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Reducing the man-made impact of hydrate formation inhibitors on the environment by applying gas hydrate technologies

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Reducing the man-made impact of hydrate formation inhibitors on the environment by applying gas hydrate technologies

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Abstract. The extraction of hydrocarbons is significantly complicated by the threat of clogging of technological lines with gas hydrates. Due to its undeniable effectiveness, the most common inhibitor of hydrate formation is methanol. However, due to its potential negative impact on the environment and the health of personnel, the search for effective substitutes for methanol is an urgent task. A comparative analysis of the effectiveness for the mixture of hydrate formation inhibitors of kinetic and thermodynamic action (poly-N-vinylcaprolactam and ethanol) was carried out on the basis of experimental studies. Parameters for the effective use of a mixture of poly-N-vinylcaprolactam and ethanol have been established. Taking into account the low thermal stability of poly-N-vinylcaprolactam, a method of regeneration of spent aqueous solutions for a mixture of kinetic and thermodynamic inhibitors based on gas-hydrate concentration technology is proposed and substantiated. The criteria for effective separation of gas hydrate crystal suspension and concentrated solution are established. Propane is proposed as a hydrate-forming gas. The principle scheme of the research and industrial device for its implementation is proposed and the main parameters of the process are substantiated.

1. Introduction

The processes of extraction, preparation, storage and transportation of oil and gas can be complicated by the formation of man-made gas hydrates. As a result, the technological process is disrupted or becomes impossible. Today, the main method of preventing hydrate formation is the use of inhibitors of this process. At the same time, methanol is the most effective inhibitor of thermodynamic action. It is also practically indispensable in the case of combating the formed hydrate plugs in process lines. However, the methanol used has a number of significant disadvantages. Methanol is a strong poison that can cause a significant negative impact on the environment. In addition, the low boiling point and significant volatility of the substance contribute to its significant losses in technological processes.

Therefore, the use of more ecological and at the same time effective hydrate formation inhibitors is relevant for the oil and gas industry. One the types of such substances are low-dose inhibitors of kinetic action (for example, polyvinylpyrrolidone (PVP), polyvinylpiperidone (PVPip), polyvinylcaprolactam (PVCap) and polyvinylazacyclooctanone (PVACO) [1]). However, the physical properties of these substances determine the expediency of their use in a mixture with thermodynamic inhibitors (for example, ethanol). At the same time, relatively low thermal stability of known kinetic hydrate formation inhibitors requires improvement of technologies for their regeneration from aqueous solutions.

The purpose of the work is a comparative analysis of the effectiveness of kinetic hydrate formation inhibitors, as well as an analysis of ways to improve the technology their regeneration.

2. Methods

2.1. Justification of the methanol alternative

In addition to methanol, glycols are widely used as thermodynamic inhibitors. Their advantage is low solubility in the gas phase and the possibility of regeneration [2, 3]. Disadvantages of glycols are high cost, formation of emulsions with condensate, relatively high viscosity and tendency to foaming [3, 4]. Also, in recent years, the use of ethanol has been expanding to prevent hydrate formation. Similarly to methanol, at low concentrations, ethanol acts as a catalyst for the process of hydrate formation, suppresses the effect of self-preservation for the formed hydrate and increases the rate its dissociation at negative temperatures [5]. The advantage of ethanol is its low toxicity. This is especially relevant in the development of marine deposits [1].

Unlike thermodynamic inhibitors, which shift the hydrate equilibrium curve to lower temperatures, kinetic inhibitors slow down the gas hydrate nucleation process by blocking the crystallization centers with a polymer molecule. However, kinetic inhibitors cannot completely prevent this process [6].

Kinetic inhibitors are effective at much lower concentrations (0.1-1.0 wt.%) than thermodynamic inhibitors (40-60%). They belong to the "ecological" category, which reduces the risks of contamination during their transportation and storage. They also have a low corrosion rate and are compatible with reservoir fluids. Due to these advantages, the popularity of kinetic inhibitors is growing [3, 6-8].

