Research of Processes of Formation and Dissociation of Natural Gas Hydrates

Evgeny P. Zaporozhets and Nikita A. Shostak

Institute of oil, gas and energy
Kuban State Technological University
Krasnodar, Russia
shostak@kubstu.ru

Abstract—**Technogenic hydrates are mostly a negative factor in the oil and gas industry. Their formation in the bottomhole well zone and in wellbores complicates the extraction, reducing their production rate. In the hydrocarbons collection systems, the hydrates in certain thermobaric conditions deposit on the gas pipeline walls and raise their hydraulic resistance, thus increasing energy costs. The presence of hydrates in the streams of the fluid, extracted from subsoil, increases the wear of production headers, reducing their resource. In the systems of field treatment of hydrocarbons, hydratation negatively affects the technological processes. Hydrate formation in machinery and aggregates of gathering facilities and processing systems leads to accidents. Hydrate deposition in gas pipelines decreases work efficiency. For solving the problems related to prevention and elimination of technogenic hydrates, it is necessary to be able to define the basic parameters of hydrate formation and dissociation. This article is devoted to the research of the processes of formation and dissociation of hydrates. The research was performed using the physical and mathematical models, published in several works, from which it is possible to calculate the main parameters of hydrate formation and dissociation in a wide range of thermobaric conditions. The most widespread conditions of formation and dissociation of hydrates in the development and exploitation of gas and condensate fields were analyzed in this article.**

Keywords—dissociation; elimination; formation; hydrates; natural gas

I. INTRODUCTION

Technogenic hydrates are mostly a negative factor in the oil and gas industry. The formation of hydrates in the bottomhole well zone and in wellbores complicates the extraction of carbohydrates, reducing the flow rates. In the gas collection systems, the hydrates in certain thermobaric conditions deposit on the gas pipeline walls and raise their hydraulic resistance, thus increasing energy costs. The presence of hydrates in the streams of the fluid, extracted from subsoil, increases the wear of production headers, reducing their resource. In the systems of field treatment of hydrocarbons (in heat exchangers, separators, throttle devices, ejectors), hydratation negatively affects the technological processes. The formation of hydrates in machines and aggregates (compressor, pressure-reducing valves) systems of gathering facilities and processing systems leads to accidents. Hydrate deposition in gas pipelines decreases work efficiency.

For solving the problems related to prevention and elimination of technogenic hydrates, it is necessary to be able to define the basic parameters of hydrate formation and dissociation. The research was performed using the physical and mathematical models published in several works [1, 2], from which it is possible to calculate the main parameters of hydrate formation and dissociation in a wide range of thermobaric conditions. The most widespread conditions of formation and dissociation of hydrates in the development and exploitation of gas and condensate fields were analyzed.

The model of the formation of hydrates from multicomponent gas for the thermobaric conditions, in which all its components transfer to hydrate condition, is based on the following ideas. First, the hydrate cavities of the ice-like associates of water molecules are formed in the gas – the liquid phase of the water system around the separate molecules of gas components and water vapors being in the state of equilibrium with the liquid phase of water. The gas molecule is enclosed within the cavity and cannot spontaneously leave it. Such association of molecules is a robust frame in the corresponding thermobaric processes of hydrate formation.

The process of hydrate cavity formation is similar to the process of gas molecule adsorption on solid surface – in this case, the local ice-like associates of water molecules. The local ice-like associates of water molecules are independent (i.e. one of them does not influence the absorbing qualities of others) and identical.

During the formation of each hydrate cavity at the temperature of hydrate formation the pressure increase from the pressure of gas-water system to the pressure of saturated vapors of absorbed components occurs in it. If the thermobaric conditions of hydrate formation correspond to the supercritical temperatures and subcritical pressures of the absorbed component, its saturated vapors in the hydrate cavity are condensed with the heat energy release. If the thermobaric conditions of hydrate formation correspond to the supercritical temperatures and pressures of the absorbed component, then during its absorption by the cavity the release of heat energy, which is equal to the change of the component's enthalpy or inner energy, takes place. The process of molecule absorption is in the energetic (dynamic) equilibrium with the reverse process (desorption).

It made the authors suggest that the process of cavity formation in respect of energy is similar to the adsorption process, and it is possible to use Langmuir constants for defining the levels of filling the hydrate cavities [2].

