Measurement and Prediction of Condensate Gas Hydrates Formation Conditions – A Study Case

Samer Said¹, Belloum Mohamed¹, Otmanine Ghazi², Mimoun Hadj² and Khodja Mohamed³

1. Laboratory of Materials Science (LCMVAR), Dpt of Chemistry, Faculty of Science, University Hadj Lakhdar, Batna 05000, Algeria

2. Laboratory of Hydrocarbons technology, Dpt of Chemistry, Faculty of Hydrocarbons & Chemistry, University Mhamed Bouguerra, Boumerdes 35000, Algeria

3. Division Technology and Development (DTD), Boumerdes 35000, Algeria

Abstract: A new field of gas condensate recently discovered in south of Algeria caused a lot of difficulties and even accidents during its operation due to unexpected hydrates plug formation. To prevent such damage, we carried out an experimental study using a visual high pressure PVT (pressure-volume-temperature) cell to investigate the thermodynamic conditions of gas hydrates formation and stability, then we established hydrate formation curves, identifying safety zones, allowing operators to work safely. The influence of inhibitors on gas hydrate formation was also investigated. This study was gathered with a numerical analysis using PVTsim (pressure-volume-temperature simulator) commercial software to confirm our experimental results.

Key words: Hydrates, gas condensate, plug, PVT, safety.

1. Introduction

Hydrates belong to the class of clathrates, which are inclusion compounds. Clathrates are crystallized solids, in which some atoms or molecules are trapped in cages created by the assembly of another type of molecules. When the crystal lattice is formed by water molecules linked together by hydrogen bonds and the cavities are occupied by gaseous molecules, the formed clathrates are called hydrates [1]. The most common gas hydrates morphology is methane hydrate. There are other gas molecules including ethane, propane, butane, isobutane, pentane, nitrogen, carbon dioxide and hydrogen sulfide. Three different crystal lattice structures have been identified: cubic structure sI, cubic structure sII and hexagonal structure sH [2-5].

Because of their accidental occurrence, hydrates are considered as a nuisance because they block

transmission lines, plug blowout preventers, endanger the foundations of deepwater platforms and pipelines, cause tubing and casing collapse, and foul process heat exchangers, valves, and expanders [6].

In 1934, *Hammerschmidt* [7] recognized first that natural gas transport lines failure was due to the formation of hydrate plugs. Since that time, the gas industry has invested significant human and material resources in research to determine the conditions of hydrate formation, then took a number of preventive measures.

A new field of gas condensate recently discovered in south of Algeria caused a lot of technical difficulties and even accidents during its operation, due to hydrates formation (Fig. 1 shows an accident during the well flow back test). This accident caused the pipe destroying, with one death and two injuries. This is why identifying the conditions of gas hydrates formation in this field and possible solutions to prevent their formation have become imperative.

To clearly define the type of hydrates, predict their

Corresponding author: Samer said, assistant professor, research fields: hydrocarbons technology and materials science. E-mail: saidpg2006@gmail.com.

Fig. 1 Damage caused during the well flow back test (Algeria).

equilibrium conditions, and determine the relationship between pressure and temperature under which those hydrates form and dissociate, equilibrium curves were used. These curves can be generated by a series of laboratory experiments, or are more commonly deduced using thermodynamic software such as PVTsim (pressure-volume-temperature simulator), based on the hydrocarbons composition and aqueous phases in the system [8, 9].

Two sampling methods are applied today; down-hole sampling and surface sampling [10-13].

Regarding the samples validation, for the separator liquid, we should first determine bottles opening pressure and saturation pressure at the separation temperature, which must be identical to the separation pressure. Since our gas is a condensate gas, we should determine the saturation pressure of the separator liquid which is performed by a CME (constant mass expansion) test. It should be noted that the CME is a conventional study conducted at separation temperature to determine the saturation pressure of the separator liquid [10]. Validation of separator gas is performed by chromatographic analysis. The opening pressure should be equal or close to the separation pressure [10].

