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MAIN FEATURES OF GAS HYDRATES

Introduction

Natural gas hydrates are specific combinations of two very common substances: water and natural gas. If these substances come into contact at high pressure and low temperature, the solid mass is formed, similar to ice. Huge amounts of hydrate deposits are found in the seabed of the ocean floor and in the polar zones, where they are kept in the thermobaric conditions that permit formation of gas hydrates.

Synonymous with the term "hydrate" are gas hydrates, methane hydrates, or clathrates (from the Greek "frame"). The basic structural element of hydrates is crystal lattice of water molecules, inside of which gas molecules are located. Hydrate structure is similar to the structure of ice, but differs from the latter by the fact that gas molecules are located inside the crystal cells rather than between them. Outside hydrates are looking like ice, although they can be seen not frequently. They do not behave like ice. If a match is brought to them, they flash.

When conventional hydrocarbon reserves can not provide energy to the growing economy and population, then they will be substituted with the so-called unconventional hydrocarbon reserves in the form of gas hydrates.

Review of recent research sources and publications

All gas hydrate research performed for 120 years (until the early thirties of XX c.) had been of purely academic nature.

Gas hydrates were not used in industry, they did not interfere with technological processes of those times and found no practical application. In the thirties, rapid development of gas production industry set before the researchers a serious task of studying gas hydrates, primarily, in order to develop methods to prevent their formation and accumulation in pipelines and in equipment at gas extraction and transportation.

The period of applied gas hydrates study lasted over 20 years. During this time, almost all known methods of hydrates controlling have been developed. In recent decades, studies of some gas hydrates properties have been performed using modern instrumental methods, serious theoretical studies are being developed, resulting not only in the improved methods of controlling hydrates, but also in developed ways of their practical use in various industrial processes.

A special place in the hydrate study is occupied by research related to the discovery of gas hydrate deposits in the sedimentary layer of the earth's crust, performed by a group of scientists: V.H. Vasyliev, Yu.F Makohon, F.A. Trebinye, A.A. Trofymuk and N.V. Cherskyi [1, 2].

In studying of the gas hydrates problem significant contribution has been made by Soviet scientists, among them: B.A. Nikitin, I.N. Stryzhov, I.B. Khodanovych, M.Kh. Shakhnazarov, G.A. Sarkysiants, P.A. Tesnera, F.A. Trebinye, Yu.P. Korotaev, N.V. Cherskyi, F.K. Andryushchenko, V.A. Khoroshylov, S.S. Byk, V.I. Fomin, V.P. Tsarev, V.P. Vasylchenko, V.I. Shahaydenko, A.M. Kuliyev, R.M. Musayev A. Javadov, A. Aliyev and others [6, 7].

Setting up previously unsolved aspects of the problem

In order to develop efficient technologies for transportation and storage of gas in the form of gas hydrate, a scientific basis should be created to control the process of gas hydrates formation and decomposition. It is important to understand the mechanisms of gas hydrates decomposition, which permits to develop technologies of gas hydrates conservation, to suggest new methods of phase equilibria studies, etc. As a first step, it is advisable to analyze the thermodynamic conditions for the appearance of metastable water phases during the gas hydrates decomposition and to compare them with the available experimental data.

Such an approach permits to specify trends for further studies of the gas hydrates decomposition kinetics (including the self-conservation effect) in view of possible practical applications.

Statement of assignment

The aim of the study is to analyze the features of hydrate formation and controlling them both in wells and in pipelines.

Basic material and results

Gas molecules are bound with water backbone by means of Van der Waals bonds. In general, the composition of gas hydrates is described by $M \cdot n \cdot H_2O$ formula, where M is a molecule of gas hydrating agent, n is a number of water molecules per a single included gas molecule, meanwhile n is variable number depending on the type hydrating agent, pressure and temperature.

Cavities, combining with each other, form a continuous structure of different types (Fig. 1). According to the accepted classification, they are called CS, TS, HS – according cubic, tetragonal and hexagonal structures. In nature, the most common types of hydrates are CS-I, CS-II, while others are metastable.

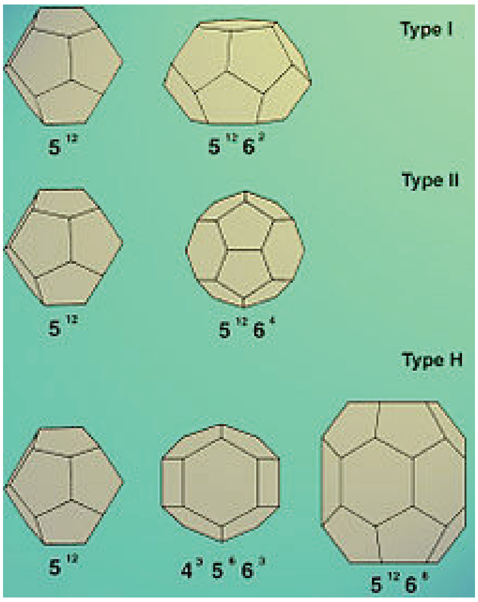

***FIGURE 1.** Gas hydrates crystal modifications*

Hydrating agents' molecules are held in the cavities between the assemblies of associated water molecules of the hydrate lattice by means of Van der Waals gravitative attraction forces. Hydrates compounds can be formed as two structures, whose cavities are filled with hydrating agent's molecules partially or completely (Fig. 2).

