

## **EXPERIMENTAL METHOD FOR DETERMINATION OF THE RESIDUAL EQUILIBRIUM WATER CONTENT IN HYDRATE-SATURATED NATURAL SEDIMENTS**

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### **ABSTRACT**

The equilibrium “pore water in sediment–gas hydrate-former–bulk gas hydrate” was experimentally studied. This residual pore water corresponds to a minimal possible amount of water in the sediment, which is in thermodynamic equilibrium with both gas and the bulk hydrate phase. This pore water can be defined as non-clathrated water by analogy to unfrozen water widely used in geocryological science. The amount of non-clathrated water depends on pressure, temperature, type of sediment, and gas hydrate former. The presence of residual pore water influences the thermodynamic properties of hydrate-saturated samples. The paper’s purpose is to describe a new experimental method for determining the amount of non-clathrated water in sediments at different pressure/temperature conditions. This method is based on measuring the equilibrium water content in an initially air-dried sediment plate that has been placed in close contact with an ice plate under isothermal, hydrate-forming gas pressure conditions. This method was used to measure the non-clathrated water content in kaolinite clay in equilibrium with methane hydrate and CO<sub>2</sub> hydrate at a temperature of –7.5° C in a range of gas pressures from 0.1 to 8.7 MPa for methane and from 0.1 to 2.5 MPa for CO<sub>2</sub>. Experimental data show that at the fixed temperature the non-clathrated water in hydrate-containing sediments sharply reduces when gas pressure increases. The experiment demonstrates that the non-clathrated water content strongly depends on temperature, the mineral structure of sediment, and the hydrate-forming gas.

*Keywords:* gas hydrates, equilibrium water content, unfrozen water, non-clathrated water, sediment, ice.

### **NOMENCLATURE**

$P_{\text{exp}}$  experimental pressure [MPa]  
 $S$  salinity [%]

$T$  temperature [°C]  
 $\rho_s$  particle density [g/cm<sup>3</sup>]

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## INTRODUCTION

It is known that pore water can freeze in some temperature range below the freezing point of bulk water. In geocryological science this amount of water is called “unfrozen”. Under each fixed value of negative Celsius temperature, phase equilibrium takes place between ice, water and water vapor in the porous medium [1,2], that is, there is a dependence curve of unfrozen water content on temperature. The amount of unfrozen water in frozen sediments depends on their composition, structure and pressure-temperature conditions. In other words, the chemical potential of pore water depends on sediment type, water content and temperature. However, the pressure effect is not taken into account because experiments in geocryology are usually prepared under atmospheric pressure. As a rule, the external pressure influence on the phase equilibrium “water-ice” is not large, which can be confirmed by the fact that to change the equilibrium by 1 °C, 13 MPa pressure must be applied. Several methods have been developed for determining the unfrozen water content in a porous medium as a function of temperature; these methods include calorimetry, dielectric, nuclear magnetic resonance (NMR), and others. In general, these methods can be modified to study the gas hydrate equilibria between the gas hydrate, gas and water dispersed in pores. Up to now in gas hydrate science the traditional approach to gas hydrate equilibrium study consisted of two stages. The first stage is preparation of gas hydrates in a pressure chamber; the second stage is decomposition of hydrates and determination of equilibrium pressure-temperature parameters. This traditional approach for studying equilibria in porous media leads to loss of accuracy because of the small amount of hydrates formed in the dispersion medium.

Researchers have experimentally studied the effects of porous media on hydrate stability. The first experimental data were offered by Yu.F. Makogon on the conditions of gas hydrate formation and dissociation in a porous medium [3]. Makogon showed that thermo-baric conditions of methane hydrate formation and decomposition in small pores move to the area of higher pressures and lower temperatures. After that, conditions of gas hydrate existence in porous medium were studied by Cherskii et al. [4], Handa and Stupin [5], Uchida et al. [6-8], Clennell et al. [9], Ostergaard et al. [10], Anderson et al. [11-12] and many others. During this research of critical pore

size, the water content of dispersion media was found when thermobaric conditions of porous hydrate decomposition differed from that of bulk hydrate. As a whole, the study of gas hydrate phase equilibrium in porous media in these works was carried out by obtaining thermobaric parameters of hydrate formation or decomposition under certain given water content. The experimental results reflect a low level of accuracy. The traditional approach leads to loss of accuracy because of the small amount of hydrates formed in the dispersion medium. Moreover, there are serious methodological difficulties about completeness of the pore water transition to hydrate at the stage of hydrate preparation phase. Sometimes this approach gives too high an amount of water in the dispersion medium (taken as equilibrium water content).

