

Peculiarities of natural gas hydrate formation from ice in reactors under high pressure

M Ye Semenov¹, I K Ivanova^{1,2} and V V Koryakina¹

¹ Institute of Oil and Gas Problems, Siberian Branch, Russian Academy of Sciences, Yakutsk, Russia

² M. Ammosov North-Eastern Federal University, Yakutsk

E-mail: xotoy_82@mail.ru

Abstract. Experimental results of natural gas hydrates formation from ice obtained under static conditions in the batch reactor applying the method of thermal cycling have been given. Hydrate forms subdivided according to their morphological features have been shown: powder and layered growth, retained ice shapes, and whisker crystals. The conducted experiments have defined effects of the thermal cycling regime on forms of obtained hydrates: decreased rates of heating/cooling results in an increase of a share of whisker crystals. The rate of decomposition of loose retained ice shapes in the form of hydrate has been defined to be 2.3 times faster than that of powder and dense layered hydrates.

1. Introduction

Gas hydrates are known to be solid crystalline compounds formed under certain thermobaric conditions from water and gas with low molecular weight and characterized by the ability to contain gas in a concentrated state [1, 2]. The rationale and comparative calculations of the prospects for natural gas use in a hydrate (solid) state for transportation and storage in oil and gas industry are given in [3].

From the technological point of view, an important parameter of gas hydrates is the specific gas content that depends on a molecular weight of the gas forming agent, type of structure and content, degree of hydrate cavity filling, as well as the presence of foreign inclusions and crystal lattice defects [4, 5]. At a 100% of the hydrate structure filling with methane molecules ($\text{CH}_4 \cdot 5.75\text{H}_2\text{O}$), the specific gas content of hydrate makes $164 \text{ m}^3/\text{m}^3$. [2].

Transportation and storage of natural/associated gas in the northern regions of Russia are promising technologies due to the self-preservation effect of gas hydrates, i.e. slow decomposition of hydrates at negative temperatures [6]. The most stable, under the same storage conditions, are massive forms of gas hydrates [7]. The following regularity has emerged: at a specific gas content of more than $130 \text{ cm}^3/\text{g}$, the hydrate maintains a high stability under non-equilibrium conditions at negative temperatures. The temperature boundaries of "the anomalous conservation area" of methane hydrate are determined in [8].

Despite existing technologies for industrial production of gas hydrates [9, 10], the issue of production of the gas hydrate ready for storage and transportation directly in the reactor itself is still unsolved [11]. Therefore, study of mechanisms of growth and forms of hydrate formation is a significant aspect of development of the gas hydrate production technology, and it is of fundamental importance [12]. It is assumed that [13] compensation is possible for the heat of phase transitions during hydrate formation and with maintenance of low temperatures during their accumulation,



making use of naturally low temperatures of the North of Russia. Hence, there are prerequisites for simplification of the means of formation of synthetic gas hydrates and reduction of energy costs in the technological cycle of their production [14].

It is known [15-20] that at elevated pressures of a gas-hydrate forming agent, it is possible to transfer practically the entire solid-ice phase ($0.18 \div 0.5$ mm) into hydrates via thermal cycling in the batch reactor of high pressure. However, obtaining and preparation of finely ground ice particles is a laborious process, and the obtained particles of synthetic hydrates are unstable and rapidly decomposing products [11]. Currently, the review of literature has showed that, an absence of experimental data and quantitative parameters of natural gas hydrate (NGH) synthesis from larger ice fractions (> 5 mm).

Thus, the objective of this paper is an experimental study of formation of natural gas hydrates (NGH) from formed ice at various temperature regimes of synthesis and estimation of rates of the obtained hydrate decomposition.

2. Experimental part

The natural gas from the Srednevelyuskoe field with the following composition $\text{CH}_4 - 92,89$, $\text{C}_2\text{H}_6 - 5,25$, $\text{C}_3\text{H}_8 - 1,21$, $i\text{-C}_4\text{H}_{10} - 0,102$, $n\text{-C}_4\text{H}_{10} - 0,12$, $\text{N}_2 - 0,38$, $\text{CO}_2 - 0,048$ (total %). has been used in this research. The equilibrium condition of hydrate formation has been calculated on the basis of the natural gas composition applying the Sloan method [4]. Ice samples, 30 mm in diameter, were obtained by freezing distilled water in 10 ml forms (Fig. 1a). Four identical cylindrical reactor chambers with a volume of 1113 cm^3 were used. Cooling of reagent-loaded reactors was carried out in a SANYO MIR-254 refrigerated incubator (Fig. 1b), where the thermal cycling mode could be set up.

