Experimental Study of the Effects of Various Intensifiers on the Process of Methane Replacement with Carbon Dioxide in Gas Hydrate

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Abstract. The experimental data of replacement of methane with carbon dioxide in gas hydrate using various intensifiers of the substitution process are represented in this article. When nitrogen was used as the gas of the intensifier of the substitution process, a growth of 15% in the volume of carbon dioxide substituted for methane was revealed in a 30/70% ratio for the same period of time and the same experimental conditions. When atmospheric air was used as a gas intensifier for the substitution process, as a cheaper alternative component, a 36% increase was detected in the volume of carbon dioxide that replaced methane at a ratio for the same period of time and the same experimental conditions. When applying thermal stimulation and substitution using preheated carbon dioxide, the growth was 44% and 52%, respectively.

1. Introduction
Gas hydrates is concentrated form of gas storage. One cubic meter of gas hydrate can contain up to 164 cubic meters of gas [1]. A large concentration of natural gas in the form of hydrates can be a very attractive source of energy if it can be dissociated in an environmentally friendly way for the production of gas and its delivery to the market.

Now days, there is interest in gas hydrates as energy sources in countries that do not have their own conventional sources of natural gas, such as Japan, China, Canada, the Netherlands and India. These countries are conducting research on gas hydrate development technologies. Trial development of gas hydrate deposits is underway. In May 2017, Japan Oil, Gas and Metals Corp. did a test production of natural gas from methane hydrate deposits in the Nanai fault off the eastern coast of Japan. Estimated gas reserves are 1.1 trillion m3 of gas. In the same year, Chinese oil industry workers produced test production of natural gas from gas hydrate deposits in the South China Sea. The production of natural gas from gas hydrate deposits is today one of the most technologically challenging procedures in the oil and gas industry. There is a wide range of problems: from the clogging of mining equipment with sand, to the possibility of uncontrolled dissociation.
2. Experimental equipment
All measurements are carried out with the high precision French equipment Fluid Eval Autoclave GHA from Vinci Technology.

The laboratory facility consists of two main parts:
- Thermostatic bath;
- Cell: stainless steel cylinder with a volume of 250 cm³, upper end with fitting connections, stereoscopic camera, thermocouple, digital manometer, safety valve, exhaust and inlet valves, magnetic stirrer, set of magnetic stirrers, outlet.

OPTIONAL EQUIPMENT
- The BTSP piston pump is used to monitor the water level is injected into the cell.
- A RD.2D vacuum pump with blades in the oil bath made from DVP Vacuum technologies is used to extract air from the cell.
- A gas booster model DLE 75-1 (Vinci Technologies, France) used for gas injection.
- To control the temperature of the thermostatic bath used the Huber MPC submersible cooler in conjunction with the Unichiller MRC (regulator).

Figure 1. Schematic diagram of the experiment on the replacement of CH₄ by CO₂ in gas hydrate. 1 - thermostatic bath; 2 - the GHA cell; 3 - mesh cell; 4 - thermostat; 5 - thermocouple; 6 - upper connection port; 7 - lower connection port; 8 - manometer; 9 - needle valve; 10 - rheometer; 11 - gas booster DLE 75-1; 12 - cylinder with CO₂.

3. Experimental description

3.1. Experimental study of gas hydrate formation
In order to simulate a gas hydrate deposit, a mesh metal cell filled with fine-grained quartz sand of a fraction of 0.3-0.6 mm in the amount of 100 g was constructed. The sand was placed in a 20 cm³ hand-made iron mesh cylindrical container shown in Figure 2. The sand was compacted until a porosity coefficient of 0.72 is reached.
Using the data obtained in [2], a simulation of the conditions of the existence of a gas hydrate field in northern Alaska was carried. Field conditions: reservoir type - sandstone, temperature - 5 °C, pressure - 7.3 MPa, thickness - 9.1 m, hydrate saturation - 72%.

