

EXPERIMENTAL SIMULATION OF FROZEN HYDRATE-CONTAINING SEDIMENTS FORMATION

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ABSTRACT

In paper on the basis of experimental investigations the main factors and conditions influence on hydrate accumulation in freezing methane-saturated sediments are revealed. The parameters quantitatively characterized the process of methane hydrate accumulation in porous media are received. The important characteristic for understanding of process of hydrate accumulation in sediment porous space is the hydration coefficient -portion of porous water, transformed into hydrate. Experimental researches show, that the hydration coefficient depends on structure porous spaces of dispersed sediments, connection energy of water with a surface of mineral particles, the "gas-water" contact surface and gas permeability of porous media and also pressure/temperature regime of hydrate formation. The model of hydrate and ice formation in porous media of methane-saturated sediments is suggested.

Keywords: methane hydrate, hydrate accumulation, freezing, kinetic, hydrate saturated sediments.

INTRODUCTION

Great deal of data, regarding natural gas hydrate, which are ice-like crystalline compounds, consisted of water and gas have received recently. It's known, that gas hydrate formation and existence fields confined to zones of the Earth's crust cooling. They occur in submarine conditions and also in the permafrost regions, where a part of the gas hydrate stability zone (GHSZ) is within permafrost intervals [1].

The methane gas hydrates are the most widespread in nature. Currently methane hydrate accumulations have indentified either by direct evidences (hydrate-containing core sample) or indirect evidences in various regions of the world (Arctic coast of Canada, Alaska, the North of Siberia etc.). The hydrate-containing samples occurred within permafrost intervals were recovered in the Mackenzie delta territories [2,3]. Visible inpermafrost hydrate forms have been collected in the Taglu gas field from GHSZ at 330-350 m. Moreover, there are some data about methane hydrate findings in upper layers of pemafrst sediments (119 m), which occur in

GHSZ [3] and preserved due to self-preservation effect under negative temperature section condition.

High gas-saturation, intensive gas releases from permafrost intervals at low level of free porosity and some links between gas-saturation sediments and their composition, structure and properties of permafrost sediments [4] are indirect evidences of gas hydrate accumulations. Frequent shallow hydrate-shows fixed from depths above 200 m have been documented through the North of West Siberia territories and other regions of Russia [5].

Some models of gas hydrate formation in permafrost have been proposed at this moment. As a rule, they associate with sea transgression, regional ice cover formation, freezing of gas-saturated talik zones, permafrost sediments formation etc. [6,4].

However mechanisms of gas hydrate accumulation within and under permafrost sediments are poorly investigated. Physical modeling of gas hydrate and ice formation in dispersed sediments has an

considerable importance to successful solution to this problem. It allows expanding our ideas about hydrate accumulation in natural condition.

METHODS

The physical modeling of water phase transitions in gas-saturated sediments was carried by using experimental set-up which included following main components: the pressure chamber with volume of 420 cm³, refrigerator for maintaining thermal regime of the pressure chamber, analog-to-digital converter for pressure and temperature sensors signals and computer [7]. The experimental set-up allows the pressure and temperature values registering of any time step automatically.

Disturbed composition sediments were used in the experiments. Model sediments were quartz sand, kaolinite and montmorillonite clay and also sand-clay mixture consisted mainly of sand up to 7% of clay content represented by kaolinite and montmorillonite.

Sample of the sediment with predetermined parameters was prepared for each test. Incomplete pore filling sediments were generally used, that provides sufficient gas-water contact in porous space of sediments. Prepared sample of sediment with a diameter of 4,5 cm and height of 9 cm was placed into the pressure chamber. After complete purged of air pressure chamber with sediment inside was filled with methane till pressure came to 8-10 MP.

