

HYDRATE FORMATION

GAS PERMEABILITY VARIATIONS IN GAS-FILLED SOILS  
UPON HYDRATE FORMATION AND FREEZING: AN EXPERIMENTAL STUDY

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Variations in gas permeability of laboratory-formed sand samples exposed to hydrate saturation and freezing are studied experimentally. The experiments are performed in a specially designed system to evaluate the permeability of pressurized wet disperse materials during formation and dissociation of pore gas hydrates, as well as during freezing and thawing of hydrate-bearing samples. Permeability depends on the fraction of pore water converted to hydrate, and the dependence is different as a function of lithology and initial water saturation. Consuming 70–80 % of pore water by hydrate formation reduces the gas permeability of sand and silt with the initial water content 14–18 % by one or two orders of magnitude. Freezing of hydrate-bearing samples makes their permeability times lower upon freezing of residual pore water and additional hydrate formation.

*Gas permeability, gas hydrate, ice, sand, silt, hydrate formation, freezing*

INTRODUCTION

Knowledge of permeability and porosity in hydrate-bearing sediments is indispensable for technological advances in gas production from natural hydrates. It is also important for the conventional production of natural gas in high latitudes, in areas of permafrost where the reservoirs are relatively cold and lie close to the permafrost base and to zones of gas hydrate stability. In these conditions, reservoir rocks at the bottom of producing wells often reach the temperatures of hydrate or ice formation.

Permeability is a key reservoir property for evaluating economically feasible gas recovery processes, including from hydrate-bearing formations, as well as for predicting the presence of hydrates in producing reservoirs. Permeability can be treated with respect to gas or to water. The earliest experiments on gas permeability in Russia began in the 1970-s [*Skhalyakho, 1974; Beznosikov, 1978*] and yielded empirical relationships between permeability and hydrate saturation in sand. The permeability of sand was shown to decrease with hydrate saturation, till complete impermeability to gas at a saturation of 0.65–0.70.

The first estimates of permeability to water belong to *Nenakhov [1982]* who obtained a nonlinear relationship between the relative permeability of hydrate-bearing sand and the pressure gradient between the sample ends. *Nenakhov* explained the non-linearity by viscoplastic rather than Newtonian water behavior in hydrate-saturated samples [*Istomin and Yakushev, 1992*].

In the 1990-s, permeability was measured experimentally during saline water flushing through a sample before and after it was saturated with hydrate [*Larionov et al., 1993*]. The permeability of hydrate-saturated rocks turned out to be three or more orders of magnitude lower than that of hydrate-free samples. Namely, hydrate saturation led to permeability reduction from 3.8 to  $8 \cdot 10^{-3}$  mD in samples with 10 % porosity and 30 % initial water content and from 4.0 to  $3.5 \cdot 10^{-3}$  mD in those with 15 % porosity containing initially 80 % pore water [*Larionov et al., 1993*].

Studies of hydrate-saturated rocks have been progressively increasing worldwide since the 2000-s, often as part of special national programs for gas hydrate research.

*Kneafsey et al. [2008]* studied gas and water permeability of dry, moist, frozen, and hydrate-bearing sand samples exposed to hydrate saturation. Formation of pore gas hydrates reduced permeability to instrumentally irresolvable limits in samples with an initial water content of 90 % and to very low though measurable values in slightly less moist sand (75–80 %).

*Kumar et al. [2010]* experimentally determined the permeability to gas at varying hydrate saturations and parameters of hydrate dissociation in a porous medium made of packed glass beads. It was found out that hydrate tended to form either on grain surfaces or in pores at the initial water saturations less or greater than 35 %, respectively [*Kumar et al., 2010*].

The permeability of the sample material decreased ten-fold (from 50 to 5 mD) upon hydrate saturation to 40 %. The experimental permeability values were correlated with several other models: the parallel capillary model of *Kleinberg et al.* [2003], the permeability-porosity equation of Kozeny [*Ibid.*], as well as with the model of *Masuda et al.* [2002]. The best fit was with the model implying exponential hydrate saturation dependence of permeability [*Masuda et al.*, 2002].

