CO2 capture by using hydrates: 4) From experimental evidences to economic impossibility as a post combustion process

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4) FROM EXPERIMENTAL EVIDENCES TO ECONOMIC IMPOSSIBILITY AS A POST
COMBUSTION PROCESS

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ABSTRACT
The post-combustion CO2 capture by using clathrates is a method which takes profit of the CO2 selectivity
in gas hydrate to separate it from nitrogen, or other exhausting gases from gas combustion or coal
combustion. The bottleneck is the operative pressure which still remains high and needs to be drop down to
0.5 MPa in order to compete with the reference case using Amines. After two national projects
(SECOHYA, ACACIA) and an European program (iCAP), we tested different classes of thermodynamic
additives, organic ones (water non soluble cyclopentane, water soluble THF) which form classical gas
hydrates with structure SII, and ionic ones (Tetra-N-Butyl Ammonium Bromide, TBAB) which forms new
types of structures, and mixture of promoters. In this presentation, we present a flow-sheet for a CO2
capture process, with two stages, a bulk and a finisher. After sizing, we emphasize that the volume of the
bulk is similar to the volume of an Amine Process because the crystallization operates in a Gas/liquid
transfer limitation regime. But, the volume of solvent to handle is much too large to be reasonable.

Keywords: semi clathrates hydrates, CO2 capture, sizing, costing

INTRODUCTION
The main motivation for CO2 capture via hydrates
formation is a reduction of the heat duty, which
strongly reduces the power plant efficiency when
using an absorption processes with chemical
solvent.

Nevertheless, hydrates formation requires high
pressure levels and low temperatures in the
absorber: so, flue gas conditioning is necessary.
The principle of the design of the process (without
flue gas conditioning) is shown in Figure 1. The
main components are the vessel for hydrates
formation, the vessel for hydrates dissociation and
the slurry pump that tranfers the hydrate slurry
from the formation vessel to the dissociation one.
Preliminary assumptions were the following:

- dissociation may be realised at 50 bar and 20 °C,
- the heat for dissociation does not affect the
efficiency of the power plant, given that the
temperature level is close to ambient conditions.

Figure 1: Design of the capture process with
hydrates
To provide for the right flue gas conditions in the hydrates formation vessel (5 bars and 0 °C) three main steps are necessary:
- Compression;
- Drying (to avoid freezing);
- Cooling.

The drying is essential as surfaces in the heat exchanger of the last cooling stage have temperatures below the freezing point of water. Even if a temperature approach of 10 °C is used between flue gas and cooling medium, local freezing might still harm the components and affect the flow conditions in the heat exchanger. Three different cooling strategies have been investigated and Figure 2 presents the variant with the lowest impact on the energy penalty of the power station.

![Figure 2: Flow scheme of the flue gas conditioning section](image)

Within this variant, the flue gas leaving the FGD unit is cooled by the clean gas leaving the hydrates formation column and is sent to the compression train. Only one intercooler is foreseen to reach a high temperature level downstream of the compression train. A high temperature level is required to heat up the clean gas before it enters the clean gas expander. Downstream of the second flue gas cooler and the liquid-water knock-off drum, the flue gas is dried in an adsorptive drying unit. The flue gas is then directly cooled using a flue gas expander. The backpressure of the expander is determined by the requirements for hydrates formation. The flue pressure at the outlet of the compression train can be varied to reach the desired temperature at the inlet of the hydrates formation column.

The energy penalty corresponding to this flue gas conditioning has been evaluated. For the CO₂ capture based on hydrate formation flue gas conditioning represents the largest contributor to the overall efficiency penalty. In this section all interface quantities of the flue gas conditioning (i.e., the electrical energy for pumps and compressors, the steam for the adsorptive drying unit, the cooling water pumps) and CO₂ compression are considered without taking into account any energy requirement for the capture unit itself (e.g. slurry pump). The break down of the corresponding efficiency penalty is shown in Figure 3.

