



CO₂ capture by using hydrates: 1) The benefice and the counterpart of thermodynamic additives

Aurélie Galfré, Pedro Brantuas, Ana Cameirão, Yamina Ouabbas, Baptiste Bouillot,
Jean-Michel Herri, Peter Jørgensen Herslund, Nicolas von Solms

► To cite this version:

Aurélie Galfré, Pedro Brantuas, Ana Cameirão, Yamina Ouabbas, Baptiste Bouillot, et al.. CO₂ capture by using hydrates: 1) The benefice and the counterpart of thermodynamic additives. The 8th International Conference on Gas Hydrates, Jul 2014, Pékin, China. pp.T1-73. <hal-01068432>

HAL Id: hal-01068432

<https://hal.science/hal-01068432v1>

Submitted on 29 Sep 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

CO₂ CAPTURE BY USING HYDRATES:

1) THE BENEFICE AND THE COUNTERPART OF THERMODYNAMIC ADDITIVES

GALFRE Aurélie, BRANTUAS, Pedro, CAMEIRAO Ana, OUABBAS Yamina, BOUILLOT Baptiste,
HERRI Jean-Michel^(*)

Gas Hydrate Dynamics Centre, Ecole Nationale Supérieure des Mines de Saint-Etienne, 158 Cours Fauriel,
42023 Saint-Etienne, France

(*) corresponding author: herri@emse.fr

HERSLUND Peter, Von SOLMS Nicolas

Department of Chemical and Biochemical Engineering, Center for Energy Resources Engineering
(CERE), Technical University of Denmark, Kgs. Lyngby DK2800, Denmark

ABSTRACT

CO₂ capture by using clathrates is a method which benefits from the CO₂ selectivity in gas hydrates to separate it from nitrogen, or other exhaust gases from gas or coal combustion. The bottleneck is the operating pressure which still remains high and needs to drop to 0.5 MPa in order to compete with the reference case using amines. As part of two national projects (SECOHYA, ACACIA) and a European program (iCAP), we tested different classes of thermodynamic additives, organic (water insoluble cyclopentane, water soluble THF) which form classical gas hydrates with structure SII, and ionic (Tetra-N-Butyl Ammonium Bromide, TBAB) which forms new types of structures.

In this presentation, we show experimental results that clearly demonstrate that the operating pressure can be reduced to atmospheric pressure, and we emphasize that the CO₂ selectivity is enhanced, with cyclopentane as an additive, but also especially by using TBAB where the selectivity can be boosted up to 100%.

We also show that the experimental conditions of pressure and temperature need to be selected outside the region of formation of the single additive hydrate. If not, the gas storage capacity drops to a negligible value.

We conclude the presentation by showing the physical impossibility to find a thermodynamic additive to drop the operative pressure without dropping the storage capacity.

Keywords: clathrates and semi clathrates hydrates, thermodynamic additives, gas separation

Introduction

Greenhouse gas emissions have been identified as the major source of global warming. Among the greenhouse gases emitted into the atmosphere due to anthropogenic activities, carbon dioxide (CO₂) plays a major role. One possible way to reduce the global CO₂ emissions is to establish suitable capture processes that can be integrated in existing plants and equipment and by which carbon dioxide can be removed from the considered flue gas streams. Flue gas mixtures of conventional post-combustion power plants are characterised by low carbon dioxide mole fractions ranging from 0.05 to 0.15. In addition, the respective gas streams are typically emitted at high flow rate. The challenge is to develop CO₂ capture technologies by which

both energetic and capital costs (size of the units) are minimized. An innovative technology for gas separation and capture could be based on a process making use of gas hydrate formation.

For the typical case of a steel making plant, an energetic costing performed by Duc et al (2007) showed that the process making use of the semi-clathrate hydrate approach can be competitive compared to conventional capture technologies. The separation cost is mainly due to the gas compression stages. Hence, the objective is to lower the operational pressure.

We tested different additives as a thermodynamic additive, tetrahydrofuran which is perfectly miscible with water and forms a SII clathrate hydrate (Herslund et al, 2013),

cyclopentane which no miscible with water and forms also a SII clathrate hydrate (Galfré et al, 2013), and lastly quaternary ammonium salts which form semi-clathrate hydrates (Herri et al, 2014). In each case, we can drop the operating pressure, sometimes we can enhance the selectivity of the CO₂ separation. But also we systematically drop the hydrate storage capacity to a value that is incompatible with an industrial application as explained in the fourth paper of this series of four papers.

Tetrahydrofuran: An example of water soluble additive

Tetrahydrofuran (THF) forms structure II hydrates in which THF occupies the large cavity $5^{12}6^4$ and gas competes with THF for the occupation of the large cavity and/or occupies the small cavity. THF is a water-soluble additive. With water, they are completely miscible in the liquid state over the whole composition range in the pressure and temperature domain of hydrate formation (Riesco *et al.*, 2005). The equilibrium pressure reduction effect to form hydrates is dependent on the relative concentration of THF. It is important to notice that in presence of pressurized carbon dioxide (temperature above 290 K and a pressure above 2.0 MPa), Sabil *et al.*, 2010 observed that water and THF phase split in two liquids phases (in presence of a solution of 5% mole of THF in water). Over the years, many authors reported hydrate dissociation data of the system {THF + water + gas}. Only works where nitrogen and carbon dioxide were used are presented in the following paragraph..

Benefits of THF on the equilibrium of pure gases:

Seo *et al.* (2001, 2008) studied the hydrate dissociation pressure – temperature data {H₂O + THF + pure gas (CO₂ or N₂)} for several compositions of THF (1 to 5 %mol of THF in water) and the hydrate dissociation pressure – temperature data {H₂O + THF + CH₄} for 3 %mol of THF.

Firstly, their studies focused on showing the stabilization effect of THF on hydrate formation compared to the effect of others water miscible promoters (propylene oxide, 1,4-dioxane, acetone). For a concentration of promoter of 3 %mol, THF was found to be the most interesting for each gas (CO₂, N₂ and CH₄).

Secondly, the effect of THF concentration from 1 to 5 %mol on the equilibrium hydrate dissociation pressure-temperature data has been studied. The

pressure decreased rapidly up to 1 %mol of THF, but very slowly above 1 %mol for each case study (CO₂ and N₂).

Delahaye *et al.* (2006) also investigated the hydrate dissociation pressure – temperature data {H₂O + THF + CO₂} for THF concentration in the range of 1.6 to 3.0 %mol, and the latent heat of dissociation of the mixed hydrates (CO₂/THF/water). Like Seo *et al.* (2008) the authors observed the drastic reduction of the hydrate pressure formation with a few mole of THF in the system.