Taking into account the problems of traditional experimental technique, researchers have started to use sensitive methods for fixing the hydrate dissociation process, for instance, studying hydrate decomposition in disperse medium in a calorimetric cell [13, 14]. The productivity of such an approach was pointed out in Istomin and Yakushev’s monograph [15] and in a pioneer calorimetric paper by Handa and Stupin [5].

The difference is seldom clarified between equilibrium of pore water and disperse or bulk hydrate phase. Considering that these two types of equilibria (with bulk or pore hydrate) are different, when studying them experimentally in the presence of pore water it must be stated clearly which equilibrium is being studied. Developing methods has become important for studying phase equilibria of gas hydrates in natural porous media (sediments). The experience of geocryological science in determining unfrozen water content for real (not model) porous media may be useful. Modification and specification of elaborated geocryology methods for investigating gas hydrate equilibria may be a new direction in the experimental research of gas hydrates in porous media.

The term “non-clathrated water content”, which appears as an analog to unfrozen water, needs to be discussed. Non-clathrated water content is an equilibrium amount of pore water in sediment which is in equilibrium with gas phase (gas hydrate former) and gas hydrate in bulk phase. Taking into account that metastable pore water state is possible in hydrate-bearing sediments, it can be said that equilibrium water content (the so-

called non-clathrated water) in hydrate-bearing media corresponds to the minimum possible amount of pore water in the concerned sediment system. The liquid water amount in equilibrium with pore hydrate differs from the equilibrium water content in three-phase equilibrium “pore water–gas–bulk gas hydrate.” Thus, it is necessary to develop experimental methods to determine the equilibrium water content for both types of equilibriums. Considering the difficulty in setting up such research, this work considered only the equilibrium of pore water and bulk hydrate. Additionally, this work considers the possibility of using sorption methods to study hydrate equilibrium when hydrate in pore medium does not form at all. A type of sorption method used for the quantitative study of unfrozen water content in geocryology, called the contact method, was elaborated in the midst of 1970’s by Russian geocryologists [16, 17].

The essence of the contact method is based on reaching the equilibrium between ice, unfrozen water, and vapor at the isothermal contact between plates of dry sediment and ice. As these experiments show, the saturation of sediment by water at the contact between soil and ice occurs by means of both vapor transition and film-capillary water transition [16]. Thermodynamic three-phase equilibrium (ice, unfrozen water, and vapor) and stopping the saturation by water of initially “dry” sediment occur at some point. At that point, total water content of initially “dry” sediment corresponds to the equilibrium amount of unfrozen water at the given negative temperature. According to geocryology research, the real saturation stabilization time in the range of  $-0.5$  to  $-20$  °C is about 24 hours for the majority of sediments [17]. Usually, the contact time between dry sediment plates and ice at the determination of unfrozen water content is 1 to 3 days. Nowadays, the contact method is successfully used in geocryological research in Russia for determining unfrozen water content.

This work proposes for the first time using the contact method to study non-clathrated water content. The equilibrium pore-water content was determined in a porous medium in the presence of a three-phase equilibrium: pore water–gas–bulk gas hydrate. The suggested method fundamentally allows for determining equilibrium water content over a wide range of temperatures and pressures. At fixed temperatures, pressure influence can be experimentally estimated on equilibrium water

content; and at the fixed gas pressure, temperature dependence can be obtained for the equilibrium pore water content change in the range of negative and positive temperatures.

