

THERMAL PROPERTIES OF METHANE HYDRATE BY EXPERIMENT AND MODELING AND IMPACTS UPON TECHNOLOGY

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ABSTRACT

Thermal properties of pure methane hydrate, under conditions similar to naturally occurring hydrate-bearing sediments being considered for potential production, have been determined both by a new experimental technique and by advanced molecular dynamics simulation (MDS). A novel single-sided, Transient Plane Source (TPS) technique has been developed and used to measure thermal conductivity and thermal diffusivity values of low-porosity methane hydrate formed in the laboratory. The experimental thermal conductivity data are closely matched by results from an equilibrium MDS method using in-plane polarization of the water molecules. MDS was also performed using a non-equilibrium model with a fully polarizable force field for water. The calculated thermal conductivity values from this latter approach were similar to the experimental data. The impact of thermal conductivity on gas production from a hydrate-bearing reservoir was also evaluated using the Tough+/Hydrate reservoir simulator.

Keywords: gas hydrates, thermal conductivity, thermal diffusivity, molecular modeling, reservoir simulation

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NOMENCLATURE

C_p Specific heat capacity
 k Thermal conductivity
 S Pore saturation
 α Thermal diffusivity
 ϕ Porosity of the rock phase

Subscripts

H Hydrate phase
 I Ice phase
 Rd Dry rock phase
 Rw Wet rock phase
 W Water phase
 Θ Composite property

INTRODUCTION

The National Energy Technology Laboratory (NETL) has been involved in hydrate research since the early 1980s [1]. The current effort involves both experimental and theoretical research that is focused on obtaining pertinent, high-quality information on gas hydrates that will benefit the development of models and methods for predicting the behavior of gas hydrates in their natural environment under production or climate change scenarios. The modeling effort comprises both fundamental and reservoir scale simulations and economic modeling. NETL has also recently established a new virtual Institute for Advanced Energy Studies (IAES) that includes research on gas hydrates in their natural environment. The IAES involves professors and students from universities in the western Pennsylvania and northern West Virginia region.

The emphasis of part of the hydrate research at NETL has been on obtaining thermal properties of methane hydrate. These properties are important for hydrate production, seafloor stability, and climate change scenarios. In particular, the emphasis has been on thermal conductivity. The purpose of this paper is to present the results of recent work in this area by NETL and others and indicate the importance of these findings to understanding the thermal behavior of methane hydrate and how this behavior impacts technology. The paper will describe recent research using laboratory experiments, molecular level modeling, and reservoir simulation. A brief background will be provided in each of these sections.

EXPERIMENTAL MEASUREMENTS

Thermal conductivity

Stoll and Bryan were the first to measure and note the unusual thermal conductivity behavior of clathrate hydrates [2]. Unlike ice that has a higher conductivity than water, the conductivity of both methane and propane hydrate were about 30% lower than water. They made a similar observation when ice/sand and hydrate/sand samples were compared. Ross et al., were the first to observe the unusual temperature dependence of clathrate hydrates [3]. Unlike other crystalline, non-metallic solids at temperatures greater than 100 K, the conductivity of THF hydrate increased with temperature. Other investigations since then have in general also observed these unusual properties with various clathrate hydrates [4-20]. Some of this experimental work was performed at temperatures down to 2 K to help elucidate the mechanisms for the anomalous behavior of clathrate hydrates compared to ice. However, no theoretical model currently exists that permits a quantitative description of the thermal conductivity of clathrate hydrates over a wide range of temperatures [12].

With respect to naturally-occurring clathrate hydrates, of which methane is generally the predominant guest species, the thermal conductivity of methane hydrate at geologically relevant conditions have only been measured by a small number of investigators owing to the difficulties encountered at working at the pressures required to form and stabilize methane hydrate in a manner suitable for thermal property measurements.

Stoll and Bryan first measured the thermal conductivity of a porous sample of methane hydrate formed from water and methane using a needle probe based on the technique of von Herzen and Maxwell [2, 21]. Based on the limited information in this paper, they obtained a value similar to that for tests with a somewhat compacted sample of propane hydrate, which was $0.39 \text{ W m}^{-1} \text{ K}^{-1}$ at 275 K. Cook and Leaist, using a guarded hot plate cell, obtained a value of $0.45 \text{ W m}^{-1} \text{ K}^{-1}$ at 216 K on a disc-shaped sample of methane hydrate that may have contained some ice [8]. The sample was prepared in a mold using methane hydrate powder under a mechanical pressure of 100 MPa. Waite et al. [16], synthesized porous methane hydrate around a