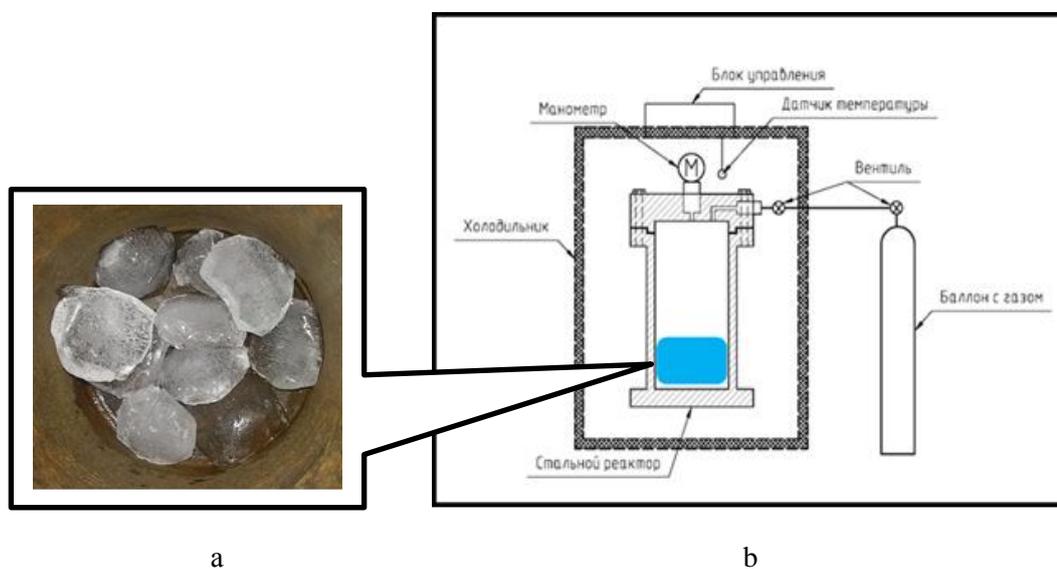


Figure 1. Formed ice samples (a) and the scheme of experimental installation for gas hydrate production (b).

Since it is during the ice melting process [17-19], when the intensive hydrate formation occurs, the temperature range of thermal cycling is selected with transition through the melting point of ice from -5 to $+5^\circ\text{C}$. To select the optimal temperature regime for production of NGH from formed ice, five modes of 96 hour temperature effects on the system were used (from 4 to $\frac{1}{2}$ cycles of heating/cooling for a day), according to the procedure described in [21, 22].

After the hydrate formation process was over, the reactor was opened in a freezer at a temperature of -10°C to fix the native structure and select hydrate samples for subsequent weighing and decomposition. The morphology of gas hydrates was recorded with a Pentax K200D digital camera. Kinetics of hydrate decomposition was studied applying a volumetric method at $+25^\circ\text{C}$, for this

purpose, a sample of the hydrate with a given weight was placed under a glass dome located in the refrigerated heated bath circulator Huber CC 410, the dome, in its turn, was connected to a gas meter.

The specific gas content of the obtained hydrate (v , sm^3/g) was calculated as a ratio of the measured volume of the gas released from the hydrate to the amount of the sample from the obtained gas [7]:

$$v = \frac{V_{\text{gas}}}{m_{\text{hydrate}}}; \quad (1)$$

v is the specific gas content of the sample, V_{gas} is a volume of the gas released from the hydrate, m_{hydrate} is the weight of the hydrate sample.