## TECHNIQUE OF NON-CLATHRATED WATER IN SEDIMENTS STUDYING

The technique for determining non-clathrated water content is based on measuring the equilibrium water content in an initially air-dry sediment plate placed in close contact with an ice plate under isothermal, hydrate-forming pressure conditions. According to experimental research, gas hydrates appear on the ice surface under these conditions, and the three-phase equilibrium (pore water–gas–bulk gas hydrate) stabilizes.

Several methodical experiments were conducted to improve the contact method for determining equilibrium non-clathrated water content. As a result, a technique was created for experimentally determining non-clathrated water content in a porous medium. The technique includes preparation methods of sediment and ice plates for the experiment and data processing. Model sediments with well-known properties were used as test subjects: kaolinite clay and sand-clay mixes consisting of quartz sand with kaolinite or montmorillonite clay particles (Tables 1, 2)

Type of sediment	Particle size distribution/%		
	1-0.05 mm	0.05-0.001mm	<0.001 mm
Quartz sand	94.8	3.1	2.1
Kaolinite clay	4.5	70.9	24.6
Montmorillonite clay	0.3	46.2	53.5

Table 1. Characteristics of sediments

Type of sediment	Mineral composition	$\rho_s$ g/cm <sup>3</sup>	S/%
Quartz sand	Quartz >90%	2.65	0.012
Kaolinite clay	Kaolinite 92% Quartz 6% Muscovite 2%	2.66	0.043
Montmorillonite clay	Montmorillonite 93.4% Andesite 2.9% Biotite 2.9% Calcite 0.8%	2.45	1.988

Table 2. Characteristics of sediments

Most of the experiments were performed on the kaolinite clay samples. During preparation of the sand-clay mixes, the weight content of clay particles was set at 14, 25, and 40%.

To prepare sediment plates for the experiment, initially wet sediment inside a special container was stepwise consolidated in a compression frame under 0.4 MPa pressure. Then sediment plates 4 cm in diameter and 0.5–0.8 cm thick were cut out of the consolidated wet sediment and dried to air-dry condition. This produces homogeneous sediment plates with 40–45% porosity. Ice plates were prepared by freezing distilled water in cylinder cups of 4-cm diameter and about 1-cm thick. The air-dried sediment plates and ice plates were cooled in a cold room at  $-8$  to  $-10^{\circ}\text{C}$  and in contact under the isothermal conditions. Each dry sediment plate was in contact between two ice plates to form laminated cassettes (Figure 1).

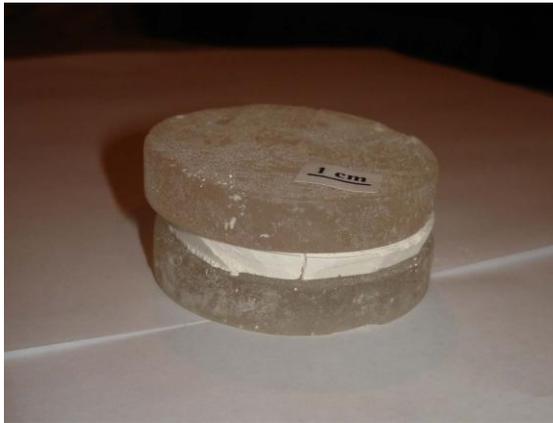


Figure 1 General view of an ice-sediment cassette

The prepared ice-sediment cassette was covered with polyethylene film, fixed by a thin elastic band, and placed into a special pressure chamber cooled to the experimental temperature. The experimental pressure chamber filled with the ice-sediment cassettes was pressurized at a negative temperature ( $-8^{\circ}\text{C}$  to  $-10^{\circ}\text{C}$ ). Then the chamber was evacuated and subsequently saturated with cool hydrate-forming gas (methane or  $\text{CO}_2$ ). During methane pressurization, the initial gas pressure registered in the range from 0.1 to 8.7 MPa and for  $\text{CO}_2$  from 0.1 to 2.5 MPa. The pressure chamber containing the ice-sediment cassettes was supplementary isolated by special thermal insulation and placed into a cooling chamber with a constant negative temperature. The system of thermostating used in these experiments