Kinetic hydrate formation inhibitors are used in the form of aqueous solutions. PVP and PVCap (figure 1) at a pressure of 7-9 MPa provide a level of subcooling of the system in the range of 3-4 °C [1, 9]. Therefore, to increase efficiency, they are used together with synergists. This allows you to increase the temperature of the subcooling for the system and extend the induction period.
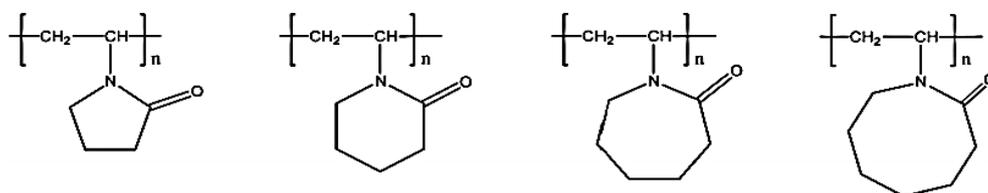
Figure 1. Typical polymers (N-vinyllactam): PVP, PVPip, PVCap and PVACO [1].

Glycols and lower aliphatic alcohols (methanol, ethanol, etc.), salt solutions, biological additives, etc. are used as synergists. As a result, each component of the mixture makes its additive contribution to the antihydration activity. In this case, the effectiveness of the mixture of kinetic and thermodynamic inhibitors is determined by the duration of the induction period of crystal hydrate growth, as well as the temperature of supercooling.

During the analysis of literary sources, the following reasons for the low efficiency of the use of pure inhibitors of kinetic action were established:

– high viscosity, which prevents the use of a concentration higher than 2%;

– the freezing point of aqueous solutions is close to 0˚C;

– insufficient slowing down of the induction period of hydrate formation when the system is significantly supercooling [8]. There are reports in the literature that kinetic inhibitors can work at hypothermia not higher than $\Delta T = 15\text{-}23$ °C [9];

– low rate of biological decomposition [10, 11];

– the application is limited by the temperature and degree of mineralization of the water [12];

– the stoppage time of treated wells should not exceed the time of their effective operation [12].

The industrial use of inhibitors of hydrate formation of kinetic action is limited by their high cost and insufficient level of biological decomposition. For example, for use in the North Sea, it is required that the kinetic inhibitor and its synergists have more than 20% by weight. substances capable of

biological decomposition within 28 days [10]. However, none of the kinetic inhibitors on the market have this level of degradation. In this regard, technologies for their effective utilization or regeneration are relevant, and taking into account their presence in a mixture with a synergist.

At the same time, regeneration of the inhibitor is a priority, as it provides the possibility of its repeated use, minimization of environmental risks and environmental burden, reduction of operating costs and increase of production stability. At the same time, the cost of regeneration should be much lower than the production of the inhibitor.

At the moment, the method of extracting methanol from a water-methanol mixture by rectification has become widespread. However, this method cannot be used for the regeneration of this inhibitors mixture because the maximum permissible heating temperature for kinetic inhibitors (PVP, PVCap – 50 °C) is much lower than the boiling point of lower alcohols (ethanol 78 °C) [1].

However, their regeneration by the method of gas-hydrate concentration can be quite promising.

2.2. Technology of gas-hydrate concentration

As is known, the processes of formation of hydrocarbon gas hydrates and their dissociation can be used in energy and environmental aspects, such as gas storage and transportation, energy accumulation, seawater desalination [13, 14].

Gas hydrate technologies are based on the property of gas hydrates to push all molecules of the gas-liquid mixture out of their crystal lattice, except for molecules of water and hydrate-forming gas.

All other molecules are pushed out of the crystal structure of the gas hydrate. As a result, the concentration of these molecules in the solution occurs outside the hydrate crystals. The liquid aqueous concentrate can be separated from the solid phase of the gas hydrate. If the goal of the technology is desalination of the solution (for example, desalination of seawater), the target product will be the separated gas hydrate. If it is necessary to isolate the dissolved components or concentrate them, the target product will be a concentrate [15, 16].

In work [17], a variant of desalination based on hydrates is proposed for the separation of heavy metal salts from industrial effluents. Also, work [18] suggested using gas hydrates to concentrate sensitive products, mainly liquids.

