

## Peculiarities of Methane Hydrate Formation/Dissociation P/T Conditions in Sediments of Different Composition

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New experimental data on hydrate formation and dissociation in artificially methane-saturated sediments are represented. These data allow to evaluate role of the basic geological factors that influence conditions of gas hydrate formation and existence in porous space of various sediments. Physical modeling of hydrate formation and decomposition in dispersed sediments has been conducted in special pressure chamber. The chamber is equipped with automatic system of pressure and temperature registration. Pure methane was used to form hydrate. Gas hydrate formation/decomposition took place under cyclical temperature alteration at certain initial pressure conditions. Sediments of various salinity, grain size and mineral composition were used in experiments. The data on kinetics and thermodynamics of water phase transitions under methane pressure were obtained during experiments. It was found out that only a part of ground water transforms to hydrate and the rest of the water freezes at subzero temperature. Temperature and pressure parameters of gas hydrate formation and decomposition in porous space were measured for investigated sediments. Influence of soil salinity, grain size and mineral composition on P/T conditions of gas hydrate existence is quantitatively shown. Detected deviations of P/T conditions of gas hydrate existence in porous space in comparison with free volume (water - gas) were not constant. The values of these deviations increase with temperature and pressure. Experimental data on phase equilibria of methane hydrate in sediments indicate the necessity of taking into consideration dispersed medium parameters while evaluating gas hydrate stability zone in nature.

### 1 Introduction

Gas hydrates as well as ice are widely spread in sediments. Both can be in the form of cement, various inclusions and separate bodies within sediments. Many physical properties of hydrate-containing soils are equal to properties of frozen soils. However, in contrast to freezing, hydrate formation process in soils is investigated extremely poorly. First of all it is connected to complexity of modeling of hydrate formation in dispersed soils and also with influence of the different factors on formation and existence of gas hydrate in soils. The problem of studying thermobaric conditions of formation and decomposition of gas hydrates in pore space of sediments remains debatable. Many researchers noted the influence of soil grain size on conditions of gas hydrate existence (Makogon, 1974; Cha et al, 1988; Handa & Stupin, 1992; Melnikov and Nesterov, 1996, 2001; Uchida et al, 1998; Wright et al, 1998, 1999; Clennell et al., 1999; Tohidi et al., 2000; Chuvilin et al, 2001, etc.). The majority of the authors received data on the shift of gas hydrate formation and decomposition conditions to the field of lower temperature and higher pressure comparing to the system "pure methane-free water". However these data usually describe only specific soil media, often artificial (silica gel spheres etc.), and do not allow developing regularities of gas hydrate formation and decomposition P/T conditions change depending on the soil characteristics. The attempt to discuss of kinetics and P/T conditions of hydrate formation and decomposition in soils of different grain

size, mineral structure and salinity is undertaken in this paper.

### 2 Methods

Physical modeling of hydrate formation and decomposition processes in dispersed sediments has been conducted in the special pressure chamber. The chamber is equipped by pressure and temperature sensors connected to data acquisition system able to record incoming data to computer at any step on time scale.

Pressure inside the chamber was regulated via connection with gas cylinder (methane 99,98%, P = 15 MPa). Gas hydrate formation/decomposition took place under cyclical temperature variations at certain initial pressure.

Each experiment included testing of 2 samples: one in experimental chamber (hydrate-containing) and control sample of the same composition and structure outside the chamber (ice-containing), but at the same temperature conditions as first one. Samples were prepared using layer-by-layer consolidation method.

The procedure of hydrate-containing samples production included following steps:

1. Loading of prepared sample into the chamber and chamber assembling;
2. Soil saturation by methane and pressure rise inside the chamber up to 8-9 MPa;
3. Placement of the chamber and control sample into refrigerator and temperature reduction down to  $+0.5 \div +4^{\circ}\text{C}$ ;

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4. Storage of the chamber and control sample at this temperature until pressure stabilization within chamber (primary hydrate formation);

5. Temperature reduction in refrigerator down to  $-7 \div -9^{\circ}\text{C}$  and samples freezing;

6. Temperature gradual elevation in refrigerator up to  $+17 \div +20^{\circ}\text{C}$  (ice melting, hydrate decomposition).

Last step was the end of one complete cycle of hydrate and ice formation/decomposition. After hydrate decomposition the pressure was reduced in 1,5-2 MPa and steps were repeated to receive new P/T equilibrium points. Other cycles repeated the steps mentioned from the step 4.

