Freezing Technology for Laboratory Study of Hydrate-Saturated Sediments and it's Application to Gas Industry

Main author
E.M. Chuvilin
Moscow State University, Moscow,
Russia
IGRC2008@gasunie.nl
Co-author
V.A. Istomin,

Joint-stock company "Novatek", Moscow,

Russia

1. Abstract

When a core sample of hydrate-bearing sediments is recovered for laboratory researches, there appears a serious problem of its temporary storage (before studying of its properties by means of different physicochemical methods) without significant alteration of the sample's internal structure and properties. Well-known technology of long-term storage in liquid nitrogen without gas hydrates decomposition leads to significant changing of sample's pore space microstructure. In this paper we consider an alternative technique which consists in freezing the hydrate-bearing core samples up to temperature -7…-20 ^{o}C at atmospheric pressure. This technique allows to decrease significantly the rate of hydrate dissociation in frozen sediment samples. To develop the technique we need some experimental data concerning the behavior of gas hydrate inclusions in porous media under temperature below 0 ^{o}C. During experimental research the factors and conditions for promoting of gas hydrates preservation in frozen sediments has been revealed. The obtained experimental data are used for improving the technique of gas hydrate preservation in hydrate-bearing natural sample with minimal violation of its internal structure.

C O N T E N T S

2. BODY OF PAPER

2.1. Introduction

At present natural gas hydrates is considered by IGU as one of the prospective unconventional gas resource. Gas hydrates of methane and other hydrocarbons are stable at appropriate temperature and pressure conditions. As known gas hydrates in sediments are widely spread in nature both at offshore and onshore conditions (i.e. in marine sediments and in permafrost zone). Gas hydrates may be also considered as a specific marker of below-situated productive collectors with conventional natural gas. To estimate hydrate reserves and to propose a technology for gas recovery from hydrate-containing deposits it should be studied some physical and chemical properties of natural hydrate-containing core samples. From this point of view the important problem is how to prevent the rapid decomposition of gas hydrates in the samples and how to provide the preservation of their properties during storage and laboratory testing.

Laboratory testing of hydrate-containing sediments is difficult and laborious procedure. So we need to use an appropriate technology without serious property's changing during sediment storage. It seems that the quick freezing of the samples in liquid nitrogen may be a good candidate for such technology. Unfortunately quick freezing may alter the inner structure of porous media and also may change significantly the physical properties of the sample (including gas hydrate decomposition kinetics). More safety technology is to freeze a hydrate-saturated sediment about minus 5 ÷ minus 10 degrees centigrade at atmospheric pressure which is allow to reduce the velocity of decomposition process significantly. Another words, it means understanding when and why a self-preservation and related effects may be used in practice in context of long-storage hydrate-saturated sediments without significant decomposition. Also it means the necessarily of detailed study of the hydrate decomposition kinetics in sediments at different conditions. Similar hot problem is the possibility of carbon dioxide long storage in gas-hydrate state in permafrost zone.

Firstly the subject of the paper is to provide an additional experimental data of decomposition kinetics of hydrate-saturated sediments at pressure below three phase "gas – ice - hydrate" equilibrium pressure (for instance, at atmospheric pressure) and subzero temperatures. So we present experimental data on stability of frozen gas hydrate-containing sediments at negative (on degrees centigrade scale) temperatures. The experiments included the following stages: hydrate-saturation process of porous soils, their slowly freezing and than the determination of decomposition velocities during storage at different pressure and negative temperatures.

2.2. Methods of experimental research

The experimental technique has been based on physical modeling of phase transitions of pore water in methane-saturated sediment in pressure chamber (Chuvilin et al. 2005). Artificially prepared hydrate-saturated samples were carried out in two pressure chambers with wet soils inside. In the first chamber the size of sample of a soil made 4,6 cm in diameter and about 9 cm in length, in the second chamber of 6,8 and 9 cm accordingly. Different soils were used in experiments: silty sand, quartz sand and sandy-clay mixes consisting of quartz sand with kaolinite or montmorillonite clay particles. The weight content of clay component in the soils was chosen as

7 % and 14 %. The initial water content of soil was set in a range from 10 % to 17 %, ensuring a well-developed gas-water interfacial area in the pore space. Pure methane and carbon dioxide were used as hydrate-forming gases.

