DETERMINATION OF REAGENT FLOW RATE DURING NATURAL GAS TRANSPORT

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Abstract

The complications arise due to the variation of thermodynamic parameters during the production, collection and transportation of gas under the marine environment. As a result, these complications prevent the normal operation of gas transportation equipment and create an emergency situation in the gas network. Investigations were carried out in gas condensate fields and the complex preparation of gas for transportation was studied in order to improve gas treatment. We determined the optimum methanol consumption rate to prevent hydrate bridging and made estimates to improve gas treatment. This paper presents the results of the calculation of the optimum methanol consumption for gas treatment to prevent hydrate bridging.

Keywords: gas condensate, methanol, hydrate, consumption rate, thermodynamics

I. Introduction

One of the operating costs incurred during the production, storage and transportation of oil and natural gas in offshore fields is the consumption of chemicals used to prevent hydrate formation and other technological difficulties. This increases the cost of produced gas in large volumes. Therefore, the regulation of qualitative and quantitative indicators of reagents used to ensure the unhindered transportation of gases is one of the urgent and important issues of oil and gas production.

Taking into account the above, research and mining work was carried out to improve the principle of operation of installations and the technological system for regulating the consumption rates of reagents used in the process of producing, drying and transporting gas from gas condensate fields, as well as the development of new scientific and technical proposals. Research was conducted on several fronts. When studying the operation of individual apparatuses of the gas treatment plant operating at the PA OGPD, it was found that methodological reports for regulating the flow of reagents used in the system were not carried out taking into account the actual indicators [1-5].

The results of studies conducted at offshore fields showed that since the production, collection and transportation of gas condensate is carried out under difficult conditions, it is advisable to improve the composition and technologies of reagents used to prevent hydrate formation in the process system.

II. Features of automation for the liquid fuel use supplied to the tube furnace

The general approach to thermodynamic modeling of phase equilibrium with aqueous and gas hydrates is relevant for the study of vapor-liquid equilibrium in the "natural gas-hydrocarbon condensate" system. However, modeling of the balance of the condensed water phase - water, chilled water, an aqueous solution of inhibitors, the application of a methodological approach to the transformation of the ice phase into a hydrate and a separate thermodynamic state of each contact phase - was studied. This method has several advantages for thermodynamic gas treatment in the well, which ensures the accuracy of the phase balance report and the normalization of hydration inhibitors. Accurate accounting of phase imbalances in mining conditions requires accurate accounting of volatile or non-volatile components of the gas phase, including CO_2, H_2S, N_2, H_2O, and methanol. For this purpose, a modified thermodynamic model has been developed based on the Redlix-Kvong equation for the gas phase with a hydrocarbon or non-hydrocarbon component. According to the modification, the model used includes secondary viral coefficients and additional parameters characterized by the compression coefficient of gas mixtures at high pressure. The parameterization of the modification equation shows that the calculation of the volatile components of natural gas results in an error of 1-2%, which is more accurately calculated by the Peng-Robinson equation.

III. Selection and justification of process parameters used in the designed automation and control scheme

The advantage of modifying the equation of state is that when conducting new tests, additional changes caused by secondary coefficients are easily added, and the disadvantage is high parameters. This is characterized by an increase in the exact description of the Gibbs energy in the gas phase. Interval of effective use of equation -40°C ÷ +100-150°C, pressure is 0,1MPa÷12-14 MPa.

Recent chemical potential differences - $\Delta\mu^0$ and water-ice enthalpy of empty hydrate hydrate network - Δh^0, On the basis of more accurate data, the Langmuir coefficient of individual components of natural gas mixtures was recalibrated, since updating the parameterization of the hydrate phase model is considered important. Currently, the new prices are as follows:

For structure I: $\Delta\mu^0$ =1203 J/mol,; Δh^0 =1170 J/mol; T=273,15° K temprature;

For structure II: $\Delta\mu^0$ =1077 J/mol; Δh^0 =1294 J/mol; T=273,15° K temperaturda.

Ice enthalpy is equal to Δh^f 6008 J/mol.

Using the new data, the Langmuir coefficient was reconstructed, that is, the parameters of the gas hydrate phase were updated, which improved the description of the three-phase balance "gas hydrate" for the complex gas phase, but did not affect the description of the three-phase balance with pure gases. Based on the above models, a comprehensive program has been developed for taking into account the balance of natural gas with water, the specified pressure and temperature for individual hydrate compounds or gas mixtures in the gas industry.

