Hydrate Formation and Dissociation via Depressurization in Simulated and Field Samples

Interim Report
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Abstract: A series of end-member experiments in sand and natural permafrost sediments have been conducted within ORNL's Seafloor Process Simulator at 275-277 K and 10 MPa to determine the effects of methane flux on hydrate accumulation. Methane flux through a 60 cm long, 4.8 cm diameter sediment column was controlled by flow of methane-saturated water and/or bubbling of free methane gas. Initial experiments were conducted in commercially available black sand (< 500 micron grain size) and Ottowa sand containing Snowmax. Methane saturated water was cycled through the sediment column at ~10 ml/min; in these water flow experiments no hydrate formation was visible in the column within 3-6 hours. Temperature and conductivity data collected within the sediment also did not show conclusive evidence of hydrate formation. However, in experiments where free methane gas was bubbled through the sediment column (with or without water flow) hydrate formation was visibly observed within 10-40 minutes in sediment void spaces. A single experiment in which the sediment column was placed at the gas-water interface within the vessel also formed hydrate in the sediment over a similar time scale. Substituting an inert gas phase (nitrogen) did not stimulate hydrate formation in the same manner observed in free methane gas experiments; similar to the water flow only experiments, hydrate formation was not observed over the several hour timescale of the experiment. These results suggest that free methane gas within the sediment, either as bubbles or at the water-gas interface, greatly increases the likelihood that hydrate will nucleate, therefore decreasing the observed induction time.

Introduction: The effects of differing rates and mechanisms of methane flux (free gas vs. methane saturated water) on hydrate nucleation and accumulation in sediment systems was investigated at the mesoscale using ORNL's 72 liter Seafloor Process Simulator (SPS; Phelps et al. 2001). The effects of heterogeneous fluid flux and sediment conditions has been noted in field observations (Ruppel et al. 2005, Borowski, 2004, Gorman et al. 2002) but few laboratory experiments have focused on the effects of varying methane flux on hydrate accumulation within sediments. This study addresses the effects of varying forms of methane flux on hydrate accumulation in mesoscale synthetic and natural sediments to better understand the rate and distribution of hydrate accumulation. The results of these experiments will provide input to reservoir-scale models of hydrate accumulation and estimates of potential resources.

The SPS is a unique experimental facility, ideally suited to the determination of rates, thermophysical and mechanical properties of methane hydrates that are relevant to understanding their resource potential, environmental significance and their effects on the mechanical stability of the seafloor. Not only can the physical conditions be controlled, but the size and design of the vessel permit direct observation of the hydrate formation processes, and investigation of how these processes are influenced by the heterogeneities that can be expected in nature. Recent work has demonstrated that kinetic studies conducted within the SPS result in faster nucleation times, smaller standard deviations in the results and lower overpressures required for hydrate formation compared to parallel experiments conducted in a 450 ml Parr vessel (McCallum et al. 2006).

Methods: A series of experiments have been conducted within ORNL's 72 liter Seafloor Process Simulator (SPS) to investigate the effects of varying the type and rate of methane flux on hydrate accumulation. The effects of free gas and water flow were investigated in a series of sediment column experiments at 1500 psi (10.3 MPa, 900 psi or 6.2 MPa above the stability point) and temperatures between 275 and 278K. Hydrate accumulation was observed in both synthetic sediments (Ottawa sand and black sand), as well as natural samples of permafrost sediments from the Hot Ice-1 GIP were investigated within the SPS.

The SPS vessel was reconfigured to hold the core materials in a glass column for strict control of sediment experiments (Figure 1a). Initial experiments were conducted in commercially available Ottawa sand and black aquarium sand (<500 micron grain size) with and without Snowmax® (a natural protein used as a nucleator in snowmaking operations). Sediments retrieved from the Hot Ice 1 JIP permafrost production project were also investigated in collaboration with NETL. Cores were received from Alaska, shared with NETL, logged into custody and a subset of cores remain frozen.