allowed for maintaining a constant negative temperature in a pressure chamber with an accuracy of  $\pm 0.2^{\circ}\text{C}$  throughout the experiment. The determination of non-clathrated water content in different model sediments and the estimation of gas-pressure influence on non-clathrated water content were carried out at  $-7.5^{\circ}\text{C}$ . Temperature dependence on the change of non-clathrated water content in model sediments was carried out under the fixed gas pressure for methane saturated samples of 4.3 to 4.1 MPa, and for  $\text{CO}_2$  saturated samples, of 1.65 to 1.6 MPa. Under the given conditions, temperature influence was studied in methane saturated samples in the range of  $-1.2$  to  $-13.5^{\circ}\text{C}$  and for  $\text{CO}_2$  saturated samples of  $-3.5$  to  $-13.5^{\circ}\text{C}$ .

The experiment's duration was about 14 days. During the experiment, the cooling chamber's temperature remained constant and the pressure chamber's pressure was fixed. As a rule, in the beginning of the experiment, pressure in the pressure chamber slightly reduced because of hydrate formation on the ice plate's surfaces.

At the end of the experiment, pressure was released, and the pressure chamber was opened in the cold room. The sediment and ice plates (covered by hydrate under the pressure of hydrate-forming gas) were separated from each other. The gas content of the ice reached 20 to 30  $\text{cm}^3/\text{g}$  at the experiment's end. Then sediment plates (average weight of about 15 to 20 g) were cleared and the equilibrium water content was determined using an electronic balance with an accuracy of 0.001 g. Determination of non-clathrated water content was replicated two or three times.

Special methodological experiments were conducted on estimating equilibrium state stabilization time in sediment plates. These showed that during the experiment (14 days) the equilibrium water content was reached for all the sediment samples independent of their composition and experimental conditions (Figure 2).

Thus, during the longer 29-day interaction time between sediment and ice plates, the non-clathrated water content did not exceed the value obtained for the 14-day interaction time even for samples with high montmorillonite particle content. Along with this, equilibrium water content of kaolinite clay samples was reached 4 days after the experiment began.

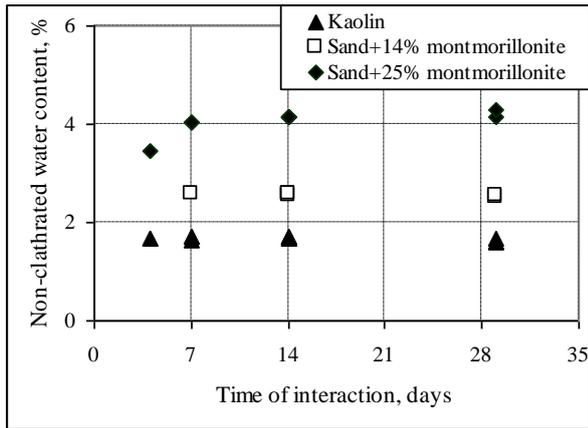


Figure 2 Influence of time of interaction of sediment plate with ice plate on moisture content in sediment samples

Hence, all the water content values in the experiments are at thermodynamic equilibrium and characterize non-clathrated water content in a hydrate-containing medium.

### RESULTS AND DISCUSSION

Based on the methods described above, a complex of experiments was carried out on the estimation of non-clathrated water at three-phase equilibrium conditions (gas–liquid water–bulk CH<sub>4</sub> or CO<sub>2</sub> hydrate) in model sediments. Table 3 and Figure 3 present the results of non-clathrated water determinations in methane-saturated kaolinite clay at a pressure range of 0.1 to 8.7 MPa and a temperature of -7.5°C.

As the experimental data shows, the non-clathrated water content in kaolinite clay reduces pressure increases. In the pressure range of 2 to 4 MPa, this decrease is abrupt enough, virtually by two times. Then at a pressure increase of 4 to 8.7 MPa, the equilibrium water content reduction becomes negligible.

