

Determination of Hydrate Phase Equilibrium Curve Using High-Pressure Visual Cell

Gharesheiklou, Ali Asghar⁺; Mahmoodian, Hassan; Ghalyaghy-Zadeh, Reza*

Research Institute of Petroleum Industry (RIPI), P.O. Box 18745-4163 Tehran, I.R. IRAN

ABSTRACT: *This study aimed to construct the hydrate three-phase equilibrium curves for two typical Iranian gas reservoir samples using a high-pressure visual cell. To do so, complete analysis of the reservoir fluids was obtained by different techniques of composition analysis i.e. gas chromatography (GC) and detailed hydrocarbon analysis (DHA). Using high-pressure visual cell the hydrate phase equilibrium curve was obtained by measuring the hydrate formation temperature in each pressure level. By means of commercial hydrate software, hydrate formation temperature was predicted in each specified pressure level. Comparing the results showed that the experimental data are in good agreement with the simulator results. Using the experiments results, hydrate phase equilibrium curves were constructed in order to depict the safe and unsafe regions of the hydrate formation zones for two typical Iranian gas reservoir samples.*

KEY WORDS: *Hydrates, Clathrates, High-pressure visual cell, Hydrate phase equilibrium curve.*

INTRODUCTION

Gas clathrates (commonly called hydrates) are crystalline compounds that occur when water forms a cage-like structure around smaller guest molecules. Hydrate formation is possible in any place where water exists in natural or artificial environments and at temperatures above and below 0 °C when the pressure is elevated (see Fig. 1). Hydrates are considered 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. Common examples of preventive measures are the regulation of pipeline water content, unusual drilling-mud

compositions, and large quantities of methanol injection into pipelines [1]. *Hammerschmidt* first identified hydrates as the primary cause of plugging in gas transmission lines in 1934 [2]. Since that time the natural gas industry has committed significant resources to the understanding of hydrate formation and prediction of hydrate equilibrium conditions [3-6]. Historically, the main hydrate research work has done to predict hydrate equilibrium conditions, typically the hydrate stability curves. Several attempts have already been done in order to measure and predict the hydrate phase equilibrium curve experimentally. The majority of them have been done through constant volume pressure Depletion in high pressure non-visual

** To whom correspondence should be addressed.*

+ E-mail: shikhlooa@ripi.ir

1021-9986/07/1/107

6/\$/2.60

Table 1: Composition of gas sample one (Experimental data obtained by gas chromatography).

No.	Component	MW [g/mol]	Separator Gas	Reservoir Fluid
			mol %	mol %
			Sum=100.00	Sum=100.00
1	N ₂	28.013	5.5	5.49
2	CO ₂	44.01	1.41	1.4
3	H _{2s}	34.076	0.01	0.01
4	C ₁	16.043	86.55	86.36
5	C ₂	30.07	3.58	3.58
6	C ₃	44.097	1.07	1.07
7	i-C ₄	58.124	0.27	0.27
8	n-C ₄	58.124	0.39	0.4
9	i-C ₅	72.151	0.21	0.21
10	n-C ₅	72.151	0.17	0.18
11	C ₆	86.18	0.27	0.29
12	C ⁷⁺	185.20	0.57	0.74

cells [6]. But the recent work has focused on determining the hydrate phase equilibrium curve using high-pressure visual cell.

EXPERIMENTAL SET-UP

The high-pressure visual cell was used to measure the hydrate formation conditions in a static condition. The experimental set-up mainly consisted of a high-pressure visual cell. The maximum working pressure and temperature of the high pressure visual cell was around 1000 atm and 300 °C, respectively. It has been made in Canada by DBR Oil Phase Company (see Fig. 2).

The high-pressure cell had been connected to a high pressure hydraulic 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 was in an air bath and the temperature of the cell could be stabilized by a digital temperature controller very precisely. The internal volume of high-pressure cell was divided into two separated parts. They were separated from each other by a sealed piston. One side of the piston was connected to the hydraulic pump and the other side had been filled with the gas sample and connate water (see table 1 and 2).

Table 2: Composition of gas sample two (Experimental data obtained by gas chromatography).

