].

One of the possibilities to promote or enhance hydrate formation is the use of chemical additives. Conventionally, water-soluble additives are classified either as kinetic or as thermodynamic additives. The latter, which typically consist of organic compounds such as cyclic ether or quaternary ammonium salts, have the tendency to displace the equilibrium conditions towards higher temperatures or lower pressures [3,4]. Kinetic additives consist typically of surfactant molecules and have the effect to accelerate hydrate formation.

Sodium dodecyl sulfate (SDS) is an anionic surfactant which has been widely studied and used as a kinetic hydrate promoter. Gayet *et al.* (2005) [11] and Kalogerakis *et al.* (1993) [12] noted that a small concentration of SDS added to the aqueous phase drastically increases the kinetics of methane hydrate formation, without changing the hydrate equilibrium conditions.

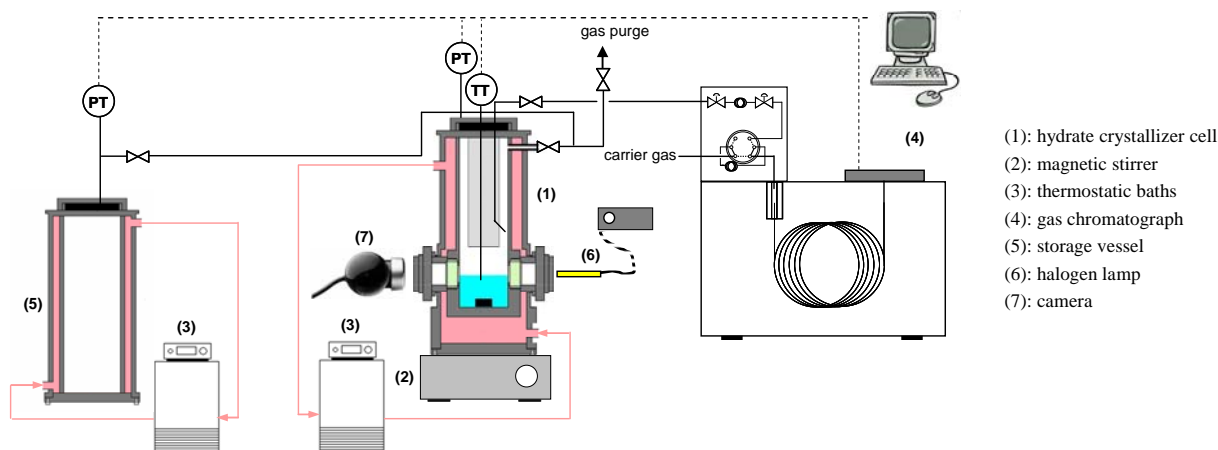
Various studies [13,14] report a significant reduction of hydrate equilibrium pressures at a given temperature by adding small amounts of tetrahydrofuran (THF) in the aqueous phase. For instance, 1 mol% THF has been shown by Lee *et al.* (2009) [5] to be the optimum concentration to promote the CO<sub>2</sub> separation from CO<sub>2</sub> – H<sub>2</sub> gas mixture via hydrate crystallization. Recently, Liu *et al.* (2008) [15] and Torr e *et al.* (2011) [16] showed that THF and SDS used in combination are efficient additives for promoting CO<sub>2</sub> hydrate formation.

This paper presents a study of the influence of THF concentration and gas loading pressure on CO<sub>2</sub> capture by hydrate formation from a CO<sub>2</sub>-CH<sub>4</sub> gas mixture. The range of THF concentrations and gas loading pressures investigated in this study were 0 – 4 wt% THF and 30.1 – 46.4 bar, respectively. In all experiments, SDS is used at the concentration of 3000 ppm and the target temperature is 2°C: these parameters are based on a previous study performed in this laboratory with pure CO<sub>2</sub> as the gas phase [16].

## EXPERIMENTAL SECTION

### Materials

The gas mixture containing CO<sub>2</sub> (75 mol%) and CH<sub>4</sub> (25 mol%) was supplied by Air Liquide, France. Tetrahydrofuran (THF) (purity > 99.9%) and sodium dodecyl sulfate (SDS) were supplied by Sigma - Aldrich, France and Chem Lab, Belgium, respectively. The solutions were prepared with ultra-pure water (18.2 mΩ\*cm), produced in this laboratory by a PureLab Classic<sup>®</sup> from ELGA Labwater, France. An electronic balance with a readability of ± 0.001 mg is used to weigh the mass of water and additives required for preparing the solutions.