Desalination technology based on gas hydrates consists of three stages: the formation of hydrate crystals in a salt water solution, the separation of the hydrate from the residual salt water concentrate, and the dissociation of the gas hydrate [19]. Previous experimental studies have shown that the desalination process will be unsatisfactory without effective separation of the produced gas hydrate from the concentrated brine [20, 21]. Theoretically, this can be done using various mechanical methods, such as centrifugation, extrusion, and others [22]. But problems arose during the implementation of this stage of the technology [17].

In order to solve the difficulties of separating the components of the technology in [23], equipment for the rapid separation of dehydrated gas hydrates of high density from the hydrate suspension is proposed. This equipment option allows continuous production of CO_2 gas hydrate and its granulation using a double-cylinder press.

The importance of setting gas hydrate filtering parameters, the principle and parameters of the washing column for separating brine residues and hydrate formation promoters, which allow the process to be carried out at relatively low pressure and higher temperature, is also emphasized in the works [20, 24].

For increase the rate of hydrate formation in [25], it was proposed to use promoters of this process. In work [26] it is proposed to use cyclohexane and cyclopentane as auxiliary components to increase the temperature of formation of CO_2 hydrates from -2 °C to 6-7 °C. In addition, it was established that the addition of these components allows 16 and 22 times to increase in the rate of hydrate formation of the mixture compared to pure CO_2, as well as an increase in the efficiency of salt removal.

At the same time, due to slow kinetics, difficulty in separating hydrate crystals from brine, and higher energy costs associated with cooling, the desalination process based on gas hydrates has not yet found industrial implementation [3, 22]. However, when applying this technology to concentrate a

number of process fluids in the oil and gas industry, this technology, in our opinion, will be quite competitive.

2.3. Research object and equipment
Since the object of study was a mixture of kinetic and thermodynamic inhibitors, which have a different mechanism of preventing hydrate formation, their effectiveness was studied according to the method described in [27]. An aqueous solution of a mixture of 0.5% mass was studied. PVCap and ethanol, with a concentration in the range of 10 - 60% vol.

When choosing the composition of the studied mixture to study the features of the technology of gas-hydrate concentration of the spent inhibitor solution, it was assumed that, in addition to condensation water, mineralized formation water can enter the solution. Therefore, water with a salt concentration of 10 g/l was studied. At the same time, the initial concentration of the mixture of inhibitors was 0.5% wt. PVCap and 40 - 42% vol. of ethanol, which corresponds to the lower limit of its concentration for the anhydrous operation of the plumes of gas production wells (the rationale is given below).

The research was carried out on a laboratory setup, the schematic diagram of which is presented in figure 2.
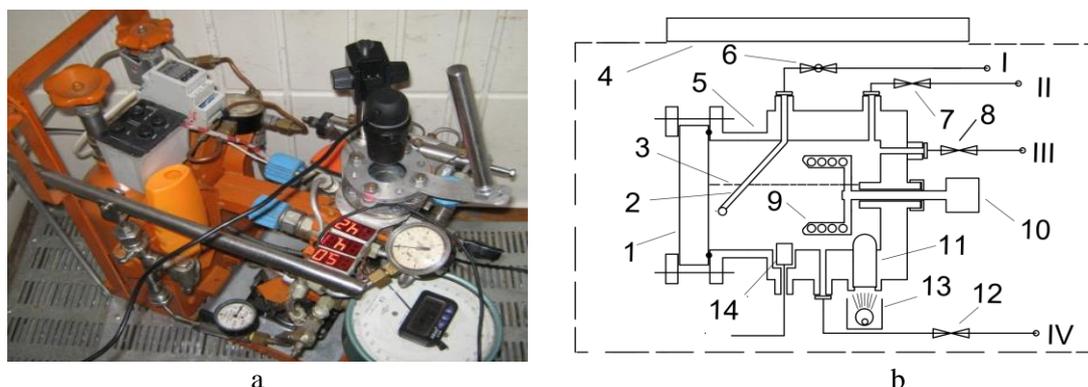
Figure 2. Laboratory setup for studying hydrate formation processes: a – photo; b – scheme; 1 – transparent window; 2 – capillary for introducing gas into the liquid; 3 – liquid level in the reactor; 4 – temperature control system in the reactor; 5 – reactor body; 6 – valve for fine adjustment of gas supply; 7, 8, 12 – valve; 9 – mixer rotor; 10 – mixer drive; 11 – reactor lighting system; 13 – external light source; 14 – temperature sensor; flows: I, II – gas supply; III – introduction of liquid samples; IV – sample selection.