Sabil *et al.* (2010) also examined the complete hydrates dissociation lines for the systems {H₂O + CO₂} and {H₂O + THF + CO₂} at a THF concentration of 5 %mol for different carbon dioxide concentrations. The authors discovered a four-phase equilibrium region with three fluid phases at temperatures above 290K and pressures above 2.0 MPa : a water-rich with a constant amount of carbon dioxide, a carbon dioxide in an organic-rich, the vapor phase and the hydrate phase.

Finally, Yang *et al.*, 2011 studied the hydrate dissociation pressure – temperature data {H₂O + THF + pure gas (N₂)} for THF concentration of 5 %mol. The authors also provided equilibrium phase hydrate data for {O₂ + THF + water}, {air + THF + water}. Their research focused on finding valuable information on the air separation by hydrate crystallization.

Benefits of THF on gas mixtures:

Recovering CO₂ from a gas mixture of CO₂/N₂ in presence of THF was the purpose of the works of (Kang and Lee, 2000, 2001 and Linga *et al.*, 2007). The authors measured the hydrate dissociation data for several mixtures of CO₂ and N₂ without any promoter and in presence of THF. As for pure gases, with aqueous solutions containing 1 and 3 %mol of THF, a drastic drop of equilibrium dissociation pressure has been observed from the moment the THF concentration reached 1 mole percent (Kang and Lee, 2000, 2001). Moreover, a benefit of THF is observed on the selectivity of the separation. Pressure-composition diagrams of the {H₂O + THF + CO₂/N₂}. The respective hydrate compositions of the mixed hydrates with and without THF have been added on the diagrams. Kang and Lee (2000) showed that the CO₂ selectivity in the mixed hydrate phase has been lowered in the mixed hydrate when the THF has been used as a hydrate promoter.

Linga *et al.* (2007) tested a THF concentration of 1 %mol and studied the gas uptake and the rate of the crystallization. THF reduced the induction time but also the growth rate of the crystallization.

The authors did not estimate the carbon dioxide selectivity and did not calculate the gas storage capacity.

Finally, Linga *et al.* (2010) investigated the formation of gas hydrate with one composition of gas mixture at THF concentrations of 1 and 1.5 %mol. The authors estimated the gas uptake and the CO₂ recovery and compared them to the results reported in the literature with tetra-n-butyl ammonium bromide and tetra-n-butyl ammonium fluoride (Fan *et al.*, 2009; Li *et al.*, 2009).

Cyclopentane: an immiscible organic additive

Cyclopentane (CP) is described in the literature as an excellent thermodynamic promoter. It forms structure II hydrate without any gas (Nakajima *et al.*, 2008) but competes with CO₂ to occupy the large cavity 5¹²6⁴. Cyclopentane is a hydrophobic compound and needs to be dispersed in water. So, the main difference with THF is the low solubility of CP in water.

Fan *et al.* (2001) were the first to report the quadruple equilibrium point (CP hydrate-liquid water-organic liquid-vapor) at a temperature of 280.22 K and a pressure of 0.0198 MPa (abs).

As for THF, many authors reported the hydrate dissociation data of the system (THF + water + pure CO₂, pure N₂, or CO₂+N₂): their works are detailed in the following paragraph.

Zhang *et al.* (2009a, b) determined hydrate dissociation data for {H₂O + CO₂+CP} system. Dissociation conditions for {H₂O + CO₂+CP} hydrate have been compared with the dissociation data for {H₂O + CO₂+TBAB} with a TBAB weight fraction of 0.427 (Arjmandi *et al.*, 2007) and for {H₂O + CO₂+THF} with a THF molar fraction of 3 percent (Delahaye *et al.*, 2006). CP appears to be a better additive than TBAB to decrease the equilibrium pressure.

Zhang & Lee (2009c) also studied the potential of using CP as a kinetic promoter in a static autoclave at a low temperature.

Mohammadi *et al.* (2010) compared the stabilization effect of CP on hydrate formation of {H₂O + CO₂+CP} gas hydrate to the effect of several organic promoters (example: methyl-cyclopentane, methyl-cyclohexane, and cyclohexane). For volume fraction of promoter of 10% in water, among the promoters, CP promotion

effect was the highest. Experimental dissociation data for clathrate hydrates of cyclopentane and carbon dioxide have been also reported. Data were in good agreement with the study of Zhang *et al.* (2009a, b).

Experimental hydrate dissociation data for {H₂O + N₂+CP} system were first published by Tohidi *et al.* (1997). They tested the potential of using cyclopentane to decrease the equilibrium pressure when gas hydrates of nitrogen and promoter (cyclopentane or neopentane) are formed. CP promotion effect has also been compared in that case to several organic promoters of the literature (cyclohexane and benzene). It was found to be the strongest promoter, just above neopentane.

Mohammandi *et al.* (2011) and Du *et al.* (2010) completed the experimental hydrate dissociation data for {H₂O + N₂+CP} system and their results were in good agreement.

For CO₂/N₂ gas mixture, Li *et al.* (2010) preliminary showed that gas hydrates could be enriched in CO₂ in presence of cyclopentane. The authors studied two different situations: CP dispersed in an emulsion or a buoyant CP phase on the top of the liquid water phase. Differences in the separation efficiency have been reported. This difference implies that the authors have not reached the thermodynamic equilibrium in their work. In fact, we will comment this point in our discussion, but it appears that the formed hydrate from a gas mixture are not at equilibrium, and that its composition is directly dependent on kinetic considerations, and so is indirectly dependent on the geometry of the system.

Galfré *et al.* (2014) shows the “selectivity curve” (Figure 1) in which for the system {H₂O + CP + CO₂ + N₂} under the condition of H-L_w-L_{hc}-G four phase equilibrium, the binary mole fraction of CO₂ in the mixed CO₂ + N₂ + CP hydrate phase, $z'_{\text{CO}_2} = n_{\text{CO}_2}^{\text{H}} / (n_{\text{CO}_2}^{\text{H}} + n_{\text{N}_2}^{\text{H}})$, is plotted against the binary mole fraction of CO₂ in the gas phase $y'_{\text{CO}_2} = n_{\text{CO}_2}^{\text{G}} / (n_{\text{CO}_2}^{\text{G}} + n_{\text{N}_2}^{\text{G}})$. This curve covers the temperature range from 283.5 K to 287.5 K and the pressure range from 0.76 MPa to 2.23 MPa. In addition to the experimental data, Figure 1 shows corresponding curves calculated via a simulation for the system without cyclopentane, i.e. for the system {H₂O + CO₂ + N₂}, by means of the in-house

programme “GasHyDyn” (Herri et al, 2011) at four different temperatures T .

