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Experimental Study of Self-Preservation Mechanisms and Relict Gas Hydrates Formation in Porous Media

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Natural gas hydrates are formed under appropriate thermodynamic conditions in bottom sediments of seas and oceans as well as in permafrost regions. Hydrate stability zone in permafrost starts at depth 200-250m and spreads to under-permafrost layers till depth 800-1500 m. It was established the possibility of methane hydrates existence in metastable state (so called "relict gas hydrates") in layers of frozen sediments above stability zone (up to 200-250 m). The metastable hydrates may exist in permafrost at negative (on Celsius) temperatures for a long time due to the self-preservation effect (very low hydrate decomposition due to ice covering of hydrate particles).
Presence of relict gas hydrates in the permafrost of the Arctic zone can significantly increase its energy resources. On the other hand relict gas hydrates at shallow depth in the permafrost can be a serious geological hazard at natural or technogeneous degradation of the permafrost. Large quantity of methane (greenhouse gas) can be thrown out to the atmosphere when hydrates are decomposed. Moreover, some technical problems (blow out of gas or sediments, fires) can take place while drilling and exploitation of production wells in the Arctic regions.
Previously we already discussed the mechanisms of bulk hydrate decomposition process for different gases at atmospheric pressure and negative temperatures. We find that some gases (nitrogen, methane, natural gases, carbon dioxide) show self-preservation effect, but some gases (propane, i-butane, etc.) do not show. Sometime self-preservation process may be considered as stochastic. Theoretical estimations show that the "good preservation" of hydrate particles include the appearance of metastable (supercooled) liquid water at the initial stage of decomposition and then water freezing and ice film formation. If decomposition process proceed directly to ice and gas (without appearance of intermediate phase of liquid water), the preservation of hydrate particles is not so good. As for hydrate decomposition in porous media it still need in additional experimental studies.
A complex of special experiments has been carried out to study frozen hydrate-bearing sediments under non-equilibrium conditions. It included artificial saturation of freezing sediments by methane or carbon dioxide hydrates, research of gas- and hydrate-content of frozen hydrate-bearing sediments when gas pressure was reduced below equilibrium pressure and fixed (at different levels, up to 0.1 MPa), estimation of change in thermal conductivity of hydrate-bearing sediments under non-equilibrium conditions. We used sediments of different composition and structure, including core samples recovered from gas-showing horizons of frozen sediments in Yamburg, Bovanenkovo and Zapoliarnoe gas-condensate field.
Experimental research of hydrate decomposition in frozen sediments when pressure is reduced below equilibrium value allowed revealing some features of the self-preservation effect in sediments at negative (on Celsius) temperatures. It was shown, that the self-preservation of gas hydrates in frozen sediments depends on many factors, such as thermodynamic conditions, ice content, phase composition, gas permeability, composition of organo-mineral matrix, salinity, structure-textural peculiarities of hydrate-bearing sediments, including micro-morphology of hydrates. Freezing of residual pore water (not transformed to hydrate) plays the important role in self-preservation of hydrates. Ice occurrence provides the increase of hydrate stability and their initial preservation in porous media.

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