Estimation and measurement of permeability inside methane hydrate mimicking porous media

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Abstract
The objective of this study is to mimic methane hydrate cores at atmospheric pressure conditions with the same permeability as oceanic methane hydrate cores. This became possible by freezing a solution of water, ethanol, and sodium bicarbonate in Toyoura sand at -10°C. First, partial freeze was measured and theoretically evaluated in a solution of water, NaHCO₃ and ethanol. Then, the permeability of the methane hydrate core mimicking samples was evaluated based on the partial freeze evaluation. Finally, the permeability of the methane hydrate core mimicking samples was measured by injecting a solution of water and ethanol at -10°C inside the partially frozen samples. The experimental results suggested that it is possible to control the permeability of the created porous media by changing the volume fraction of ethanol in the solution. Furthermore, the permeability of the methane hydrate core mimicking samples was of the same order as that of real oceanic methane hydrate cores for a weight percent of ethanol in the solution of 8wt%.

Key words: Methane hydrate, Porous media, Permeability, Control, Freezing point, Fractional freezing

1. Introduction

Methane hydrate (MH) is a crystalline structure comprising a water cage that is occupied by methane gas. MH is stable under high pressure and in low temperatures, and is thus found in extreme environments such as the Siberian arctic or in the deep sea bed. These hydrates are considered to be one of the promising future energy resources for the current century and have attracted much attention because they exist in large quantities around the world (Milkov et al., 2004). The two principal methods for extracting MH from the deep ocean are depressurization and thermal stimulation (Kurihara et al., 2005). The depressurization method has high energy efficiency but leads to low production rates whereas the thermal stimulation method is more productive but with a low energy efficiency (Narita, 2011). Maruyama et al. have proposed an innovative low CO₂ emission power generation system utilizing MH using the depressurization and thermal stimulation simultaneously as shown in Fig. 1 (Maruyama et al., 2012).

To estimate the amount of extractable methane gas precisely, the study of heat and mass transfer in porous media is necessary. Nevertheless, conducting dissociation experiments on real MH requires either large pressure (10 MPa) or low temperatures. Furthermore, the permeability of MH has been reported to be of several miliDarcies (Oyama et al., 2012), and it takes up to several months in order to artificially create MH with the same permeability (Konno et al., 2012).
Conducting dissociation experiments on real MH at a meter scale has thus proven to be time consuming and to require a high level of complexity.

In order to upscale the study of gas production mechanism from MH, Sasaki et al. have shown that it is possible to mimic a MH bearing reservoir by making samples of frozen solutions of sodium bicarbonate (NaHCO$_3$) in sand (Sasaki et al., 2009). Hot hydrochloric acid (HCl) is then injected in these samples, reacted with aqueous NaHCO$_3$ and generated carbon dioxide (CO$_2$), which is a way of mimicking the generation of methane gas from MH. Using this technique, it is possible to mimic gas production from a medium mimicking MH at the atmospheric pressure and conduct meter scale dissociation experiments. Nevertheless, it is not possible to control the permeability of the created medium such that it fits in the oceanic MH permeability range.

In the present study, an effort is being made to experimentally mimic MH bearing layers and the control permeability of this porous medium in order to conduct dissociation experiments considering the permeability variability in an actual MH bearing layer. This was made possible by creating a unique porous medium made of a frozen mixture of water, ethanol and NaHCO$_3$ in Toyoura sand. By changing the amount of ethanol and thus displacing the freezing point of the solution and changing the amount of ice which is formed, the permeability of the created sample can be controlled.

![Image: Concept of the power generation system utilizing methane hydrate (Maruyama et al., 2012).](image)

**Fig.1** Concept of the power generation system utilizing methane hydrate (Maruyama et al., 2012).

### 2. Permeability prediction

#### 2.1. Control of ice formation

In order to study the fractional freeze in the MH core mimicking samples, samples composed of ethanol, water and NaHCO$_3$ were created by precisely measuring the amount of each compound with a milligram-precise weighting scale. These samples were then placed in an isothermal bath and kept at -10°C ±0.2°C for 48 h. Some solutions were partially frozen and the liquid and solid phases were carefully separated using the apparatus shown in Fig. 2. During the separation process, the temperature of the whole apparatus was kept at -10°C to avoid any melting of the formed solid. Nevertheless, some liquid was not retrieved because it was absorbed by the filter or was stuck in the solid phase.

