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Effective thermal conductivity of methane hydrate-bearing sediments: Experiments and correlations

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HIGHLIGHTS

- The effective thermal conductivity of gas hydrate-bearing sediments was measured.
- Various effective medium models were evaluated with our experimental data.
- A hybrid fitting model combining three forms of self-consistent models was proposed.
- The PIKAIA genetic algorithm was employed to obtain the optimal weighting parameter.

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ABSTRACT

Thermal properties of gas hydrate-bearing sediments directly govern the heat transfer process during hydrate decomposition which couples with phase transitions and multiphase flows. The effective thermal conductivity of a multiphase system represents the composite capacity to conduct heat. Here we report on point heat source measurements of the effective thermal conductivity of methane hydrate-bearing sediments through a thermistor-based method combining with X-ray CT observations. Methane hydrates were formed at different saturations, with various initial water contents, and in porous matrices simulated by grains with differing thermal conductivities. It is indicated that the effective thermal conductivity of sediments negatively correlated with the hydrate saturation, while an increase of initial water contents and thermal conductivity of grains has a positive impact on the elevation of the effective thermal conductivity. Moreover, the effective thermal conductivity was found to slightly increase with the proceeding of hydrate decomposition. Typical effective medium models were evaluated with the measurements of this study, and a hybrid fitting model combining three forms of self-consistent models was proposed, with the optimal weighting parameters determined *via* the genetic algorithm. The effective prediction of the measurements in this work and results in literatures corroborates the feasibility of the model. This study could help in understanding the evolutions of sediment thermal properties during gas production and their effects on large-scale hydrate decomposition when expanded to field scale tests.

1. Introduction

Their enormous energy reserves, high purity, and environmental friendliness have made natural gas hydrates an potentially alternative source of future energy [1,2]. Gas molecules are trapped into a crystalline cage structured by hydrogen-bonded water molecules under a high pressure and/or low temperature to form gas hydrates [3]. Basic nature involving thermal, mechanical, acoustic and electrical properties of gas hydrates in/without porous media could help in explaining the kinetics of hydrate formation/decomposition, control mechanism of gas production, and engineering applications of gas hydrates including gas separation, gas storage and transportation, as well as plugging problems in natural gas pipelines [1,4–6]. Given the fact that heat transfer is considered the dominant mechanism controlling gas hydrate decomposition, a number of attempts have been made on the analysis of heat conduction and convection process during gas production [7–10]. Analytic models have also been proposed to predict gas production behavior considering heat and mass transfer [11,12]. The specific heat capacity and thermal conductivity are widely employed as initial parameters in simulations on hydrate decomposition to study the effects of sensible and latent heat on the gas production behavior [13–16]. However, the effective thermal conductivity (ETC) of a multi-phase system involving gas, hydrates, water, and porous matrices is largely unknown and the

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empirical data by simply combining the thermal conductivity of each component are commonly ambiguous. Considerable work has been conducted on measurements of the thermal conductivity of pure hydrates without the presence of porous matrices [17–19]. Tetrahydrofuran hydrates are generally employed as substitutes for gas hydrates on account of similar physical properties and mild formation conditions [20–22]. Their thermal conductivity has been measured through a steady-state potentiometric method at a wide temperature range [19]; similar work has also been conducted using a transient hot-wire method [23]. The glass-like temperature dependent characteristics of their thermal conductivity were identified [19,23]. Moreover, the formation of THF hydrates appeared to have a positive effect on the increase of the effective thermal conductivity of sediments [24]. Efforts have also been exerted on the determination of gas hydrate thermal conductivities in/without porous matrices [17,18,25]. The thermal conductivity of pure methane hydrates was measured to be 0.575 W/(m K) at 0 °C and 6.6 MPa, and an inhomogeneous formation of gas hydrates was found to have a significant impact on the effective thermal conductivity of the sample [17]. Notable numerical and experimental work has been conducted on the composite thermal conductivity of gas hydrate-bearing sediments as well [10,25–28]. The agreements between simulated results and measured data were illustrated and analyzed [25,26]. A recent study provided experimental measurements of the effective thermal conductivity of methane hydrate-bearing sediments, and found that the ETC showed little dependence on hydrate saturations in samples with high water contents [29]. It is also suggested that the thermal conductivity is likely to significantly drop when residual hydrate/water saturation declines below ~40% [30]. The abovementioned work has provided a better description of the thermal conductivity of hydrates and hydrate-bearing sediments, which would help in numerical simulations on gas production behavior on field scale. However, little further discussion on the effects of component volume fraction and thermal property on the effective thermal conductivity was provided, which would have implications in understanding the evolution of the ETC during hydrate decomposition. In addition, these studies were all conducted using a plate heat source method or a transient hot-wire method, which likely has limitations in reflecting local properties arising from the measuring principle, and little research is found to be conducted through a point heat source method with a smaller heating probe and thermally affected region.