Hydrate-saturation of sediment samples in a pressure chamber (7 ÷ 8 MPa for CH_4 and 3 ÷ 4 MPa for $CO_{2)}$ was carried out at low positive temperature (plus 0,5 ÷ 2,0 ^{o}C). When hydrate formation finished, the pressure chamber was cooled to -8 ^{o}C in a refrigerating room. Then the pressure in a chamber with frozen hydrate saturated sample was released up to atmospheric pressure, the pressure chamber was opened frozen hydrate sample was taken from a chamber and was exposed to detailed petrophysical researches. Petrophysical researches included macro-and micromorphological supervision, definition and calculation of water content, density, gas and hydrate content (H_v), porosity, hydrate coefficient (K_h) (share of pore water which has transformed in hydrate), hydrate (S_h) and ice (S_i) saturation. Gas content was measured by thawing in NaCl saturated solution. Another part of frozen hydrate-bearing sediment sample was stored on weighing devices for long time at negative temperatures. Sublimation of the ice was reduced by a thin ice particles coating on the samples. Samples were monitored during a month or so.

2.3.   Results and discussion

Experimental data on methane hydrate dissociation in frozen samples after pressure release shows that in the first moment after pressure release there is rather intensive decomposition of pore hydrate, then intensity of decomposition falls, and later practically fades (fig. 1). It is characteristic both for methane hydrate saturated samples, and for samples sated by hydrates CO_2 too. Incomplete decomposition of pore hydrate, caused by self-preservation display effect is observed.
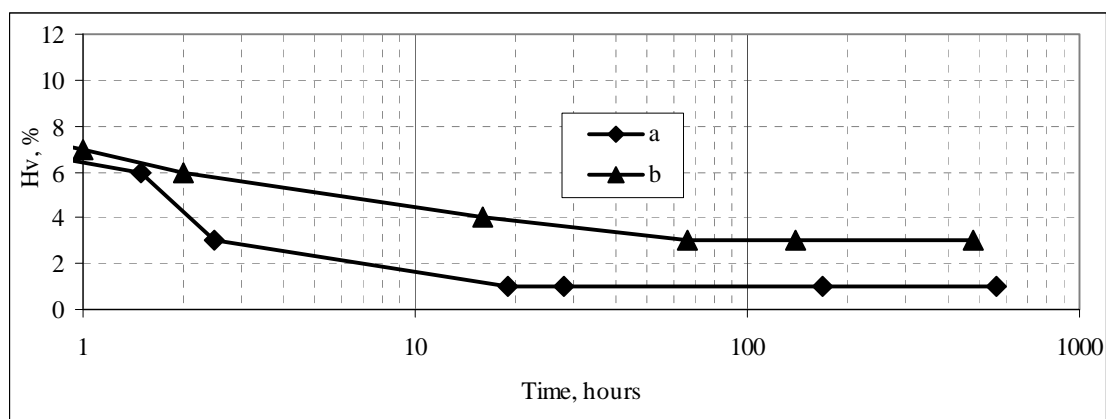

Figure 1. Kinetic of methane hydrate dissociation in frozen sand with 7% montmorillonite clay samples after gas pressure release (P=0,1MPa, t=-8 ^{o}C); a and b initial gravimetric water content of samples W_{in}=17%, W_{in}=10%, initial volumetric hydrate content of samples (Hv)=10%.

The self-preservation effect consists in formation of ice pellicle around gas hydrate particles during its initial surface decomposition at negative temperatures. As the result a remained part of

not decomposed pore hydrate can exist in metastable state for a long time (Ershov et al. 1991; Istomin et al. 2006, Chuvilin et al. 2008).

Our experimental data show that self-preservation effect reduces the decomposition velocities of pore hydrate in all soil samples.