The amount of NaHCO$_3$ that can be dissolved inside water at 20°C is 96 kg·m$^{-3}$ while it is almost insoluble inside ethanol (Haynes et al., 2015). Thus, it can be assumed that almost all the NaHCO$_3$ that is inserted in the samples will only be dissolved inside water. However, the amounts of NaHCO$_3$ that can be dissolved inside water and ethanol are
not given for -10°C in the references, and no reference about the ternary solution of water, ethanol and NaHCO$_3$ was found. In this study, it was assumed that the solubility of NaHCO$_3$ and ethanol do not change between binary and ternary solutions of water, ethanol and NaHCO$_3$ and there might thus be errors arising from these approximations. Moreover, the amount of NaHCO$_3$ that can be dissolved in water is diminishing to 69 kg·m$^{-3}$ when the temperature is reduced to 0°C (UNEP, 2002). For that reason, a weight percentage of NaHCO$_3$ of 5 wt% relative to water was chosen so that NaHCO$_3$ remains entirely aqueous even by reducing the temperature to -10°C, and this was verified experimentally.

The freezing points of ethanol and water at atmospheric pressure are respectively -114.6°C (Pauling, 1970) and 0°C. Previous studies have shown that the freezing point of a solution of ethanol and water can be predicted depending on the molar ratio of the two compounds (Ott et al., 1978). In this study, the experimental temperature is kept at -10°C±1°C, the weight percent of ethanol at the freezing point between these values can be evaluated using the expression given in Eq. (1). This expression fits the measured values of freezing temperature depression for a mixture of ethanol and water, and it also fits Hoff’s Law (Behschnitt, 1996).

$$\Delta T = -0.1765786 + 101.5153x + 323.1374x^2 - 709.7395x^3,$$  \hspace{1cm} (1)

where $\Delta T$ [K] is the freezing temperature depression for the mixture of ethanol and water and $x$ [-] is the mole fraction of ethanol in the binary solution. By inverting the Eq. (1) and changing the mole concentration to the weight percent, the weight percent of ethanol at the freezing point for a temperature at -10°C±1°C was between predicted to be between 18.8 wt% and 20.1 wt%.

When the previously prepared samples of water, ethanol and NaHCO$_3$ were frozen, multiple freezing behaviors were observed. When the mass percentage of ethanol in this ternary solution is inferior to 5 wt%, the solution totally freezes and when it is higher than 19.5 wt%, the solution does not freeze. In fact, 19.5 wt% corresponds to the weight percent of ethanol from which a solution of water and ethanol starts freezing under the condition of temperature of -10°C as was shown using Eq. (1). When the weight percent of ethanol is between 5 wt% and 19.5 wt%, a partial freeze of the ternary solution is experimentally observed and the volumetric ratio of frozen ternary solution depending on the weight percent of ethanol could be measured as shown in Fig. 3. The experimental data is quite dispersed because sometimes some liquid is trapped in ice and was not measured in the beaker. The ratio of ice diminishes when the amount of ethanol increases.

![Apparatus used for liquid-solid separation and measurement.](image)

Fig. 2  Apparatus used for liquid-solid separation and measurement.
2.2. Estimation of solid formation during fractional freeze

It is necessary to know the amount of ice formed in the samples in order to theoretically predict the permeability of the MH mimicking samples composed of water, ethanol and NaHCO$_3$ solutions. In the following parts $w_0$ refers to the weight percentage of ethanol in the water, ethanol and NaHCO$_3$ solution and $w_1$ and $w_2$ refer to the upper and lower limit of the weight percentage $w_0$ of ethanol that makes the ternary solution partially frozen under the temperature of -10°C. By assuming the following, it is possible to quantify the volume of ice formed in the solution:

1. The ternary solution of water, ethanol and NaHCO$_3$ has the same freezing behavior as the binary solution of water and ethanol.
2. The solid formed when the ternary solution is partially freezing has a weight percentage of ethanol in ice of $w_2 = 5$ wt%.
3. Ice starts forming when the weight percentage of ethanol in the solution is decreased to $w_1 = 19.5$ wt%.