The reconstitution of a representative reservoir fluid requires a PVT (pressure-volume-temperature) study of separator gas and separator liquid [14].

2. Experimental Setup

The PVT apparatus was employed to (i) validate samples, (ii) reconstitute reservoir fluid and (iii) measure the hydrate formation conditions. This apparatus (Fig. 2) is composed of many elements; the

Fig. 2 PVT Apparatus (Jefri).

most important of them are: the volumetric pump, the visual high pressure cell, the displacement and volume measurement system, the air bath and the sampling cylinder.

The visual high-pressure cell was connected to a volumetric pump and therefore the pressure of the cell could be controlled by injecting and withdrawing the hydraulic fluid to the hydraulic fluid side. On the other hand, the high pressure cell temperature was very precisely stabilized by a digital controller ($\pm 0.2^\circ\text{C}$). The cells internal volume was divided into two compartments, separated from each other by a sealed piston. One side of the piston was connected to a volumetric pump and the other side was filled with the fluid sample and water.

2.1 Samples Validation

The reservoir samples are two bottles containing 20 liters of separator gas, two cylinders containing 700 ml of separator liquid and one cylinder containing 700 ml of separator water. The samples were heated to the separator temperature (39°C), stirred and stabilized. The opening pressure was measured using a pump pressure indicator.

2.2 CME Test

A constant mass expansion test was performed on both separator liquid samples at separator temperature to determine the saturation pressure, which would

normally correspond to the separation pressure. For this, a volume of 40 cm³ was introduced at 3000 psig in the PVT visual cell heated to the separator temperature (39 °C) in an air bath, set up at ± 0.2 °C and after stabilizing in temperature and pressure, a progressive decreasing in the pressure with recording the corresponding fluid volume at regular time was performed. The break point on the pressure-volume curve corresponds to the saturation pressure “Pb”.

2.3 PVT Study of Separator Gas

The validated separator gas sample was analyzed using gas phase chromatography.

2.4 PVT Study of Separator Liquid

During this experiment, 40 cm³ of validated separator liquid samples were introduced in the visual high pressure cell, heated to separator temperature (39 ± 0.2 °C) in an air bath, set up to a higher pressure than the separation pressure (3000 psig) to ensure a single-phase transfer of the sample. After the stabilization of temperature and pressure, the mass of the empty pycnometer was measured. A volume of 14.9 cm³ of separator liquid was transferred from the PVT cell towards the pycnometer at 3000 psig, under separation temperature (39 °C), then a mass of the pycnometer after the transfer was measured.

2.5 Measurement of Gas Hydrates Formation Temperature

A volume of 60 cm³ of reservoir fluid (gas) was introduced at a pressure of 5000 psig in the visual high pressure cell to the reservoir temperature (104 °C) in an air bath, set up to ± 0.2 °C, then a volume of 3 cm³ of separator water was injected at the base of the PVT cell using the volumetric pump and after stabilizing on temperature and pressure by a magnetic stirrer, the pressure was reduced. The pressure increase was done by the pump positive displacement. For each pressure level, a reduction of the temperature of the fluid with

agitating the high pressure cell fluid was performed until the hydrate formation (Fig. 3). Hydrate formation causes a rapid decrease of pressure in the visual high pressure cell. For each pressure level and after hydrates formation, a process of dissociation of formed hydrates by increasing temperature in the high pressure cell was carried out.

2.6 Measurement of Gas Hydrates Formation Temperature with Increasing of Produced Water Amount

In each experiment, a volume 60 cm³ of reservoir gas was introduced into the visual high pressure cell at a pressure of 5000 psig and reservoir temperature (104 °C), after that and at the bottom of the cell, using the volumetric pump a volume of 3 cm³ (5% vol), 6 cm³ (10% vol), 9 cm³ (15% vol) and 12 cm³ (20% vol) of produced water for the last test was injected. After temperature stabilization by a magnetic stirring, a decreasing in pressure was performed. Then, the cooling process of the fluid into the cell with agitation was carried out until hydrates formation.