![Figure 3: Break down of the efficiency penalty for flue gas conditioning and the CO₂ compression (assumed CO₂ pressure at CO₂ compressor inlet = 50 bar)](image)

The influence of the desired flue gas pressure in the hydrates formation column is shown in Figure 4. For a flue gas pressure above 15 bar, the energy penalty for flue gas conditioning is higher than energy penalty of a MEA based capture process unit (10 points). So, a capture process based on hydrate formation must be operated at a pressure under 15 bar in order to compete with a capture process based on chemical solvent.
Figure 4: Influence of the desired flue gas pressure on the efficiency penalty (desired flue gas temperature = 0 °C, assumed CO\textsubscript{2} pressure at CO\textsubscript{2} compressor inlet = 50 bar). The efficiency penalty does not include the capture process.

We propose here (see ANNEX) a flow sheet in two stages, a bulk reactor and a finisher. The bulk reactor operates with a gas phase at a mole fraction higher than 0.2 in order to form a pure CO\textsubscript{2} hydrate (see Figure 5 and Paper 1/4 of this series). The finisher captures the remaining CO\textsubscript{2} in order to meet the specifications, especially to recover CO\textsubscript{2} up to a fraction hereafter called RECOV.

The Liquid solution is TBAB solution at a weight fraction of \( w_{TBAB}^{L} = 0.32 \). It crystallizes a S38 structure (see paper 2/4 of this series) below a temperature of 10.38°C, corresponding to the eutectic point. The water and TBAB composition remains the same in the liquid and in the solid.

The Hard-Coal gas has been chosen as a base case flue gas for the design of the hydrate formation process. It is defined as:
- Flowrate (kg/s) 772.8
- Pressure (bara) 1.018
- Temperature(°C) 49
- Composition (wt.%): 67.26% N\textsubscript{2}; 3.58% O\textsubscript{2}; 20.58% CO\textsubscript{2}; 7.43% H\textsubscript{2}O; 1.14% Ar

The process will be designed with an overall 90% CO\textsubscript{2} removal efficiency, a typical CO\textsubscript{2} recovery in reference carbon dioxide capture and storage (Thambimuthu et al, 2005; Oexmann, 2012; Liebenthal, 2011)

The CO\textsubscript{2} mole fraction (\( y_{CO_{2}}^{dry\;flue\;gas} \)) of the Flue Gas after drying, the mole flow rate \( F_{dry\;flue\;gas} \) remains lower than 0.2. So, a recycling of pure CO\textsubscript{2} (mole flow rate \( F_{Recycling} \)) is injected before entering the bulk in order to increase the CO\textsubscript{2} content so that the bulk reactor can operate at a CO\textsubscript{2} gas molar fraction of 0.2. It is a key point of the process to crystallize hydrate with 100% CO\textsubscript{2}. The quantity of hydrate to crystallize is consequently increased. It brings a penalty from two point of views: 1) the slurry to handle at the exit of the bulk reactor is increased, 2) the size of the reactor is increased too.

\[
F_{OUT,\;bulk}^{CO_{2,\;hyd}} = RECOV \cdot F_{dry\;flue\;gas}^{CO_{2}} + F_{Recycling}^{CO_{2}} \quad (1)
\]

OPERATIVE CONDITIONS OF THE BULK REACTOR

We recall here the numeric data and correlations given in the paper number 2/4 of this series of four papers.

The maximum gas storage capacity of the TBAB, 38H\textsubscript{2}O structure is:

\[
n_{S_{38,\;Max}}^{STORAGE} = 3191 \; mole.m^{-3} \quad (2)
\]

The effective storage capacity takes into account the occupancy of cavities \( \theta_j \) by component j. It depends on thermodynamics.

\[
n_{S_{38,\;j}}^{STORAGE} = \theta_j \cdot n_{S_{38,\;Max}}^{STORAGE} \quad (3)
\]

The Liquid solution is TBAB solution at a weight fraction of \( w_{TBAB}^{L} = 0.32 \). We can evaluate the mole number of water per volume of liquid solution:

\[
n_{water,\;L}^{STORAGE} = 38954 \; mole.m^{-3} \quad (4)
\]

So, the Liquid storage capacity of gas components j is given by:

\[
n_{j,\;L}^{STORAGE} = n_{water,\;L}^{STORAGE} \cdot x_{j,\;L} \quad (5)
\]
\( x_{j,L} \text{ [mole of component } j \text{ / mole of water]} \) is the solubility of the component \( j \).