The first assumption can be justified by the fact that NaHCO$_3$ is almost insoluble inside ethanol. It is thus possible to consider that the interaction between ethanol and water are not affected by the presence of NaHCO$_3$ in the solution.

The second assumption can be justified by the results of Fig. 3. When the weight percent of ethanol in the solution is lower than $w_0 = 5$ wt%, there is a total freeze. This implies that the solid, which is formed, is not pure ice but a solid made of a mixture of ethanol and water as was observed in the precedent research on fractional freezing of solutions containing water and ethanol. If we assume that the amount of ethanol included in this solid is always the same, it can be naturally assumed that it is in fact equal to $w_2$.

The third assumption is actually justifiable with Eq. (1) and the first assumption.

When the volume of solid in the solution is different from 0, the volume ratio of the solid that is formed in the sample is expressed as

$$S = \frac{V_s}{V_s + V_l} = \frac{\frac{1}{1+\frac{m_s}{m_l}\rho_l}}{1+\frac{m_s}{m_l}\rho_l},$$

where $S$ [-] is the volume ratio of solid, $V_s$ [m$^3$] is the volume of solid, $V_l$ [m$^3$] is the volume of liquid, $m_s$ [kg] is the mass of solid, $m_l$ [kg] is the mass of liquid, $\rho_s$ [kg m$^{-3}$] is the density of solid, and $\rho_l$ [kg m$^{-3}$] is the density of liquid.

The lever rule is the usual way of determining weight percentages of the phases present in a binary equilibrium phase diagram (Smith, 2006). The relationship between the weight percentages of water and ethanol in the solid and liquid phases can be expressed as

![Fig. 3](image_url)
where $W_s$ is the weight percentage of the solid in the whole solution. Thus, by rearranging Eq. (3) the ratio between the liquid and solid mass can be written as

$$\frac{m_l}{m_l + m_s} = \frac{W_l}{W_l - W_s},$$

(4)

Finally, by substituting Eq. (4) in Eq. (2), the volume ratio of solid in the fractionally frozen solution can be expressed as

$$S = \frac{1}{1 + \frac{\rho_s W_s}{\rho_l W_l - W_s}}.$$

(5)

### 2.3. Estimation of methane hydrate core mimicking sample permeability

In this section, a MH core mimicking sample made out of a mixture of sand and a partially frozen solution of water, ethanol and NaHCO$_3$ is considered in order to estimate the permeability of this core.

First, by considering that the tube is only filled with sand and by letting $n$ [-] denote the number of sand particles in the tube; $\varepsilon$ [-] the porosity of the tube filled only with sand; $V_s$ [m$^3$], the volume of sand in the sample and $V_{\text{poro}}$ [m$^3$], the volume occupied by pores,

$$V_s = n \frac{4}{3} \pi \left( \frac{d}{2} \right)^3,$$

(6)

$$V_{\text{poro}} = \varepsilon V_s.$$

(7)

The porous areas are partially filled with ice. With the proportion of ice in the porous space being $S$ [-] (0 < $S$ < 1), the total volume of ice $V_i$ [m$^3$] can be written as

$$V_i = SV_{\text{poro}} = V_s \frac{S\varepsilon}{1 - \varepsilon}.$$

(8)

Considering that $d_s$ [m] is the average diameter of the individually existing ice particles and supposing that there are $m$ [-] times more individually existing ice particles than sand particles, the total volume of ice is also expressed by the following equation:

$$V_i = nm \frac{4}{3} \pi \left( \frac{d_s}{2} \right)^3.$$

(9)

By substituting (6) and (9) in (8) the average diameter of the individually existing ice particles can be expressed as

$$d_s = \sqrt[3]{\frac{S\varepsilon}{m(1 - \varepsilon)}} d.$$  

(10)

Finally, the average diameter $d$ [m] of the particles inside the studied porous medium can be expressed as

$$d = \frac{nd_s + nmd}{n + nm} = \frac{1 + \frac{S\varepsilon m^2}{(1 - \varepsilon)}}{1 + m} d_s.$$

(11)
In this study, it is assumed that the sample is constituted of a porous structure of representative cross-sectional area and representative length without destroying it. By using these assumptions, Darcy’s law is applicable (Bethke, 1989) and it is expressed as (Darcy, 1856)

\[ Q = \frac{K\Delta p}{\mu L}, \]  

