INVESTIGATION OF GAS HYDRATE FORMATION IN FROZEN AND THAWING GAS SATURATED SEDIMENTS

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ABSTRACT
A special experimental technique was elaborated to perform physical modeling of hydrate formation conditions in cryogenic ice-containing sediments. Experimental data shows that after attenuation of hydrate formation in frozen sediments the considerable activation of hydrate accumulation processes during the increasing of temperature above 0 °C can occur. That leads to the thawing of porous ice, which does not turn into hydrate, and attendant this process structural-textural changes result in appearance of new gas-water contacts. As a result there is second hydrate formation on background of thawing of ice. In the course of experiments the influence of thermobaric conditions, porous media composition and ice-saturation on the kinetics of hydrate accumulation in porous media of frozen and thawing rocks were considered.

Based on analysis of geological data and experimental researches the possible model of gas hydrates formation in shallow permafrost under the sea transgression can be presented. In consideration of high gas-saturation of frozen sediments, the active processes of hydrate formation in permafrost during the transgression of arctic seas under conditions of relict submarine permafrost formation can be expected.

Keywords: gas hydrates, frozen gas saturated sediments, gas hydrate formation, kinetic, ice

NOMENCLATURE
Hv volumetric hydrate content [%]
Kh hydrate coefficient [u.f.]
n porosity of the sediment sample [u.f.]
Sh hydrate saturation [%]
Si ice-saturation [%]
W gravimetric water content of sample [%]
W_H amount of water that transformed into hydrate [% to weight of dry sample]
ρ density of the sediment sample [g/cm³]
ρ_H density of hydrate [g/cm³]

INTRODUCTION
In natural conditions gas hydrates form mainly in seafloor sediments and also in permafrost area below frost penetration, i.e under positive (Centigrade) temperatures. However there are some cases when gas hydrates formation can occur under negative temperatures, for example in glacial Arctic and Antarctic sheets and permafrost strata as well[1,2,3]. Taking into account high gas-saturation of frozen sediments (mainly methane with admixture of carbon dioxide and nitrogen), the active processes of hydrate formation in permafrost under the influence of pressure factor, caused by arctic seas transgression and ice sheets extension, can be expected [4,5]. As a result, gas-saturated frozen rocks imbedded in comparatively low depth get into gas hydrate stability zone and intra-permafrost free gas accumulations transfer into gas hydrates.

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Possibility of hydrates formation from natural gases (mainly CH₄ and CO₂) under sub-zero temperatures in bulk (on surface between ice and gas) was shown in considerable amount of experimental works. Thus Stern et al. [6] showed the possibility of almost 97% fine-crystalline (200-350 µm) ice transformation into methane hydrate during 8 hours under high pressure (271,5 K и 27,3 MPa). Formation of gas hydrates under temperature range from -1 to -10 °C during interaction of CH₄ and CO₂ gases with dispersed ice (ice particles size 10-30 µm) was observed by T.Komai et al.[7]. Kinetics of hydrate formation during interaction of ice particles with CH₄ and CO₂ gases was described in works by X.Wang with co-authors [8], F. Kuhs et.al.[9], D.K.Staykova [10] and others.

However, the process of hydrate formation in porous ice-containing media is studied poorly. Possibility of gas hydrate formation in porous media of freezing and frozen rocks was shown in works by Wright et al.[11], Chuvilin et al.[12,13], T.Komai et al.[14]. It was determined that reduction of negative temperature of frozen gas-saturated sediments leads to decreasing of hydrate formation intensity, but it remains quite high for significant hydrate accumulation.

Paying attention to insufficient knowledge of hydrate formation processes in frozen and thawing rocks, we worked out special experimental technology of physical modeling of hydrate formation conditions in cryogenic rocks.

METHODS
For experimental modeling of gas hydrates formation in frozen sediments we used experimental installation consisting of the following basic elements: a pressure chamber (about 420 cm³) with sample container (diameter 4,6 cm and length about 10 cm), a thermostat to provide temperature conditions of pressure chamber, a converter of temperature and pressure gauge electrical signals into digital data, a computer. This experimental installation allowed automatic registration of temperature and pressure. Accuracy of temperature sensors was 0,05 °C, and pressure sensors was 0,005 MPa.

As a subject of research we used natural quartz sand -sand 1-, sandy loam from Vorkuta - sandy loam 1- and some sediments, which were collected from gas-containing horizons in Permafrost areas in the North of West Siberia -sand 2 (Yamburg gas field) and sandy loam 2 (Zapolyarnoe gas field). Their characteristics are shown in Table 1, 2.