**Figure 1.** Schematic diagram of the experimental setup

## Apparatus

The hydrate crystallizer cell consists of a titanium cylindrical vessel equipped with two see-through sapphire windows (20 mm in diameter) allowing the direct observation of hydrate formation inside the cell. The cell has a capacity of 176.1 ml and is designed to be operated at pressures up to 200 bar. The solution inside the cell is stirred by means of a magnetic agitator driven by a magnetic stirrer (Hei-Mix D model from Heidolph). The cell temperature is controlled by circulating through the cell jacket an aqueous solution of propylene glycol coming from a thermostatic bath (Polystat, Fischer Scientific) with a stability of  $\pm 0.02$  °C. The cell temperature is measured with two PT 100 probes immersed in the liquid phase and gas phase, respectively. The uncertainty of the temperature measurement is  $\pm 0.1$  °C.

The cell pressure is measured by a KELLER PA23SY pressure transducer (0 – 100 bar) with an accuracy of  $\pm 0.1$  bar. A high pressure storage tank is used to load the gas mixture into the hydrate crystallizer cell. The composition of the gas phase is determined by a gas chromatograph (Agilent GC6980) equipped with a thermal conductivity detector (TCD). A high pressure valve system directly connected to the cell hydrate crystallizer cell is used to sample gas for GC measurements. The pressure drop caused by each gas sampling is about 0.01 bar. The temperature and pressure are recorded every second via a standard PC and a LabView® interface. The hydrate formation process is

continuously recorded by means of a CCD camera all along the experiments.

## Experimental procedure

The aqueous solutions are prepared by first dissolving SDS in 50 ml of ultra-pure water while stirring during 5 min. The desired mass of THF is then added to the SDS solution while stirring again for 5 min. Finally, the total mass of the solution is adjusted to  $200 \pm 0.001$  g with ultra-pure water and stirred during 5 min.

The hydrate crystallizer cell is loaded with  $65 \pm 0.1$  ml of the aqueous solution using glass pipettes. This volume ensures that the gas/liquid interface is located at the middle of the sapphire windows. The cell is closed and connected to the rest of the equipment. The temperature is fixed at  $T_{init} = 20.0$  °C and the cell is purged two times with the gas mixture before pressurization at the desired pressure (called gas loading pressure ( $P_{load}$ )). Then, stirring is started (rotation speed: 600 rpm) and maintained during 2 hours to enhance thermal and mass transfers and allow complete solubilization of the gas mixture in the aqueous solution.

The gas composition after solubilization is measured through a GC sampling at high pressure, and then the cell temperature is cooled down to  $2.0 - 2.5$  °C at a cooling rate of  $0.9$  °C/min in order to promote the hydrate formation. Due to the weak agitation torque, it was observed that the agitator stopped as soon as the hydrate phase formed in the cell. Therefore, it

can be considered that the hydrate growth occurs under quiescent conditions. During the hydrate formation, the gas phase composition is measured several times all along the experiment until both the cell pressure and gas composition reach steady state or equilibrium conditions, which marks the end of the hydrate formation period. Finally, the temperature is raised to 20.0 °C to dissociate the hydrates formed.

### Number of moles of gas removed from the gas phase and separation factor

The number of moles removed from the gas phase during the hydrate formation process is calculated using the following equation:

$$\Delta n_g^i = n_g^i \Big|_{t_{init}} - n_g^i \Big|_{t_{equil}} = \frac{y^i PV}{zRT} \Big|_{t_{init}} - \frac{y^i PV}{zRT} \Big|_{t_{equil}} \quad (1)$$

where: superscript  $i$  refers to component of gas mixture,  $y^i$  is the mole composition of the component  $i$  in the gas mixture,  $z$  is the compressibility factor calculated by the Peng Robinson equation of state [17],  $P$  and  $T$  are the experimental pressure and temperature, respectively.  $V$  is the volume of gas phase,  $t_{init}$  and  $t_{equil}$  are the initial condition and equilibrium condition, respectively. The volume change due to hydrate crystallization and the presence of water and THF in the gas phase are neglected.

