1. Introduction

In modern conditions, when structural changes are carried out in our country and new economic conditions are introduced, gas and oil industries, as before, are the main industries in the fuel and energy complex of Ukraine. The development of technology for the operation of gas and gas condensate fields in the conditions of carbon dioxide corrosion and hydration requires a special approach that opens new directions in science and industry.

Extraction and preparation of gas for transportation is complicated by hydration and corrosion of metal equipment [1–6]. Carrying out work to eliminate these complications dramatically increases the cost of operating wells and hydrocarbon collection systems. Neglecting corrosion protection leads to frequent interruptions, and in some cases when the tubing is broken – stops the production of hydrocarbons. The main indirect losses from hydroformation and corrosion are the underproduction due to emergency and repair shutdowns, environmental sanctions.

The introduction of advanced technologies for the protection of operating equipment helps to reduce labor costs and material consumption, reduce the duration and cost of repair and restoration work carried out at industrial enterprises [2, 4]. These measures will ensure sustainable development in the future during the operation of oil and gas fields in the conditions of hydrate formation and carbon dioxide corrosion.
2. Problem statement

World and domestic practice shows that one of the simplest, most effective and in many cases cost-effective methods of combating the processes of hydrate formation and corrosion is the use of inhibitors. [7, 8]. According to the data of the feasibility study on the use of reagents, technologies based on the use of complex inhibitors are more efficient.

Inhibitors for industrial piping systems must have certain technological and protective properties. For example, hydration inhibitors should lower the hydration temperature by more than 25 °C, corrosion inhibitors should have high protective properties in the water and vapor phases (not less than 85% of total corrosion), not to have a negative impact on technological processes [7].

Nowadays, some experience has been gained in the use of inhibitors to prevent hydration and corrosion. Methanol, glycols and calcium chloride are mainly used as inhibitors of hydrate formation [8–11]. These solutions in their properties meet the requirements for inhibitors of hydration, but have significant disadvantages.

The main disadvantage of methanol is its high toxicity, explosion and fire hazard. In addition, low boiling point and high volatility cause significant losses of methanol in the industrial gas treatment system. The use of methanol is the source of environmental pollution [8, 9].

Compared to methanol and calcium chloride, glycols are less effective in reducing the temperature of hydration, are quite expensive, cause technological difficulties in separating the emulsion, have high viscosity and relatively high crystallization temperature [10].

The main disadvantage of calcium chloride is high corrosion activity, deposition during interaction with carbon dioxide, which is always contained in natural gas [11].

Therefore, in some cases it is advisable to use other antihydrate reagents.

In connection with the above, the current problem is the choice of process fluid, which would ensure quality and trouble-free operation of gas wells, systems for collection and preparation of hydrocarbons and at the same time would have minimal negative impact on the environment.

The authors have conducted laboratory studies on the selection of the composition of environmentally friendly complex inhibitor of hydration and corrosion (CIHC), which meets the requirements for inhibitors of hydration and corrosion.

Bischofite solution is proposed as an environmentally friendly basis for the CIHC formulation. When using thermodynamic inhibitors of hydrate formation, including bischofite, there is a change in the structural parameters of water, reducing the vapor pressure of water, which causes changes in hydration conditions [8,12,13], helps prevent the formation and destruction of hydrate deposits.

Bischofite solutions have better antihydrate activity than calcium chloride and not worse than methanol [2] (reduce the equilibrium temperature of hydration by ≈27–29 °C), as well as significantly lower corrosion aggressiveness compared to calcium chloride. Bischofite is an inexpensive, non-volatile, safe reagent [12, 13]. The inhibitory effect is achieved due to ions Mg$^{2+}$, Ca$^{2+}$ and Cl$^-$, which attract water dipoles. Bischofite solutions have a freezing point $\approx -30$ °C [12–15]. Therefore, the use of bischofite is acceptable in temperate climate deposits.