Based on the equilibrium parameters of hydrate formation of hydrocarbon gases [28], thermobaric parameters acceptable for industrial equipment, as well as the availability of hydrate-forming gas resources at industrial facilities, the following composition was adopted for the implementation of the technology, and therefore for experimental research: C_3H_8 82%, i-C_4H_8. (It is assumed that the isolation of isobutane in industrial conditions will be realized directly in the technological process of regeneration of the inhibitor due to the effect of fractionation of the gas mixture).

3. Results and discussion
3.1. Analysis of the effectiveness of kinetic and thermodynamic hydrate formation inhibitors
In the course of experimental studies, the expediency of using ethanol as a synergist for PVCap was demonstrated. The effectiveness of the mixture was determined by the subcooling temperature of the system (shift of the equilibrium curve of hydrate formation, ΔT). The last parameter characterizes the effectiveness of both components of the mixture.

The limit concentration of methanol in an aqueous solution, which satisfies the conditions of anhydrous operation of oil and gas facilities, is 40-50% vol. Therefore, the effectiveness of the

proposed kinetic inhibitor (achievable level of supercooling ΔT) was compared for a given range of its concentrations. Based on the presented in figure 3 experimental and calculated dependences of the system subcooling temperature on concentration, efficiency 0.5% wt. PVCap is equivalent to an efficiency of 22% vol. methanol solution or 30% ethanol solution.
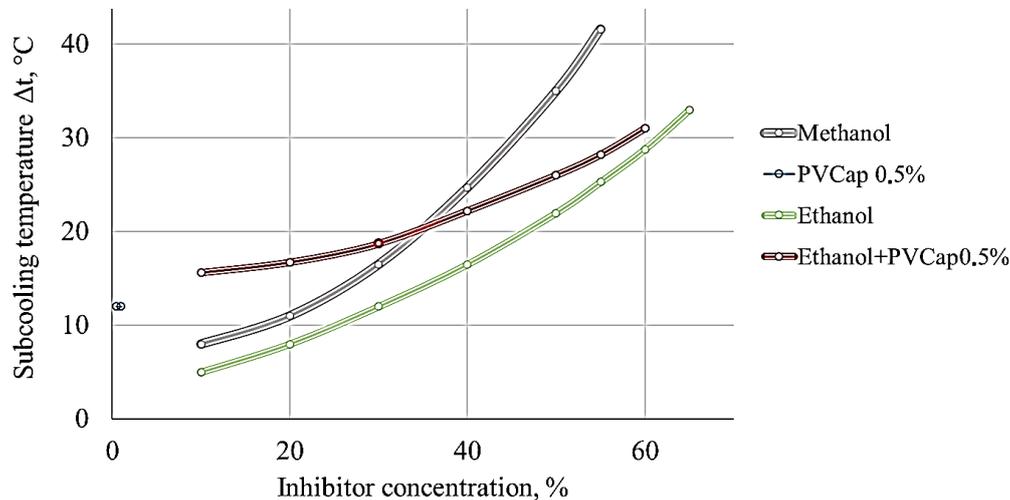
Figure 3. Dependence of the level of subcooling of the system on the concentration of the hydrate formation inhibitor.

Analysis of experimental data showed that in a mixture of 0.5 % wt. PVCap and ethanol have a slight synergistic effect. Each component of the mixture increases its influence on the process depending on the concentration. However, with an increase in the concentration of ethanol in the mixture, their effectiveness decreases The additive effect of the components on the level of subcooling of the system is observed only up to an ethanol concentration of 10-15%vol. For example, when adding up to 0.5 %wt. PVCap (ΔT = 12K) 10% ethanol solution (ΔT = 4K), the subcooling temperature of the mixture is within 16-17 K. That is, with an increase in the concentration of ethanol in the mixture, ΔT increases, but the synergistic effect of this mixture gradually decreases.

