Influence of the Model Stratum Water Mineralization on the Process of Carbon Dioxide and Natural Gas Hydrates Formation

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Abstract. The paper presents the results of an experimental study of the natural gas and carbon dioxide hydrates formation in a calcium chloride solution. It was found that the gas saturation of hydrates formed from natural gas and carbon dioxide in 15 mass. % calcium chloride solution, 3 and 4 times less, respectively, of the gas saturation of hydrates obtained in distilled water. The rate of gas hydrates formation in a calcium chloride solution is slightly higher than this one in distilled water.

1. Introduction

Currently, environmental aspects of rational subsoil use are a priority all over the world, so the development of new environmentally friendly technologies is an urgent task. The authors of [1] substantiated the idea of the carbon dioxide (CO₂) utilization and storage upon extraction of methane (CH₄) from deep-sea hydrated deposits. The idea is based on the premise that replacing CH₄ with CO₂ is a favorable process that will maintain the stability of the seabed during and after the substitution of methane for carbon dioxide, thus reducing environmental impact. In this regard, studies are carried out on the substitution of CH₄ / CO₂ in laboratory experimental installations [2], with the addition of various hydration promoters [3-4] in order to study the effect on the carbon dioxide hydrate formation. In addition, experimental studies are carried out on the kinetics of the CO₂ hydrate formation during the movement of a hydrate-forming medium through a high-pressure pipeline [5].

The authors of [6] proposed a project for temporary underground storage of the natural gas under permafrost conditions in the form of hydrate deposits. So, after the natural gas extraction from temporary storage facilities, instead of natural gas, for example, flue gases can be disposed of and stored [7]. The natural gas and carbon dioxide conversion into hydrates is possible in moist dispersed rocks, which in real conditions contain stratum water. For example, in the deposits of Yakutia, the chloride-calcium type of stratum water prevails with a salinity up to 390 g/l [8]. To assess the effect of water mineralization on the natural gas and carbon dioxide hydrate formation process, it is necessary to conduct targeted experiments with the calculation of the hydrate formation rate, as far as we know, this topic has not been studied much.

Thus, the aim of the work was to study the natural gas and carbon dioxide hydrates formation in model stratum water of calcium chloride type.
2. Experimental part
Obtaining hydrates was carried out in a solution of calcium chloride with a concentration of 15 wt.%. Pure carbon dioxide (99.99%) and natural gas from the Srednevilyuyskoye gas and condensate field were used as hydrate-forming gases. The natural gas composition (table. 1) was determined by gas adsorption chromatography according to GOST 31371.7-2008.

| Components | CH₄ | C₂H₆ | C₃H₈ | i-C₄H₁₀ | n-C₄H₁₀ | N₂ | CO₂ |
|------------|-----|------|------|---------|---------|----|-----|
| Content, vol.% | 93,9 | 4,44 | 1,10 | 0,087 | 0,108 | 0,33 | 0,0559 |

In laboratory conditions, natural gas hydrates in a solution of calcium chloride were obtained at a temperature of 278.15 K and an initial pressure of 8 MPa, and carbon dioxide hydrates at an initial pressure of 4 MPa. The experiments were carried out at the same time in 4 high-pressure chambers under static conditions according to the procedure [9].

Based on the obtained experimental data, the dependences of the pressure change in the chambers versus time were constructed (Fig. 2). It is shown that in time the experiment can be divided into two stages with different durations: the first of intensive pressure reduction due to cooling of the system and dissolution of the gas in solution; and a second, longer, smooth pressure drop due to the formation of gas hydrates.

![Figure 1](image1.jpg)

**Figure 1.** The dependence of the change in pressure in the chambers versus time:
a - for a system with natural gas, b - for carbon dioxide.

Also, to determine the P, T-conditions of the onset of hydrate formation, the dependences of the pressure in the chambers versus the temperature were constructed (Fig. 3).

![Figure 2](image2.jpg)

![Figure 3](image3.jpg)
Figure 2. Dependence of gas pressure in chambers versus temperature: A - natural gas hydrates, B - carbon dioxide hydrates, (1) from distilled water, (2) from 15 mass% calcium chloride solution.

