Efficiency evaluation of using highly mineralized reservoir waters for preventing hydrate formation of natural gas in the conditions of Zakhidno-Radchenkivske gas-condensate field

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Abstract. A comparative analysis of hydrate formation inhibitors of different types: thermodynamic, anti-agglomerate, kinetic action was performed. The advantages and disadvantages of each class of reagents are considered. The possibility of using highly mineralized reservoir waters to prevent hydrate formation in gas condensate fields is proposed. Laboratory studies were conducted to determine the decrease in equilibrium temperature in the presence of reservoir water of the well 202 of Zakhidno-Radchenkivske gas-condensate field. Experimental determination of the equilibrium parameters of the hydrates formation of technical propane for the studied formation water showed that the value of ΔT is higher than predicted. This paradoxical effect can be explained by the multicomponent combination of formation water and, probably, the synergistic action of its micro- and macro components. The results of the calculation of the antihydrate properties of the reservoir water of Zakhidno-Radchenkivske gas-condensate field are presented. The results of industrial tests of using reservoir waters for the prevention of hydrate formation in the gas preparation system at Zakhidno-Radchenkivske gas-condensate field are presented. The results of industrial tests confirmed the effectiveness of the formation of reservoir water to prevent the formation of hydrates: hydrate formation in the well and on complex gas treatment unit was not detected. In addition, due to the use of well production, the cost of preparing gas for transportation has been significantly reduced. The article substantiates the possibility of using formation waters of oil and gas fields of the south-eastern part of the Dnieper-Donetsk basin as an inhibitor of hydrate formation.

1. Introduction
The problem of hydrate formation in the processes of extraction and preparation of hydrocarbons is faced by oil and gas companies in different regions of the world, including in the Eastern oil and gas region of Ukraine [1-3]. Hydration leads to various complications associated with the precipitation of solid crystalline substances in the pipelines, which impede the movement of gas. Carrying out work to eliminate these complications dramatically increases the cost of hydrocarbons and reduces the efficiency of work [1-3]. The most unpleasant property of hydrates is their ability to be formed at a temperature well above zero. Hydrates are formed all the way from the bottom of the well to the gas collection points. This forms hydrated plugs, which partially or completely block the cross section of the pipes, and cause serious complications during the extraction and transportation of gas. Even minor
Violations of the thermobaric regime in the pipeline can lead to its tamponade with hydrates [1, 2, 4]. Therefore, the development of effective methods for preventing hydration formation in gas equipment is undoubtedly an urgent problem.

2. Critical literature review

Among the existing methods of preventing the formation of gas hydrates, the use of chemical reagents is technologically and economically justified.

In recent years, many studies have been conducted on low-dose hydration inhibitors (LDHIs) [2-5] to prevent hydration: kinetic and anti-agglomerate inhibitors. As kinetic inhibitors of low-dose hydration, polymers are used, among which the most widely studied compounds are polyvinylpyrrolidone, polyvinylcaprolactam, and polyethylene oxide. Currently, studies of additives that would show a synergistic effect with kinetic inhibitors are performed [6, 7]. The mechanism of inhibitory action of these substances is still not fully understood [5]. According to [5], kinetic inhibitors of hydrate formation delay the nucleation and growth of hydrates for a certain time, affect the equilibrium conditions of hydration and create a zone of hydrate stability.

According to Fu and co-authors, the use of these inhibitors can reduce the temperature of hydration by 11 ºC with a mass fraction of inhibitor less than 0.3%. However, some companies, such as Exxon-Nalco, have conducted experiments with this type of inhibitor in-service, and they have not yet found any practical application in the gas industry.

An alternative to kinetic inhibitors are anti-agglomerate agents – surfactants [8-11]. The data of researchers [11] show that surfactant additives in concentrations of 0.1% do not change the equilibrium conditions of hydrate formation. But in their presence, the growth rate of hydrates increases hundreds of times at the stage of mass crystallization and porous hydrates are formed.

According to [12], kinetic inhibitors and their complex mixtures are not active enough for widespread use. Other studies indicate that low-dose inhibitors have been used successfully in the oil and gas industry.

The advantage of LDHIs is that their solutions with a mass fraction of inhibitor of 0.3-0.5% compared to 10-60% of the concentrations required for conventional thermodynamic inhibitors are used. However, the industrial application of LDHIs in Ukraine is limited by their high cost and questionable efficiency.

Thermodynamic inhibitors of hydrate formation are very important and large-capacity reagents of the oil and gas industry. In terms of use, they continue to occupy one of the leading positions among other inhibitors of hydration. The action of inhibitors is based on the fact that their use changes the structural parameters of water, reduces the vapor pressure of water, which causes changes in the conditions of hydration, helps prevent the formation and destruction of hydrate deposits.

