Characterization of Methane Gas Hydrate Bearing Sediments and Hydrate Dissociation Kinetics

Monthly Report for May 2002

Task 1: Diffusion Measurements

Quotes for a 500 MHz instrument with pulsed field gradient capabilities have been completed and the purchase is underway. Current estimated arrival time of the instrument is late June, early July, with expectation to be fully operational by mid to late July. In the interim, time has been scheduled (June 19-26) on the NMR in the Environmental Molecular Sciences Laboratory (EMSL) to begin initial studies with our new PFG-NMR probe.

Task 2: Flow and Transport Properties

High pressure capable columns were fabricated for gas permeability measurements versus hydrate loading. We plan to detect hydrate formation by its thermal signature (heat of formation) during cooling of the column. Verification of hydrate formation will be performed after completion of a permeability measurement. To test this hypothesis, we conducted an experiment with the columns filled with crushed glass of particle size -20 +40 mesh. Bulk porosity was determined at 46%. One column was fully saturated with water and the other with a 20 vol% solution of tetrahydrofuran. Sufficient fluid was then drained to achieve bulk fluid saturation of 70%. The columns were then immersed in a controlled temperature bath filled with a solution of propylene glycol and water at -11°C. Temperature was recorded as a function of time from a thermocouple embedded in the porous medium.

The resulting data are shown Figure 1. For the column filled with deionized water, crystallization of ice is clearly observable from the temperature rise after approximately 15 min of immersion in the bath. Complete conversion to ice required approximately 15 minutes, whereupon the temperature then begins to decrease and asymptotically approach the bath temperature. Note that a significant degree of subcooling was required before ice formed.

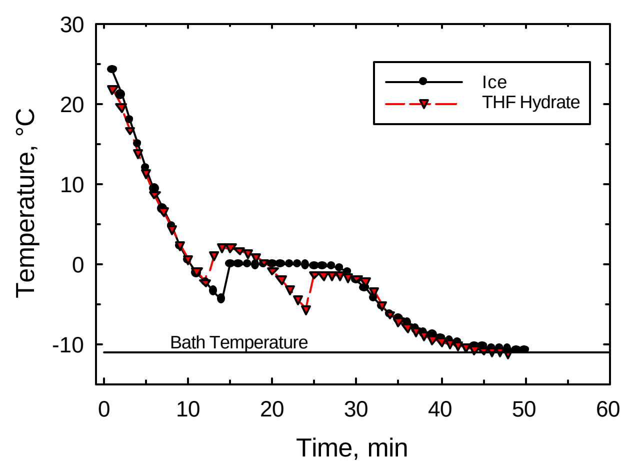


Figure 1. Time-Temperature Profile During Cooldown of Column Filled with Crushed Glass Porous Medium.

Tetrahydrofuran forms a sII hydrate with ideal composition of $C_4H_8O{\cdot}17H_2O$ at 4°C. Consequently, a solution with 23.6 wt% THF should convert completely to the hydrate form at 4°C. Our solution was made with 20 vol% THF, which is only a 17.7 wt% solution of THF. Consequently, complete conversion to THF hydrate would still leave some free water. Figure 1 shows two distinct thermal signatures for the THF solution. The first at about -1°C is almost certainly from formation of THF hydrate. The second temperature excursion begins at almost the same temperature (-5°C) as was observed for the pure water test. The second peak is almost certainly due to formation of water ice from the residual free water remaining in the column. These experiments clearly demonstrate the ability to identify hydrate and ice formation signatures in the columns as we begin to work with the hydrocarbon gases. Gas permeability measurements with these columns are currently in progress and preliminary data will be discussed next month.

We initiated work on a constitutive model for the effect of hydrate formation and dissociation on the hydraulic properties of porous media. Analytical formulations at the pore level and Darcy level are now underway. Pore-network modeling is being investigated as a tool for a realistic simulation of such phenomena and their scale-up from pore to Darcy scale.

Task 3: Hydrate Dissociation Kinetics

The ability to initiate and display spectra within LabVIEW was added to the control program for the Raman spectrometer. Reference spectra of the relevant gas, liquid, and hydrate species in the pressure cell are now being collected.