Soils of disturbed structure were used in the course of experiments. To prepare samples, the sediment was first dried and then cooled to -6 -7 °C. Cold sediment was mixed with a certain amount of ice powder. The prepared soil-ice mixture was placed into the container by method of layer-by-layer compaction. Sediment samples were characterized by different ice saturation (Si) from 29 to 80%, density (ρ) 1.37-1.85 g/cm³ and porosity (n) 0.40-0.50

### Table 1. Grain size of investigated sediments

<table>
<thead>
<tr>
<th>Type of sediment</th>
<th>Particle size distribution/%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1-0.05 mm</td>
</tr>
<tr>
<td></td>
<td>0.05-0.001 mm</td>
</tr>
<tr>
<td></td>
<td>&lt;0.001 mm</td>
</tr>
<tr>
<td>Sand 1</td>
<td>94.8</td>
</tr>
<tr>
<td>Sand 2</td>
<td>84</td>
</tr>
<tr>
<td>Sandy loam 1</td>
<td>41.8</td>
</tr>
<tr>
<td>Sandy loam 2</td>
<td>88</td>
</tr>
</tbody>
</table>

### Table 2. Characteristics of sediment samples

<table>
<thead>
<tr>
<th>Type of sediment</th>
<th>Genesis, age</th>
<th>Mineral composition, %</th>
<th>Salinity, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand 1</td>
<td>m J₃</td>
<td>&gt; 90 –Qtz</td>
<td>0,0124</td>
</tr>
<tr>
<td>Sand 2</td>
<td>mgmQ₉²-⁴</td>
<td>80 – Qtz 9 – RAS</td>
<td>0,076</td>
</tr>
<tr>
<td>Sandy loam 1</td>
<td>gmQ₉²-⁴</td>
<td>45 - Mc+ Ab 38 - Qtz</td>
<td>0,075</td>
</tr>
<tr>
<td>Sandy loam 2</td>
<td>m II₂-⁴</td>
<td>64- Qtz 9- Mc 5- Ab</td>
<td>0,20</td>
</tr>
</tbody>
</table>

The pressure chamber with the sample was frozen at -8°C and then saturated with cold gas. Experiments were carried out under constant negative temperatures from -2 °C to -9 °C. Methane (99.98%) and carbon dioxide (99.99%) were used as hydrate-former gases. Initial pressure was 4-6 MPa for CH₄ and 2.5-3 MPa for CO₂. Duration of one experiment was 10-15 day till pressure stabilization.

Analysis of pressure chamber thermo-baric conditions changes in the process of hydrate
formation allowed to detect parameters of phase transition in soil samples. The hydrate saturation (Sh), volumetric hydrate content (Hv) and hydrate coefficient (Kh - share of water transforming into hydrate) were determined from changes in thermobaric conditions incorporating compressibility according gas low recommended by State standard of Russia with account of gas solubility in pore water [15].

Volumetric hydrate content (Hv) was calculated by formula (1):

$$H_v = \frac{H \cdot \rho}{\rho_H}, \text{(\%)}$$

(1)

Hydrate saturation (Sh) was calculated by formula (2):

$$Sh = \frac{H_v}{n}, \text{(\%)}$$

(2)

Hydrate coefficient (Kh) was calculated by formula (3):

$$K_h = \frac{W_H}{W}, \text{(u.f.)}$$

(3)

We used hydrate number 5.9 for CH₄ and 6.1 for CO₂ to perform the calculations.

RESULTS

Kinetics of pore gas hydrate accumulation in frozen sediments

Under conditions of negative temperatures after saturation of pressure chamber with cold gas, hydrate accumulation in porous media of frozen sediments was observed as soon as gas pressure exceeded equilibrium. And it was determined that in frozen gas-saturated sediments hydrates form from porous ice.

Typical kinetic curves of changes in hydrate- and ice-saturation with time during formation of methane hydrate in sample of sandy loam 2 are presented in the Figure 1 (initial ice saturation 59%).

There are three typical segments on the curves in figure 1. They correspond to different stages of hydrate formation: 1 - linear segment of intensive hydrate formation with the rate of hydrate formation 5 \%/hour; 2 – slower intermediate segment when the rate of hydrate formation goes down to 0.8 \%/hour, and 3 – segment when hydrate formation ceasing and the rate of hydrate formation does not exceed 0.07 \%/hour.

