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CO2 CAPTURE BY USING HYDRATES: 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 CO_2 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:

- with appropriate additives, it is possible to operate hydrates formation at 5 bar and 0 °C,
- 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.

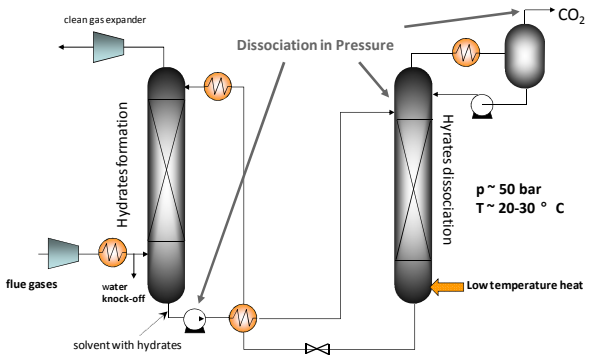


Figure 1: Design of the capture process with hydrates

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.

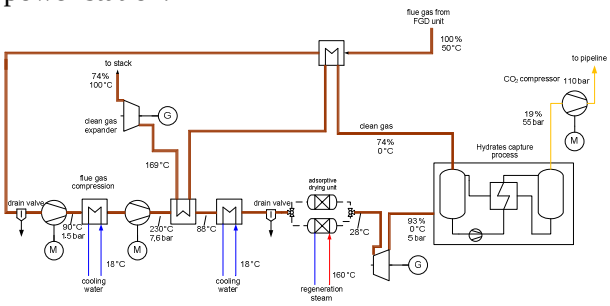


Figure 2: Flow scheme of the flue gas conditioning section

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 CO_2 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 CO_2 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.

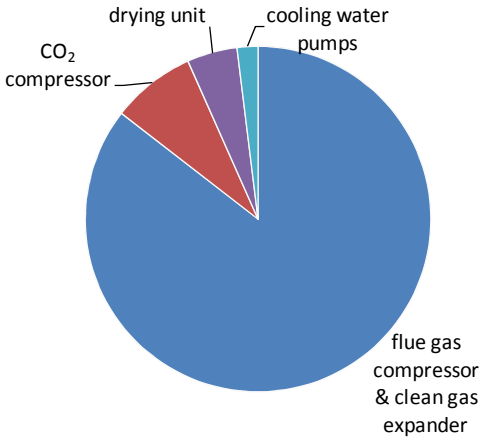


Figure 3: Break down of the efficiency penalty for flue gas conditioning and the CO_2 compression (assumed CO_2 pressure at CO_2 compressor inlet = 50 bar)

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.

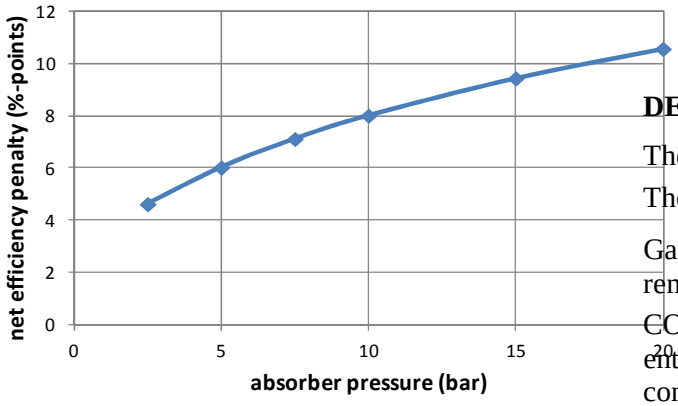


Figure 4: Influence of the desired flue gas pressure on the efficiency penalty (desired flue gas temperature = 0 °C, assumed CO_2 pressure at CO_2 compressor inlet = 50 bar). The efficiency penalty does not include the capture process.