The equilibrium pressure is fixed by the difference of temperature between the operative temperature \( \Theta_{\text{Bulk}} \text{ [°C]} \) and the value of 10.38°C at which the pure TBAB semi-clathrate of structure S38 can form from a liquid solution at a TBAB mass fraction of 0.32. From the complete thermodynamic modeling, we have determined the operative pressure of a capture process \( P_{\text{Bulk,eq}} \text{ [MPa]} \) from the following correlation:

\[
P_{\text{Bulk,eq}} = 3.687 \times 10^{-3} (\Theta_{\text{Bulk}} - 10.38)^3 \\
- 7.839 \times 10^{-3} (\Theta_{\text{Bulk}} - 10.38)^2 \\
+ 2.035 \times 10^{-1} (\Theta_{\text{Bulk}} - 10.38)
\] (6)

The operative pressure cannot be lower than \( P_{\text{Bulk,eq}} \text{ [MPa]} \) given in Eq.7:

\[
P_{\text{Bulk}} = q \cdot P_{\text{Bulk,eq}} \text{ / } y_{\text{CO}_2}
\] (7)

Also, the thermodynamic modeling has allowed determining the occupancy factor of the cavities, independently of the gas hydrate former.

\[
\theta = -3.719 \times 10^{-3} (\Theta_{\text{Bulk}} - 10.38)^2 \\
+ 9.926 \times 10^{-1} (\Theta_{\text{Bulk}} - 10.38)
\] (8)

It is assumed that the bulk reactor operates in a Gas/liquid transfer limited regime. The temperature in the bulk reactor is \( \Theta_{\text{Bulk}} \text{ [°C]} \) and the corresponding equilibrium pressure of the pure \( \text{CO}_2 \) semi-clathrate hydrate of TBAB is \( P_{\text{Bulk,eq}} \text{ [MPa]} \), given in Eq. 6:

\[
x_{\text{CO}_2,L} \text{ OUT, Bulk} = \frac{\phi_G \text{ P}_{\text{Bulk,eq}}}{k_{\text{H,CO}_2,w} \left( T_{\text{Bulk}} \cdot p_w^{0,\sigma} \right)}
\] (9)

The values of the Henry constants \( k_{\text{H,CO}_2,w} \left( T \cdot p_w^{0,\sigma} \right) \) are retrieved from experimental values, or from correlations (Galfré et al, 2014). It is assumed that the solubility of gaseous component into TBAB solution is similar to the solubility of gaseous components in pure water. \( \phi_G \text{CO}_2 \) is the fugacity coefficient.

The bulk reactor is assuming to work at a \( \text{CO}_2 \) mole fraction \( y_{\text{CO}_2,\text{bulk}}^{\text{OUT}} = 0.2 \). At such a composition, the semi-clathrate hydrate is a practically pure \( \text{CO}_2 \) hydrate (see paper 1/4 of this series of 4 papers). The other gas components are not consumed during the crystallization, and they are in physical equilibrium with the liquid phase at pressure \( P_{\text{bulk}} \text{ [MPa]} \) given in Eq.7:

\[
\phi_G \text{CO}_2 \text{ OUT, Bulk} = \frac{y_{\text{Bulk}} \text{ CO}_2 \phi_G \text{ P}_{\text{Bulk}}}{k_{\text{H,CO}_2,w} \left( T_{\text{Bulk}} \cdot p_w^{0,\sigma} \right)}
\] (10)