needle probe from granular ice according to the method of Stern et al. [22, 23] and found the conductivity to range from 0.36 to 0.34 $\text{W m}^{-1} \text{K}^{-1}$ over a temperature range of 253 to 278 K, respectively. Waite et al., also reported results for compacted samples of methane hydrate in their device [18, 19]. For a sample prepared in a similar manner and radially compacted around the needle probe at 32 MPa, they obtained values that ranged from 0.456 to 0.452 $\text{W m}^{-1} \text{K}^{-1}$ over a temperature range from 243 to 268 K [18]. In the same system modified to apply more uniform radial compaction pressure they more recently obtained values of 0.62 to 0.63 $\text{W m}^{-1} \text{K}^{-1}$ over a temperature range from 253 to 290 K for a sample compacted at ~ 102 MPa [19]. Using a commercially available transient-plane-source (TPS) instrument based on the technique developed by Gustafsson [24, 25], Huang and Fan formed a sample of methane hydrate from methane and water around a relatively flat TPS sensor with the aid of a surfactant (0.971 mol m^{-3} aqueous sodium dodecyl sulfate) [15]. They obtained conductivity results over a temperature range from 263 to 278 K of 0.334 to 0.381 $\text{W m}^{-1} \text{K}^{-1}$ for the sample without compaction and 0.564 to 0.587 $\text{W m}^{-1} \text{K}^{-1}$ with compaction at 2 MPa.

With respect to all of the above techniques, the needle probe has been the only one successfully used for in-situ measurements in geologic samples [21]. Using such a probe in hydrate-cemented sediments requires precision drilling and sealing [26] or otherwise good contact with a solid surface [17]. NETL has recently developed a modified TPS technique that may be more suitable for in-situ or field measurements [27]. In this approach, a single-sided TPS technique is used in which the TPS element, two configurations of which are shown in Fig. 1, is mounted onto an insulating support to permit the device to be used as a contact sensor. The TPS element also requires less sample

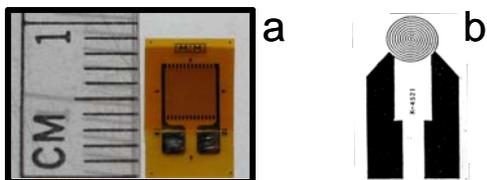


Figure 1. (a) Rectangular TPS element used in NETL research [20]. (b) Schematic of double-spiral element similar to that used in the work of Huang and Fan [15].

contact area than a needle probe.

A sensor similar to that shown in Fig. 1a was mounted to a polyvinylchloride (PVC) base and used to measure the thermal properties of a small, disc-shaped sample of methane hydrate [20]. The NETL device also permitted direct mechanical compaction of the sample to effectively minimize porosity. Thermal conductivity results of $0.68 \pm 0.01 \text{ W m}^{-1} \text{K}^{-1}$ over a temperature range of 261.5 to 277.4 K were obtained after the sample was compacted onto the TPS element at 45 MPa.

Figure 2 illustrates the thermal conductivity data for methane hydrate obtained using the NETL device and compares it to the more recent published data or correlations of others discussed above at temperatures typically encountered in hydrate-bearing formations. Also shown in this

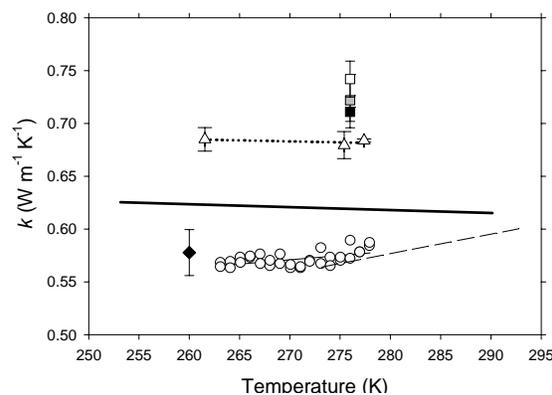


Figure 2. Thermal conductivity data as a function of temperature. **Experimental:** methane hydrate: Δ NETL [20]; $—$ Correlation of Waite, et al. [19]; \circ Huang and Fan [15]; $---$ water: NIST [28]. **MDS:** Methane Hydrate: \blacksquare TIP4P-FQ, 100% occupied, \square 90%, \square 80% [20]; \blacklozenge COS/G2 100% [29].

