Research of Influence Preliminary Water Compression to the Processes of Methane-Containing Gas Mixtures Hydrate Formation

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Abstract. Currently, the supply of a thermodynamic hydrate inhibitor (THI) increasing is the most common measure to prevent the formation of hydrates of gas transmission systems. It is proposed to improve the test procedure for calculating the consumption of inhibitors. By the method of Kinetic (K) and Hydrate Stability Zone (HSZ) the study of the formation and decomposition of gas hydrate phase was led in the mercury-free installation of GHA (Vinci Technologies, France). The moment of formation and decomposition of the gas hydrate phase is determined by the method of recording the pressure deviation from the reference one and duplicated visually.

The substance of the methane-containing gas mixture is determined by the results of the analysis using a chromatograph SHIMADZU GC 2014. The gas mixture as natural gas of the Yuzhno-Kirinskoye Gas Condensate Field is used in the studies as follows: Methane [CH4] 91.28%, Ethane [C2H6] 3.74%, Propane [C3H8] 1.61%, Carbon dioxide [CO2] 1.87%, Butanes [C4H10] 0.37%, [i-C4H10] 0.28%, Pentanes [C5H12] 0.04%, [i-C5H12] 0.09%, [neo-C5H12] 0.001%.

The measurements are carried out in the temperature range from -2°C to 20°C and pressures from 6 MPa to 11 MPa (930-1560 PSI). Cycles of the formation and decomposition of the gas hydrate phase are carried out in samples with water previously subjected to a pressure of 50 MPa and 10 MPa. The difference in experiments is described by the methods of Kinetics (K) and Hydrate Stability Zone (HSZ).

It has been established that during the calculation of THI concentration, it is necessary to carry out additional tests of samples of the gas mixture and water, which was subjected to the preliminary exposure to high pressure, to prevent hydrate formation. The formation of hydrates in such samples occurs earlier than in standard tests.

The increase in the incubation period of hydrate formation in repeated experiments with pre-prepared water indicates the flow of the equilibrium process of redistribution of the proportions of the cubic structures I and II. The process takes place in the system for a long time during several cycles of formation and destruction of the hydrate phase.

1. Introduction
The gas of the Yuzhno-Kirinskoye Gas-Condensate Field, which constitutes the main part of the natural gas stream of the main gas transmission system Sakhalin-Khabarovsk-Vladivostok (MGTS SKV) is
classified as methane type ([CH₄] 83-84% vol., [C₂H₆] 4.5-4.8% vol., [C₃H₈] 2.6-3.03% vol., [C₄H₁₀ + i-C₄H₁₀] 1.4-1.8% vol. e.g. [6]).

Thermodynamic hydrate inhibitors (THI) are used to prevent hydrate formation in gas transmission systems. The most common of them are methanol [C₂H₅OH] and monoethylene glycol (Me-OH) [C₂H₄(OH)₂]. Data on the conditions of hydrate formation in the pipeline, obtained in laboratory studies, are the basis of recommendations for the calculation of volumes of THI.

Calculations of hydrate stability zones, testing of samples are conducted and recommendations are made, taking into account the results of the existing practice of preventing hydrate deposits in gas pipelines. However, literary sources describe incidents registers, which indicate the need for a deeper study of the hydrate formation factors during natural gas transportation (e.g. [9]).

1.1. Method of determining conditions of education of gas hydrates in methane-containing gas mixtures

To conduct tests of hydrate formation conditions, using Kinetics (K) and Hydrate Stability Zone (HSZ) methods, a mercury-free plant for the formation and decomposition of the GHA gas phase (Vinci Technologies, France) is used.

The installation consists of a high-pressure cell that is placed in a thermostatic bath with a glycerol solution. The cell is made of SS 316L stainless steel and equipped with a PT100 sensor for measuring temperature through the RS232 port with an accuracy of ± 0.1°C. The design of the cell allows to mix the magnetic stirrer in the range of rotation frequencies from 0 to 1000 rpm. The maximum pressure of the safety valve of the cell is 21.3 MPa (3000 PSI).