The bulk and finisher reactors are considered as homogeneous reactions in which the crystallization rate is limited by the gas/liquid mass transfer. From paper 3/4 of this series, we showed that the volume of the reactor is given by:

\[
V_L = \frac{r_{\text{CO}_2}}{k_L(x_{\text{CO}_2,\text{ext}} - x_{\text{CO}_2,\text{bulk}})C_{\text{H}_2\text{O}}}
\] (11)

Where \( r_{\text{CO}_2} \text{ [mol s}^{-1}] \) is the rate of \( \text{CO}_2 \) capture in the hydrate phase (Eq.1)

\[
r_{\text{CO}_2} = r_{\text{CO}_2,\text{hyd}}
\] (12)

Once the operative temperature is fixed, the equilibrium pressure is fixed (Eq. 6), and the occupancy of gas in the hydrate structure (Eq.8) is also fixed. So, we can evaluate the flow rate of hydrate to be handled from the rate of gas,

\[
Q_{\text{hyd}} = \frac{r_{\text{CO}_2}}{\phi_G \text{CO}_2 \text{ STORAGE}}
\] (13)

It is also possible to evaluate the liquid flow rate from the consideration that the slurry viscosity cannot be too high. So the solid content can not exceed a value \( \Phi_{\text{MAX}} \) (to be designed precisely) which can be around the value of \( \Phi_{\text{MAX}} = 0.3 \) (see paper 3/4 of this series).
\[ Q_{L \text{Out.Bulk}} = \frac{1 - \Phi_{\text{Max}}}{\Phi_{\text{Max}}} Q_{\text{Hyd}}^{\text{Out.Bulk}} \] (14)

**FLUE GASES**

The mole fraction of chemical species in the flue gases, dimensionless, is given by \( y_i^{\text{wet flue gas}} \) and \( y_i^{\text{dry flue gas}} \) respectively before and after the drying stage.

**SPECIFICATIONS**

\( \text{RECOV} \) is the CO\(_2\) recovery ratio expressed as the ratio between the recovered molar flow rate (\( F_{\text{CO}_2}^{\text{OUT.BOTTM}} \)) and the CO\(_2\) molar flow rate in the flue gas (\( F_{\text{wet flue gas}} y_{\text{CO}_2}^{\text{wet flue gas}} \) or \( F_{\text{dry flue gas}} y_{\text{CO}_2}^{\text{dry flue gas}} \))

\[ \text{RECOV} = \frac{F_{\text{OUT.BOTTM}}^{\text{CO}_2}}{F_{\text{dry flue gas}} y_{\text{CO}_2}^{\text{dry flue gas}}} \] (15)

**TOP GAS**

The top gas is composed of the non recovered CO\(_2\) at a molar flow rate \( F_{\text{CO}_2}^{\text{OUT.TOP}} \) and mole fraction \( y_{\text{CO}_2}^{\text{OUT.TOP}} \). The other components are the component to be exhausted from the unit without being captured, mainly N\(_2\), O\(_2\), Ar and other components.

The TOP Gas CO\(_2\) mole fraction can be easily determined. In fact

**BOTTOM FLOW**

The bottom flow gas is composed of pure CO\(_2\)

\[ F_{\text{CO}_2}^{\text{OUT.BOTTM}} = \text{RECOV} F_{\text{dry flue gas}} y_{\text{CO}_2}^{\text{dry flue gas}} \] (18)

Figure 5 : Selectivity of the separation of CO\(_2\) from N\(_2\) during crystallization of semi-clathrate hydrates from TBAB solution, and comparison to the selectivity of clathrate hydrate of structure SI (Herri et al, 2014)

From the experimental results of Herri et al (2014) reported in Figure 5, it is assumed that the hydrates are filled with 100% CO\(_2\) if the flue gas contains more than 20% CO\(_2\).

\[ y_{\text{CO}_2} > 0.2 \Rightarrow z_{\text{CO}_2} = 1; \quad z_{\text{other components}} = 0 \] (16)

If the gas phase is lower than 20% CO\(_2\).