When pressure inside the experimental chamber was dropped down to atmospheric value at temperature below  $0^{\circ}\text{C}$  there was incomplete decomposition of methane hydrate due to gas hydrate self-preservation phenomenon. This phenomenon made it possible to study produced hydrate-containing samples in a cold room at subzero temperature and atmospheric pressure and apply procedures developed for study of frozen sediments.

Sediments of various salinity, grain size and mineral composition were used in experiments. Their main parameters are shown in Table 1.

Montmorillonite (bentonite) and kaolinite clays with water content close to the plasticity limit values for these clays were used in the experiments. Initial water content of montmorillonite was in the range 70 - 130% (relatively to weight of dry sediment) and for kaolinite - about 35%. Quartz fine-medium-grained sand was used. In some experiments quartz fine-medium-grained sand was used for producing mixtures with montmorillonite clay. Clay content of the mixtures was 7% (from dry sand weight). Initial water content for sand and its mixtures was the same in all experiments - 17%. Kaolinite clay of different salinity was used in the experiments. Salt content for these samples was 0,2%, 0,4%, 1% and 2% (from dry clay weight).

The data on temperature and pressure conditions changes with time in investigated sediments were used for kinetics study of gas hydrate formation and dissociation. Experimental data of pressure and temperature changes inside pressure chamber allow to calculate by the Mendelev-Claeyron equation gas quantity which was consumed for hydrate formation or released during decomposition. Gas quantity changes on

different moments allow to define hydrate formation/dissociation rate in sediments.

Besides, volume of sediment water transformed to hydrate (hydrate ratio) was calculated for investigated sediments.

### 3 Results and Discussion

**3.1 Kinetics of The Gas Hydrate Formation and Dissociation in Sediments.** Observation of temperature and pressure condition changes with time in wet methane-saturated soil samples under cyclic cooling and heating allows to investigate the kinetic of water phase transitions in soil porous space. It is found that the transition of part of soil water to hydrate is registered at cooling stage of soil system taking place under methane pressure. The rest of the water transforms to ice during the further subzero cooling. We can see the thawing of the porous ice and further gas hydrate decomposition at a heating stage (Chuvilin et al, 2000).

The analysis of P/T conditions change with time allows to investigate hydrate-accumulation intensity in various ground mediums and to estimate a part of water, which was transformed to hydrate under the certain experiment conditions. The experimental data show that only a part of pore water in investigated sediments is transformed to hydrate. On data calculated with use of P/T conditions the maximum quantity of water which was transformed to hydrate (about 80% of water) was detected in sandy samples ( $W_{\text{int}}=17\%$ ). In kaolinite clay ( $W_{\text{int}}=35\%$ ) this value was about 45%. The minimum water quantity (about 15%) was transformed to hydrate in montmorillonite clay ( $W_{\text{int}}=70\%$ ). So, hydrate ratio naturally decreased in accordance with rise of bonding energy of pore water and mineral surface. Decrease of the quantity of hydrate-transformed water was also observed with sediment salinity increase. So, the portion of water, which was transformed in hydrate decreased up to 2% in kaolinite clay salted by solution of NaCl ( $D_{\text{sol}}=2\%$ ).

The rates of methane absorption (hydrate formation) at cooling of gas-saturated dispersed sediments were calculated by experimental curves of P/T conditions change with time (fig. 1A). The diagram shows that the maximum rate of hydrate formation takes place in sandy samples. Two sections are obviously to allocate on this diagram.

Table 1 - Grain size and micro-aggregate composition of the researched sediments.

| Sediment title                   | Grain size distribution, %<br>Grain size, mm |              |              |              |                |                |                |                | Soil title according to grain size classifications of V.V.Okhotin for clay-containing sediments and E.M.Sergeev – for pure sand |
|----------------------------------|--|--------------|--------------|--------------|----------------|----------------|----------------|----------------|---|
|                                  | 1 - 0,5                                      | 0,5 - 0,25   | 0,25 - 0,1   | 0,1 - 0,05   | 0,05 - 0,01    | 0,01 - 0,005   | 0,005 - 0,001  | < 0,001        |   |
| Quartz sand                      | 1  | 53           | 45           | 1            | -              | -              | -              | -              | Fine/medium grain size sand   |
| Montmorillonite (bentonite) clay | 0,0<br>(2,0)                                 | 0,0<br>(1,0) | 0,2<br>(1,3) | 0,1<br>(8,5) | 18,8<br>(15,6) | 7,3<br>(5,9)   | 20,1<br>(15,4) | 53,5<br>(50,3) | Heavy clay  |
| Kaolinite clay                   | 0,7<br>(1,5)                                 | 0,5<br>(0,2) | 0,4<br>(0,2) | 2,9<br>(1,2) | 19,5<br>(32,2) | 11,2<br>(24,0) | 40,2<br>(34,5) | 24,6<br>(6,2)  | Silty clay  |

Values: 0,1 – content of certain grain size particles (%);

(8,5) – content of micro-aggregates of certain diameter (%).