Kinetic characteristics of hydrate decomposition were calculated applying the Avrami-Erofeev-Kolmogorov equation [23], most often used for analysis of isothermal solid phase reactions [24:]

$$\alpha = 1 - \exp(-k\tau^n), \quad (2)$$

where α is a degree of conversion, n is the kinetic parameter characterizing the mechanism of the process, k is the generalized rate constant, and τ is time. Kinetic parameters n and k can be determined by double-logarithm of the equation and presented as follows:

$$\lg[-\lg(1 - \alpha)] = n\lg\tau + \lg k + \lg(\lg e). \quad (3)$$

The equation (2) in this form (3) makes a direct line, thus allowing us to calculate values of the parameters n and k constructing logarithmic anamorphoses. And, the parameter n characterizes the mechanism of the reaction under study, thus, with $n > 1$, the process predominantly occurs in the kinetic area, and with $n < 1$ – in the diffusional one.

Substituting the determined kinetic parameters (n and k) into the Sakovich formula (4), the rate constants of the decomposition reaction of natural gas hydrates (K) have been calculated as:

$$K = nk^{1/n}. \quad (4)$$

3. Results and discussions

Under the temperature regime with 4 heating/cooling cycles per day, only hydrate inclusions are distinct on the well preserved ice surface, which evidences that the ice does have time to melt under the given regime of thermal cycling. Under the temperature regime with 3 cycles per day, the major mass of ice retains its shape, and thin branched growths occur on the ice surface. Hence, under the above-mentioned temperature regimes, following a rapid temperature change in the refrigerated incubator, the temperature inside the reactor does not have time to rise to positive degrees, so ice samples in the reactor do not melt.

Under the temperature regime with 2 heating/cooling cycles per day, destruction of the original ice forms occurs, and white porous snow-like structures of NGH with a small amount of thin branched growths (Fig. 2) are observed.



Figure 2. Images of the change in shapes of NGH depending on the thermal cycle of synthesis.

It has been identified that upon NGH synthesis from formed ice, elongation and enlargement of branched growths with the direction of crystal growth upwards from the ice surface (Fig. 2) occur, as the number of heating/cooling cycles decreases (from 2 cycles to ½ cycle).

Upon obtaining NGH from ice under the temperature regimes with 1 and ½ heating/cooling cycles, three major shapes of ice-hydrate associates are found to be formed: fine powder and layered growths at the chamber bottom, a retained ice form, and whisker crystals of hydrates (Fig. 3).



Figure 3. Images of various forms of NGH obtained from ice: whiskers, form of ice, powder and layered growths.

The specific gas content of synthesized NGH (Table 1) has been calculated on the basis of measurements of the volume of the emitted gas from the hydrate samples obtained under the temperature regime with one heating/cooling cycle per day during 96 hours.

Table 1. Specific gas content of synthesized natural gas hydrates in accordance with their forms

Forms of hydrate	m, g	V _{gas} , cm ³	v, cm ³ /g	χ, %
Whiskers	4,8	-*		
Forms of ice	24	2220	92.5	60
Hydrate from reactor bottom (layered growths, powder)	80	9000	112.5	73.5

It is worthwhile to note here that, regretfully, the precision of the measurement equipment did not allow us to measure a small amount of gas emitted from whiskers. The value of the specific gas content of the retained ice forms is 92.5 cm³/g, and that of hydrates in the form of powder and dense layered growth at the reactor bottom is 112.5 cm³/g. It has been found out that 75 wt% of hydrates have been accumulated at the bottom of the reactor as a powder and dense layered growth, with 22.2 wt % being in the well-preserved original ice form, and 2.8 wt% of the hydrates are growing as whiskers (Table 1).

Based on the measurement of a gas volume evolved during decomposition of various forms of hydrates, kinetic parameters of disassociation of natural gas hydrates have been calculated (Table 2), and logarithmic anamorphoses have been constructed according to the equation (3) (Fig. 4). High values of reliability approximation (0.99) demonstrate the validity of this equation for description of kinetics of decomposition of natural gas hydrates.