The relative fraction of gas removed from the gas phase ( $n_{removed}^i$ ) is expressed in percentage using the following expression:

$$n_{removed}^i = \frac{\Delta n_g^i}{n_g^i \Big|_{t_{initial}}} \cdot 100 \quad (2)$$

The separation factor ( $\eta$ ) is defined as:

$$\eta = \frac{n_{removed}^{CO_2}}{n_{removed}^{CH_4}} \quad (3)$$

This factor is used to estimate the selectivity of the hydrate formation process with regard to CO<sub>2</sub> capture: a higher value of  $\eta$  means a more efficient gas mixture decontamination from CO<sub>2</sub> [2,18].

## RESULTS AND DISCUSSION

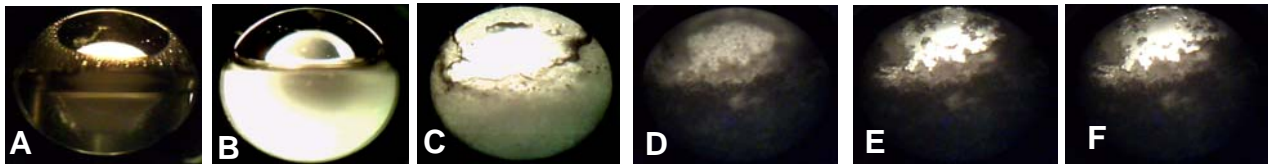
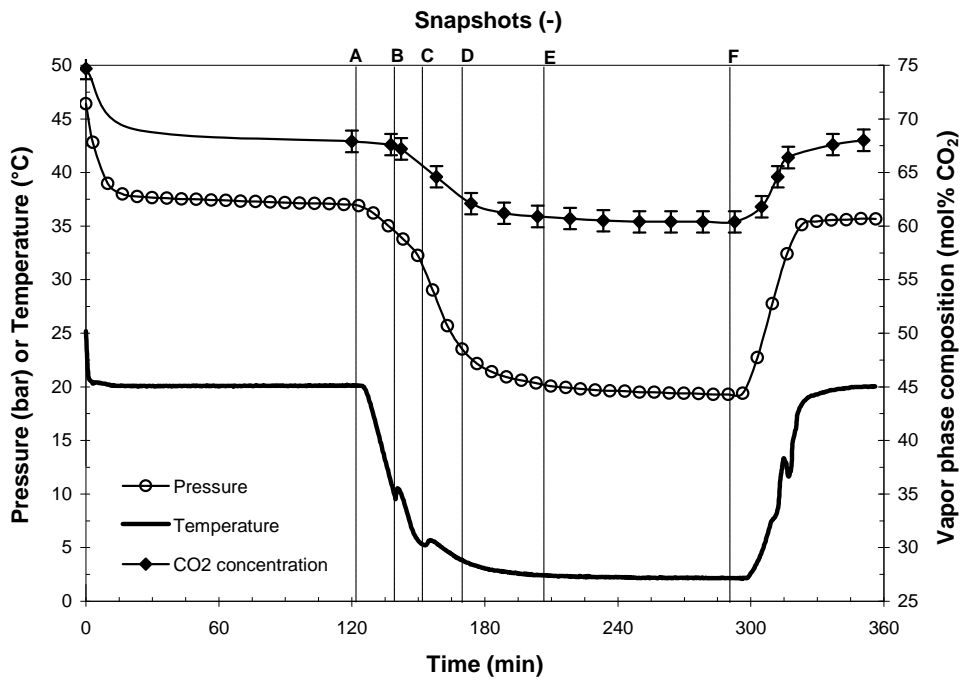
### Example of typical experimental curves

Figure 2 shows the variation with elapsed time of the cell temperature, pressure and gas phase composition in a typical experiment, together with selected images (snapshots) through the sapphire window. During the first 30 min, the pressure and the CO<sub>2</sub> content in the vapor phase decrease quickly, due to the gas solubilization into the aqueous solution. Then a plateau is reached that corresponds to solubilization equilibrium between the aqueous phase and the gas phase at 20°C. At point A, the cell is cooled down to 2.0 °C. From A to B, the observed decrease in pressure results from both the gas phase contraction and the gas solubilization into the aqueous solution.

