Permeability of Ottawa sand specimens containing R-11 gas hydrates

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ABSTRACT

Permeability is an important parameter when modeling the production of natural gas from gas hydrate reservoirs. This paper illustrates permeability variation in Ottawa sand samples at different hydrate concentrations. Samples were prepared with synthetic R-11 (CCl_3F) hydrate, which stabilizes at temperatures below 8 °C and at atmospheric pressure. Concentrations ranging from 0% to 60% of hydrate pore occupancy were tested. Results of the experimental program indicate that permeability is highly dependent on the hydrate concentration. Comparison of experimental results against previous models allowed us a better understanding of hydrate growth habits (grain coating, pore-center filling).

RÉSUMÉ

La perméabilité est un important paramètre lors de la modélisation de la production de gaz naturel en provenance des réservoirs d'hydrates de gaz. Ce papier illustre les variations de perméabilité dans des échantillons de sable d'Ottawa avec des concentrations différentes en hydrates. Les échantillons sont préparés avec l'hydrate synthétique R-11 (CCl_3F), qui se stabilise à des températures au-dessous de 8°C et à la pression atmosphérique. Des concentrations en hydrates de 0% à 60% de remplissage des pores sont testées. Les résultats des expérimentations indiquent que la perméabilité dépend grandement de la concentration en hydrates. Une comparaison de ces résultats avec des modèles précédents nous permet de mieux comprendre les habitudes de croissance des hydrates (revêtement des grains, centre de remplissage des pores).

1 INTRODUCTION

Natural gas hydrates consist of methane trapped within a lattice of water molecules. Low temperature and high pressures are required for hydrates to stabilize; conditions found in permafrost areas at high latitudes and in deep water at ocean and lake-bottoms (Kataoka et al. 2008). Estimates of the quantity of natural gas present in hydrate accumulations vary between 10^{16} and 10^{19} SCF(standard cubic feet), and even the most conservative estimates double the energy content of currently recoverable worldwide fossil fuels (Sloan 2008).

Producing natural gas from gas hydrates reserves is considered a viable potential energy source, especially for regions that lack sufficient conventional fossil fuels. Countries such as Japan, India, Russia, U.S.A, Canada and Germany are investing in research to find an economically viable method to exploit this potential source. Gas hydrate production research at the Mallik field, in Northwest Territories, Canada, proved “proof of concept” for extracting methane from hydrate reserves. Analysis of the project results is ongoing, investigating aspects such as production rate, reservoir modelling, environmental impact, etc.

One important aspect of production scenarios is the development of mathematical models that enable gas production rate estimates from hydrate reserves under different operating conditions in addition to gaining insight on the role of different parameters on hydrate decomposition. Previous research highlights that permeability is an important parameter for predicting gas flow rates from hydrates (Pooladi-Darvish and Hong 2005; Masuda et al. 1997). However, the relation between permeability of a porous medium and hydrates saturation is poorly understood, and current models use permeability values based on assumptions, estimations and indirect measurements.

Permeability is the ability of a soil to transmit fluids. In this research the fluid is water, thus the permeability is synonymous with hydraulic conductivity. Permeability can be determined in the lab by application of Darcy's law under steady state conditions. Pooladi-Darvish andHong (2005) illustrates the variation of gas production predictions depending on initial permeability input (Figure 1). Permeability depends on the hydrate content of the soil, and its behaviour depends significantly on the hydrates growth habit. Several models have been developed, each one assuming different growth habit, to estimate initial permeability and the permeability estimates for determined hydrate contents are significantly different from model to model, leading to the necessity of finding a reliable initial permeability value in hydrate bearing soils, which is the principal target of this research paper.