Alcohols, glycols and electrolytes are mostly used as thermodynamic inhibitors of hydrate formation during industrial extraction and preparation of gas for transportation [1, 7, 12]. Let’s consider their main advantages and disadvantages.

A widespread use of methanol as an inhibitor of hydration is due to the following reasons: methanol has a high antihydrate activity, low freezing point, low viscosity, low solubility in unstable condensate. The main disadvantage of methanol is its high toxicity, explosion and fire hazard. In addition, the low boiling point and high volatility leads to significant losses of methanol in the system of industrial preparation of gas for transportation.

The use of methanol is a source of environmental pollution [1, 2, 13]. In the conditions of industrial gas treatment, glycols are also used as dehumidifier and hydrate formation inhibitor: C_2H_5O (EG), C_4H_9O_2 (DEG), C_6H_14O_4 (TEG), HO[-CH=CH(CH_3)O]_nH (PPG). The main properties of glycols are considered in [1, 16]. Their positive property is low solubility in the gas phase, detailed systems for regeneration of spent solution.

The disadvantages of glycols compared to methanol and calcium chloride are that they reduce the hydration temperature less effectively, are quite expensive, cause technological difficulties in
separating the glycol emulsion with unstable condensate, have high viscosity and relatively high crystallization temperature. At high gas velocities, glycols sometimes form foams and emulsions [14].

Currently, there is a tendency to return to use of electrolyte solutions as inhibitors of hydrate formation [15-16].

F.K. Andrushchenko, V.P. Vasylichenko, B.I. Shahaidenko evaluate the electrolyte in terms of antihydrate efficiency, which is based on the comparison of the binding strength of its ions and water molecules with the strength of crystal hydrates [17].

Calcium, magnesium and aluminum nitrates can be used along with their chlorides. The disadvantage of nitrates is their rather high cost and oxidative effect. Besides, sodium nitrate is quite hygroscopic [1]. The main disadvantage of aluminum chloride as an inhibitor of hydrate formation is that it is easily hydrolyzed and therefore corrosive. Potassium chloride is more expensive than calcium chloride and sodium chloride, the viscosity of which is higher [17].

Among individual electrolytes, calcium chloride solution is one of the most common antihydrate reagents. It is non-toxic, produced in large quantities, non-volatile, so the use of calcium chloride heated to 60-80 °C provides additional advantages in the elimination of hydrate plaques in wells by hot washing [17]. Comparison of the data of lowering the equilibrium temperature of hydrate formation in the presence of solutions of calcium chloride, methanol, EG, DEG show that solutions with a mass fraction of calcium chloride up to 40% are much more effective than solutions of glycols [12].

The main disadvantage of calcium chloride is that its solutions corrode steel in the presence of oxygen, therefore, when using it, it is necessary to ensure a decrease in its corrosivity [1]. Another disadvantage is that when calcium chloride interacts with carbon dioxide, which is always present in natural gas, carbonates are formed in the form of deposits. In addition, it can precipitate with saline reservoir waters [17], therefore, in the practical use of calcium chloride solutions, special attention should be paid to the observance of the solution preparation technology in industrial conditions and to reduce its corrosivity.

Antihydrate activity of magnesium chloride is higher than calcium chloride by 20-30%, and corrosion activity is much lower. Despite this, the use of individual substance MgCl₂ as an inhibitor of hydrate formation has not been widely used due to the lack of an industrial method of production.

Many authors suggest using the antihydrate activity of natural mineral salts.

V.I. Siomin studied the antihydrate activity of bischofite, the main component of which is magnesium chloride with impurities of calcium chloride and other salts [18].

M.Sh. Mirzaev, S.V. Kozlov, A.A. Komarovsky analyzed the possibility of using the antihydrate activity of highly mineralized reservoir waters in the deposits of the Perm region [19]. According to V.A. Khoshilova reservoir waters, which reduce the equilibrium temperature of hydration by 11 °C, can be used as inhibitors of hydration in summer [17-19]. Wastewater from chemical industries, such as epoxy resins, is acceptable as mineralized reservoir water.

The purpose of the article is the investigation of the antihydrate properties of reservoir waters of the Zakhidno-Radchenkivske gas condensate field and the possibility of their use to prevent hydrate formation in the system of extraction and preparation of natural gas for transportation.

The authors propose to use highly mineralized formation waters for effective, ecological and economic prevention of hydrate formation. To evaluate the antihydrate properties of formation waters, it is proposed to use known empirical dependences. A generalized sequence of such calculations is given.

3. Methodology and results

In order to determine the possibility of using highly mineralized waters to prevent hydration formation at the Zakhidno-Radchenkivske gas condensate field, the reservoir water of the well 202 was used in the gas preparation system. The quantitative composition of the substances dissolved in it are shown in table 1.