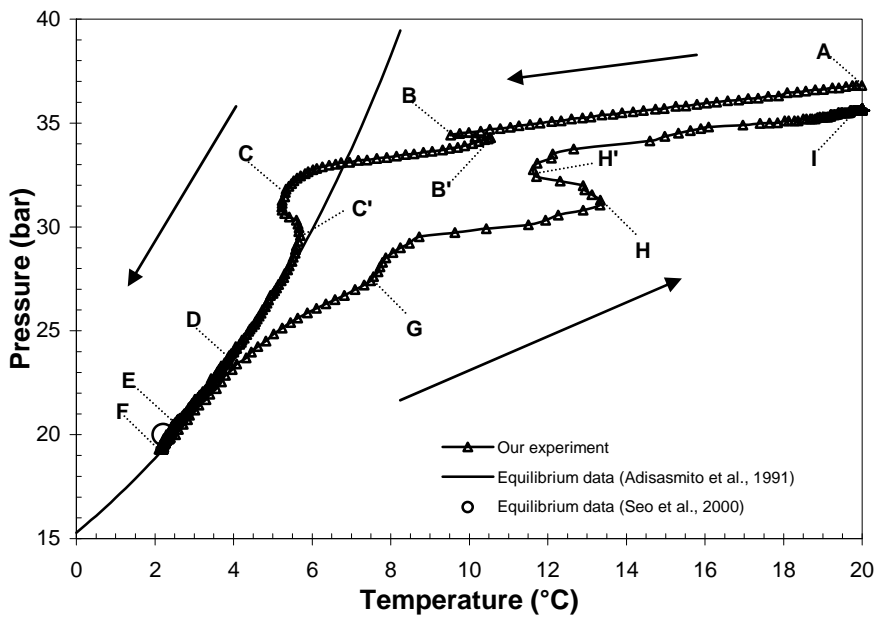
At point B, the observed increase in temperature corresponds to a first hydrate crystallization in the system, which is confirmed by the direct observation through the sapphire windows (snapshot B). When the heat released by hydrate crystallization is offset by the cell cooling, the temperature of the system decreases to point C, where a second hydrate crystallization takes place. These two steps are very similar to those observed with pure CO<sub>2</sub> (see ref. [16]).

From C to E, the cell pressure and the CO<sub>2</sub> content in the vapor phase decrease significantly, and changes in the physical aspect of the hydrates are observed (snapshots C, D and E). At F, the pressure, temperature and gas composition reach almost constant values, indicating that the enclathration reaction has finished and an equilibrium state is reached. In the presented example, the pressure and gas composition at F are 19.3 bar and 60.4 mol% CO<sub>2</sub>, respectively.

The temperature of the system is then raised to its initial value (20.0 °C) to dissociate the hydrates formed. In this heating process, two endothermic perturbations are observed in the temperature profile corresponding to the decomposition of the hydrates. Meanwhile, the pressure increases in the cell. Finally, the pressure recovers its initial value when temperature reaches 20°C. The small pressure difference being due to the multiple GC samplings carried out during the experiment.



**Figure 2.** Variation of pressure, temperature, vapor phase composition as a function of time and snapshots made during a typical experiment.  $P_{load} = 46.3$  bar,  $[SDS] = 3000$  ppm and  $[THF] = 4$  wt%



**Figure 3.** Pressure versus temperature for a hydrate formation/dissociation cycle.  $P_{load} = 46.3$  bar,  $[SDS] = 3000$  ppm and  $[THF] = 4$  wt%. (The three phase equilibrium curve (full line) corresponds to the composition  $CH_4$  (40 mol%) and  $CO_2$  (60 mol%) of the gas mixture)

## P-T curve

In Figure 3 the variation of pressure is plotted versus temperature for the above formation/dissociation cycle, starting from (and ending with) the solubilization equilibrium between the aqueous phase and the gas phase at 20.0 °C.