The cavity merger forms the hydrate crystal lattices of structures I and II. According to Gibbs' phase rule, structures I and II can exist both separately (only I or II) and conjointly (I and II) [3]. Energy is emitted in the process of crystallization.

During hydrate formation in the gas – ice system, the formation of hydrate cavities occurs without emitting the heat energy of molecule absorption by means of transforming the crystal lattice of ice into the hydrate one. The transformation of ice into the hydrate crystal lattice of structure I is an exothermic process, and its transformation into structure II is an endothermic process [1].

II. HYDRATE FORMATION

A. HYDRATE FORMATION IN THE DIRECT CONTACT OF GAS AND WATER

The direct contact of gas and water is observed, for example, in the wellbore areas and in wellbores, production headers, condensation heat exchangers, as well as in the hydrate reaction vessels in the laboratory and industrial conditions.

The speed of hydrate formation, mol./s, in the direct contact in the gas – water (liquid, ice) systems, is defined by the following formula:

$$W_{\text{form}_{1,2\,I,II}} = \frac{K \cdot f \cdot (T_{\text{eq}} - T_{\text{r}})}{\Delta H_{1,2\,I,II}}, \qquad (1)$$

where K is the heat transfer coefficient, W/(m^2·K); f is the area of contact of gas with water or ice, m^2; T_{eq}, T_r are the temperatures of hydrate equilibrium and of refrigerant, K; $\Delta H_{1,2\,I,II}$ is the latent heat emitted in the process of hydrate formation of structures I and II in the gas – liquid water and gas – ice system, kJ/mol.

As seen from this formula, the speed of hydrate formation directly depends on the area of contact of gas with water or ice f. The hydrate growth intensifies with the speed increase. The increase of the interphase contact area is achieved by the turbulization of contacting phases, their intermixing, dispergation, vibration effect etc.

This effect is observed in the performed [3] experiments on obtaining hydrates in the reaction vessels equipped with mechanic and magnet stirrers. The experiment was performed at the variable stirrer rotation speeds (from 0 to 600 rot./min) in the constant thermobaric conditions. In both experiments the intensification of hydrate growth was observed. The surface area increases by approximately 1.67 times with the change in the rotation number up to 600 rot./min.

The intensive heat removal from the forming hydrated is performed by means of intermixing [4]. In such conditions, the coefficient of heat transfer between the contacting phases changes from $6 \div 8$ W/(m^2·degr.) for the convection heat transfer in stationary conditions to $14 \div 20$ W/(m^2·degr.) for the forced motion, i.e. the heat transfer coefficient changes $\approx 2 \div 2.5$ times.

Having inserted into equation (1) the values of changing the interphase contact area 1.67 and the change of the value of the average heat transfer coefficient 2.25 for $\frac{(T_{\text{eq}} - T_{\text{r}})}{\Delta H_{1,2\,I,II}} = const$, one shall obtain the 3.75-time increase of hydrate formation speed, which perfectly correlates with the experiment data [3].

The increase in the speed of hydrate formation in the case of intensive shaking of the gas – ice system with metal balls in the experiment described in the work [4] can be explained by changing the area of interphase contact and the coefficient value. By intensive shaking the hydrate crust on the surface of ice crystals is destroyed, and the conditions of heat and mass transfer are significantly improved.

To provide an example, Fig. 1 shows the graphic dependencies of changing the relative speed of the methane hydrate growth $\overline{W} = \dfrac{W_i}{W_0}$ ($W_0 = 0.0005$ mol./s) on changing the relative area of the contact $\bar{f} = \dfrac{f_i}{f_0}$ ($f_0 = 1$ m^2) for the degree of supercooling $\Delta T = T_{eq} - T_r = 3$ K in the stationary conditions with heat transfer coefficient, considered equal to 2 W/(m^2·degr.). Fig. 1 shows that, first, the speed is higher for the formation of hydrate from ice than for the formation of hydrate from water and, second, the speed increases rectilinearly with the increase in $\bar{f}$.
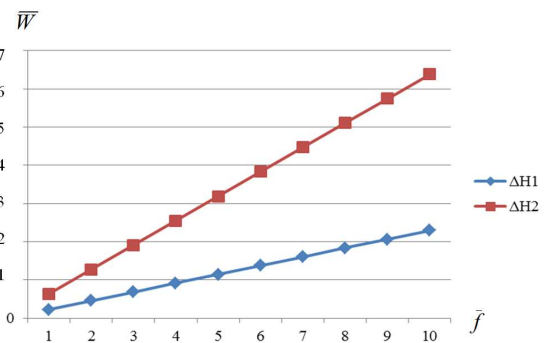