Using a comprehensive reporting program, simple and appropriate analytical relationships were obtained in order to determine the rate of consumption of natural gas mixtures, hydration, hydrate inhibitors in the gas collection and processing system from various fields. To confirm the results of calculation of the gas-hydrate balance of gases of complex composition, it is advisable to use the thermodynamic method of comparative calculation, including the method of empirical correction of the thermodynamic model of the gas-hydrate phase using the hydration curve of the complex gas composition. At negative or positive temperature in a wide temperature range, the method of thermodynamic extrapolation of spatial data of equilibrium tests with a pressure of 100 MPa and higher is used.

Analysis of the thermodynamic model shows that test data obtained under the condition that the degree of filling of the gas hydrate cavity does not exceed 1 are calculated as follows [6-9].

$$\ln f - H(p,T) - \frac{\Delta V\ p}{(\nu_1+\nu_2)RT} \div \frac{1}{T}$$

f -component volatility; ΔV – difference in molar volumes of water and hydrate, sm^3; p – pressure, MPa ; $H(p,T)$ – Henri constant ;

ν_1, ν_2 –crystal-chemical constants (characterizing the type of hydrate structure).

Coordinate system approximation constraint:

$$Y = A + \frac{B}{T} + C \cdot \ln(T);$$

here: A, B, C – coefficients that also describe the data in more detail at the test points, allowing extrapolation of the relationship obtained at negative or positive temperatures over a wide range of cases. The equilibrium pressure at given temperature is determined by the following formula.

$$A + \frac{B}{T} + C \cdot \ln(T) = \ln(f) - \frac{p \cdot \Delta V}{(\nu_1 + \nu_2) \cdot RT} + \frac{\ln x_{H_2O}}{\nu_1 + \nu_2}$$

Determination of gas volatility at high pressure, water density and water solubility in gas is mandatory. The extrapolation method was carried out for two gases (methane, nitrogen), and the results obtained are sufficient in the range of the temperature balance of the hydrate compound for methane. For methan ~307° K (110 MPa) , for nitrogen ~301°K (230 MPa), percentage of errors in the report ~ 5-6% - dir (for pressure).

The thermodynamic properties of the metasabit phase are shown with respect to hexogonal ice, chilled water, and ice cube. Chilled water and ice cubes are formed by separating the gas hydrate as an intermediate phase. Hexogonal ice temperature as standard is T_0=273,15° K.

The thermodynamic account of the difference in chemical potentials between hexogonal ice and chilled water is based on the thermodynamic properties of the condensed water phase based on test data reported in the literature. Several phase equilibrium reports used to report the chemical potential difference between a cube of chilled water and ice % with error 240 – 273° K in the temperature range The slow hydrate separation model is presented and the main test data is concentrated. Detailed explanations of theoretical model typing and hydrate separation mechanism and gas hydrate surface separation properties are given.

In order to expand the possibility of gas hydrate preservation technology, V.A.Istomin must cover its upper surface with another solid-phase thermodynamic stable coating, unlike the hexonal ice layer, in order to slow down the release of gas hydrate [10-12]. The implementation of the kinetic mechanism of extraction depends on the composition of the gas in the hydrate, the morphology and structure of the hydrate, the thermobaric conditions of its formation and extraction. The leading power of the splitting process is determined in several ways: for example, ΔT - the temperature difference between the process of separation and separation of the hydrate into gas and aquoeous phase is calculated:

$$\Delta G = RT \ln f / f_0 \approx RT \ln p / p_0 ,$$

f, p - flight capability and gas pressure in the system,

f_0, p_0 - balancing value of flight capability and pressure.

When conducting tests at the initial stage, the driving power may change, the results of these tests show the properties of the mechanism of the process of separation of gas hydrates and kinetics at negative temperatures:

- staged (conservation effect leading to the first rapid stage and subsequent slow separation stage);
- clear image of the effect of self-preservation of hydrated methane and natural gas in a certain temperature range;
- formation of different metasabitic aqueous phases in the first separation step.
- formation of metasabit surface phase at different times depending on thermobaric conditions.

Depending on the test conditions, the mechanism of separation of gas hydrates at negative temperatures can be divided into options.

- To accurately separate the effect of preservation at the initial stage, release the hydrate into gas and chilled water, and then crystallize the chilled water coating under optimal conditions.