Normal operation of the gas pipeline can be provided with high-quality drying of natural gas in the processing facilities: the presence of moisture in the gas at its inadequate removal is often the cause of gas hydrates formation.

In practice, the conditions for hydrates formation are determined by means of the equilibrium diagrams or by calculation: according to the balance constant and using the graphic-analytical method according to the Barrer-Stewart equation.

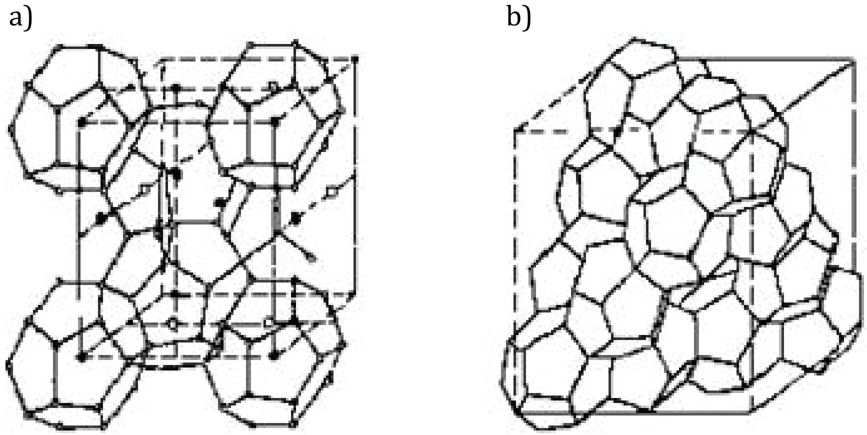

FIGURE 2. *Structure of natural gas hydrates formation: a) type I, b) type II*

The higher the density of the gas is, the lower is the hydrate formation pressure. "Heavy" components of natural gas, such as propane and butane, react with hydrate formation at the temperature of 0-4°C and the overpressure of 0.3 MPa. The presence of "germ" crystals promotes the formation of methane hydrate.

The formation of gas hydrates is a process of simultaneous fixation of gas hydrating agent's free molecules and water. Figure 3 shows schematically the formation of an ordered gas hydrate structure of free gas and water molecules, obtained by the innovative method of molecular dynamics simulation, which permits to study the structure and properties of molecules by means of computational methods followed by visualization of the results, and to provide their three-dimensional representation under the conditions given in the calculation.

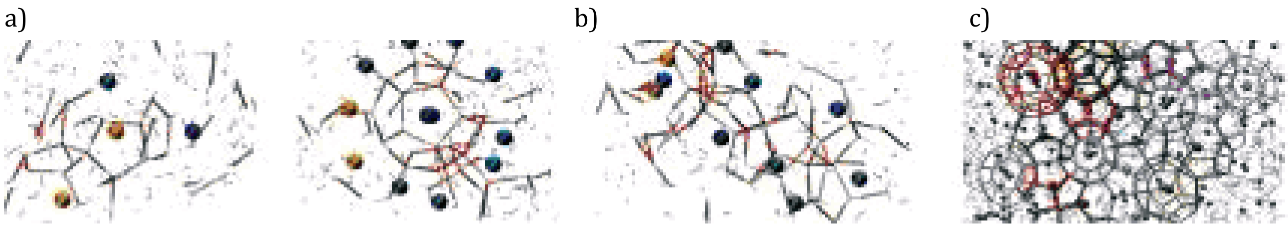

FIGURE 3. *Diagram of the multi-staged gas hydrate formation process: a) free gas and water, b) transient state, c) hydrate*

Formation of hydrate structure is accompanied by fluctuations in the internal energy of the system, while between the states of gas and water in free and bound forms, there is an energy barrier corresponding to the transient state; however, as a whole, the gas hydrates formation is exothermic. Gas hydrates are formed at low temperature and high pressure under the condition of sufficient hydrate gas and water amounts. In the process of hydrate structure formation, specific volume of gas decreases rapidly, it is compressed from the external hydrating agent's pressure to the gas pressure in the hydration state.

Many studies, both in Ukraine [6, 7] and abroad [4], are dedicated to the methodology for determining the equilibrium conditions of simple and complex gas hydrates formation and decomposition, taking into account the hydrate types and their non-stoichiometry. To build a thermodynamic model, the hydrate formation process can be presented in two stages. At the first stage, a blank hydrate lattice is formed out of the pure water; the second stage is its filling.

Conditions of natural gas hydrates formation are determined according to the equilibrium constant by the formula:

$$r = y / K \tag{1}$$

where: r, y – the component's molar fraction in accordance with the hydrate's composition and the gas phase; K – the equilibrium constant.