Hydrate-saturation falls at decomposition of hydrate in pore space. In turn it makes active the transition of the residual water into ice. So while the reducing of sample hydrate-saturation take plays its ice saturation is increasing (fig. 2).
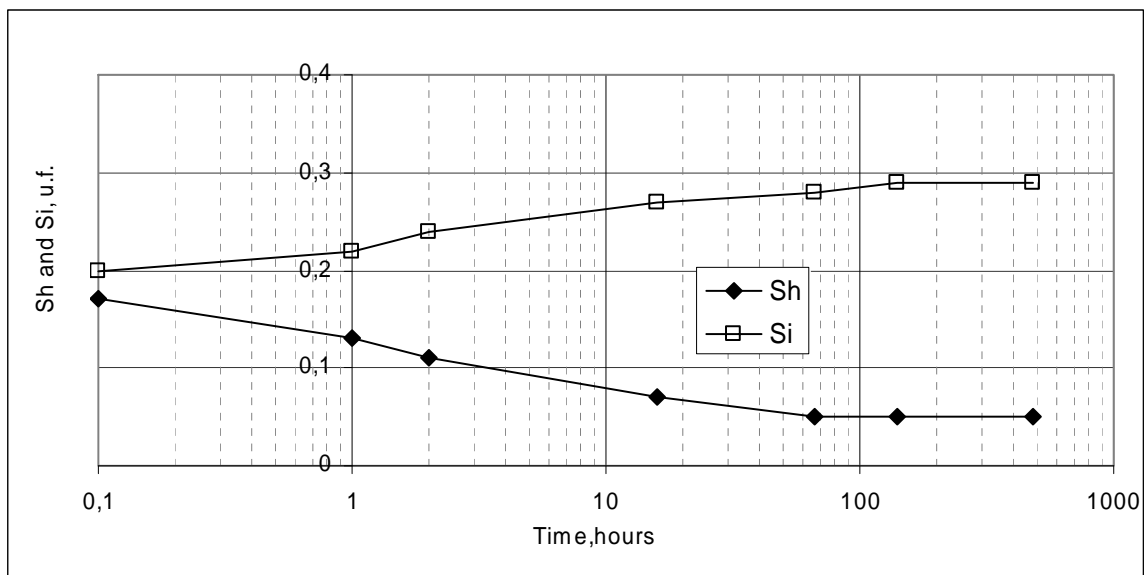

Figure 2. Methane hydrate dissociation kinetic in frozen sediment sample after pressure releases to 0,1 MPa; sand with 7% montmorillonite clay (W_{in}=17%), t=-8 ^oC, Sh и Si – hydrate saturation and ice saturation.

At the beginning of the experiment (before decomposition process) hydrate saturation was about 18%, and ice saturation was 20%. During 390 hours, gas hydrate saturation was decreased up to 5%, and the ice saturation was increased to 28%.

As known, preservation of gas hydrate in frozen sediment depends on many factors such as thermobaric conditions, hydrate and ice saturation, gas permeability, structure of organ-mineral skeleton of sediment, pore water salinity, and structure of hydrate, including micromorphology (Chuvilin et al. 2008). Ice which is formed during freezing of residual pore water (which has not transformed into hydrate) plays an important role in the self-preservation of gas hydrates. This ice promotes gas hydrate stability in a porous medium. As a rule, frozen hydrate-containing samples with greater ice content after pressure release are more prone to self-preservation.

For gas permeability reduction and prevention of ice sublimation from the surface of the samples it is reasonable to use the technique of artificial freezing-out an ice film on the surface of hydrate-bearing samples wrapped in a thin polypropylene fabric. This technique may increase the stability of gas hydrates in frozen samples. To freeze-out an ice film, frozen hydrate-bearing sample is periodically put into vessel with slightly supercooled water (water temperature from -1 to -5 ^oC). According to experiments, the optimum thickness of artificially grown ice film around the sample is several mm.

Results of experiments on frozen hydrate-contained samples show that intensity of pore gas hydrate dissociation sharply decreases with lower temperatures. In the silty sand sample

(W_{in}=14 %, initially about 45% hydrate saturation at all temperatures) hydrate-saturation after pressure release fell to 5% at -2°C in 20 hours, 28% at -4 °C, and 43% at -7 °C (Fig. 3). After 150 hours at -2°C, little hydrate amount remained, however, at -4 °C and -7 °C decomposition was significantly decreased.