The sediment bearing columns were bounded top and bottom with glass beads to equilibrate and disperse fluid flow through the sedimentary materials (Figure 1b). Vessel water (methane saturated due to communication with the headspace gas) was

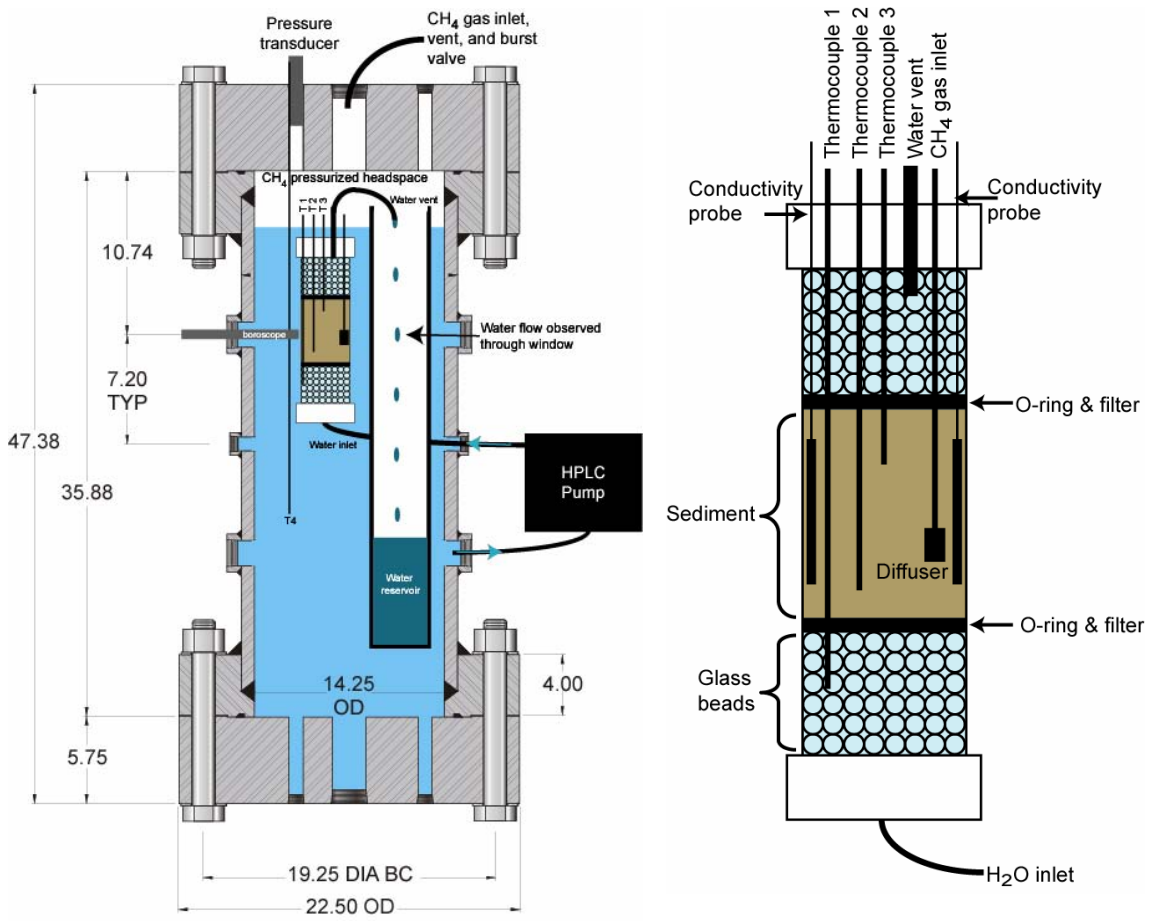

Figure 1. (A) Flow-through sediment column experiments within the SPS. A 60 cm glass column (diameter 4.8 cm) was filled with sediment and glass beads as spacers and suspended within the SPS. Methane-saturated water flow was controlled by an external HPLC pump; methane gas was injected into the sediment in some experiments (vessel measurements in inches). **(B) Sediment column design.** Ottawa sand, black sand, or permafrost sediments from the HotIce-1 field experiment were packed into the column and separated from the glass beads using filters and O-rings. Thermocouples and a conductivity meter were inserted to monitor the sediments for fluctuations indicative of hydrate formation.

removed from the vessel and circulated through an HPLC pump and the reinjected directly into the sediment containing glass column at rates between 0.1 and 9.9 ml min (Figure 1A). Methane flux was controlled by flow of methane-saturated water and/or bubbling of free methane gas through a 60 cm long, 4.8 cm diameter sediment column. Effluent water exiting the column was collected within a separate vessel in the SPS such that any fines exiting the sedimentary column were not redistributed throughout the SPS to avoid issues with turbidity. This experimental design allowed flux experiments to be conducted using recirculated waters that were in equilibrium with vessel PT conditions and the methane gas headspace without any volume change after hours of operation. Free methane gas or nitrogen was also introduced in some experiments through a diffuser placed in or below the sediment.

