

Improvement of the Efficiency of Development of Gas Hydrate Deposits

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Abstract — Natural hydrates are one of the existence forms of gas in earth depths. Nowadays about 250 hydrate deposits are known with a total reserves of about 20 peta-cubic meters of natural gas. The technologies of extracting gas from natural hydrates with the help of borehole underground mining of their continental deposits (underground and subwater) differ from the extraction of traditional reserves of natural gas and the collection of bottom sediments. The choice of technology depends on the specific geological and physical conditions of their occurrence. Today have been developed many technologies, the technical essence of which is based on changing the pressure-temperature conditions of hydrate existence by the following methods: depression (lowering reservoir pressure below balanced), thermal (raising temperature of hydrate above balanced), chemical and combined. Based on the analysis of existing and promising technologies, the authors developed a comprehensive technology for extracting gas from hydrates based on the theoretical foundations of their dissociation, methods of calculating optimal temperature and pressure conditions and determining the effectiveness of using chemical methods to minimize the costs of antihydrate reagents (solutions of alcohols, salts, nitrogen compounds).

Keywords— *gas hydrates; gas-hydrate deposit; natural hydrates; existence conditions of hydrates; gas extraction from hydrates*

I. INTRODUCTION

Natural hydrates are one of the forms of gas in the earth depths. Nearly 250 hydrate deposits with a total reserves of about $2 \cdot 10^{16}$ m³ are discovered worldwide [1]. The deposits of this type are attributed to unconventional sources of hydrocarbons, which in modern technical, economic and social conditions have not yet found wide practical application, but there is a possibility of their use if new technologies appear for which their development becomes economically efficient.

The technologies of gas extraction from natural hydrates by borehole underground exploitation of their continental deposits (underground and subwater) differ from the extraction of traditional reserves of natural gas and the collection of bottom sediments. The choice of technology depends on the specific geological and physical conditions of their occurrence. Nowadays many technologies have been developed, the technical essence of which is based on

changing the pressure-temperature conditions for the existence of hydrates by the following methods: depression (lowering reservoir pressure below balanced) [2], thermal (raising temperature of hydrate above balanced) [3], chemical [4] and combined [5].

Currently the leading positions in the development of such technologies are occupied by Japan, Canada, China, India and the United States of America. South Korea, Norway, France, Germany, Italy and Australia are actively increasing their investments in this direction.

The depression method, based on the reduction of reservoir pressure, has been carried out at the Messoyakha field since 1967 [6]. The main disadvantage of the depression method is its high energy consumption. Due to the fact that the produced gas has a low pressure, it is necessary to expend additional amount of energy to compress it, in order to prepare it and transport. This ultimately increases the cost of gas and makes its production unprofitable in comparison to traditional. It is necessary to take into account that when reservoir pressure drops according to the Joule-Thomson effect, the reservoir temperature decreases and the formation of technogenic hydrates usually occurs in the bottom-hole zone, which may be reasoned by additional complications. However, the depression method seems to be possible for reservoirs that are in balanced hydrate formation conditions, in which there are three phases together: hydrate - gas - liquid water.

The thermal method is based on the heating of hydrate-containing rocks with the help of heat-transfer medium introduced into formation. With the use of this method, reservoir pressure is preserved and even maintained. A heat-transfer medium can be supplied from the surface or generated in reservoir conditions. Supply of heat transfer from surface to bottom of a well is accompanied by large heat losses along its trunk. Under frozen conditions, this can lead to additional complications.

Nearby natural thermal sources can serve as a heat transfers. The thermal method is suitable for formations having a high content of hydrates in pores. However, thermal effects on the reservoir through the bottom of a vertical well are ineffective. It is reasoned by small area of contact of heat transfer with reservoir at the bottom. The amount of heat transferred through a small area is little, and

the heating of the rocks enclosing hydrates, roofs and the bottom of the reservoir is calculated in the first meters. In order to increase the contact area of heat transfer with a rock, it is necessary to use wells with inclined and horizontal termination.