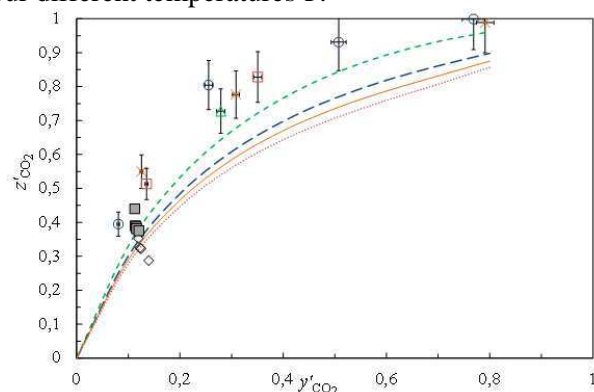


Figure 1. Mole fraction of CO_2 in the hydrate phase z'_{CO_2} as function of the corresponding mole fraction of CO_2 in the gas phase y'_{CO_2} , both at equilibrium, for different temperatures T between 282.5 K to 287.5 K. Symbols correspond to experimental data at (Δ) 282.5 K, (\circ) 285.3 K, (\times) 286.2 K and (\square) 287.3 K. Literature data of Li et al. (2010) for (\diamond) emulsion system, and (\blacksquare) system containing two “macroscopic” liquid phases. Simulations obtained by means of the in-house software “GasHyDyn” (Herri et al, 2011) for the corresponding system without cyclopentane at (----) 282.5 K, (— · —) 285.3 K, (—) 286.2 K and (····) 287.3 K.

It can be seen in Figure 1 that the carbon dioxide selectivity in the mixed $\text{CO}_2 + \text{N}_2 + \text{CP}$ hydrates is significantly increased compared to the theoretical selectivity of the gas hydrates without any promoter. For example, the mole fraction of CO_2 relative to the system $\{\text{CO}_2 + \text{N}_2\}$ present in the hydrate phase z'_{CO_2} approaches 0.931 for a corresponding mole fraction of CO_2 in the gas phase y'_{CO_2} of 0.507.

Experimental data presented by Li et al. (2010) for mixed $\text{CO}_2 + \text{N}_2 + \text{CP}$ hydrates are also reported in Figure 1. and appear to give a lower selectivity. In their article, Galfré et al (2013) argued that the data of Li et al. (2010) are not at equilibrium and cannot directly be compared to the data presented in their work.

In Figure 2, the gas storage has been reported by Galfré et al (2014) against the composition of the $\text{CO}_2 + \text{N}_2$ gas phase in terms of y'_{CO_2} . In this diagram, it can be seen that the Gas Storage

Capacity is in the range of $(20\text{--}60) \text{ m}^3 \text{ gas.m}^{-3} \text{ hydrate}$, scattered around a mean value of $40 \text{ m}^3 \text{ gas.m}^{-3} \text{ hydrate}$.

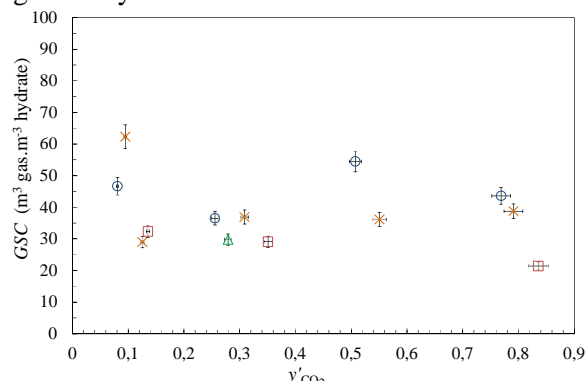


Figure 2. Gas storage capacity for $\text{CO}_2 + \text{N}_2$ gas mixtures from 282.5 K to 287.5 K as function of the mole fraction of CO_2 in the gas phase y'_{CO_2} (with respect to the total amount of $\text{CO}_2 + \text{N}_2$, i.e., $y'_{\text{CO}_2} + y'_{\text{N}_2} = 1$). Symbols correspond to experimental data at (Δ) 282.5 K, (\circ) 285.3 K, (\times) 286.2 K, (\square) 287.3 K.

Lastly, Herslund et al (2013) have reported that below 281 K, we can observe a competition in between the crystallization of pure cyclopentane sII hydrates and mixed carbon dioxide–cyclopentane hydrates. It is due to the stability of pure CP clathrate hydrate, and contributes significantly to decrease again the storage capacity if the temperature is decreased too much.

Semi clathrate hydrates

Another class of clathrates, called semi-clathrates, can be formed in presence of electrolytes, such as alkyls Ammonium salts or alkyls Phosphonium salts (Sato et al, 2013). It forms, in presence of water, and without any gas, a semi-clathrates hydrate crystal, even at atmospheric pressure (McMullan and Jeffrey, 1959). They are qualified as peralkylonium polyhydrates and have been the research project of the Russian team of Dyadin and co-workers over decades and were only published in English in 1984, 1985 and 1995. In contrast to gas hydrates, the cation is the guest situated in the framework cavities and separated from the host- molecules by the distance not less than the sum of the Van der Waals radii (Dyadin and Udachin, 1984).

So, they are called semi-clathrates due to the fact that the crystalline water network is broken in order to incorporate the cation of the compound. For instance, in the case of TBAB hydrate, the

nitrogen atom at the center of the four butyl radicals takes the place of a water molecule effectively, “breaking” the four surrounding cages and creating a larger cavity made from smaller ones. Therefore the hydration number will change regarding gas hydrates because less water molecules in a similar structure, due to their replacement by the cation of the semi-clathrate, will be present. Bromide atoms and water molecules form the cage structure. Tetra-*n*-butyl ammonium is located at the centre of four cages (Shimada *et al.*, 2005b) and the butyl groups occupy the cavities. There is a large number of semi-clathrate compounds due to the different cation and anion they possess (Herri *et al.*, 2014)

With a wide range of anions and cations that can compose a semi-clathrate, it is not a surprise that many different crystalline structures can be formed. A detailed review has been made by Dyadin and Udachin in 1987 which continues to be the reference on the subject.

Tetra-*N*-Butyl ammonium Bromure has been extensively studied in reason of a direct application for air conditioning as a phase change material (Lipkowski *et al.*, 2002, Oyama *et al.*, 2005, Kamata *et al.*, 2004, Darbouret *et al.* 2005, Lin *et al.*, 2008, Arjmandi *et al.*, 2007 and Li *et al.*, 2009). Tetra butyl ammonium bromide salt forms at least four different structures with hydration number of 24, 26, 32 and 36 (Lipkowski *et al.*, 2002). Only one of the crystallographic structures of semi-clathrate hydrates has been determined precisely by McMullan and Jeffrey (1959) and completed by Shimada (2005b). A complete reviewing off all the equilibrium data can be in Sato *et al.* (2013)

Davidson (1973) suggested that these semi-clathrates crystals do not encage gas molecules, but Shimada *et al.*, (2005a) and Duc *et al.*, (2007) have given opposite results or opinions. Shimada *et al.*, (2003, 2005a) has supposed that TBAB semi-clathrates could encage small gas molecules. In fact, based on the structure analyze of pure TBAB semi-clathrates (formula $(n-C_4H_9)_4N^+Br^- \cdot 38H_2O$), they supposed that the structure could encapsulate the gas in the free cavities (Figure 3). Duc *et al.*, (2007) have experimentally confirmed that semi clathrates can encapsulate up to 40 M³ STP of gas per cubic meter of solid.