Experimental investigation of gas-water relative permeability for gas-hydrate-bearing sediments from the Mount Elbert Gas Hydrate Stratigraphic Test Well, Alaska North Slope [*Johnson et al.*, 2011] showed the permeability to be 0.65 at hydrate saturation 1.5 % and to decrease further to 0.1 at 36 % of pore hydrates. The results of *Johnson et al.* [2011] agree with the experiments of *Ahn et al.* [2005] (relative permeability from 0.05 to 0.6), but gas permeability turns out to be much lower in the latter.

There were several experimental studies of relative permeability in core samples from the Mallik 5L-38 gas hydrate production research well (Mackenzie delta). For instance, *Minagawa et al.* [2005] described water flushing through hydrate-saturated samples. The permeability to water was 1–2 mD initially, approached 5–7 mD after clay particles of drilling mud were flushed away, and reached 7–17 mD after hydrate dissociation. For the Mallik samples, *Murray et al.* [2006] received effective water permeability of 1–6 mD at 10–20 % hydrate saturation.

*Minagawa et al.* [2008] studied hydrate saturation dependence of relative water permeability in experiments with deformed sand samples and compared the results with different models. Gas permeability first decreased abruptly (5 % hydrate saturation corresponded to relative gas permeability 0.1) and then more smoothly only being 0.03 at 34 % of pore hy-

drates. The obtained data are consistent with the parallel capillary model.

The dependence of relative water permeability on hydrate saturation in Mallik core samples with 10 to 70 % of pore hydrates was also tested with a magnetic resonance system [*Kleinberg et al.*, 2005].

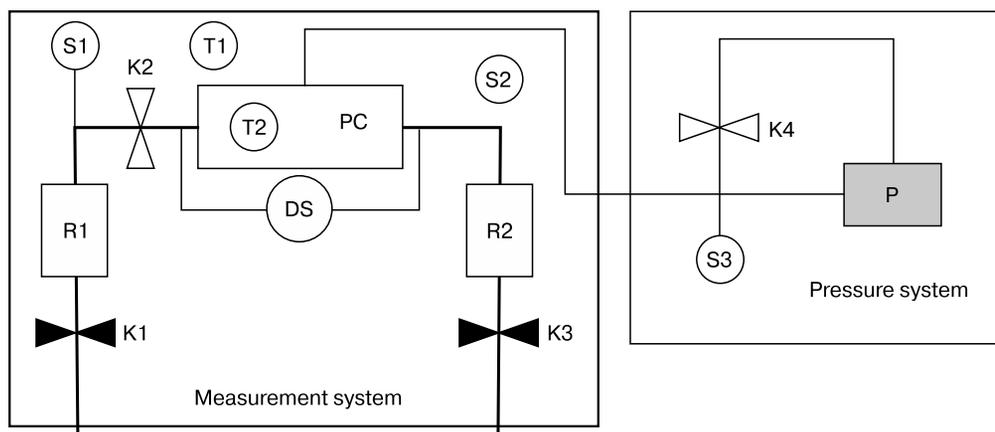
However, in spite of the abundant experimental evidence, permeability of hydrate-bearing soils in general, and gas permeability of freezing hydrate-saturated sediments in particular, remains insufficiently constrained.

## METHODS

Gas permeability variations in hydrate-bearing sediments were studied by means of gas flushing, using a method designed by the authors jointly with people from the Schlumberger Company [*Chuvilin et al.*, 2013]. The procedure consisted of several steps: (i) preconditioning of samples to provide user-specified water content and to saturate them with hydrate-forming gas in a special vessel; (ii) creating pressures and temperatures of hydrate and/or ice formation; (iii) testing the samples for gas permeability at different gas pressures and temperatures; (iv) processing the experimental data.

The system designed by the *EkoGeosProm* LLC (Fig. 1) can provide sample temperatures and pressures from  $-15$  to  $+30$  °C and up to 100 bar, respectively. It consists of a pressure vessel which can accommodate samples up to 30 mm in diameter and 50 mm long; a control, monitoring, and recording unit; a cold storage box maintaining the preset temperature of samples; a compressor and an oil pump for creating overburden pressure; an ADC; a gas bomb; and a PC (Figs. 2, 3).