At a pressure rise of 4.3 to 8.7 MPa, the non-clathrated water content decrease is only 0.35%. At a pressure above 6 MPa this decrease is not more than 0.1%. The power character of its change is traced by approximating the data obtained about non-clathrated water content for kaolinite clay depending on methane pressure. Non-clathrated water content depending on pressure is determined mainly by dispersion and mineral composition of sediment. The experiment on estimation of non-clathrated water content in sandy-clay mixtures showed that at the same content of clay particles

distinguished by mineral composition, the non-clathrated water content may change by an order (Figure 3).

$P_{exp}/\text{MPa}$	Non-clathrated water content/%
8.69	1.36
7.35	1.43
7.35	1.46
7.35	1.41
6.85	1.47
6.85	1.47
6.20	1.51
5.90	1.51
5.90	1.52
4.34	1.66
4.34	1.68
4.34	1.71
4.34	1.71
3.10	2.00
3.10	1.95
3.10	1.96
2.59	2.39
2.59	2.38
1.83	3.09
1.83	3.17
1.83	3.21
0.10	3.80

Table 3. Experimental data of pressure influence on non-clathrated water content in kaolinite clay at the fixed temperature -7.5°C.

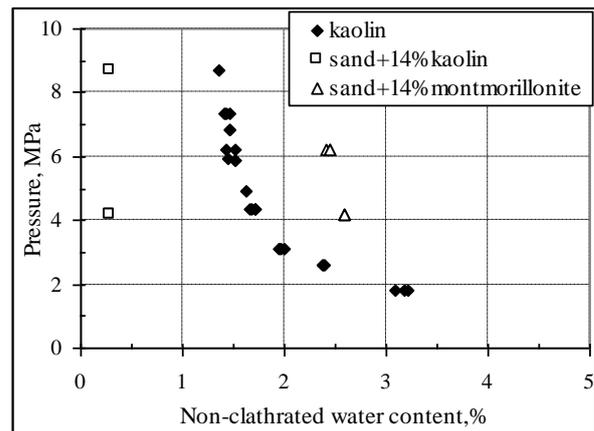


Figure 3 Change of non-clathrated water content depending on gas (methane) pressure in model sediment samples (kaolinite clay, sand with 14% kaolinite particles and sand with 14% montmorillonite particles) at temperature -7.5 °C. In quartz sand with 14% of kaolinite particles at methane pressure of 4.2 MPa, the equilibrium

liquid-phase content was about 0.3%. At the same conditions in sand samples with 14% montmorillonite particles it was up to 2.6%. The sharp difference in non-clathrated water content is explained by the energetic characteristics of clay additives, mainly by the specific active area that determines the quantity of bound water. Considering the data about gas adsorption of nitrogen the specific active surface for kaolinite clay was 12 m/g, and the value of the outer specific active area for montmorillonite clay was equal to 70 m/g.

Characteristically, non-clathrated water content is practically unchanged in samples of sand with kaolinite particles at a rise of atmospheric methane pressure from 4.2 to 8.7 MPa. For a sand sample with montmorillonite particles at a lower pressure change of 4.2 to 6.2 MPa, the quantity of non-clathrated water markedly decreases (Figure 3).

The change in non-clathrated water content in sand samples with an increase kaolinite content and montmorillonite particles at the fixed methane pressure of 4.1 to 4.4 MPa and temperature  $-7.5^{\circ}\text{C}$  is shown in Figure 4. The experimental data show that non-clathrated water content in sediment samples linearly increases with the increase in clay particles. The non-clathrated water content increases more intensively in samples with kaolinite clay. According to data obtained, the non-clathrated water content can be estimated in montmorillonite clay at the defined thermobaric conditions of about 14%.