Particularly rational from the economic point of view is the use of this effective inhibitor of hydration in the case of its direct extraction on the territory of gas fields or bischofite fields in the surrounding areas. In deposits characterized by high cryolithozone capacity (up to 700 m) and low geothermal gradient (1.5–2.5 °C per 100 m), the use of bischofite may be appropriate in hydrocarbon collection systems.

In Ukraine, large deposits of bischofite have been explored in Poltava and Chernihiv regions. In Russia – in Saratov, Volgograd and other regions. These bischofite reserves are almost inexhaustible.

The use of bischofite in gas production companies is often limited due to its irrational use. Highly concentrated solutions of bischofite, untreated from sulfate ions and iron compounds,
without corrosion inhibitor cause corrosion of equipment and salt deposits.

Research on these issues and the development of economic technologies for the use of complex reagents based on bischofite will improve the environmental performance and performance of gas collection and treatment systems.

**The purpose of the study**: prevention of hydration and carbon dioxide corrosion during the operation of gas condensate fields by the use of domestic, available, inexpensive raw materials instead of expensive methanol and corrosion inhibitors.

3. **Materials and methods**

Bischofite solutions with a mass fraction of MgCl₂ 24% from well №1 of Zaturyn area were used as a carrier of the complex inhibitor.

Primary selection of reagents was performed. Analysis of the technical and economic characteristics of more than one hundred surfactants allowed to identify the following reagents for further experiments: KI-1M, sulforocanol (SRK), emily (EM), cocamide propylbetaine (CAPB) and stentex (St). The following acids and complexes were selected as stabilizers of iron ions: hydrochloric acid, acetic acid, formic acid, citric acid, oxalic acid, sodium salt of ethylenediaminetetraacetic acid (EDTA).

The process of hydrate deposition was studied under dynamic conditions on an experimental setup (figure 1).

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

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 – outlet valve; 14 – refrigerator.
Technical propane and surfactant solutions in double-distilled water and bischofite were used to obtain hydrates. The main element of the installation is a sealed reactor, which has the shape of a cylindrical glass with a useful volume of 300 cm$^3$, made of organic glass. The reactor was filled with thawed cooled test liquid with solid phase crystals. Gas from the cylinder through the outlet valve 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. The temperature in the chamber was created and regulated by the coolant supplied to the reactor jacket. The experiment ended when all the liquid in the reactor turned into a solid phase, the conditions and time of hydration were recorded.

Bischofite solution with a mass fraction of 24% MgCl$_2$ + 3 g/dm$^3$ CH$_3$COOH was used to study effectiveness of the corrosion inhibitors. Concentration of acetic acid was chosen because of the maximum content of low molecular weight carboxylic acids in the formation waters of wells of Northeastern Ukraine. Lighted condensate was used as hydrocarbon phase, as it has neutral reaction of medium and constant fractional composition and carbon dioxide as gaseous medium.

One of the main parameters influencing the corrosion rate is the ionic composition of the aqueous phase [4]. The main component of formation waters of North-Eastern Ukraine is sodium chloride NaCl [7]. Therefore, a solution of 0.5 M NaCl + 3 g/dm$^3$ CH$_3$COOH in distilled water was chosen as the model medium for model formation water.

Corrosion studies were carried out in a thermostatic installation (figure 2) The installation is designed at the All-Union Scientific Research Institute of Natural Gases and Gas Technologies (VNIIGAZ) for determination of corrosion rate in the simulated conditions of industrial pipelines [7]. It is a glass vessel in which the test solution was poured and a fluoroplastic cylinder with witness samples and a propeller stirrer was placed.
The cell was attached to an electric motor that rotated the stirrer. During rotation of the stirrer, circular fluid motions in the laminar mode were created in the fluoroplast cylinder with a flow rate of 0.3–0.5 m/s. When the propeller was mounted below the bottom of the cylinder, it was rotated at a speed of 1400 revolutions per second. There was a circular motion of the fluid in turbulent mode. The speed of stream flow in the area of placement of metal piece was 7–8 m/s. In addition to circular motion, fluid was also circulated through the small cylinder by creating irritation during rotation of the stirrer.