The effective medium theory (EMT) has been commonly employed to predict the approximations of bulk properties of a multi-component system by averaging the physical data of each component based on its volume fraction [31–33]. A number of researches have been reported on the determination of physical properties according to various effective medium models. Numerically validated models for the prediction of the effective index of refraction and absorption index of nanocomposite thin films were developed through the effective medium theory, and fine agreements between the proposed models with the widely used models were obtained [34,35]. Other attempts to gain the elastic properties of rocks or sediments have been reported by the combination of the effective medium theory with other approximation theories [31,36,37]. The velocity of two-phase flow was also calculated by using an analogy of effective property models [38]. Moreover, attentions were also placed to the prediction of the effective thermal conductivity of a multi-component system based on the EMT [39–42]. In the context of the ETC of THF hydrate-bearing sediments, the measured data were compared with six typical prediction models, and the *Woodside* model was evaluated to best agree with the measurements [17]. Curves of seven prediction models were illustrated for the water saturated quartz system at a porosity range from 0 to 1, which would provide implications when expanded to sediments containing hydrates [43]. However, these studies do not provide any support for the effective prediction of the ETC of sediments containing gas hydrates, involving a gas phase with high pressure in the multi-phase system. This would nevertheless significantly contribute to the analysis of heat transfer process during gas production from natural reserves where a gas phase with pressure is present as well. Furthermore, the typical effective medium models were commonly found powerless in predicting a complicated system containing gas hydrates [44]. Yet little work is reported on proposing a prediction model with a wide applicability, which would help in realizing the basic physical properties of natural gas hydrate deposits without measurements. The volume fraction and homogeneity of hydrate-bearing sediments play a significant role in local effective properties, and it would be helpful to directly observe the distribution of each component by means of a visualization method, yet still few studies were found to make connections between observations and effective thermal conductivity measurements.

Therefore in the following, a thermistor-based point heat source measuring method was developed for the determination of the effective thermal conductivity of methane hydrate-bearing sediments. Various grains with differing thermal conductivities were employed to simulate porous matrices for the formation of methane hydrates with different saturations and initial water contents. Furthermore, the effective thermal conductivity of sediments during hydrate decomposition was investigated. The X-ray computed tomography (CT) technique was used to observe the homogeneity of hydrate-bearing sediments and acquire content saturations. The agreements between measured results and typical EMT models were illustrated, and a hybrid model by linearly combining the existing models was proposed with the fitting parameters calculated through the genetic algorithm. The effective prediction of data from other researchers validated the feasibility of the model.

2. Experiments and measurement methods

2.1. Experimental apparatus

The schematic of the experimental system is shown in Fig. 1. A 120-ml pressure vessel made of polyether ether ketone (PEEK) with an inner diameter of 40 mm was used for gas hydrate formation and decomposition, CT scanning, as well as thermal conductivity measurements, the size of which is sufficiently large to be considered infinite relative to the thermally affected region of a thermistor [45]. A water bath (FP51, Julabo Co., Germany) with a precision of 0.01 °C was employed to control the temperature during hydrate formation and decomposition. A high pressure control system (260D, ISCO Inc., USA) was established for gas and water injections. A thermistor (Shibaura Electronics Co., Japan) with the chip size of ~0.5 ± 0.05 mm functions simultaneously as a point heat source and a temperature sensor; the measuring method and the uncertainty have been validated and provided in the previous work [46,47]. A data acquisition system (34972A, Agilent Co., USA) was used to collect the electrical signal feedbacks of the thermistor for thermal conductivity calculation. A microfocus X-ray CT system (SMX-225CTX-SV, Shimadzu Co., Japan) with a limit resolution of 4 μm/pixel was responsible for observing the homogeneity of samples and acquiring component saturations. A liquid nitrogen spraying system was developed to prevent possible decomposition of samples during scanning.

2.2. Experimental materials

Various grains with almost same size distributions but differing thermal conductivities were used for hydrate formation, the details