Investigations on hydrate and ice formation and dissociation in gas-saturated samples were carried at cyclic temperature fluctuations: from near +22 to low positive (near +1-3°C), then to negative temperatures (-7°C÷-8°C)

and to +22 °C again. During experiment not less than two cycles were conducted. The experiment final took place after complete sample froze and pressure in the test cell released to atmospheric values.

After the tests finishing obtained experimental data processing was performed. Processing included analysis time change of temperature and pressure in the chamber, determination of phase transition parameters, estimation of water phase composition and also observations of petrophysical characteristics of frozen hydrate-containing sediments.

The types of structure of frozen artificial hydrate saturated samples are presented on figure 1.

RESULTS AND DISCUSSION

During cooling of water and hydrate-containing sediments under gas pressure which is higher than equilibrium, gas hydrate nucleation conditions were formed in porous space of sediments and at further cooling to negative temperature ice formation was controlled additionally [7]. Water phase transition into hydrate as in case of hydrate formation attended by a certain supercooling of system required for the first nucleation center initiation. The porous water supercooling degree (ΔT_{sc}^h) and also rate of hydrate crystals growth in dispersed sediments depended on cooling system conditions, process cyclic, water- and gas-saturated sediments composition and properties. As a rule, at repeated hydrate cycles value of the porous water supercooling degree decreased, that was motivated by water structure memory (table 1).

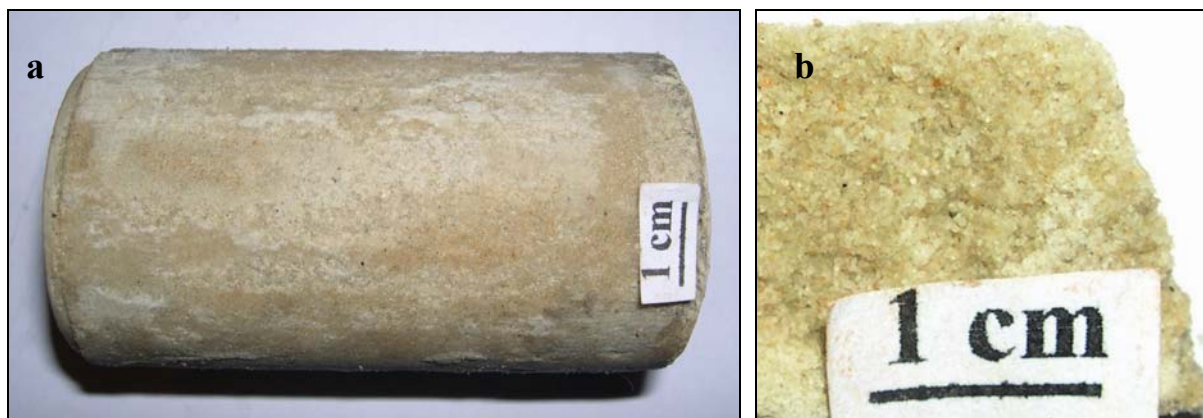


Figure 1. General view (a) and detail view (b) of frozen hydrate-saturated sample (sand with 3% of montmorillonite clay particles, $W_{in}=17\%$, $H_v=8\%$, $t=-8^\circ\text{C}$).

Sediment characteristics	1 cycle	2 cycle
Sand ($W_{in}=10\%$)	1,80	0,66
Sand with 3% of montmorillonite clay ($W_{in}=10\%$)	1,64	1,27
Sand with 7% of montmorillonite clay ($W_{in}=10\%$)	1,23	0,42
Sand with 7% kaolinite clay ($W_{in}=10\%$)	0,29	0,18

Table 1. The porous water supercooling degree (ΔT_{sc}^h) at hydrate formation in methane-saturated sediments.

Influence of mineral composition on initiation of hydrate crystallization centers in pore space could be observed in case of sand-clay mixture. Addition of clay particles (to 7%) in sand with initial water content of 10% the porous water supercooling degree reduced. The most decreasing was documented due to addition of kaolinite clay particles in comparison with montmorillonite one, that was induced by influence of crystal-chemical composition of mineral skeleton on porous water energy state and process of hydrate crystals growth (table 1).