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_2 hydrate (see Figure 5 and Paper 1/4 of this series). The finisher captures the remaining CO_2 in order to feet the specifications, especially to recover CO_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_2; 3.58% O_2; 20.58% CO_2; 7.43% H_2O; 1.14% Ar

The process will be designed with an overall 90% CO_2 removal efficiency, a typical CO_2 recovery in reference carbon dioxide capture and storage (Thambimuthu et al, 2005; Oexmann, 2012; Liebenthal, 2011)

DETAILS ON THE FLOWSHEET

The flow sheet is given in ANNEX.
The CO_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_2 (mole flow rate $F^{Recycling}$) is injected before entering the bulk in order to increase the CO_2 content so that the bulk reactor can operate at a CO_2 gas molar fraction of 0.2. It is a key point of the process to crystallize hydrate with 100% CO_2. The quantity of hydrate to crystallize is consequently increased. It brings s 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.

$$F_{CO_2,hyd}^{OUT,bulk} = RECOV \bullet F^{dry\ flue\ gas} y_{CO_2}^{dry\ flue\ gas} + F^{Recycling} \quad (1)$$

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, $38H_2O$ structure is:

$$n_{S38,Max}^{STORAGE} = 3191\ mole.m^{-3} \quad (2)$$

The effective storage capacity takes into account the occupancy of cavities θ_j by component j. It depends on thermodynamics.

$$n_{S38,j}^{STORAGE} = \theta_j \cdot n_{S38,Max}^{STORAGE} \quad (3)$$

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:

$$n_{j,L}^{STORAGE} = n_{water,L}^{STORAGE} x_{j,L} \quad (5)$$

$x_{j,L}\left[mole\ of\ component\ j / mole\ of\ water\right]$ is the solubility of the component j.

The equilibrium pressure is fixed by the difference of temperature between the operative temperature $\Theta_{Bulk}\left[°C\right]$ 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 $\mathrm{P}_{Bulk,eq}\ \left[MPa\right]$ from the following correlation:

$$\begin{aligned}\mathrm{P}_{Bulk,eq} &= 3.687\cdot10^{-3}\left(\Theta_{Bulk}-10.38\right)^3 \\ &- 7.839\cdot10^{-3}\left(\Theta_{Bulk}-10.38\right)^2 \\ &+ 2.035\cdot10^{-1}\left(\Theta_{Bulk}-10.38\right)\end{aligned} \quad (6)$$

The operative pressure cannot be lower than $\mathrm{P}_{Bulk,eq}/y_{CO_2}^{Bulk}$ where $y_{CO_2}^{Bulk}$ is the average mole fraction of CO_2 in the gas phase of the bubble column. We assume the operative pressure to be higher and fixed by a coefficient *q*:

$$\mathrm{P}_{Bulk} = q.\mathrm{P}_{Bulk,eq}/y_{CO_2}^{Bulk} \quad (7)$$

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

$$\begin{aligned}\theta &= -3.719\cdot10^{-3}\left(\Theta_{Bulk}-10.38\right)^2 \\ &+ 9.926\cdot10^{-1}\left(\Theta_{Bulk}-10.38\right)\end{aligned} \quad (8)$$

It is assumed that the bulk reactor operates in a Gas/liquid transfer limited regime. The temperature in the bulk reactor is $\Theta_{Bulk}\left[°C\right]$ and the corresponding equilibrium pressure of the pure CO_2 semi clathrate hydrate of TBAB is $P_{Bulk,eq}\left[MPa\right]$, given in Eq. 6:

$$x_{CO_2,L}^{OUT,Bulk} = \frac{\phi_{CO_2}^{G} P_{Bulk,eq}}{k_{\mathrm{H},CO_2,\mathrm{w}}^{\mathrm{L_w}}(T_{Bulk}, p_{\mathrm{w}}^{\mathrm{o},\sigma})} \quad (9)$$

The values of the Henry constants $k_{\mathrm{H},j,\mathrm{w}}^{\mathrm{L_w}}(T, p_{\mathrm{w}}^{\mathrm{o},\sigma})$ 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. $\phi_{CO_2}^{G}$ is the fugacity coefficient.

