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# Thermodynamic study of clathrates hydrates from hydrocarbon gas mixtures consequences for CO<sub>2</sub> capture and flow assurance

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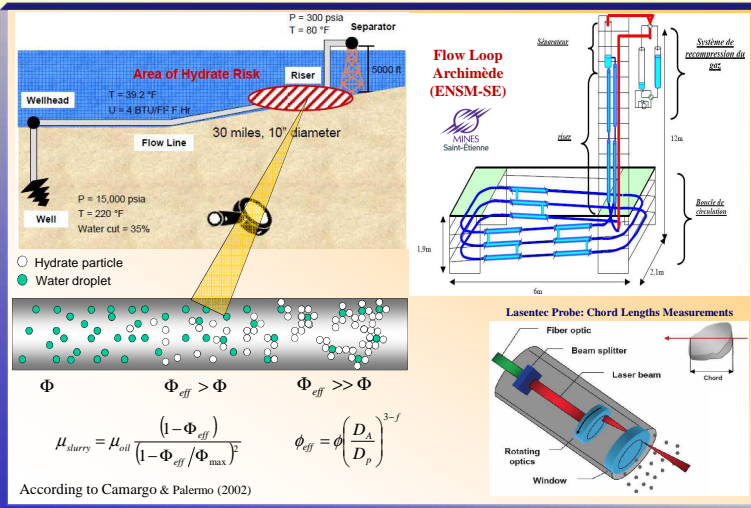
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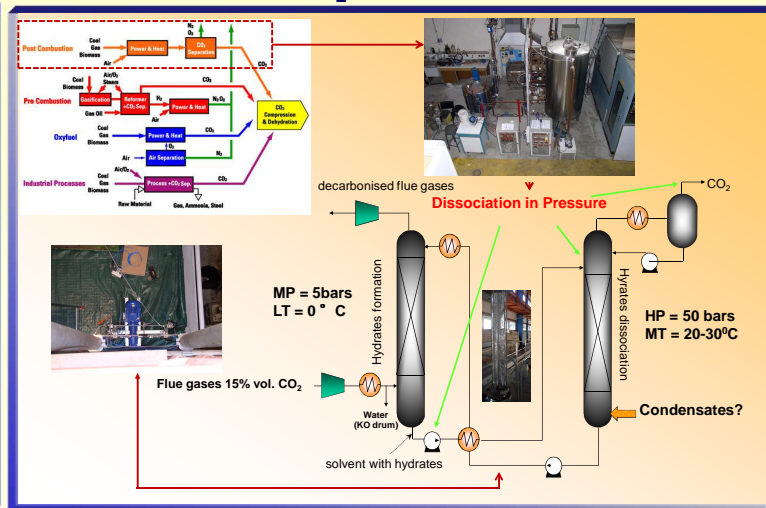
Centre SPIN, Department GENERIC, École Nationale Supérieure des Mines de SAINT-ETIENNE, 158 cours Fauriel, 42023 Saint-Etienne Cedex 02, France

This work presents details on the experimental procedure to measure the composition of the hydrate that crystallizes from a hydrocarbon gas mixture. We show that the results are time dependent and tend to thermodynamic equilibrium as time tends to infinity. An immediate consequence concerns two major domains of applications, CO<sub>2</sub> capture from power plants, as well as flow assurance in the oil and gas industry. In fact, in both the cases, the crystallization is under non equilibrium conditions, and we conclude here that it necessarily leads to the formation of hydrates with a composition which is not predicted by classical modeling.

## FLOW ASSURANCE

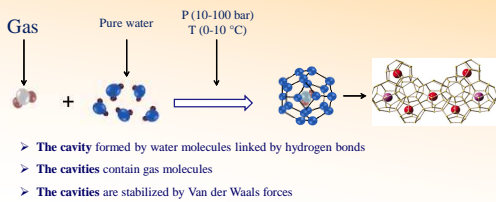


## CO<sub>2</sub> CAPTURE

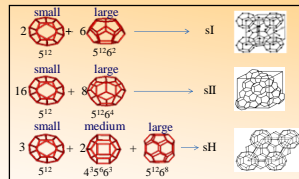


## GAS HYDRATES FORMATION

### 1 - Conditions needed for the gas hydrate to form



### 2 - Hydrate structure



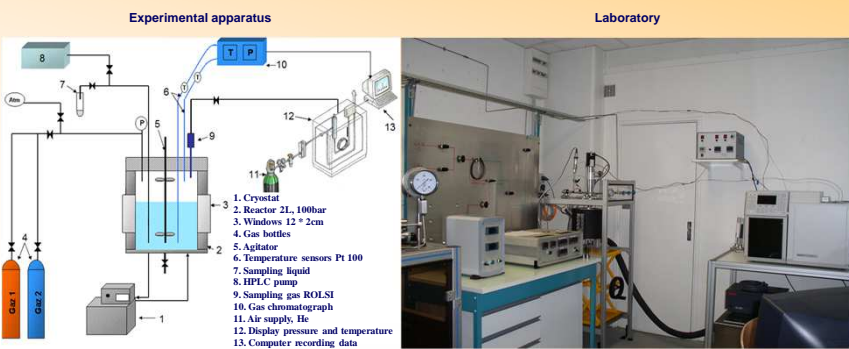
### 3 - Clathrate hydrate

Clathrate hydrate structures	S <sub>I</sub>		S <sub>II</sub>		S <sub>H</sub>	
Cavity	Small	Large	Small	Large	Small	Medium
Description	5 <sup>12</sup>	5 <sup>12</sup> 6 <sup>2</sup>	5 <sup>12</sup>	5 <sup>12</sup> 6 <sup>4</sup>	5 <sup>12</sup>	4 <sup>5</sup> 6 <sup>3</sup>
Number per unit cell (m.)	2	6	16	8	3	2
Average cavity radius (Å)	3,95	4,33	3,91	4,73	3,91 <sup>a</sup>	4,06 <sup>c</sup>
Coordination number <sup>a</sup>	20	24	20	28	20	36