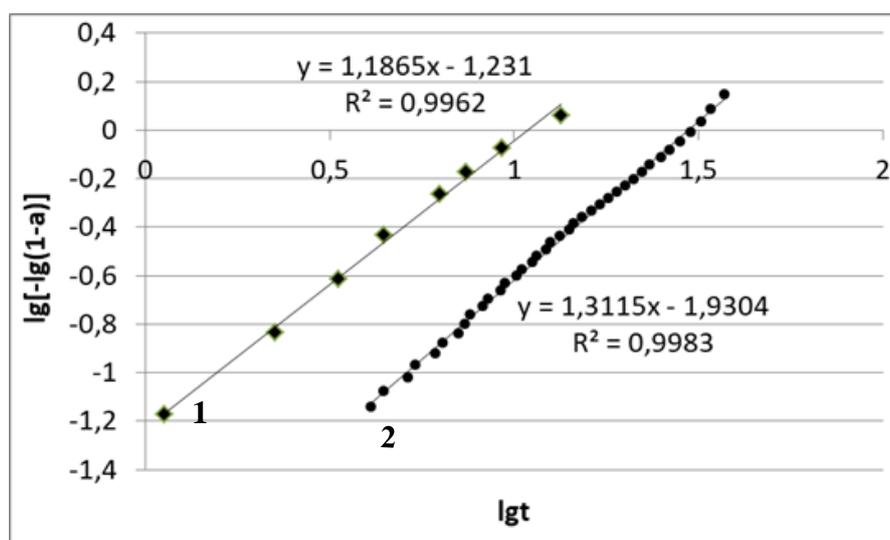


Figure 4. Kinetics of decomposition of various forms of hydrates at $T=25^{\circ}\text{C}$: 1 – hydrates in the form of ice; 2- hydrates in the form of powder and layered growths.

At the atmospheric pressure and room temperature, hydrates in the form of powder and layered growth from the bottom of the reactor are identified to be completely decomposed within 50 min, and hydrates as preserved forms of ice completely decompose within 25 minutes.

Decomposition of synthesized forms of hydrates has been determined to occur in the kinetic area ($n>1$). Wherein, the rate of decomposition of hydrates in the form of ice is 2.3 times higher than that of hydrates from the bottom of the reactor in the form of layered growth and powder. The half-life of hydrates in the form of ice is 3.5 minutes, and that of hydrates from the bottom of the reactor makes 13 minutes (Table 2).

Table 2. Kinetic parameters of decomposition of various forms of natural gas hydrates, obtained from formed ice

Sample	Melting			
	n_{squ}	$K_{\text{squ}}, \text{min}^{-1}$	$\tau^{1/2}$	R^2
Hydrate in the form of ice	1.004	0.207	3.5	0.99
Hydrate from the reactor bottom (lawyered growth, powder)	1.414	0.089	13	0.99

Thus, it has been identified that the most thermodynamically stable forms of hydrates at the air pressure and at 25°C are hydrates from the bottom of the reactor in the form of powder and a dense layered growth.

4. Conclusions

Thus, it has been defined that natural gas hydrates with gas saturation over 70% can be obtained by thermal cycling of the "formed ice + natural gas" system during 96 hours. While producing NGH from formed ice at the temperature regime with 1 heating/cooling cycle from -5 to $+5^{\circ}\text{C}$, hydrates are shown to be formed in the form of powder and a layered growth, in the form of ice, as well as whiskered crystal hydrates. Their mass redistribution in the reactor has been determined. It has been concluded that hydrates in the form of powder and dense layered growth at the bottom of the reactor possess the greatest thermodynamic stability.

Acknowledgments

The study has been conducted within the framework of the State Task №0377-2016-003. The research has been performed with the financial support provided by Russian Foundation for Basic Research (RFBR) and the Government of the Sakha Republic (Yakutia) within the framework of the Scientific Project № 18-45-140035.