Based on the composition of reservoir water, it can be assumed that the decrease in the temperature of hydration should be greater than in NaCl solution with the appropriate concentration, due to the
presence of chlorides and iodides of calcium and magnesium, whose antihydrate properties are higher; freezing point – lower (table 2). The content of the main components of the studied reservoir water in% is as follows: NaCl is 18.461, CaCl₂ – 3.305, others <1, so the predicted values of ΔT are not less than 19 ºC.

Table 1. The composition of the basic salts dissolved in the reservoir water of the Well 202 of the Zakhidno-Radchenkivske gas condensate field.

| Components of mineralization | cations | mg/l      | anions | mg/l      |
|-------------------------------|---------|-----------|--------|-----------|
| Na⁺ + K⁺                      | 85883.70967 | Cl⁻    | 159570 |
| Ca²⁺                          | 14028 | Br⁻     | 111.5 |
| Mg²⁺                          | 912 | B⁻      | 1.61  |
| Fe⁴⁺                          | 139.6 | HCO₃⁻   | 536.8 |
| Fe³⁺                          | 7.444 | CO₂⁻₂   | 0     |

Density 1.178 g/cm³
Total mineralization 22.165 %

Table 2. The value of the decrease in the equilibrium temperature of hydrate formation ΔT depending on the electrolyte concentration [19].

| Electrolyte | Electrolyte concentration (C), % mass. |
|-------------|--------------------------------------|
|             | 5     | 10   | 15   | 20   | 25   | 30   | 35   |
| LiCl        | 3.50  | 13.20| 26.50| –    | –    | –    | –    |
| NaCl        | 1.80  | 5.00 | 10.00| 19.00| –    | –    | –    |
| MgCl₂       | 2.90  | 8.70 | 18.00| 29.00| –    | –    | –    |
| CaCl₂       | 1.50  | 4.00 | 8.00 | 12.50| 25.00| –    | –    |
| Ca(NO₃)₂    | 1.00  | 2.50 | 4.40 | 6.50 | 9.70 | 15.00| 21.00|

A study was conducted to determine the decrease in equilibrium temperature in the presence of reservoir water of the well 202 of the Zakhidno-Radchenkivske gas condensate field.

As a model of hydrate-forming gas, propane was used, the hydrates of which have a type of crystal lattice KS-II close to natural gas hydrates with a propane content of more than 0.2%. At the same time, relatively low equilibrium pressures for the three-phase water-hydrate-propane system (t = -11.8 ºC, Pₑq = 100 kPa) allowed to visualize the process of hydrate formation.

The process of hydrate formation was investigated under dynamic conditions on an experimental setup. The main element is a reactor in the form of a cylindrical glass made of organic glass. The reactor was filled with thawed cooled test liquid. The gas from the cylinder at a pressure of 0.4 MPa was fed to the reactor and released under a pressure of 0.35 MPa at a given temperature, which was maintained by a thermostat.

The experiment ended when all the liquid in the reactor went into a solid phase. The conditions and time of hydration were recorded [20].

Experimental determination of equilibrium parameters of technical propane hydrates formation for the studied reservoir water of the well 202 of the Zakhidno-Radchenkivske gas condensate field showed that the value of ΔT is 29 ºC and is 10 ºC is higher than predicted. This paradoxical effect can be explained by the multicomponent combination of reservoir water and, probably, the synergistic action of its micro- and macrocomponents.
To assess the possibility of using reservoir water at industrial plants for integrated gas treatment, the calculation of the hydrate formation temperature was performed. Industrial values of pressure in places of probable hydration formation were taken for calculation.

Equilibrium hydrate formation temperature for natural gas from the well 202 of the Zakhidno-Radchenkivske gas condensate field (table 3), which has a density of 0.72 kg/m³ was calculated by the formula of Makogon-Shalyako [1]:

\[ \log P = \beta + \alpha(t_h + k t_h^2) \] (1)

where, \( P \) – pressure, bar; \( t_h \) – temperature of hydration, ºC ; \( k = 0.03; \alpha = 0.0497; \beta = \log P_{ex}^0 \).

Figure. 1. The scheme of the experimental installation for the study of hydrate formation:

1 – gas cylinder; 2 – buffer tank with gas (thermostated); 3, 4 – gas reducer; 5 – inlet valve; 6, 13 – manometer; 7 – housing; 8 – cooling chamber; 9 – reactor; 10 – cover; 11 – thermometer; 12 – the final crane; 14 – refrigerator reservoir water.