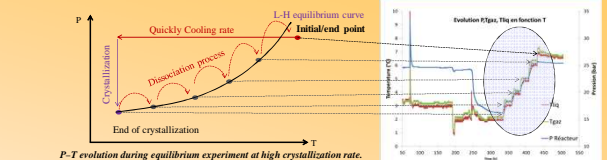
(a) The number of oxygen atom per cavity

## Experimental procedure and set-up

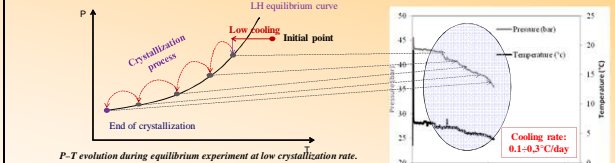
### ✓ Experimental apparatus and laboratory



### ✓ Experimental procedure at high driving force



### ✓ Experimental procedure at low driving force



## COMPARING: Results from experiment AND simulated GASHYDYN Predictions

### ✓ Results (at high crystallization rate) N<sub>2</sub> - CO<sub>2</sub>

Experimental Equilibrium Data			
T (°C)	P (MPa)	xCO <sub>2</sub>	xN <sub>2</sub>
2.3	2.46	0.667	0.333
3.1	2.6	0.689	0.311
3.3	2.66	0.699	0.301
4.3	2.87	0.723	0.277
5.2	3.13	0.747	0.253
6.0	3.38	0.768	0.232

GASHYDYN Predictions			
Structure	P (MPa)	xCO <sub>2</sub>	xN <sub>2</sub>
SI	2.53	0.955	0.045
SI	2.69	0.958	0.042
SI	2.73	0.960	0.040
SI	2.99	0.962	0.038
SI	3.22	0.966	0.034
SI	3.48	0.968	0.032

Mean Deviation (%): %D=3.0, %D=1.0, %D=15.0

### ✓ Results (at high crystallization rate) CO<sub>2</sub>+CH<sub>4</sub>+C<sub>2</sub>H<sub>6</sub>

Experimental Equilibrium Data				
T (°C)	P (MPa)	xCO <sub>2</sub>	xCH <sub>4</sub>	xC <sub>2</sub> H <sub>6</sub>
2.75	3.54	0.144	0.769	0.087
3.65	3.81	0.144	0.769	0.087
5.15	4.23	0.141	0.774	0.085
6.55	4.56	0.141	0.777	0.089
7.80	5.12	0.135	0.777	0.089
9.25	5.99	0.049	0.804	0.148

GASHYDYN Predictions				
Structure	P (MPa)	xCO <sub>2</sub>	xCH <sub>4</sub>	xC <sub>2</sub> H <sub>6</sub>
SI	2.72	0.097	0.739	0.164
SI	2.90	0.103	0.717	0.180
SI	3.22	0.106	0.683	0.210
SI	3.64	0.107	0.669	0.224
SI	4.11	0.112	0.662	0.226
SI	4.83	0.127	0.661	0.211

Mean Deviation (%): %D=22, %D=48, %D=11, %D=130

### ✓ Results (at low crystallization rate) CO<sub>2</sub>+CH<sub>4</sub>+C<sub>2</sub>H<sub>6</sub>

Experimental Equilibrium Data				
T (°C)	P (MPa)	xCO <sub>2</sub>	xCH <sub>4</sub>	xC <sub>2</sub> H <sub>6</sub>
2.75	3.78	0.086	0.780	0.134
3.65	3.56	0.086	0.815	0.099
5.15	3.18	0.077	0.843	0.080
6.55	3.04	0.079	0.848	0.073
7.80	2.76	0.077	0.858	0.065
9.25	3.57	0.063	0.835	0.102

GASHYDYN Predictions				
Structure	P (MPa)	xCO <sub>2</sub>	xCH <sub>4</sub>	xC <sub>2</sub> H <sub>6</sub>
SI	4.12	0.062	0.811	0.127
SI	3.64	0.062	0.843	0.095
SI	3.51	0.061	0.846	0.093
SI	3.28	0.061	0.869	0.070
SI	3.03	0.059	0.871	0.070
SI	2.75	0.057	0.885	0.058

Mean Deviation (%): %D=1.8, %D=28.0, %D=13.0, %D=18.0

✓ Hydrate equilibria are given (T, P, gas and hydrate compositions) following two procedures.

✓ The two procedures used (high and low crystallization rates) highlight the kinetic effect on hydrate formation.

✓ In the end this work, there is a questioning about the validity of measurements: Are they thermodynamic of kinetic measurements? This is why the present data were analyzed using a thermodynamic model in an in-house software to discuss the possibility to crystallize gas hydrate at thermodynamic equilibrium at a low and high crystallization rate [Herri et al., 2014]

## Conclusions