Fig. 1. Dependencies of changing the relative speed of the methane hydrate growth on changing the relative area of the contact

$\overline{W}$ – relative speed of hydrate growth; $\bar{f}$ – relative area of the contact; $\Delta H1$ – heat for the formation of hydrate from water; $\Delta H2$ – heat for the formation of hydrate from ice

Fig. 2 shows the graphic dependency of the increase in the relative speed of methane hydrate growth on the relative value of heat transfer coefficient in case of direct contact in the gas – water systems.
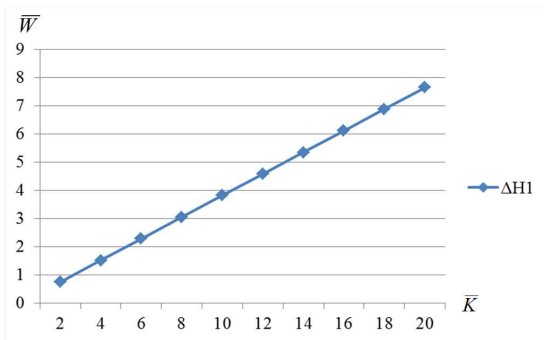
Fig. 2. Dependency of increase in the relative speed of methane hydrate growth on the relative value of heat transfer coefficient for the direct contact in the gas – water (liquid, ice) systems

$\overline{W}$ – relative speed of hydrate growth; $\overline{K}$ – relative value of heat transfer coefficient; ΔH1 – heat of formation of hydrate from water

Taking into consideration the fact that the heat transfer coefficient depends on the intensiveness of intermixing the contacting phases, the graph (Fig. 2) of dependency of the relative speed of methane hydrate growth $\overline{W} = \dfrac{W_i}{W_0}$ ($W_0 = 0.00015$ mol./s) on the relative value of heat transfer coefficient $\overline{K} = \dfrac{K_i}{K_0}$ ($K_0 = 1$ W/(m²·grad.)) was built.

The comparison of the experimental data given in the work [3] and reflected in graph 2, Fig. 1 and the graph in Fig. 2 shows that the value of heat transfer coefficient can be compared with the number of stirrer rotations. The dependency of the values of the relative coefficient of heat transfer $\overline{K}$ on the number of stirrer rotations is presented in Fig. 3.
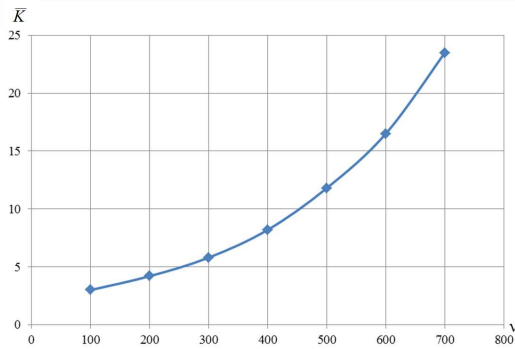

Fig. 3. Dependency of the heat transfer relative coefficient values on the number of stirrer rotations

$\overline{K}$ – relative value of heat transfer coefficient; ν – number of stirrer rotations

The analytical expression (2) for the heat transfer coefficient, based on the graph (Fig. 3), was obtained:

$$K = 2,1 \cdot e^{0,0034 \cdot \nu}, \qquad (2)$$

where ν is the number of stirrer rotations.

It should be noted that stirring the hydrate formation system negatively affects the properties of inhibitors [6, 7].

In order to diminish the speed of hydrate formation, according to (1), it is necessary to diminish the area of contact between gas and liquid and to select the hydrogasodynamic conditions, in which the heat transfer coefficient will be minimal.

