Investigation of the Formation and Decomposition Processes of the Sredneviluiisky GCF Natural Gas Hydrates in Dispersed Media

L P Kalacheva¹, I K Ivanova¹, A S Portnyagin¹, S A Solovieva¹
D R Egorov², A A Vasiliev², A A Chaynikova²

¹Institute of Oil and Gas Problems, Siberian Branch, Russian Academy of Sciences, Federal Research Center “Yakut Scientific Centre SB RAS”, Yakutsk, Russia
²Ammosov North-Eastern Federal University, Yakutsk, Russia

E-mail: iva-izabella@yandex.ru

Abstract. In this paper the processes of formation and decomposition of natural gas hydrates in wet salted sand samples were studied. Investigations of phase transitions were performed on a specially assembled DTA installation. It is shown that with decrease of the humidity and increase of the salinity of media the degree of supercooling decreases, and the amount of the gas bound to hydrate decreases. It has been found that in comparison with the water-gas system in dispersed rocks there is a shift of thermobaric conditions of hydrate formation to the area of high pressures and low temperatures.

1. Introduction
It is known that the regions of gas hydrate existence are concentrated on the shelf of the world ocean, as well as in the cryolitosone, where part of the zone of gas hydrates stability can be located directly in frozen rocks. Gas hydrates formation in frozen thicknesses will affect their properties and structure. Thermobaric parameters of gas hydrates formation and decomposition in dispersed rocks can be used in mathematical modeling of hydrate formation processes in dispersed systems for the creation of underground storage of natural, associated and greenhouse gases.

2. Experimental Part
The objects of the study were natural gas hydrates obtained in samples of the sand produced in the Lena River with different specified humidity and salinity. The sand is light brown and round. The determination of the grain size [1] of the sand showed that the 55,58% of the total weight of the sample was per fraction of 0.4-0.315 mm. The true and bulk densities of the sand determined by pycnometric method [2] are 2.61 g/cm³ and 1.65 g/cm³, porosity – 36.74%. To obtain hydrates, the sand samples were set to humidity and salinity. For this purpose distilled water and solutions of calcium chloride with concentrations of 5% and 15% by weight were used, that corresponds to mineralization of chloride-calcium type stratum waters of Yakutia deposits. Depending on the solution concentration, soil weight humidity was 17.7-15%, salinity – 0.89-2.65%.
The natural gas of the Srednevilyuysky gas condensate field (GCF) of the following composition (% mol.): CH₄ - 93.9; C₂H₆ - 4.44; C₃H₈ - 1.10; i-C₄H₁₀ - 0.087; n-C₄H₁₀ - 0.108; CO₂ - 0.0559; N₂ - 0.33 was used to obtain gas hydrates.

A study of the phase transitions occurring during the formation and dissociation of natural gas hydrates in a porous medium was carried out in a specially assembled DTA analysis installation, the scheme of which is shown in figure 1. The distinctive feature of this installation is the less complex structure of the measuring cell, compared to its analogues described in [3], [4]. The main element of this installation, as in [3], [4], is a high-pressure chamber, inside which there is a measuring cell (4) consisting of two equal cuvettes of the inert polymer (3), which are equidistant from the walls of the chamber. The high pressure chamber is made of a stainless steel according to the design developed in the laboratory of clathrate compounds of the Institute of Inorganic Chemistry named after A.V. Nikolayev SB RAS (Novosibirsk). The chamber is provided with the actuator type sealing method, which ensures sealing of chamber up to 15 MPa of excessive pressure. Chamber consists of the sleeve (1) with useful volume of 220 cm³, cover (2) with integrated in it two thermocouples CTCA (cable thermocouple chromel-alumel) (6, 7).

The chamber is filled with a hydrate-forming gas from a balloon (12) connected to the external filling port of the chamber (9) by a flexible high-pressure hose. The filling port of chamber is equipped with a shutoff valve, technical analogue pressure gauge and highly sensitive pressure sensor (10). The filling port, in turn, is connected to the chamber by a steel tube twisted into a spring providing more convenient use of the chamber.

Collection and the processing of the primary data from pressure and temperature sensors is performed by means of the precision multichannel temperature meter «MIT – 8» (13) equipped with special software complex and connected to the computer. The change and a maintenance of the set temperature was carried out by placing a high pressure chamber with a measuring cell in the air thermostat «MIR – 256» of Sanyo (Japan) (11), with the accuracy of the maintained temperature equal to 0,1 °C.

The procedure of the experiment is as follows: 21.7 g of the sieved sand was placed in one of the cuvettes located in the measurement cell, to which a predetermined amount of the salt solution was added. The second comparison cuvette remained empty. Further, the measuring cell was placed in the sleeve of the pressure chamber and closed with a cap with thermocouples integrated therein so that the thermocouples were placed in the center of the section of the cuvettes and immersed to half the level of the substance placed in the cuvette. The chamber was then sealed and the gas was fed to an instrument pressure of 8 MPa. The chamber was then placed in an air thermostat programmed to cool the system from 20.0 to -6.0 °С at a rate of 3 deg/h. During the experiment, temperature and pressure values were recorded every 40 seconds.

