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

To cite this version:


HAL Id: emse-01089986
https://hal-emse.ccsd.cnrs.fr/emse-01089986
Submitted on 2 Dec 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
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: herri@emse.fr (J.-M. Herri).
Centre SPIN, Department GENERIC, Ecole Nationale Superieure des Mines de SAINT-ETIENNE, 158 cours Fauvet, 4203 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; CO₂ 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 modelling.

FLOW ASSURANCE

CO₂ CAPTURE

GAS HYDRATES FORMATION

1 – Conditions needed for the gas hydrate to form
Gas
Pure water
P (10-100 bar)
T (5-60 °C)

> The cavity formed by water molecules linked by hydrogen bonds
> The cavity contains gas molecules
> The cavities are stabilized by van der Waals forces

2 – Hydrate structure

3 – Clathrate hydrate

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

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 this end this work, there is a question 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 hydrates at thermodynamic equilibrium at a low and high crystallization rate [Herri et al., 2014].