The minimal coefficients of heat transfer are observed in static conditions, when the hydrate formation system is immobile. That is why, in static conditions low speeds of hydrate formation are observed, for example, at the pressure of 5.0 MPa and the temperature of 7°C 100 ml, gas become hydrate in 2.6 h; at the same temperature and the pressure of 7.0 MPa – in 1 h; at the temperature of minus 2°C and the pressure of 7.0 MPa – in 0.5 h [3].

The speed of hydrate growth is influenced by the temperature difference – $(T_{eq} - T_r)$. The greater this value is, the higher is the hydrate formation speed. In the works [8, 9], the values of about 0.05 – 0.7 mm/s (in static conditions) depending on the supercooling value are given. After covering all the free water – gas surface by the hydrate film being 5-10 µm thick [10, 11] (i.e. by the formed hydrate), the coefficient of heat transfer decreases rapidly, so the hydrate growth speed gets lower and reaches about $(0.28 – 0.83) \cdot 10^{-3}$ mm/s [8]. The decrease in speed can be explained by the fact that the water contacting the gas above the film of hydrate comes from below due to capillary forces through the hydrate film slowly. As the film grows, the hydrate formation speed diminishes practically to zero. By the moment when the hydrate formation finishes, the thickness of the film increases up to 50-150 µm.

For the gases, which are soluble in water (e.g. CO_2), the ultimate thickness of the hydrate film formed on the hydrating agent – water interphase surface has the value of about 800 µm [12]. The growth speeds for the hydrate crystallization film of methane [8, 9], ethane [8], carbon dioxide [13] on the pure water – gas interphase surface in case of supercooling $\Delta T = 3$ K are given in Table I.

TABLE I. GROWTH SPEED FOR THE HYDRATE CRYSTALLIZATION FILM IN CASE OF CONSTANT SUPERCOOLING ΔT = 3 K

System	Film location	Data source	Hydrate crystallization film growth speed, µm/s
water - methane	water-gas interphase surface	[8]	60-200 (depending on pressure)
water - methane	water-gas interphase surface	[9]	90
water - ethane	water-gas interphase surface	[8]	90-180 (depending on pressure)
water - CO_2	water-gas (liquid CO_2) interphase surface	[13]	$2.0\ (3.0) \cdot 10^3$

The difference to certain extent characterizes the process of heat transfer. Depending on the speed of heat transfer on the hydrate formation system, the time of hydrate formation increases or decreases.

In practice, it takes place in the following cases:

- heat transfer from the gas-liquid system through the wall;

- isenthalpic expansion (Joule-Thomson effect) of gas, containing water in the vapor and drip condition;

- isentropic (adiabatic) expansion of gas, containing water in the vapor and drip condition.

B. Hydrate Formation in Case of Heat Transfer from Hydrates through the Wall

The process of hydrate formation in case of heat transfer from hydrates through the wall takes place in wellbores, in permafrost intervals, in pipelines cooled by outside environment, in heat exchangers and separators of the hydrocarbon gathering and processing systems.

The equation for the time of formation of 1 mole of hydrate by means of heat transfer from the system through the wall is as follows (3):

$$\tau_{form_{1,2_{I,II}}} = \frac{\Delta H_{1,2_{I,II}}}{K_{WA} \cdot f_{WA} \cdot \Delta T}, \qquad (3)$$

where f_{WA} is the surface area of the wall through which heat is transferred from the hydrate formation system, m^2; ΔT is the temperature difference between the hydrate formation system and the cooling agent, K; K_{WA} is the coefficient of heat transfer from the system through the wall, J/(m•K•s).

The heat conductivity on the walls depends on the kind of heat-transfer medium, its temperature and speed, as well as on the wall material, heating environment temperature, and the duration of running the equipment without cleaning, i.e. eventually on the kind of sediment and corrosion product. The exact data can be obtained only in the experimental way. It is possible to take into account the influence of wall pollution approximately, based on the estimated values of the heat conductivity of pollutions.

The time of hydrate formation while transferring the heat from the wall depends on the value of heat load – the denominator of the (3), which, in its turn, depends on the wall area, the coefficient of heat conductivity, and the temperature gradient (temperature drop). If the surface area is developed, as, for example, in heat exchangers, ΔT is more than 15 degrees, the hydrogasodynamic conditions contribute to heat transfer, and the wall material has large heat conductivity, hydrates are formed in a small period of time.