The autoclave is cooled and heated under the control of the HUBER microprocessor unit (Huber, France) with a precision of maintaining the set temperature ± 0.1°C. The autoclave operates with a coolant (water + glycol 15%) to reach an operating temperature of -10°C to 60 °C. In addition, the RS232 interface allows monitoring and recording of data via the "AppliLab" software interface.

In the study, the moment of formation and decomposition of the gas hydrate phase is determined by the method of recording the deviation of pressure from the reference one. For this purpose the unit is equipped with an electronic manometer Keller LEX 1 with a relative measurement error of ≤0.05% FS and an absolute measurement error of ≤0.025% FS.

Visual observation and video recording of the occurring processes is carried out using a port, which equipped with a quartz glass with a thickness of more than 20 mm.

To create high pressures for gases and liquids, the system is equipped with a Floxlab BTSP 100-10 piston pump (Floxlab, France). With the help of a piston pump, excess pressures in the liquid medium are created up to a value of 70 MPa (10000 PSI). In addition, the liquid phase of the sample is dosed with a piston pump with high accuracy. The flow meter allows to record fluid flow rates up to ± 0.0001 ml. The cell is cleaned from atmospheric gases by a vacuum pump RD.2D (D.V.P. Vacuum Technology S.r.l., Italy). The unit includes a GB700 gasifier (Vinci Technologies, France), which creates excess pressures of up to 70 MPa (10,000 PSI) in inert and hydrocarbon gases.

Gas Meter (Vinci Technologies, France) is used to determine the volume of the gas phase of the sample. The range of measured pressures is from -15 to 20 PSI with an accuracy of ± 0.2% FS. The measured volume is not less than 4000 cm³, at a resolution of ± 0.1cm³. Temperature range from 0 to 40 °C with a measurement accuracy of ± 0.1 °C (PT100).

Verification experiments were performed to determine instrumental errors in the equipment. The results of studies of a gas mixture with a high content of the main component [CH₄] 98.44% vol agree well with the generally accepted research results. Fig. 1 shows the results of the experiments of formation and decomposition of the hydrate phase in comparison with other data of the studies [CH₄] 98.9-99.9% vol (e.g. [10]).
The analysis of the compositions of the explored gases is carried out using a chromatograph SHIMADZU GC 2014.

According to the method of the Hydrates Stability Zone (HSZ) experiment, the cell with the sample is slowly cooled to an intermediate temperature and maintained for a certain time, while stabilizing the pressure inside. The operation is repeated until the set temperature is reached. Further, the system starts heating the cell to achieve intermediate temperatures and stabilizing the pressure at each of the points. The data is recorded in a table format. The result of the experiment is an array of data on the values of the stable pressure in the intermediate temperatures of the sample. Based on the data obtained, a diagram of the hydrate stability zones in the gas pipeline is formed. Comparison of the diagram of zones of hydrate stability with technological conditions of gas transportation makes it possible to develop recommendations for changing the concentration of TIG in a gas pipeline.

The Kinetics (K) experiment is performed to evaluate the rate and intensity of hydrate formation in the sample. To do this, the cell with the sample is cooled until a predetermined temperature is reached, and the pressure and temperature inside values are recorded with an equal time interval. The data obtained reflect changes in the rate of decrease in temperature and pressure. Calculating the decrease or increase in the gas phase over a certain time allows us to evaluate the effectiveness of TIG.

The method of preparing a sample for the study includes several stages. The first stage is the preparation of the cell, during which the cell is dried and degassed by a vacuum pump. The second stage of preparation is to make a sample. The sample for the study consists of water and the test gas mixture. Exemplary characteristics of the used components of the sample are given in Tables 1 and 2. The used liquid phase quantity is 30 ml. The hydrogen index (pH) is 5.52.

The error in measuring temperature and pressure is calculated according to a standard procedure (e.g. [1]).