\[ y_{\text{CO}_2} < 0.2 \Rightarrow z_{\text{CO}_2} = 5 \cdot y_{\text{CO}_2}; \quad z_{\text{other components}} = 1 - 5 \cdot y_{\text{CO}_2} \] (17)
Recycling Flow

The bulk reactor is assumed to run with a minimum gas CO₂ mole fraction of \( y_{\text{CO}_2,\text{min}} = 0.2 \). In fact, at this concentration, it has been observed that the hydrate which is formed can be considered 100% CO₂. Consequently, the feed gas entering the bulk reactor needs to be at higher concentration (\( y_{\text{CO}_2}^{\text{IN, Bulk}} > y_{\text{CO}_2,\text{min}} \)) so that a reaction can be operated. The mole fraction in the feed gas (\( y_{\text{CO}_2}^{\text{dry, flue gas}} \)) is probably at a lower concentration than \( y_{\text{CO}_2}^{\text{IN, Bulk}} \) and the flow entering the bulk reactor needs to be completed with a recycling of pure CO₂ gas in order to reach the \( y_{\text{CO}_2}^{\text{IN, Bulk}} \) value.

\[
y_{\text{CO}_2}^{\text{IN, Bulk}} = \frac{F_{\text{dry, flue gas}} y_{\text{CO}_2}^{\text{dry, flue gas}} + F_{\text{Recycling}}}{F_{\text{dry, flue gas}} + F_{\text{Recycling}}} (24)
\]

\[
F_{\text{CO}_2} \quad \text{corresponds to the non recovered CO}_2:\nF_{\text{CO}_2} = (1 - \text{RECOV}) F_{\text{dry, flue gas}} y_{\text{CO}_2}^{\text{dry, flue gas}} (20)
\]

\[
F_{\text{other components}} \quad \text{corresponds to the gases which are not recovered in the CO}_2 \text{ capture unit, and the flow rate is assumed to be flow rate in the flue gas} :\nF_{\text{other components}} = F_{\text{dry, flue gas}} (1 - y_{\text{CO}_2}^{\text{dry, flue gas}}) (21)
\]

Finally, we can express the total top gas flow rate:

\[
F_{\text{OUT, TOP}} = \frac{F_{\text{OUT, TOP}}^{\text{CO}_2}}{y_{\text{CO}_2}^{\text{OUT, TOP}}} = \frac{F_{\text{dry, flue gas}} y_{\text{CO}_2}^{\text{dry, flue gas}}}{1 - y_{\text{CO}_2}^{\text{dry, flue gas}}} (22)
\]

\[
F_{\text{Recycling}} = F_{\text{dry, flue gas}} \frac{y_{\text{IN, Bulk}}^{\text{CO}_2} - y_{\text{CO}_2}^{\text{dry, flue gas}}}{1 - y_{\text{IN, Bulk}}^{\text{CO}_2}} (25)
\]

Finisher Reactor

CO₂ Mole Balance

\[
F_{\text{OUT, Bulk, CO}_2,\text{Gas}} = F_{\text{OUT, Finisher, CO}_2,\text{hyd}} + F_{\text{OUT, Finisher, CO}_2,\text{L}} + F_{\text{CO}_2} (26)
\]

\[
F_{\text{CO}_2} \quad \text{is given from the process specification, following Eq.20, so:}\nF_{\text{OUT, Bulk, CO}_2,\text{Gas}} - F_{\text{OUT, Finisher, CO}_2,\text{hyd}} - F_{\text{OUT, Finisher, CO}_2,\text{L}} = (1 - \text{RECOV}) F_{\text{dry, flue gas}} y_{\text{CO}_2}^{\text{dry, flue gas}} (27)
\]

Other Components Mole Balance

Other components are N₂, O₂ and Ar.

\[
F_{\text{OUT, Bulk, other components, Gas}} = F_{\text{OUT, Finisher, other components, hyd}} + F_{\text{OUT, Finisher, other components, L}} + F_{\text{other components}} (28)
\]

\[
F_{\text{other components}} \quad \text{is given from the process specification, all the other components being not involved in the capture process:}\nF_{\text{OUT, Bulk, other components, Gas}} - F_{\text{OUT, Finisher, other components, hyd}} - F_{\text{other components, L}} = (1 - y_{\text{CO}_2}^{\text{dry, flue gas}}) F_{\text{dry, flue gas}} (29)
\]