When the concentration of the ethanol solution is about 60%, the effect of 0.5 %wt. PVCap at ΔT is lost. This fact is explained by the shift of the equilibrium curve to negative temperatures, at which kinetic inhibitors become ineffective. Therefore, the use of a mixture of 0.5%wt. PVCap and ethanol, with a concentration of more than 60% vol. is impractical.

3.2. Regeneration of a mixture of low-dose kinetic and thermodynamic inhibitors

As mentioned above, a temperature above 50 ºC negatively affects the stability of solutions of PVCap, PVR and other kinetic inhibitors [1]. There is a change in the structure of molecules and the loss of their original properties. At the same time, one of the alternative regeneration methods of the spent aqueous solution of a PVCap and ethanol mixture can be the gas-hydrate concentration technology.

The works [29] proposed a technology for the production of gas hydrate, which involves the implementation of intensive interphase contact "liquid – gas" based on jet technology with the simultaneous maintenance of optimal thermobaric process conditions, the removal of process heat, the selection of water hydrate suspension from the reactor and its separation. This technology is also suitable for the process of concentration of inhibitor solutions. The schematic diagram of the laboratory setup for physical modeling of this technology is shown in figure 4.

The process is implemented as follows.

After filling the reactor 1 (figure 4) with liquid and supplying gas to the reactor through the bubbling device 8, the pump 17 is turned on, which pumps the liquid along the line: reactor 1 – separator 12 – heat exchanger 18 (section 1) – pump 17 – heat exchanger 18 (section 2) – jet device 4 – reactor 1. The limiting factor of the hydrate formation process is the removal rate heat of the

process. Therefore, the suspension formed in the reactor in the process of circulation performs the function of a heat carrier for its removal from the reaction zone. Based on the (above) anti-hydrating characteristics of the mixture of 0.5%wt. PVCap and ethanol, the depth of concentration of its aqueous solution should be at least 70% vol. The temperature of the process for the guaranteed achievement of this concentration, based on the equilibrium parameters for the given gas composition, should not exceed minus 25 ℃ [30].
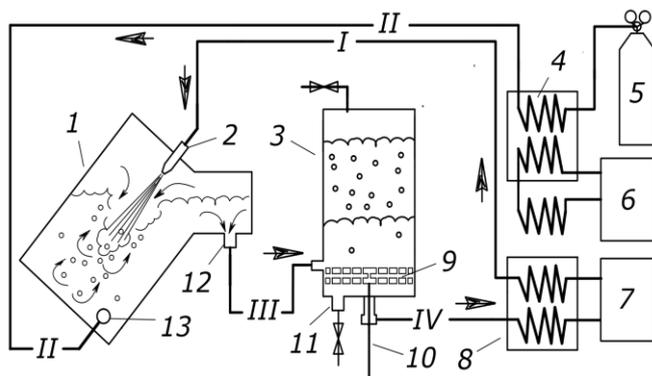
Figure 4. Scheme of a laboratory installation for the production and separation of gas hydrate [29]: 1 – reactor; 2 – jet device; 3 – separator; 4, 8 – heat exchangers; 5 – gas source; 6 – refrigerator; 7 – pump; 9 – a piston with a filter element; 9 – press rod; 11 – concentrate discharge connector; 12 – suspension outlet fitting; 13 – bubbling device; streams: I – inhibitor solution; II – hydrate-forming gas; III – liquid-hydrate mixture.

After filling the separator 12 with the solid phase of gas hydrate, the process will stop. Next, piston 11 with a built-in filter squeezes a concentrated solution of a mixture of inhibitors from the gas hydrate. Then a coolant (water) with a temperature of 60 - 95 °C is supplied to the separator to melt the gas hydrate. The released gas is returned to the process. Water after melting the hydrate will contain a minimal amount of inhibitor.

However, as mentioned above, hydrate separation is one of the problems of gas hydrate technology. This is confirmed by the analysis of the photo (figure 5) of the gas-hydrate mass separation process presented in [31].

Figure 5. Gas hydrate separation process [31].

In figure 5 cloudiness of the liquid under the filter indicates a significant content of the solid hydrate phase in it (concentrate). Therefore, after the dissociation of this hydrate residue, the regenerated inhibitor solution will again be diluted with a certain amount of water. Given that the value of the regenerated inhibitor for reuse lies in its maximally high concentration, the resulting concentrate will require further concentration steps.