Hydrate formation thermodynamic parameters in porous space obtained

experimentally showed that in comparison with bulk water there is a shift to the field of higher pressures and lower temperatures. The tend of deviation increasing for experimental samples ($W_{in}=10\%$) is observed in the row: sand-sand with montmorillonite particles-sand with kaolinite particles. Intensity of pore space hydrate accumulation, which could be estimated by rate of methane absorption at hydrate formation, reduced in case of clay particles addition. The most decreasing took place due to addition montmorillonite particles that is caused by porous water energy changes (fig. 2).

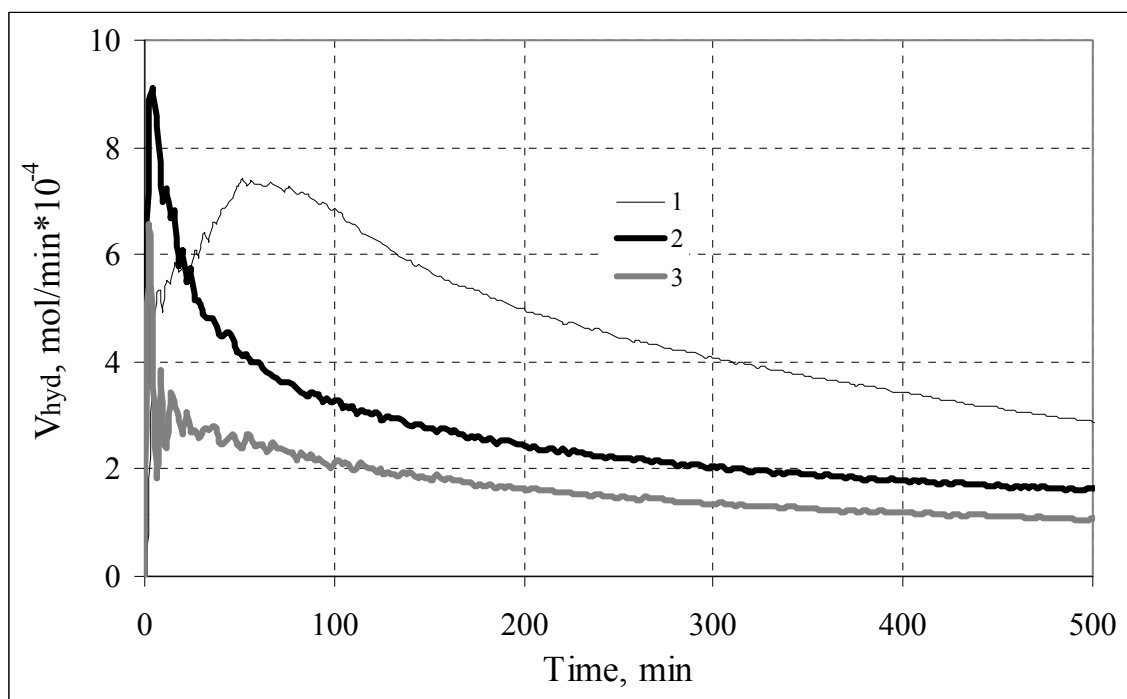


Figure 2. Intensity of methane consumption (V_{hyd}) in sample under hydrate formation: 1 – sand, $W_{in}=10\%$; 2 и 3 – accordingly, sand with 7% of kaolinite and montmorillonite clay particles, $W_{in}=10\%$.

