Effects of temperature cycling on the phase transition of water in gas-saturated sediments


Abstract: Experimental results on hydrate- and ice-formation conditions in the pores of sandy sediments that have undergone temperature cycles are presented. Thermodynamic parameters of gas hydrate and ice formation in porous space were determined for CH₄ and CO₂ saturated sandy sediments. The experiments indicate that temperature and freezing cycles affect the thermodynamics of hydrate and water–ice in gas-saturated sediments. Temperature cycles increased the hydrate accumulation in the pore space of sediments and reduce the freezing temperature of the remaining pore water.


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1. Introduction

When wet, gas-saturated sediments cool, some water transforms to gas hydrates and some to ice [1,2]. Hydrates often form above 0°C in gas-saturated, porous media at sufficiently high pressures. Further cooling of hydrate-containing sediments below 0°C generally results in ice growth because hydrates use only some of the pore water. Collett and Dallimore [3] showed that similar processes can occur in permafrost areas and in hydrate-containing marine deposits near 0°C where the partial decomposition of hydrate in pores can significantly cool the deposits and thus cause pore water to freeze. Because of such widespread applications and the little amount of experimental work in this area, we did an experimental
study of hydrate and ice formation in porous media. In this paper, we present some experimental results on hydrate and ice formation in gas-saturated sediments that undergo cyclic fluctuations of temperature under pressure.

In nature, the top several hundred metres of hydrate-containing sediment often has cyclic temperature fluctuations about 0°C [4]. In this connection, research on hydrate and ice formation with cyclic fluctuations of temperature has direct applications to important problems related to hydrates in nature.

2. Experimental methods

Fine-grained, natural quartz sand with an average diameter of about 0.32 mm was used in the experiments (Fig. 1). The soil samples were cylindrical with a diameter of either 6.4 or 7.3 cm and lengths of about 13.0–14.5 cm. Samples were prepared in a cylindrical Plexiglas container using a layer-by-layer consolidation method. The container with the soil sample was then loaded into a high-pressure chamber. This pressure chamber was made of stainless steel with a total volume of 1000 cm³. Pressure and temperature sensors in the chamber were connected to a recording system. The chamber was equipped with a jacket connected to a Haake model N8 circulating cooler for cooling and heating the test sample during the experiments.

We made samples with a soil porosity of 40–50% and initial gravimetric water content of 14–18%, which would result in pore saturation levels of 45–60%. Unsaturated pores allow the hydrate gases to penetrate into interior pore spaces. Two hydrate-forming gases, CH₄ and CO₂, were used in the experiments.

After assembling the chamber with the sample inside, the cell was purged of air and filled with either CH₄ or CO₂ gas. If CH₄ was used, the initial pressure inside the chamber was 8–9 MPa; if CO₂ was used, the initial pressure was 3.5–4.0 MPa.

During an experiment, the pressurized chamber with the sample was gradually cooled and heated such that the sample experienced temperatures between −10 and +20°C. Decrease of temperature in the chamber below the equilibrium hydrate temperature (phase transition (P/T) point) caused gas-hydrate formation. Further decrease of temperature below 0°C caused ice formation. In the experiments, the P/T conditions of formation and decomposition of gas hydrate and ice in the sediment samples were defined using the curve of change of temperature and pressure in sandy samples. Figure 2 shows the characteristics in the temperature and pressure data that were used to interpret the water-phase transitions in these porous media consisting of gas-saturated sediments with cooling and heating cycles. During cooling, the chamber pressure and temperature first decreased according to the ideal gas law. Then, after time A, the decrease in chamber pressure was greater than that which could be accounted for by changes in temperature alone, indicating that methane gas was being used to form hydrates. The freezing of the
remaining pore water during cooling caused a sharp increase of sample temperature at time B due to the release of latent heat during freezing. Hydrate formation also releases latent heat, but we argue that ice formed at B because the pressure increased due to the volume expansion upon freezing, which does not occur during hydrate formation because the hydrate consumes gas. During heating, the ice melts at time C and the flow of heat to the ice reduced the rate of temperature increase. Further warming of the chamber results in decomposition of the gas hydrate beginning at time D. After this time, the release of gas into the free volume sharply increased the pressure in the chamber. Our experiments generally included several cycles of temperature above and below 0°C (Fig. 3). We finished each experiment by completely freezing the sample at −10°C. Then, the pressure inside the chamber was reduced to atmospheric pressure, and samples were removed in the cold room at −10°C. The samples were stable due to the self-preservation effect of gas hydrate [5,6]; hence, we could use these stable samples to study the structure changes that occurred during hydrate and ice formation. These hydrate-containing samples were described, cut into 6–7 pieces, then the density; the water, gas, hydrate content; and hydrate ratio (amount of pore water transformed into hydrate) of each piece were determined. After the experiments, the distribution of pore water and the pore saturation levels in the samples were nonuniform. This redistribution of water is due to gravity and also the mass transfer during the phase transformations of hydrate and ice.