References

1. Byk S SH 1980 *Gazovye gidraty* (Moscow: Himiya) p 296
2. Dyadin Yu A and Bondaryuk I V 1995 Stoichiometry of clathrates *Journal of Structural Chemistry* 1088-1141
3. Gudmundsson J 2002 *Proc. 4 Int. Conf. on Gas Hydrates* (Japan) pp 997-1002
4. Havkin A YA 2010 Perspektivy sozdaniya gazogidratnoj promyshlennosti *Vestnik RAEN* 43-45
5. Sloan E D and Koh C A 2008 *Clathrate hydrates of natural gases* (CRC Press) p 720
6. Makogon Yu F 1974 *Hydrates of natural gases* (Moscow: Subsoil) p 204
7. Istomin V A and Yakushev V S 2006 *Effekt samokonservacii gazovyh gidratov* (Moscow: Gazovaya promyshlennost) pp 36-46
8. Yakushev V S 2009 *Prirodnyj gaz i gazovye gidraty v kriolitozone* (Moscow: Gazprom VNIIGAZ) p 192
9. Stern L A, Circone S, Kirby S H and Durham W B 2001 Anomalous preservation of pure methane hydrate at 1 atm *J. Phys. Chem. B.* **105** 1756-1762
10. Horiguchi K and Watanabe S 2011 *Proc. Int. Conf. on Gas Hydrates (Edinburgh United Kingdom)* vol 1 (Electronic Materials) p 75
11. Murayama T and Iwabuchi W 2011 *Proc. Int. Conf. on Gas Hydrates (Edinburgh United Kingdom)* vol 1 (Electronic Materials) p 187
12. Yakushev V S, Kvon V G, Gerasimov Yu A and Istomin V A 2008 *Sovremennoe sostoyanie gazogidratnyh tekhnologij* (Moscow: IRC Gazprom) p 88
13. Yakushev B C, Kvon V G, Dolgaev S I, Podenok S E and Istomin V A 2009 *Gidratnye tekhnologii dlya gazifikacii regionov Rossii* (Moscow: Gazovaya promyshlennost) pp 75-79
14. Istomin V A 2010 *Fiziko-himicheskie osnovy i problemy razrabotki gazogidratnyh tekhnologij* (Moscow: OOO Gazprom ehkspo) p 48
15. Semenov M E, Shitz E Yu and Portnyagin A S 2016 *Sposob polucheniya gidratov prirodnogo gaza i razrabotka na ego osnove konceptual'noj tekhnologicheskoy skhemy processa ih proizvodstva* (Transport i hranenie nefteproduktov i uglevodorodnogo syr'ya) vol 3 pp 53-58
16. Grojsman A G 1985 *Teplofizicheskie svojstva gazovyh gidratov* (Novosibirsk: Nauka) p 94
17. Stupin D Yu 1979 Dielektricheskie svojstva $\text{CCl}_2\text{F}_2 \cdot 17\text{H}_2\text{O}$ i $\text{CCl}_2\text{F}_2 \cdot 17\text{D}_2\text{O}$ *Izv. vuzov. Himiya i him Tekhnologiya* **2** 170-173
18. Stern L A 1996 Peculiarities of methane clathrate hydrate formation and solid-state deformation, including possible superheating of water ice *Science* **273** (5283) 1843-1848
19. Stern L A, Kirby S H, Circone S and Durham W B 2004 Scanning Electron Microscopy investigations of laboratory-grown gas clathrate hydrates formed from melting ice, and comparison to natural hydrates *American Mineralogist* **89** 1162-1175
20. Liu W and Wang L 2014 *Proc. Int. Conf. on Applied Energy (ICAE2014)* vol 61 pp 619-623
21. Nesterov A N 2006 *Dis. d-ra him. nauk: 02.00.04 Nesterov Anatolij Nikolaevich* (Tyumen) p 280
22. Semenov M E, Portnyagin A S and Shitz E Yu 2017 Poluchenie sinteticheskikh gidratov prirodnogo gaza iz l'da v zakrytyh reaktorah pri termociklovanii *Nauka i obrazovanie* **3** 76-81
23. Semenov M E and Shitz E Yu 2015 Vliyanie fazovogo sostoyaniya i sostava odnogo iz komponentov na morfologiyu sinteticheskikh gidratov prirodnogo gaza *Mezhd. nauchno-issl. Zhurnal* **38** (7) 96-101
24. Rozovskij A YA 1974 *Kinetika topohimicheskikh reakcij* (Moskva: Himiya) p 224
25. Talatory Sh and Barth T 2012 Rate of hydrate formation in crude oil/gas/water emulsions with different water cuts *Journal of Petroleum Science and Engineering* 32-40