At the same time, the analysis of data from visual observations of the kinetics of formation of hydrate structures from a solution of inhibitors and their sedimentation from a water-hydrated suspension gave grounds to propose a method of selecting a part of the inhibitor solution of the maximum (for the given thermobaric conditions of hydrate formation) concentration. The essence of the method follows from the peculiarities of the sedimentation process of hydrate crystals depending on the density of the liquid concentrate. The density of the hydrate (propane-isobutane mixture in this

case) is 906 kg/m^3 [3]. An increase in the depth of concentration and initial mineralization of reservoir waters additionally increases the difference in the density of gas hydrate and liquid concentrate. As a result, the formed gas hydrate floats to the surface of the liquid in the reactor (figure 6).

At the same time, in the course of experimental studies, the peculiarities of the formation of the solid phase of the hydrate in an aqueous solution of a mixture of ethanol and low-dose PVCap were established, which are suggested to be taken into account in the process of its concentration. As you know, the density of concentrated ethanol (789 kg/m^3) is much lower than the density of gas hydrate. When a certain limit concentration of ethanol and salt ions in the concentrated solution is reached in the process of hydrate formation, its density will become lower than the density of the hydrate. Therefore, after the stages of growth and agglomeration of hydrate crystals, their sedimentation will be observed. After a certain time (from several minutes to several hours), the formation of sediment at the bottom of the reactor will be recorded (figure 7).

**Figure 6.** Gas hydrate formed in distilled water.

Figure 7. Gas hydrate formed in an aqueous solution of ethanol and high concentration PVCap.

At the same time, the upper part of the reactor contents will be gradually cleared of the solid phase (it will become transparent). At the same time, the concentration of ethanol in the upper layer of the reactor contents will be maximum and will correspond to the thermobaric parameters of the process. Based on the analysis of the density of the samples taken from the reactor and visual observations, the gravitational sedimentation of the main part of the hydrate lasts within 2-10 hours. At the same time, the concentration of ethanol, despite a certain increase in the density of the liquid phase caused by the simultaneous concentration of salt content (up to 5-10 g/l), was from 68 to 82% vol. The analysis of the ratio of the density of gas hydrate (the investigated composition) and the aqueous solution of a mixture of PVCap, ethanol and salt ions depending on the concentration in the process of gas hydrate concentration is shown in figure 8.

However, in the course of experimental studies, it was established that the presence of a known proportion of water (about 60% by volume) in the solution entering the regeneration leads to the rapid formation of a significant amount of gas hydrate of high dispersion in the reactor. The reactor is filled with a homogeneous hydrate mass (figure 9). At the same time, the liquid is captured between the crystals and held by capillary forces. This makes it impossible to apply gravity separation.