The calculations showed that the total error of the temperature measurement was ≈1.22%, and the error of the pressure measurement was ≈0.79%.
Table 1. H₂O mineral consistence of the test sample liquid phase.

|           | mg/l  | kOhm/cm³ | pH | ml |
|-----------|-------|----------|----|----|
| NaCl      | 1.230 |          |    |    |
| KCl       | 1.300 |          |    |    |
| CaCl₂     | 3.390 |          |    |    |
| NaNO₃     | 3.390 |          |    |    |
| Conductivity, |    |          | 298.6 |    |

Table 2. Gas mix consistence of the test sample gas phase.

| Component          | Concentration, % vol |
|--------------------|----------------------|
| Methane [CH₄],     | 98.4431              |
| Ethane [C₂H₆],     | 1.5313               |
| Propane [C₃H₈]     | 0.0215               |
| Butane [C₄H₁₀]     | 0.0019               |
| i-Butane [i-C₄H₁₀] | 0.0022               |

Processing of the obtained data and determination of hydrate formation points is carried out according to the above procedure. Based on the obtained series of experimental data, we calculate the relative differential pressure and temperature between neighboring samples (j is the reference number), according to the following scheme:

\[
\frac{dP}{P} = \frac{P_{j+1} - P_j}{2P_j}, \quad (1)
\]

\[
\frac{dT}{T} = \frac{T_{j+1} - T_j}{2T_j}, \quad (2)
\]

The contact between changes in pressure, temperature and quantity of substance in the gas phase is expressed as follows: in the measurements made, the total volume V available for the gas phase does not change. The amount of substance n changes due to the release of sorbed methane and the dissociation of gas hydrates, i.e. the molar volume changes. Differentiation of this formula gives us an expression of the change in the molar volume:

\[
\frac{dv}{n} = -\frac{\partial n}{\partial v}, \quad (3)
\]

Using the Van der Waals equation, we express the pressure and take the total differential from both parts. Thus, we obtain the equation:

\[
dP = \frac{R}{v-b} \, dT + \left( \frac{RTv}{(v-b)^2} - \frac{2a}{v^3} \right) \frac{dn}{n} \quad (4)
\]

After identical transformations, the same equation looks like this:

\[
\frac{dn}{n} = \left( \frac{dP}{P} \left( 1 + \frac{a}{Pv^2} \right) \frac{dT}{T} \right) \left( 1 + \frac{b}{v-b} \frac{a}{P(v-b)} \right) \quad (5)
\]
The molar volume of the gas phase, based on pressure and temperature measurements, is calculated by the van der Waals equation. Thus, we have obtained an image of the experimental changes in the relative values of pressure and temperature, we can calculate, using equation (5), the value of the relative increase in the amount of matter in the gas phase. To reduce the influence of fluctuations in the measured quantities, every second measurement is taken. The constants of Van der Waals: \( a \), \( \text{Hm}^4/\text{mole}^2 \) 0.22560; \( b \), \( \text{m}^3/\text{mole} \) 0.04272 \( 10^{-3} \), (e.g. [4]).

In view of the fact that the rate of change of temperature is kept constant, the diagrams show a small change in the relative value of the temperature. However, near the point of formation of gas hydrates, there is a large deviation in the change in the relative pressure in the gas phase due to a sharp decrease in the amount of material in the gas phase.

Based on the data obtained, diagrams of the differential dynamics of the amount of matter in the gas phase of the test sample for the cooling process Fig. 2 and for the process of heating the system Fig. 3 are plotted.

The obtained diagrams clearly demonstrate a decrease in the volume of the gas phase in the region of 8.0°C (283.15°K) at a pressure in the system of 7.0394 MPa (1021 PSI), which corresponds to the beginning of the zone of stable existence of gas hydrates Fig. 2. The increase in the volume of the gas phase approximately 9.0°C (283.85°K) at a pressure of 6.8119 MPa (988 PSI) in the system corresponds to the end of the zone of stable hydrate existence Fig. 3. The obtained data are taken as the basis for estimating the boundary conditions for the stable existence of gas hydrates.