The first section (the section of intensive hydrate formation) is characterized by high and constant rate (about 0,02 g/min). General hydrate formation takes place on this section. Apparently, the growth of characteristic superficial hydrate accumulations ("gas hydrate caps") in sand takes place in this period (Chuvilin et al, 2000). The second section corresponds to attenuation of hydrate formation process (hydrate formation rate decreases up to 0,007 g/min).

The smoother character of the diagram is observed in sandy samples containing montmorillonite clay (7% of weight)(fig. 1A). The rate of hydrate formation in the initial period of time (100 minutes) is significantly less (0,006 g/min) in comparison with pure sand and it decreases up to 0,002 g/min on section of attenuation. Low hydrate formation rates for clay sediments were also documented. So, the hydrate formation rate did not exceed 0,006 g/min for montmorillonite clay in the initial period of time. This rate was decreased to 0,003 g/min in the section of stabilization.

In the case of kaolinite clay the process of hydrate formation does not reach attenuation stage for long time, therefore characteristic sections are not distinguished (fig. 1A). The average rate of hydrate formation in the period of time 300 min was about 0,002 g/min. The hydrate formation rate is minimum in the saline kaolinite

clay ( $D_{sol}=0,2\%$ ) in the row of investigated sediments and it was about 0,001 g/min in the period of time 300 min.

Such character of change of hydrate formation rate with time is caused by influence of chemical-mineral structure of mineral sediment skeleton and energy condition of ground water on process of gas hydrate accumulations growth in pore space.

The differences in kinetics of gas hydrate accumulation in investigated sediments are confirmed by hydrate ratio values (table 2).

The hydrate decomposition rates and gas releasing are also decreasing from sand to clay and when salinity rise (fig.1B). However, hydrate decomposition in a sediment is characterized by a special feature. It can be observed on an example of montmorillonite clay and sand with clay particles. Figure 1B shows that in the first period of time the rate of hydrate decomposition is very small. It does not exceed 0,002 g/min in both sediments. Then the rate is sharply increased up to 0,01 g/min in montmorillonite clay and up to 0,007 g/min in sand with clay particles. Then the dissociation rate fades away. Such character of hydrate dissociation can be caused by conditions of hydrate existence in a sediment (B. Tohidi et al, 2000). Hydrate is present in the form of porous cement and various inclusions also in our case.

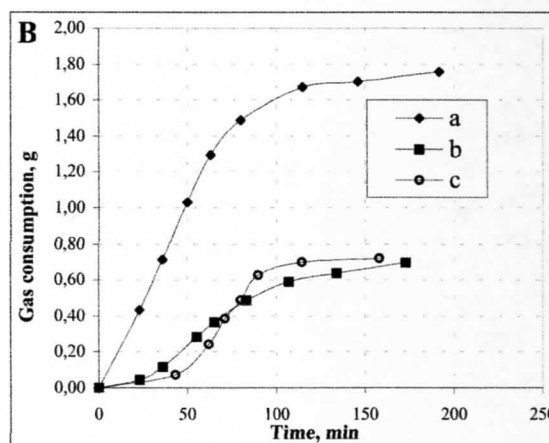
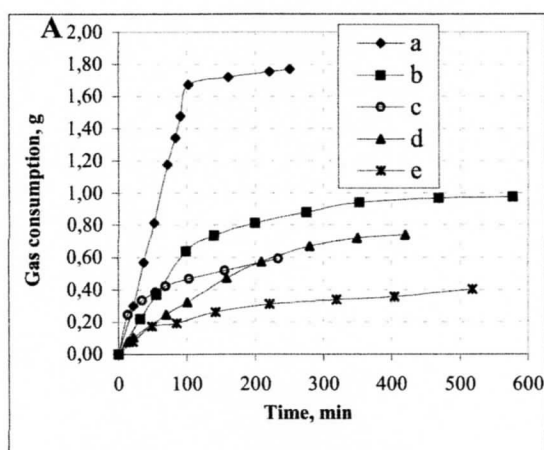


Fig. 1. The rate of methane hydrate formation (A) and dissociation (B) in investigated sediments: a – sand ( $W_{int}=17\%$ ); b – sand with 7% of montmorillonite clay ( $W_{int}=17\%$ ); c – montmorillonite clay ( $W_{int}=70\%$ ); d – kaolinite clay ( $W_{int}=35\%$ ); e – kaolinite clay ( $W_{int}=35\%$ ,  $D_{sol}=0.2\%$ ).

