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GAS HYDRATE FORMATION AND ITS PREVENTION IN GAS-FIELD OPERATIONS

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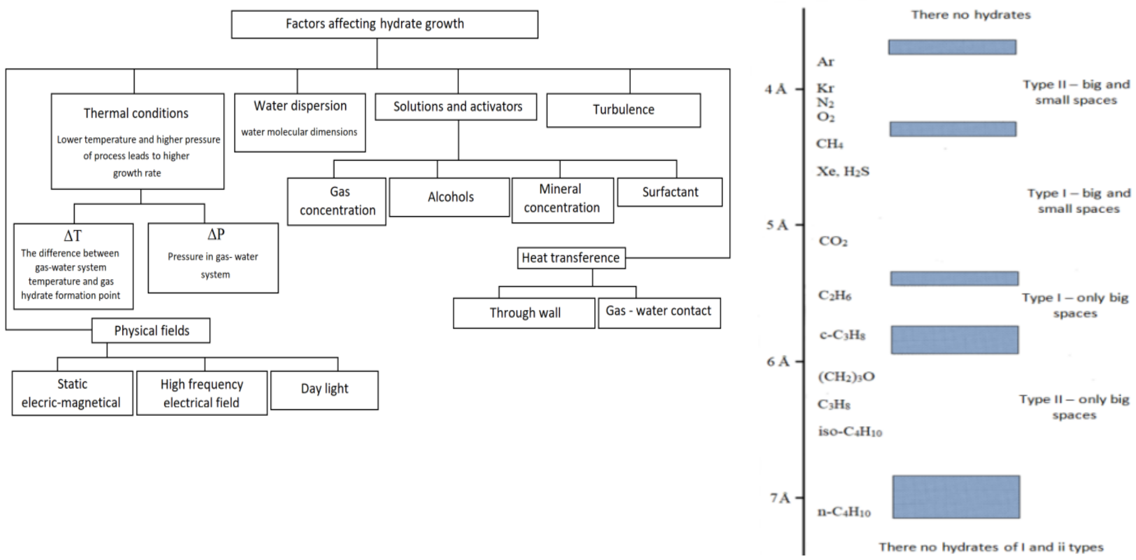
Gas hydrate formation is the one of negative factors in gas production. It reduces service operating life of the gas-gathering main and decreases its capacity; hydrate formation complicates or makes refining process impossible, decreases efficiency of gas transportation, and leads to emergencies in the field facilities. All these necessitate studying the mechanism of gas hydrate formation and choosing methods for its prevention and elimination.

Factors affecting formation time of gas hydrate formation rate and molecular dimension dependence on the gas hydrate structure

Three conditions are obligatory for gas hydrate formation in the pipelines: certain temperature and pressure, an agent which can create a hydrate structure and enough amount of water. Growth rate of gas hydrate formation depends on some factors shown in Figure 1 (a).



a) ***b)***

Fig. 1 The classification of main factors affecting hydrate growth rate of natural and oil gas (a) and molecular dimensions dependence on the gas hydrate type 1Å = 10-10 m (b)

Scheme in Figure 1 (b) shows the dependence between molecular dimensions and hydrate structures. According to this scheme, a molecule having a diameter more than 3.8 Å (hydrogen, helium) and less than 7 Å (C5, C6 and more) can't form any gas hydrate structure. The main components of natural gas (methane, ethane) form the hydrate structure I.

Calculations of gas hydrate formation probability and estimates of temperature and pressure distribution

We can use the formula (1) for determining possible hydrate formation in some sections of pipelines and gas hydrate formation point of hydrate development.

$$\Delta = {\mu_w}^{\alpha} - {\mu_w}^{H} = {\mu_w}^{\beta-H} - {\mu_w}^{\beta-\alpha} =$$

$$= \ln a_w - R_\mu T\left(\sum_{i=1}^{2} v_i \ln\left(1-\sum_{j=1}^{C}\theta_{ij}\right) - \frac{\Delta\mu_w^0}{R_\mu T_0} + \int_{T_0}^{T}\frac{\Delta H_w}{R_\mu T^2}dT - \int_0^p \frac{\Delta V_w}{R_\mu T}dp\right) \quad (1)$$

if $\mu^{\alpha} - \mu^{H} > 0$, it is possible to have gas hydrate formed in pipeline section under study; if $\mu^{\alpha} - \mu^{H} < 0$ it is not possible; if $\mu^{\alpha} - \mu^{H} = 0$, there is an equal balance, as rule there is no case in industry, this is theoretical case for unreal conditions.

In order to use the formula (1), we need to know temperature and pressure distribution along the entire pipeline section. This formula is often used for determining gas hydrates either in wells or pipeline sections. Improved exponential dependence (2-3) can be used to estimate temperature and pressure along the pipeline under study.

$$T_{k+1} = T_{out} + (T_k - T_{out})\left(\frac{\sqrt{L}+\alpha}{\alpha}\right)^{\alpha\beta} \cdot e^{-\beta\sqrt{L}} \quad (2)$$

$$p_{k+1} = \frac{p_k}{2T_k}\left(T_k - T_{k+1} + \sqrt{(T_k - T_{k+1})^2 + 4T_k\left(T_{k+1} - \frac{S_k}{{p_k}^2}\right)}\right) \quad (3)$$

Kinetic hydrate inhibitors (KHI) application

In order to replace standart methanol, many companies are looking for the alternative ways to prevent hydrate formation using kinetic inhibitors. One of the commonly used substances for making inhibitor solution is polyvinyl caproloktam (PVCap). In addition, interpolymer with PVP (polyvinyl pyrrolidone) shown in Figure 2 can be applied instead. These substances were studied either in the laboratory or in the field. In the first case, they were found in commercial solutions Luvicap 55W and Luvicap EG produced by BASF Company (Germany). Luvicap 55W is interpolymer of PVCap and PVP in 55% water solution, whereas Luvicap EG is solution of PVCap in MEG. The results of studies are presented in Table 1.

Table 1

Researches of kinetic inhibitor based on PVCap

Research technique	Results
In the laboratory (commercial Luvicap 55W, Luvicap EG)	KHI allows preventing hydrate formation during 48 hours, with temperature difference being 13°C. It takes 0.5 - 1 % kinetic inhibitor concentration. In comparison, methanol needs ten times more, about 6 – 30 % in the same condition. KHI is less poisonous and doesn't require high expenses. KHI is not applicable to prevent hydrate formation under permafrost and low temperatures conditions. In that case methanol is more effective.
In the field (inhibitor based on PVP)	According to the previous estimate, if methanol is replaced by KHI, it can lead to expenses decrease in 7-8 times. For wells drilled at high hydrogen sulfide deposits, it is necessary to use methanol instead of KHI during certain periods.

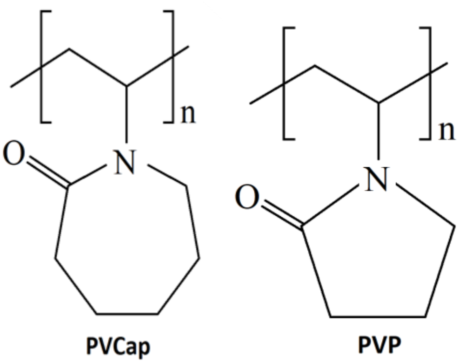


Fig. 2 Chemical structure of main components of KHI

It is necessary to know properties of gas hydrate to choose proper prevention and elimination methods and be able to calculate conditions for gas hydrate formation. Studying hydrate formation mechanism allows creating new methods or improving current ones. It is possible to replace standartl methanol by more beneficial kinetic hydrate inhibitor under certain conditions.

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