The obtained in the Kinetic experiment data demonstrate an increase in the rate of transition of the gas phase to the hydrate at the 52nd minute of the experiment, at 6.0°C (279.15°K) and at pressure 7.1566 MPa (1038 PSI) in the system corresponds to the beginning of the hydrate formation process. The decrease in the rate of reduction of the gas phase at the 66th minute of cooling, at a temperature of 3.5°C (276.65°K) and pressure in the system of 7.0325 MPa (1020 PSI) corresponds to the completion of the hydrate formation process in Fig. 4. The control time in the diagrams is marked by larger markers.
Figure 4. $dP/P - \tau$, $dT/T - \tau$ diagram (temp. decrease).

The increase in the rate of addition of the gas phase at 96 minutes, at a temperature of 4.2°C (277.35°C) at a pressure in the system 7.1015 MPa (1030 PSI), corresponds to the beginning of the hydrate decomposition in Fig.5.

Figure 5. $dP/P - \tau$, $dT/T - \tau$ diagram (temp. increase).

The obtained data allow to estimate the rate of hydrate formation and the effect of inhibitors on it.

2. Statement of the research problem

During the experiments in the industrial laboratory local conditions of the gas pipeline are recreated, the influence of pressures and temperatures during transportation of gas is simulated. Thus, the research determines the hydrate formation conditions for components which are torn from the context of previous events. Other methods for inhibiting and intensifying hydrate formation are also considered below, using modern techniques and materials that are taken into account in the study.

A process of the hydration slowdown with the use of thermodynamic hydrate inhibitors (THIs), kinetic hydrate inhibitors (KHI) and anti-agglomerants (AA) have been accepted as the most preferred methods (e.g. [8]). Reduction and total loss of fluidity of the environment is the main risk in forecasting natural gas transportation regimes. The mobility or complete decomposition of agglomerated hydrates can be achieved by several known methods: thermodynamic inhibition and the addition of a kinetic inhibitor (e.g. [10]). In some cases, the state of the system may take an intermediate value - to maintain mobility in the zone of hydrate stability. Small hydrate particles stabilize without the formation of large agglomerates (e.g. [2]; [11]). In the metastable states of the existence system (the gas + water + hydrate), the kinetic processes of the formation, decomposition and transformation of gas hydrates from the structure of $s_{II}$ to $s_I$ are of interest. Research of methane-containing gas mixtures with a concentration of 71-99.3% of mass shows a slight decrease in the activation energy of decay in the structure of $s_{II}$ in comparison with the structure of $s_I$. However, the reason for the decrease in activation energy is not entirely clear (e.g. [12]).

Another interesting area of research is the intensification of hydrate formation processes. Methods of chemical action on the formation of elementary cells of hydrate structures, by reducing the surface tension forces using surfactant solutions research is being conducted. The work of the hydrate promoter of sodium dodecyl sulfate ($C_{12}H_{25}SO_4Na$, SDS) is described. We add it to the sample from water and methane, and it allows to accelerate and intensify hydrate formation (1000 ppm SDS, 43.16 mMole methane per 1 mole
water at 7.5MPa (1088PSI)) (e.g. [5]). The increase in the contact area of the hydrate-forming agent and water molecules due to the porous structure of mechanical impurities also increases the rate and volume of formation of the hydrate. The use of a powder of porous quartz with a specific surface area of 2.4 m$^2$/g enabled to increase a maintenance of the methane in the hydrate at 14.5% from the theoretically possible (e.g. [7]). It is established that the combination of methods for increasing the contact surface and reducing the surface tension forces gives additive results.

The use of coal that impregnated with SDS solution significantly increases the rate of hydrate formation (methane absorption 58.26 cm$^3$/min) (e.g. [2]).

The current study relates to the field of studying the kinetic inhibition of the formation of the hydrate phase. Analysis of known methods for intensifying hydrate formation demonstrates a low probability of their accidental reproduction under the conditions of the main gas pipeline. However, early hydrate formation against the background of the measures taken to prevent it keeps the need to search for the reasons for the discrepancy between recommendations and actual conditions in the pipeline. Analysis of calculation of hydrate stability zones in gas pipeline conditions has shown that when predicting the time of their formation, the preliminary effect of technological pressure on condensed water is not taken into account. To determine the role of this factor, of the effect of high pressures on water samples for the formation of hydrates a study was made.