The corrosion rate of the metal was calculated by the equation (1) [7]:

\[ v = \frac{\Delta m}{S \tau} \]  

where \( v \) – the corrosion rate g/(m\(^2\)·h); \( \Delta m \) – the loss of the metal piece, g; \( S \) – the surface area of the coupon, m\(^2\); \( \tau \) – the test duration, h.

Protective effect of test reagents in bischofite solution \((Z)\) was calculated by the equation (2) [7]:

\[ Z = \frac{v_0 - v_1}{v_0} 100 \]  

where, \( v_0 \) – corrosion rate of the metal piece without the corrosion inhibitor e, g/(m\(^2\)·h); \( v_1 \) – corrosion rate of the metal piece with the corrosion inhibitor, g/m\(^2\)·h.

The stability of soluble forms of iron under the action of reagents was determined by colorimetric method in accordance with GND 211.1.4.040-95. The effect of surfactants on the rate and completeness of calcium sulfate deposition was performed in accordance with the standards for determining the content of sulfates in the sediment and solution by gravimetric method according to GOST 7759-73. Based on the results obtained, the degree of precipitation of calcium sulfate relative to the initial amount of sulfate ions in solution was calculated. Phase equilibria in the studied systems were studied by the isothermal solubility method, which allows to establish the exact molecular ratio of the components.

The quantitative indicators obtained in the experiments were analyzed using the methods of mathematical statistics.

4. Experimental laboratory results

It is known that surfactant additives with a concentration of 0.1% do not change the equilibrium conditions of gases hydration [8, 16]. The conclusion follows from the fact that surfactants in low concentrations can not significantly affect the chemical potential of water in solution, which is defined as the equation (3):

\[ \mu = \mu_0 + RT \ln(1 - x) \]  

where, \( \mu_0 \) – chemical potential of pure water, \( x \) – is the molar fraction of surfactants in the solution.

To elucidate the nature of the hydroformation process in the processes of gas production and treatment, the temperature of hydrate formation \((p = \text{const})\) was determined under dynamic conditions under the action of distilled water, aqueous solutions of surfactants 0.1% wt., bischofite solution 10% wt. and a mixture of bischofite 10 wt%. with surfactant 0.1% wt.

It was found that the introduction of a complex inhibitor based on bischofite as an anti-agglomerate inhibitor of hydration of cationic surfactants CAPB and KI-1M, mass fraction of which in solution is 0.1%, the temperature of deposition of hydrates decreases by 6 °C, hydrate
Figure 3. Hydrate in the surfactant system – bischofite/water – propane:
1 – propane hydrate obtained from water; 2 – propane hydrate obtained from a surfactant solution of 0.1% wt.; 3 – propane hydrate obtained from bischofite 10% wt.; 4 – propane hydrate obtained from a solution of bischofite 10% wt. with the addition of surfactants 0.1% wt.

is formed on the solution surface and on the walls of the reactor (figure 3). The adhesion of such hydrates to the reactor walls is negligible. In a distilled water control experiment, the hydrate is formed as a solid throughout the volume of the liquid-filled reactor. A similar hydrate was obtained from bischofite. Our data are confirmed by studies of the authors [16–18], who determined the effect of surfactants on the kinetics of hydrate formation.

In order to eliminate the main technological shortcomings of bischofite, a number of laboratory studies were carried out.

The results of studies on the protective effect of surfactants showed that in the complex inhibitor of hydration and corrosion instead of high-quality imported corrosion inhibitors it is possible to use surfactants of domestic production, which significantly reduce the cost of inhibitor and do not impair its technological properties. It was found that all surfactants studied in the model environment of formation waters show a protective effect of more than 90% with a dosage of 1 g/dm³ (figure 4a), which satisfies the requirements of regulatory documents for corrosion inhibitors.

It is established that the protective properties of surfactants in bischofite solution are 1.01–2.50 times less effective than in the model environment of formation waters. The degree of surfactant protection of SRK, EM and CAPB is reduced by 2.45–2.50 times. The degree of
Figure 4a. The degree of protection against corrosion of steel P-110 in the presence of surfactants in bischofite solution and model environment of formation waters [7].