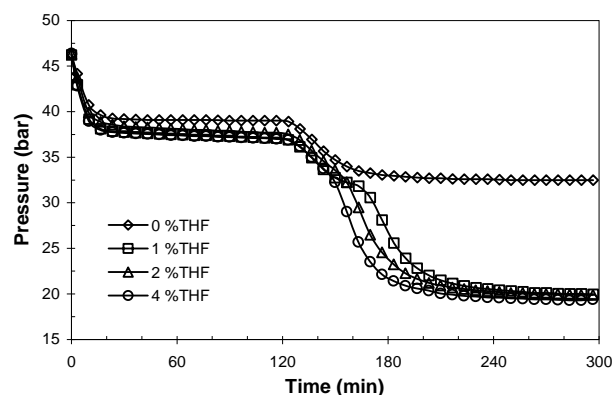
As already observed in Figure 2, the largest drop of pressure occurs after the second hydrate crystallization (point C'). Interestingly, the values of pressure and temperature at equilibrium (point F) agree with the values predicted by using the equation proposed by Adisasmito *et al.* (1991) [19] for a gas phase composition of 60 mol% CO<sub>2</sub> (i.e., 40 mol% CH<sub>4</sub>), which is the composition measured by GC at the end of the crystallization process. The experimental equilibrium P-T conditions measured by Seo *et al.* (2000) [9] for a gas phase composition of 60.7 mol% CO<sub>2</sub> (i.e., 39.3 mol% CH<sub>4</sub>) are also reported in Figure 3: they are consistent with the results presented here.

Therefore, the hydrate equilibrium conditions for the CH<sub>4</sub>-CO<sub>2</sub>-water system do not depend on the presence of THF and SDS, at least in the concentration range investigated in this study (3000 ppm SDS and 1-4 wt% THF). These results are similar with those obtained by Torr  *et al.* (2011) [16] on the CO<sub>2</sub>-water hydrate system in the presence of the same additives and with those obtained by Shin *et al.* (2009) [14] on the CO<sub>2</sub>-water hydrate system in the presence of THF and 1,4-dioxane as additives.

## Effect of THF concentration

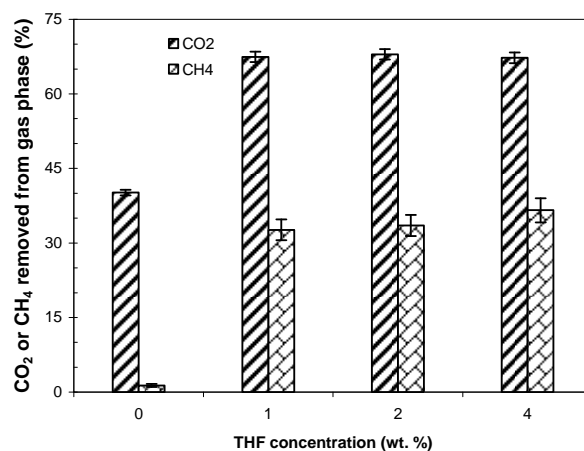
The variation of cell pressure as a function of time for THF concentrations between 0 and 4 wt% THF is shown in Figure 4. For these experiments, the gas loading pressure is equal to 46.3 bar. In all experiments, the target temperature at the end of the hydrate formation cycle is 2.1 °C. As observed in the previous experiments, the pressure decreases quickly during the first 30 min, and then stabilizes. At the end of the solubilization stage, the equilibrium pressure is observed to be smaller when some THF is present in the aqueous phase. This behavior can be related to the chemical affinity

between the THF and CO<sub>2</sub> molecules, which promotes the solubilization of CO<sub>2</sub> into the aqueous phase [3,19].



**Figure 4.** Pressure evolution for various THF concentrations.  $P_{load} = 46.3$  bar, [SDS] = 3000 ppm and [THF] = variable

As shown in Figure 4, hydrates are not formed in the absence of THF in the aqueous phase, even if the system is left for 24 hours at 2.1 °C. In the presence of THF hydrate formation is observed and the pressure drop decrease rate is observed to increase with THF concentration. However, at the end of the hydrate formation, the pressure reaches almost the same value (~19.5 bar) in all systems containing THF. The amount of CO<sub>2</sub> removed from the gas phase is found on average to be equal to 68 % when some THF is present in the aqueous phase (Figure 5). This CO<sub>2</sub> removal is accompanied by a significant removal of CH<sub>4</sub> (35 % on average) from the gas phase as well.