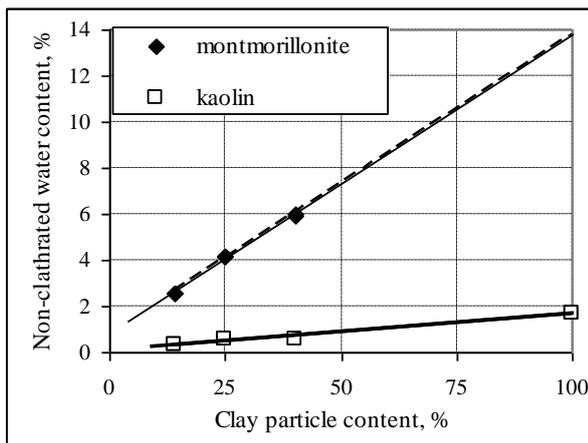


Figure 4 Influence of clay minerals on non-clathrated water content in methane-saturated sand samples ( $P=4.1-4.4$  MPa,  $T=-7.5^{\circ}\text{C}$ )

The equilibrium liquid phase content in hydrate-containing sediments at fixed gas pressure depends

on temperature. In Table 3 and Figure 5 it is possible to trace the change of non-clathrated water content in methane-saturated kaolinite clay at fixed pressure of about 4.1 to 4.3 MPa. As follows from obtained data, the increase of equilibrium temperature from  $-10.6^{\circ}\text{C}$  to  $-1.2^{\circ}\text{C}$  led to the rise of non-clathrated water content by 1.6 times.

$T/^{\circ}\text{C}$	$P_{\text{exp}}/\text{MPa}$	Non-clathrated water content, %
-1.2	4.2	2.42; 2.57
-3.3	4.11	2.26; 2.28; 2.28
-7.5	4.34	1.68; 1.71; 1.71
-10.6	4.20	1.63; 1.62

Table 3. Temperature influence on non-clathrated water content in kaolinite clay under methane pressure.

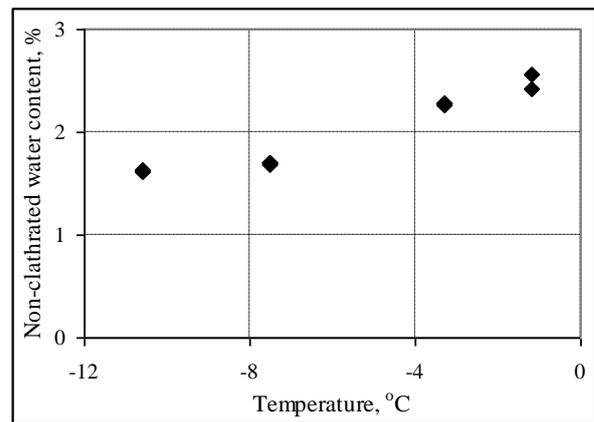


Figure 5 Temperature influence on non-clathrated water content in kaolinite clay under methane pressure ( $P=4.1-4.3$  MPa)

Using a contact method for defining non-clathrated waters, experimentally defined is the equilibrium maintenance porous water in kaolinite clay under hydrate-forming  $\text{CO}_2$  gas pressure. These results are presented in Figure 6. As seen from the obtained experimental data, non-clathrated water content in kaolinite clay reduces under increasing pressure. In the pressure range of 0.9 to 1.6 MPa, this decrease is abrupt enough, virtually by two times. Then at a pressure increase of 1.6 to 2.5 MPa, the equilibrium water content reduction becomes negligible. At a pressure above 1.6 MPa this decrease is not more than 0.1%.

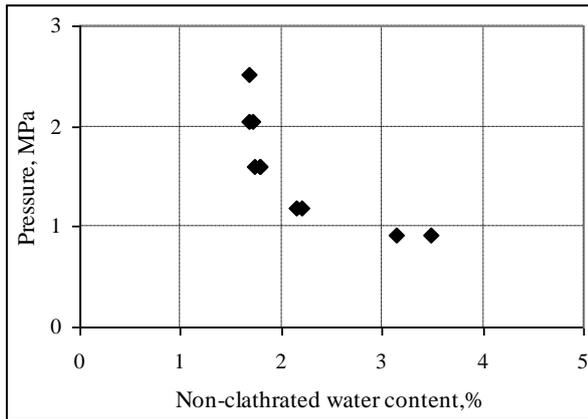


Figure 6 Change of non-clathrated water content depending on CO<sub>2</sub> gas pressure in kaolinite clay at temperature  $-7.5^{\circ}\text{C}$ .