The sand was moistened to 20% with demineralized water and then placed in the steel cell of the GHA Autoclave, described in detail in chapter 2 of this thesis. The cell was sealed, air was evacuated using a vacuum pump for 10 minutes. The cell temperature was kept in the region of 15 °C in order to avoid hydrate formation during the subsequent injection of methane hydrate. Then methane was fed into the cell until a pressure of 4.5 MPa was reached and was maintained for several seconds to compensate the amount of gas dissolved in water. After that, two different experiments were carried out.

In the first experiment, the temperature was dropped to 0 °C and was maintained for 12 hours. Then the system returned to its original state outside the hydrate formation line and was maintained until the hydrate was completely dissociated. The data are presented in Figure 3.

**Figure 2.** Metal mesh container with send for simulating a gas hydrate reservoir.

**Figure 3.** Measurement of pressure and temperature during the experiment.
As a result of the experiment, experimental data were obtained that made it possible to estimate the amount of substance that went into the formation of gas hydrate by measuring the difference in pressure and temperature in the system. The calculations were carried out according to the Klaiperon-Mendeleev equations, where the amount of substance was calculated as part of the hydrate formation and decomposition processes. The results are presented in table form on table 1.

**Table 1.** Calculation of the amount of basics transferred to the formation of gas hydrate.

|               | Pressure, Pa | Temperature, K° | Amount, Mol | Gas volume, L |
|---------------|--------------|-----------------|-------------|---------------|
| **Exp Start** | 4212000      | 288,1           | 0,43961762  | -             |
| **Exp End**   | 3850000      | 274,5           | 0,42174347  | -             |
| **Volume difference** | -      | -               | 0,01787415  | 0,40038       |

In second experiment, the hydrate formation process was intensified by conducting a thermal cycling process. After the cell was loaded with gas, the temperature of the system was cyclically decreased and increased into the boundaries of the existence of methane hydrate, according to the graph presented in Figure 4. The obtained pressure and temperature data during the experiment are presented in Figure 5.

**Figure 4.** Experiment condition. **Figure 5.** Measurement of pressure and temperature during the experiment.

As a result of the experiments, experimental data were obtained that made it possible to estimate the amount of substances measured depending on the pressures and temperatures in the system. Calculations of derivatives according to the Kliiperon-Mendeleev equations, where the amount of substances was calculated as part of the hydrate formation and decomposition processes. The results are presented in table form in table 2.

**Table 2.** Calculation of the amount of basics transferred to the formation of gas hydrate.

|               | Pressure, Pa | Temperature, K° | Amount, Mol | Gas volume, L |
|---------------|--------------|-----------------|-------------|---------------|
| **Exp Start** | 4207000      | 287,9           | 0,43940079  | -             |
| **Exp End**   | 3705000      | 273             | 0,40808963  | -             |
| **Volume difference** | -      | -               | 0,03131117  | 0,70137021    |
3.2. Experimental study of gas hydrate replacement by carbon dioxide
The formation of methane hydrate took place under the conditions described in the second paragraph of chapter 3.1, using thermal cycling. After completion of the hydrate formation process, the system was cooled to -10 °C, then methane was lowered into the atmosphere and the cell was evacuated for 3 minutes. Then, pre-compressed and heated CO2 was injected into the system till the pressure reached 2.5 MPa. Then the cell was kept at a temperature of -10 C for 54 hours for the course of the substitution reaction. The Macro connected to the sensors made marks in the table and plotted in real time, with an interval of 15 minutes. After a specified period of time, the cell was evacuated, heated to +25, allowing the hydrated structure to completely dissociate. Then, a chromatography of the gas mixture obtained by decomposition of the hydrate was carried out. The results are presented in table 3, the dependence of pressure on temperature is presented in figure 6.

| Component | Square | Concentration,% |
|-----------|--------|-----------------|
| C2H6      | 1017889 | 2.83952        |
| C3H8      | 16221.5 | 0.03059        |
| i-C4H10   | 2966.34 | 0.00423        |
| i-C5H12   | 206.548 | 0.00023        |
| O2+Ar     | 114.066 | 0.06481        |
| N2        | 778.113 | 0.42343        |
| CH4-2     | 77692.1 | 57.93148       |
| CO2       | 494851  | 37.26317       |

Figure 6. Measurement of pressure and temperature during the experiment.

