Thermodynamic study of clathrates hydrates from hydrocarbon gas mixtures consequences for CO2 capture and flow assurance

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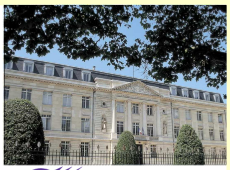
THERMODYNAMIC STUDY OF CLATHRATES HYDRATES FROM HYDROCARBON GAS MIXTURES CONSEQUENCES FOR CO_2 CAPTURE AND FLOW ASSURANCE

Du LE-QUANG, Duyen LE-QUANG, Baptiste BOUILLOT, **Jean-Michel HERRI***

* Corresponding author. Tel.: +33 4 77 42 02 92; fax: +33 4 77 49 96 92. E-mail address: herri@emse.fr (J.-M. Herri).

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



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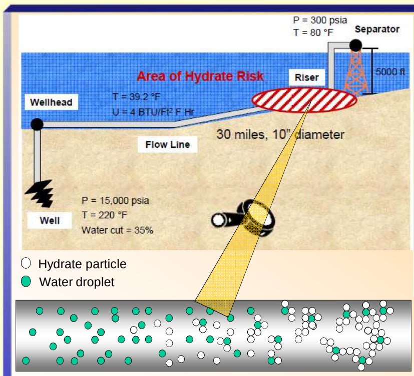
This work presents details on the experimental procedure to measure the composition of the hydrate that crystallizes from a hydrocarbon gas mixture. We show that the results are time dependent and tend to thermodynamic equilibrium as time tends to infinity. An immediate consequence concerns two major domains of applications, CO_2 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.

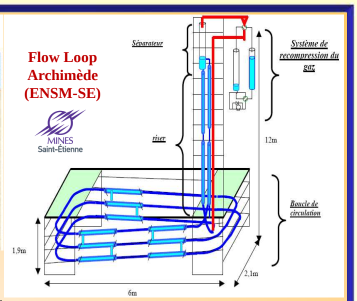
FLOW ASSURANCE



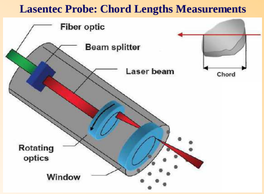
Φ $\quad \Phi_{eff} > \Phi$ $\quad \Phi_{eff} >> \Phi$

$$\mu_{slurry} = \mu_{oil} \frac{(1-\Phi_{eff})}{(1-\Phi_{eff}/\Phi_{max})^2} \qquad \phi_{eff} = \phi \left(\frac{D_A}{D_p}\right)^{3-f}$$

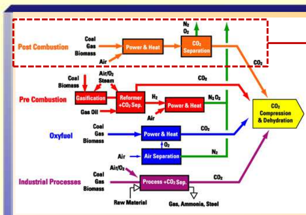
According to Camargo & Palermo (2002)

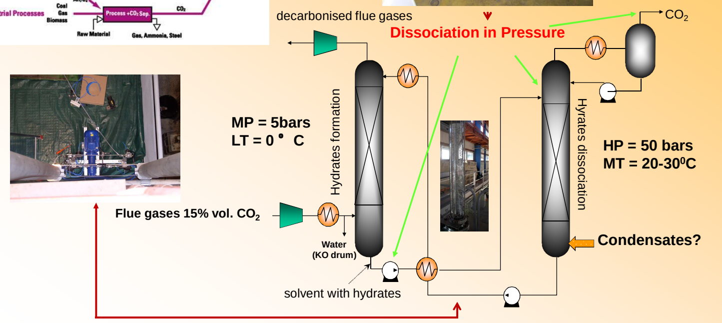


Lasentec Probe: Chord Lengths Measurements



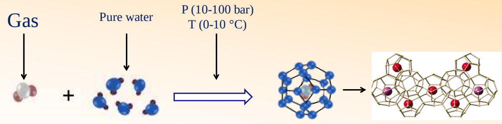
CO_2 CAPTURE





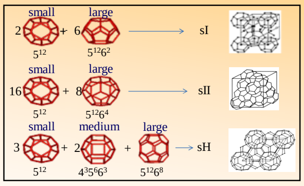
GAS HYDRATES FORMATION

1 – Conditions needed for the gas hydrate to form

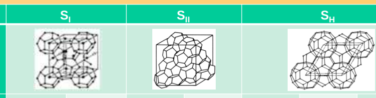


- **The cavity** formed by water molecules linked by hydrogen bonds
- **The cavities** contain gas molecules
- **The cavities** are stabilized by Van der Waals forces