Figure 4b. The degree of protection against corrosion of steel P-110 in the presence of surfactants in the solutions of complex inhibitors of hydrate formation and corrosion on bischofite basis relatively to the model environment of formation waters [7].

Protection of more than 90% was detected in the presence of St and KI-1M. Reagent KI-1M in bischofite solutions practically does not change its efficiency (increases by 1.05 times). All studied complex systems provide a degree of protection of the metal more than 90 °C (figure 4b). The most effective corrosion inhibitor is a complex inhibitor containing MgCl$_2$ 24% and KI-1M 0.1%, which showed a degree of protection of the metal of 99.57% relative to the model environment of formation waters.

When choosing an iron stabilizer, a number of organic and inorganic acids has been studied. The study found that the most effective reagents are EDTA, oxalic and citric acids, which form
Figure 5. Characteristics of iron stabilizers: 1 – hydrochloric acid; 2 – acetic acid; 3 – formic acid; 4 – oxalic acid; 5 – citric acid; 6 – ETDA.

stable soluble forms of iron, provide a degree of iron ions retention in the soluble state of 96.5–98.4% for 30 days (figure 5). Based on the calculation results of the effective concentration of stabilizers shown in figure 5, citric and oxalic acids were isolated, so much so that to maintain the same amount of iron ions requires 1.68 citric acid, and oxalic acid – 1.94 times less than EDTA.

For the final choice, corrosion studies of reagents at a temperature of 106 °C. As a result of the study, data were obtained that allowed to choose citric acid, which causes 1.81 times less corrosion than oxalic acid, as a stabilizer of iron ions for bischofite solutions.

Table 1. The degree of calcium silicate precipitation in the presence of surfactants and stabilizers of iron ions, T=20 °C.

| Environment | Stabilizer of iron ions (w=0.5%) | Degree of precipitation CaSO₄, % | Surfactant (w=0.1%) | Surfactant (w=0.1%) |
|-------------|---------------------------------|---------------------------------|---------------------|---------------------|
|             |                                 |                                 | KI-1M   | St     | SRK    | EM     | CAPB   |             |
| Bischofite  | (w(MgCl₂)=24%)                  |                                 | 12.10   | 3.60   | 10.30  | 48.20  | 68.20  | 88.96      |
| Hydrochloric acid | 12.00 | 2.30 | 8.40 | 7.80 | 8.30 | 8.50 |
| Acetic acid | 11.30 | 3.20 | 9.60 | 7.90 | 9.30 | 9.60 |
| Formic acid | 10.80 | 2.50 | 8.35 | 7.81 | 8.29 | 8.75 |
| Citric acid | 11.20 | 4.50 | 11.20 | 20.21 | 55.52 | 78.91 |
| Oxalic acid | 83.09 | 70.85 | 78.67 | 68.60 | 88.95 | 97.62 |
| EDTA        | 94.94 | 30.50 | 75.29 | 76.35 | 98.56 | 99.69 |
Further research was aimed at removing sulfates from bischofite solutions. For this purpose, the effect of surfactants on the crystallization of calcium sulfate in an aqueous solution of bischofite – 24 mass % solution, was studied. Determined the degree of precipitation, phase distribution rate and the effect of reagents on the precipitation of chlorides. It was found that during bisulfite desulfation, EM, CAPB and SRK reagents effectively improve calcium sulfate precipitation and prevent chloride salting.

The mutual influence of iron ion stabilizers and surfactants on the process of desulfation of bischofite solutions has been studied. Based on research, it has been determined (table 1) that surfactants EM, SRK and CAPB have a complexing effect on alkaline earth metal ions. This is confirmed by the fact that in the presence of strong acids, the degree of precipitation of calcium sulfates decreases sharply due to the destruction of complex compounds, supersaturation of CaCl$_2$ solution and precipitation of chlorides.