It's experimentally found that at cooling stage of gas-saturated sediment only a part of porous water transformed into hydrate. It could be estimated by the hydration coefficient (K_H). As experiments showed the hydration coefficient and also of the total hydrate accumulation depended on pore space structure, gas-water contact surface, bond energy of porous water with mineral surface and thermodynamic conditions of hydrate formation. For example addition in sand ($W_{in}=10\%$ and 17%) of 7% of kaolinite clay particles in comparison with montmorillonite ones promoted the hydration coefficient (fig. 3). It could be explained by increasing pore space of sediment made growth of hydrate forms conditions possible. In additional clay particles induced porous water structure-energy changing, which also influence on condition of water phase transform into hydrate. Similar tendency was typical for kaolinite and montmorillonite clay samples ($W_{in}=35\%$) (fig. 3).

In the performed experiments maximal values of the hydration coefficient ($0,7-0,9$) characterized sand and sand-clay mixture. The

hydration coefficient values of the clay sediments (kaolinite and bentonite) were considerable lower and generally didn't exceed $0,5$ that attended by low gas permeability and imperfect gas-water contact.

Incomplete water transform into hydrate is also characterized for natural conditions. Using methodic studies on the hydration coefficient estimation, calculations for under permafrost gas hydrate forms in the Mackenzie delta were made. The field data analysis revealed that the hydration coefficient for Mackenzie 2L-38 [3] gas hydrate research well varied from $0,04$ at the pore hydrate-saturation (G_h) of 5% to $0,81$ at $G_h=75\%$ (table 2). Minimal values of the hydration coefficient for Mackenzie 5L-38 gas hydrate research well [8] amounted to $0,08$ at $G_h=10\%$ and maximal values of $0,63$ was accomplished at 80% of the pore hydrate-saturation (table 2). In fact that in natural condition as well as in laboratory experiments the hydration coefficient was maximal for sandy sediments and their values were found to be similar.

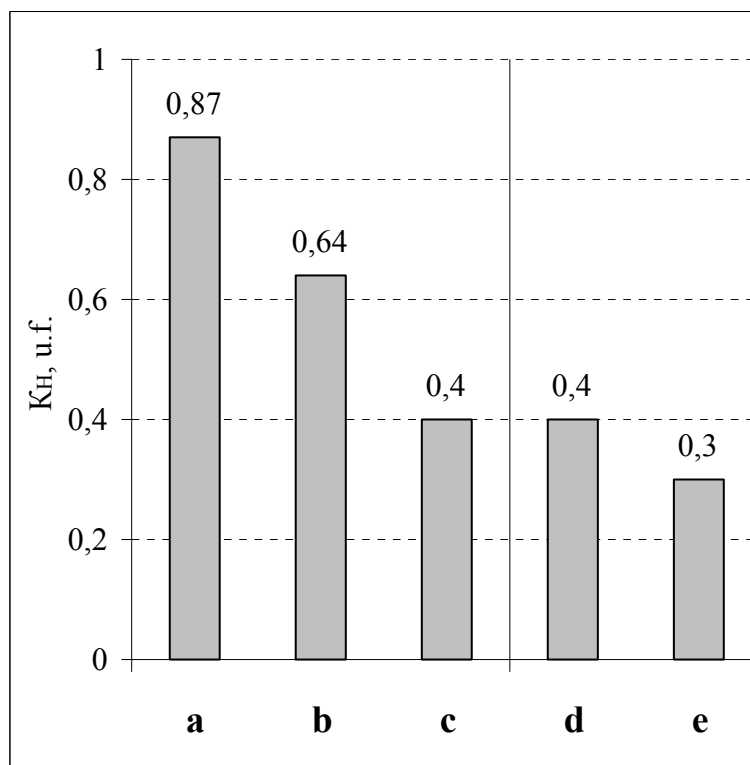


Figure 3. Hydration coefficient (K_H) for investigated sediments:

a – sand, $W_{in}=10\%$; b – sand with 7% of kaolinite clay particles, $W_{in}=10\%$; c – sand with 7% of montmorillonite clay particles, $W_{in}=10\%$; d – kaolinite clay, $W_{in}=35\%$; e – montmorillonite clay, $W_{in}=35\%$.

