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CO₂ capture by gas hydrate crystallization

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Abstract

Gas hydrates are formed at low temperature and high pressure. They are crystalline solid formed from mixtures of liquid water and low molecular weight gases. The water molecules that form the lattice are strongly hydrogen bonded and form a network of cavities in which the gas can be engaged. The gas molecules interact with the water molecules through van der Waals type dispersion forces, in a way which is similar to Langmuir absorption.

Hydrate occurrence is a problem of flow assurance for decades in the domain of natural gas and oil transportation. So, the thermodynamic has been intensively studied, especially for hydrocarbon gases. The well known model of Van der Waals and Platteeuw (VWD-P) was proposed in 1959. It is based on classical statistical thermodynamics. However, several limitations of this model have been reported in the literature. The first is that the cavities and the gas molecules are not necessarily spherical and a new approach has been proposed by Holder *et al.* to correct this limitation. Secondly, a new concept, which is a combination of thermodynamic and kinetic considerations was proposed by Chen and Guo. Furthermore, experimental measurements of several different hydrates show that the volume of cavities depends on the hydrate guest (while Van der Waals and Platteeuw model supposes a common size without deformation). To improve the (VDW-P) model, Sloan *et al.* have proposed a new model based on equality of fugacities of water taking into account the non-ideality of water in the hydrate phase by introducing an activity coefficient.

Our laboratory at Ecole Nationale Supérieure des Mines de Saint-Etienne has developed a new apparatus (fig 1) to study the kinetic and thermodynamic formation of hydrates from pure or mixture of gases, here CO₂-N₂ and CO₂-CH₄. This work studies the effect of presence of TBAB in the liquid mixture and shows that it reduces the operation pressure by a factor up to 16. Thermodynamic data collected during this work is presented in the paper and compared with corresponding data obtained from a software package (fig 2) (GasHyDyn software), also developed in our laboratory. This program predicts the thermodynamic equilibrium (Pressure, temperature) and phase composition (hydrate, liquid, gas). The comparison (fig 3) shows a good agreement between the experimental results and predicted data by the GasHydyn software.