The samples were synthetically prepared from earth materials of different lithologies: fine quartz



**Fig. 1. Sketch of experimental setup for evaluating gas permeability in samples saturated with hydrate.**

K1–K3 are membrane valves for gas input; K4 is ball valve of hydraulic system; R1, R2 gas receivers; S1–S3 are pressure sensors; DS is differential pressure sensor; P is hydraulic pump with an oil tank; PC is pressure vessel; T1, T2 are temperature sensors.

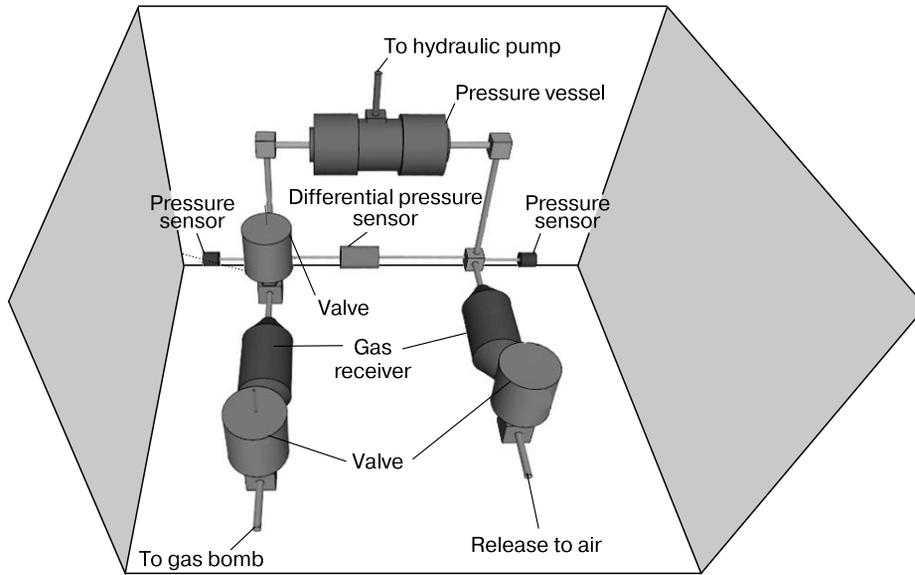


Fig. 2. Experimental setup.

sand, sand-clay mixes of sand with 7 % kaolin clay or 7 % bentonite, and silt. Each sample was measured for water content, water saturation, density, and porosity (Table 1). The initial porosity was from 0.38 to 0.44 and water content from 14 to 18 wt. % (Table 2). Hydrate formation was with carbon dioxide (99.99 %) stored in a bomb at a pressure ~ 3–4 MPa.

The preconditioned samples with different water contents were sealed tightly in the pressure vessel; the vessel was vacuumed and filled with the hydrate-forming gas (CO<sub>2</sub>); then temperature and pressure conditions were set at the level required for formation of pore hydrate and ice in the samples.

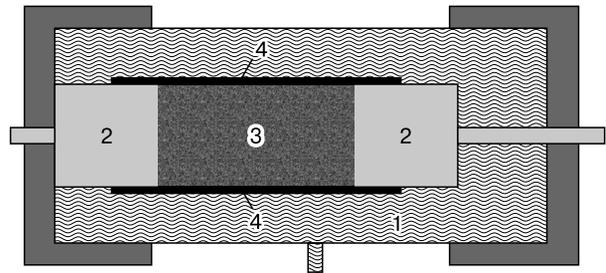


Fig. 3. Pressure vessel:

1 – hydraulic chamber; 2 – gas input system; 3 – soil sample; 4 – rubber seal.

Table 1. Properties of earth materials used for preparation of samples

Soil type	Grain size fractions, %			Mineralogy, %		Salinity, %
	1–0.05 mm	0.05–0.001 mm	<0.001 mm			
Sand	94.8	3.1	2.1	Quartz	>90	0.012
Kaolin	4.5	70.9	24.6	Kaolinite	92	0.043
Bentonite	0.3	46.2	53.5	Montmorillonite	93	1.988
Silt	41.8	53.7	4.5	Quartz	38	0.075
				Microcline + albite	55	

Table 2. Properties of soil samples used in experiments

Sample	Water content, %	Density of soil skeleton, g/cm <sup>3</sup>	Porosity	Water saturation, %
Sand with 7 % bentonite	18	1.48	0.44	60
Silt	16	1.66	0.39	70
Sand	14	1.58	0.41	51
Sand with 7 % kaolin	15	1.64	0.39	59