The bulk reactor is assuming to work at a CO_2 mole fraction $y_{CO_2,\min}^{Bulk} = 0.2$. At such a composition, the semi-clathrate hydrate is a practically pure 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 $P_{bulk}\left[MPa\right]$ given in Eq.7:

$$x_{j,L}^{OUT,Bulk} = \frac{y_j^{Bulk}\phi_j^{G} P_{Bulk}}{k_{\mathrm{H},j,\mathrm{w}}^{\mathrm{L_w}}(T_{Bulk}, p_{\mathrm{w}}^{\mathrm{o},\sigma})} \quad (10)$$

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:

$$V_L = \frac{r_{CO_2}}{\frac{k_L^{CO_2}}{d_b}6\frac{\varepsilon_G}{1-\varepsilon_G}\left(x_{CO_2,ext}-x_{CO_2,bulk}\right)C_{H_2O}} \quad (11)$$

Where $r_{CO_2}\left[mol.s^{-1}\right]$ is the rate of CO_2 capture in the hydrate phase (Eq.1)

$$r_{CO_2} = F_{CO_2,hyd}^{OUT,bulk} \quad (12)$$

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 rate of gas, $r_{CO_2}\left[mol.s^{-1}\right]$, which has been captured:

$$Q_{hyd}^{OUT,Bulk} = \frac{r_{CO_2}}{\theta_j \cdot n_{S38,Max}^{STORAGE}} \quad (13)$$

It is also possible to evaluate the liquid flow rate from the consideration that the slurry viscosity can not be too high. So the solid content can not exceed a value Φ_{MAX} (to be designed precisely) which can be around the value of $\Phi_{MAX} = 0.3$ (see paper 3/4 of this series).

$$Q_L^{OUT,Bulk} = \frac{1-\Phi_{MAX}}{\Phi_{MAX}} Q_{hyd}^{OUT,Bulk} \quad (14)$$

FLUE GASES

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

SPECIFICATIONS

RECOV is the CO_2 recovery ratio expressed as the ratio between the recovered molar flow rate ($F_{CO_2}^{OUT,BOTTOM}$) and the CO_2 molar flow rate in the flue gas ($F^{wet\ flue\ gas} y_{CO_2}^{wet\ flue\ gas}$ or $F^{dry\ flue\ gas} y_{CO_2}^{dry\ flue\ gas}$)

$$RECOV = \frac{F_{CO_2}^{OUT,BOTTOM}}{F^{dry\ flue\ gas} y_{CO_2}^{dry\ flue\ gas}} \quad (15)$$

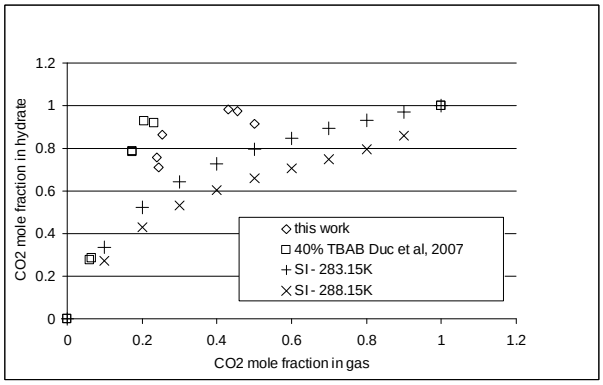


Figure 5 : Selectivity of the separation of CO_2 from N_2 during crystallization of semi-clathrate hydrates from TBAB solution, and comparison to the selectivity of clathrate hydrate of structure SI (Herri et al, 2014)

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

$$y_{CO_2} > 0.2 \Rightarrow \quad z_{CO_2} = 1; \quad z_{other\ components} = 0 \quad (16)$$

If the gas phase is lower than 20% CO_2.

$$y_{CO_2} < 0.2 \Rightarrow \quad z_{CO_2} = 5 \times y_{CO_2}; \quad z_{other\ components} = 1 - 5 \times y_{CO_2} \quad (17)$$

BOTTOM FLOW

The bottom flow gas is composed of pure CO_2

$$F_{CO_2}^{OUT,BOTTOM} = RECOV^{dry\ flue\ gas} y_{CO_2}^{dry\ flue\ gas} \quad (18)$$