3. Obtaining experimental data
The experiments are carried out according to the block diagram which has shown in Fig. 6.

We made additions to the sample testing procedure - Kinetics (K) concerning the preparation of water. For K-test Exp. 1 the water is not exposed to any influences. For K-test Exp. 2.1, the liquid phase of the sample is pre-conditioned at a pressure of 50 MPa (7300PSI) for 120 minutes. For K-test Exp. 2.2, 2.3, 2.4 are used components of K-test Exp. 2.1 after the cycle of formation-dissociation of gas hydrates.

For K-test Exp. 3, water is not affected any influences. For K-test Exp. 4.1 water is pre-conditioned at a pressure of 10 MPa (1450PSI) for 60 minutes. For K-test Exp. 4.2 the components K-test Exp. 4.1 are used after the formation-dissociation cycle of gas hydrates.

A sample is prepared in the cell from the water and natural gas of MGTS SKV. First, the cell is fed with water and degassed by a vacuum pump. The cell reaches a pressure of -0.1027MPa (-15PSI) at a temperature of 19.5°C (292.65K) and is maintained for 10 minutes. To intensify the release of gases from water, the sample is stirred by a magnetic stirrer with an intensity of 650 rpm. In this case, bubbles of dissolved gases and water vapor are emitted. Next, a gas mixture is brought into the cell with water at a temperature of 19.5°C (292.65K) under pressure of 7.5841MPa (1100PSI) and is maintained for 10 minutes. To intensify the dissolution of the gas mixture in water, the sample is stirred by a magnetic stirrer with an intensity of 650 rpm.
The cycle of cooling and heating of the system is carried out with the registration of temperature, pressure and visual status with an interval of 1 minute. In view of the fact that the system cools more slowly than it heats up - every second dimension is considered on cooling.

The gas phase of the sample is made from natural gas MGTS SKV. Analysis of a sample of the natural gas composition of MGTS SKV, showed a predominance of 91.28% vol in methane [CH₄], significant concentrations of ethane [C₂H₆] 3.74% vol, propane [C₃H₈] 1.61%, and carbon dioxide [CO₂] 1.87% vol. The remaining hydrocarbon components are contained in the trace concentration. Table 3.

| Component      | Chemical formula | Concentrations, % vol |
|----------------|------------------|----------------------|
| Methane        | [CH₄]            | 91.28                |
| Ethane         | [C₂H₆]           | 3.74                 |
| Propane        | [C₃H₈]           | 1.61                 |
| Carbon dioxide | [CO₂]            | 1.87                 |
| Butane         | [C₄H₁₀]          | 0.37                 |
| i-Butane       | [i-C₄H₁₀]        | 0.28                 |
| Pentane        | [C₅H₁₂]          | 0.04                 |
| i-Pentane      | [i-C₅H₁₂]        | 0.09                 |
| neo-Pentane    | [neo-C₅H₁₂]      | 0.001                |

The dynamics of the dew point temperature determines the natural gas of MGTS SCV as wet Fig. 9, containing moisture more than 150 g/m³, in accordance with the requirements of GOST R 8.668-2009.

Experimental data are obtained by performing Kinetics and HSZ tests. Kinetic tests are carried out in two stages: K-test Exp. 1-2 and K-test Exp. 3-4.
3.1 Kinetics tests

K-test Exp. 1 is carried out with a sample which is consisting of water and natural gas MGTS SKV. The beginning of the hydrate formation process was noted at the 66th minute, at a temperature in the system of 4.1°C (277.25 K) and a pressure of 6.8671 MPa (955 PSI). The process ends at 83 minutes, at a temperature of 0.6°C (273.75 K) and a pressure of 6.6258 MPa (961 PSI) Fig.10.