No.	Component	MW [g/mol]	Separator Gas	Reservoir Fluid
			mol %	mol %
			Sum=100.00	Sum=100.00
1	N ₂	28.013	5.47	5.43
2	CO ₂	44.01	1.75	1.74
3	H _{2s}	34.076	0.04	0.04
4	C ₁	16.043	84.37	83.8
5	C ₂	30.07	3.98	3.99
6	C ₃	44.097	1.32	1.33
7	i-C ₄	58.124	0.38	0.38
8	n-C ₄	58.124	0.57	0.59
9	i-C ₅	72.151	0.31	0.33
10	n-C ₅	72.151	0.28	0.3
11	C ₆	86.18	0.45	0.49
12	C ⁷⁺	185.20	1.08	1.58

In this experimental research, total volume of the visual cell was 100 cm³ and about 25 cm³ of this volume was filled by connate water and the rest (75 cm³) was filled by gas reservoir sample. As a rule of thumb, the ratio of connate water volume respect to the gas sample volume was 1/3. To perform the experiments, the high-pressure visual cell was thoroughly cleaned and evacuated before being filled with the sample. The hydrocarbon fluid to be tested was introduced to the cell and at the same time the cell volume was increased until the desired pressure and temperature was attained. A high-pressure pump was then used to inject water into the base of the cell [7].

EXPERIMENTAL PROCEDURE

The visual capability of the hydrate experimental set-up enabled us to measure the hydrate phase equilibrium curve using a high-pressure visual cell (see Fig. 8).

The routine procedure for measuring them has already been done through fixed volume pressure depletion. To do so, the hydrocarbon fluid to be tested is introduced to cell and at the same time the cell volume is increased until the desired pressure and volume is attained. An HPLC pump is then used to inject the water into the base of the cell. With the cell contents being mixed, the

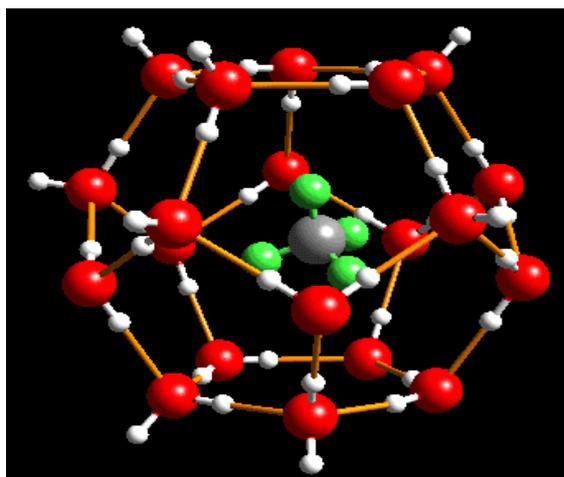


Fig. 1: Clathrate structure of methane hydrate.



Fig. 2: Visual high-pressure cell.

temperature is then lowered to form hydrates. The formation of the hydrates caused a rapid decline in pressure dramatically. The temperature is then raised stepwise, allowing at least 3 hours for equilibrium to be reached at each temperature. The temperature, T and the pressure, P , are logged continuously and the equilibrium data is plotted on a scatter-gram. The point at which the slope of P versus T plot sharply changed is considered as the hydrate dissociation point [7-10].

But the visual capacity of the hydrate experimental set-up enabled us to measure the hydrate formation temperature in each fixed pressure step. In other words, during the experiment the pressure was kept constant and three different steps were considered to pinpoint the hydrate formation temperature with an acceptable accuracy. The experimental procedure for determining the conjugates of the hydrate formation pressures and temperatures has been described through the following steps:

1- Cooling down and heating up the mixture of connate water and gas sample in the visual hydrate cell, just to sub-cool and melt the hydrate, respectively. During this step, the hydrate formation temperature and melting temperature are measured by monitoring the visual hydrate cell with ± 1.0 °C accuracy. Once forming the hydrate, the temperature of the cell should be adjusted close to the melting temperature to keep hydrate seeds in the water.

2- Setting the temperature 4-5 °C below the formation temperature and holding this temperature until the time that corresponds to the crystals growth (crystal growth

effect). Once confirming this part, set the temperature back to within 2 °C of the suspected melting temperature immediately. Then, increase the temperature in 0.5 °C steps holding for about 15 minutes after the temperature is stable to confirm that there is no melting. Continue this process until melting is confirmed. Melt most but not all of the hydrate.

3- Set the temperature 2-3 °C below the formation temperature and hold until one can see crystal growth. Once confirming that the crystals are growing, set the temperature back to within 2 °C of the suspected melting temperature immediately. Then increase the temperature in 0.2 °C steps holding for about 15 minutes after the temperature is stable to confirm that there is no melting. Continue this process until melting is confirmed [11, 12].

It should be reminded that the above-mentioned steps complete the accuracy of measuring the hydrate formation temperature step by step. First step can predict the hydrate formation temperature with ± 1.0 °C and the second and the third step should be done in order to increase the accuracy of hydrate formation conditions (see Fig. 3).