Relationship in between variables

The composition of the hydrate slurry is fixed by thermodynamic, and especially the ratio between CO₂ and other components. At gas CO₂ mole fraction lower than \( y_{\text{CO}_2}^{\text{Finisher}} = 0.2 \), we know from Eq.17 that:

\[
\frac{F_{\text{OUT, Finisher, CO}_2,\text{hyd}}}{F_{\text{OUT, Finisher, other components, hyd}}} = \frac{5y_{\text{CO}_2}^{\text{OUT, TOP}}}{1 - 5y_{\text{CO}_2}^{\text{OUT, TOP}}} (30)
\]

Another relationship can be given of mole flow \( F_{\text{OUT, Bulk, Gas}} \):

\[
\frac{F_{\text{OUT, Bulk, CO}_2,\text{Gas}}}{F_{\text{OUT, Bulk, other components, Gas}}} = \frac{y_{\text{CO}_2}^{\text{Bulk}}}{1 - y_{\text{CO}_2}^{\text{Bulk}}} (31)
\]
Also, we can give a relation between $F_{OUT, FIN}^{j, hyd}$ and $F_{j, L}^{OUT, FIN}$ for every components $j$, CO$_2$ and other components, because:

$$F_{OUT, FIN}^{j, hyd} = Q_{hyd}^{OUT, FIN} n_{j, 38, MAX}^{STORAGE} \theta_j$$

(32)

$\theta_j$ is the occupancy of cavities by component $j$.  

So

$$Q_{hyd}^{OUT, FIN} = F_{j, L}^{OUT, FIN} \frac{1 - \Phi}{\Phi}$$

(33)

The volume liquid flow rate is given from Eq.14 by:

$$Q_{L}^{OUT, FIN} = Q_{hyd}^{OUT, FIN} \frac{1 - \Phi}{\Phi}$$

And, finally, from Eq 5., Eq.33 and Eq.14, we can evaluate the mole flow of gas components in the liquid phase: $F_{j, L}^{OUT, FIN}$

$$F_{CO_2, L}^{OUT, FIN} = F_{CO_2, hyd}^{OUT, FIN} \frac{1 - \Phi}{\Phi} n_{j, 38, MAX}^{STORAGE} \Phi n_{water, L}^{STORAGE} x_{CO_2}$$

(34)

or after summation over all the other components:

$$F_{other, components, L}^{OUT, FIN} = \sum_{j \neq CO_2} F_{j, L}^{OUT, FIN}$$

(36)

$$F_{other, components, L}^{OUT, FIN} = F_{CO_2, hyd}^{OUT, FIN} \frac{1 - \Phi}{\Phi} n_{j, 38, MAX}^{STORAGE} \Phi n_{water, L}^{STORAGE} \sum_{j \neq CO_2} x_j$$

In the end, the mole balance on CO$_2$ given in Eq.27 yields to:

$$F_{CO_2, Gas}^{OUT, Bulk} = \left(1 + \frac{1}{n_{j, 38, MAX}^{STORAGE} \theta_{CO_2}} \frac{1 - \Phi}{\Phi} n_{water, L}^{STORAGE} x_{CO_2} \right) F_{CO_2, hyd}^{OUT, FIN}$$

(37)

And the mole balance on other components given in Eq.29 yields to:

$$1 - \sum_{j \neq CO_2} F_{j, L}^{OUT, FIN}$$

$$= \left(1 - \frac{1 - \Phi}{\Phi} \sum_{j \neq CO_2} n_{water, L}^{STORAGE} \theta_{CO_2} \sum_{j \neq CO_2} x_j \right) F_{CO_2, hyd}^{OUT, FIN}$$

$$= (1 - RECOV) F_{dry \ flue \ gas}^{dry \ flue \ gas} x_{CO_2}$$

(38)

Eq.37 and Eq.38 consist of a system of two equations with two unknowns ($F_{CO_2, Gas}^{OUT, Bulk}$ and $F_{CO_2, hyd}^{OUT, FIN}$) which can be solved analytically, provided that $\theta_{CO_2}$ and $x_j$ are calculated elsewhere.