In case humid gas contains asphaltenes, gums, and paraffines, in certain thermobaric conditions and hydrogasodymanic states of the flow of such gas, their sediments, having high heat-transfer resistance, are deposited on the walls. It ultimately leads to the increase in time of hydrate formation. In case there is humid gas containing salts and mechanic admixtures with low heat-transfer resistance, as well as their sediments deposited of the walls, the time of hydrate formation decreases.

C. Hydrate Formation in the Conditions of Humid Gas Throttling

Hydrate formation in the conditions of humid gas throttling is observed in the wellbore area in case of considerable reservoir and bottomhole pressure difference, in various throttle devices (chokes), for example, those installed in the well mouths and in the low-temperature separation units.

For throttling 1 mole of humid gas (the integral Joule-Thomson effect), taking water condensation into account, the formula looks as follows:

$$\tau_{form_{1_{I,II}}} = \frac{\Delta H_{1_{I,II}}}{G \cdot C_{PM} \cdot \sigma \cdot (P_0 - P_C)}, \qquad (4)$$

where G is the discharge rate of the gas-liquid mixture, mol./s; T_0, P_0 are the initial temperature and pressure of humid gas before throttling, K, Pa; σ is the integral Joule-Thomson effect, degr./Pa; P_C is the system pressure after throttling, Pa; is the molar heat capacity of humid gas, J/(mol.•K).

The denominator of the (4) shows the change in the quantity of heat in the gas-water system depending on the difference between the pressures of initial and expanded gas. Therefore, the greater the difference is, the lesser is the time of formation, i.e. the hydrate growth speed is higher. It is the inverse value of time:

$$W_{form_{1_{I,II}}} = \frac{1}{\tau_{form_{1_{I,II}}}}. \qquad (5)$$

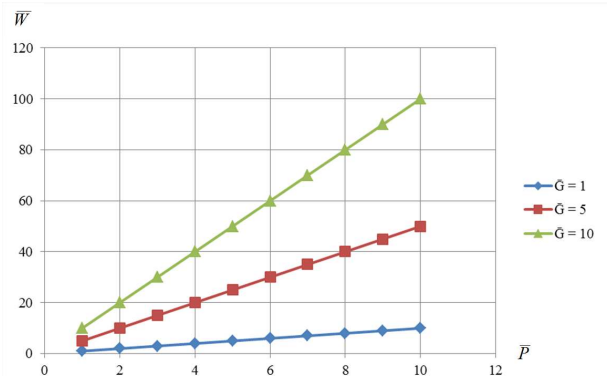The process of hydrate growth is graphically presented in Fig. 4, 5.

Fig. 4. Dependencies of the relative speed of methane hydrate growth on relative pressure difference $\overline{P}$ of the gas phase for the fixed relative discharge rates of gas phase $\overline{G}$ ($G_0 = 1$ mol./s)

$\overline{W}$ – relative speed of methane hydrate growth; $\overline{P} = \dfrac{P_0 - P_C}{P_C}$ – relative pressure difference of the gas phase; $\overline{G} = \dfrac{G_i}{G_0}$ – relative discharge rate of the gas phase
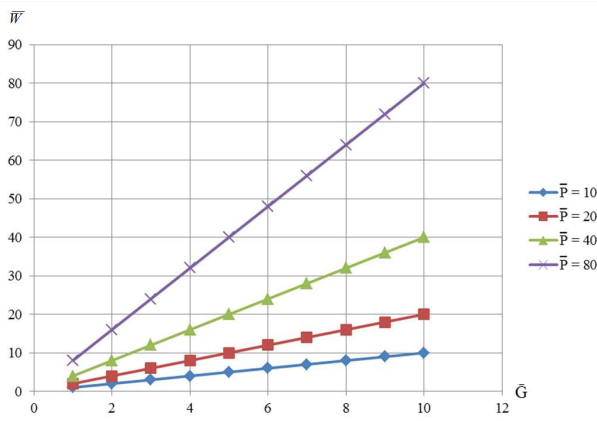
Fig. 5. Dependencies of relative speed $\overline{W}$ of methane hydrate growth on relative discharge rate $\overline{G}$ of the gas phase for fixed relative pressure differences $\overline{P}$