SIMULATION SOFTWARE

Before experimental measuring the hydrate formation conditions, it was necessary to have an estimate about the hydrate formation temperatures in each pre-determined pressure. To do so, we used in-house hydrate simulation software in order to predict the hydrate formation temperature in each operating pressure.

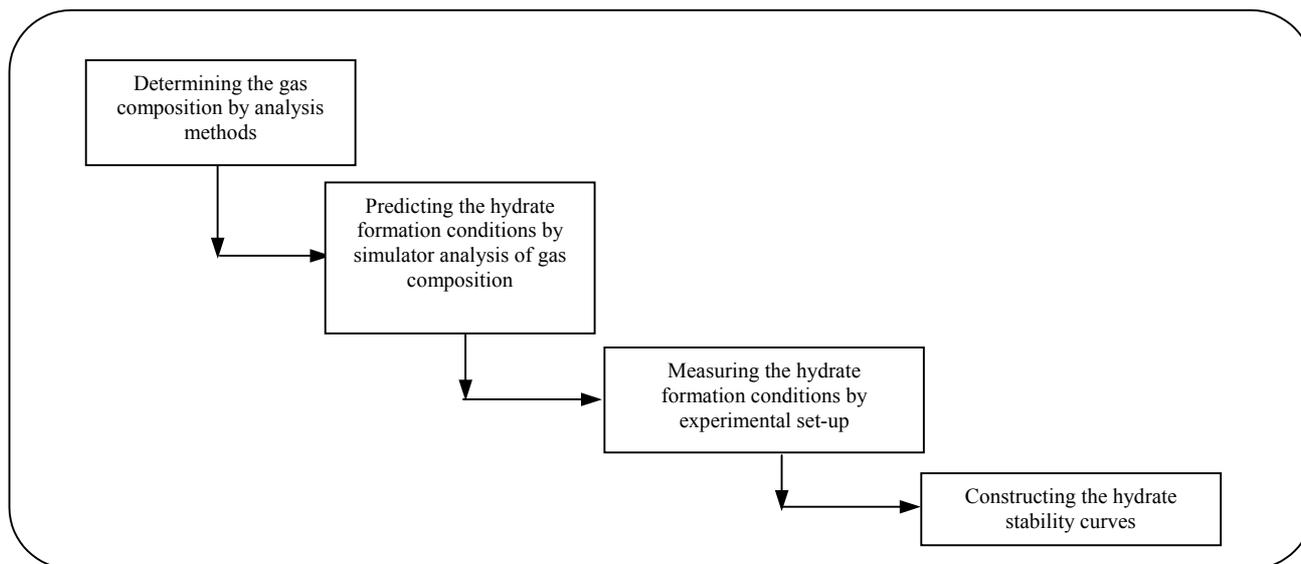


Fig. 3: Flow chart showing different steps needed for constructing the hydrate phase equilibrium curves.

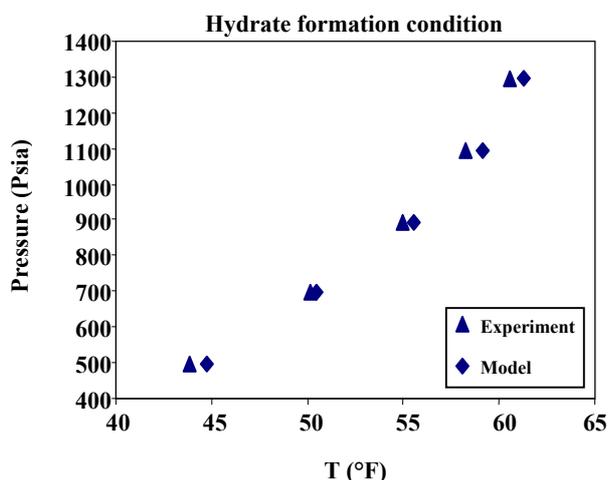


Fig. 4: Comparison between the experimental data and simulation results for gas sample no.1.

