Prevention of hydrates formation in associated petroleum gases by their metanization

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Abstract. The paper presents the method to prevent the formation of hydrates in associated petroleum gases by introducing some amount of methane. The method of calculation of temperature-pressure conditions of hydrate formation taking into account the content of methane in multicomponent gas is developed for practical application. Dependency diagrams of equilibrium conditions of hydrates formation on relative density of associated petroleum gases for methane are presented for express assessment of methane supply influence.

1. Introduction

Petroleum industry tackles various technological and technical tasks related to the prevention of hydrates formation in the production and transportation of associated petroleum gases (APG). These tasks are traditionally bound to the introduction of hydrate-forming inhibitors into the APG flows. Such inhibitors mainly include alcohols, the majority of which represent expensive and toxic substances regenerated after being used in special energy-intensive facilities.

Due to the fact that APG usually has low pressure, when the working pressure does not exceed 1.5-2.0 MPa, the introduction of inhibitors in quantities permitted for recovery units is not always justified from the point of view of energy and operation costs, including losses of such reagents. It should also be mentioned that these toxic substances ultimately appear in the ecosystem.

2. Main part

To reduce energy costs and eliminate toxic inhibitors in the ecosystem it is suggested to exclude their application for further prevention of hydrates formation in low pressure associated gas flows. Instead of chemical inhibitors it is proposed to introduce dehydrated methane into APG flows, with the formation of gas mixture where the equilibrium conditions of hydrate formation are displaced towards higher pressure and lower temperature than those of the initial values [1].

The amount of introduced methane into APG is calculated [2] based on equilibrium equations of hydrate formation, hence, below or above 273.15 K:

\[ P_1 = 0.5 \cdot \sum_{i=1}^{n} \left( Y_i \cdot P_i \right) \]

\[ P_2 = 0.5 \cdot \sum_{i=1}^{n} \left( Y_i \cdot P_{i2} \right) \]

where \( P_1, P_2, P_{i1}, P_{i2} \) – pressure (Pa) of hydrate formation in multicomponent mixture and...
individual gases, respectively, at temperatures $T_1 \leq 273.15 \text{ K}$ and $T_2 > 273.15 \text{ K}$; $Y_i$ – molar fraction of each hydrate-forming component in a mixture.

\[ P_{i_1} = a \cdot T_i^b, \]
\[ P_{i_2} = c \cdot e^{d T_i}, \]

where $e = 2.71828$ – base of the natural logarithm;
$a, b, c, d$ – coefficients defined by experiments are given below.

| Gas              | $a$        | $b$         | $c$         | $d$     |
|------------------|------------|-------------|-------------|---------|
| Methane          | $4 \times 10^{-17}$ | 9.3415     | $10^{-7}$   | 0.1128  |
| Ethane           | $3 \times 10^{-26}$ | 12.8130    | $6 \times 10^{-10}$ | 0.1256  |
| Propane          | $2 \times 10^{-28}$ | 13.4980    | $8 \times 10^{-20}$ | 0.2052  |
| i-butane         | $2 \times 10^{-32}$ | 15.0760    | $3 \times 10^{-20}$ | 0.2078  |
| Dioxide          | $10^{-21}$  | 11.0890     | $8 \times 10^{-10}$ | 0.1281  |
| Hydrogen sulphide| $10^{-23}$  | 11.4690     | $2 \times 10^{-8}$ | 0.1064  |
| Nitrogen         | $2 \times 10^{-12}$ | 7.7171     | $10^{-8}$   | 0.1015  |
| Argon            | $8 \times 10^{-12}$ | 7.4047     | $10^{-7}$   | 0.1168  |
| Krypton          | $5 \times 10^{-26}$ | 12.8900    | $2 \times 10^{-6}$ | 0.0990  |
| Xenon            | $2 \times 10^{-24}$ | 11.8380    | $3 \times 10^{-7}$ | 0.0993  |

3. Results

The figure shows the calculated diagrams of equilibrium pressure-temperature conditions of hydrates formation in associated petroleum and natural gases depending on their relative density for methane. It is clear that with the increase of methane concentration in a multicomponent mixture, the equilibrium conditions of hydrate formation are displaced towards higher pressure and lower temperature. The given graphic dependences are used for express assessment of methane supply influence, and expressions (1) – (4) – for precise calculation of its quantity.
For example, in field conditions the water-saturated associated petroleum multicomponent gas is transported through a gathering line to the installation to be prepared for its further transportation. The pipeline pressure is maintained within 0.3 MPa. The petroleum gas is transported during summer at positive temperatures higher than 273 K, and in autumn, spring and especially in winter the pipeline temperature may drop to 263 K, thus causing a risk of hydrates formation. To prevent this, methane is additionally injected into the associated petroleum multicomponent gas, where the hydrates are formed at higher pressure and lower temperature than those than in the initial system. The methane is introduced in the amount of 25-30% wt. of the amount of initial petroleum gas. The hydrates in the obtained mixture may only be formed at a temperature of 260 K and at a pressure of 0.4 – 0.45 MPa. Thus, the obtained mixture does not lead to hydrates formation under initial pressure-temperature conditions.

4. Conclusions
Using results of the given study, it is possible:
- to use methane as an inhibitor to prevent hydrates formation in APG;
- to calculate the precise amount of methane introduced into APG for this purpose;
- to exclude negative impact of toxic inhibitors on the ecosystem.
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References
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