Progress Report

PROPERTIES OF SEDIMENTS CONTAINING METHANE HYDRATE, WATER, AND GAS SUBJECTED TO CHANGING GAS COMPOSITIONS

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WORK PERFORMED UNDER

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SUBMITTED BY

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INTRODUCTION

The objective of this work is to measure physical, chemical, mechanical, and hydrologic property changes in sediments containing methane hydrate, water, and gas subjected to injection of carbon dioxide and nitrogen. Because the replacement of methane by carbon dioxide and nitrogen is thermodynamically favored in some cases, these gases are considered to enhance the extraction of methane from hydrate, and to simultaneously sequester carbon dioxide. DOE has participated in a field test in Alaska in which nitrogen and carbon dioxide were introduced into a reservoir containing methane hydrate, water, and gas, and then gas was extracted. Analysis and modeling of the data and processes observed are expected to be performed for some time resulting in questions that can be efficiently answered in the laboratory. We propose to make measurements that will support these investigations. We will share our results with those analyzing the field test, and the scientific community, and communicate with those analyzing the field test to ensure our tests are on target to answer their questions.

Studies performed to date have examined basic thermodynamic and methane hydrate structural changes upon introduction of other hydrate forming molecules showing that carbon dioxide tends to replace methane in large cages ideally resulting in about 64% methane replacement, and nitrogen replaces methane in small cages resulting in an additional 21% replacement. Few studies have been performed to examine changes to the physical, mechanical, and hydrological properties of hydrate-bearing sediments undergoing gas exchange. Laboratory tests examining methane replacement by mixed nitrogen/carbon dioxide in a porous medium containing methane hydrate, water, and methane gas have not yet been performed.

GENERAL STATEMENT

Our schedule has been impacted in the last quarter by personnel changes at the lab. We lost key personnel for two of our tasks, and one task directly affects the subsequent task.

CURRENT TASKS AND PROGRESS:

Task 5.0 Measurement of kinetics of gas exchange in a hydrate/water/gas system

Title:	Complete measurements of gas exchange and hydrologic properties of media containing methane hydrate, water, and gas subjected to N_2/CO_2 gas flooding.
Planned Date:	December 31, 2013
Verification Method:	Internal review and analysis of data set.

Progress:

To date, seventeen experimental runs of this gas exchange have been attempted, with perhaps eight being marginally successful at achieving our goal here. Compared to the water-free hydrate samples, in the replicates with water present, less methane was eluted from the sample and the exchange rates are on the order of a order of magnitude lower than the “dry” hydrate (with water present, on the order of $4x10^{-8}$ moles methane/(mole water*s), with no water present, on the order of $2x10^{-7}$ moles methane/(mole water*s) (Note that in these rates, the moles of water refers to water originally held in the hydrate.)

Technical challenges: These tests have been difficult to perform. To establish a three-phase environment (water, gas, hydrate) requires that the experimental conditions be on the equilibrium curve. Our pressures are typically at 538 psi after forming hydrate. To perform the gas flood with stable conditions requires a significantly higher pressure ~1400 psi. We have had difficulties with the transition. If we keep pure methane in the vessel, we will make hydrate and lose water. If we pressurize with the mixed gas, we still have excess methane in at least one third of the column, possibly forming hydrate. We have seen many tests with significant permeability changes. This may be from the residual methane in concentrated zones forming more hydrate on pressurization. This will be examined in Task 6.

Personnel challenges: In January, a key member of our team on this task left LBNL. Although the required skill set remains at the lab, the correct combination of time availability and skills has not been easy to assemble.

Task 6.0 Investigation of mechanical and hydrologic property changes of media containing methane hydrate, water, and gas subjected to nitrogen and CO2 flushing

Title:	Complete geophysical measurements of media containing methane hydrate, water, and gas subjected to N_2/CO_2 gas flooding.
Planned Date:	February 28, 2014
Verification Method:	Report containing description of tests, results, and interpretation.

Progress:
Selection of experimental parameters is based on the results of Task 5. This test has not begun. Discussions with Carolyn Koh (Colorado School of Mines, and an LBNL Affiliate) have identified a current CSM graduate student working on a similar problem. We are now working out details that would allow the student to participate in the experiment, to be conducted this summer.

Task 7.0 Grain-scale Computation of Hydrate-Bearing Sand Properties Based on microCT Sample Description (collaboration with NETL)

Title:	Obtain Finite Element Code and perform / demonstrate code usage.
Planned Date:	February December 31, 2013
Verification Method:	Internal review of preliminary results.