Gas permeability was measured at each cooling and heating cycle while temperature and pressure were monitored continuously during the experiment. The gas permeability measurements were applied first before hydrate formation after saturation with CO<sub>2</sub> at a temperature about +20 °C, and then during hydrate accumulation as the pressure vessel was cooled down to +1...+2 °C. After the hydrate formation process ended, the pressure vessel was cooled to -4...-5 °C, which led to freezing of residual water not consumed by hydrate. Gas permeability was measured also in frozen hydrate-bearing samples. Each sample was subjected to several cooling and heating cycles.

The fraction of pore water changed to hydrate (hydrate coefficient  $K_h$ , in unit fractions) was estimated from pressure and temperature (PVT) changes [Chuvilin and Guryeva, 2009]:

$$K_h = \frac{W_h}{W},$$

where  $W_h$  is the percentage of water converted to hydrate relative to the dry weight (%);  $W$  is the water content, wt. %.

The effective permeability of the sample in the pressure vessel was inferred from pressure drop in receivers with the known gas volume, by solving the differential equation of mass transfer through the sample under the pressure gradient:

$$k = \frac{2\eta LV_1 p_1 (p_{10} - p_{1k})}{Sp_{10} (p_1^2 - p_2^2) t_1},$$

where  $\eta$  is the dynamic viscosity of gas, Pa·s;  $L$  is the length of sample, cm;  $S$  is the cross section area of sample, cm<sup>2</sup>;  $V_1$  is the receiver volume, cm<sup>3</sup>;  $p_1$  is the pressure at sensor 1 (Fig. 1) at the time  $t_1$ , bar;  $p_2$  is

the pressure at sensor 2 at the time  $t_1$ , bar;  $p_{10}$  is the pressure at sensor 1 at the start time, bar;  $p_{1k}$  is the pressure at sensor 1 at the end time, bar;  $k$  is the gas permeability, mD.

The quality of the gas permeability estimates was checked by gauging against ceramic samples with known absolute permeabilities [Chuvilin *et al.*, 2013]. Thus estimated error was within 15 %.

## RESULTS

**Effect of hydrate formation.** The gas permeability was found out to depend on the fraction of pore water in samples converted to hydrate ( $K_h$ ), at the initial water content 14–18 %. The permeability became one or two orders of magnitude lower when hydrate formation consumed 70–80 % of pore water ( $K_h = 0.7–0.8$ ), the initial water saturation being 50–60 % (Fig. 4). The reduction was smaller at  $K_h < 0.3–0.4$  than at higher  $K_h$  (Fig. 3), specifically for the sand sample it was 1.5 times at  $K_h$  from 0 to 0.36 but 25 times on further  $K_h$  increase to 0.76. Wet sand with 7 % kaolin was initially less permeable than the pure sand sample because it had lower porosity and water content and contained clay particles. The permeability difference became times as great at  $K_h = 0.7$ : sand with 7 % kaolin had a gas permeability of 0.09 mD while that in pure sand was 1.8 mD (Fig. 4).

Highly porous samples showed the greatest permeability reduction: it was from 14 to 0.4 mD (at  $K_h = 0.74$ ) in sand with 7 % kaolin and the initial water content 18 %, and from 7.92 to 0.1 mD (at  $K_h = 0.70$ ) for sand with 7 % kaolin and the initial water content 15 % (Fig. 5, a).

The gas permeabilities of sand samples containing different clay minerals were different, possibly because clay mineralogy controls the conditions for hydrate formation in the pore space.

The permeability values decreased from 37.07 to 0.4 mD in gas-saturated sand with the initial water content 14 % at  $K_h = 0.9$  (Fig. 5, b) and from 1.2 to 0.02 mD in the case of silt bearing 16 % water, at  $K_h = 0.75$  (Fig. 5, b). The low permeability of silt was due to high contents of silt and clay particles and high initial water saturation (70 %).

Permeability reduction during hydrate formation has several controls: soil microstructure, uncontrollable changes in active porosity, and different mechanisms depending on pore size, etc.