Table 2 – Hydrate ratio in investigated sediments.

| Sediment characteristic                    |                  | Hydrate ratio, %                       |
|--|------------------|--|
| Sediments name                             | Water content, % | Part of water in the porous hydrate, % |
| Quartz sand                                | 17               | 77 (41, in hydrate cap)                |
| Quartz sand with 7% of monmorillonite clay | 10               | 57                                     |
| Montmorillonite clay                       | 130              | 6                                      |
| -  | 70               | 15                                     |
| Kaolinite clay                             | 35               | 44                                     |
| Kaolinite clay, $D_{sol}=0,4\%$            | 35               | 21                                     |
| Kaolinite clay, $D_{sol}=1\%$              | 35               | 21                                     |
| Kaolinite clay, $D_{sol}=2\%$              | 35               | 2                                      |

Apparently, the first step corresponds to dissociation of hydrate cement (porous hydrate) and the second step associates with dissociation of various gas hydrate inclusions.

### 3.2 Temperature and Pressure Conditions of Hydrate Formation in Sediments.

The temperature and pressure conditions of gas hydrate formation in dispersed sediments depend on the whole row of factors, which are determined by energy state of pore water and opportunity of its phase transition to hydrate. These factors are grain size and mineral structure of sediment medium, the water content, salinity and kinetic factors. Often, the influence of these factors is complex. It can result in considerable range of experimental data. The analysis of experimental data have shown obvious shift of P/T equilibrium conditions of hydrate formation in sediment pore space to the field of higher pressures and lower temperatures when compared to the system "water (ice) - free gas - gas hydrate" (P/T<sub>g-w</sub>). This shift is not constant and it is growing with rise of environment temperature. Apparently, it could be attributed to energy condition of pore water of sediments and change of physical-chemical properties of the sediment at higher temperatures.

Cyclic phase transition influences on P/T points of water phase transitions in hydrate-containing sediment. So, the tendency of increasing of P/T deviation is traced from the first cycle to next. Apparently, this could be attributed to structural transformations of the sediment during the first and following cycles. Probably, water memory effect influences on shift increase (Chuvilin et al, 2000).

It was received that the shift of P/T parameters to the field of higher pressures and low temperatures increases with increase of the clay particles content in sandy sediments. Shift of temperature ( $\Delta T$ ) and pressure ( $\Delta P$ ) is 1,0-1,5°C and 0,7 MPa, accordingly, in pure sand ( $W_{int}=17\%$ ). These values increase in sand with montmorillonite particles ( $W_{int}=17\%$ ). The shift reached 1,6-2°C in temperatures scale and 0,7-1,5 MPa in pressure scale. Such distinction is explained by increase of bonding energy of pore water with mineral surface and, correspondingly, more complicated conditions of its transition to hydrate.

The influence of mineral structure can be consider on an example of clay sediments of montmorillonite and kaolinite structure. It was revealed that the shift of P/T conditions of formation and decomposition in montmorillonite clay is more than in kaolinite clay in spite of the large initial humidity of montmorillonite clay. So, the shift on a temperature scale is 3-4,5°C for montmorillonite clay ( $W_{int}=70\%$ ) and 2,5-3°C for kaolinite clay ( $W_{int}=35\%$ ). The value of the pressure shift reaches 3,0 MPa and 1,8 MPa for montmorillonite and kaolinite clay, accordingly. It is marked that the values of P/T parameters shift of gas hydrate formation are minimal both for montmorillonite and kaolinite clays in area of lower temperatures (+1 - +3°C) (in comparison with free volume) and are close to

each other. The similar behavior of montmorillonite clay is caused by its crystal-chemical structure. It owes of active crystal lattice and a high specific active surface (up to 600 m<sup>2</sup>/g). Therefore it can strongly tie a great quantity of porous water. In case of kaolinite clay hydration occurs only on external surfaces of particles. The specific active surface of kaolinite does not exceed 30 m<sup>2</sup>/g. Therefore porous water is less subjected by energy influence of a mineral surface and conditions of its transition to hydrate are more favorable.