Table 3. Gas composition of Zakhidno-Ranchenkiivske gas condensate field.

| Natural gas components | %     |
|------------------------|-------|
| Methane                | 82.3  |
| Ethan                  | 5.28  |
| Propane                | 2.49  |
| iso-Bhutan             | 0.42  |
| n-Bhutan               | 0.22  |
| Pentane + above        | 0.81  |
| N₂                     | 4.36  |
| CO₂                    | 4.04  |
According to the method of Dickens and Quinby-Hunt (equation 2), the hydrate formation temperature was calculated at the presence of reservoir water [2].

\[
\frac{1}{T_w} - \frac{1}{T_s} = \frac{6008n}{\Delta H} \left[ \frac{1}{273.15} - \frac{1}{T_{fs}} \right]
\]  

(2)

where \( T_w \) – temperature of hydration without the inhibitor; \( T_s \) – temperature of hydration formation with the inhibitor; \( \Delta H \) – heat of hydrate dissociation; \( T_{fs} \) – freezing point of saline solution; \( n \) – hydrate number.

The freezing point of the saline solution was calculated by Rankin's formula (3) [20]. As the experiment showed, the calculated freezing temperature corresponds quite well to the practical results, and is \(-31 \pm 1 \) °C.

\[
T = \frac{10^7}{36608 - 3279 \ln a_0 - 74302(\ln a_0)^2 - 607310(\ln a_0)^3}
\]  

(3)

The activity of water for electrolytes was calculated from the model Enlezos Bishnoi (1988) (equation 4) [2].

\[
\ln a_w = -\frac{18\nu m}{1000} \left[ 1 + z_z z_- \theta_1 + m \theta_2 + m^2 \beta_2 \right]
\]  

(4)

where \( m \) is the molarity of the electrolyte in solution, \( \nu \) is the stoichiometric number of ions in one mole of salt; \( z \) is the charge of each salt ion; \( I \) – ionic strength of the solution; \( \beta_0, \beta_i, \beta_2 \) – calculated parameters of the Pitzer model; \( A_\phi \) – Debye-Huckel coefficient.

\[
\theta_1 = -\frac{A_\phi I^{0.5}}{I + 12I^{0.5}}
\]  

(5)

\[
\theta_2 = \beta_0 + \beta_I \exp(-2I^{0.5})
\]  

(6)

The activity of water for a mixture of electrolytes was calculated using the method of Patwardhan and Kumar (equation 7)

\[
\ln a_w = \sum \left( \frac{m_k}{m_k^0} \right) \ln a_{w,k}^0
\]  

(7)

Experimentally, the efficiency of reservoir waters for the prevention of hydrate formation was determined at complex gas treating plant of the Zakhidno-Radchenkivske field, where gas preparation is carried out by the method of low-temperature separation.

**Table 4. Hydration formation conditions of Zakhidno-Radchenkivske gas condensate field.**

| Separator pressure | Hydration temperature without inhibitor, °C | Hydration temperature with inhibitor, °C |
|------------------|------------------------------------------|----------------------------------------|
|                  | in the separator | design | in the separator | design |
| І lev. – 12      | +21                        | +21 | -10                   | -12    |
| ІІ lev. – 3      | +12                       | +11 | -20                   | -22.8  |

The calculation results of the hydration formation process according to the given formulas and actual data are given in Table 4. The calculation results showed that the equilibrium hydration
formation temperature in the presence of reservoir water of Zakhidno-Radchenkivske field decreases by a sufficient amount, providing hydrate-free wells and complex gas treating plant.

The results of industrial tests confirmed the effectiveness of the formation of reservoir water to prevent the formation of hydrates: hydrate formation in the well and on complex gas treating plant was not detected. In addition, due to the use of well products, the cost of preparing gas for transport has decreased significantly.

It should be noted that such a decrease in the equilibrium temperature of hydrate formation of highly mineralized reservoir waters is manifested in isolated cases, which allowed them to be used both in the well and complex gas treating plant. According to V.A. Khoroshilova reservoir waters, which reduce the equilibrium temperature of hydration by 11 ºC, can be used to prevent hydration of wellbores, plumes, in-reservoirs.

4. Conclusions

Similar opportunities to reduce for hydrates control are in many areas where there are highly mineralized reservoir waters of chlorine-calcium type. The specifics of each field should be taken into consideration when using reservoir water. For their application it is necessary to determine: freezing point of water; composition of solutes; the possibility of precipitation due to cooling; equilibrium conditions of hydrate formation in the presence of reservoir waters. These data are quite sufficient for the development of technology for the control of hydrates using reservoir waters.

Prospects for further research are related to the study of the effect of reservoir water mineralization on the reduction of the equilibrium temperature of hydrate formation in gas condensate fields of Ukraine and the search for new effective antihydrate compositions based on them.

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