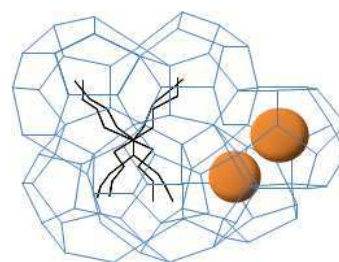


Figure 3 : Structure of gas TBAB semi-clathrates (Shimada *et al.*, 2005b).

Since this period, a huge quantity of experimental results have been produced which gives evidence of the enclathration of gases in the TBAB structure. The question that remains is which structure is formed. In fact, facing the variety of possibilities, and except the work of Shimada *et al.*, (2005b) who clearly identified one structure in presence of gas, we do not have evidence of the crystallographic structure formed.

(Pressure-Temperature) equilibrium with TBAB, CO₂ and N₂

In recent years, many experimental data have been produced about the equilibrium of TBAB semi-clathrate in presence of pure CO₂ and pure N₂ gas. Also, a model has been produced by Paricaud (2011) to predict the pressure and temperature of equilibrium as a function of the TBAB mass fraction for only one type of hydrate structure. Arjmandi *et al.*, (2007) have given CO₂-TBAB semi clathrate equilibrium data at TBAB mass fraction of 0.1 and 0.4. Duc *et al.*, (2007) have determined few points at TBAB mass fraction of 0.05, 0.09, 0.5 and 0.65. Lin *et al.*, (2008) did a complete study for TBAB mass fraction of 0.044, 0.07 and 0.05. Oyama *et al.*, (2008) gave equilibrium data of CO₂ semi clathrate at TBAB mass fraction of 0.1. But also, they produced data at very low mass fraction of 0.01, 0.02, 0.03 and 0.045 without formation of the semi clathrate hydrate but only formation of the clathrate hydrate. Lastly, Deschamps and Dalmazzone (2009) have given few points at TBAB mass fraction of 0.4.

Experiments about N₂-TBAB semi clathrate equilibrium are less numerous. Arjmandi *et al.*, (2007) have given N₂-TBAB semi clathrate equilibrium data at TBAB mass fraction of 0.1. Duc *et al.*, (2007) have determined few points at TBAB mass fraction of 0.05, 0.09, 0.5 and 0.65. Deschamps and Dalmazzone (2009) have given few points at TBAB mass fraction of 0.4.

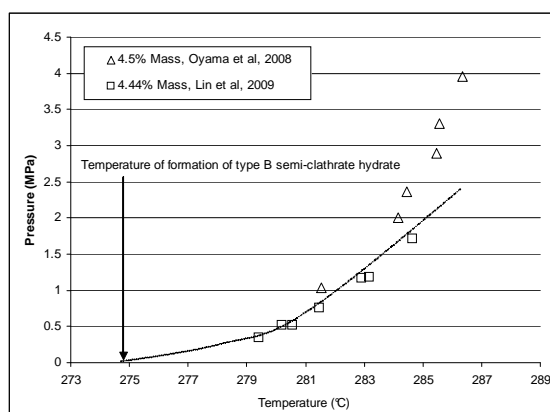


Figure 4: CO₂-TBAB semi clathrate equilibrium curve at TBAB mass fraction of 4.44-4.5%, from Oyama *et al.* (2008) and Lin *et al.* (2009)

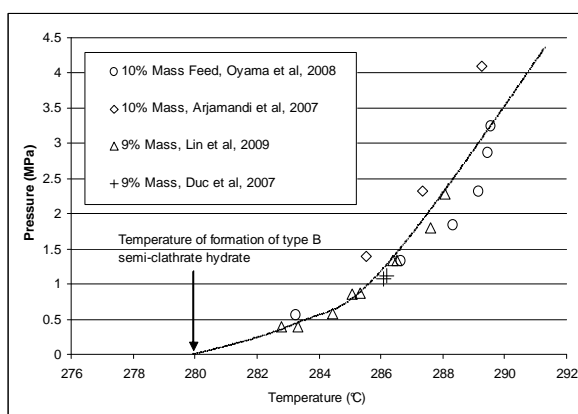


Figure 5: CO₂-TBAB semi clathrate equilibrium curve at TBAB mass fraction of 9-10 percent, from Arjmandi *et al.* (2007), Duc *et al.* (2007), Oyama *et al.*, 2008 and Lin *et al.* (2009)

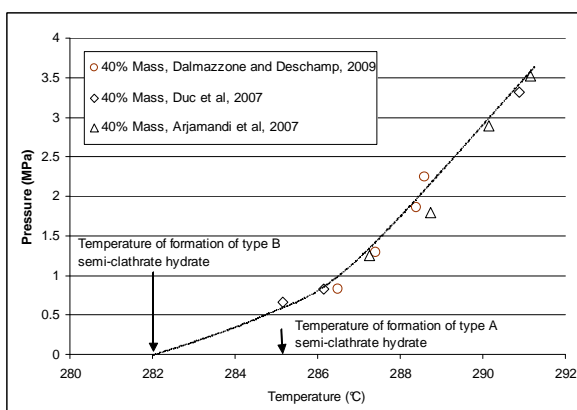


Figure 6: CO₂-TBAB semi clathrate equilibrium curve at TBAB mass fraction of 40 percent, from Arjmandi *et al.*, 2007, Duc *et al.*, 2007, Dalmazzone and Deschamps, 2009

Figure 4, Figure 5 and Figure 6 show some of the experimental data for CO₂-TBAB semi clathrate. All the data are not coherent. On Figure 4, for two similar TBAB mass fractions, we can distinguish two different equilibrium curves (Oyama *et al.* in 2008, and Lin *et al.* in 2009). At TBAB mass fraction of 9-10 percent (Figure 5), the equilibrium data of Arjmandi *et al.*, (2007), Duc *et al.*, (2007), Oyama *et al.*, (2008) and Lin *et al.*, (2009) do not seem in coherence together. But, at TBAB mass fraction of 0.4 (Figure 6), the data from Arjmandi *et al.*, (2007), Duc *et al.* (2007) and Dalmazzone and Deschamps (2009) appear to be coherent together. The difference between the authors can be explained by the difficulty to crystallize the same structure. In fact, as we underlined before, the TBAB semi-clathrate can crystallize under 4 structures, and at least two of them can capture gas (Paricaud, 2009).

Independently of the difference between the experiments, it can be stated that the equilibrium pressure decreases as the temperature decreases. The different authors reported equilibrium pressure down to 0.5 MPa, but never close to the atmospheric pressure. In fact, at low pressure, the kinetics slow down and the crystallization time becomes too much long to be observed. But, from a theoretical point of view (Herri *et al.*, 2014), the equilibrium pressure tends to 0 as the temperature tends to the temperature of equilibrium of the pure TBAB clathrate hydrate.