Experimental data show that increase of dispersed sediment salinity also causes shift of temperature and pressure conditions of hydrate formation to the field of higher pressures and low temperatures. So, in a row: pure kaolinite clay - kaolinite clay salted by NaCl solution with  $D_{sol} = 0.2\%$  - kaolinite clay salted by NaCl solution with  $D_{sol}=2\%$ , the shift on temperature scale changed from 2,5°C (for pure kaolinite clay) up to 5,5°C (kaolinite clay with  $D_{sol}=2\%$ ) and on pressure scale - from 1,8 MPa up to 4,5 MPa, accordingly. Apparently, it could be attributed to the salt ions dissociated during interaction with water and connected to water polar molecules. Therefore, the energy condition of pore water varies. It becomes the osmotically connected water. Its transition to hydrate requires more energy expenses in comparison with free water. Therefore, the more concentration of pore solution, the more water will be tied by salt ions and the conditions of hydrate formation will became more difficult.

It is necessary to note that P/T conditions of gas hydrate formation are very close in all sediments in the field of low positive temperatures (up to +1,5°C). P/T shift increases with increase of environment temperature.

### 3.3 Temperature and Pressure Conditions of Hydrate Dissociation in Sediments.

The analysis of methane hydrate decomposition conditions in the investigated sediments has shown that temperature and pressure parameters of gas hydrate decomposition are also different from those in free volume and are shifted to the field of higher pressures and low temperatures. These deviations are significantly less on amplitude and poorly are subjected by P/T fluctuations when compared to hydrate formation stage. Therefore, they have good reproducibility.

Figures 2, 3, 4 show the experimental data on P/T conditions of methane hydrate dissociation in investigated sediments. The experimental data show that phase parameters of gas hydrate dissociation in sediments are differ from that for free volume. In the case of kaolinite clay ( $W_{int}=35\%$ ) deviation on pressure scale ( $\Delta P$ ) does not exceed 0,1 MPa at temperature - 0,2°C and it reaches 2,1 MPa at temperature 12,1°C (fig. 2). The shift on temperature scale ( $\Delta T$ ) to the field of lower temperatures varies from 0,2°C at  $t = -0,2^\circ\text{C}$  up to 2°C at  $t = 12,1^\circ\text{C}$  in kaolinite clay at these conditions. Obviously, this shift is dependent on sediment grain size, chemical-mineral structure and humidity.



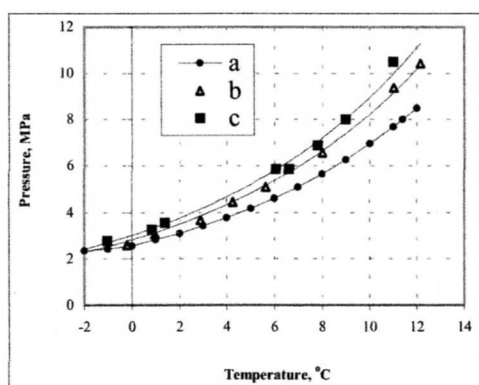


Fig. 2. Temperature and pressure conditions of methane hydrate decomposition in kaolinite and montmorillonite clay: a - P/T conditions in system "gas-water"; b - P/T conditions in kaolinite clay ( $W_{int}=35\%$ ); c - P/T conditions in montmorillonite clay ( $W_{int}=70\%$ ).

This shift is registered even in fine-medium-grain sand ( $W_{int}=17\%$ ), where the deviation reaches  $0,6 - 1,2^{\circ}\text{C}$  on temperature scale and  $0,4-0,6$  MPa on pressure scale. Increase of montmorillonite clay particles content at the fixed value of humidity ( $W_{int}=17\%$ ) in sand causes increase of the deviation both on temperature and pressure scales. In sand with 7 % of montmorillonite clay particles  $\Delta T$  reaches  $1,3^{\circ}\text{C}$  and  $\Delta P - 1$  MPa (fig. 3).