**Effect of freezing.** Formation of hydrate and ice in the pores makes samples about hundred times less permeable to gas, which corresponds to almost impermeable reservoirs in natural conditions. Note that hydrate-saturated samples show slight  $K_h$  increase upon freezing as residual pore water freezes up and favors additional hydrate formation [Chuvilin *et al.*, 2007; Chuvilin and Guryeva, 2009].

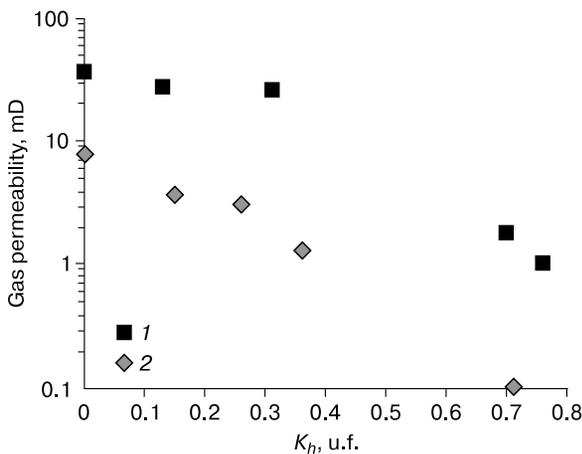
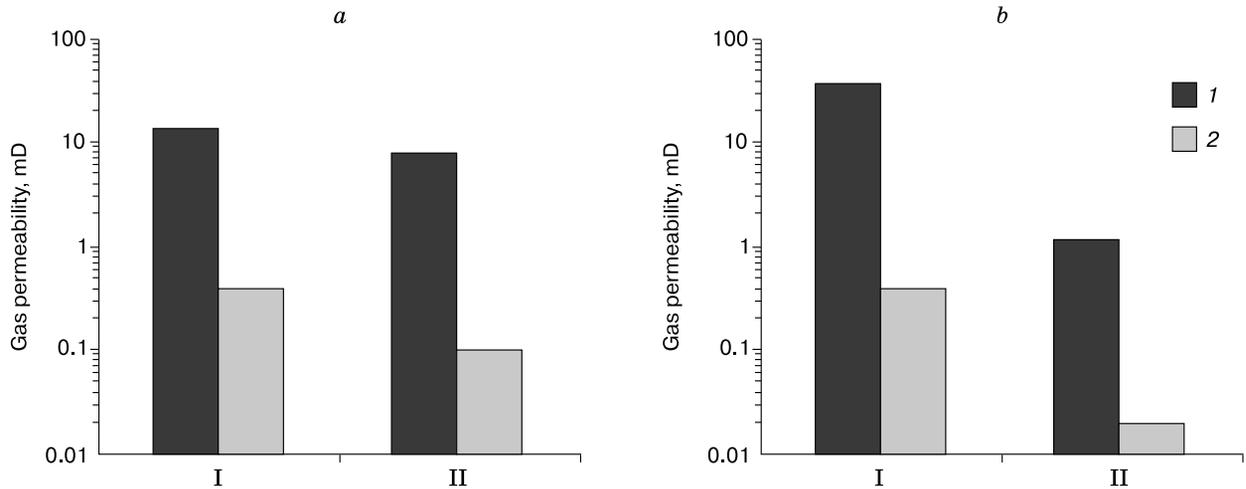