The decrease of temperature of hydrate-bearing sample storage below minus 30 °C (beyond the temperature range of "good quality" self-preservation effect) leads to the activation of the processes of pore hydrates dissociation. At the figure 4 the results of experimental study of changes in hydrate saturation in sediments samples are presented. It is showed that at temperature -50 °C the intensity of dissociation is significantly higher then at -7 °C (fig. 4). After 22 hours from the beginning of hydrate-bearing samples storage at negative temperatures and atmospheric pressure, hydrate saturation at -50 oC became half in comparison at temperature -7oC. After 50 hours this difference became more then 4 times.
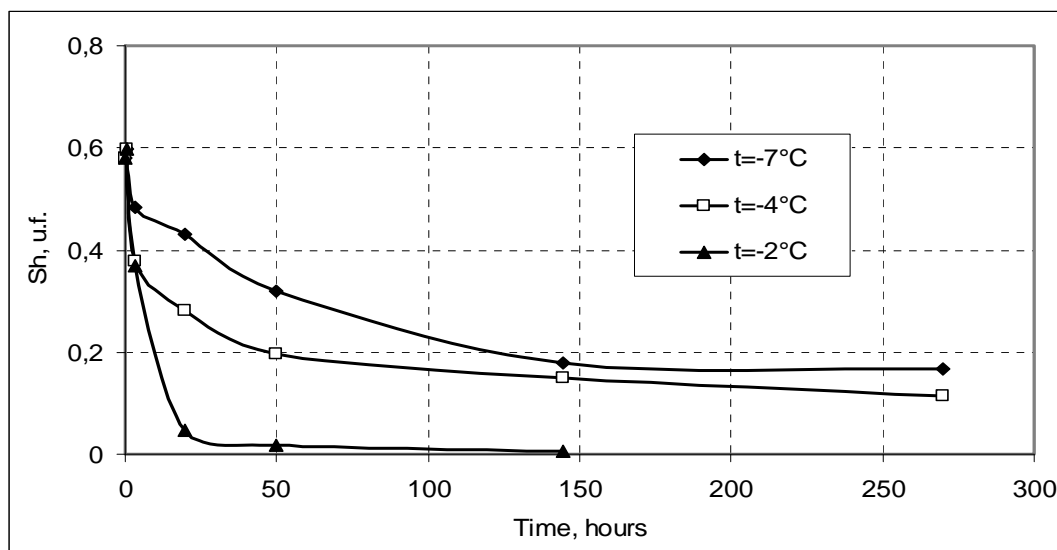

Figure 3. Methane hydrate dissociation kinetics in artificially hydrate-saturated frozen silty sand (W_{in}=14%) after pressure release to 0,1 MPa at different temperature.
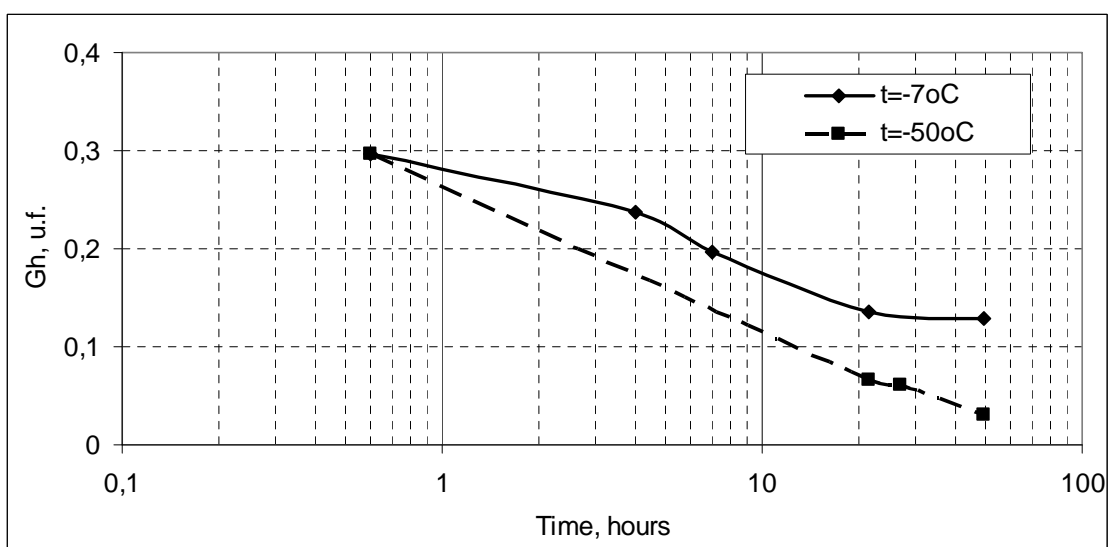

Figure 4. Temperature influence on methane hydrate dissociation kinetic in frozen hydrate saturated sandy samples (sand with 7% montmorillonite, W_{in}=17%) after pressure release to 0,1 MPa.