TOP GAS

The top gas is composed of the non recovered CO_2 at a molar flow rate $F_{CO_2}^{OUT,TOP}$ and mole fraction $y_{CO_2}^{OUT,TOP}$. 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

$$y_{CO_2}^{OUT,TOP} = \frac{F_{CO_2}^{OUT,TOP}}{F_{CO_2}^{OUT,TOP} + F_{other\ components}^{OUT,TOP}} \quad (19)$$

$F_{CO_2}^{OUT,TOP}$ corresponds to the non recovered CO_2 :

$$F_{CO_2}^{OUT,TOP} = (1 - RECOV) F^{dry\ flue\ gas} y_{CO_2}^{dry\ flue\ gas} \quad (20)$$

$F_{other\ components}^{OUT,TOP}$ corresponds to the gases which are not recovered in the CO_2 capture unit, and the flow rate is assumed to be flow rate in the flue gas :

$$F_{other\ components}^{OUT,TOP} = F^{dry\ flue\ gas} \left(1 - y_{CO_2}^{dry\ flue\ gas}\right) \quad (21)$$

$$y_{CO_2}^{OUT,TOP} = \frac{(1 - RECOV) y_{CO_2}^{dry\ flue\ gas}}{(1 - RECOV) y_{CO_2}^{dry\ flue\ gas} + \left(1 - y_{CO_2}^{dry\ flue\ gas}\right)} \quad (22)$$

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

$$F^{OUT,TOP} = \frac{F_{CO_2}^{OUT,TOP}}{y_{CO_2}^{OUT,TOP}} = F^{dry\ flue\ gas} \left[\begin{array}{l} (1 - RECOV) y_{CO_2}^{dry\ flue\ gas} \\ + \left(1 - y_{CO_2}^{dry\ flue\ gas}\right) \end{array} \right] \quad (23)$$

RECYCLING FLOW

The bulk reactor is assumed to run with a minimum gas CO_2 mole fraction of $y_{CO_2,\min}^{Bulk} = 0.2$. In fact, at this concentration, it has been observed that the hydrate which is formed can be considered 100% CO_2. Consequently, the feed gas entering the bulk reactor needs to be at higher concentration ($y_{CO_2}^{IN,Bulk} > y_{CO_2,\min}^{Bulk}$) so that a reaction can be operated. The mole fraction in the feed gas ($y_{CO_2}^{dry\ flue\ gas}$) is probably at a lower concentration that $y_{CO_2}^{IN,Bulk}$ and the flow entering the bulk reactor needs to be completed with a recycling of pure CO_2 gas in order to reach the $y_{CO_2}^{IN,Bulk}$ value.

$$y_{CO_2}^{IN,Bulk} = \frac{F^{dry\ flue\ gas} y_{CO_2}^{dry\ flue\ gas} + F^{Recycling}}{F^{dry\ flue\ gas} + F^{Recycling}} \quad (24)$$

$$F^{Recycling} = F^{dry\ flue\ gas} \frac{y_{CO_2}^{IN,Bulk} - y_{CO_2}^{dry\ flue\ gas}}{1 - y_{CO_2}^{IN,Bulk}} \quad (25)$$

FINISHER REACTOR

CO_2 Mole Balance

$$F_{CO_2,Gas}^{OUT,Bulk} = F_{CO_2,hyd}^{OUT,Finisher} + F_{CO_2,L}^{OUT,Finisher} + F_{CO_2}^{OUT,TOP} \quad (26)$$

$F_{CO_2}^{OUT,TOP}$ is given from the process specification, following Eq.20, so:

$$F_{CO_2,Gas}^{OUT,Bulk} - F_{CO_2,hyd}^{OUT,Finisher} - F_{CO_2,L}^{OUT,Finisher} = (1 - RECOV) F^{dry\ flue\ gas} y_{CO_2}^{dry\ flue\ gas} \quad (27)$$

Other components Mole Balance

Other components are N_2,O_2 and Ar.