Hydrates are formed in the following sites:

– in the connectors directly after the gas reduction at the pressure of about 6.5 MPa and at the temperature lower than +17°C;
– in the pipe fitting to separators (with the intense heat emission from the gas stream to the soil);
– in the separators (the flow rate in the inlet ducts of the cyclone separators reaches 120 m/s);
– in the gas flow-lines, gas pipelines, including wells, for industrial gas-separating header;
– in the industrial gas-separating header in the sites of abrupt changes in gas flow velocity;
– at the end of pipeline valves.

The main way to prevent the formation of gas hydrate plugs is gas dehydration. Deep purification of natural gas from water vapor requires expensive equipment and is expensive.

The method of natural gas dehydration, including its separation from the condensed moisture, gas dehydration by means of moisture absorption with concentrated aqueous glycol solution, regeneration of saturated glycol by moisture evaporating from it and condensation of the moisture evaporated.

The main disadvantage of this method is absorbent impurity with salts contained in the condensed moisture that is partially carried up after the primary separation phase to the final dehydration phase.

The method of gas dehydration is an absorption method using the sulfuric acid solution as an absorbent, i.e. it is a method including the direct contact of the gas to be dehydrated and sulfuric acid.

This method possesses so significant drawbacks that it has not found practical use for the purpose of gas dehydration and is only used in laboratory conditions. Its disadvantages are as follows. If it is not difficult to select the necessary sulfuric acid concentration for deep natural gas dehydration, it is almost impossible to implement this process with the support of this composition during the process.

Meanwhile, dependence of water vapor's partial pressure over the acid upon its concentration is so significant that a sufficient acid concentration reduction in the process is unacceptable, because the requirements to the water vapor content in natural gas are not complied with. Regeneration of the acid is associated with its evaporation, the process is complicated enough, expensive and requires special techniques to meet the environmental requirements of production.

There are several ways of destroying gas hydrate plugs. One of the simplest is the method of pressure reducing. Its essence is in violation of hydrate's equilibrium state, resulting in their decomposition. Pressure is lowered in three ways:

– disable the pipeline site where plug has formed, and deflate gas through the "candles" on both sides;
– close the pipeline valve on one side and deflate the gas, accumulated between the plug and one of the closed valves, into the atmosphere;
– disable the pipeline on the both sides of the plug and deflate the gas, concentrated between the plug and one of the closed valves, into the atmosphere.

The disadvantages of this method are considerable duration of the process and emission of gas into the atmosphere, which adversely affects the environment, so it is necessary to develop an alternative method that does not have negative environmental aspect.

Another common method of removing gas hydrate plugs is the use of methanol. Methanol with water vapor, saturate gas, forms alcohol-hydrogenic solutions which freezing temperature is significantly below zero.

Since the amount of water vapor contained in the gas is reduced, the condensation point is decreased, the risk of hydrates setting out is significantly lower.

However, it should be kept in mind that methanol dissolves in water. If it is present in the well, methanol dissolves in it completely and becomes less effective.

Advantages:

- relatively low cost;
- well-developed industrial base;
- production of methanol can be entered directly in the area of consumption;
- there is no need for reagent preparation unit;
- the highest among the known inhibitors anti-hydration activity that is maintained even at low temperatures;
- very low freezing temperature of concentrated methanol solutions and their extremely low viscosity even at temperatures below -50°C;
- relatively low methanol solubility in unstable condensate (especially at the contact of unstable gas condensate with the outspent (saturated) aqueous methanol solution with concentration of less than 50 wt.%);
- non-corrosive methanol and its aqueous solution;
- quite simple process flow sheets of outspent solutions regeneration.
- high efficiency of the reagent not only to prevent hydrate formation, but also to eliminate discontinuous hydrate plugs emerging when technological regime is violated in industrial communications (wells, gas flow-lines, collectors, APO, heat-exchange equipment).

Disadvantages:

- very high toxicity (both as vapor and when getting in contact with skin and inside the body);
- high fire hazard;
- possibility of salts setting out when mixed with strongly mineralized reservoir water and the resulting scaling in industrial communications;
- the effect of accelerated crystal growth in the presence of diluted aqueous solutions of methanol with insufficient concentration to prevent hydrates;
- high elasticity of methanol vapors (normal boiling point is ~65°C), due to that its very high solubility in compressed natural gas and, accordingly, increased specific consumption of methanol.

Conclusions

Gas hydrates are the only undeveloped source of natural gas in the Earth that can provide a real competition to traditional deposits. Significant potential resources of gas in hydrate deposits will permanently provide mankind with high-quality energy feedstock.

Review of the existing methods of gas hydrates decomposition in gas pipelines (removal of gas hydrate plugs) demonstrates the presence of significant technical and environmental problems and the need for research and development of ecologically cleaner methods of gas hydrate plugs removing from distribution gas pipelines of gas-transport systems.

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