K-test Exp. 2.1, conducted with the liquid phase of a sample subjected to a high-pressure treatment of 50 MPa, early formation of hydrates was noted. The beginning of the event was recorded on the 45th minute of the test, which corresponds to a temperature in the system of 7.3°C (280.45 K) and a pressure of 7.0532 MPa (1023 PSI). The diagram shows the beginning of the hydrate formation process, its development, the peak of the process and the completion at the 76th minute, which corresponds to the temperature in the system -0.1°C (273.05 K) and pressure 6.5775 MPa (954 PSI). Fig.11.

K-test Exp. 2.2 is performed with the components of sample K-test Exp. 2.1. Between the end and the beginning of the next test, a time interval of 30 minutes was maintained. In K-test Exp. 2.2. The formation of hydrates started at 70 minutes, which corresponds to a temperature in the system of 4.0°C (277.15 K) and a pressure of 6.8740 MPa (997 PSI). End at 90 minutes, which corresponds to a system temperature of -0.2°C (272.95 K) and a pressure of 6.6120 MPa (959 PSI). Fig. 12.
Results K-test Exp. 2.3 and K-test Exp. 2.4, and the results of the described tests, are summarized in Table 5. Comparison of the obtained data makes it possible to state that in the sample with water subjected to pressure, the hydrate formation process starts 20 minutes earlier than in the sample with water not subjected to pressure. Subsequent tests demonstrate the return of sample characteristics to the original parameters.

Table 4. Results of kinetic tests 1 and 2.

| Exp. No.          | Cr. Start. | Temp.. | Pres.. | Cr. Fin.. | Temp.. | Pres.. | Duration, min |
|-------------------|------------|--------|--------|-----------|--------|--------|---------------|
| K-test Exp. 1     | 66         | 4.1    | 6.8671 | 83        | 0.6    | 6.6258 | 17            |
| K-test Exp. 2.1   | 45         | 7.3    | 7.0532 | 76        | -0.1   | 6.5775 | 31            |
| K-test Exp. 2.2   | 70         | 4.0    | 6.8740 | 90        | -0.2   | 6.6120 | 20            |
| K-test Exp. 2.3   | 73         | 2.2    | 6.7774 | 85        | -0.1   | 6.5844 | 12            |
| K-test Exp. 2.4   | 67         | 3.5    | 6.8464 | 83        | 0      | 6.6120 | 16            |

K-test Exp. 3 is carried out with a sample consisting of water without preliminary pressure preparation. Gas phase is natural gas of MGTS SKV. The beginning of the hydrate formation process at 60 minutes, at a temperature in the system of 5.8°C (278.95 K) and pressure of 6.9360 MPa (1006 PSI). The hydrate formation ends at 83rd minutes, at a temperature of 0.5°C (273.65 K) and a pressure of 6.6051 MPa (958 PSI) Fig. 13.

In K-test Exp. 4.1, conducted with the liquid phase of a sample subjected to a processing pressure of 10 MPa, formation of hydrates on a 50 minute test was observed, that corresponds to a system temperature of 5.7°C (278.85 K) and a pressure of 6.9774 MPa (1012 PSI). The diagram shows the moment of the beginning of the hydrate formation process, its development, the peak of the process and the completion at the 79th minute, which corresponds to a temperature in the system of -0.6°C (272.55 K) and a pressure of 6.5085 MPa (944 PSI). Pic 14.
K-test Exp. 4.2 is performed on the components of sample K-test Exp. 4.1. Between the end and the beginning of the next test, a time interval of 30 minutes was maintained. In K-test Exp. 4.2, the formation of hydrates started at 61 minutes, which corresponds to a temperature in the system of 5.4°C (278.55°K) and a pressure of 6.9153 MPa (1003 PSI).

The end at 83 minutes, that corresponds to a system temperature of 0.2°C (273.35°K) and a pressure of 6.5982 MPa (957 PSI). Fig. 15.