Chemical methods are based on the introduction into the reservoir of antihydrate reagents, which change the balanced temperature and pressure parameters of hydrates. Applying chemical methods it is necessary to strictly follow all the norms and requirements of the protection of subsoil and environment, as well as safety regulations.

Combined methods consist of several dissociation approaches.

Depression and thermal methods were implemented technically. In 2002, researchers tested a thermal method for the extraction of gas from hydrates under real-life conditions on the Mallik area in the Canadian Arctic region [7]. However, the energy costs of the thermal method turned out to be greater than the energy received from the produced gas. In March 2008, Canadian engineers used the depression method in order to extract 13 thousand m³ of methane for six days from a field located at a depth of 1.8 km [8]. A year earlier, in South Korea, the pressure reduction method was used to extract methane from hydrates in the Ulleung Basin in Sea of Japan. In 2013, after ten years of exploration the Japan Oil, Gas and Metals Corporation produced 120 thousand m³ of gas from methane hydrate on

the territory of shore of Aichi Prefecture [9]. Apart from the technical difficulties associated with the clogging of the equipment of particles of bottom rocks containing hydrates, the infrastructure necessary for offshore mining was practically absent in Japan. However in 2017, test production of hydrate gas in the Nankai Fault off the east shore was restarted.

The analysis of existing and promising technologies led to the direction of further research of authors, the purpose of which was to find the optimal temperature and pressure conditions for the extraction of gas from hydrates and to determine the effectiveness of using chemical methods in order to minimize the costs of reagents.

II. EXISTENCE CONDITIONS OF HYDRATES

During the development of the calculation method [10] of pressure-temperature conditions for the decomposition of hydrates, physical and mathematical models, experimental studies and practical applications in this field from 1780 to the present time were analyzed. They are properly described in the works of the authors [11], which brings together 1,000 references. The analysis of the data on the balanced pressure-temperature conditions for the dissociation (formation) of hydrates of individual gases revealed three characteristic ranges (see Fig. 1).

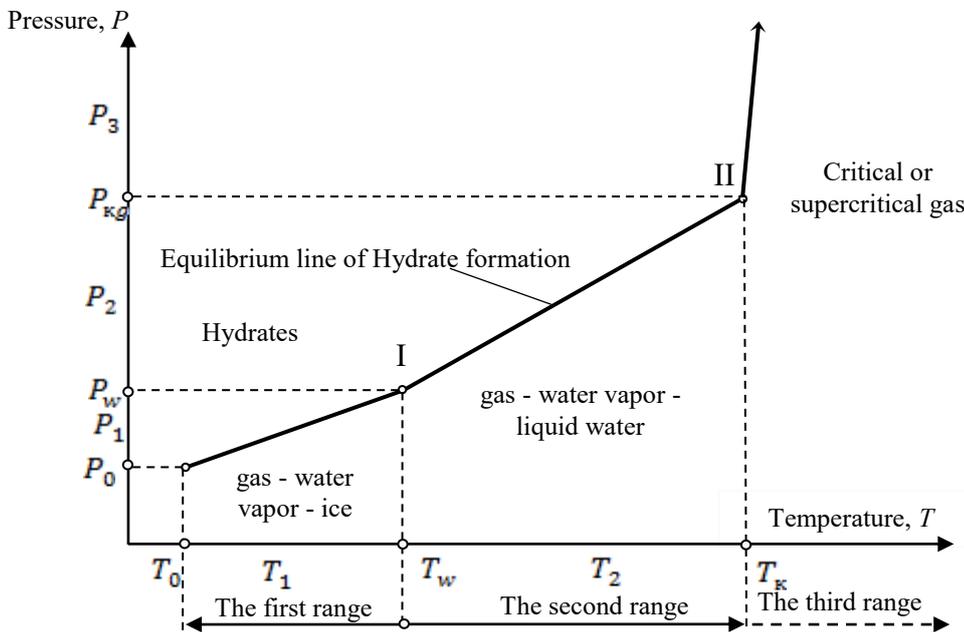


Fig. 1. The diagram of balanced pressure-temperature conditions for the existence of hydrates.

The first and the second ranges are separated by the quadrupole point (I), with coordinates T_w and P_w , which are, respectively, the temperature and pressure of crystallization of pure water.