h, m	Type of sediment	Water content, %	Density, g/cm ³	Porosity, u.f.	G _h , u.f.	K _H , u.f.
Mallik 2L-38						
896,70	Sand	20	2,10	0,39	8	0,07
898,65	Sand	18	2,00	0,33	80	0,68
901,60	Sand	23	1,95	0,42	61	0,55
902,08	Sand	18	2,10	0,37	75	0,68
902,22	Silty sand	18	2,10	0,35	75	0,64
902,97	Sand	22	1,85	0,42	64	0,63
903,79	Silt	21	2,00	0,40	40	0,36
904,52	Sand	20	1,95	0,45	75	0,81
905,20	Pebbly sand	19	1,90	0,30	83	0,64
905,88	Sand	21	1,90	0,39	78	0,72
906,70	Silt	20	2,10	0,38	20	0,17
912,10	Silty sand	18	2,10	0,33	60	0,48
914,44	Gravel sand	18	2,15	0,33	75	0,59
920	Fine sand	20	2,00	0,37	76	0,66
921,58	Fine sand	28	1,85	0,42	60	0,49
922,43	Sand	24	1,95	0,37	45	0,35
926,81	Sandstone	1	2,70	0,34	5	0,50
927,01	Clayey silt	19	2,20	0,34	5	0,04
927,60	Clayey silt	18	2,25	0,31	5	0,04
Mallik 5L-38						
921	Sand with gravel	17	2,15	0,30	80	0,63
1022	Siltstone with sand	21	2	0,34	10	0,08
1097	Sand with siltstone	19	2	0,33	45	0,36

Table 2. Hydrate-containing layers characteristics for Mackenzie 2L-38 [3] and 5L-38 [8] gas hydrate research wells, applied for the coefficient hydration estimation

During experimental process it was found out that hydrate formation in pore space of sediments could continue also at negative temperature when the remaining porous water freezing. The rate of additional methane hydrate formed during freezing could come up to 10-20% at the total rate of hydrate accumulation [9].

THE MODEL OF FROZEN HYDRATE-CONTAINING SEDIMENT FORMATION

Experimental investigations analysis allowed predicting the special model dealing with hydrate and gas formation in porous space of methane-saturated dispersed sediments at cooling (fig. 4).

The main factors for methane hydrate formation in dispersed sediments are thermodynamic conditions and presence of gas-water contact that is available in circumstances of

incomplete degree of pore water filling. Water-gas phase boundary in porous space is a zone of pore hydrate form origin and growth. At that the basic growth of crystals processes within pores. Disturbance and liquidation of gas-water contact during hydrate growing initiates a hydrate formation damping. If certain structure forming processes activating and generating of new gas-water contacts didn't take place, hydrate formation could full stop, in spite of the water existence. Further cooling of hydrate-containing system to negative temperature induced ice formation. Enclosing hydrate ice would originate from the remaining bulk water and interfacial water located on the particles and aggregates surface. The primary hydrate preservation will occur by surrounding ice.