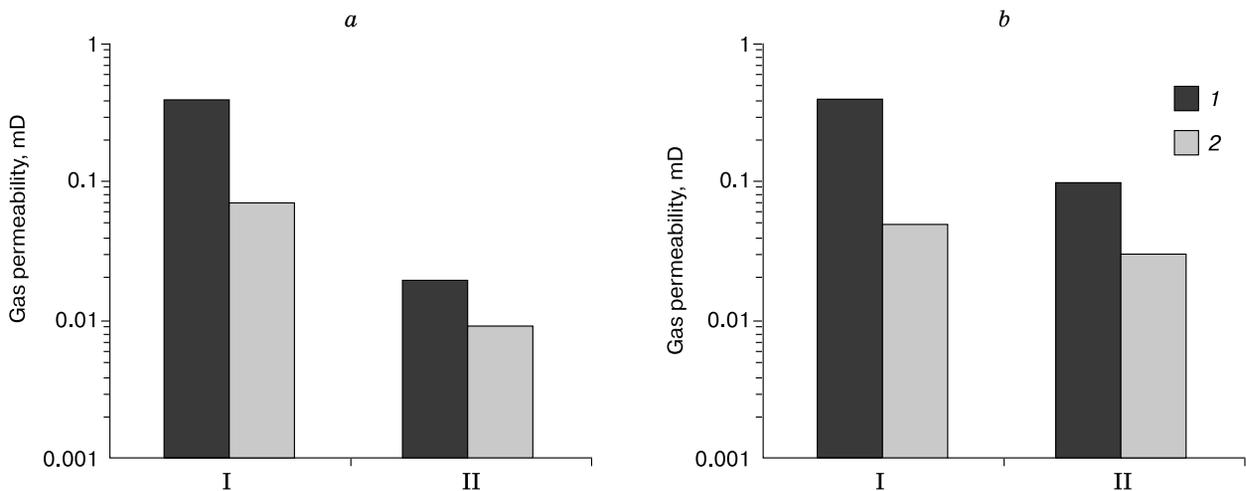
Fig. 4. Gas permeability of sand samples as a function of  $K_h$ .

1 – sand; 2 – sand with 7 % kaolin.



**Fig. 5. Behavior of gas permeability in samples exposed to hydrate saturation.**

*a*: I – sand with 7 % kaolin ( $W = 15\%$ ), after hydrate saturation,  $K_h = 0.70$ ; II – sand with 7 % bentonite ( $W = 18\%$ ), after hydrate saturation,  $K_h = 0.74$ ; *b*: I – sand ( $W = 14\%$ ), after hydrate saturation,  $K_h = 0.90$ ; II – silt ( $W = 16\%$ ), after hydrate saturation,  $K_h = 0.75$ . Samples before (1) and after (2) freezing.



**Fig. 6. Behavior of gas permeability in samples exposed to freezing.**

*a*: I – sand ( $W = 14\%$ ),  $K_h = 0.90$  before freezing and  $K_h = 0.91$  after freezing; II – silt ( $W = 16\%$ ),  $K_h = 0.75$  before freezing and  $K_h = 0.81$  after freezing; *b*: I – sand with 7 % kaolin ( $W = 15\%$ ),  $K_h = 0.74$  before freezing and  $K_h = 0.79$  after freezing; II – sand with 7 % bentonite ( $W = 18\%$ ),  $K_h = 0.71$  before freezing and  $K_h = 0.81$  after freezing. Samples before (1) and after (2) freezing.

In our experiments, freezing led to gas permeability reduction from 0.4 to 0.07 mD in hydrate-saturated sand (Fig. 6, *a*) and from 0.02 to 0.01 mD in silt. The changes for the sand-clay mixes were within 0.40–0.05 mD and 0.10–0.03 mD for sand with 7 % bentonite and 7 % kaolin, respectively (Fig. 6, *b*). The freezing-induced reduction was the greatest in sand with 7 % bentonite (8 times).

Generally, gas permeability changes in hydrate-bearing soil samples exposed to freezing depend on ice content and on the amount of residual pore water able to freeze up with formation of additional hydrate.

Changes to structure and texture of samples also play some role, but it is worth a separate study.

## CONCLUSIONS

The behavior of gas permeability in laboratory-formed sand and silt samples exposed to hydrate saturation and freezing was tested using a specially designed experimental system. The study included tailoring of the system to the research objectives, updating the sample preconditioning procedure, estimation of soil parameters, and design of the permeability evaluation algorithms.

Gas permeability was tested for sensitivity to the amount of pore water consumed by hydrate formation, as well as to freezing of residual pore water in hydrate-saturated samples.

The samples with the initial water content  $W = 14\text{--}18\%$  became ten to hundred times less permeable to gas as  $70\text{--}80\%$  of pore water converted to hydrate. Gas permeability was the lowest in samples rich in clay and silt particles. Namely, the gas permeability of a silt sample with  $W = 16\%$  reduced to  $0.02\text{ mD}$  at  $K_h = 0.75$ .

Freezing of hydrate-saturated samples likewise led to gas permeability reduction resulting from freezing of residual pore water and additional hydrate formation upon water-ice phase transitions.

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