Thermocouples placed within the sediment column as well as the body of the vessel monitored temperature variations. A conductivity meter was also tested within the sediment column; however no definitive response to hydrate formation was recorded. A boroscope was inserted through one of several ports into the SPS enabling close-in

photographs with near 20um resolution. Lower resolution photographs were also taken thru the Lexan/Sapphire windows using our Nikon digital camera with C-mount adapted lenses providing resolution.

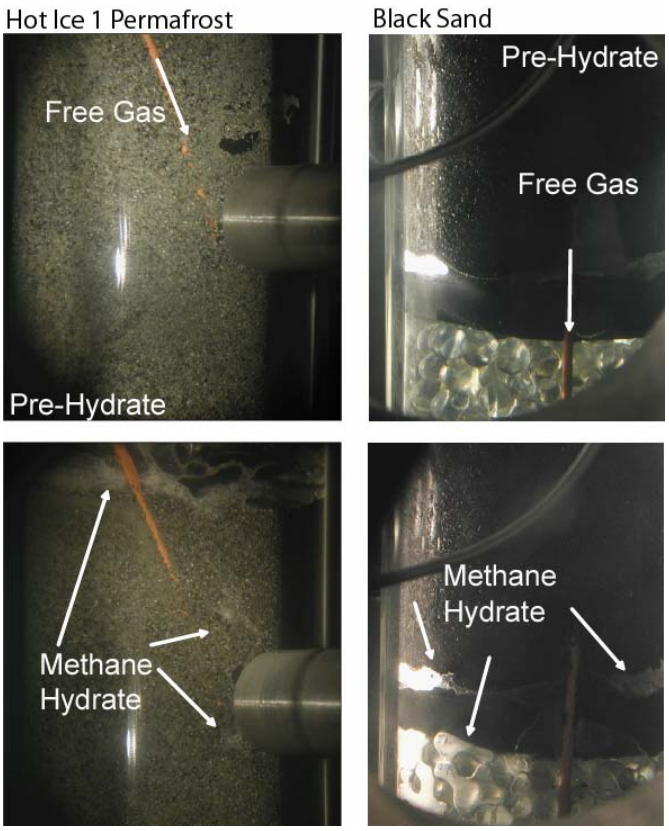

Figure 2. Boroscope images of hydrate formation within the sediment columns containing Hot Ice-I permafrost sediments (A and B) and synthetic black sand sediments (C and D). Hydrate was first observed as a film around bubbles in void spaces, then later grew into sediment pore spaces.

Results: The initial series of experiments examined hydrate accumulation within commercially available black sand (< 500 micron grain size) with 200 mg of Snowmax (a natural protein which acts as an ice/hydrate nucleator) added to the sediment under methane-saturated flow conditions. In these experiments without a free methane gas phase, no hydrate formation was observed within the 3-6 hour timeframe of the experiments. In experiments where free methane gas was bubbled through the sediment column (with or without water flow) hydrate formation was visibly observed within 10-40 minutes (Figure 2 a and b). An experiment in which the sediment column was placed at the gas-water interface within the vessel also formed hydrate within the sediment over a similar time scale. We also conducted an experiment in which nitrogen gas was bubbled through the sediment along with flow of methane saturated water. Similar to the water flow only experiments, hydrate formation was not observed over the timescale of the experiment.

A second set of experiments was conducted using permafrost sediments collected during the Hot Ice-1 JIP. No nucleators were used in these experiments. Again, hydrate formed readily when free methane gas was present in the system, but was not observed in when only methane-saturated water was used. The results of the full series of experiments are summarized in the table below.

Methane Hydrate Nucleation Experiments

Sediment	Water flow	Free gas	T (C)	P (psi)	Duration (hr)	Nucleator	Hydrate observed
Ottawa sand	X		4.5	1500	6.5		
Ottawa sand	X		3.5	1500	6.75		
Ottawa sand	X		3	1500	4.25	Thawed water	
Black sand			6	1500	5		
Black sand	X	gas/water interface	3.2	1500	5		X
Black sand	X		4.5	1500	4.5	Snowmax	
Black sand	X	CH_4	2	1500	4		?*
Black sand	X	CH_4	4.5	1500	2	Snowmax	X
Black sand	X	N_2	2.5	1500	3	Snowmax	
Black sand	X	CH_4	2	1500	1	Snowmax	X
Permafrost	X	CH_4	2.5	1500	1		X
Permafrost	X		3.7	1500	3		

*Gas diffuser paced at base of column in the glass beads. Hydrate may have formed below the sediment within the glass beads, but was not visible in the sediment.