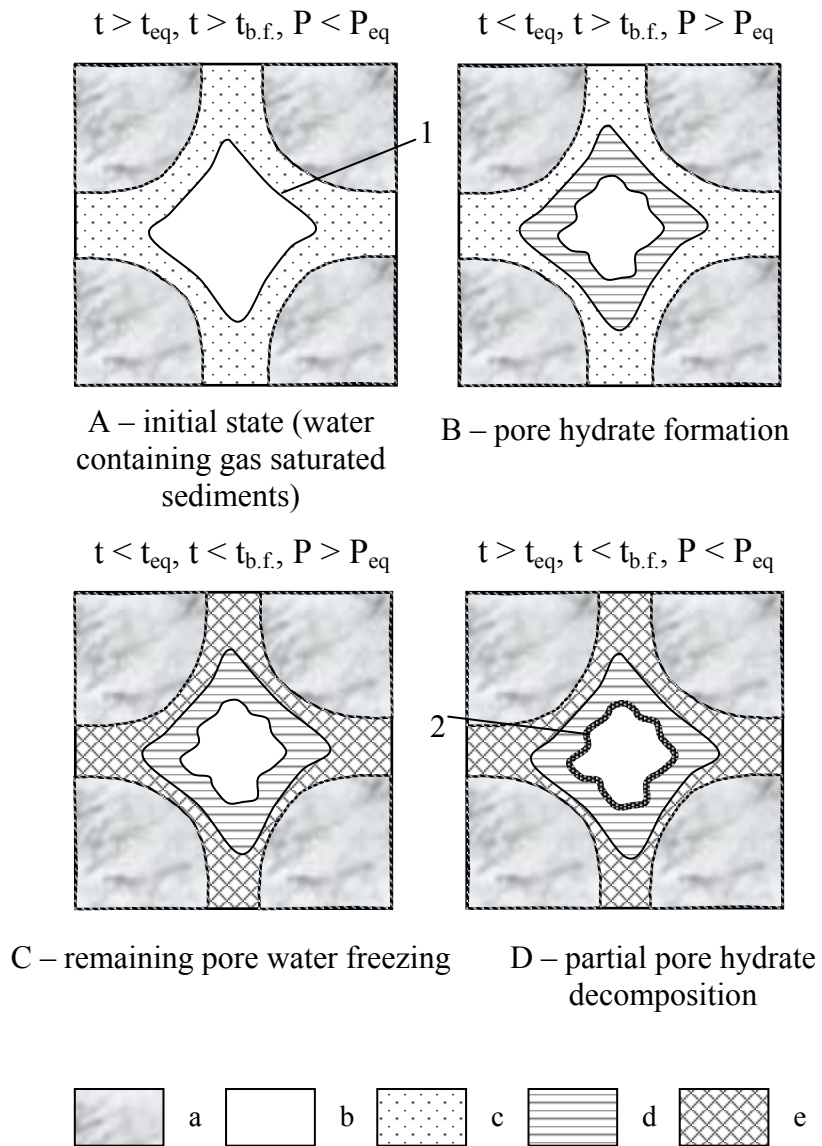


Figure 4. Mechanism of hydrate and ice formation in porous media of methane saturated sediments: a – sediment particle; b – free gas; c – pore water; d – hydrate; e – ice;

- 1 – the place of gas hydrate crystal nucleation (gas-water contact);
- 2 – the ice formed from partial hydrate dissociation (self-preservation effect).

t and P – existence thermodynamic conditions;
 t_{eq} and P_{eq} – equilibrium temperature and pressure under hydrate formation;
 $t_{b.f.}$ – temperature of pore water beginning freezing.

The remaining porous water freezing and some processes according it (blowouts of dissolved gas, deformation of mineral structure, structure formation etc.) facilitated new gas-water contact appearance and elevation of sediment gas-saturation on the whole. Under thermodynamic non-equilibrium conditions for hydrate existence (pressure reducing to atmosphere level) secondary preservation of pore hydrate would be occurred due to partially hydrate dissociation. This phenomenon was described earlier as self-preservation effect at negative temperature.

CONCLUSIONS

Quantitative parameters on kinetics of hydrate accumulation in dispersed sediments at their cooling investigated on base of performed experiments. The influence of composition of mineral skeleton on the porous water supercooling degree, conditions and rate of methane hydrate crystals growth and also on the hydration coefficient in the studied samples was shown. It was found out that maximal rate of water transformed into hydrate was typical for sandy sediment that was supported by the same data for natural hydrate-contained sediments. It was mentioned that hydrate formation process in dispersed sediments could be activated by freezing of the remaining porous water and cyclic thermodynamic effects.

Experimental studies resulted in predicting model of hydrate and ice formation in porous space of methane-saturated dispersed sediments at cooling.

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