Testing the effects of methane gas and methane-saturated water flux on hydrate formation kinetics within sediments

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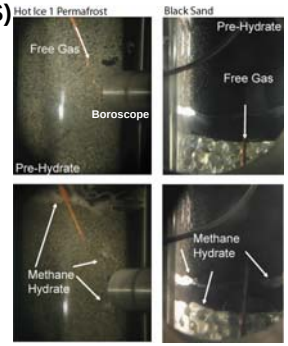
Sediment flow-through experiments in the Seafloor Process Simulator (SPS)

It has long been recognized that hydrates form much more quickly in aqueous systems when there is a flux of free methane gas. However, the effect of gas-saturated water flux on methane hydrate nucleation kinetics has remained unexplored. A series of end-member experiments in sand have been conducted within ORNL's Seafloor Process Simulator (SPS; Phelps et al. 2001) at 275-277 K and 10 MPa methane pressure to determine the effects of methane flux on hydrate formation kinetics.

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. 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. Methane saturated water was cycled through the sediment column at ~6 ml/min using an external HPLC pump. 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.

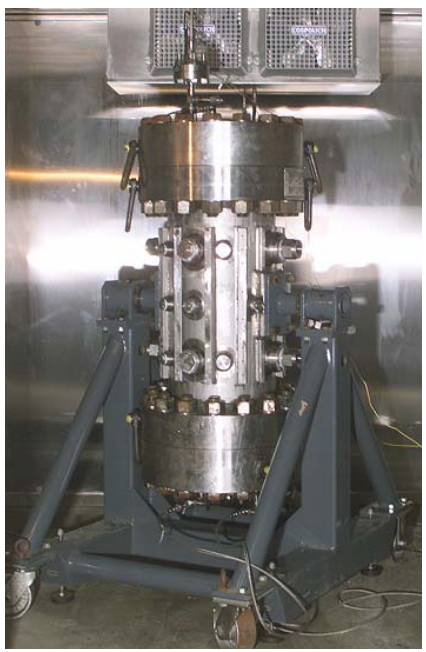


Boroscope images of hydrate formation within the sediment column. Hydrate first observed as a film around bubbles in void spaces, then later grows into sediment pore spaces.

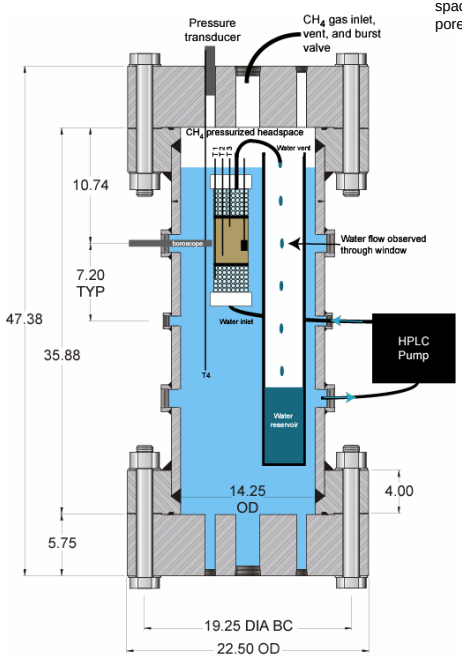
Methane Hydrate Nucleation Experiments

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		

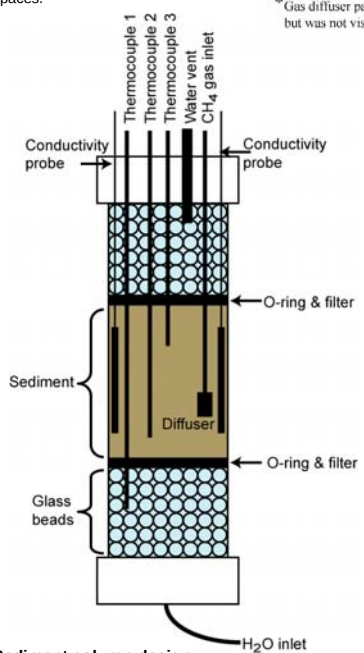
*Gas diffuser paced at base of column in the glass beads. Hydrate may have formed below the sediment within the glass beads, but was not visible in the sediment.



ORNL's 72-liter Seafloor Process Simulator (SPS)
The vessel is constructed of corrosion-resistant Hastelloy. Forty vessel ports and windows allow for characterization and monitoring of the sediment column *in situ*. The large experimental volume decreases the standard deviation observed in kinetic experiments as well as the overpressures required for hydrate formation (McCallum et al. 2006).



Flow-through sediment column experiments
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).



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.

Effects of free gas and methane saturated water flow on hydrate nucleation:

The effects of free gas and water flow were investigated in a series of sediment column experiments at 1500 psi (10.3 MPa) and temperatures between 275 and 278K. Temperature and conductivity data collected within the sediment did not show conclusive evidence of hydrate formation. Methane-saturated water flow alone did not result in visible hydrate deposits in any experiments to date. 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.

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.

References: McCallum, S.D, Riestenberg, D.E., Zatsepina O, and Phelps, T.J. (In Press). Mesoscale research of gas hydrates. *J. Petroleum Science and Eng.* (2006); Phelps, T. J., D. J. Peters, S. L. Marshall, V. Alexiades, G. K. Jacobs, J. G. Blencoe, M. T. Naney, J. L. Heck, and O. R. West (2001) A new experimental facility for investigating the formation and properties of gas hydrates under simulated seafloor conditions. *Review of Scientific Instruments* **72,** 1514-1521.

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