During the process of hydrate accumulation, gradual decreasing of pores ice filling degree was observed. Thus, in the sample of sandy loam 2 initial ice-saturation was 59% (Figure 1). On the stage of intensive CH₄-hydrate formation after 3 hours of experiment value of Sh reached 11, but Si decreased till 48%. Then hydrate accumulation slowed down and during the next 120 hours hydrate-saturation in porous media of sandy loam sample reached 40%, but ice-saturation reduced till 19%. Ceasing segment of kinetic curve indicates completion of hydrate accumulation and on this stage after 250 hours of experiment 46% of porous media was filled with gas hydrate and residual Si did not exceed 13%. Thus partial transition of pore ice into gas hydrate was observed.

Based on the theoretical and experimental elaborations on hydrate formation in the system gas - ice particles, the mechanism of hydrate formation in the porous media of ice-containing sediments, can be described as follows.

On the first stage, when thermo-baric conditions reach equilibrium a film mechanism of hydrate formation takes place. Gas hydrate that appears in the most favorable conditions spreads as a film on surface of pore ice contacting gas. After the interface between ice and gas is covered by hydrate the second stage begins. The only way to maintain the clathration reaction is the transport of gas molecules through the intervening hydrate layer to the ice-hydrate interface and/or water molecules from the ice to the outer hydrate-gas interface. The clathration reaction itself together with the gas and water transfer over the phase boundaries may be the rate-limiting step(s) that follows the initial coverage. Then on the third stage (diffusion-limited) the process of hydrate formation allowed to detect parameters of phase transition in soil samples. The hydrate saturation (Sh), volumetric hydrate content (Hv) and hydrate coefficient (Kh - share of water transforming into hydrate) were determined from changes in thermobaric conditions incorporating compressibility according gas low recommended by State standard of Russia with account of gas solubility in pore water [15].
formation is limited by gas permeability of hydrate layer that formed on the surface of pore ice[16,17]. At that partial transition of pore ice into hydrate was observed.

**Particularities of gas hydrates accumulation in frozen sediments**

The performed experiments allow to estimate influence of temperature, excessive pressure, ice-saturation and hydrate-forming gas on the processes of hydrate formation in porous media. The rate of hydrate formation under negative temperatures is slower then under positive temperatures, however it subsides slower when hydrate forms from pore ice (Figure 2).

![Figure 2. Kinetics of methane hydrate accumulation in porous media of sandy-loam 1 (Si=69%) under different temperatures.](image)

Figure 2. Kinetics of methane hydrate accumulation in porous media of sandy-loam 1 (Si=69%) under different temperatures.

Thus, high rate of hydrate formation under positive temperature +2 °C was observed only during first 10 hours of the experiment. As one can see from figure 3, the rate of hydrate formation decreases with the decrease of temperature from +2 to -8 °C during this period. But then, after 50 hours of hydrate formation the process almost ceased under positive temperature whereas under negative temperature hydrate was still accumulating with noticeable rate. As a result, total hydrate-saturations at the end of experiments do not differ much. Hydrate coefficient at the end of experiments under negative temperatures was 0,39-0,44, and under positive temperatures did not exceed 0,46.

With the decrease of temperature from -3.7 to -8 °C the decrease of the rate of hydrate formation was observed at the first stage of the experiment, but it subsides slower at -8 °C. Thus, the time of active processes of hydrate formation increases with the decrease of experimental temperature. On one hand, it can be explained by the increase of excessive (above equilibrium) pressure with the decrease of temperature when initial pressure is the same in both experiments, because it increases the driving force of hydrate formation. On the other hand, slow subside of hydrate formation at low temperatures can be explained by permeability of the hydrate layer that forms on pore ice surface. It has a more porous structure at lower negative temperatures which ensures better permeability and higher rate of diffusion of gas towards ice surface.

Factor of pressure is also an important parameter which influences on the process of hydrate formation. Excessive pressure of hydrate-forming gas (pressure that exceeds equilibrium for particular temperature) determines driving force of hydrate formation. With the increase of excessive pressure at constant negative temperature (-3,8 °C) the share of ice transformed into hydrate and hydrate-saturation increase [18]. Thus, with the increase of excessive pressure from 2 to 3.4 MPa hydrate saturation in the sample of sand 1 (with initial ice-saturation 63%) increased by 14%.

During the experiments it was determined that intensity of hydrate accumulation depends on degree of ice filling of pores, which defines a surface of ice-gas interface. It was experimentally shown that maximum hydrate-saturation of porous media occurs at optimum value of ice-saturation (Figure 3).