2.7 Measurement of Gas Hydrates Formations Temperature in Presence of Different Inhibitors

The influence of some inhibitors on reducing the hydrate formation temperature has been investigated

3. Experimental Results

3.1 Samples Validation

The representative sample (validated) is the first one and it can be used for recombination to obtain reservoir fluid.

Fig. 3 Hydrates formation process in the visual high pressure cell at a pressure of 3000 psig and a temperature of 24 °C.

Table 1 Molar composition of the reservoir fluid obtained by recombination of separator gas and separator liquid.

Component	Molar mass “Mi” (g/mol)	Sep gas molar composition (%)	Sep liquid molar composition (%)	Reservoir fluid molar composition (%)
N2	28.014	1.17	0.69	1.16
CO2	44.010	1.59	0.26	1.55
C1	16.043	81.35	5.33	79.07
C2	30.070	10.31	6.09	10.18
C3	44.097	3.54	7.95	3.67
iC4	58.124	0.49	2.62	0.55
nC4	58.124	0.86	6.95	1.04
iC5	72.151	0.27	4.82	0.41
nC5	72.151	0.23	5.06	0.38
C6	86.178	0.13	10.50	0.44
C7	96.000	0.06	14.63	0.50
C8	107.00	0.00	9.90	0.30
C9	121.00	0.00	8.41	0.25
C10	134.00	0.00	5.12	0.15
C11	147.00	0.00	3.23	0.10
C12	161.00	0.00	2.17	0.07
C13	175.00	0.00	1.67	0.05
C14	190.00	0.00	1.18	0.04
C15	206.00	0.00	0.88	0.03
C16	222.00	0.00	0.65	0.02
C17	237.00	0.00	0.49	0.02
C18	251.00	0.00	0.37	0.01
C19	263.00	0.00	0.29	0.01
C20	275.00	0.00	0.21	0.01
C21	291.00	0.00	0.16	0.01
C22	305.00	0.00	0.12	0.00
C23	318.00	0.00	0.08	0.00
C24	331.00	0.00	0.07	0.00
C25	345.00	0.00	0.05	0.00
C26	359.00	0.00	0.03	0.00
C27	374.00	0.00	0.02	0.00
C28	388.00	0.00	0.01	0.00
C29	402.00	0.00	0.01	0.00
C30+	580.00	0.00	0.01	0.00
Total		100.00	100.00	100.00
Average molar mass “Mm” (g/mol)		20.05	91.74	22.21

3.2 Reservoir Fluid Reconstitution

The molar composition of the reservoir fluid obtained by recombination of separator gas and separator liquid is shown in Table 1.

3.3 Measurement of Hydrate Formation Temperature

The obtained results regarding the measurement of hydrate formation temperature are shown on Fig. 4.

3.4 Measurement of Hydrate Formation Temperature with Increasing of Produced Water Amount

The obtained results regarding the measurement of hydrate formation temperature for different amount of produced water are shown on Fig. 5.

3.5 Measurement of Hydrate Formation Temperature in Presence of Different Inhibitors

The obtained results regarding the measurement of hydrate formation temperature in presence of different inhibitors are shown on Figs. 6, 7 and 8.

Fig. 4 Curve P-T of hydrates formation of gas condensate.

Fig. 5 Curves P-T of hydrates formation of gas condensate with increasing of produced water amount.

Fig. 6 Curves P-T of hydrates formation of gas condensate in presence of Methanol.

Fig. 7 Curves P-T of hydrates formation of gas condensate in presence of TEG.

Fig. 8 Curves P-T of hydrates formation of gas condensate in presence of DEG (Di-Ethylene Glycol).