To analyze the disadvantages of sample storage in liquid nitrogen we carried out a number of model experiments. Thus, we observed the frozen hydrate-bearing samples which had experienced a strong cooling in liquid nitrogen during 1-2 hours. These samples after their removal out of liquid nitrogen were characterized by higher rate of hydrate dissociation then the samples, which had not been exposed to liquid nitrogen (comparative experiments on hydrate dissociation were carried out at temperature -8°C). As an example let's consider hydrate-bearing sand samples (sand sample with 14% of kaolinite clay particles, W_{in}=10%). Their initial hydrate saturation was about 30 %. The sample, which had contact with liquid nitrogen after 5 hours of storage at temperature -8°C had hydrate saturation of about 2% which was 5 times less then the similar sample without contact with liquid nitrogen. And after 93 hours hydrate content in this sample is equal to 0.

Also we study the influence of dispersity and mineral composition on the pore gas hydrates dissociation kinetics and self presentation effect. The intensity of dissociation is reduced in the line "sand with 7% of kaolinite – sand with 7% of montmorillonite – sand". The increasing of clay particles content as well as salinity of the sample promotes the reducing of the stability of pore methane hydrate (increases the intensity of hydrate dissociation).

Recent investigations (Klapproth et al 2007) have shown that microporous gas hydrates often form in sediments with high content of clay particles, which are less stable under non-equilibrium conditions. Comparative analysis of the self preservation effect in frozen sediments containing methane or CO_2 hydrates at similar experiment conditions (t=-7 °C) showed increased stability of methane hydrate in comparison to CO_2 hydrate (Chuvilin et al., 2007). Thus, in sand samples (W_{in}=10%) at the initial time (under equilibrium conditions) there was similar hydrate saturation for methane and CO_2 hydrates (about 33%). However, after 5 hours from the beginning of the hydrate decomposition process, hydrate saturation in methane-bearing sample was 27% but in CO_2- bearing sand was 17% (fig. 5).

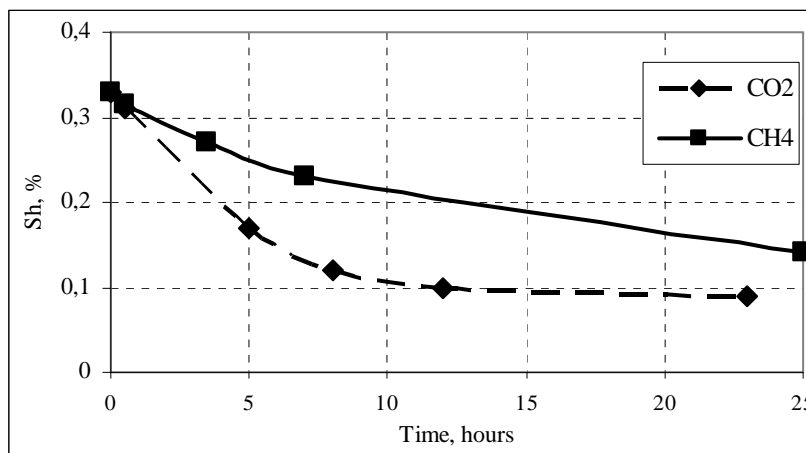Figure 5. Dissociation kinetics of CH_4 and CO_2 hydrates in sand sample (W_{in}=10%) after pressure release up to atmospheric (t=-8 °C).

After that it was observed the attenuation of CO_2 hydrate dissociation process. But, as the experimental data showed, in CO_2-saturated samples dissociation process was less long as in in methane saturated sample.

2.4. Conclusions

During our experimental research it was shown that after freezing of gas hydrates samples in porous media (soil samples) self preservation effect also may take place as well as in bulk gas hydrates. It was determined the main factors and conditions for unusual stability of frozen samples. These factors are: initial ice and hydrate contents, gas permeability, dispersity, salinity, temperature range for "good self preservation", liquid nitrogen treatment, hydrate-forming gas etc.

The analyses of experimental data give us possibilities to propose the special technique for good storage of hydrate-containing core samples before field and/or laboratory testing.

The technology includes two main steps. The first step is freezing the hydrate-bearing sediment sample wrapped in a thin film of polypropylene fabric at negative temperature from $-7\ ^{o}C$ to -20 ^{o}C. The second step is additional isolation of hydrate-bearing sample by freezing-out an ice film on the sample surface. Further this sample is stored at a constant negative temperature at a range from -7 to -20 ^{o}C.

The technique allows to store samples without significant altering of inner structure and substantially simplify transportation and temporary storage of recovered hydrate-bearing samples.

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Figure 5. Кинетика диссоциации гидратов CH_4 и CO_2 в образце песка (W_{in}=10%) после сброса давления до атмосферного (t=-8 ^{o}C).