**PARAMETRIC STUDY**

The Figure 6 shows the pure CO$_2$ hydrate equilibrium pressure versus the temperature, given as the difference between the operative temperature and the temperature at the congruent point (10.38°C).

The bulk reactor is assumed to form a pure CO$_2$ hydrate because it is operating at a CO$_2$ molar fraction higher than 0.2 (Eq.16). The Figure 6 shows also the corresponding operative pressure in
the bulk reactor at constant $q=1.5$, ($q$ is defined in Eq.7).

The bulk reactor pressure can not be superior to 1.5 MPa because the energy penalty for flue gas conditioning is higher than energy penalty of a MEA based capture process unit (10 points), see Figure 4.

On Figure 7, we show the liquid volume in the bulk reactor, and the bottom hydrate volume flow rate, as function of the total pressure. Both values decrease dramatically as the pressure is increased. At a pressure of 1.5 MPa, the volume of the bulk reactor is in the range of 5000-6000 m$^3$. The corresponding bottom hydrate flow rate is 40 m$^3$/s, which is a very high value.

![Figure 7: Bulk reactor liquid volume and hydrate bottom volume flow rate. The over pressure coefficient $q$ is given in Eq.7.](image)

The reason to explain such a high volume of hydrate to handle comes from the gas storage capacity of the hydrate. From paper 2 of this series, we got the Figure 8 which gives the hydrate storage capacity. At a pressure of 1.5 MPa, the solid can not store more than 500 moles of CO$_2$ in a volume of 1 m$^3$, to be compared to the value of 2500 moles/m$^3$ for an MEA Amines (Lecomte et al, 2009). More, if we assume the slurry to be concentrated at a solid fraction of $\Phi_{\text{MAX}}=0.33$, given Eq. 14, the total bottom flow rate will be 120 m$^3$/s, which is not realistic.

![Figure 8: Storage capacity. [mole CO$_2$/m$^3$ hyd] in the hydrate phase and liquid phase (from paper 2 of this series)](image)

**CONCLUSION**

Experimental work has shown that it is possible (see paper 1 of this series, here Figure 5) to enhance the selectivity of CO$_2$ in the hydrate structure. The best thermodynamic additive is TBAB, a quaternary ammonium salt.

Among the additives that we tested, allowing to form a stable hydrate without gas (for example THF, cyclopentane, TBAB), it can be said that each of them can form a gas hydrate at atmospheric pressure, with an enrichment of CO2 regarding the gas gformer composition. However the counterpart of the low pressure is the storage capacity that tends to vanish. From a specific thermodynamic modelling on TBAB semi-clathrate hydrate (paper 2 of this series), we proposed a correlation to calculate the storage capacity at a given operative pressure, or a given operative temperature.

In paper 3 of this series, we gave the correlations to design a bubble column running a CO2 separation from TBAB semi-clathrate hydrate.

With a 2 stages process including a finisher, it is possible to produce pure CO$_2$ (this paper)

Nevertheless the volume of the reactor and the liquid flow rate handled is linked to the total pressure (Figure 7). The pressure can not be superior to 1.5 MPa because the energy penalty for flue gas conditioning is higher than energy penalty...
of a MEA based capture process unit (10 points), see Figure 4.
The low storage capacity of TBAB semi-clathrate hydrate increases the size of the equipment and the flow rates to handle. CAPEX and OPEX for an industrial CO$_2$ post combustion capture unit by hydrates would be too high.

So, it appears now obvious that hydrates are not adapted for CO$_2$ capture in post-combustion. We need to increase the pressure to decrease the size of the capture unit which increases the energy penalty linked to flue gas conditioning.
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