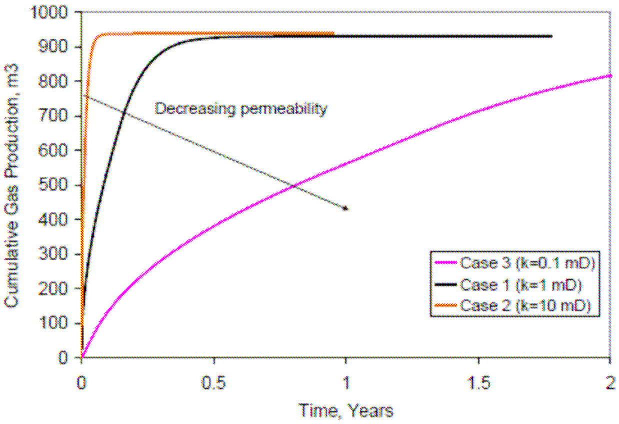

Figure 1. Effect of permeability on gas production (Pooladi-Darvish and Hong 2005)

Trichlorofluoromethane hydrate (synthetic R-11hydrate) belongs to the ice-like family of solid hydrates compounds, in which water molecules form a three-dimensional hydrogen-bonded network of cages (host) stabilized by the occupation of some or all cages by small molecules (guests) (Fouconnier et al. 2006). Synthetic R-11 hydrates have the advantage of crystallizing into a well known cubic structure II at atmospheric pressure and low temperatures. The generation of R-11 hydrates is simpler since there is no need to apply any confinement and R-11 hydrates also require shorter time to form than methane/carbon-dioxide hydrates. For these reasons synthetic R-11 hydrates are a good candidate to analyze the permeability of hydrate-bearing soils.

This research consists of analyzing specimen permeability at different hydrate contents (10, 20, 30, 50 and 60%). The results will enable us to better understand the behaviour of the permeability variation as hydrate saturation is increasing. In addition, the results will help to determine the accuracy of permeability estimation among several models, each one with different hydrate growth habit assumptions.

2 PERMEABILITY MODELS

Permeability in hydrate bearing soils vary widely, partially because there are several ways in which hydrate can interact with the host soil: (1) hydrate forms preferentially at grain contacts, acting as a cement even in small particles; (2) hydrate coats grains more or less uniformly, progressively cementing them as the hydrate increases; (3) hydrate grows in the interior of pores partially supporting the frame; (4) hydrate grows without significant interaction with the frame (Kleinberg et al. 2003).

Depending growth habit assumption there are two main permeability models: Parallel Capillary Models and Kozeny Grain Models. Parallel Capillary Models consists of a bundle of straight, parallel cylindrical capillaries having inner radius and length, these models are: Hydrate Coats Capillary Walls, in this model hydrate uniformly coats the walls of each capillary and the radius of the water-filled pore space is reduced; and Hydrate Occupies Capillary Centers, in which hydrate avoids grain surfaces and forms in the centers of cylindrical pores, leaving an annular flow path for water. Kozeny Grain Models assume that pore spaces are irregular, and flow paths are longer than the straight-line distance that defines the pressure gradient, these models are: Hydrate Coats Grains, where the surface area of the water-filled pore volume diminishes as the hydrate saturation increases; and Hydrate Occupies Pore Centers, where just before hydrate fills the pore, the surface area is double its original value. Other hydrate permeability models that do not fall into any of the previous groups are: University of Tokyo Model (Masuda et al. 1997), where the capillary tube is taken as a starting point and hydrate is assumed to line the walls of the capillary; and Lawrence Berkeley National Laboratory Model, that uses previously published relative permeability model in which they adapted a equation to estimate the relative permeability for unsaturated soils (van Genuchten 1980; Parker et al. 1987). Further details on these modles can be found in Kleinberg et al. (2003). Nuclear magnetic resonance (NMR) estimates of relative permeability, are based on the Kenyon relationship hydrate (Kenyon 1992; Straley et al. 1994), “The Kenyon relationship is empirical, based on measurements of several thousand water-saturated sandstone core plugs. Its application to rocks and sediments partially saturated with hydrate must be considered carefully. The effect of hydrate on the porosity term is reasonably simple. With respect to flow, hydrate acts as an addition to the solid grain space. Thus it is sensible to use the NMR-apparent porosity, which excludes the volume of applied to rocks and assuming pore occupancy” (Kleinberg et al. 2003).