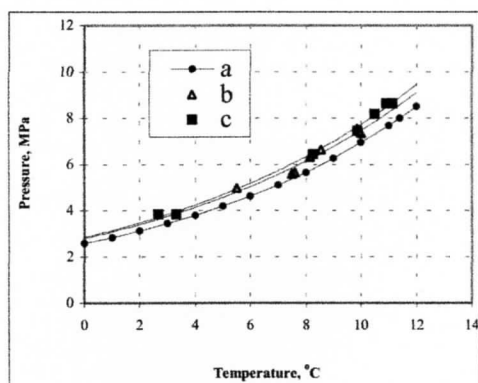


Fig. 3. Temperature and pressure conditions of methane hydrate decomposition in sand and sand with montmorillonite clay: a - P/T conditions in system "gas-water"; b - P/T conditions in sand ( $W_{int}=17\%$ ); c - P/T conditions in sand with 7% of montmorillonite clay ( $W_{int}=17\%$ ).

It could be explained by increasing of bonding energy of mineral surface when addition of montmorillonite particles with high superficial energy. Larger shift of P/T parameters of hydrate decomposition was registered for pure montmorillonite clay in spite of rather high humidity ( $W_{in}=70\%$ ). It reached  $2,5^{\circ}\text{C}$  on temperature scale and 2,8 MPa on pressure scale (fig. 3),

that is much higher than in other investigated soils. It testifies large role of mineral surface properties when existence conditions of gas hydrate in pore space of the soils are considered.

The experimental data on salinity influence on conditions of gas hydrate decomposition are presented in fig. 4. These data show that in salted soils the deviation of P/T conditions extends with salinity increase. So in salted kaolinite clay ( $D_{sol}=0,2\%$ ) the deviation on temperature and pressure scales changes from  $1,3^{\circ}\text{C}$  up to  $2,5^{\circ}\text{C}$  and from 1,4 MPa up to 2,2 MPa accordingly. At salinity 2 %  $\Delta T$  reaches  $3,6^{\circ}\text{C}$  and  $\Delta P - 3$  MPa (fig. 4). It is typical that the influence of salinity in free volume (solution) and in pore space is not identical. In pore water solution the shift is more than in free volume that indicate joint influence of salts and mineral skeleton on conditions of gas hydrate decomposition in pore space. The received experimental data on P/T conditions of methane hydrate decomposition in pore space point to necessity of dispersed medium parameters considering when possibility of gas hydrate existence is discussed. Apparently, this can be of significance when estimation of gas hydrate stability zones.

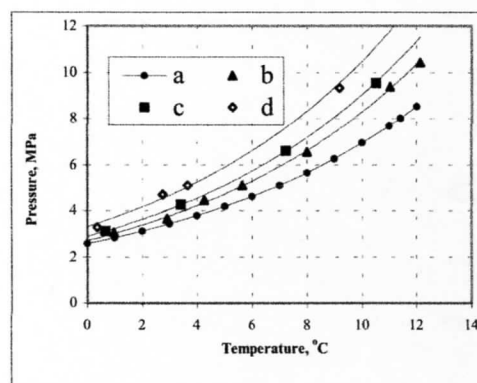


Fig. 4. Temperature and pressure conditions of methane hydrate decomposition in saline kaolinite clay: a - P/T conditions in system "gas-water"; b - P/T conditions in unsaline kaolinite clay ( $W_{int}=35\%$ ); c - P/T conditions in saline kaolinite clay ( $W_{int}=35\%$ ,  $D_{sol}=0.2\%$ ); d - P/T conditions in saline kaolinite clay ( $W_{int}=35\%$ ,  $D_{sol}=2\%$ ).

#### 4 Conclusion

Main received experimental results are following:

1. Only part of pore water is transformed to hydrate in methane-saturated sediments when downturn of temperature. The portion of water transformed to hydrate is maximum (about 80 %) in sandy sediments. The share of clathrated water (water which was transformed to hydrate) gradually decreases when increasing of sediment grain size and salinity.

2. Dispersion, mineral structure and salinity of sediments are exerted appreciable influence on kinetic of hydrate formation and decomposition. The rate of methane hydrate formation and decomposition is reduced from sand to clay and at salinity rise.

3. Temperature and pressure conditions of gas hydrate formation/decomposition in dispersed sediments are shifted to the field of higher pressures and low temperatures in comparison with system "free water - pure gas". This shift is not constant. It is increasing with environment temperature rise.

4. The various sediment characteristics, such as grain size, mineral structure, salinity influence on the value of the P/T shift. The value of this shift is increasing at increase of clay particles content in sediment, at transition from kaolinite clay to montmorillonite clay, at salinity rise. This is caused by changes of pore water energy.

5. Received P/T parameters of methane hydrate dissociation in sediments point the necessity of accounting of the sediment factor when estimation of gas hydrate stability zones in nature.

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