![Figure 3 Influence of initial ice-saturation (Si) on methane hydrate accumulation (Sh) in sandy-loam 2 under the temperature -2,9 °C](image)

Figure 3 Influence of initial ice-saturation (Si) on methane hydrate accumulation (Sh) in sandy-loam 2 under the temperature -2,9 °C.

The most favorable degree of ice pores filling is in range of 45-65%. If value of ice-saturation is more than this, hydrate formation reduces in consequence of decreasing of gas-ice surface. When degree of ice pores filling is more than 80%, the process of hydrate accumulation is depressed because of insignificant amount of hydrate-forming gas in the sample and decreased permeability. When ice saturation is low, less than 20%, rate of hydrate formation is also low because...
of low ice content, although the share of ice transformed into hydrate (Kh) increases. Also the type of hydrate-forming gas has an influence on the kinetics of hydrate formation in porous media of ice saturated sediments. According to our previous work[18] intensity of CO₂ hydrate accumulation and amount of accumulated hydrate are higher than for CH₄ hydrate and the differences in the rate of hydrate accumulation appear from the beginning of the experiment. This can be connected with considerably higher reaction capacity of CO₂ in comparison with methane, therefore the reaction of hydrate formation runs faster [16]. And also carbon dioxide has higher solubility as compared with methane and the process of volume-diffusion hydrate formation with carbon dioxide runs better [13].

**Influence of thawing of residual pore ice**

Experimental data show that after attenuation of hydrate formation in frozen sediments the considerable activation of hydrate accumulation processes during the thawing of residual pore ice, which does not turn into hydrate, can occur (Figure 4).

![Figure 4. The kinetics of CH₄ hydrate accumulation in sandy-loam 2 (Si=66%) at the constant temperature -3 °C and during increasing of temperature from -3 to +4,1 °C.](image)

Thus in the sandy loam sample (Si=66%) after 270 hours of the experiment under the constant negative temperature -3 °C hydrate saturation was 17%. Then during the process of heating from -3 °C to +4,1 °C after 17 hours of experiments 54% of accumulated hydrate formed and to the end of the test hydrate saturation was 43%. And as experimental investigations show the higher initial ice saturation the more quantity of gas hydrate forms during the thawing of pore ice. Up to experimental data, in the sample of sandy loam 2 (Si=80%) after 290 hours of the experiment under constant negative temperature -2,9 °C only 3% of methane hydrate accumulated. That can be explained by high degree of ice saturation and insignificant surface of ice-gas interface. However in the result of phase translations (ice-water) during the heating from -2,9 to +0,7 °C dramatic activation of methane hydrate accumulation was observed and after 7 hours, in the course of pore ice thawing, 90% of accumulated hydrate formed. By the end of the test hydrate saturation was 36%. (Figure 5).

Probably this is connected with the formation of new crystallization centres and appearance of new gas-water contacts, in the course of pore ice thawing, which leads to hydrate formation activation.

![Figure 5. The kinetics of CH₄ hydrate accumulation in sandy-loam 2 (Si=80%) at the constant temperature -2,9 °C and during increasing of temperature from -2,9 to +0,7 °C.](image)

But when initial ice-saturation was comparatively insignificant the dramatic activation of second hydrate formation wasn’t observed. Thus in the sample of sandy loam 2 (Si=43%) after the heating from -3 °C to +1 °C and thawing of the pore ice in the sample only 4,5 % of accumulated hydrate formed. This can be explained by the fact that in the sample with low ice-saturation, considerable part of pore ice turns into gas hydrate during hydrate formation under constant negative temperatures. As a result thawing of pore ice doesn’t lead to the active surface of ice-water interface and new crystallization centres formation.

**DISCUSSION**

Performed experimental data shows that hydrate formation can develop actively not only in moist dispersed sediments under positive (above 0°C) temperatures, but also under negative temperatures.
in porous media of gas-saturated frozen sediments. This allows to say about possibility of hydrate formation in upper gas-saturated horizons (up to 100-200 m) of permafrost under the influence of pressure factor. Existence of gas accumulations in frozen rocks strata, along with gas hydrates, was indicated in north regions of Western and Eastern Siberia, on Arctic seaboard of Canada, in Alaska by many researchers [19,20]. These gas accumulations consist of methane mainly with some admixture of carbon dioxide and others gases. There is great number of information about high gas saturation of upper permafrost horizons in north regions of Western Siberia, where particular permafrost investigations were held during exploration and development of oil and gas fields. Hydrate formation on low depths in permafrost can be connected with long-term frost penetration of sediments and as a result appearance of high pressure due to crystallization of pore liquid in gas saturated layers and also this can be connected with appearance of additional external pressure (pressure factor) onto concentrated (due to frost penetration) gas accumulations in frozen rocks [21,19].