figure are results for water at 5.5 MPa pressure [28], which was the average gas phase pressure in the NETL experiments, and the results from molecular dynamics simulations that will be discussed below [20, 29]. These experimental and theoretical values for methane hydrate are all above the thermal conductivity of water and have an average value of $0.65 \text{ W m}^{-1} \text{K}^{-1}$. The differences in the experimental values may be due to the differences in the techniques used to prepare the samples and to determine the thermal conductivity. The porosity of sample of Huang

and Fan is likely higher than the other samples owing to the low compaction pressures used [15]. The NETL sample is also the smallest, being only about 1 cm^3 [20]; whereas, the sample of Waite et al. was 175 cm^3 [19] and that of Huang and Fan was similar ($\sim 200 \text{ cm}^3$) [15]. The compaction of the NETL sample was likely more efficient and is evident in the fact that the slope of the data is the lowest of the three data sets.

The thermal conductivity of a laboratory-formed porous sample of methane hydrate was recently determined by inverse modeling of temperature measurements during thermal cycling of the sample [30]. X-ray computed tomography scans were also taken that permitted assessment of the density of the sample. An arithmetic mixing model was also used by these authors to predict the zero-porosity thermal conductivity of methane hydrate, which was $0.70 \pm 0.04 \text{ W m}^{-1} \text{ K}^{-1}$.

As documented above, the thermal conductivity of low-porosity methane hydrate has now been determined in a manner that precludes removal of the sample for compaction or other handling, thus preventing deterioration of the sample by contamination or decomposition. These measurements were performed using two separate measurement techniques and arrived at similar values that are both higher than previously determined values. The results are also close to values predicted by molecular simulation and an average value that includes both experiment and simulation results is given above. If only the values of Rosenbaum et al. [20] and Waite et al. [19] are averaged, the value is the same, $0.65 \text{ W m}^{-1} \text{ K}^{-1}$. The NETL experimental and theoretical values for thermal conductivity, $0.68 \pm 0.01 \text{ W m}^{-1} \text{ K}^{-1}$ and $0.74 \pm 0.02 \text{ W m}^{-1} \text{ K}^{-1}$, respectively, bracket the value of $0.70 \pm 0.04 \text{ W m}^{-1} \text{ K}^{-1}$ determined by inverse modeling [30]. Owing to the observed insensitivity to temperature over the range of temperatures of geological interest, no temperature correlations appear to be necessary for most modeling and simulation purposes.

Thermal Diffusivity

Compared to the efforts described above for thermal conductivity, fewer attempts have been made to determine the thermal diffusivity of hydrates. Figure 3 contains all of the thermal diffusivity measurements for methane hydrate on both unconsolidated and compacted samples. The

first measurements were made by deMartin on a sample of methane hydrate that was compacted in a separate apparatus outside of hydrate equilibrium conditions and appeared to have been contaminated with ice, which began to melt at the highest temperatures investigated [31].

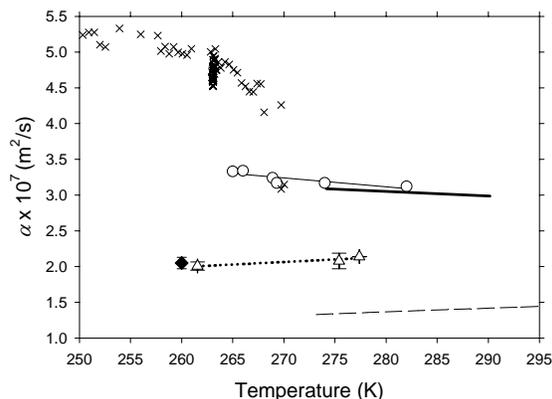


Figure 3. Thermal diffusivity data as a function of temperature. **Experimental:** Methane Hydrate: Δ NETL [20]; — Correlation of Waite, et al. [19]; \circ Kumar, et al. [33]; \times deMartin [31]. Water: --- Calculated from NIST data [28]. **MDS:** \blacklozenge COS/G2 [29].

Data for ice, which are about an order of magnitude higher than water, are not shown in Fig. 3. In the temperature range investigated, the diffusivity of ice is about $1.2 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ [32].

The data of Waite et al. on a compacted sample [19] and of Kumar et al. on a porous sample [33] are close and fall in the same range as the last two, supposedly ice free, data points of deMartin [31]. This would indicate that porosity has little effect on thermal diffusivity as discussed by Waite et al.