The second and the third ranges are separated by a quadrupole point (II) with coordinates T_K and P_{Kg} - the critical temperature for the gas and the hydrate formation pressure under it.

Formalizing the balanced pressure and temperature parameters, the authors revealed that the pressure and

temperature parameters of hydrate formation of individual gases change:

- in the first temperature range they change in power dependencies:

$$P_{i_1} = a \cdot T_1^b, \quad (1)$$

$$T_{i_1} = \left(\frac{P_1}{a} \right)^b, \quad (2)$$

where P_{i_1} , T_{i_1} – line pressure and temperature values of i -gas in the first range;

T_1 , P_1 – temperature (including T_w) and pressure of hydrates-forming system of gas – water vapor – solid state of water (ice);

a , b – coefficients determined experimentally;

- in the second temperature range they change in exponential dependencies:

$$P_{i_2} = c \cdot e^{d \cdot T_2}, \quad (3)$$

$$T_{i_2} = \frac{\ln\left(\frac{P_2}{c}\right)}{d}, \quad (4)$$

where P_{i_2} , T_{i_2} – line pressure and temperature values of i -gas in the second range;

T_2 , P_2 – temperature and pressure of hydrates-forming system of gas – water vapor – fluid water;

where P_{i_2} and T_2 pressure (Pa) and temperature (K) in the second thermic range;

$e = 2,718$ – the basis of natural logarithm;

c , d – coefficients determined experimentally;

- in the third (non-calculated) range where $T_K \approx const$.

The critical temperature of individual gas is found or calculated by known dependencies from the reference literature.

The numerical values of the coefficients a , b , c , d for some gases forming hydrates are given in Table 1.

TABLE I. VALUES OF COEFFICIENTS FOR EQUATIONS (1)–(4)

Gas	a	b	c	d
Methane	$4 \cdot 10^{-17}$	9.3415	10^{-7}	0.1128
Ethane	$3 \cdot 10^{-26}$	12.8130	$6 \cdot 10^{-10}$	0.1256
Propane	$2 \cdot 10^{-28}$	13.4980	$8 \cdot 10^{-20}$	0.2052
<i>i</i> -butane	$2 \cdot 10^{-32}$	15.0760	$3 \cdot 10^{-20}$	0.2078

Gas	a	b	c	d
Carbon dioxide	10^{-21}	11.0890	$8 \cdot 10^{-10}$	0.1281
Hydrogen sulphide	10^{-23}	11.4690	$2 \cdot 10^{-8}$	0.1064
Nitrogen	$2 \cdot 10^{-12}$	7.7171	10^{-5}	0.1015
Argon	$8 \cdot 10^{-12}$	7.4047	10^{-7}	0.1168
Krypton	$5 \cdot 10^{-26}$	12.8900	$2 \cdot 10^{-6}$	0.0990
Xenon	$2 \cdot 10^{-24}$	11.8380	$3 \cdot 10^{-7}$	0.0993

The pressure and temperature parameters of the existence of hydrates in a multicomponent gas-water system are described by the equations for the ranges of its phase states, respectively (Fig. 1):

$$P_j = \sum_{i=1}^n (Y_i \cdot P_{i_j}), \quad (5)$$

$$T_j = \sum_{i=1}^n (Y_i \cdot T_{i_j}), \quad (6)$$

where j – the value of range – 1; 2; 3.

In the case when in a multicomponent mixture some components belong to the first range, others - to the second and / or third ranges, the balanced temperature of such a mixture is calculated by the formula:

$$T = T_1 + T_2 + T_3, \quad (7)$$

III. DETERMINATION OF THE EFFICIENCY OF THE USE OF CHEMICAL REAGENTS

The use of chemical methods allows changing the thermal conditions of the existence of hydrates. The developed method [12] for the determination the effectiveness of chemical reagents (solutions of alcohols, salts, nitrogen compounds) allows estimating its required concentration. In addition, it makes it possible to accurately determine the temperature of hydrate formation and freezing of water solution of an inhibitor of the corresponding concentration.