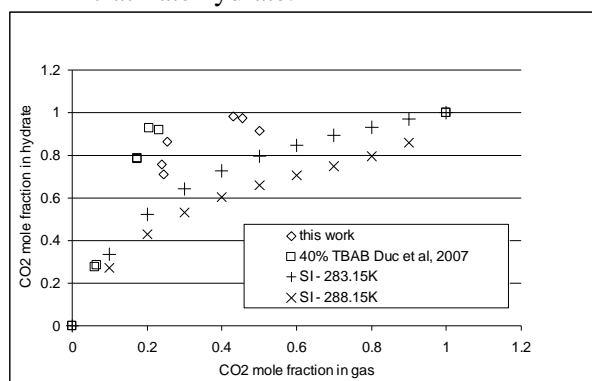


Figure 7: Selectivity of the separation of CO₂ from N₂ during crystallization of semi-clathrate hydrates from TBAB solution, and comparison to the selectivity of clathrate hydrate of structure SI.

Figure 7 presents the selectivity of the separation of CO₂ from N₂ during crystallization of semi-clathrate hydrates from TBAB solution, from Herri

et al (2014). The data from this work are compared to the results from Duc *et al.*, (2007). All the experimental points of this study and from Duc *et al.*, (2007) are in the range of temperature [283.4-288.6K]. Herri et al (2014) plotted a reference case consisting in the molar fraction of CO₂ in the SI structure (pure water clathrate hydrate), at two temperatures of 283.15K and 288.15 K. We can observe an enhancement of the content in CO₂ in the case of the semi-clathrate hydrate of TBAB, even at low molar fraction of CO₂. However, it is observed a difference between the data of this work and the results of Duc *et al.*, (2007). The data from Duc *et al.*, (2007) has been determined with a liquid solution at TBAB mass fraction of 0.4. In our work, the TBAB mass fraction is in the range [0.07-0.18] and could explain the difference. But independently of the differences, it can be underlined that the semi-clathrate hydrate of TBAB has a better affinity to CO₂ in comparison to pure water clathrate hydrate.

For example, at a gas molar fraction of CO₂ around 0.2, the CO₂ molar fraction in the clathrate hydrate is in the range of 0.43 (T=288.15K) to 0.42 (T=283.15K) whereas the CO₂ molar fraction in the TBAB semi-clathrate hydrate can be up to 0.93 (from Duc *et al.*, (2007) at a temperature of 286.15K).

Similarly, at gas molar fraction of CO₂ around the value of 0.5, the CO₂ molar fraction in the clathrate hydrate is in the range 0.66 (T=288.15) to 0.79 (T=283.15) whereas the CO₂ molar fraction in the TBAB semi-clathrate hydrate can be up to 0.96 (Herri et al, 2014) at a temperature of 285.5K).

Brantuas (2013) has also reported the Gas Storage Capacity of some quaternary ammonium salts. The first experimental fact is the low value in the range of [30-60 m³/m³], but also that there is no clear relationship in between the pressure and the Gas Storage Capacity.

Table 1 CO₂ Gas Storage Capacity of Quaternary Ammonium Salts (From Brantuas, 2013)

Experiment	CO ₂ pressure (bars)	Gas Storage Capacity (m ³ /m ³)
TBAB	8.5	33.6
TBPB (experiment 1)	6.3	30.6
TBPB (experiment 2)	7.9	57.0
TBPB (experiment 3)	4.9	61.4
TBACl (experiment 1)	13.8	39.4
TBACl (experiment 2)	10.1	23.5
TBACl (experiment 3)	8.1	44.7
TBACl (experiment 4)	7.8	45.7
TBACl (experiment 5)	8.3	45.4
TBAF	13.6	45.3

CONCLUSIONS

The main conclusions regarding the benefits and drawbacks of thermodynamic additives can be summarized as follows:

- the operating temperature cannot be lower than the temperature of formation of the pure promoter hydrate, for example 281K for Cyclopentane, or 285K for the TBAB. At lower temperature, there is a competition between the pure promoter hydrate, and the mix gas promoter hydrate which affects the Gas Storage Capacity of the hydrate phase,
- the selectivity of the CO₂ separation is slightly enhanced in presence of CP, and very slightly enhanced in presence of TBAB,
- the equilibrium pressure depends on the difference of temperature ΔT between the operating temperature and the temperature of formation of the pure promoter hydrate,
- the equilibrium pressure tends to 0 as ΔT tends to 0,
- the storage capacity is low. From a theoretical point of view (see paper 2 in this series of 4 papers), the storage capacity vanishes as the pressure tends to 0.

So, there is a fundamental contradiction between the benefits of a thermodynamic additive to drop the operating pressure, and the drawback in terms of gas storage capacity which decreases, as the pressure drops.

Acknowledgements:

This work has been carried out within the ANR (French Research Agency) project CO2 SECOHYA and the FUI ACACIA project. The FP7 European project iCAP (GA n°241393) has also supported this work.