$$F_{other\ components,Gas}^{OUT,Bulk} = F_{other\ components,hyd}^{OUT,Finisher} + F_{other\ components,L}^{OUT,Finisher} + F_{other\ components}^{OUT,TOP} \quad (28)$$

$F_{other\ components}^{OUT,TOP}$ is given from the process specification, all the other components being not involved in the capture process:

$$F_{other\ components,Gas}^{OUT,Bulk} - F_{other\ components,hyd}^{OUT,Finisher} - F_{other\ components,L}^{OUT,Finisher} = \left(1 - y_{CO_2}^{dry\ flue\ gas}\right) F^{dry\ flue\ gas} \quad (29)$$

Relationship in between variables

The composition of the hydrate slurry is fixed by thermodynamic, and especially the ratio between CO_2 and other components. At gas CO_2 mole fraction lower than $y_{CO_2,\min}^{Finisher} = 0.2$, we know from Eq.17 that:

$$\frac{F_{CO_2,hyd}^{OUT,Finisher}}{F_{other\ components,hyd}^{OUT,Finisher}} = \frac{5 y_{CO_2}^{OUT,TOP}}{1 - 5 y_{CO_2}^{OUT,TOP}} \quad (30)$$

Another relationship can be given of mole flow $F_{Gas}^{OUT,Bulk}$

$$\frac{F_{CO_2,Gas}^{OUT,Bulk}}{F_{other\ components,Gas}^{OUT,Bulk}} = \frac{y_{CO_2}^{Bulk}}{1 - y_{CO_2}^{Bulk}} \quad (31)$$

Also, we can give a relation between $F_{j,hyd}^{OUT,Finisher}$ and $F_{j,L}^{OUT,Finisher}$ for every components j, CO_2 and other components, because:

$$F_{j,hyd}^{OUT,Finisher} = Q_{hyd}^{OUT,Finisher} n_{S38,MAX}^{STORAGE} \theta_j \quad (32)$$

θ_j is the occupancy of cavities by component *j*. So

$$Q_{hyd}^{OUT,Finisher} = \frac{F_{CO_2,hyd}^{OUT,Finisher}}{n_{S38,MAX}^{STORAGE} \theta_{CO_2}} \quad (33)$$

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

$$Q_L^{OUT,Finisher} = Q_{hyd}^{OUT,Finisher} \frac{1-\Phi}{\Phi}$$

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

$$F_{j,L}^{OUT,Finisher} = \frac{F_{CO_2,hyd}^{OUT,Finisher}}{n_{S38,MAX}^{STORAGE} \theta_{CO_2}} \frac{1-\Phi}{\Phi} n_{water,L}^{STORAGE} x_j \quad (34)$$

Eq. 34 can be applied directly to CO_2

$$F_{CO_2,L}^{OUT,Finisher} = \frac{F_{CO_2,hyd}^{OUT,Finisher}}{n_{S38,MAX}^{STORAGE} \theta_{CO_2}} \frac{1-\Phi}{\Phi} n_{water,L}^{STORAGE} x_{CO_2} \quad (35)$$

or after summation over all the *other components*:

$$F_{other\ components,L}^{OUT,Finisher} = \sum_{other\ components} F_{j,L}^{OUT,Finisher}$$
$$= \frac{F_{CO_2,hyd}^{OUT,Finisher}}{n_{S38,MAX}^{STORAGE} \theta_{CO_2}} \frac{1-\Phi}{\Phi} n_{water,L}^{STORAGE} \sum_{other\ components} x_j \quad (36)$$

In the end, the mole balance on CO_2 given in Eq.27 yields to:

$$F_{CO_2,Gas}^{OUT,Bulk} - \left(1 + \frac{1}{n_{S38,MAX}^{STORAGE} \theta_{CO_2}} \frac{1-\Phi}{\Phi} n_{water,L}^{STORAGE} x_{CO_2}\right) F_{CO_2,hyd}^{OUT,Finisher} = \left(1 - RECOV\right) F^{dry\ flue\ gas} y_{CO_2}^{dry\ flue\ gas} \quad (37)$$