[19]. Both the NETL experimental and modeling data are lower. The NETL experimental data also have a slope similar to that of water. As discussed in Rosenbaum et al. [20], finite difference modeling of the single-sided TPS technique with PVC as the support material show that these data are likely lower than they should be owing to the sample having a higher thermal diffusivity than the PVC. We are continuing to study this issue and expect a resolution of this problem soon. The thermal diffusivity data of Waite et al. [19] are at present the only reliable data set for low-porosity methane hydrate.

Specific Heat Capacity

Only one set of measurements have been made of the specific heat capacity of methane hydrate. Handa determined this value, along with values for ethane and propane hydrate in a heat flow calorimeter over the temperature range of 85 to 270 K [34]. His values along with those calculated by Waite et al. [19] from their data are shown in Fig. 4. In this figure, the correlation by Waite et al. [19] was determined only from the data above 273 K; however, it is extended below this temperature for comparison purposes.

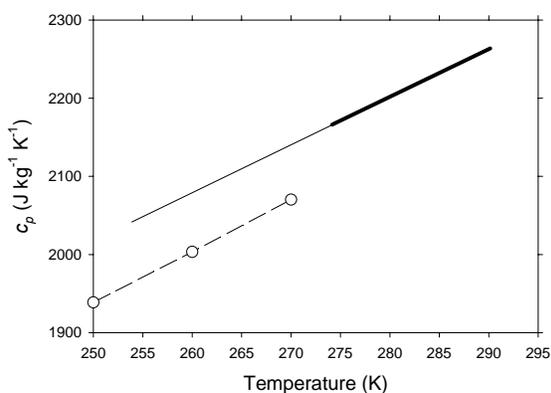


Figure 4. Specific heat capacity data as a function of temperature for methane hydrate: — correlation of Waite, et al. [19]; ○ Handa [34].

MOLECULAR DYNAMIC SIMULATIONS

MDS has been used at NETL to study the thermal properties of methane hydrate. Rosenbaum et al. reported the use of three rigid potential models to determine the thermal conductivity of methane hydrate at 276 K and at pressures from 0.1 to 100 MPa [20]. One of the models, TIP4P-FQ, includes the effects of in-plane polarization of water. The simulations were performed with 80, 90, and 100% occupancy of the lattice cavities. Simulations were also performed on water and ice, which are shown in Table 1 along with experimental values from the literature [20, 29].

The thermal conductivity results obtained with the TIP4P-FQ model at a pressure of 10 MPa are shown in Fig. 2 along with the previously discussed experimental data. The results are slightly higher than the experimental data as would be expected for a hydrate crystal as compared to

the experimental samples that likely contained some structural defects and residual porosity. The removal of methane from the lattice cages appears to result in a slightly higher thermal conductivity, although the trend is almost within the simulation variability.

	Water	Ice
TIP4P-FQ	0.67 ± 0.03^a	2.42 ± 0.04^b
Experiment	0.61^a	2.2^b
COS/G2	0.62 ± 0.01^c	2.2 ± 0.02^d
Experiment	0.61^c	4.3^d

Table 1. Comparison of the thermal conductivity of values obtained by simulation for water and ice with values obtained from the literature (in $\text{W m}^{-1} \text{K}^{-1}$). ^a298 K, 100 kPa [20]. ^b273 K, 0 MPa [20]. ^c298 K [29]. ^d150 K [29].

Recently, more extensive simulations of the thermal properties of methane hydrate have been performed by NETL [29] using the COS/G2 model that allows for both in-plane and out-of-plane polarization of the water molecules [35]. In this work, a range of temperatures was employed from 30 to 270 K. Simulations with ice at 150 K and water at 298 K were also performed and these results are contained in Table 1. The lower ice results are likely due to quantum effects [36].

The thermal conductivity of methane hydrate obtained using the COS/G2 model in the temperature range of geologic interest is shown in Fig. 2. It is close to the experimental values of Huang and Fan [15] and lower than the experimental values of Waite et al. [19] and Rosenbaum et al. [20]. A complete account of this more recent MDS work has been submitted for review and publication [29].

RESERVOIR SIMULATION

An accurate knowledge of the thermal properties of methane hydrate is important for predictions involving resource production, greenhouse gas evolution impacting climate change, and seafloor stability. Concise descriptions of the importance of these thermal properties and scenarios have been published [19, 37].

With respect to the technology of gas production from hydrate-containing reservoirs, the inclusion of the hydrate phase has only recently been added

to advanced simulation codes [38, 39]. A recent assessment also highlights the importance of having accurate thermal properties for methane hydrates, both pure and in porous media [39].