The rates of the gas transition to the hydrate phase were calculated by pressure change during a hydrate formation process according to the procedure [5].

![Figure 1](image_url)
Figure 2 shows DTA thermograms of formation and decomposition processes of the Srednevilyuysky (GCF) natural gas hydrates in wet salted sand samples. Temperature and pressure of supercooling, a start of the hydrate formation and equilibrium temperature and pressure of the hydrate decomposition are determined based on the thermograms (Table 1). Experimental data show that during the hydrate formation, the system is supercooled (T<sub>s-cool</sub>), that is one of the determining factors for the first hydrate crystals formation. The formation of nucleates and the first hydrate microcrystals is associated with the release of the crystallization heat, which causes the temperature of the system to the jumping start of the hydrate formation (T<sub>f</sub>). As the salinity of the system increases and the humidity of the supercooling temperature decreases and the hydrate formation begins, the amount of absorbed gas decreases (Table 1). The degree of supercooling (ΔT<sub>s-cool</sub>) defined as a difference between temperatures of supercooling and the beginning of the hydrate formation affects the intensity of the hydrate formation in a system. As the degree of supercooling increases, the hydrate formation rate increases, hence increasing the salinity of the dispersion system leads to a decrease of the hydrate formation rate.

**Table 1.** Characteristics of the samples and parameters of the natural gas hydrates formation process in the dispersed media.

| Sample          | Initial humidit y, % | Salinit y, % | T<sub>s-cool</sub>, °C | T<sub>f</sub>, °C | ΔT<sub>s-cool</sub>, °C | n<sub>cons. gas</sub>, mol |
|-----------------|----------------------|--------------|------------------------|------------------|--------------------------|--------------------------|
| Sand+ water     | 17,7                 | 0            | 4,8                    | 6,8              | 2,04                     | 2,897*1                  |
| Sand+ 5% CaCl₂ solution | 16,8                 | 0,89         | 4,0                    | 5,9              | 1,95                     | 1,387*1                  |
| Sand+ 15% CaCl₂ solution | 15,0                 | 2,65         | 0,8                    | 1,6              | 0,81                     | 7,884*1                  |

**Figure 2.** DTA - thermograms of natural gas hydrates formation and decomposition in the sand: A - distilled water; B - 5% calcium chloride solution; C - 15% calcium chloride solution.
Table 2 shows the equilibrium conditions of the hydrate formation in the dispersed medium compared to the values of the hydrate formation in the free volume. P, T - conditions of the natural gas hydrate formation in dispersed media are shifted to the area of higher pressures and low temperatures.

Table 2. Equilibrium conditions of the hydrate formation in the free volume and in the dispersed medium.

| Sample          | In the free volume | In the dispersed medium |
|-----------------|--------------------|-------------------------|
|                 | \( T_{\text{equil.}} \) \(^\circ\text{C} \) | \( P_{\text{equil.}} \) \text{MPa} |                  | \( T_{\text{equil.}} \) \(^\circ\text{C} \) | \( P_{\text{equil.}} \) \text{MPa} |
| Sand+w+ater     | 9,93               | 3,64                    | Sand+w+ater     | 9,939             | 7,390                  |
| 5% CaCl\(_2\) solution | 9,66               | 4,30                    | 5% CaCl\(_2\) solution | 9,668             | 7,488                  |
| 15% CaCl\(_2\) solution | 5,60               | 5,52                    | 15% CaCl\(_2\) solution | 5,604             | 7,370                  |

The process of the hydrate formation in the dispersed media proceeds with a certain degree of supercooling of the system necessary for the formation of crystallization centers. At that, the degree of supercooling and the amount of the gas bound to the hydrate decreases with a decrease of the moisture content and an increase of the salinity of medium. When gas hydrates are formed and decomposed in dispersed rocks, thermobaric conditions are shifted in comparison with the water-gas system towards higher pressures and lower temperatures.

3. References
[1] GOST 12536-2014 Soils Laboratory methods for determining particle size distribution (grain) and microaggregate composition (Moscow) 25 p
[2] Mukheno I P, Dobkin E I, Deryuzhkin V I and Soroko V E 1979 Catalyst Technology, Leningrad: Chemistry 328 p
[3] Groisman A G 1985 Thermophysical properties of gas hydrates (Novosibirsk: Science) 94 p
[4] Filippov D D, Shishkin A S, Malishev A V and Bolshev K N 2006 Modernization of the differential thermal analysis installation developed for the study of equilibrium conditions of the hydrate formation Science and education 1(41) pp 41-44
[5] Fitzgerald G C, Castaldi M J and Schicks J M 2014 Methane hydrate formation and thermal based dissociation behavior in silica glass bead porous media I&ES research vol 53 pp 6840-6854

Acknowledgment
The work was carried out with the financial support of the project Reg. No. NIOKTR AAAA-A17-117040710035-7 and RFBR No. 18-45-140035 r _ a «Justification for the creation of underground natural gas storage facilities in the hydrate state in permafrost aquifers».