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

$$\frac{1-y_{CO_2}^{Bulk}}{y_{CO_2}^{Bulk}} F_{CO_2,Gas}^{OUT,Bulk} - \left(\frac{1-5y_{CO_2}^{OUT,TOP}}{5y_{CO_2}^{OUT,TOP}} + \frac{1}{n_{S38,MAX}^{STORAGE} \theta_{CO_2}} \frac{1-\Phi}{\Phi} n_{water,L}^{STORAGE} \sum_{other\ components} x_j \right) F_{CO_2,hyd}^{OUT,Finisher} = \left(1 - y_{CO_2}^{dry\ flue\ gas}\right) F^{dry\ flue\ gas} \quad (38)$$

Eq.37 and Eq.38 consist of a system of two equations with two unknowns ($F_{CO_2,Gas}^{OUT,Bulk}$ and $F_{CO_2,hyd}^{OUT,Finisher}$) which can be solved analytically, provided that θ_{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).

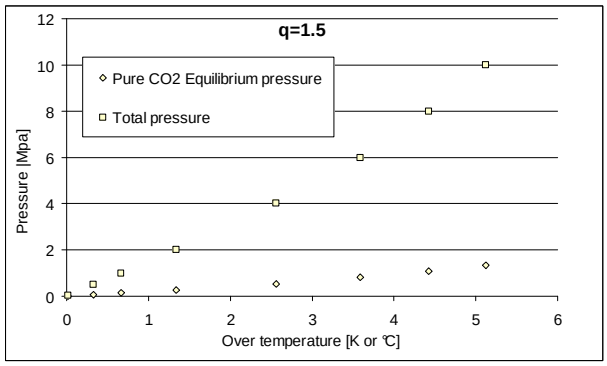


Figure 6: Bulk reactor operative conditions The over pressure coefficient q is given in Eq.7. The over temperature is the difference between the operative temperature and the temperature at the congruent point (10.38°C).

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.

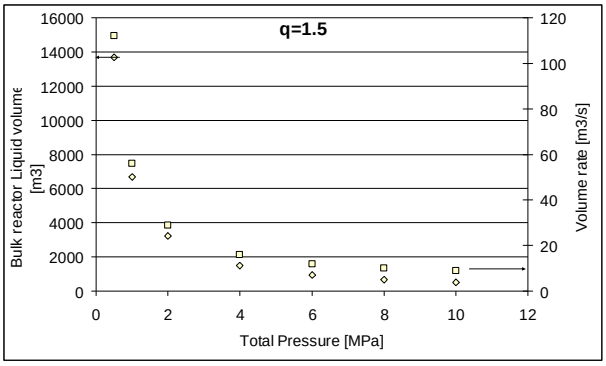


Figure 7: Bulk reactor liquid volume and hydrate bottom volume flow rate. The over pressure coefficient q is given in Eq.7.

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 Φ_{MAX} =0.33, given Eq. 14, the total bottom flow rate will be 120 m^3/s, which is not realistic.

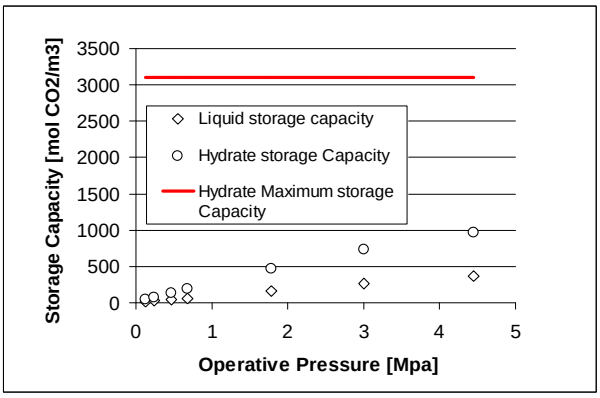


Figure 8: Storage capacity. [mole CO_2/m^3 *hyd*] in the hydrate phase and liquid phase (from paper 2 of this series)

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)