After comparing the permeability values estimated by NMR method (hydrates in sandstones) to the models above it was found that pore filling models most closely matched the experimental estimates. Figure 6 present a plot of values of relative permeability from NMR and also the four principal models.

3 EXPERIMENTAL METHODS

In order to experimentally verify the proposed models, permeability testing on hydrate-bearing samples using synthetic R-11 hydrates at different saturation levels in Ottawa sand specimens were investigated. The constant head test was used to determine permeability values and the equipment consisted of a cooling chamber (2 to 4 ^{o}C) surrounding the sample and a cooling chamber for water storage which is maintained at a constant head. In order to avoid hydrate dissociation, water temperatures were maintained below the dissociation temperature (8^{o}C). R-11 hydrates have the advantage of stabilizing at atmospheric pressures, thus no confining pressure is required to the cell. The inner diameter of the cell is 7.62 cm and the cell height is15.24 cm; yielding typical sample volumes of 579±1 cm^3.

A constant hydraulic gradient was applied across the length of the sample using a continuous water supply at constant pressure head. Flow was calculated by collecting water from the sample top and permeability (k) calculated by following Darcy's law (i.e. $k=Q\cdot L/(A\cdot \Delta H\cdot \Delta t)$ where Q is the volume of collected water, A the cross sectional area of the sample, Δt is the time of collection of the water, L is the height of the sample, and ΔH is the difference in head pressures as indicated in the schematic (Figure 3)).

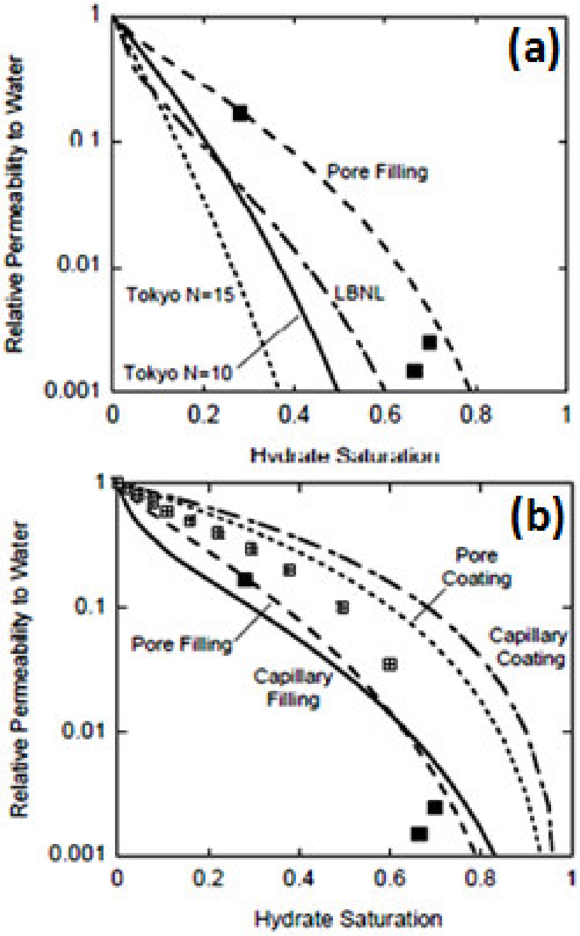

Figure 2. Relative permeability to water of porous media in the presence of hydrate (a) capillary and Kozeny models (b) Tokyo and LBNL models (Kleinberg et al. 2003

A schematic of the constant head test, and photographs of the cell and the actual permeability setup equipment, are presented in figure 3.