The calculation of the criterion of reagent effectiveness is performed according to the following formula:

$$\eta = \frac{T_w - T}{T_h}, \quad (8)$$

Where T – temperature of the onset of crystallization of water in freezing water solution of an inhibitor, K; T_h – balanced temperature of hydrate formation in the system of gas - pure water, K; T_w – temperature, K, crystallization of water, which can be accurately calculated in the pressure range $P = 0.1 - 210$ MPa from the dependence obtained by the authors:

$$T_w = 273,16 - 0,0731 \cdot P - 0,0002 \cdot P^2, \quad (9)$$

The temperature of the onset of crystallization of water in freezing water solution of inhibitor is determined by the type of dependence developed:

$$T = \alpha \cdot X^2 + \beta \cdot X + \gamma, \quad (10)$$

where α , β , γ – empirical coefficients for various antihydrate reagents (Table 2); X – mass concentration of inhibitor in the solution.

TABLE II. COEFFICIENTS TO EQUATION (10)

Reagent	Reagent concentration in solution	Coefficients		
		α	β	γ
<i>Alcohols</i>				
methanol	0.10 – 0.60	-138.93	-40.15	271.89
ethanol	0.025 – 0.719	-10.40	-70.26	275.93
propanol	0.08 – 0.65	28.83	-63.80	274.40
ethylene glycol	0.02 – 0.663	-160.62	11.44	270.20
diethylenglycol	0.02 – 0.62	-131.77	13.14	271.73
triethyleneglycol	0.02 – 0.50	-101.47	7.41	272.16
propylene glycol	0.05 – 0.59	-153.29	16.51	269.72
glycerine	0.050 – 0.667	-116.58	14.74	270.78
<i>salts</i>				
lithium chloride	0.05 – 0.25	-1130.70	19.79	270.55
magnesium chloride	0.014 – 0.206	-840.22	16.46	271.84
sodium chloride	0.015 – 0.224	-212.97	-45.24	272.86
calcium chloride	0.059 – 0.284	-840.90	126.63	263.66
calcium nitrate	0.02 – 0.35	-102.86	-16.29	272.86
calcium permanganate	0.05 – 0.42	-295.6	48.35	269.16
<i>nitrogen compounds</i>				
ammonia	0.02 – 0.33	-937.69	28.37	268.27
monoethanol amine	0.10 – 0.50	-480.14	122.40	262.47
diethanoamine	0.10 – 0.50	-153.57	30.64	269.65

Thus, the criterion of the effectiveness of inhibitor allows evaluating the effect of inhibitor in a dimensionless

form: the larger the η value, the more effective the reagent. The comparison of the values of the criteria for different inhibitors presents an express method for the choice of the optimal one.

IV. TECHNOLOGY OF GAS PRODUCTION FROM HYDRATES

The complex technology proposed by the authors [11], the principal technological scheme of which is presented in Fig. 2 includes the creation of non-balanced pressure and temperature conditions in the hydrate deposit where hydrates dissociate.

Non-balanced pressure and temperature conditions create a decrease in pressure in hydrate reservoir and / or an increase in temperature. The heat supply is carried out by supplying a heat transfer from outside (for example, heated dry gas) or from a local heating source located in a well. The decrease in pressure is produced by the fact that outside the zone of occurrence of hydrates the region of reduced pressure is formed, for example, in a phase separator in which the value of the permissible pressure drop is maintained. Gas and formation fluid (water) are removed from the zone of decomposing hydrates. Gas is cleaned and dried. After that, a part of the prepared gas is supplied to a consumer; the other part is supplied to power plant and for technological needs. In order to intensify the dissociation of hydrates, antihydrate reagents are added to the zone of their occurrence. To increase the efficiency of gas production from hydrates, a heat transfer with high heat released during condensation, for example, C_{3+g} hydrocarbons, is added to the injected hot dry gas.

V. CONCLUSION

During the course of the research the existing technologies of development of gas hydrate deposits were analyzed. A comprehensive technology for gas extraction from hydrates was proposed, based on the theoretical bases of their dissociation, methods for calculating optimal pressure and temperature conditions and determining the effectiveness of using chemical methods in order to minimize the cost of antihydrate reagents (solutions of alcohols, salts, nitrogen compounds). The developed technological solutions briefly presented in the article can be used in the design of the development of deposits of natural hydrates.