Based on analysis of geological data and experimental researches the possible model of gas hydrates formation in shallow permafrost under the sea transgression can be presented. Formation of thick strata of frozen rocks and gas hydrate stability zone took place during arctic sea regression. Shelf permafrost had maximum thickness during the last, Sartan regression of the sea [5], in the coldest period of the Late Pleistocene stage in the development of the cryolithic zone (27-15 ka). In the shelf, drained to depths of 100 m or greater, frost penetration of rocks went on at air temperatures -18-(-20)°C. The pick of cold was 20-18 ka [22,23,24], during the period of maximum buildup in the thickness (up to 500-700m) of the shelf cryolitic zone. At the same time in top layers of frozen sediments above hydrate stability zone partial concentration of gas could occur in horizons with good reservoir properties. And also local formation of separate gas hydrate accumulations due to cryogenic factor during frost penetration of sediments and relict gas hydrate formation in icy strata were possible (Figure 6.A)

During the subsequent transgression, which began about 15 ka [24,25], formed in subaerial conditions permafrost submerged to a water depth of 120-140 m and the last degradation stage started the development (Figure 6.B). In the time of sea transgression the temperature of rocks rose up to the value of sea water temperature, so profile of temperature distribution with the depth had no trend [26]. And from above thawing of frozen sediments under the influence of sea water with negative temperatures was insignificant, therefore shelf permafrost thickness decreased mainly from the bottom. In whole taking into account quite large thickness of frozen rocks and low arctic seas temperature the process of subaqual permafrost degradation was quite slow, and as a result relict shelf permafrost could exist for a long period of time.

Due to sea transgression, the pressure over underlying frozen sediments increased, this activated the processes of hydrate formation in submarine conditions and led to expansion of gas hydrate stability zone. As a result, gas-saturated frozen rocks imbedded in comparatively low depth (70-80 m) got into gas hydrate stability zone and intra-permafrost free gas accumulations transfer into gas hydrates (Figure 6.B).

Further, due to warming effect of deep thermal flow, permafrost degradation from below took place. Horizons of frozen rocks on the depth of 400-500 m began to thaw, but increasing of temperatures up to positive values stimulated the processes of hydrate formation. This led to deep gases accumulation, transition of free gases into gas hydrate state and increasing in size of gas hydrate deposits (Figure 6.C.).

During the transgression period of the Late Pleistocene-Holocene, i.e. for the last 12-14 ka, partial or total degradation of relict frozen sediments went on. This was accompanied by lowering of HSZ upper boundary, gas hydrate decomposition and saturation of upper layers with free gas. That led to active gas emission from thawing sediments.

In consideration of energy consumption during gas hydrates decomposition, temperature of thawed sediments could decrease. As a result degradation of permafrost became slower. This led to some stabilization of relict frozen rocks and to self preservation of undecomposed gas hydrates in frozen horizons outside of HSZ (Figure 6.D.)
CONCLUSIONS

Experiments show that hydrate formation in gas saturated sediments occurs actively not only in freezing sediments (under positive temperatures) but also in frozen sediments, under negative temperatures (to -8°C). Intensity of hydrate formation in frozen sediments depends on such factors as ice-saturation, thermobaric conditions and gas composition. Thawing of residual pore ice activates considerably the processes of hydrate accumulation in porous media.

Experimental investigations show that long existence of relict submarine permafrost on Arctic seas can lead to considerable accumulation of gas hydrates in frozen and cooled deposits on the Arctic shelf.

Based on analysis of geological data and experimental researches possible geological model of gas hydrates formation in shallow permafrost under the sea transgression was presented.

Figure 6. The possible model of gas hydrates formation in shallow permafrost under the sea transgression:

A-formation of onshore permafrost and hydrate stability zone in Arctic after sea regression; B-beginning of sea transgression, formation of shelf permafrost, expansion of HSZ; C-progress of sea transgression, beginning of submarine permafrost degradation, hydrate formation in frozen and thawing sediments; D- partial or total degradation of relict permafrost, gas hydrates decomposition, active gas emission from thawing sediments.
REFERENCES