The results were taken into account when developing the technology of a complex inhibitor preparation. The use of amphoteric surfactant CAPB with a mass fraction of 0.1% in the preparation of bischofite as a catalyst for sulfate precipitation and a chloride precipitation inhibitor allows to increase the degree of CaSO$_4$ precipitation by 76.86% and reduce the volume of precipitate formed by 9.4 times. According to the results of laboratory studies, the following component composition of the complex inhibitor of hydration and corrosion OV-07 (mass fraction, %): magnesium chloride – 23–25, amphoteric surfactant CAPB – 0.1–0.2, cationic surfactant KI-1M – 0.1–0.2 and citric acid – 0.2–0.5.

The composition is designed simultaneously to prevent hydration and corrosion in the conditions of well removal of formation waters with an initial high content of iron ions <600 mg/dm$^3$.

5. Industrial tests

Industrial tests of the complex inhibitor of hydration and corrosion OV-07, which is proposed by the author to increase the reliability of gas wells operation in the conditions of hydration and corrosion, conducted at Kaverdynske gas condensate field. Methanol was previously used as an inhibitor of hydrate formation at this field. Well operating parameters: gas flow rate – 206 thous. m$^3$/day, water quantity 1.5 m$^3$/day, volume fraction of CO$_2$ – 5.3%, organic acid content – 167 mg per liter of water products. According to the calculations, the equilibrium temperature of hydration formation for C-1 conditions at a pressure of 120 kg/cm$^2$ is 20 ℃, the corrosion rate is 6.3 g/(m$^2$·h). The supply of the inhibitor was carried out centrally at the wellhead and in front of the heat exchanger of gas delivery station through the inhibitor lines dosing pumps ND/63/400 with a capacity of 0.063 m$^3$/h; the average supply of OV-07 to the wellhead was about 0.055 m$^3$/h, in front of the heat exchanger – 0.06 m$^3$/h.

The effectiveness of the complex inhibitor in preventing hydrate formation was determined by controlling the operation of well №2 in hydrate mode without the supply of inhibitor. The dewpoint of the gas was determined by a moisture meter «Kharkiv-2M», the intensity of corrosion – by witness samples, which were installed in the samplers at the mouth of the well.

The results of industrial tests confirmed the effectiveness of the technology of corrosion prevention and hydration with the use of a complex inhibitor based on bischofite:

1) the rate of uniform corrosion with constant circulation of the inhibitor in the system did not exceed 0.01 mm/year. The OV-07 inhibitor effectively inhibits corrosion of tubular steel;
2) formation of hydrates in the well and at gas delivery station was not found. The use of the complex inhibitor OV-07 instead of methanol makes it possible to prevent hydrates formation and obtain a treated gas dew point corresponding to the use of methanol.

There is also a significant environmental effect due to the prevention of pollution of petroleum products and disposal of used reagents.
6. Conclusions
1. Laboratory studies of the effect of surfactants on antihydrate, corrosion and technological properties of bischofite solutions. It was found that the introduction into the solution of bischofite amphoteric surfactant CAPB provides a decrease in the temperature of deposition of hydrates by 6 °C and increase the degree of precipitation of CaSO₄ by 76.86%; cationic surfactant KI-1M – a high degree (99.6%) of metal protection against corrosion; citric acid – the degree of retention of iron ions 96.5%.

2. Based on bischofite solutions, a new formulation of a complex inhibitor of hydrates formation and corrosion OV-07 was developed, including (mass fraction, %): magnesium chloride – 23-25, amphoteric surfactant CAPB – 0.1–0.2, cationic surfactant KI 1M – 0.1–0.2 and citric acid – 0.2–0.5.

3. Industrial tests show that the introduction of technological schemes for the use of complex inhibitors based on bischofite allowed to obtain an annual economic effect of 356.1 thous. UAH/year due to the use of cheap raw materials (bischofite, surfactants) instead of expensive methanol and inhibitors corrosion, reduction of the number of injections of two inhibitors and a significant environmental effect due to the prevention of pollution of petroleum products and disposal of used reagents.

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