It was established that during the cooling of the chambers, the hydrate formation was not detected, and the characteristic kink of the curve indicating the beginning of the hydrate formation process corresponds to a given experiment temperature equal to 278.15 K, both in the case of the natural gas and carbon dioxide. The influence of the hydrate formation medium mineralization on the solubility of gases in it was also determined. It is shown that under the conditions of the experiment, the solubility of the gas in the mineralized solution decreases by 8.6% for natural gas, and 3.6% for carbon dioxide. At the same time, the magnitude of the pressure change that occurred after reaching the set experiment temperature is a quantitative estimate of the gas saturation of the resulting hydrates.

Based on the foregoing, in this case we can not consider data related to the cooling stage, but use only those data that reflect the stage of the hydrate formation. This assumption will surely distort the true value of the gas bound to the hydrate, since it does not take into account the amount of the gas dissolved in the hydrate formation medium, but for comparative analysis of the experimental results of the with each other, this method is applicable, provided that the difference in solubility of the gases in distilled water and 15 wt% calcium chloride solution in the calculations of hydrate formation parameters is taken into account.

Therefore, based on the data related to the stage of the hydrate formation, the volumes of the gas bound into the hydrate were calculated (Fig. 3), the gas saturation of the obtained hydrates, and the rate of their formation according to the procedure [10], presented in Table 2.

Figure 3. The dependence of the volume of gas bound into hydrates as a function of time: a - for a system with natural gas, b - for carbon dioxide.

Figure 3 shows the time dependences of the volume of the gas bound into hydrates for both systems under consideration. During the carbon dioxide hydrates formation in the first 50 hours of the experiment, the hydrate formation does not occur, which indicates a process with a certain induction period, the duration of which does not depend on the salinity of the initial solution. The formation of the natural gas hydrates begins from the observation moment without an induction period. At the same
time, the intensity of the gas binding to the hydrate in the system with a solution of calcium chloride at the initial stage is higher than during the formation of hydrates from distilled water.

Table 2. The rate of the hydrate formation and the parameters of the obtained natural gas and carbon dioxide hydrates.

| Characteristic                              | Natural gas | CO₂                      |
|---------------------------------------------|-------------|--------------------------|
|                                             | Dist. water | 15 mass% CaCl₂ Dist. water | 15 mass% CaCl₂ |
| The volume of the gas bound to the hydrate, dm³ | 5,89        | 2,12                     | 3,03           | 0,79          |
| Gas saturation of the hydrate, %            | 36,85       | 13,25                    | 18,93          | 4,94          |
| The average rate of the hydrate formation, mol / s * 10⁻⁵ | 186,23      | 226,55                   | 6,32           | 6,94          |

It was established that the presence of calcium chloride in the hydrate formation medium leads to a significant decrease in the gas saturation of the resulting hydrates. Thus, the gas saturation of hydrates formed from natural gas decreased by more than 2.8 times, and carbon hydrates by 3.8 times. Moreover, the rate of the gas hydrates formation from a mineralized solution is slightly higher than the hydrates formation rate from distilled water in both cases. The increase in the rate of the hydrate formation in mineralized solutions is attributed to the presence of structured water formed during hydration of calcium chloride, which facilitates the hydrate formation process and thereby shortens the nucleation period during the natural gas and carbon dioxide hydrates formation.

Thus, it was found that under the given experimental conditions, natural gas and carbon dioxide hydrates do not form during the cooling of the reactors, and the hydrates formation begins only when the set temperature of 278.15 K is reached in all considered cases. It was determined that under the conditions of the experiment, the solubility of the gas in the mineralized solution decreases by 8.6% for natural gas, and 3.6% for carbon dioxide. It is also shown that the gas saturation of hydrates formed by natural gas and carbon dioxide and a 15 mass% solution of calcium chloride is 3 and 4 times less, respectively, of the gas saturation of hydrates obtained from distilled water. The rate of gas hydrates formation from the mineralized solution is slightly higher than the rate of hydrates formation from distilled water. Therefore, model stratum water, using the example of a 15 mass% solution of calcium chloride, under the given conditions of the hydrate formation, exhibits the properties of an inhibitor in the formation of natural gas and carbon dioxide hydrates.

3. References

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