(12)

where \( Q [\text{m}^3\text{s}^{-1}] \) is the flow rate of a fluid passing through the sample, \( K [\text{m}^2] \) is the permeability of the sample, \( \Delta p [\text{Pa}] \) is the pressure loss in the sample, \( \mu [\text{Pa}\cdot\text{s}] \) is the viscosity of the fluid, \( A [\text{m}^2] \) is the cross-sectional area and \( L [\text{m}] \) is the length of the sample. In this study, the porous medium is shaped as its container, namely a cylindrical tube with the cross-sectional area \( A [\text{m}^2] \) and length \( L [\text{m}] \). Therefore, the speed \( u [\text{m} \cdot \text{s}^{-1}] \) inside the porous medium can be expressed as

\[ u = \frac{Q}{A}. \]  

(13)

The Kozeny-Carman equation is applicable to a phenomenon involving a packed bed of spherical particles (Carman, 1937) and can be expressed as in Eq. (14). Nevertheless, its application to a system with differently sized particles can only be justified if the size difference is small.

\[ \frac{\Delta p}{L} = 5u\mu \left( \frac{6}{d} \right)^2 \left( 1 - \varepsilon' \right)^2 \varepsilon^{-3}, \]  

(14)

where \( \varepsilon' [-] \) is the porosity of the porous medium. In this study, the porous medium is partially filled with non-permeable ice that is considered as a part of the porous matrix. Thus, the Kozeny-Carman equation can be expressed as follows in this case:

\[ \frac{\Delta p}{L} = 5u\mu \left( 1 - \varepsilon \left( 1 - S \right) \right)^2 \left( \frac{6}{d} \right)^2 \varepsilon^{-3}. \]  

(15)

Finally, by combining (12), (13) and (15), the permeability of the studied porous medium can be expressed as

\[ K = \frac{5 \left( 1 - \varepsilon \left( 1 - S \right) \right)^2 \left( \frac{6}{d} \right)^2 \varepsilon^{-3}}{5 \left( 1 - \varepsilon \left( 1 - S \right) \right)^2 \left( \frac{6}{d} \right)^2 \varepsilon^{-3}}. \]  

(16)

3. Permeability measurement

3.1. Creation of methane hydrate core mimicking sample

In this research, MH core mimicking samples were created using NaHCO₃ to mimic MH and ethanol was used in the samples to control their permeability.

At first, a solution composed of water, ethanol and NaHCO₃ was created by measuring precisely the mass of each compound with a milligram precision weighing scale. As explained, the same weight percent of NaHCO₃ to water was used to make every sample and it was equal to 5wt%. Only the weight percent of ethanol to the whole solution was changed and varied from 7 wt% to 20 wt%.

Then, the solution was mixed for 10 min. In fact, it took that amount of time so that NaHCO₃ becomes aqueous and totally dissolves in the solution. The whole process was carried out in a room where a constant temperature of 20°C±1°C was kept so that it is assured that the amount of accidentally evaporated ethanol or water does not vary from one experiment to another. To prevent the accidental evaporation, the prepared solutions were covered by a plastic film after their mixing.
During that time, a stainless pipe was closed on one side. The stainless pipe had a cylindrical shape with a length of 0.200 m and a diameter of 0.0254 m (1 inch). A filter with a pore size of 2µm was used in order to avoid any leak of Toyoura sand (average diameter of 150 µm) in the experiment and placed between the pipe couplings and the pipe.

Then, Toyoura sand and the previously prepared solution were mixed in the stainless pipe. In order to prevent water bubbles from forming, the solution of water, ethanol and NaHCO$_3$ was first poured in the pipe until it reached about one third of the total height.

Then, sand was added to that solution using a funnel. Furthermore, the mixture was mixed with a medicine spoon so that the position of the sand particles was as regular as possible.

These steps were repeated until the pipe was totally filled with the solution and sand. In order to obtain a reliable estimate of the porosity, the pipe was filled as explained previously 10 times in the same conditions. The porosity of the sample was always of 0.44±0.004, which validates the repeatability of this method. Further, the amount of solution poured in the sample was always filling the remaining 44±0.4% of the total space, and it was thus verified with a very good repeatability that no air bubbles were remaining in the porous space after this step.