**Figure 5.** Effect of THF concentration on CO<sub>2</sub> and CH<sub>4</sub> removed from the gas phase.  $P_{load} = 46.3$  bar, [SDS] = 3000 ppm and [THF] = variable

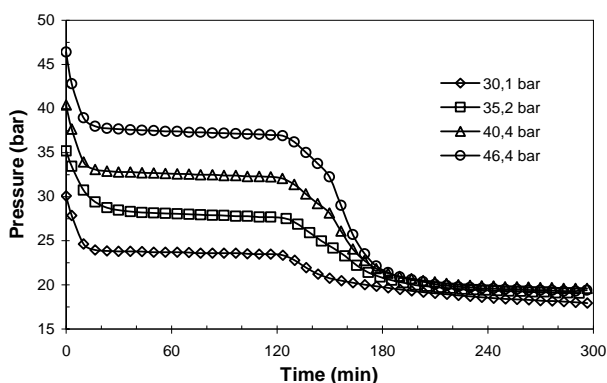


One can note that in the absence of THF, 40% of the CO<sub>2</sub> and only 1% of the CH<sub>4</sub> initially present in the gas phase are removed from this phase. This is explained by the fact that, without hydrate formation, gas removal is totally controlled by the solubilization in the aqueous phase. As a matter of fact, the solubility of CO<sub>2</sub> in water is approximately 30 times that of CH<sub>4</sub> at 2.1 °C [3].

### Effect of gas loading pressure

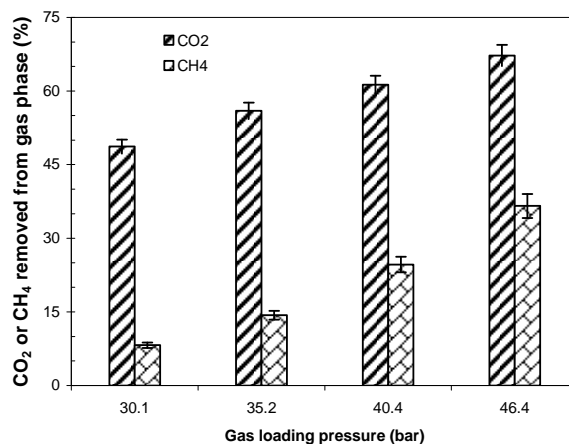
Figure 6 shows the variation of cell pressure as a function of time in four different experiments in which the initial loading pressures has been varied in the range of 30.1 to 46.4 bar. In all experiments, the additives concentrations are equal to 4 wt% THF and 0.3 wt% SDS, respectively, and the target (or final) temperature is 2.1 °C. The decrease in pressure due to the hydrate formation corresponds to the times greater than 130 min.

One can observe that the pressure drop increases with the load pressure. However, the pressure at equilibrium conditions seems not to depend significantly on the gas loading pressure. This result suggests that the gas phase composition, and therefore, the selectivity of the capture will not drastically vary with the gas loading pressure.



**Figure 6.** Pressure versus time for different gas loading pressures. [SDS] = 3000 ppm and [THF] = 4 wt%

The influence of the gas loading pressure on CO<sub>2</sub> and CH<sub>4</sub> removal from the gas phase at equilibrium (calculated using equation (2)) is shown in Figure 7.



**Figure 7.** Effect of gas loading pressure on CO<sub>2</sub> and CH<sub>4</sub> removed from the gas phase. [SDS] = 3000 ppm and [THF] = 4 wt%

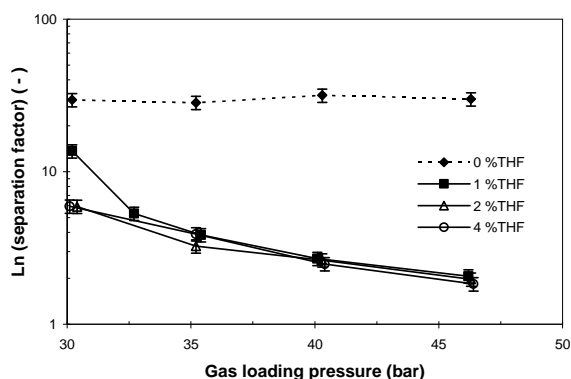
Actually, it can be observed that the higher the gas loading pressure, the higher is the amount of CO<sub>2</sub> removed from the gas phase. Similarly, the amount of CH<sub>4</sub> removed from the gas phase increases with the loading pressure, showing that 8 % and 37 % of CH<sub>4</sub> are removed for initial loading pressures of 30.1 bar and 46.4 bar, respectively..