The hydrate simulation software is user-friendly software, which is able to simulate and predict the hydrate formation conditions with and without using inhibitors. It can predict incipient hydrate formation potentials using detailed algorithm based on a statistical thermodynamic model. The software has been developed from a calculation scheme suggested by Parrish and Prausnitz, which is modified and extended by Robinson. The gas hydrate routine is based on a procedure developed by Robinson. The Peng-Robinson equation of state is used for all property calculations through the structure of the simulator. Before measuring the hydrate formation temperature in each specific pressure, it was

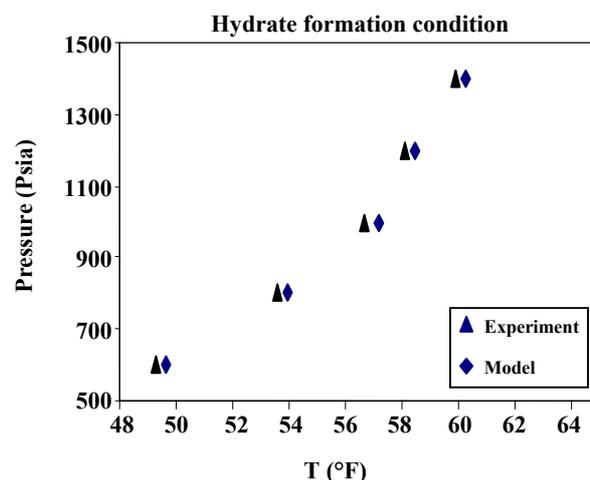


Fig. 5: Comparison between the experimental data and simulation results for gas sample no.2.

necessary to have an estimate using the available hydrate simulation software.

RESULTS AND DISCUSSION

Measuring the hydrate formation temperature in each specified pressure led to determine the conjugates of hydrate formation pressure and temperature. Afterwards, the hydrate formation points were fitted and hydrate phase equilibrium curves were depicted for each reservoir fluid sample. Using the experiments results, hydrate three-phase equilibrium curves were constructed in order to depict the safe and unsafe regions of the hydrate formation zones.

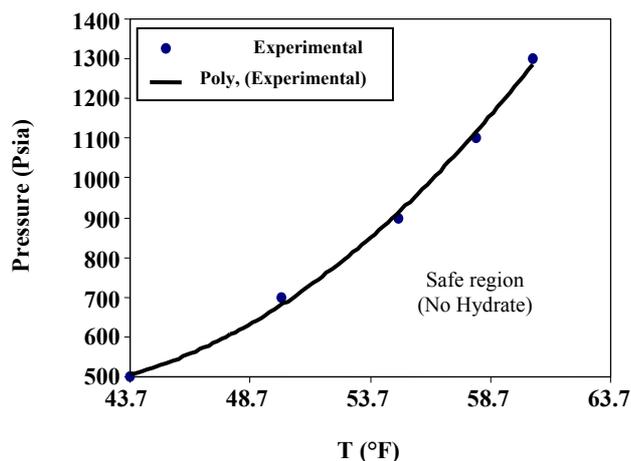


Fig. 6: Hydrate phase equilibrium curve of gas sample no. 1.

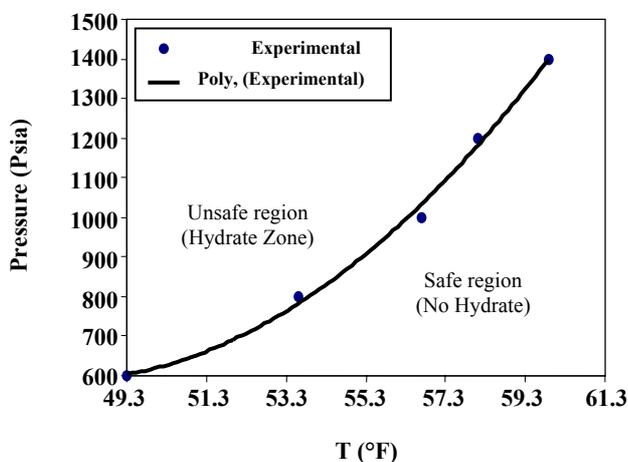


Fig. 7: Hydrate phase equilibrium curve of gas sample no. 2.

The results showed that the experimental data are reasonably in good agreement with the simulator results (see Fig. 4 and Fig. 5). As it was expected, hydrate zone was detected at high pressures and low temperatures, (above the stability curve), and the safe zone (below the stability curves) was depicted at low pressures and high temperatures for each reservoir gas sample (see Fig. 6 and Fig. 7). Using the results of the stability curves, one can determine the possibility of the hydrate formation in different operating conditions of temperatures and pressures. In other words, the stability curves can be used as a rule of thumb in order to design the field operating conditions within the hydrate free zone.