Results K-test Exp. 3, K-test Exp. 4.1 and K-test Exp. 4.2 are presented in the summary Table 6. Analysis of the obtained data allows to state that in the sample with water subjected to the pressure, the hydrate formation process starts 10 minutes earlier than in the sample with water not subjected to pressure. Subsequent tests demonstrate the return of sample characteristics to the original parameters.

| Exp. No.     | Cr. start. | Temp. | Pres. | Cr. Fin. | Temp. | Pres. | Duration |
|--------------|------------|-------|-------|----------|-------|-------|----------|
| K-test Exp. 3| 60         | 4.8   | 6.9360| 83       | 0.5   | 6.6051| 23       |
| K-test Exp. 4.1| 50        | 5.7   | 6.9774| 79       | -0.6  | 6.5085| 29       |
| K-test Exp. 4.2| 61        | 5.4   | 6.9153| 83       | 0.2   | 6.5982| 22       |

3.2 HZS test

HZS tests are also carried out in two stages HZS-test Exp. 5.1-5.2 and HZS-test Exp. 6.

We made changes to the HZS test procedure related to the preparation of water. For HZS-test Exp. 6, water is not subject to any influence. For HZS-test Exp. 5.1 the liquid phase of the sample is preconditioned at a pressure of 50MPa (7300PSI) for 120 minutes. For HZS-test Exp. 5.2 the components HZS-test Exp. 5.1.
In HZS-test Exp. 5.1, the stable formation of hydrates in a sample with prepared water starts at the
193-minute test, at a system temperature of 11.5°C (284.65 K) and a pressure of 8.5563 MPa (1241 PSI).
The process ends at 386 minutes, at a temperature of 4.1°C (277.25 K) and a pressure of 7.9702 MPa
(1156 PSI). Fig.16.

In HZS-test Exp. 5.2, the stable formation of hydrates in the sample with the components of
Experiment 3-1 begins at 230 minutes of the test, at a system temperature of 10.1°C (283.25 K) and a
pressure of 8.4597 MPa (1227 PSI). The process ends at 399 minutes, at a temperature of 3.6°C
(276.75 K) and a pressure of 7.9288 MPa (1150 PSI). Fig.17.

In HZS-test Exp. 6, with a sample from the liquid without preparation, the stable formation of hydrates
begins at 265 minutes, at a temperature of 10.9°C (283.25 K) and a pressure of 8.4597 MPa (1227 PSI).
The end of the process is 411 minutes, at a temperature of 5.5°C (278.65 K) and a pressure of 7.9702 MPa
(1156 PSI). Fig.18.

A comparative analysis of the results of HZS tests shows that the zone of stable hydrate formation in
the sample with water previously exposed to process pressure starts 72 minutes earlier than in the sample
without preparation, and the duration of hydrate formation is 47 minutes longer than in the similar test
with water without preparation. There is also a tendency to return the characteristics of the sample to the
initial, prior to the impact of process pressure Table 7.
Table 6. Results of HSZ tests 5 and 6.

| Exp. No.          | Cr. start, min | Temp., °C | Pres., MPa | Cr. Fin., min | Temp., °C | Pres., MPa | Duration, min |
|-------------------|----------------|-----------|------------|--------------|-----------|------------|---------------|
| HZS-test Exp. 5.1 | 193            | 11.5      | 8.5563     | 386          | 4.1       | 7.9702     | 193           |
| HZS-test Exp. 5.2 | 230            | 10.1      | 8.4597     | 399          | 3.6       | 7.9288     | 169           |
| HZS-test Exp. 6   | 265            | 10.9      | 8.4115     | 411          | 5.5       | 7.9702     | 146           |

4. Conclusions

The carried-out researches have shown that the process of hydrate formation significantly changes in water treated beforehand by creating high pressures of 10-50 MPa. The acceleration of the process of hydrate formation is 26-32% compared to the control one without the preliminary action of high pressure on water.

The results of experiments in kinetic tests and HSZ tests prove the effect of preliminary water compression on the intensity of hydrate formation.

The change in hydrate formation conditions indicates an increase in the amount of hydrates of the cubic structure $s_{II}$, towards to hydrates of the cubic structure $s_{I}$.

The obtained results testify to the need to take into account the pressure at which the medium was before the moment of hydrate formation and to make an adjustment to the calculation of the required amount of the thermodynamic hydrate inhibitor (THI).

5. References

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