3.1 Relative Permeability Measurements

Relative permeability in hydrate bearing samples is defined as the ratio of permeability of the sample at a particular hydrate saturation (k_{SH}) over the permeability of the sample at 0% hydrate saturation (k_o) and thus equal to k_{SH}/k_o. Permeability is a constant of proportionality in Darcy's law, that depends on both water and soil properties, and can be calculated based on equation 1:

$$k=q/i\cdot A \qquad [1]$$

where "*i"* is the gradient (non dimensional quantity used to express the head loss between two points), "A" the cross sectional area, and "q" is the flow rate of the water passing through the soil. Coefficient of permeability was calculated for each sample before and after hydrate formation. With these two measurements, relative permeability for each hydrate saturation was calculated.

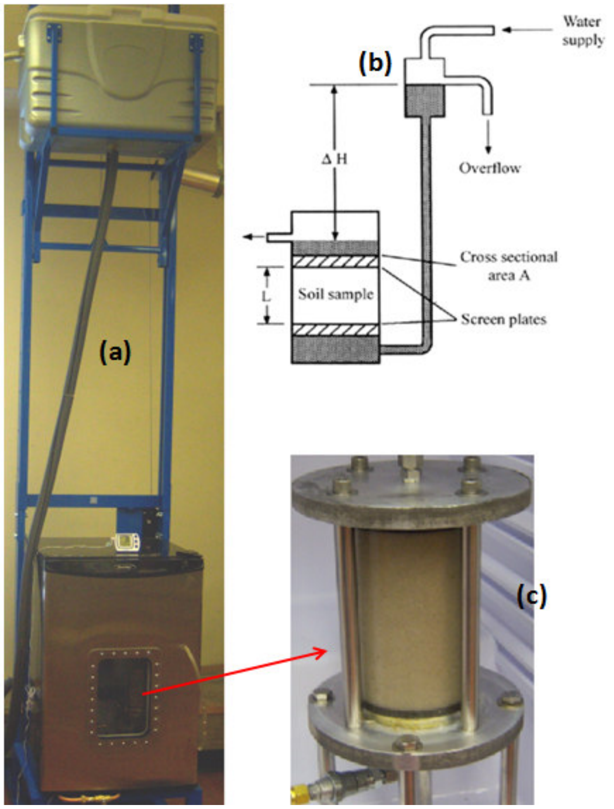

Figure 3. Constant head permeability test apparatus (a) permeability setup photograph, (b) constant head schematic, (c)sample

3.2 Production of R-11 hydrate-bearing specimens

Poorly graded Ottawa sand (particles between 0.85-0.42 mm) was used. The humidity of the sand was checked by heating three samples at 120 °C for 24 hours. The average weight loss was 0.1 %. After this the sand was used without drying it.

The procedure to prepare the samples was as follows:

- Dry Ottawa sand was packed into the cell
- The samples were purged with carbon dioxide to replace the air contained in the voids
- De-aired distilled water (three times the volume of voids, approx 200 ml) was passed through the sample

- The sample was left to equilibrate, allowing solution of the carbon dioxide into the water
- Another two times the volume of voids of de-air distilled water was passed through the sample
- Using the constant head, steady state conditions were achieved and the permeability determined from the volume of outflow water (water at 6-7 ^{o}C) collected within a specified time increment
- R-11 was added to the sample to achieve the desired hydrate saturation, the volume of R-11 (V_{R-11}) added was determined using the saturated volume of voids (V_{vsat}) as per Equation 2, based on volume ratio water/R-11 equal to 3.41 (Mork et al. 2000):

$$V_{R-11} = V_{Vsat} \cdot \%HC/(4.41) \qquad [2]$$

- After the R-11 was added, the sample was left at a 2 to 4 ^{o}C for 48-52 hours to allow hydrate formation
- Cold water, at the same constant head at steady state conditions used to estimate permeability before hydrates were added, was passed through the sample and the permeability at the particular hydrate saturation determined

4 RESULTS AND DISCUSSION

Table 1 and Figure 4 present a summary of current experimental results at 10, 20, 30, 40 and 50% hydrate saturation.