All samples were characterized as a massive cryohydrate structure (i.e., without visible ice-hydrate inclusions) as described earlier in Chuvilin et al. [2, 7]. Porphyr-like ice-hydrate inclusions, which did not exceed a few millimetres, were rare. Hydrate content in the samples was calculated from the weight changes of sample before and after the experiment. In addition, the hydrate content for methane-hydrate-saturated samples was also determined from the gas-content data.

3. Results and discussion

In our wet, sandy samples, the hydrate formed at higher pressures (or, equivalently lower temperatures) than the equilibrium values for free-water plus hydrate-forming gas. This shift to higher pressure $\Delta P$ was 1.6 MPa for CH$_4$ but only 0.5 MPa or less for CO$_2$-saturated samples. Equivalently, the shift to lower temperature $\Delta T$ was 2°C for CH$_4$ but only 1.1–1.3°C or less for the CO$_2$-saturated samples (Fig. 4). The smaller deviations in the CO$_2$ samples is related to the higher solubility of CO$_2$ in pore
Fig. 3. Kinetic curve showing the changes in the P/T conditions for the experiment with CO$_2$-saturated sandy sample ($W_m = 17\%$).

Fig. 4. P/T conditions of gas-hydrate formation in the sandy samples ($W_m = 14–18\%$). Samples underwent 1–3 temperature cycles.

The higher solubility does not require significant supercooling for nucleation of gas-hydrate crystals and, therefore, conditions of gas-hydrate formation are near equilibrium.

Only some of the pore water was converted into hydrate during cooling of the sediment; the remaining water froze into ice during freezing. The portion of water transformed to hydrate (hydrate ratio) in sandy sediments varied from 30 to 90\% (Fig. 5a). This variation is influenced by the gas saturation of pore water, cyclic fluctuations of temperature, and on some other factors related to hydrate accumulation (e.g., rate of cooling and presence of additional gas-hydrate formation during the melting of ice).
data show that the maximum gas-hydrate content occurs near the highest water contents (Fig. 5b). At water contents above about 22%, the hydrate ratio and hydrate accumulation decrease. This is probably connected with the increase in the amount of pore filling by water that decreases the area of the gas–water interface in the pore space. However, this requires additional study because there are presently not enough data to describe this trend.

Figure 6 shows the relation between the freezing temperature of the remaining pore water and the melting temperature of the pore ice for a range of gas pressures for CO₂- and CH₄-saturated sandy samples. Each data point represents a freezing or melting point found from curves such as those in Fig. 2. For a given pressure, data points at lower temperatures are generally from samples that underwent one or more freeze–melt cycles. The freezing temperature of this water depends on its quantity, the pore space, and the gas pressure [7]. Our data in Fig. 6 show that freezing and melting temperatures depend not only on pressure but also strongly depend on the type of gas. The lowest temperatures of freezing and melting are in CO₂-saturated sandy samples. For example, the freezing temperature of the remaining water in all CO₂ hydrate samples was below −1°C, despite the pressures being less than 2.5 MPa. The data in Fig. 6 indicate that freezing in the CO₂ samples varied over a wider range at the same pressure than that in the CH₄ samples. Also, the CH₄-saturated samples froze and melted at temperature above −1°C, even at a gas pressure of 7 MPa, which is significantly higher than the corresponding temperature for the CO₂ samples. The trends of melting and freezing temperatures with pressure also differed for the two gases; the CO₂ samples tended to have temperatures that increased with increasing pressure, whereas the CH₄ samples tended to decrease. This freezing behavior of the samples might be explained by the different solubility of gases in pore water and processes that occur with the dissolved gases. For example, the solubility of CO₂ in water is 10 times that of CH₄. In addition, the dissolution of CO₂ in water involves the interaction of CO₂ with ions of water that lead to the formation of carbonic acid ions HCO₃⁻. These acid ions create acidic conditions in the solution that decrease the freezing temperature [8].