- Long-term storage of chilled water in a non-crystallized state, except for the complete release of a hydrate particle into chilled water and gas. In this case, it is impossible to stop the process. With the conservation effect, part of the hydrated particles is completely separated, and the other part is preserved independently.

If the first surface of the hydrate is separated by ice and gas, a layer of ice forms in the upper layer of the hydrate, and, despite the slowdown of the process, no abrupt flow occurs.

The process of surface separation of gas hydrates at negative temperatures is divided into three main stages: the first stage is the stage of separation into the metasabit phase, the stage of crystallization or recrystallization of the metasabit phase of water and the subsequent stage of slow separation with a diffusion mechanism. Sometimes the stages may not take place or the separation stage may end in the first stage. For wider implementation of the initial stage of the methane hydrate separation process is low (272,95°K) three-phase accounting of the water phase and the hydrated part of methane was carried out. Analysis of the results of the report allows us to determine the area of possible formation of very cold water and ice on the decomposing methane hydrate and, thus, analyze the reasons for the formation of the "self-preservation" effect in various conditions. The following are the temperature ranges for the presence of chilled water in the methane-methane-hydrate-chilled water system at various pressures.

Table 1: *Pressure reduction and methane hydrate splitting Thermobaric conditions for the existence of chilled water*

Pressure, MPa	**Temprature diapason, °K**
0,1	~240 – 272,95
0,5	~256 – 272,95
1,0	~263 – 272,95
1,5	~266 – 272,95
2,0	~270 –272,95
2,5	not available

When the system is transferred from 1 region to 3 regions (Fig. 1.) And in the presence of ice in the hydrate as a result of the release of methane hydrate in the first stage, it goes into the chilled water stage, and the water directly crystallizes and turns into ice. If the water creates a dynamic layer between the hydrate and the ice, the separation rate decreases, the water layer softens and disappears, and thus a hydrate preservation step occurs.

It should be noted that the formation of chilled water looks visually (in the window of the hydrate pressure chamber, "darkening" of hydrate particles in transmitted light is observed). This visual representation of the decomposition process allows us to study the experimental line of the gas (methane, propane) - hydrate - chilled water band.

Similar studies were conducted for hydrates of other gases in order to determine the possible temperature range of the self-preservation effect. Propane, ethane, isopropane were also reported for another temperature range (Table 2). As can be seen from Table 2, the lower available cooling water frame for the obtained nitrogen hydrate is lower ~ 240 K from the theoretical point of view, in which case there is practically no cooling water. Therefore, the determination of the temperature range when depressurizing atmospheric pressure is an important element in the optimization and search for a method for preserving hydrate of various gases.

Thermodynamic analysis of the surface separation of the hydrate shows that its transition to the preservation method and process control are possible. The main parameter here is pressure. A decrease in pressure leads to the formation of cooling water in the upper hydrate layer. One of the leading parameters of the conservation effect is the temperature, the increase of which in the studies leads to the separation of the hydrate surface in the network of three-phase equilibrium lines "gas-hexogonal ice-hydrate" and "gas-cooled water-hydrate" in the appropriate sequence.

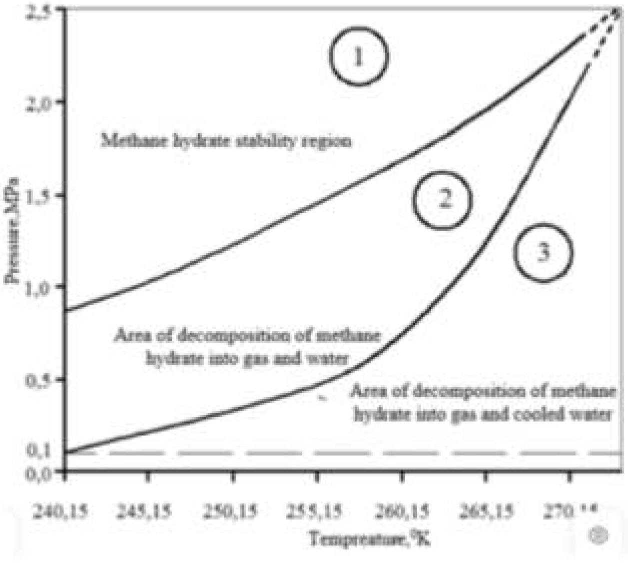

Figure 1: *As a result of methane hydrate pressure increase separation into gas-ice and gas-cooled water phases in different thermobaric.*