$\overline{W}$ – relative speed of methane hydrate growth; $\overline{P} = \dfrac{P_0 - P_C}{P_C}$ – relative pressure difference of the gas phase; $\overline{G} = \dfrac{G_i}{G_0}$ – relative discharge rate of the gas phase

D. Hydrate Formation in the Conditions of Adiabatic Expansion of Humid Gas

In case of deep treatment of gas by the methods of low-temperature cooling, the isentropic expansion of gas in pressure-reducing valves or in de Laval nozzles is used (Fig. 6) [14]. In this connection, it is necessary to define the speeds of hydrate formation.
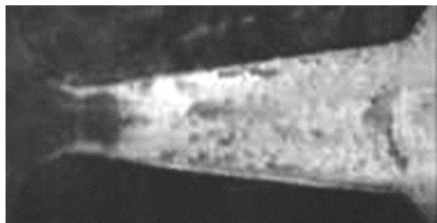

Fig. 6. Hydrate formation in case of supersonic gas flow

In case of adiabatic (isentropic) humid gas expansion, the temperature change is described by the formula:

$$\Delta T = T_0 \cdot \left[1 - \left(\frac{P_0}{P_C} \right)^{\frac{1-k}{k}} \right], \qquad (6)$$

Taking (6) into account, the formula looks as follows (7):

$$\tau_{form_{1,2_{I,II}}} = \frac{\Delta H_{1,2_{I,II}}}{G \cdot C_{PM} \cdot T_0 \cdot \left[1 - \left(\dfrac{P_0}{P_C} \right)^{\frac{1-k}{k}} \right]}, \qquad (7)$$

$$k = k_W \cdot X + k_G \cdot Y, \qquad (8)$$

where k_W and k_G are the adiabatic indicators of water vapor and gas; X, Y are the molar fractions of water vapor and gas.

With the increase in the level of gas expansion, the amount of the removed heat and the speed of hydrate growth increase as well. The graphic dependencies of the relative speed of hydrate growth on the level of gas (methane) expansion for the fixed values of relative discharge rate are presented in Fig. 7.
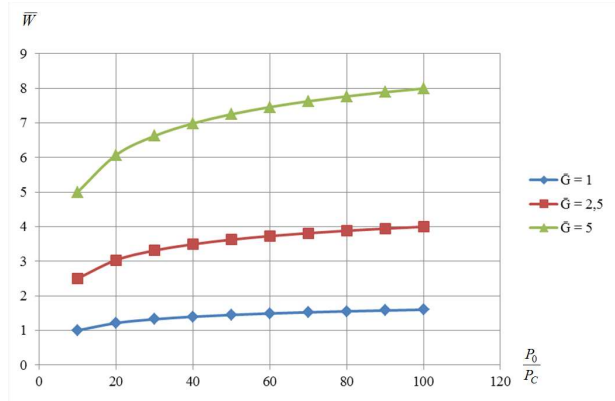

Fig. 7. Dependencies of the relative speed of hydrate growth $\overline{W}$ on the level of gas (methane) expansion for the fixed values of relative discharge rate $\overline{G}$

$\overline{W}$ – relative speed of hydrate growth; $\dfrac{P_0}{P_C}$ – on the level of gas expansion;

$\overline{G} = \dfrac{G_i}{G_0}$ – relative discharge rate of the gas phase

In nozzles, the expansion of gas occurs with supersonic speed, the decrease of the temperature of the expanded gas depends on Mach number M being defined as follows:

$$T = \frac{T_0}{1 + 0{,}5 \cdot M^2 \cdot (k-1)}, \qquad (9)$$

$$M^2 = \frac{2}{k-1} \cdot \left[\left(\frac{P_0}{P} \right)^{\frac{k-1}{k}} - 1 \right]. \qquad (10)$$

Taking the (8) into account, the formula for defining the time of forming a mole of hydrate in case of the isentropic expansion of humid gas, for example, in nozzles, will look as follows:

$$\tau_{form_{1,2_{I,II}}} = \frac{\Delta H_{1,2_{I,II}}}{G \cdot C_{PM} \cdot T_0 \cdot \left(1 - \dfrac{1}{1 + 0,5 \cdot M^2 \cdot (k-1)}\right)} . \quad (11)$$

In case of supersonic flows of humid gas the hydrate formation time is very small.