BIBIOGRAPHY

- Arjmandi, M.; Chapoy, A.; Tohidi, B.; 2007, Equilibrium Data of Hydrogen, Methane, Nitrogen, Carbon Dioxide, and Natural Gas in Semi-Clathrate Hydrates of Tetrabutyl Ammonium Bromide. *J. Chem. Eng. Data*, 52, 2153-2158
- Belandria, V., Mohammadi, A. H., Richon, D., 2009. Volumetric properties of the (tetrahydrofuran + water) and (tetra-*n*-butyl ammonium bromide + water) systems: Experimental measurements and correlations. *J. Chem. Thermodyn.* (41) 1382-1386.
- Bollas, G. M., Chen, C. C., Barton, P. I., 2008, Refined Electrolyte-NRTL Model: Activity Coefficient Expressions for Application to Multi-Electrolyte Systems; *AIChE J.* 54, 1608-1624.
- Brantuas, P., 2013, Captage du dioxyde de carbone par des semiclathrates hydrates : modélisation, expérimentation et dimensionnement d'une unité pilote, Ph.D. Ecole Doctorale de Saint-Etienne, France
- Brinchi, L., Castellani, B., Cotana, F., Filipponi, M., Rossi, F., Investigation of a novel reactor for gas hydrate production, *Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011)*, Edinburgh, Scotland, United Kingdom, July 17-21
- Chen, C.-C.; Britt, H. I.; Boston, J. F.; Evans, L.B.; 1982, Local Composition Model for Excess Gibbs Energy of Electrolyte Systems; *AIChE J.* 28, 588-596.
- Chen, C.-C., Evans, L. B., 1986, A Local Composition Model for the Excess Gibbs Energy of Aqueous Electrolyte Systems; *AIChE J.* 32, 444-454.
- Compingt, A., Blanc, P., Quidort, A., 2009. Slurry for Refrigeration Industrial Kitchen Application. *Proceedings of 8th IIR Conference on Phase Change Material and Slurries for Refrigeration and Air Conditioning*, Karlsruhe, 2009.
- Danesh, A.; "PVT and Phase Behaviour of Petroleum Reservoir Fluids"; 1998, Elsevier
- Darbouret, M., 2005a. Etude rhéologique d'une suspension d'hydrates en tant que fluide frigoporteur diphasique Résultats expérimentaux et modélisation. Ph.D., Ecole Nationale Supérieure des Mines de Saint-Etienne, France.
- Darbouret, M., Cournil, M., Herri, J. M., 2005b. Rheological study of TBAB hydrate slurries as secondary two-phase refrigerants. *Int. J. Refrig.* 28 (5), 663-671.
- Davidson, D. W.; 1973, Clathrate Hydrates. In *Water, a comprehensive treatise*; Vol. 2; *Water in crystalline hydrates; aqueous solutions of simple nonelectrolytes*; Franks, F., Ed.; Plenum Press: New York 140-146.
- Delahaye, A., Fournaison, L., Marinha, S., Chatti, I., Petit, J.-P., Dalmazzone, D., Fürst, W., 2006, Effect of THF on equilibrium pressure and dissociation enthalpy of CO2 hydrates applied to secondary refrigeration. *Industrial & engineering chemistry research*, 45(1), p.391-397.
- Deppe, S.S. Tam, R.P. Currier, J.S. Young, G.K. Anderson, L. Le, D.F. Spencer., 2002, A high pressure carbon dioxide separation process in an IGCC Plant, *Future Energy System and Technology for CO2 abatement*, Antwerpen, Belgique, November 18-19.
- Deschamps and Dalmazzone, 2009, Dissociation enthalpies and phase equilibrium for TBAB semi-clathrates of N₂, CO₂, N₂+CO₂ and CH₄+CO₂, *Therm Anal Calorim*, Vol. 98, pages 113-118
- Douzet, J., 2011, Conception, construction, experimentation et modélisation d'un banc d'essai grandeur nature de climatisation utilisant un fluide frigoporteur diphasique à base d'hydrates de TBAB, Ph.D., Ecole Nationale Supérieure des Mines de Saint-Etienne, France.
- Douzet, J., Brantuas, P., Herri, J.-M., 2011, Crystallisation and flowing of high concentrated slurries of quaternary ammonium semi-clathrates. Application to air conditioning and CO2 capture, *Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011)*, Edinburgh, Scotland, United Kingdom, July 17-21

- Douzet, J. ; Kwaterski, M. ; Lallemand, A. ; Chauvy, F. ; Flick, D. ; Herri, J.M., 2013, Prototyping of a real size air-conditioning system using a tetra-n-butylammonium bromide semiclathrate hydrate slurry as secondary two-phase refrigerant - Experimental investigations and modeling, *International Journal of Refrigeration*, 2013, doi: 10.1016/j.ijrefrig.2013.04.015
- Du, J., Liang, D., Li, D., 2010. Experimental Determination of the Equilibrium Conditions of Binary Gas Hydrates of Cyclopentane plus Oxygen, Cyclopentane plus Nitrogen, and Cyclopentane plus Hydrogen. *INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH*, 49(22), p.11797-11800.
- Duc N.G., Chauvy F., Herri J.-M.. CO₂ Capture by Hydrate crystallization - A potential Solution for Gas emission of Steelmaking Industry. *Energy Conversion and Management* 2007; 48, 1313–1322.
- Dwain F. Spencer. US Patent: methods of selectively separating CO₂ from a multicomponent gaseous stream; 2000.
- Dyadin, Yu.A. , Udachin, K.A., 1984, Clathrate formation in water-peralkylonium systems, *Journal of Inclusion Phenomena* 2, 61-72.
- Dyadin, Yu.A. , Udachin, K.A., 1987, , Clathrate polyhydrates of peralkylonium salts and their analogs, *Translated from Zhurnal Strukturnoi Khimii*, Vol. 28, No. 3, pp. 75-116, May-June, 1987
- Dyadin, Yu. A. , Bondaryuk, I. V. , Aladko, L. S., 1995, Stoechiometry of clathrates, *Journal of Structural Chemistry*, Vol 36, No. 6
- Fan, S., Liang, D. & Guo, K., 2001. Hydrate Equilibrium Conditions for Cyclopentane and a Quaternary Cyclopentane-Rich Mixture - *Journal of Chemical & Engineering Data* (ACS Publications). *Journal of chemical engineering Data*, p.930-932.
- Galfré, A., Kwaterski, M., Brantuas, P., Cameirao, A., Herri, J.M. 2014, Clathrate hydrate equilibrium data for the gas mixture of carbon dioxide and nitrogen in the presence of an emulsion of cyclopentane in water, *Journal of Chemical & Engineering Data*, 59 (2014) 592–602
- Galindo, A.; Gil-Villegas, A.; Jackson, G.; Burgess, A. N., 1999, SAFT-VRE: Phase behavior of electrolyte solutions with the statistical associating fluid theory for potentials of variable range. *J. Phys. Chem. B* 103, 10272-10281.
- Gayet, P., Dicharry, C., et al., 2005. Experimental determination of methane hydrate dissociation curve up to 55 MPa by using a small amount of surfactant as hydrate promotor. *Chemical Engineering & Science* 60, 21, 5751.
- Gibert, V., 2006. Ice Slurry, Axima Refrigeration Experience. 7th Conference on Phase Change Materials and Slurries for Refrigeration and Air Conditioning, 13-15 September 2006, Dinan, France.
- Herri, J.-M. , Bouchemoua, A., Kwaterski , M., Fezoua, A., Ouabbas, Y., Cameirao, A., 2011, Gas Hydrate Equilibria from CO₂-N₂ and CO₂-CH₄ gas mixtures, – Experimental studies and Thermodynamic Modelling, *Fluid Phase Equilibria* (301) 171-190
- Herri, J.M., Kwaterski, M., 2011, Thermodynamic modelling of gas semi-clathrate hydrates using the electrolyte NRTL model, *Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011)*, Edinburgh, Scotland, United Kingdom, July 17-21
- Herri, J.M., Kwaterski, M., 2012, Derivation of a Langmuir type of model to describe the intrinsic growth rate of gas hydrates during crystallization from gas mixtures, *Chemical Engineering Science* (81)28-37
- Herri, J.-M., Bouchemoua, A., Kwaterski, M., Brântuas , Galfré, A., P., Bouillot, B., Douzet, J., Ouabbas, Y., Cameirao, A. 2014, Enhanced selectivity of the separation of CO₂ from NE during crystallization of semi-clathrate hydrates from quaternary ammonium, *Oil and Gas*, Accepted
- Herslund, P.J., a, Thomsen, K., Abildskov, J., von Solms, N., Galfré A., Brântuas, P., Kwaterski, M., Herri, J.M., 2013, Thermodynamic promotion of carbon dioxide-clathrate hydrate formation by tetrahydrofuran, cyclopentane and their mixtures, *International Journal of Greenhouse Gas Control* (17) 397–410
- Holder, G.D., Zetts, S.P. & Pradhan, N., 1988. Phase Behavior in Systems Containing Clathrate Hydrates: A Review. *Reviews in Chemical Engineering*, 5(1-4), p.1–70.