### The separation factor

The separation factor ( $\eta$ ) has been defined as the ratio between the number of moles of CO<sub>2</sub> and CH<sub>4</sub> removed from the gas phase (see equation (3)). A process to capture CO<sub>2</sub> from CO<sub>2</sub> – CH<sub>4</sub> gas mixtures can be considered as a selective process when  $\eta \gg 1$ , i.e., the amount of CO<sub>2</sub> captured should be much greater than the amount of CH<sub>4</sub> captured.

Figure 8 depicts the separation factor measured as a function of gas loading pressure for the different THF concentrations investigated.

In the absence of THF in the aqueous phase, hydrate formation does not take place, and the gas removal process is totally controlled by the solubility of CO<sub>2</sub> and CH<sub>4</sub> into the aqueous phase. The large separation factors ( $\eta > 28$ ) observed reflects the fact that CH<sub>4</sub> solubility in water is much lower than CO<sub>2</sub> solubility.



**Figure 8.** Influence of gas loading pressure on separation factor at different THF concentrations

In the presence of THF, the formation of hydrates, which are much less selective towards  $\text{CO}_2$  than aqueous phase solubilization, results in a lower selectivity in comparison to the situation where no hydrates are formed (absence of THF). The decrease of the separation factor with increasing gas loading pressure results from the proportional increase of the amount of  $\text{CH}_4$  removed (Figure 5). This result is consistent with that obtained by van Denderen *et al.* [6] and by Li *et al.* (2009) [20], who provide evidence for a higher  $\text{CO}_2$  capture selectivity at low pressure. This effect is merely due to the fact that a lesser quantity of hydrates form and therefore more unconverted (or ‘free’) water remains in which a much larger proportion of  $\text{CO}_2$  is dissolved.

Except for the lowest gas loading pressure investigated in this work,  $\text{CO}_2$  capture selectivity does not appear to depend on THF concentration. The experiment carried out with aqueous solutions containing 1 wt% THF and a gas loading pressure of 30.2 bar shows a higher separation factor compared to the experiments carried out with more concentrated solutions (and same loading pressure). As pointed out above, this large separation factor is likely to result from a lower conversion of water into hydrate or, equivalently, a larger quantity of ‘free’ water able to dissolve much more  $\text{CO}_2$  than methane. In fact, a direct visual observation through the sapphire windows reveals in this case the presence of a large amount of “free” water at the end of the hydrate formation.

We infer from these results that the  $\text{CO}_2$  selectivity of the hydrate phase at the equilibrium

does not depend on THF concentration, at least in the range of concentrations considered in this study (1 – 4 wt% THF).

## CONCLUSION

In this work, a study of the influence of THF concentration in water and the gas loading pressure on  $\text{CO}_2$  capture by hydrate formation from a  $\text{CO}_2$ - $\text{CH}_4$  gas mixture has been presented.

The presence of THF in the aqueous phase is mandatory for hydrate formation to occur. The rate of hydrate formation is observed to increase with THF concentration.

The separation factor, i.e. the selectivity of  $\text{CO}_2$  removal by hydrate crystallization, is found to be constant in the range of THF concentrations studied (i.e., from 1 to 4 wt% THF), and to decrease when the gas loading pressure increases.

Further investigations with others  $\text{CH}_4$  –  $\text{CO}_2$  gas mixtures and a relevant choice of different additives are needed to better characterize the separation process and its efficiency for capturing  $\text{CO}_2$  from  $\text{CH}_4$  –  $\text{CO}_2$  streams. In complement, experiments with pure fluids are also needed for a better understanding of the driving mechanisms. An effort is done in this direction with pure  $\text{CO}_2$  and THF and SDS as additives in the companion paper by Torr  and co-workers [21].

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