Table 2: *The presence of cooling water in the temperature range when the pressure drops to atmospheric pressure when separating various gas hydrates.*

Gas	**Temprature, °K**
Methane	~240 – 272,95*
Nitrogen	~223 – 271,85*
Ethane	~258 – 273,15*
CO2	~251 – 273,0*
C3H8	~270,5 – 273,15*
Iso-buthane	Not available

In the "Gas-chilled water-hydrate" network, the hydrate turns into chilled water. Under optimal conditions, it is important to crystallize this water. At low process power, water crystallization is accelerated, for example, recooling of the system or a combination of cooling with increasing pressure can be accelerated. The presence of ice in the hydrate allows it to control the separation process and enter the conservation stage, since ice leads to crystallization of chilled water.

Process paths can be selected for each gas hydrate. The hydrate sample is preheated in the pressure chamber of the hydrate oven. The temperature change of the chamber depends on pressure stabilization, which means that the hydrate separation process is completed. The process then continues at higher temperatures. At each temperature step, a separation process occurs whereby the pressure of the hydrated sample increases or becomes constant. When the pressure in the upper layer of the first hydrate sample increases, regeneration from the gas phase and water occurs. (composition of the new hydrate film is different). Thus, the separation process of the initial hydrate continues stably, and the pressure in the system is stabilized. From these tests it can be seen that a hydrate of one composition is converted to a hydrate of another composition by preservation. The process results in a hydrated hydrate preservation effect.

Depending on the conditions, the lower hydrate is released, a hydrate is formed from the gas dissolved in water, which prevents the partial release of the primary hydrate as a stable hydrate of a new composition. To control the effect of slowing hydrate separation, another method was discovered, which consists in coating one hydrate with another at positive temperatures under thermobaric and stable thermodynamic conditions. It can be seen from the reports that one hydrate can be preserved with another hydrate and its pressure is below that of the other hydrate compound.

So, the composition of the gas mixture: 98% methane +2% propan; 95% methane +5% nitrogen; 70% isobutan + 30% nitrogen və 90% methane + 10% CO_2)

Analysis and thermodynamic reports show that the following conditions are possible for the effect of slow separation of gas hydrates:

- development of new methods of gas-hydrate balance study;
- hydrated gas storage and transportation technology;
- seasonality conditions of gas hydrates in metasabit conditions.
- Methodical approach to normalization of hydration inhibitors and their additional properties using volatile inhibitors.

All information on normalization of inhibitor consumption contains information on its process losses and other production needs. Production losses of inhibitor occurring during regeneration, storage, transportation are determined by the trial statistical method, other losses are determined by the reporting and analytical method.

To return the spent reagent to the process cycle, it is necessary to install a spent inhibitor regeneration unit, develop a recycling technology for the use of hydration inhibitors.

The methodical approach to normalizing the inhibitor is as follows.

The consumption of chemicals in the production of all gas production is determined in the form of group (H) as follows:

$$H = \frac{\sum H_i \cdot Q_i}{\sum Q_i},$$

here: H_i - individual consumption of chemicals per each device, kg/1000 m^3;

Q_i -any time (month, quarter, year) gas production for each facility,mln.m^3.

Chemical consumption H_i shows the specific flow rate for each device:

$$H_i = H_T - H_B + \sum g_i ,$$

here: H_T – inhibitor consumption rate in the process;

H_B – rate of specific consumption, chemical reagent returned by the cycle;

$\sum g_i$ – rate of final production losses.

The rate of inhibitor spent on the process for each device in the well is determined by the sum of inhibitor consumption in each individual process in accordance with the well plume.

The rate of inhibitor consumption in each individual area is determined by the following formula:

$$H_{T,i} = G \cdot K,$$

here: G – specific consumption of the minimum important (theoretical) inhibitor;K – reserve ratio in the range of 1.05-1.25 for unaccounted factors;

K- coefficient of distribution by phase of components at non-isothermal and non-stationary flow of gas-liquid mixture is determined by tests.