Gas hydrates will form in the pipeline linked the manifold and the separator (arrival at the processing center) and upstream the manifold.

The increasing of produced water amount will increase slightly the hydrates formation temperature, this means that the increasing of produced water amount affect the amount of gas hydrates but not the formation temperature.

The injection of methanol, TEG (Tri-Ethylene Glycol) and DEG (Di-Ethylene Glycol) decrease the hydrates formation temperature and consequently decrease the hydrates formation stability zone.

To prevent the formation of hydrates at manifold, it is necessary to inject at least 25% vol of methanol or more than 25% vol of TEG or 25% vol of DEG.

To prevent the hydrates formation at separator, it is necessary to inject at least 50% vol of methanol or 75% vol of TEG or 75% vol of DEG.

4. Conclusions

Experimental evidence shows that under design

conditions, gas hydrates formation is thermodynamically favored. Consequently, the plugging of pipelines and gas treatment equipment is possible. The plugging may occur without proper mitigation, it may occur from the manifold to the arrival at the processing center, and even before the manifold. With time, an increase in the amount of produced water will increase slightly the temperature of hydrates formation.

To prevent the formation of hydrates at manifold temperature, it is necessary to inject at least 25% vol of methanol or more than 25% vol of TEG or 25% vol of DEG. While to prevent the hydrates formation at separator temperature, it is necessary to inject at least 50% vol of methanol or 75% vol of TEG or 75% vol of DEG.

We finally conclude that, our experimental results are in line with those obtained by simulation, and are in good agreement with those reported in the literature.

References

- [1] Mooijer, M. M. 2004. "Phase Behaviour and Structural Aspects of Ternary Clathrate Hydrates Systems." PhD thesis, Technische Universiteit Delft.
- [2] Berez, E., and Bella-achs, M. 1983. *Gas Hydrates*. Edition Elsevier.
- [3] Rojey, A., and Naturel, L. G. 1994. *Production, Traitement et Transport*. Paris: Editions Technip.
- [4] Jeon, Y. H., Kim, N. J., Chum, W. G., Lim, S. H., Kim, C. B., and Hur, B. K. 2006. "A Study of the Kinetic Characteristics of Natural Gas Hydrate." *Ind. Eng. Chem.* 12 (5): 733-8.
- [5] Sloan, E. D., and Koh, C. A. 2008. *Clathrate hydrates of Natural Gases*. Third Edition, Taylor and Francis Group.
- [6] Sloan, E. D. 1953. "Natural Gas Hydrates." *Colorado of Mines, SPE paper* 2356.
- [7] Hammerschmidt, E. G. 1934. "Formation of Gas Hydrates in Natural Gas Transmission Lines." *Ind. Eng. Chem.* 26: 851-5.
- [8] Cochran, S., and Gudimetla, R. 2004. "Hydrate Management: Its Importance to Deepwater Gas Development Success." *World Oil* 225: 55-61.
- [9] Pickering, P. F., Edmonds, B., Moorwood, R. A. S., Szczepanski, R., and Watson, M. J. 2001. "Evaluating New Chemicals and Alternatives for Mitigating Hydrates in Oil and gas Production." *Ultradeep Eng Supplement to offshore Magazine* 7-10.
- [10] Gravier, J. F. 1986. *Properties of Reservoir Fluids*. Paris: Technip Edition.
- [11] Nagarajan, N. R., Honarpour, M. M., and Sampath, K. 2007. "Reservoir-Fluid Sampling and Characterization." *Society of Petroleum Engineers*.
- [12] Donnez, P. 2007. *Essentials of Reservoir Engineering*. Paris: Technip Edition.
- [13] Williams, J. M. 1998. "Fluid Sampling under Adverse Conditions." *Review of French Institute of Petroleum* 53 (3): 355.
- [14] Danesh, A. 1998. "PVT and Phase Behavior of Petroleum Reservoir Fluids." *Developments in Petroleum Science* 47.