Thermodynamic study of clathrates hydrates from hydrocarbon gas mixtures consequences for CO2 capture and flow assurance
Quanq-Du Le, Duyen Le Quang, Baptiste Bouillot, Jean-Michel Herri

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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, CO2 capture from power plants, as well as flow assurance in the oil and gas industry. In fact, in both 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**

**CO2 CAPTURE**

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**Experimental procedure and set-up**

- **Experimental apparatus and laboratory**
- **Experimental procedure at high driving force**
- **Experimental procedure at low driving force**

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**COMPARING:** Results from experiment AND simulated GASHYDYN Predictions

- **Results (at high crystallization rate) N2 - CO2**
- **Results (at high crystallization rate) CO2 + CH4 + C2H6**
- **Results (at low crystallization rate) CO2 + CH4 + C2H6**

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**Conclusions**

- Hydrate equilibria are given/fit, P, gas and hydrate composition following two procedures.
- The two procedures used (high and low crystallization rates) highlight the kinetic effect on hydrate formation.
- In the end, this work is a questioning about the validity of measurements: Are they thermodynamic or kinetic measurements? This is why the present data are analyzed using a thermodynamic model in an in-house software to discuss the possibility of crystallizes gas hydrate at thermodynamic equilibrium at a low and high crystallization rate [Henri et al., 2014].

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**GAS HYDRATES FORMATION**

1. Conditions needed for the gas hydrate to form
   - P (10-100 bars)
   - T (5-40 °C)
   - Gas
   - Pure water
   - The cavity formed by water molecules linked by hydrogen bonds
   - The cavities contain gas molecules
   - The cavities are filled by Van der Waals forces

2. Hydrate structure
   - Clathrate hydrate structures
   - Small
   - Large
   - Cavity
   - Description
   - Small
   - Large
   - Small
   - Large
   - Small
   - Large
   - Average cavity radius (Å)
   - Coordination number
   - The number of oxygen atoms per cavity

3. Clathrate hydrate
   - Phase transition
   - Dissociation in Pressure
   - MP = 5 bars
   - LT = 0 °C
   - HP = 50 bars
   - MT = 20-30 °C

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**THERMODYNAMIC STUDY OF CLATHRATES HYDRATES FROM HYDROCARBON GAS MIXTURES CONSEQUENCES FOR CO2 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: henri@emse.fr (J.-M. Henri).

Centre SP2N, Department GENERIC, Ecole Nationale Superieure des Mines de SAINT-ETIENNE, 158 cours Faustel, 42023 Saint-Etienne Cedex 02, France