Maximum initial field development cost is equal to 1,10÷1,25, When automating production processes, the inhibitor consumption is reduced to a factor of 1.05. The theoretical inhibitor flow rate for a single area of the process chain and the protected point aqueous phase flow rate are determined by the following formula: [13,14].

$$G = \frac{G_1 \cdot (X_2 - X_1) + G_1^{recycle} \cdot (X_2 - X_1^{recycle}) + (W_1 - W_2) \cdot X_2}{X - X_2} + \frac{100 - X_2}{X - X_2} \cdot [(Q_2 - Q_1) + (q_2 - q_1)]$$

$$G_2 = \frac{X}{X_2} + \frac{G_1 \cdot X_1 + G_1^{recycle} \cdot X_1^{recycle} + 100 \cdot [(Q_1 - Q_2) + (q_1 - q_2)]}{X_2}$$

G - specific consumption of the minimum important inhibitor, hardness *X*, kg/1000 m^3;

G_1 - special quantity entering 1 point of liquid-water phase from previous inhibitor process area, kg/1000 m^3;

$G_1^{recycle}$ - specific amount of inhibitor recycle aqueous solution to point 1, kg/1000 m^3;

G_2 - specific amount of inhibitor recycle aqueous solution to point 2, kg/1000 m^3;

X_1, X_2 – density of the inhibitor aqueous phase before point 1 and point 2, respectively,% mass;

X – inhibitor concentration per 1 point, % mass;

$X_1^{recycle}$ – concentration of treated inhibitor per 1 point, % mass;

W_1, W_2 – gas humidity at points 1 and 2 (balanced with liquid phase), kg/1000m^3;

Q_1, Q_2 - amount of inhibitor in gas phase at points 1 and 2,kg/1000m^3;

q_1, q_2 - amount of inhibitor in gas phase at points 1 and 2, kg/1000m^3;

G_1, $G_1^{recycle}$, X_1, X_2, $X_1^{recycle}$, *X is assumed to be known values,*

G and G_2 and their values are found by calculation.

In practice, the theoretical inhibitor consumption is reported several times, that is, reports are kept at several technological points, and the prices obtained are summarized.

Here, the technique aims to facilitate the thermodynamic equation of the gas hydrate phase. Parameters were selected by formula based on test data. You can use the above-mentioned reporting methods to report hydration conditions.

In gas and gas condensate fields, the calculation of the concentration of hydration inhibitors at a given pressure and (K) at the protection point and the dependence between hydration temperatures on movement is determined as follows:

$$\Delta T = -A \cdot \ln \frac{(100-X)/18}{(X/M + (100-X)/18)},$$

A - empirical coefficient depending on gas pressure, its composition, structure of formed hydrates. This coefficient depends on the composition and pressure of the gas phase and is selected individually.

The humidity of complex natural gas can be calculated using the following formula:

$$W = a_1 \cdot W_0 = \gamma_1 \cdot x_1 \cdot W_0$$

here: γ_1 - water activity coefficient in water-methanol solution;

x_1 - molar part of water in water-methanol solution;

a_1 - water activity in water-methanol solution;

W_0 – humidity of natural gas in balance with clean water, kg/1000 m^3.

An analysis of the methodological approach to the practical use of volatile and non-volatile inhibitors for the hydration inhibitors discussed above revealed a number of advantages. The advantages of a volatile inhibitor are its uneven distribution of methanol in phases depending on temperature and pressure. To protect against hydrates in gas treatment units used in low-temperature processes, methanol injection ensures hydrate-free operation of the unit. To calculate the rate of consumption of volatile hydration inhibitors, it is important to calculate the dependence of the inhibitor flow on the operation of the heating apparatus under thermobaric conditions and select the maximumfunction for calculating the inhibitor flow.

IV. Conclusıon

Thermodynamic models and software have been developed, the condensed water phase of hydrocarbon systems, including the metasabit phase, allows reporting of three- and two-phase equilibrium.

A method is proposed to correct the reported model of test data, thermodynamic extrapolation to improve the description of the three-phase gas-condensed water-hydrate balance.

Surface evolution of gas hydrates at negative temperatures of various gases thermodynamic analysis has been developed, methods for controlling the process of separating gas hydrates and preserving them have been proposed.

Developed on the basis of a trial analysis and a general base of methods for normalizing the flow rate of hydrate compound inhibitors and analyzing the main characteristics of its use for gas preparation technology.

Technological methods have been developed to reduce the specific consumption of methanol.

CONFLICT OF INTEREST.

Authors declare that they do not have any conflict of interest.

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