3.3. Experimental study of gas hydrate replacement by carbon dioxide and nitrogen as intensifier
The formation of methane hydrate took place under the conditions described in the second paragraph of chapter 3.1, by using thermal cycling. After completion of the hydrate formation process, the system was cooled to -10 °C, then methane was lowered into the atmosphere and the cell was evacuated for 3 minutes. Then CO2 was injected into the system or, in the second case, a pre-prepared mixture of CO2 / N2 in a ratio of 70/30% up to the pressure of 2.5 MPa to avoid liquefaction of carbon dioxide. Then the cell was maintained at a temperature of -10 C for 54 and 94 hours for each experiment, respectively, for the course of the substitution reaction. The Macro connected to the sensors made marks in the table and plotted in real time, with an interval of 15 minutes. After a specified period of time, the cell was evacuated, heated to +25, allowing the hydrated structure to
completely dissociate. Then, a chromatography of the gas mixture obtained by decomposition of the hydrate was carried out. The results are presented in table 4.

Table 4. Chromatogram of gas mixture a result of decomposition of gas hydrates.

| Component | Square | Concentration, % |
|-----------|--------|------------------|
| C2H6      | 1017889| 2.83952          |
| C3H8      | 16221.5| 0.03059          |
| i-C4H10   | 2966.34| 0.00423          |
| i-C5H12   | 206.548| 0.00023          |
| O2+Ar     | 114.066| 0.06481          |
| N2        | 778.113| 0.42343          |
| CH4-2     | 77692.1| 57.93148         |
| CO2       | 494851 | 37.26317         |

| Component | Square | Concentration, % |
|-----------|--------|------------------|
| C2H6      | 1270866.767| 3.53238 |
| C3H8      | 31194.821 | 0.05861          |
| C4H10     | 2992.788  | 0.00425          |
| C5H12     | 38.085   | 0.00004          |
| O2+Ar     | 159.792  | 0.09046          |
| N2        | 3942.377 | 2.13759          |
| CH4-2     | 85472.239| 52.84977         |
| CO2       | 421553.170| 43.90145        |

Table 4 should be read as follows: a) Chromatographic analysis of decomposition products of hydrate after replacement (CO2) after 54 hours of experiment b) Chromatographic analysis of decomposition products of hydrate after replacement (CO2 + N2) after 54 hours of experiment c) Chromatographic analysis of decomposition products hydrate after replacement (CO2) after 94 hours of experiment d) The result of chromatographic analysis of the decomposition products of hydrate after replacement (CO + N2) after 94 hours of experiment.

3.4. Experimental study of gas hydrate replacement by oxygen as intensifier

The formation of methane hydrate was carried out according to the method described in the first paragraph of chapter 2.1, using pressure reduction and was maintained for 12 hours. Pure methane was used, the moisture amount of the sand was 23.2%. After completion of the hydrate formation process, the system remained the temperature at 0 °C, then methane was released into the atmosphere. The cell was not evacuated. Then, a pre-prepared mixture of CO2 and atmospheric air was injected into the system, the results of chromatographic analysis of the mixture are presented in Table 5 to a pressure of 3.1 MPa.

Table 5. Chromatogram of gas hydration gas.

| Component | Square | Concentration, % |
|-----------|--------|------------------|
| CO2       | 443655 | 79.2135          |
| O2        | 1028   | 1.0450           |
| N2        | 30115  | 20.0053          |

Then, the cell temperature was maintained at the same level for 54 hours. The pressure was not maintained. Macros connected to sensors made marks in the table and compiled diagrams in real time, with an interval of 1 minute. A diagram of the dependence of pressure and temperature on time throughout the experiment is presented in Figure 7.
Figure 7. Measurement of pressure and temperature during the experiment.

After a specified period of time, the cell was evacuated, the temperature increased to +20, allowing the hydrated structure to completely dissociate [4]. Then, a chromatographic analysis of the gas mixture obtained by decomposition of the hydrate was carried out. The results of chromatographic analysis of the decomposition products of the hydrate after the substitution are presented in table 6.