To assess the impact of thermal conductivity on gas production from a hydrate-bearing reservoir, simulations were performed at NETL using the Tough+Hydrate (T+H) simulator [40] with two different values for thermal conductivity, 0.50 and 0.68 $\text{W m}^{-1} \text{K}^{-1}$. To accomplish this, we had to use a different expression for composite thermal conductivity, k_θ , than is currently used in this simulator [41], which is shown in the following equation.

$$k_\theta = k_{Rd} + \left(\sqrt{S_H} + \sqrt{S_W} \right) (k_{Rw} - k_{Rd}) + \phi S_I k_I \quad (1)$$

In this equation ϕ represents the porosity of the sediment (rock) phase, S_H , S_W , and S_I represent the hydrate, water, and ice saturations in the pores, respectively, and k_{Rw} , k_{Rd} , and k_I represent the thermal conductivities of wet rock, dry rock, and ice in the reservoir, respectively. However, Equation (1) does not specifically account for the thermal conductivity of the hydrate phase. An arithmetic model [41, 42] was used instead and is shown in the equation below.

$$k_\theta = k_{Rd} + \phi (S_W k_W + S_H k_H + S_I k_I) \quad (2)$$

In this equation k_W and k_H represent the thermal conductivities of the water and hydrate phases, respectively. Equation (1) is currently preferred over Eq. (2) for hydrate reservoirs [41]; however Moridis, et al., acknowledge that there is significant room for new relationships for k_θ to be developed [39].

Figure 5 depicts the simulation results for gas production from a Class 3 [39] hydrate-bearing formation induced by the depressurization method [39] coupled with thermal stimulation provided by constant temperature boundaries. Equation (2) was used to describe the composite thermal conductivity of the hydrate-containing formation. This type of formation does not contain any underlying free gas or water layer; it only consists of the hydrate-containing sediment with overburden and underburden that are impermeable to fluid flow. Thermal conductivities of 0.50 and 0.68 $\text{W m}^{-1} \text{K}^{-1}$ were used in the simulations.

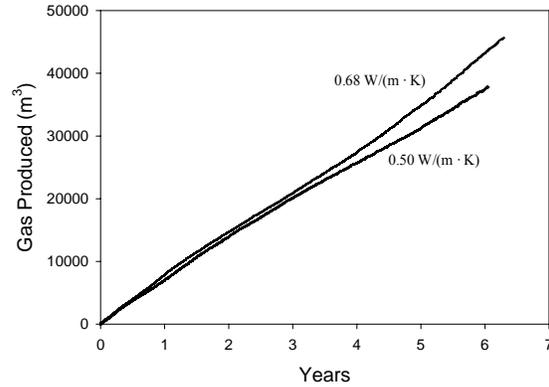


Figure 5. Simulation of production from a Class 3 hydrate-containing reservoir using two different values for thermal conductivity.

The simulation results show that initially the variation of thermal conductivities has a negligible effect on the production of methane as the hydrate area affected by the thermal stimulation is relatively small. As years progress, the thermal stimulation affects substantial hydrate area and the effect of thermal conductivity on the methane production becomes apparent. As shown in Figure 5, after five years the production of methane increases by 14% when the thermal conductivity is increased from 0.50 to 0.68 $\text{W m}^{-1} \text{K}^{-1}$. It is anticipated that similar observations would be made if higher thermal conductivity values were used in climate change or sea-floor stability simulations, i.e., the rate of hydrate dissociation would be proportional to the thermal conductivity value used in the simulation.

CONCLUSIONS

Experimental and theoretical research over the past several years has helped refine the thermal properties of methane hydrate. This is especially true for the thermal conductivity of methane hydrate. Based on experiment, molecular simulation, and inverse modeling it is recommended that values in the range of 0.65 to 0.70 $\text{W m}^{-1} \text{K}^{-1}$ should be used in simulations of systems that contain low-porosity methane hydrate.

With respect to the other thermal properties, there have been only a few measurements or simulations of thermal diffusivity and only one set of measurements that permitted calculation of the specific heat of methane hydrate. At this time, the

values obtained by Waite, et al. should be used for simulation purposes [19]. Additional experimental and theoretical simulations are warranted in this area to provide additional validation of these results. Such research is being conducted at NETL.

The TPS technique under development at NETL is also in the process of being adapted to devices for field use. The one-sided approach makes it particularly attractive for this application in natural hydrate-bearing systems.

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