UDC 622.276.5

Kudym A.V. master of specialty 185 Oil and gas engineering and technologies
Scientific supervisor: Pashchenko O.A., Ph.D., Associate Professor of the Oil and Gas Engineering and Drilling Department
(Dnipro University of Technology, Dnipro, Ukraine)

COMBAT WITH HYDRATE FORMATION

Crystal hydrates are divided into classes depending on the structure of the crystal lattice and the arrangement of water molecules in its nodes. The compounds of the hydrate group are divided into three types: hydrates of types I and II, which are the most common and often accompany natural gas extraction processes, causing various complications. The third type of hydrates: H structure is rare.

Type I hydrate molecules are characterized by a more obvious structural structure than other compounds. The structure of the crystal lattice is formed by planes, collectively forming a dodecahedron. The planes-faces of crystal hydrate molecules have the shape of a geometrically regular pentahedron.

The next representative of type I hydrates has a tetrahedron (tetrakaidecahedron) as the basis of its crystal structure. The faces of the dodecahedron are inferior in size to the tetrakaidecahedral, in connection with which small and large structural planes are distinguished.

Crystal hydrates of type II are also formed by two types of cells, but they differ in their complicated structure. Cells of the lattice of hydrates are lined up in the form of dodecahedrons and hexahedra, that is, they are dodecahedrons and hexakaidkekahedra, respectively.

Hydrate-forming substances for the structures of types I and II of crystal hydrates are: structures of type I, which are formed due to the placement of molecules of methane (CH_4), ethane (C_2H_6), hydrogen sulfide (H_2S), carbon dioxide (CO_2). The formation of type II hydrates requires the presence of propane (C_3H_8), isobutane (C_4H_{10}), and nitrogen molecules (N_2) in the mixture of compounds.

On the other hand, the chemical properties of substances that are not capable of forming crystal hydrate compounds should be noted. A distinctive feature of such substances is their inability to form hydrogen bonds, even if the molecules are small. First of all, it is worth noting gases that are well soluble in water, examples can be ammonia, hydrogen chloride. And also compounds whose molecules are already connected by hydrogen bonds, examples are methanol, calcium chloride, which prevent the formation of new hydrogen bonds between water molecules.

For quite a long time, it was not possible to reliably study the structure of crystal lattices of hydrates due to their non-stoichiometry. Or otherwise, there is a possibility of the formation of a structure in which vacant cavities will remain, but even the partial absence of hydrate-forming molecules does not affect the stability of the compound. The degree of filling of vacant cavities is determined by the concentration of molecules, but mainly by thermobaric conditions. As mentioned earlier, the process of formation of natural gas hydrates occurs only if the following conditions are met thermobaric conditions prone to hydrate formation (low temperature, high pressure), the presence of a hydrate-forming substance in the mixture, and a sufficient number of water molecules in the system. In addition, the intensity of the hydrate formation process and thermobaric conditions depend on the component composition of natural gas and the characteristics of the three-phase system.

Critical points of hydrate formation are distinguished on the diagram of phase states Rk and R'k are the upper and lower critical points, respectively. The upper critical point is called quadrupole or quadrupole, because thermobaric conditions cause the coexistence in equilibrium of four phases at once: water, gas, crystal hydrates, and condensate. In addition, an increase in temperature above the upper critical point is not accompanied by the formation of hydrates at an arbitrarily high increase in pressure, in which case the gas hydrate former enters the liquid phase and is in equilibrium with water molecules.

The lower critical point of hydrate formation also corresponds to thermobaric conditions under which four phases are in equilibrium: hydrate-forming gas, ice, hydrates, and water. The temperature of this point is close to zero on the Celsius scale, and the pressure of the hydrate decomposition corresponds to the elasticity of the moisture-saturated gas that forms the crystal hydrate. It should be remembered that the formation of crystal hydrates causes the processes of accumulation of solid substances in the cavities of industrial equipment. Accumulations of hydrates are mainly formed in the areas of changes in the geometry of the internal cavity of the equipment: on shut-off valves, chokes. And not in all cases, the zones of formation of crystal hydrates coincide with the areas of accumulation: most often, solid compounds are transported by the flow of the medium, the effect is especially strong in the presence of a liquid phase in the flow. Accumulations of crystal hydrates change the cross-sectional area of the pipeline or completely block it, forming hydrate plugs.

In order to prevent hydrate formation and detect the zone of hydrate formation, it is necessary to control the internal parameters of the gas-liquid mixture: moisture content, pressure, temperature, density of natural gas, component composition, and so on. Based on the given parameters and diagrams of phase states, it is possible to reliably predict the change in pressure and temperature and to determine with a high degree of accuracy the section of the pipeline where the equilibrium parameters of the system are reached.

The main technology for preventing hydrate formation is the injection of an inhibitor into the annular space of the well. The most common reagent is Degitrate 4010 of A and B brands, which serves as an excellent substitute for methanol.

Dehydrate 4010 brands A and B are inhibitors of hydroformation of thermodynamic action, the antiagglomerates of which have a fundamentally different effect - the polymer base prevents the crystallization of microparticles into larger ones and thereby completely prevents the formation of hydrate plugs.

The main reason for this choice is:

1. An alternative to methanol, but at the same time there is no precipitation of salts when mixing with highly mineralized reservoir water;
2. Prevention of hydrate deposits;
3. High duration of effect.

Dosing of Dehydrate 4010 grade A and B of the well is carried out by pumping it into the annular space of the well, in a constant or temporary mode, using a reagent dosing unit (BDR, UDR).

The technology is used in any range of water well production and liquid flow rate from 1 to 300 m^3/day, which is why it has become widely used in oil production.

References:

1. Kozhevnykov, A., Khomenko, V., Liu, B. C., Kamyshatskyi, O., & Pashchenko, O. (2020). The history of gas hydrates studies: From laboratory curiosity to a new fuel alternative. Key Engineering Materials, 844, 49-64.

2. Ratov, B. T., Fedorov, B. V., Khomenko, V. L., Baiboz, A. R., &Korgasbekov, D. R. (2020). Some features of drilling technology with PDC bits. Natsional'nyi Hirnychyi Universytet. Naukovyi Visnyk, (3), 13-18.

3. Ihnatov, A., Koroviaka, Y., Rastsvietaiev, V., &Tokar, L. (2021). Development of the rational bottomhole assemblies of the directed well drilling. In E3S Web of Conferences (Vol. 230, p. 01016). EDP Sciences.