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Methane hydrate formation and dissociation in a partially saturated core-scale sand sample

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Abstract

We performed a series of experiments to provide data for validating numerical models of gas hydrate behavior in porous media. Methane hydrate was formed and dissociated under various conditions in a large X-ray transparent pressure vessel, while pressure and temperature were monitored. In addition, X-ray computed tomography (CT) was used to determine local density changes during the experiment. The goals of the experiments were to observe changes occurring due to hydrate formation and dissociation, and to collect data to evaluate the importance of hydrate dissociation kinetics in porous media. In the series of experiments, we performed thermal perturbations on the sand/water/gas system, formed methane hydrate, performed thermal perturbations on the sand/hydrate/water/gas system resulting in hydrate formation and dissociation, formed hydrate in the resulting partially dissociated system, and dissociated the hydrate by depressurization coupled with thermal stimulation. Our CT work shows significant water migration in addition to possible shifting of mineral grains in response to hydrate formation and dissociation. The extensive data including pressure, temperatures at multiple locations, and density from CT data is described.
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Keywords: Hydrate formation; Dissociation; Porous medium; Thermal stimulation; Depressurization; X-ray computed tomography

1. Introduction

Gas hydrates in the earth's subsurface within permafrost and sub-sea environments are thought to hold a vast amount of potentially producible natural gas (Sloan, 1998). Each cubic meter of gas hydrate can hold approximately 160 m^3 of natural gas at standard temperature and pressure (STP) (National Resource Council, 2004). Because gas hydrates are unstable at STP and recovered samples have all been transported through conditions different from where they originated, measurements on the recovered samples have not provided adequate information for simulation of natural gas production from hydrate-bearing reservoirs.

Information needed to reliably predict the feasibility of producing natural gas from hydrates includes:

- Abundance of the hydrates in the selected reservoir
- Lithology and geologic structure of the reservoir

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- Presence or absence of a free gas zone
- Arrangement of hydrate within the porous medium
- Permeability, relative permeability–saturation relationships, capillary pressure–saturation relationships, and thermal conductivity of the hydrate-bearing and hydrate-free medium
- Energy required to dissociate the hydrate (how close the hydrate is to equilibrium)
- Kinetics of dissociation.

Several of these information needs are reservoir specific, but others – such as dissociation kinetics, thermal conductivity, and relative permeability – have components of general applicability that can be evaluated in the laboratory.

Both laboratory-made and natural hydrate samples can be used in laboratory studies. Natural hydrate samples are not abundantly available and can be somewhat-to-severely compromised by collection, recovery, transport, and handling. Several methods are available for making hydrates in a porous medium, including the method used by Stern et al. (1996) which converts granulated ice into hydrate by controlled melting at excess methane pressure, and the method of Handa and Stupin (1992) that converts capillary-held water into hydrate at excess methane pressure. Scanning electron microscopy has been used to compare natural samples to samples made using Stern's method, and the samples appear nearly identical (Stern et al., 2004). The conditions of these observations, however, are <105 K and 10^{-3} Pa, whereas the natural environment for the samples is moderate pressure (~ 3 to 10 MPa) and above-freezing temperatures (several °C).

Samples made in quartz sand using Handa's method are thought to cement sand grains (Waite et al., 2004), whereas hydrates at the Mallik site in northern Canada are thought to be part of the solid frame of the sediment (Winters et al., 2004). The hydrate configuration (cementing or solid frame) may affect properties such as the thermal conductivity and relative permeability of the hydrate-bearing sediment. Because natural samples have likely been at least partially compromised, and laboratory-made samples are thought to have some characteristics unlike natural hydrate bearing sediments, results from measurements on either laboratory-made or natural samples must be regarded with caution.

The kinetics of hydrate dissociation have been measured in laboratory stirred tank semibatch reactors (Kim et al., 1987; Clarke and Bishnoi, 2001). The effect of kinetics has not been experimentally investigated in porous medium samples containing hydrate, particularly in light of heat- and mass-transfer interferences. Kinetic effects may affect natural gas production from a hydrate-bearing reservoir, consequently, these effects must be considered.

In this work, we performed a sequence of tests on a partially water-saturated sand sample contained in an X-ray-transparent aluminum pressure vessel. These tests were performed to (1) observe changes that occur in response to hydrate formation and dissociation, and (2) gather information to evaluate the kinetic nature of hydrate dissociation in a partially saturated porous medium. The test sequence included preliminary tests to monitor the vessel strain during hydrate formation and dissociation, tests to allow computation of sample thermal conductivity, hydrate formation, dissociation by thermal stimulation, another hydrate formation step, and dissociation by depressurization coupled with thermal stimulation. Numerical modeling of these tests to determine thermal conductivities and kinetic parameters will be presented elsewhere (e.g. Moridis et al., 2005).

2. Equipment and materials

2.1. Pressure vessel

The pressure vessel used in this experiment was a 7.62 cm inner diameter and 8.9 cm outer diameter aluminum tube with threaded stainless steel end caps (Fig. 1). The end caps set the inner axial length to 31.75 cm. One of the end caps was machined to provide four feed-throughs for thermocouples. The other end was machined to provide a connection to the gas source. Three of four Type-T thermocouples (18 in. long, 1/16 in. diameter, stainless steel shielded ungrounded, Omega Engineering, Stamford, CT) were placed in a vertical line, with one about 0.5 cm from the top, one about 0.5 cm from the bottom, and one near the center (see Fig. 1, Section A-A′). This arrangement was selected to monitor the effect of a water saturation gradient caused by gravity in the partially saturated sand. The fourth thermocouple was placed in the horizontal midplane, approximately 0.5 cm from the vessel wall. The exact locations of the thermocouples were determined from X-ray computed tomography (CT) images (e.g., Fig. 5). System pressure was measured on the line connected to the pressure vessel using a Rosemount 1151 pressure transducer. Because water was placed in the sand prior to the experiment and the line was used only to carry gas, we assumed that pressure communication with the sample was direct and that there were no blockages in the line between the transducer and the sample.