Table 6. Chromatogram of gas mixture a result of decomposition of gas hydrates.

| Component | Square | Concentration, % |
|-----------|--------|------------------|
| CO2       | 6321854| 59.044           |
| O2        | 43438  | 0.441            |
| N2        | 391925 | 3.897            |
| CH4       | 2667859| 36.617           |

3.5. Experimental study of gas hydrate replacement by oxygen with thermostimulation

The formation of methane hydrate was carried out according to the method described in the first paragraph of chapter 3.1, by using pressure reduction and maintaining for 8 hours. Pure methane was used, the moisture amount of the sand was 23.2%. After completion of the hydrate formation process, the system remained in the process of maintaining the temperature at 0 °C, then methane was released into the atmosphere. The cell was not evacuated. Then, CO2 was injected into the system till a pressure of 3.1 MPa was reached and remained in this state for 4 hours. Then the temperature was increased to 6 °C and was maintained for two hours. After that, the temperature of the system returned to its initial state of 0 °C and was maintained for 44 hours. Pressure support was not carried out. Macros connected to sensors made marks in the table and compiled diagrams in real time, with an interval of 1 minute. A diagram of the dependence of pressure and temperature on time throughout the experiment is presented in Figure 8.
Figure 8. Measurement of pressure and temperature during the experiment.

After a specified period of time, the cell was evacuated, the temperature increased to +20, allowing the hydrated structure to completely dissociate. Then, a chromatography of the gas mixture obtained by decomposition of the hydrate was carried out. The results of chromatographic analysis of the decomposition products of the hydrate after the substitution are presented in Table 7.

Table 7. Chromatogram of gas mixture a result of decomposition of gas hydrates.

| Component | Square | Concentration, % |
|-----------|--------|-----------------|
| CO2       | 443655 | 67.0898225      |
| O2        | 167    | 0.021606        |
| N2        | 1028   | 0.16020449      |
| CH4       | 30115  | 32.72837239     |

3.6. Experimental study of gas hydrate replacement by overheated carbon dioxide

The formation of methane hydrate took place under the conditions described in the second paragraph of chapter 3.1, by using thermal cycling. Natural gas was used to form the hydrate, the results of the chromatographic analysis of which are presented in Table 8. The sand was moistened to 80% and then frozen.

Table 8. Chromatogram of gas hydration gas.

| Component | Square | Concentration, % |
|-----------|--------|-----------------|
| O2+Ar     | 1.66   | 0.158264        |
| N2        | 2.65   | 1.493001        |
| CH4       | 3.68   | 98.443169       |
| C2H6      | 5.56   | 1.971962        |
| C3H8      | 10.18  | 0.021585        |
| C4H10     | 13.68  | 0.002239        |
After the hydrate formation process was completed, the system was cooled to -10 °C, then methane was lowered into the atmosphere and the cell was evacuated for 3 minutes. Then, pre-compressed and heated CO2 was injected into the system to a pressure of 2.5 MPa. Then the cell was kept at a temperature of -10 C for 54 hours for the course of the substitution reaction. The Macro connected to the sensors made marks in the table and plotted in real time, with an interval of 15 minutes. After a specified period of time, the cell was evacuated, heated to +25, allowing the hydrated structure to completely dissociate. Then, a chromatography of the gas mixture obtained by decomposition of the hydrate was carried out. The results are presented in table 9, Pressure-temperature diagram is presented in figure 9.

Table 9. Chromatogram of gas mixture a result of decomposition of gas hydrates.

| Component | Square | Concentration, % |
|-----------|--------|-----------------|
| C2H6      | 1017889| 1.93952         |
| C3H8      | 16221.5| 0.03059         |
| i-C4H10   | 2966.34| 0.00423         |
| i-C5H12   | 206.548| 0.00023         |
| O2+Ar     | 114.066| 0.06481         |
| N2        | 778.113| 0.42343         |
| CH4·2     | 77692.1| 23.05148        |
| CO2       | 494851 | 77.95317        |

![Figure 9](image-url). Measurement of pressure and temperature during the experiment.

4. Experimental discussion
As a result of the work carried out, methods of intensifying the process of replacing methane with carbon dioxide in gas hydrates using inert gases such as nitrogen and oxygen were investigated. A series of experiments were conducted with a duration of 54 and 94 hours. Figure 10 shows the combined percentage substitution diagram as a result of the experiment with an indication of the intensifier gas.
Figure 10. Diagram of percentage displacement of methane by carbon dioxide depending on the intensifier gas used.