In this case, it is advisable to carry out the concentration in two stages. In the first, separate the main mass of water by separating the main amount of water in the composition of the hydrate in the process of its separation in accordance with the technology described in [29] and taking as a prototype the laboratory installation, the scheme of which is presented in figure 5. In the second - by settling the water-hydrate suspension and selecting of the upper layer of the liquid phase as the target product and returning the sediment to the first stage of separation.
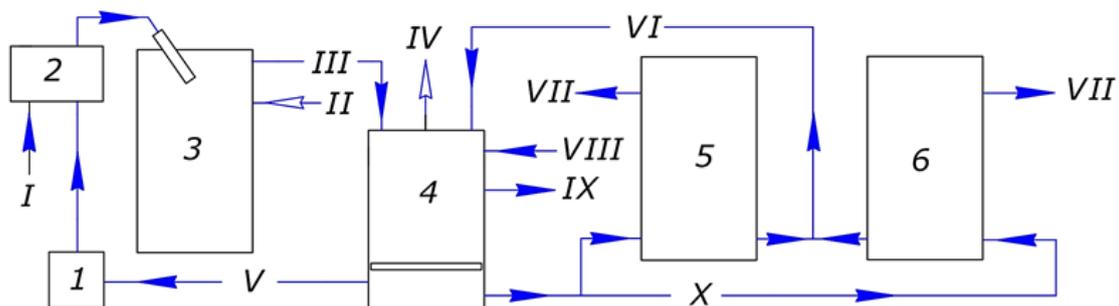
In figure 10 shows the schematic diagram of the research and industrial installation, which integrates the two-stage regeneration process of the inhibitor by the method of gas-hydrate concentration. (The specifics of the movement of material flows of the proposed process are detailed in the caption to it).
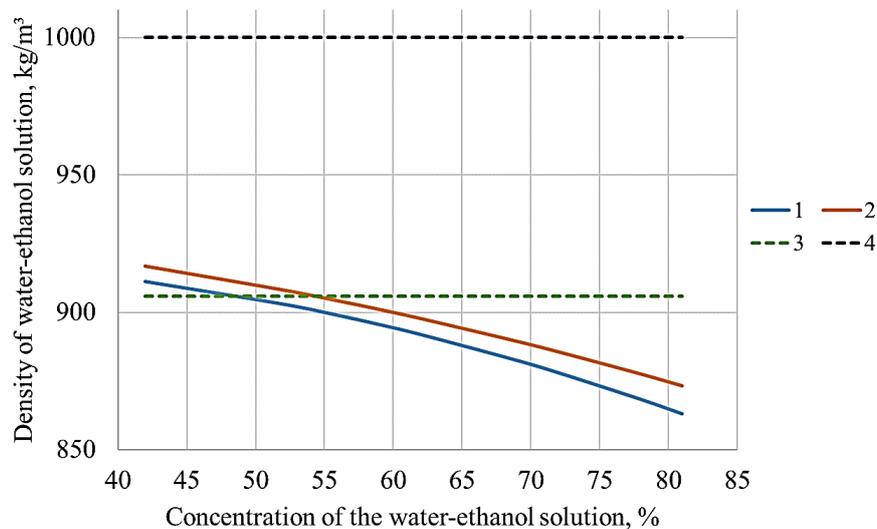
Figure 8. Analysis of the density ratio of gas hydrate and the studied aqueous solutions depending on the concentration of components in the process of gas hydrate concentration: 1 – aqueous solution of ethanol and PVCap; 2 - aqueous solution of ethanol, PVCap and salts (10 g/l); 3 – gas hydrate mixture 82% vol. propane, isobutane; 4 – distilled water.

Figure 9. The appearance of a homogeneous hydrated mass in the reactor formed from a mixture of a low-concentration inhibitor (0.5% wt of PVCap and 40% vol. ethanol).

Figure 10. Schematic diagram of the experimental and industrial plant for the regeneration of the inhibitor by the method of gas-hydrate concentration: 1 – cooling unit; 2 – pump; 3 – hydrate formation reactor; 4 – a separator with a piston in which a filter element is mounted; 5, 6 – gravity separators; flows: I – inhibitor solution for regeneration; II – gas; III – suspension of the liquid phase and gas hydrate at the first stage of separation; IV – gas after hydrate melting for reuse; V – gas hydrate-depleted suspension in the reactor; VI – sediment (suspension thickened to gas hydrate) at the first stage of separation; VII – concentrate (regenerated inhibitor); VIII – supply of coolant for hydrate melting; IH - water; X is a gas hydrate-depleted suspension for gravity separation.

4. Conclusions

1. When used as hydrate formation inhibitors, a mixture of 0.5% wt. PVCap and ethanol the synergistic effect of decreases with increasing concentration. The additivity for the level of subcooling of the system is observed only up to an ethanol concentration of 10-15% vol. As the ethanol concentration increases, ΔT of the mixture increases, but the synergistic effect for the components of the all mixture gradually decreases. When the ethanol solution concentration is about 60%, the influence of 0.5% wt. PVCap at ΔT is lost. Therefore, its use at such a concentration of ethanol is impractical.

2. Gas-hydrate concentration technology can be an effective way of regenerating the spent aqueous solution of a mixture of PVCap and ethanol. To overcome the shortcomings of the separation of gas hydrate from its mixture with the liquid phase, it is proposed to use the difference in density between the hydrate and the concentrate (in this case, a mixture of PVCap and ethanol). The possibility of gravitational separation of the solid phase of hydrate and concentrate has been confirmed experimentally. A schematic diagram of the two-stage regeneration process of the mixture of PVCap and ethanol is proposed.

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