To finish, the other side of the stainless pipe was covered with the same 2 µm filter, closed by a plug and put in an isothermal bath at -10°C± 0.1°C.

3.2. Permeability measurement of mimicking sample of methane hydrate core

Permeability in porous media is commonly measured by letting a fluid flow through the porous medium and using Darcy’s law. To determine permeability, Eq. (12) can be expressed as

\[
\frac{\dot{m}}{\rho} = \frac{KA\Delta p}{\mu L},
\]

where \(\dot{m}\) [kg·s$^{-1}$] is the mass flow rate and \(\rho\) [kg·m$^{-3}$] is the density of the measuring fluid going through the sample. The permeability of the porous medium, the length of the sample, the cross-sectional area of the sample, the viscosity and the density of the fluid used for the measurement are assumed to be constant; the only parameters that can vary in this experiment are \(\dot{m}\) and \(\Delta p\). Thus, when one parameter becomes constant the other should also theoretically become constant. This is why, when the two parameters were measured in one experiment, it was necessary to wait until both parameters become relatively constant and then evaluate the permeability of the porous medium.

Figure 4 shows the apparatus, which was developed and used in the permeability measurement experiment. During the experiment, the sample was placed as shown on the figure so that a measuring fluid can be injected in it. As expressed in Eq. (17), a pressure drop appeared before and after the sample as the fluid was pushed through it with a plunger pump, with a maximum flow rate of 2×10$^{-6}$ m$^3$·s$^{-1}$. This pressure drop was measured using a pressure transducer, which can measure the gauge pressure in the range of -0.1 MPa to 2 MPa.

The measuring fluid that was used in the permeability measurement is a mixture of water and ethanol, with a weight percentage of ethanol of 30wt%. This weight percent value was chosen for the following reasons:

- The experiment was conducted with a constant temperature of -10°C, there is thus a risk of the fluid freezing and obstructing the piping system during the permeability measurement. This affects the measurement and breaks the whole system because the pressure increases in case of total obstruction. A mixture of ethanol and water with 30wt% of ethanol starts freezing at -18.9°C (Pauling, 1970), and hence, there is no risk of freezing the mixture at -10°C.

- If a lower value of the weight percentage of ethanol is used and when the temperature gets near to the freezing point of measuring fluid, its viscosity and density change considerably and cannot be considered as constant. This is why a higher value of weight percentage was used to create the permeability measuring fluid. However, choosing this value of weight percent for ethanol has its own drawbacks. When the solution containing more ethanol reaches a solid formed with water and ethanol, there is a partial melting of this solid and thus a change in the porous structure of the sample. This affects permeability and increases it during the measurement.

The low temperature during the measurement affects the experimentally evaluated permeability because of the change of viscosity of the injected fluid. This is why the viscosity was measured specifically for a solution of water and ethanol.
ethanol with a weight percent of 30 wt%. This was measured 13 times and the measured dynamic viscosity was 0.0113±2.1×10^{-4} Pa·s.

The Reynolds number inside the sample was estimated using the maximum flow rate from the plunger pump, the diameter of sand particles, the pipe cross-sectional area and the kinematic viscosity calculated from the previously measured dynamic viscosity and density. The calculated Reynolds number was of 2 × 10^{-2}; thus, the Darcy law is valid when the Reynolds number is inferior to 1 and thus applicable in this case.

![Permeability measurement apparatus](image)