Table 1 Relative permeability at different hydrate saturations

hydrate saturation	Relative Permeability
12%	0.48
32%	0.35
42%	0.26
51%	0.14
64%	0.003

The test results to date indicate that permeability, due to the occupancy of hydrates in the specimen voids, decreases as hydrate saturation is increasing. Results suggest kozeny's pore coating model best fits the experimental data at hydrate saturations lower than 50%; and for higher percentages the data most closely matches the pore filling model (figure 5).

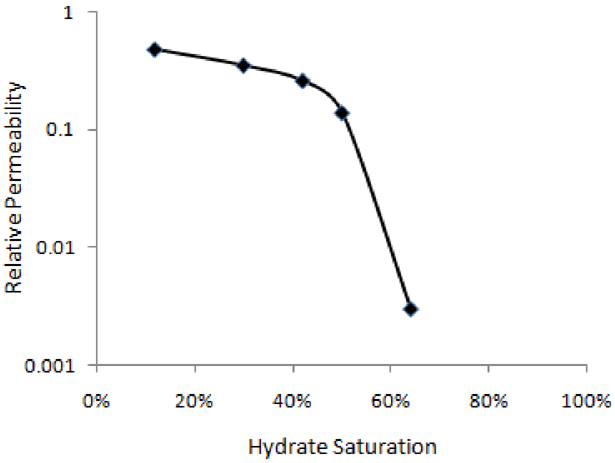

Figure 4 Relative permeability as a function of hydrate saturation.

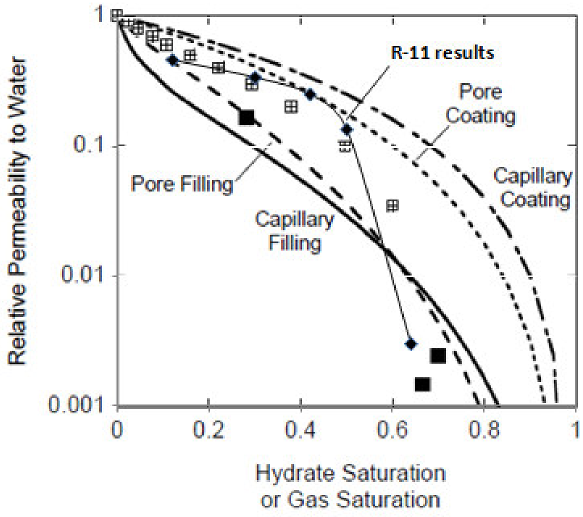

Figure 5 Comparison of R-11 results with Permeability Models

The experimental results agree with those obtained by Tohidi et al. (2001), where the progress of hydrate formation was video-taped at a micro-scale level. Evidences suggested that hydrate forms in the center of the pores, not coating the grains, it was actually found that a thin film of water is always coating the grains. Kumar (2005) also found that the relative permeability of carbon dioxide hydrate within glass beads was in agreement with the grain coating model at hydrate saturations lower than 35% and for higher hydrate saturations, his results suggested a pore filling model.

Future research on the permeability of hydrate bearing sands will include a better definition of hydrate saturation to more accurately determine the shift in growth habit, with further R-11 testing planned, particularly in the range of 40% - 60% hydrate saturations. The test results of the synthetic R-11 hydrate will then be verified using hydrates grown from a variety of different laboratory techniques, (such as from free gas, from gas saturated dissolved water, etc) in a new high pressure apparatus designed specifically to accurately measure permeability of hydrate bearing soils. New insight on the permeability of intact and dissociating hydrates, and the effects of hydrate growth habit will be obtained.

CONCLUSIONS

Permeability results showed a good correlation with the NMR estimated permeabilities following, the pore filling model trend at hydrate saturations greater than around 40 to 50%,. Below this hydrate saturation (40 to 50%) results were close to the NMR estimates and the growth habit could be assumed as a pore coating but yielding slightly lower permeability values than those predicted by this model. This can be explained with Tohidi's et al. (2001) observation of a permanent thin film of water coating the grains which could decrease the flow of the water which passes through the sample.

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