Progress:

Exploration of hydrate property alterations due to varying cementation motifs requires an approach for generation of random yet spatially realistic pore-scale volumes including the matrix, hydrate, and brine distribution. The actual pore-scale growth mechanisms of gas hydrates in a sand framework are still not well understood; 3 main conceptual models are typically used for describing hydrate distribution, linked closely to available analytical models,

1) **Pore Filling :** Nucleation starts in the center of the largest pores and the hydrates grow homogeneously from those nuclei, progressively filling the pore space starting from the bigger pores.
2) **Contact Cement :** Nucleation starts at grain contacts, and hydrates growth proceeds from the contacts of the grains outwards. This will result in a ring- shaped hydrate deposition between the grains, with subsequent coalescence while growing further.
3) **Surface Coating :** Nucleation starts on all the grain surfaces, then grows homogeneously towards the pore space: this provides a uniform coating of the sand grains with hydrates.

These three hydrate growth paradigms have been used to develop a simple computational protocol capable of providing a theoretical distribution of hydrates in an experimentally measured granular matrix, in this case a quartz sand pack imaged at the Synchrotron X-ray (SXR) microtomography beamline 8.3.2 at the Advanced Light Source (LBNL). Three slices show the measured sand pack (gray), pore space (~black), and the calculated hydrates (cyan):

1) 2) 3)

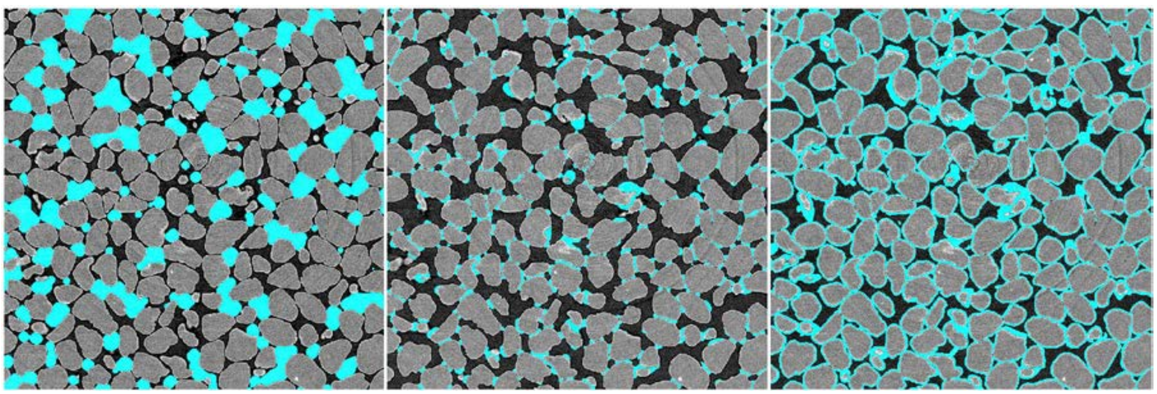

Figure 1 : 2D slices from microCT slices of a quartz sand pack with synthetic hydrate distributions showing pore-filling (1), contact cement (2), and grain coating (3) motifs.

The slices above (Figure 1) show the calculated volumes in 2D, for clarity, but the model provides 3D data appropriate for pore-scale modeling, and additional phenomenological features can be added. For example in the three volume renderings presented in Figure 2, we have added a "temperature gradient" with the bottom of the sample colder that the top therefore the growth of the hydrates is more pronounced at the bottom of the sample:

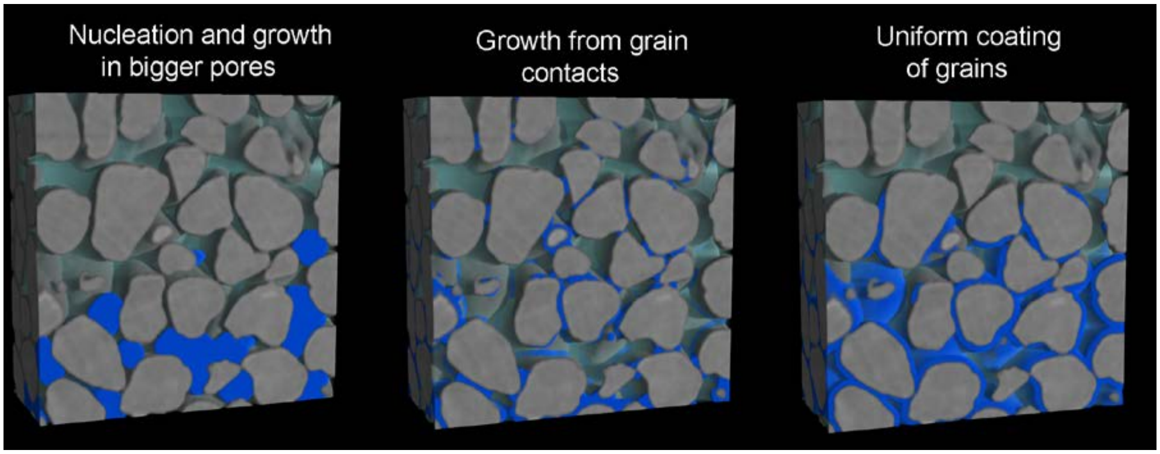

Figure 2 : The volume renderings above show sand grains in grey, water/brine in semi-transparent blue, and the modeled hydrates in dark blue. Each panel shows a different hydrate motif with the addition of a spatial gradient.