Considering the overall character of change, the non-clathrated water from pressure in CO<sub>2</sub>-saturated sediment is similar to that in methane-saturated sediment; however, quantitatively they strongly differ. This is connected with distinctions in the thermobaric conditions of hydrate CO<sub>2</sub> and CH<sub>4</sub> (Figures 3 and 6).

Temperature dependence of non-clathrated water content for CO<sub>2</sub>-saturated sediments at a fixed gas pressure (1.6 MPa) is shown in Figure 7.

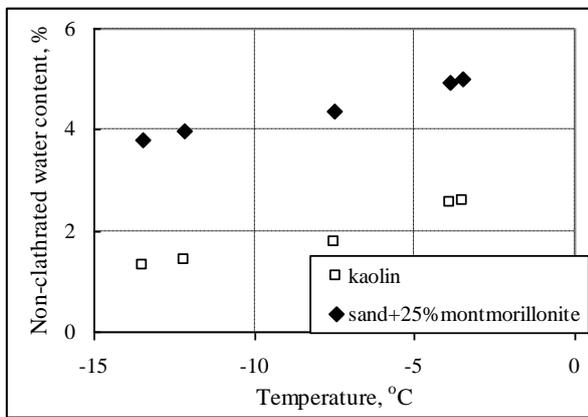


Figure 7 Temperature influence on non-clathrated water content in kaolinite clay and sand with 25% montmorillonite clay under CO<sub>2</sub> gas pressure (P=1.6 MPa)

The amount of non-clathrated water in sediment samples studied decreased as temperature decreased. This decrease was more considerable for kaolinite clay samples than for samples of sand with 25% montmorillonite clay.

Experimental data were compared on equilibrium water content for kaolinite clay at methane hydrate formation calculating non-clathrated water. Results of this comparison are presented in the paper [18], published in the same conference proceedings. The comparison shows satisfactory agreement. In particular, nonlinear dependence of non-clathrated water content on gas pressure is qualitatively confirmed.

Further we need to improve agreement between experimental data and thermodynamic description by using more detailed information concerning the soil samples and perhaps to change some parameters of the model.

### CONCLUSIONS

A new contact-absorption technique have been developed for determination of water content in sediments at three phase equilibrium “pore water – gas – bulk hydrate”. This equilibrium pore water was called as non-clathrated water. The technique is based on generalization of contact-absorption method in geocryology science. Based on the proposed technology, experimental data on non-clathrated water content in kaolinite clay in equilibrium with methane hydrate are obtained at a pressure range of 0.1 to 8.7 MPa, and also in equilibrium with CO<sub>2</sub> hydrate at a pressure range of 0.1 to 2.5 MPa at  $-7.5^{\circ}\text{C}$ . Experimental data show that at the fixed temperature, the non-clathrated water in hydrate-containing sediments sharply falls with an increase of gas-forming pressure. The extent of the character of its change can be traced by approximating the obtained data on non-clathrated water for kaolinite clay depending on methane pressure. With an increase of methane pressure higher than 4 MPa and CO<sub>2</sub> pressure higher then 1.6 MPa, the reduction rate of equilibrium water content decreases.

It is experimentally shown that the non-clathrated water content depends on the temperature and the sediment’s dispersiveness and mineral structure. The regularities of non-clathrated water content received depends on the temperature of the system in kaolinite clay in a negative temperature range of  $-1^{\circ}\text{C}$  to  $3^{\circ}\text{C}$  up to  $-11^{\circ}\text{C}$  to  $13^{\circ}\text{C}$  at a fixed pressure of hydrate-forming gas. A change was discovered in non-clathrated water content in sand with different contents of clay particles. It is shown that the equilibrium content of the liquid phase of sand is proportional to the amount of clay particles.

Further research of non-clathrated water content in hydrate-containing media should be devoted to development of determination methods for positive temperatures and saline soils.

#### ACKNOWLEDGMENTS

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