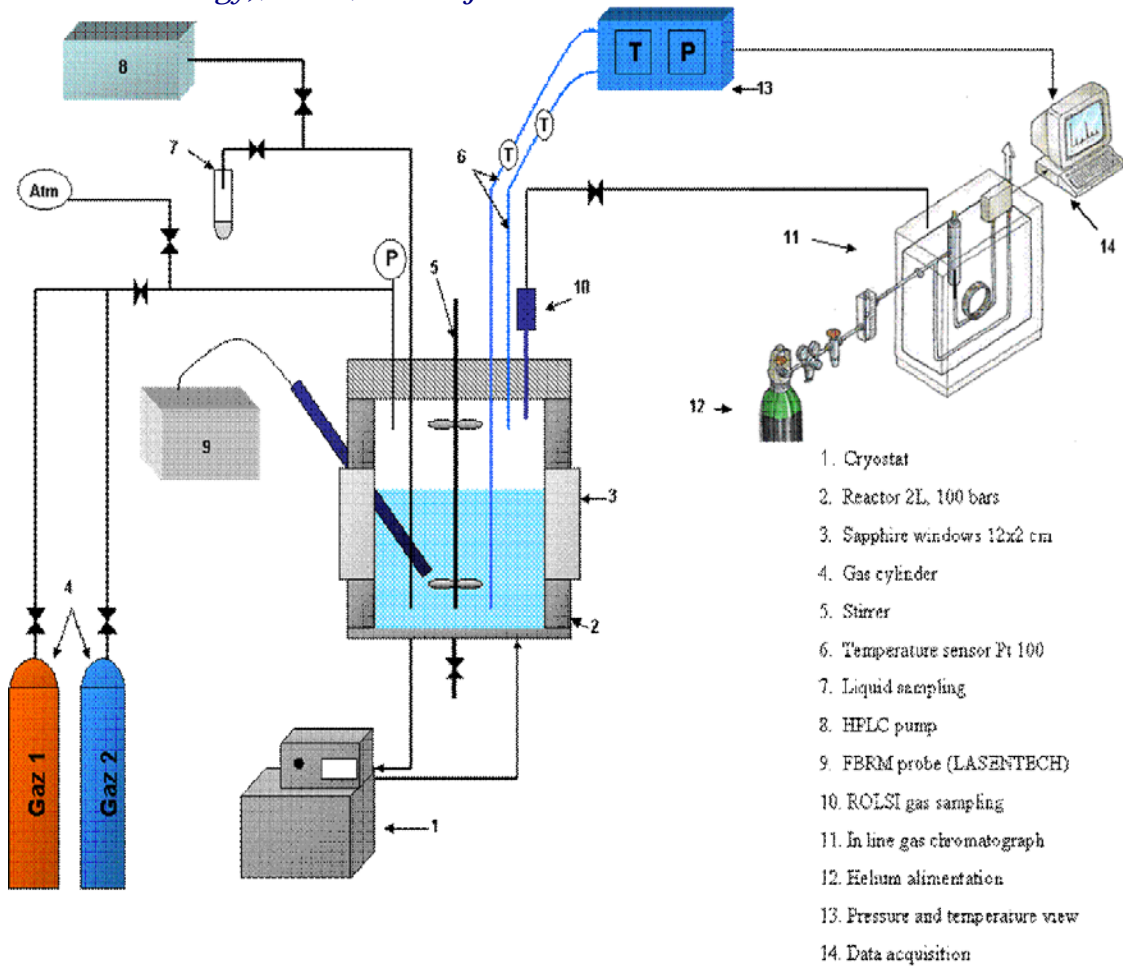


Figure 1 : Experimental apparatus

Miscellaneous Units Components Thermodynamic Models Type of calculation Thermodynamic calculation Kinetic calculation Graphical options

GasHyDyn Software from St-Etienne School of Mines

First Specification		GasHyDyn Software from St-Etienne School of Mines															
Temperature	Fix																
T (°C)	invalid	invalid															
	4	10	9														
Second specification		T [°C]	x (CO2)	x (N2)	Tc [°C]	Pc [MPa]	Peg [MPa]	Hydrate...	Tocc...	x (CO2)	x (N2)	5*12	x (CO2)	x (N2)	5*12-6*2	x (CO2)	x (N2)
Pressure	Fix	4.0	0.5	0.5	-56.11...	4.0054...	3.336600...	sl	0.95...	0.839...	0.160...	0.85...	0.4344...	0.565...	0.98171...	0.957...	0.042...
P (MPa)	invalid	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	1	10	9														
Hydrate Structure	SI is imposed	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Figure 2 : Interface of calculation from GasHyDyn

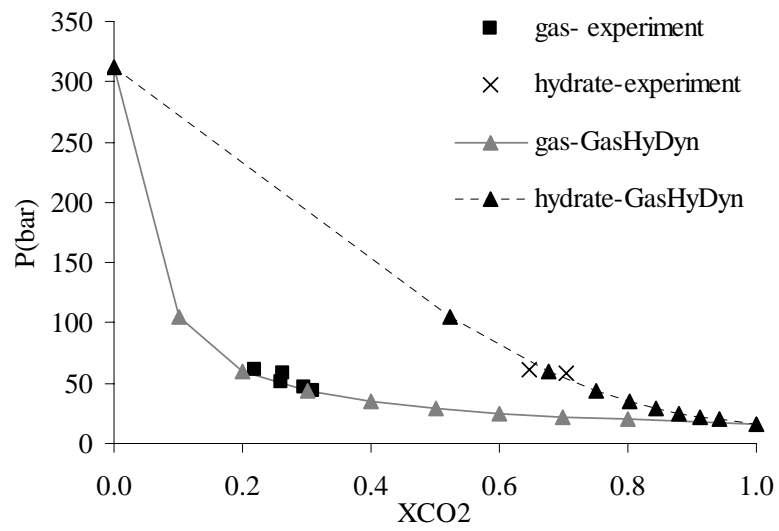


Figure 3 : Phase diagram gas- hydrate for $\text{CO}_2\text{-N}_2$ mixture at 2.7°C