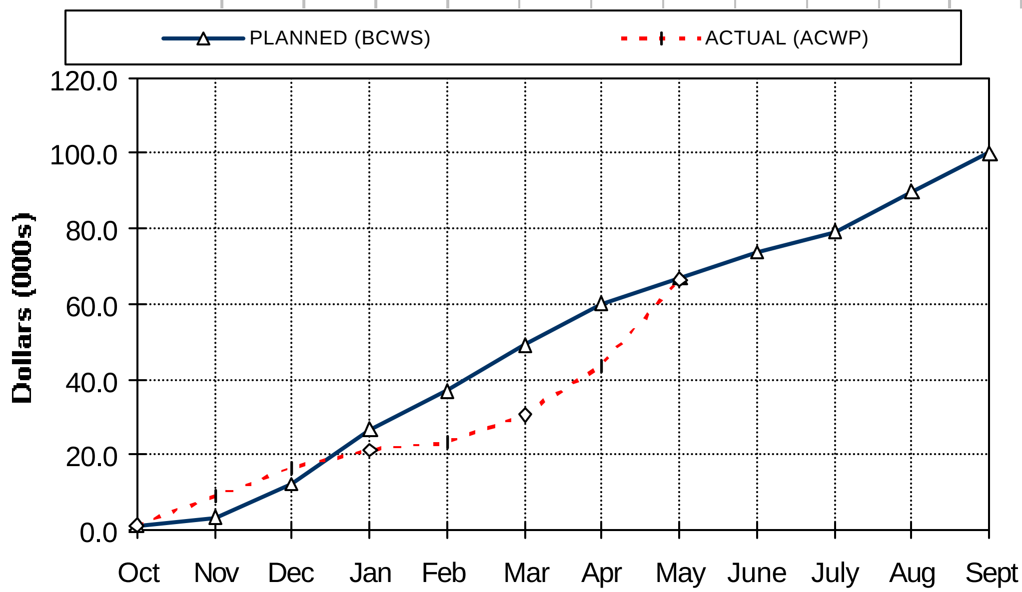
Significant Issues and Corrective Action

Milestone "High Pressure NMR Cell Design and Construction Complete" has been completed May 2002.

Milestone "Initial Hydrate Kinetics Dissociation Measurements Complete" is scheduled for completion in June 2002.

No significant cost variances to report this month.

(DOLLARS IN THOUSANDS)



($K)	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept	FY01
Planned Cost	1.3	2.0	9.2	14.2	10.1	12.2	11.2	6.8	6.9	5.5	10.7	9.9	100.0
Actual Cost	1.3	7.7	7.5	4.6	2.4	7.1	13.1	22.8					
Variance Cost	0.0	-5.7	1.7	9.6	7.7	5.1	-1.9	-16.0	6.9	5.5	10.7	9.9	
Cumulative Planned	1.3	3.3	12.5	26.7	36.8	49.0	60.2	67.0	73.9	79.4	90.1	100.0	100.0
Cumulative Actual	1.3	9.0	16.5	21.1	23.5	30.6	43.7	66.5					
Cumulative Variance	0.0	-5.7	-4.0	5.6	13.3	18.4	16.5	0.5					

Milestones	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	Jul	Aug	Sep	FY01
1) Construct PUF Reactor Test Cell Supp Appar and Data Acq Equip			☆										
2) Raman Tracer Scoping Exp to Ensure Uniform Water Content					△			☆					
3) High Pressure NMR Cell Design and Construction Complete						△		☆					
4) Initial Hydrate Kinetics Dissociation Measurements Complete									△				
5) NMR Measurements Complete												△	
6) Draft PNNL Report on Charact. of Hydrate Sediments and Hydrate Dissoc. Kinetics													
7) Final PNNL Report on Charact. of Hydrate Sediments and Hydrate Dissoc. Kinetics													
8) Monthly Reports to John Rogers (NETL)		☆	☆	☆	☆	☆	☆	☆	△	△	△	△	

LEGEND		
SCHEDULED △	DEVIATION □	COMPLETED ☆
TIME LINE ———	ELIMINATED BY REDUCTION	