The temperatures cycles changed the thermodynamic parameters of ice and gas-hydrate formation in wet, gas-saturated sediments. A previous study [7] showed that the shift in the P/T parameters for gas hydrates in sediments decreases from the first to the second and subsequent cycles of hydrate formation–decomposition. The same tendency occurs in the present study. In addition, the temperature cycles increased the amount of pore water that transformed into hydrate (hydrate ratio). In Fig. 5, the higher values of the hydrate ratio and hydrate content at the same water content are usually the samples that have undergone repeated temperature cycles. This tendency is caused by an increase of the amount of gas dissolved in the pore water with each temperature cycle. In addition, the temperature cycles can change the porosity and pore-size distribution in the sediment due to the phase changes and temperature deformations that increase the water–gas interfacial area in the pores.

The temperature cycles also decreased the freezing temperature of the remaining pore water. For example, in Fig. 6, the lower values of freezing temperature at a given pressure are from samples that
have undergone multiple temperature cycles. Furthermore, the freezing cycles generally decreased the freezing temperature for a given pressure of CO$_2$ (Fig. 7) and CH$_4$ (Fig. 8). We show the coefficient of freezing-point reduction in these figures, which is approximately the linear approximation to the slope of the melting curve for the system near 0°C. This coefficient $K_f[-1 \times (°C/MPa)]$ was calculated as the ratio of the measured freezing temperature of the remaining pore water $T_{bf} [°C]$ to the pressure $P$ at which this freezing occurred. If the amount of remaining water and the amount of dissolved gas in the pore water did not change, the value of coefficient of freezing-point reduction would not change according to the Clapeyron equation. For example, for pure water without sediments, the melting point at 2 MPa is about $-0.15°C$. Our data in Fig. 6 show that the melting point for the CO$_2$-saturated sandy sample was instead about $-1.5°C$ at this pressure. The discrepancy is primarily due to impurities in the pore water and secondarily to curvature between the sand grains. This phenomenon requires further study.

Here, we emphasize that the coefficient of freezing-point reduction under gas pressure increased with an increase in the number of freezing cycles for both the CH$_4$ and CO$_2$-saturated sandy samples.

The temperature cycles produced greater hydrate ratios and thus decreased the amount of pore water. Therefore, the decrease of freezing temperature of the pore water and the increase in $K_f$ after temperature cycles are likely caused by the decrease in the amount of remaining pore water and also the likely increase in the gas dissolved in the pore water.

4. Conclusions

By measuring the temperature and pressure conditions in wet, gas-saturated sand samples under cyclic cooling and heating, we investigated the phase transition (P/T) conditions for water and gas hydrates in the pores between sand particles. Our experiments showed that

(1) temperature cycles influenced the P/T conditions of pore water in gas-saturated sediments under pressure,

(2) temperature cycles increased the hydrate ratio and the hydrate accumulation in the pore space of sediments, and

(3) the freezing temperature of the remaining pore water depended on the type of gas in the sandy sample and this temperature decreased with an increase in the number of freezing cycles. In
Fig. 7. Influence of freezing cycles on the coefficient of freezing-point reduction under pressure for CO₂ hydrate-containing sandy samples ($W_\text{in} = 14–18\%$). Gas pressure was 1.3–2.2 MPa. Each observation point was a separate thermocouple in the sample.

Fig. 8. Influence of freezing cycles on the coefficient of freezing-point reduction under pressure for CH₄ hydrate-containing sandy samples ($W_\text{in} = 17.3\%$). Gas pressure was 5.7–6.1 MPa. Gaps in the data occur because some observation points did not clearly show all phase transformations.

particular, the freezing point under gas pressure in all CO₂ hydrate samples was less (below $-1^\circ\text{C}$) than that in CH₄ hydrate samples (above $-1^\circ\text{C}$), despite the CO₂ samples having a lower pressure (below 2.5 MPa)

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References