- Jeffrey, G. A.; 1984, "Hydrate inclusion compounds"; in Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; eds., "Inclusion compounds", I, 135-190; Academic Press, New York
- Kamata Y. Oyama H. Shimada W. Ebinuma T. Takeya S. Uchida T. Nagao J. Narita H. 2004. Gas separation method using tetra nbutylammonium bromide semi-clathrate hydrate. *Jpn J Appl Phys.* 43. 3. 62–5.
- Kang, S.-P., Lee, H., 2000, Recovery of CO₂ from Flue Gas Using Gas Hydrate: Thermodynamic Verification through Phase Equilibrium Measurements, *Environ. Sci. Technol.* 34, 4397-4400
- Kang, S.-P., Lee, H., Lee, C.-S. and Sung, W.-M., 2001, Hydrate phase equilibria of the guest mixtures containing CO₂, N₂ and tetrahydrofuran, *Fluid Phase Equilibria*, 185, 101–109.
- Kwaterski, M., Herri, J.M., 2011, Thermodynamic modelling of semi-clathrate hydrates of gas and quaternary ammonium salts, *Proceedings of the 7th International Conference on Gas Hydrates (ICGH 2011)*, Edinburgh, Scotland, United Kingdom, July 17-21, 2011.
- Li, S., Fan, S., Wang, J., Lang, X., Liang, D. 2009. CO₂ capture from binary mixture via forming hydrate with the help of tetra-n-butyl ammonium bromide. *Journal of Natural Gas Chemistry.* 18. 15-20.
- Li, S., Fan, S., Wang, J., Lang, X., Wang, Y., 2010. Clathrate Hydrate Capture of CO₂ from Simulated Flue Gas with Cyclopentane/Water Emulsion. *Chinese Journal of Chemical Engineering*, 18(2), p.202–206.
- Li X-S, et al., 2011, Hydrate-based pre-combustion carbon dioxide capture process in the system with tetra-n-butyl ammonium bromide solution in the presence of cyclopentane, *Energy*, doi:10.1016/j.energy.2011.01.034
- Li, X.-S., Xu, C.-G., Chen, Z.-Y., Jing, C., 2012. Synergic effect of cyclopentane and tetra-n-butyl ammonium bromide on hydrate-based carbon dioxide separation from fuel gas mixture by measurements of gas uptake and X-ray diffraction patterns. *International Journal of Hydrogen Energy*, 37(1), p.720–727.
- Lin. W., Delahaye. A., Fournaison. L., 2008. Phase equilibrium and dissociation enthalpy for semi-clathrate hydrate of CO₂ + TBAB. *Fluid Phase Equilibria.* 264. 1-2. 220-227.
- Linga, P., Kumar, R. & Englezos, P., 2007a. Gas hydrate formation from hydrogen/carbon dioxide and nitrogen/carbon dioxide gas mixtures. *Chemical engineering science*, 62(16), p.4268–4276.
- Linga, P., Kumar, R. & Englezos, P., 2007b. The clathrate hydrate process for post and pre-combustion capture of carbon dioxide. *Journal of hazardous materials*, 149(3), p.625–629.
- Linga, P. Kumar, R., Lee, J.-D., Ripmeester, J., Englezos, P., 2010. A new apparatus to enhance the rate of gas hydrate formation: Application to capture of carbon dioxide. *International Journal of Greenhouse Gas Control*, (4), p.630-637.
- Lipkowski J., Komorov V.Y., Rodionova T.V., Dyadin Y.A., Aladko. L.S.. The Structure of Tetrabutylammonium Bromide Hydrate. *Journal of Supramolecular Chemistry* 2002; 2: 435-439.
- McMullan. R. Jeffrey. G.A. 1959. Hydrates of the tetra n-butyl and Tetra i-amyl Quaternary Ammonium Salts. *Journal of Chemical Physics.* 31. 5. 1231-1234.
- Meunier, F., Rivet, P., Terrier, M.F., 2007. *Froid Industriel*. Ed. Dunod, Paris.
- Mizukami, T., 2010, Thermal Energy Storage system with clathrate hydrate slurry. Keio University "Global COE Program" International Symposium, Clathrate Hydrates and Technology Innovations, Challenges Toward a Symbiotic Energy Paradigm, 15 March 2010, Yokohama, Japan.
- Mohammadi, A.H. & Richon, D., 2009. Phase equilibria of clathrate hydrates of methyl cyclopentane, methyl cyclohexane, cyclopentane or cyclohexane+carbon dioxide. *Chemical Engineering Science*, 64(24), p.5319-5322.
- Mohammadi, A.H. & Richon, D., 2010. Clathrate hydrate dissociation conditions for the methane+cycloheptane/ cyclooctane+water and carbon dioxide + cycloheptane / cyclooctane + water systems. *Chemical Engineering Science*, 65 , p.3356–3361
- Mohammadi, A.H. & Richon, D., 2011. Phase equilibria of binary clathrate hydrates of nitrogen+cyclopentane/cyclohexane/methyl cyclohexane and ethane+cyclopentane/cyclohexane/methyl cyclohexane. *Chemical Engineering Science*, 66(20), p.4936-4940.