The experimental data obtained in the course of the work described in chapter 3.3 of this dissertation suggest that it takes more than 150 hours to carry out the methane substitution reaction with carbon dioxide. When nitrogen is added to carbon dioxide in a ratio of 70/30, the reaction rate increases by 15%, regardless of the length of the experiment. The data are the same for the control group of experiments lasting 54 hours, and for a series of experiments lasting 94 hours. When atmospheric air is added to carbon dioxide in a ratio of 20/80% during the methane substitution reaction in gas hydrate, the reaction rate increases by 36%.

In the course of the work, methods of intensifying the process of replacing methane with carbon dioxide in gas hydrates, such as thermal stimulation and the use of superheated carbon dioxide, described in chapters 3.5 and 3.6 of this dissertation, were also investigated. A summary diagram of the comparison of all methods of intensification of substitution processes investigated in the work is presented in Figure 11.

Figure 11. Comparative analysis of ways to intensify the processes of substitution of methane with carbon dioxide in gas hydrate.

Based on a comparative analysis, it is concluded that the use of thermal stimulation during the process of replacing methane with carbon dioxide in methane hydrate, described in detail in chapter 3.5 of this thesis, accelerates the replacement process by 44.4% and the use of superheated carbon dioxide accelerates the replacement process by 51.6%.

The use of a mixture of atmospheric air and carbon dioxide as a product for the replacement of methane in gas hydrate is more effective in view of the cost of raw materials.
5. Conclusions
The relevance of the study of gas hydrates and technologies for developing gas hydrate deposits in the near future is becoming increasingly urgent in connection with the increase in human consumption of natural gas as the main source of energy. In 2018, consumption growth amounted to about 20% [4]. With these increases in consumption and depleting reserves of conventional gas fields, the issue of developing gas hydrate deposits will soon become an issue.

Among the proposed methods by world science for the development of gas hydrate deposits (decompression, heat supply and the injection of inhibitors), the substitution of methane in gas hydrates using carbon dioxide is also the most promising from an environmental point of view. In many modern works, there is a statement of the fact of an increase in the global temperature of the planet, thawing of glaciers in the Arctic zone and the displacement of warm ocean currents. Concerning these facts, for the next century, the technology of "substitution" may become the key, both from the point of view of the industrial "burial" of carbon dioxide emitted by civilization, and from the point of view of preventing the "shot of a hydrated gun" that will occur when the temperature of the oval deposits reaches the decomposition point methane hydrate.

The technology of developing gas hydrate deposits by replacing methane with carbon dioxide in hydrate is quite long in time. The main methods of intensification of this process are considered in the work, a number of unique laboratory experiments are carried out, some patterns are deduced.

A number of experiments were carried out on the formation of gas hydrates using various techniques, such as lowering the temperature and thermal stimulation. After calculating the amount of gas transferred to the hydrate, an increase of 43% was detected in the volume of the gas transferred to the hydrate form using thermal stimulation technology.

A series of experiments was carried out on the replacement of methane with carbon dioxide in gas hydrate using various intensifiers of the substitution process. Obtained data in previous work [3] was supplemented. When nitrogen was used as the gas of the intensifier of the substitution process, a growth of 15% in the volume of carbon dioxide substituted for methane was revealed at a ratio for the same period of time and the same experimental conditions. When atmospheric air was used as a gas intensifier for the substitution process, as a cheaper alternative component, a 36% increase was detected in the volume of carbon dioxide that replaced methane in a 30/70% ratio for the same period of time and the same experimental conditions. When applying thermal stimulation and substitution using preheated carbon dioxide, the growth was 44% and 52%, respectively.

From the point of view of the mechanics of the process, substitution of methane with carbon dioxide in the hydrate is the most beneficial. However, the use of such a technology is not profitable from an economic point of view, as well as from an environmental point of view. The application of heat to the hydrated reservoir may cause an uncontrolled chain reaction of dissociation of methane hydrate.

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