CONCLUSIONS

Determining the hydrate formation conditions using the visual hydrate experimental set-up is a time-

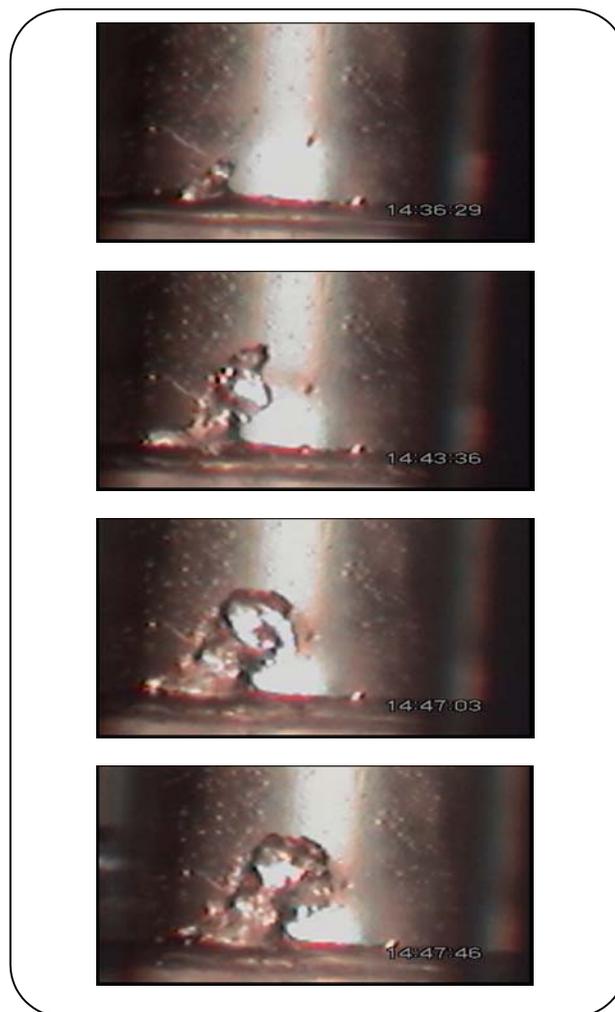


Fig. 8: Hydrate formation process inside the high-pressure visual cell.

economizing method in order to construct the hydrate phase equilibrium curves. Comparing the results of the simulation and the experiments showed that the experiment results are reasonably in good agreement with simulation data.

Nomenclatures

MCM	Million Cubic Meter
GC	Gas Chromatography
DHA	Detailed Hydrocarbon Analysis
LNG	Liquefied Natural Gas

Received : 18th September 2005 ; Accepted : 17th August 2006

REFERENCES

- [1] Sloan, E.D., Natural gas hydrates, Colorado School of Mines, SPE paper 2356, (1953).
- [2] Hammerschmidt, E. G., Formation of Gas Hydrates in Natural Gas Transmission Lines., *Ind. Eng. Chem.*, **26**, 851 (1934).
- [3] Deaton, W. M., Frost E. M., Gas Hydrates and Their Relation to the Operation of Natural Gas Pipe Lines, *U.S.B.M. Monograph 8* (1946).
- [4] Davidson, D.W., Clathrate Hydrates in Water: A Comprehensive Treatise, *Hydrate*, **2**, Chap. 3, 115 (1973).
- [5] Kobayashi, R., Vapor Liquid Equilibria in Binary Hydrocarbon-Water Systems, Ph.D. Thesis, Univ. of Mich., Ann Arbor, MI (1951).
- [6] Hubbard, R.A., Campbell, J.M., Recent developments in gas dehydration and hydrate inhibition, SPE paper 21507, (1992).
- [7] Tohidi, B. et al., Measurement and prediction of hydrate-phase equilibrium for reservoir fluids, SPE paper 31234, (1994).
- [8] Tohidi, B., Danesh, A., Todd, A.C., Predicting Pipeline Hydrate Formation, *Chem. Engineer*, September (1997).
- [9] Tohidi, B. et al., Effect of Heavy Hydrate Formers on the Hydrate-Free Zone of Real Reservoir Fluids, paper SPE 35568, presented at the 1996 SPE European Production Operations Conference and Exhibition, Stavanger, 16-17 April, (1999).
- [10] Tohidi, B. et al., Hydrate-Free Zone for Synthetic and Real Reservoir Fluids in the Presence of Saline Water, *Chem. Eng. Sci.*, **2**, p. 37 (1997).
- [11] Ng, H.-E., Chen, C.J. and Saeterstad T., Hydrate Formation and Inhibition in Gas Condensate and Hydrocarbon Liquid Systems, *Fluid Phase Equilibria*, **4**, p. 22 (1987).
- [12] Hammerschmidt, E.G., Formation of Gas Hydrates in Natural Gas Transmission Lines, *Ind. Eng. Chem.*, **6**, p. 12 (1934).