According to the (3), (4), (7) and (11), the time of hydrate formation may vary and, as it follows from the performed analysis, it depends on the type of processes occurring while gas cooling.

III. DISSOCIATION OF HYDRATES

In the conditions of development and exploitation of oil and gas deposits, the dissociation of technogenic hydrates in practical use is interesting from the point of view of their elimination, and the dissolution of natural hydrates – from the point of view of the extraction of hydrocarbon gases from them. According to the developed model, the dissociation of hydrates takes place in case of heat input to them. The mentioned dissociation processes are described in this section.

A. Dissociation of Hydrates in Case of Heat Input through the Wall to Them

The process of the dissociation of hydrates in case of heat input through the wall to them occurs when hydrates are eliminated in pipelines, heat exchangers and separators of the systems of gathering, treatment and transportation of hydrocarbons.

The speed of the dissociation of hydrates in case of heat input through the wall to them is calculated according to the formula:

$$W_{dis_{I,II}} = \frac{K_{WA} \cdot f \cdot (T_1 - T_{eq})}{\Delta H_{1,2_{I,II}}} , \quad (12)$$

where T_1 is the initial temperature of the hot heat-transfer medium, K.

B. Dissociation of Hydrates in Case of Direct Contact of Heat-Transfer Medium with Them

The process of the dissociation of hydrates in case of the direct exposure of the heat-transfer medium to them is applicable for their elimination in the wellbore area and wellbores, in production headers, in the processing facilities of oil and gas treatment systems.

The speed of the dissociation of hydrates in case of direct contact of heat-transfer medium with them is defined from:

$$W_{dis_{I,II}} = \frac{F_G \cdot C_P \cdot (T_1 - T_2)}{\Delta H_{1,2_{I,II}}} , \quad (13)$$

where F_G is the heat-transfer medium discharge rate, mol./s; C_P is the heat-transfer medium heat capacity, J/(mol.·K); T_1, T_2 are the temperatures of hot and hydrate cooled heat-transfer medium, K ($T_2 \geq T_{eq}$).

Taking into account that

$$F_G \cdot C_P \cdot (T_1 - T_2) = K_{T-H} \cdot f \cdot (T_1 - T_2), \quad (14)$$

where K_{T-H} is the coefficient of heat transfer between the heat-transfer medium and the hydrate, W/(m²·degr.); f is the area of the contact of the heat-transfer medium with the hydrate, m²;

formula (12) will look as follows:

$$W_{dis_{I,II}} = \frac{K_{T-H} \cdot f \cdot (T_1 - T_2)}{\Delta H_{1,2_{I,II}}} . \quad (15)$$

From (12), (13) and (15) it follows that with the decrease in the size of heat flow the speed of hydrate decomposition also decreases, and with N tending to zero the speed tends to zero as well. This explains the existence of natural relict hydrates in permafrost masses.

If hydrate is not provided with heat input with pressure being lower than equilibrium, the surface layer of hydrate is destroyed emitting gas and water. In connection with the fact that gas was included into hydrate in its condensed state, it is evaporated. While evaporating the gas out of the environment, heat absorption takes place. If there is no heat input from the outside, the evaporating gas takes heat from the hydrate and the liberated water. As a consequence, the hydrate-water system is cooled. The cooling speed depends on the hydrate mass: the greater the mass, the smaller the cooling speed.

IV. CONCLUSIONS

The research shows that the speeds of growth and dissociation of hydrates depend on the amount of the removed or input heat in the unit of time, i.e. on the heating power. The obtained equations reflect the kinetics of growth and dissociation of hydrates. With their help, it is possible to calculate the parameters of these processes. It makes the given equations technically applicable in the areas of extraction, gathering, treatment, transportation, and processing of carbohydrates.

Based on the conducted research, heat input is recommended to prevent hydrate formation and growth, as well as to eliminate them. Heat input can be arranged through the wall or in the direct contact. The calculation of the amount of heat-transfer medium, its temperature and delivery state (the choice of heat transfer coefficient K) can be performed according to the (12-15).

Acknowledgment

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