2 – Hydrate structure



3 –Clathrate hydrate



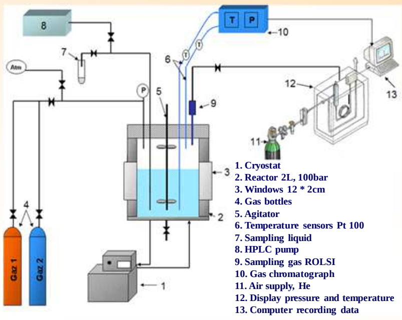
Clathrate hydrate structures	S_I		S_{II}		S_H		
Cavity	Small	Large	Small	Large	Small	Medium	Large
Description	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Number per unit cell (m_j)	2	6	16	8	3	2	1
Average cavity radius (Å)	3,95	4,33	3,91	4,73	3,91[c]	4,06[c]	5,71[c]
Coordination number[a]	20	24	20	28	20	20	36

(a)The number of oxygen atom per cavity

Experimental procedure and set-up

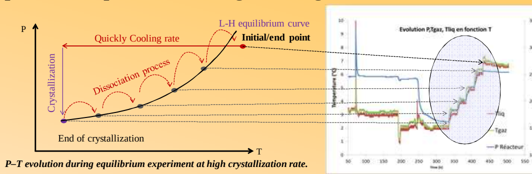
✓ Experimental apparatus and laboratory

Experimental apparatus



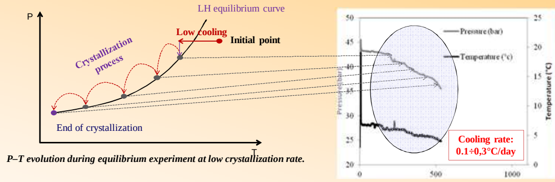
Laboratory

✓ Experimental procedure at high driving force



P–T evolution during equilibrium experiment at high crystallization rate.

✓ Experimental procedure at low driving force



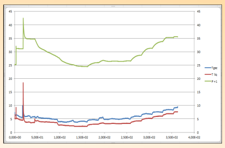
P–T evolution during equilibrium experiment at low crystallization rate.

COMPARING: Results from experiment AND simulated GASHYDYN Predictions

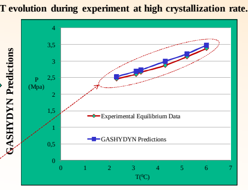
✓ Results (at high crystallization rate) N_2 - CO_2

Experimental Equilibrium Data			
T	P	Hydrate composition	
(⁰C)	(Mpa)	xCO_2	xN_2
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	Hydrate composition	
SI	(MPa)	xCO_2	xN_2
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=25.0



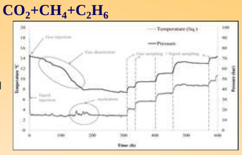
P–T evolution during experiment at high crystallization rate.



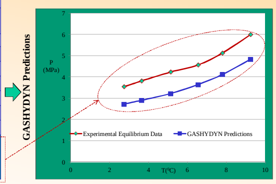
✓ Results (at high crystallization rate) $CO_2+CH_4+C_2H_6$

Experimental Equilibrium Data				
T	P	Hydrate composition		
(⁰C)	(MPa)	xCO_2	xCH_4	xC_2H_6
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	0.082
7.80	5.12	0.135	0.777	0.089
9.25	5.99	0.049	0.804	0.148

GASHYDYN Predictions				
Structure	P	Hydrate composition		
SI	(MPa)	xCO_2	xCH_4	xC_2H_6
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=120



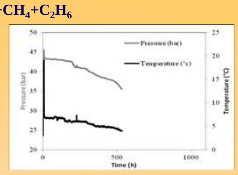
P–T evolution during experiment at high crystallization rate.



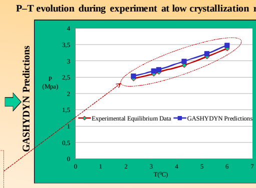
✓ Results (at low crystallization rate) $CO_2+CH_4+C_2H_6$

Experimental Equilibrium Data				
T	P	Hydrate composition		
(⁰C)	(MPa)	xCO_2	xCH_4	xC_2H_6
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	Hydrate composition		
SI	(MPa)	xCO_2	xCH_4	xC_2H_6
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



P–T evolution during experiment at low crystallization rate.



Conclusions

- ✓ 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*]