Discussion: These results suggest that free methane gas within the sediment, either as bubbles or at the water-gas interface, greatly increases the likelihood that hydrate will nucleate, therefore decreasing the observed induction time.

This kinetic affect is likely due to super-saturation of methane surrounding bubbles as the gas diffuses into the surrounding solution, thus increasing the likelihood of hydrate nucleation. Bubble surface area alone is not a significant catalyst for hydrate formation, as demonstrated by the failure of hydrate to nucleate in the presence of an inert gas phase.

These experiments also represent a significant improvement in experimental design within the SS, allowing fluids at equilibrium with vessel PT conditions and methane partial pressures to be recirculated through a sediment column, or in the future through the entire vessel volume.

Neutron Scattering Experiments: Preliminary experiments using a single crystal sapphire pressure cell specifically designed for neutron characterization studies of gas hydrates have also been initiated. A system has been designed to allow for methane hydrate synthesis and growth within the sapphire vessel for use in neutron scattering experiments. Methane hydrate was synthesized within the vessel with and without sediments. This experimental technique will be further refined as we prepare for future neutron experiments.

Future Work: Methane hydrate accumulation and production within heterogeneous sediment systems will be investigated through a series of mesoscale high pressure studies to be conducted in ORNL's 72 liter Seafloor Process Simulator (SPS) combined with neutron scattering experiments on synthetic and natural hydrate samples.

Within the SPS, hydrate accumulation and dissociation will be monitored at the cm scale using a soon-to-be acquired distributed sensing system (DSS), pressure transducers, and flow meters, as well as visual observations through a boroscope and three or more sapphire windows. Conductivity and pH sensors are also available for incorporation within the vessel. Synthetic sediment systems will be constructed within a 1 cm resolution Distributed Sensing System (DSS) grid constructed of optical fibers supported by a wire frame to simulate the effects of sediment heterogeneity (i.e. void spaces, sand lenses, fine layering) on hydrate accumulation and dissociation. Experiments conducted on natural core samples will integrate the DSS along the walls of the core or insertion of the optical fibers through the sediment core.

Hydrate accumulation and dissociation sites will be determined using the DSS. In addition, the DSS will be used to monitor possible ice formation at the cm scale during dissociation experiments. Hydrate accumulation and dissociation rates will be measured by combining temperature data with the total pressure in the system to monitor methane sequestration or release rates. Sediment stability during hydrate dissociation will be assessed using strain measurements collected by the DSS.

Neutron scattering experiments will compliment and provide data support for mesoscale experiments conducted within the SPS. Both neutron diffraction and small angle neutron scattering (SANS) experiments will be conducted on natural and synthetic samples using a single crystal sapphire pressure cell specifically designed for neutron analysis of gas hydrates (Rondinone et al. 2003). Deuterated water will be used to enhance the sensitivity of neutron scattering in all synthetic hydrate experiments. Natural hydrate samples will also be characterized using low temperature X-ray diffraction, neutron diffraction, and SANS as samples become available.

Thermal expansion (molar volume as a function of temperature) and bulk modulus (molar volume as a function of pressure) measurements will be conducted at field-relevant temperatures and pressures to determine the effects of temperature and pressure variations of hydrate volume and hence sediment stability. Hydrate accumulation and dissociation kinetics as well as ice production during depressurization will be measured through time- resolved quantitative phase analysis using neutron diffraction combined with SANS observations of crystallite nucleation and growth. These accumulation and dissociation experiments may also be conducted in synthetic sediment systems using quartz sand.

Summary: We conducted twelve flow through experiments in the SPS examining methane flux conditions and have initiated experiments in preparation for neutron scattering analysis of methane hydrate in the sapphire pressure cell. Future work includes high resolution studies of hydrate accumulation and dissociation processes in the SPS and neutron scattering experiments examining thermal expansion, bulk moduli, and phase analysis. We have met all of our deliverables for the past year.

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Presentations and Publications:

Elwood Madden, M.E., S. McCallum, T. Phelps, P. Szymcek (2006) Testing the effects of methane gas and methane-saturated water flux on hydrate formation kinetics within sediments. Science and Technology Issues in Methane Hydrate R&D Workshop, Kauai.

McCallum, S.D, Riestenberg, D.E., Zatsepina O, and Phelps, T.J. (In press) Meoscale research of gas hydrates. J. Petroleum Science and Eng.

Elwood Madden, M.E., S. McCallum, T. Phelps, P. Szymcek (in prep.) Hydrate accumulation determined by free gas pathways within sediments: observations from mesoscale experiments.