- Nakajima, M., Ohmura, R., Mori, Y.H., 2008, Clathrate Hydrate Formation from Cyclopentane-in-water emulsion, *Ind. Eng. Chem. Res.* (47) 8933-8939
- Ogoshi, H., Matsuyama, E., Miyamoto, H., Mizukami, T., 2010. Clathrate Hydrate Slurry, CHS Thermal energy storage System and Its Applications. *Proceedings of 2010 International Symposium on Next-generation Air Conditioning and Refrigeration Technology*, 17-19 February 2010, Tokyo, Japan.
- Obata, Y., Masuda, N., Joo, K., Katoh, A., 2003. Advanced Technologies Towards the New Era of Energy Industries. *NKK Tech. Rev.* (88) 103-115.
- Oyama, H., Shimada, W., Ebinuma, T., Kamata, Y., 2005. Phase diagram, latent heat, and specific heat of TBAB semiclathrate hydrate crystals. *Fluid phase Equilib.* (234) 131-135.
- Oyama, H., Ebinuma, T., Nagao, J.; Narita, H.; 2008, Phase Behavior Of TBAB Semiclathrate Hydrate Crystal under several Vapor Components. *Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008)*, Vancouver, British Columbia, CANADA, July 6-10, 2008.
- Paricaud, P. 2011, Modeling the Dissociation Conditions of Salt Hydrates and Gas Semiclathrate Hydrates: Application to Lithium Bromide, Hydrogen Iodide, and Tetra-n-butylammonium Bromide + Carbon Dioxide Systems, *J. Phys. Chem. B* 2011, 115, 288–299
- Riesco, N., Trusler, J.P.M., Novel optical flow cell for measurements of fluid phase behavior, *Fluid Phase Equilibria*, 228-229 (2005), p. 233-238.
- Sabil, K.M., Witkamp, G.-J., Peters, C.J., 2010. Phase equilibria in ternary (carbon dioxide + tetrahydrofuran + water) system in hydrate-forming region: Effects of carbon dioxide concentration and the occurrence of pseudo-retrograde hydrate phenomenon. *The Journal of Chemical Thermodynamics*, 42(1), p.8-16.
- Sato, K., Tokutomi, H., Ohmura, R., 2013, Phase Equilibrium of Ionic Semiclathrate Hydrates formed with Tetrabutylammonium Bromide and Tetrabutylammonium Chloride”, *Fluid Phase Equilibria* 337, 115-118.
- Seo, Y.-T., Kang, S.-P., Lee, H., 2001. Experimental determination and thermodynamic modeling of methane and nitrogen hydrates in the presence of THF, propylene oxide, 1,4-dioxane and acetone. *Fluid Phase Equilibria*, 189(1-2), p.99-110.
- Seo, Y., Kang, S.-P., Lee, S., Lee, H., Experimental Measurements of Hydrate Phase Equilibria for Carbon Dioxide in the Presence of THF, Propylene Oxide, and 1,4-Dioxane, *J. Chem. Eng. Data*, 53 (2008), p. 2833-2837.
- Shimada, W.; Ebinuma, T.; Oyama, H.; Kamata, Y.; Takeya, S.; Uchida, T.; Nagao, J.; Narita, H.; 2003, Separation of Gas Molecule Using Tetra-n-butyl Ammonium Bromide Semi-Clathrate Hydrate Crystals. *Jpn. J. Appl. Phys.* 42, L129-L131
- Shimada, W.; Ebinuma, T.; Oyama, H.; Kamata, S.; Narita, H.; 2005a, Free-growth forms and growth kinetics of tetra-n-butyl ammonium bromide semi-clathrate hydrate crystals. *J. Cryst. Growth* 274, 246-250
- Shimada, W., Shiro, M., Kondo, H., Takeya, S., Oyama, H., Ebinuma, T., Narita, H., 2005b, Tetra-n-butylammonium bromide-water (1/38). *acta Cryst.* C61. o65-o66
- Sloan, E.D. 1998, *Clathrate Hydrates of Natural Gases*, 2nd edition, Marcel Dekker, New York.
- Sloan, E.D.; Koh, C.A.; 2008, “Clathrate hydrates of natural gases”; 3rd ed., CRC Press, Boca Raton
- Spencer, D., 1997, Methods of selectively separating CO₂ from a multicomponent gaseous system. US patent - US 5,700,311.
- Suginaka, T., Sakamoto, H., Iino, K., Sakakibara, Y., Ohmura, R., 2013, Phase Equilibrium for Ionic Semiclathrate Hydrate Formed with CO₂, CH₄, or N₂ plus Tetrabutylphosphonium Bromide”, *Fluid Phase Equilibria*, DOI 10.1016/j.fluid.2013.01.018.
- Tajima, H., Yamasaki, A., Kiyono, F., 2004, Energy consumption estimation for greenhouse gas separation processes by clathrate hydrate formation, *Energy* 29, 1713-1729
- Takao, S., Ogoshi, H., Matsumoto, S., 2001, Air conditioning and thermal storage systems using clathrate hydrate slurry. US patent - US 6,560,971 B2.
- Takao, S., Ogoshi, H., Matsumoto, S., 2002 Air conditioning and thermal storage systems using clathrate hydrate slurry, US Patent 083720A1
- Takao, S., Ogoshi, H., Fukushima, S., H., Matsumoto, 2004, Thermal storage medium using a hydrate and apparatus thereof, and method for producing the thermal storage medium. US patent – 20050016200.

- Thiam, A., Bouchemoua, A., Chauvy, F., Herri, J.-M., Gas Hydrates Crystallization from CO₂-CH₄ gas mixtures :experiments and modelling, Proceedings of the 6th International Conference on Gas Hydrates (ICGH 2008), Vancouver, British Columbia, CANADA, July 6-10, 2008.
- Tohidi, B., Danesh, A., Todd, A. C., Burgass, R. W., Østergaard, K. K., 1997. Equilibrium data and thermodynamic modelling of cyclopentane and neopentane hydrates. *Fluid Phase Equilibria*, 138(1-2), p.241-250.
- Torre, J.P., Dicharry, C., Ricaurte, M., Daniel-David, D., Broseta, D., 2011. CO₂ capture by hydrate formation in quiescent conditions: in search of efficient kinetic additives. *Energy Procedia* 4, 621-628.
- van der Waals, J. H.; Platteeuw, J. C., Clathrate solutions"; *Adv. Chem. Phys.* 2 (1959) 1-57.
- Xu, C.G., Li, X.S., Lv, Q.N., Chen, Z.Y., Cai, J., 2012, Hydrate-based CO₂ (carbon dioxide) capture from IGCC (integrated gasification combined cycle) synthesis gas using bubble method with a set of visual equipment, *Energy* 44 p358-366
- Yang, H., Fan, S., Lang, X., Yang, Y., 2011. Phase Equilibria of Mixed Gas Hydrates of Oxygen + Tetrahydrofuran, Nitrogen + Tetrahydrofuran, and Air + Tetrahydrofuran. *Journal of Chemical & Engineering Data*, 56(11), p.4152-4156.
- Zhang & Lee, 2009a. Equilibrium of Hydrogen + Cyclopentane and Carbon Dioxide + Cyclopentane Binary Hydrates† - *Journal of Chemical & Engineering Data* (ACS Publications). *Chemical Engineering Journal*, p.659-661.
- Zhang, J., Yedlapalli, P. & Lee, J.W., 2009b. Thermodynamic analysis of hydrate-based pre-combustion capture of CO₂. *Chemical Engineering Science*, 64(22), p.4732-4736.
- Zhang, J. & Lee, J.W., 2009c. Enhanced Kinetics of CO₂ Hydrate Formation under Static Conditions. *Industrial & Engineering Chemistry Research*, 48(13), p.5934-5942.
- Zhong, Y., Rogers, R.E., 2000, Surfactant effects on gas hydrate formation. *Chemical Engineering Science*, 55(19), pp. 4175-4187.