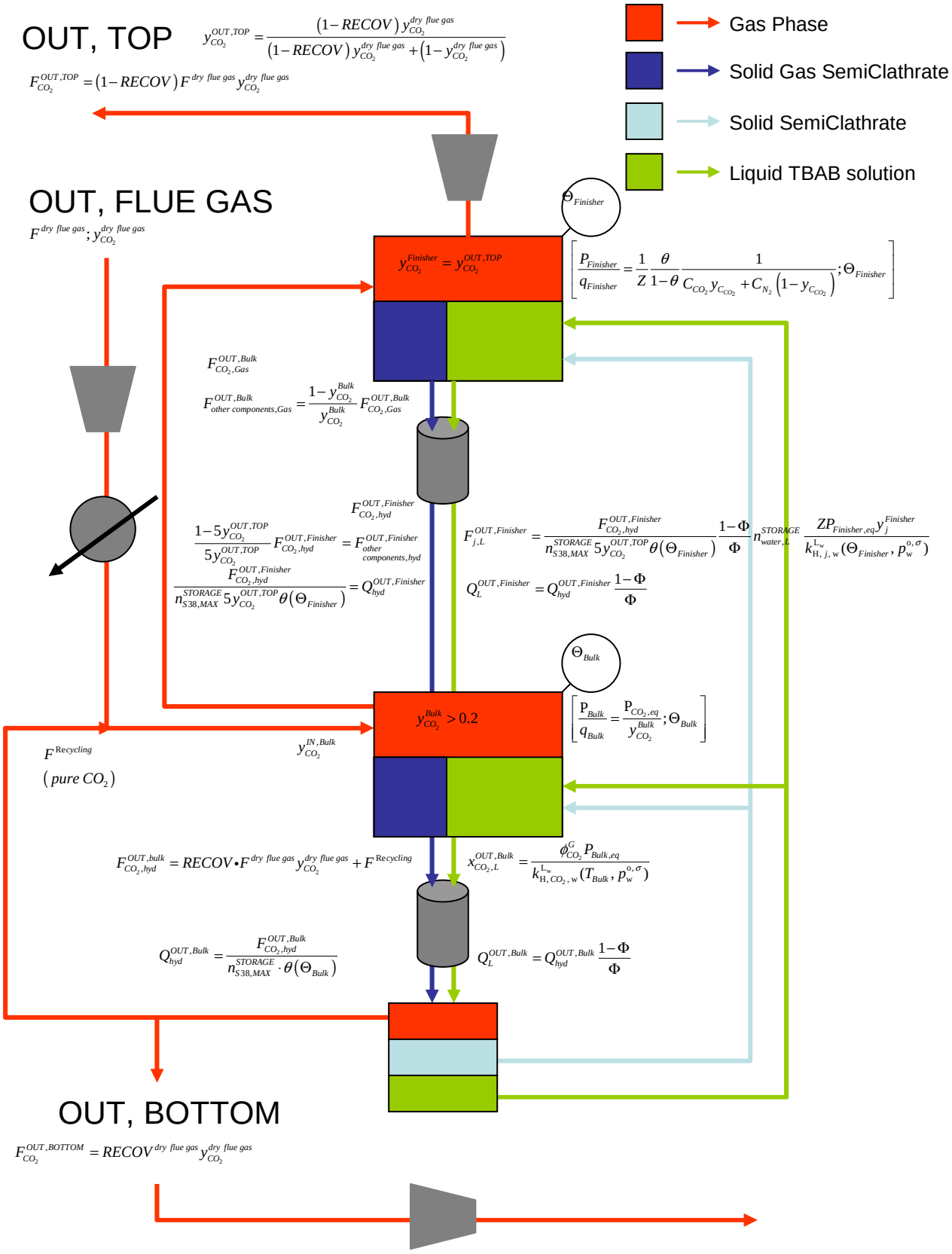
Nevertheless the volume of the reactor and the liquid flow rate handled is linked to the total pressure (**Figure 7**). The pressure can not be superior to 1.5 MPa because the energy penalty for flue gas conditioning is higher than energy penalty

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.

ANNEX : FLOWSHEET



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