**Fig. 4 Permeability measurement apparatus.**

**4. Results and discussion**

Figure 5 shows a superposed plot of the experimentally measured and theoretically estimated ratios of solid in the solution after partial freeze using Eq. (5) for different initial weight percent of ethanol in the solution. It was assumed that ρ_s was equal to the density of ice at -10°C and ρ_l was taken equal to the value measured in the case of a binary solution of water and ethanol with a weight percentage of 20wt% of ethanol at -10°C. It is verified that there is no solid in the sample when w_0 = w_1 and that there is only solid in the sample when w_0 = w_2 as stated in the preliminary assumptions. Furthermore, the ratio of solid in the solution is reducing as the initial weight percent of ethanol in the solution is increasing, as observed experimentally. Even though both plots do not show a very good agreement, this theoretical equation was used to evaluate the permeability of the MH core mimicking samples.
Since there is no evidence on which value to choose for $m$, it was assumed that the numbers of ice particles and sand particles are equal and thus $m = 1$. By making this arbitrary decision, it was possible to limit the decrease of the diameter of the ice particles to one third of the Toyoura sand particles’ diameter. It was then assumed that the Kozeny-Carman equation was applicable even though this assumption leads to great differences in the permeability values as discussed in the latter section. As shown in Fig. 6, the sand particles and ice particles are almost of the same size in the case of $m = 1$ at a low weight percentage of ethanol, whereas when $m = 9$, the size of particles is too small to be considered equal to the sand particles and the Kozeny-Carman equation is not valid. When the weight percent of ethanol in the solution is lower than 5 wt%, total freeze occurs, and there are no more flow paths inside the porous medium and the permeability tends to 0 D. As the weight percentage of ethanol increases, permeability rapidly increases and becomes constant at 35 D which is a common value for Toyoura sand. As was explained before, the permeability of an actual oceanic MH core can vary from 0.1 mD to more than 100 mD. From the theoretical estimation, it can be expected that the sample permeability will be included in this range when the initial weight percent of ethanol in the solution ranges from 6 wt% to 9 wt%.

Fig.6  Ice particle diameter as a function of the weight percent of ethanol for different values of $m$. 

Fig.5  Theoretically predicted and experimentally measured volume ratio of ice in the solution.
Figure 7 shows the measured pressure loss and mass flow rate as a function of time in the case of permeability measurement of a sample with 10 wt% of ethanol. The pressure is initially stable and there is no flow at the outlet of the pipe. This can be explained because there are very few flow paths, and the fluid first needs to overcome the surface tension inside the very low permeability porous medium. Then, the pressure decreases rapidly and the flow rate in the outlet increases; this shows that once the initial surface tension inside the porous medium has been overcome by the fluid, it flows through the sample with less resistance. The flow rate was then manually increased so that the pressure gets back to its initial value and manual adjustments are done on the plunger pump to keep this pressure as constant as possible for more than 15 min. Even if the stability was not kept for a longer time, it was supposed that it was enough to evaluate the permeability of the sample using the Darcy law. On this particular case, the pressure and mass flow rate value which were used for the permeability evaluation were the average of the approximately stabilized part of the curve from 10 to 25 min.

Figure 8 shows the variation of temperature inside the pressure proof vessel with time. It can be seen that even by using a large pressure proof vessel, the temperature is inexorably increasing and this leads to a partial melt of the sample. This had a considerably important impact on the pressure loss and the calculated permeability.

Figure 9 shows a simultaneous plot of the theoretically estimated permeability using Eqs. (5), (11) and (16) and the experimentally measured permeability values using actual MH mimicking samples. As explained before, the value of $m = 1$ was selected, and on this figure the previously measured value of porosity of 0.44 was used for the theoretical evaluation. The global tendency for both measured permeability data and theoretically evaluated permeability is almost the same. However, there is an important difference in terms of order between the measured and theoretically estimated permeability values. This can be explained by the arbitrary value of $m=1$ that was chosen previously and the approximation that was made by using the Kozeny-Carman equation in this case. Nevertheless, it is possible to see that the measured value of permeability in the case of 8 wt% of ethanol is in the range of the permeability of an actual oceanic MH core. Thus, it is possible to experimentally mimic a MH core when it comes to permeability.

![Fig.7](image_url)  
**Fig.7** Pressure and mass flow data from the permeability measurement of a sample containing 10 wt% of ethanol.
5. Concluding remarks

Methane hydrate core mimicking samples were created, their permeability was evaluated theoretically and measured.

1. It was shown that it is possible to control the amount of ice formed in samples of water, ethanol and NaHCO₃ by varying the amount of ethanol used for their creation.

2. A theory on the formation of ice in these samples was developed and a theoretical expression to estimate the amount of ice formed in the samples was derived.

3. An agreement between the tendency of the theoretically predicted permeability and the tendency of the measured permeability was found.
(4) It was shown that by using a weight percent of ethanol of 8 wt%, both theoretically estimated and experimentally measured permeability were in the range of the permeability of an actual oceanic MH core and that it is thus possible to mimic it.

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