In the volume rendering above (Figure 2) we show the sand grains in grey, the water/brine in semi-transparent light blue, and the modeled hydrates in dark blue. The cold front is at the bottom. The hydrate distribution code starts with the porous matrix and then uses geometric operations utilizing on seed locations determined by the motif type e.g. centroid of the segmented pore (pore filling), grain surface, or contact locations determined by distance maps.

The protocols developed for modeling the theoretical distribution of gas hydrates using the three main concepts in real, measured, sand 3D volumes are completed and, as it is possible to see from the pictures above, work as expected. At present, the volume generation component of the project is completed and ready for incorporation into the pore-scale modeling tool chain.

Modeling : Code Selection and Testing

Three attributes are being targeted for modeling at present, they include permeability, diffusivity/formation factor, and elastic properties. During the past quarter, the permeability and diffusivity calculation codes were tested and are considered ready for the modeling study. The permeability code is based on a FD stokes simulation while the diffusivity code uses a random walk solver. The third code set, targeting elastic properties, is a finite element solver which is still being tested and should be ready for the hydrate forward modeling study in the next quarter.

Personnel challenges: In March, a key member of the team performing numerical modeling for this task left LBNL. Options are being considered. A researcher with a similar skillset has been hired, and is being brought up to speed on the project.

COST STATUS

Cost Plan/Status

		FY13				FY14			
Baseline Reporting Quarter		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Baseline Cost Plan									
Federal Share	Task 4				2	0	0	2	
	Task 5				17	9	9		
	Task 6					0	15	16	
	Task 7				20	10	10		
Non-FederalShare					0	0	0		
Total Planned Cost					39	19	34	18	
Federal and Non-Federal					39	19	34	18	
Cumulative Baseline Cost					39	58	92	110	
Actual Incurred Costs									
Federal Share	Task 4				2	0.5	0.5		
	Task 5				16	19	3.8		
	Task 6				0	0	0		
	Task 7				6	6.3	3.4		
Non-FederalShare					0	0	0		
Total Planned Cost					39	19	34		
Federal and Non-Federal					24	25.8	7.7		
Cumulative Incurred Cost					24	49.8	57.5		
Variance									
Federal Share	Task 4				0	-0.5	-0.5		
	Task 5				1	-10	5.2		
	Task 6				0	0	15		
	Task 7				14	3.7	6.6		
Non-FederalShare					0	0	0		
Total Planned Cost					0	0	0		
Federal and Non-Federal					15	-6.8	26.3		
Cumulative Variance					15	8.2	34.5		

Table 1. Cost plan and status for the project period to date.

DELIVERABLES STATUS

Include the following list of deliverables in the SOPO document:

Deliverable	Brief Description	Frequency/Schedule
Updated Project Management Plan	Provides an update of how the project will be executed, monitored, and controlled in meeting the programmatic goals and objectives. Includes a detailed discussion about risk identification, mitigation and management.	Due 30 days **after any major project modification**
Research Performance Progress Report	Provides a narrative assessment of the technical, milestone/schedule, and cost status of the research. Measures changes in schedule or completion status of the originally planned milestones (as set forth in the Project Management Plan) and their actual completion dates. Monitors actual costs against baseline costs provided in the Project Management Plan	On or before 30th day after each quarter
Annual Research Performance Progress Report	Full account of progress, problems encountered, significant accomplishments, and approaches to be taken the following year. Includes status of milestones/schedule and cost.	Within 60 days after end of project year
Final Technical Report	Full account of all work performed during the project period in a comprehensive manner.	Within 90 days after project ends
Topical Report (as needed)	Provide a comprehensive statement of the technical results of the work performed for a specific task or subtask or detail significant new scientific or technical advances.	Within 45 days of request
Topical Report	A report documenting the design and construction of a laboratory system allowing investigation of the kinetics of gas exchange (e.g. CO2 into methane hydrate) in hydrate-bearing sediments will be submitted.	July 31, 2012 Submitted
Topical Report	A report on the changes in hydrologic and geophysical properties of methane hydrate-bearing media subjected to nitrogen or CO2 gas flooding will be submitted.	October 31, 2012 Submitted
Topical Report	A report on the changes in hydrologic and geophysical properties of porous media containing methane hydrate, water, and gas and subjected to nitrogen or CO2 gas flooding will be submitted. See Tasks 5 and 6.	February 28, 2014 Work behind schedule due to personnel issues
Topical Report	A report documenting the results of our Grain-scale Computation of Hydrate-Bearing Sand Properties Based on microCT Sample Description (collaboration with NETL) will be submitted. See Task 7.	April 30, 2014 Work behind schedule due to personnel issues
Conference Papers/ Proceedings/ Articles	Documents include conference papers, proceedings, presentations, journal articles, and press releases.	Minimum of 7 business days prior to submission
Ad hoc photos/ illustrations/ data	Photos, illustrations, diagrams, and related research data that can be used by SCC-OCP for presentations and other program documentation	As requested