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# Experimental research of methane and carbon dioxide hydrate formation in frozen and thawing sediments

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Geological studying and temperature modeling of the Arctic seas bottom conditions shows that submarine permafrost is widespread on the Arctic shelf. Continuous subsea permafrost on a shelf of northern seas can exist to isobaths 50-60 m. As the Arctic seas are shallow, the subsea permafrost occupies the large territories; sometimes its capacity reaches 200-300 m. The most of permafrost researchers believes that the submarine permafrost is relic and it was generated on the land during a cold epoch in period of deep reliction of the seas, and then has been flooded during marine transgression. Considering presence of gas components in permafrost and in some cases a high gas saturation of permafrost (gases are mainly methane with small amounts of carbon dioxide and nitrogen), especially its top horizons (to depths of 100-200 m), it is necessary to assume an active role of gas hydrate formation processes in gas saturated frozen and thawing sediments during advance of sea when relic frozen sediments exist in a gas hydrate stability zone.

Taking into account an insufficient research studying of gas hydrate formation processes on the Arctic shelf, we had been developed the special experimental program on physico-chemical modeling of hydrate formation in cryogenic shelf sediments. In the report the experimental results of hydrate formation kinetics in sediment samples are presented mainly at negative temperatures (on Celsius) with special attention of the role of water-ice phase transitions on gas hydrate accumulation in sediment samples when scanning the temperature of testing systems above zero (on Celsius). It includes the studying of mechanism and some characteristics of gas hydrates accumulation in porous space of frozen and thawing sediments (in a range of temperatures from a minus 8 up to plus 4 degrees on Celsius and gas pressure up to 8 ), and also an estimation of influence of various factors on dynamics of gas hydrates accumulation of in cryogenic sediments.

Objects of research are: sandy and loamy sand samples were collected from permafrost horizons. Thermodynamic conditions in a pressure chamber are changing during process of gas hydrate formations and it was allowed to defined some parameters of phase transitions in soil samples and also to estimate a share of moisture which transfer into a hydrate form and also to calculate a hydrate saturation of soil samples. During experiments it was detected that gas hydrates accumulation (of methane and carbon dioxide hydrates) in porous space proceeds actively both at positive and negative temperatures. It should be pointed that transition through zero degrees intensifies highly the process of hydrate accumulation in porous space of sediment samples. It may be explained the thawing of pore ice and following structurally-textural changes of the samples give some new gas-water contacts. As a result during ice thawing the secondary gas hydrate formation process can occur.

Thus the experimental data gives possibilities to estimate the influence of temperature, ice- and salt contents and types of the soil on kinetics of phase transition from pore liquid water to hydrate phase and to analyze the accumulation of methane and carbon dioxide hydrates in pore space of frozen and thawing sediment samples. Experimental results show that in frozen and thawing gas saturated sediments at appropriate thermodynamic conditions processes of hydrate accumulation in pore space can actively proceed. Long existence of relict submarine permafrost on Arctic seas probably help forward to considerable accumulation of gas hydrates in frozen and cooled deposits on the Arctic shelf. Therefore the process of relic subsea permafrost degradation and sea reliction can lead to decomposition of permafrost gas hydrates and to allocation in atmosphere of additional greenhouse gases.