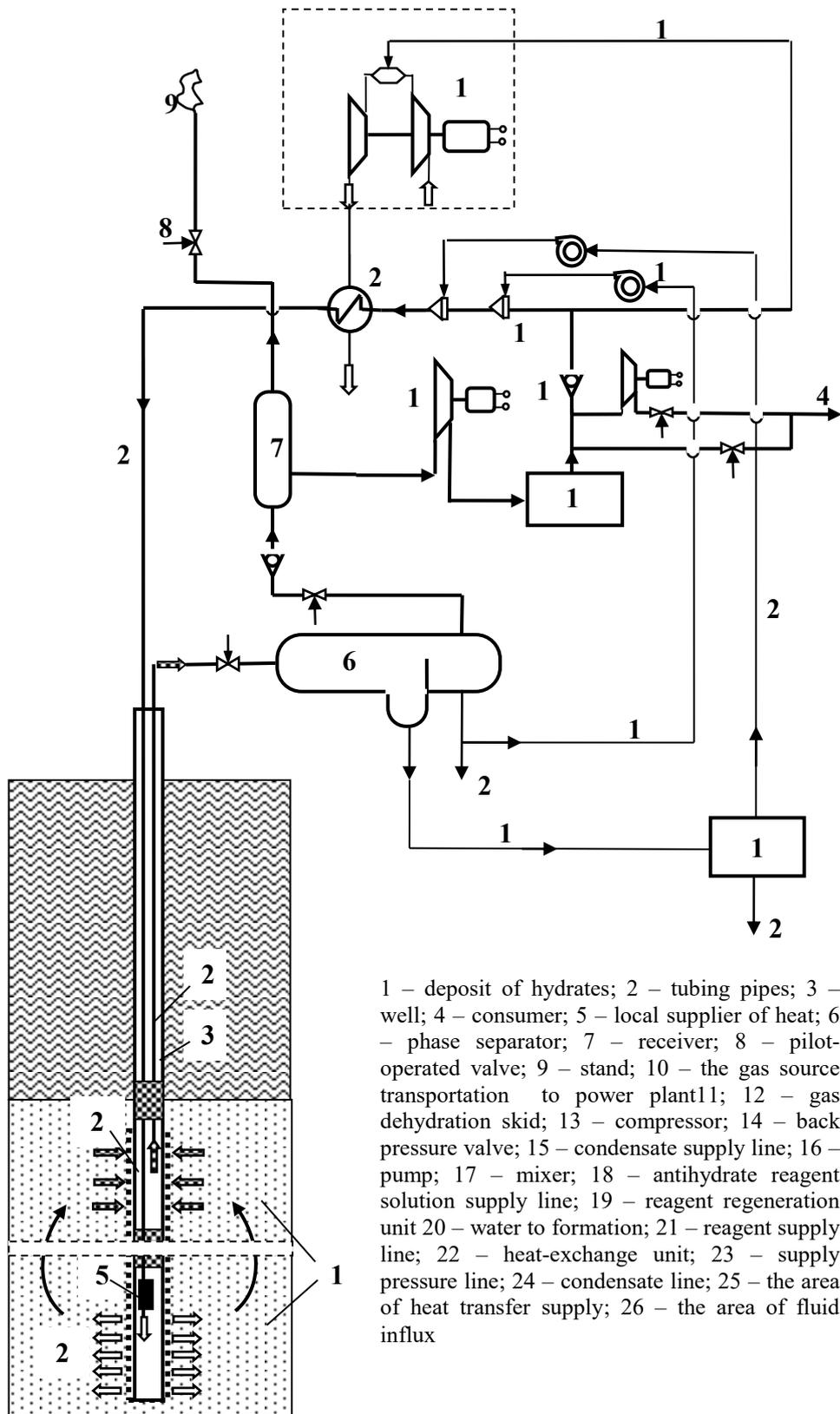


Fig. 2. Schematic diagram of gas production from hydrates.

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