Oil & Natural Gas Technology

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Quarterly Report

July 2011 to September 2011

Gas Hydrate Characterization in the GoM using Marine EM Methods

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EXECUTIVE SUMMARY

Work continued on laboratory electrical conductivity measurements of several hydrate-sediment mixtures. A meeting was held at Lawrence Livermore National Laboratories (LLNL) on Sept 29, 2011 to discuss current results from the project; determine the continuation of the project and future funding opportunities. All milestones set out for the conductivity cell have been completed. The remaining time will be spent writing up the laboratory results in a long paper with enough detail so that the project can be picked up in the future. Navigation was finalised for all surveys, 2D forward modeling commenced, and general comparisons were made between pseudosections and seismic data at GC 955.

PROGRESS, RESULTS, AND DISCUSSION

Phase 1.

Task 1.0: Project Management Plan.

Completed November 5, 2008.

Task 2.0: Technology Status Assessment.

This is embodied in the original proposal.

Task 3.0: Collect Marine CSEM Field Data.

Completed October 26, 2008.

Task 4.0: Preliminary Field Data Interpretation.

Completed October 2009.

Task 5.0: Design and Build Conductivity Cell.

Completed July 2010, results presented in Year 2, Quarterly Report 3.

Phase 2.

Task 6.0: Make Hydrate and Hydrate/Sediment Conductivity Measurement.

During this quarter we measured the electrical conductivity impedance spectra for three additional hydrate-sediment mixtures: Run 8, a 53:47 vol% hydrate and OK#1 sand mixture; Run 9, a 53:47 vol% OK#1 hydrate and bead mixture; and Run 10, a 10:90 vol% hydrate and OK#1 sand mixture. Cryogenic scanning electron microscopy (cryo-SEM) images were made to assess the sample characteristics and composition, to document grain characteristics and phase distributions, and to understand the pore structures of: (1) the ice after dissociation from hydrate for Runs 5, 6, 7, 8 and 10; and of the hydrate for Run 9. Table 1 summarized all of the samples that were made within the cell.

Table 1: Summary of samples created within the hydrate cell

Run	Sample	SEM	notes
1	100 vol% H_2O	hydrate	Thermal couple
2	100 vol% H_2O	-	impedance spectra
3	100 vol% H_2O	-	impedance spectra

4	53:47 vol% hydrate:sand	hydrate	impedance spectra
5	90:10 vol% hydrate:sand	ice	impedance spectra
6	70:30 vol% hydrate:sand	ice	impedance spectra
7	53:47 vol% hydrate:beads	hydrate	impedance spectra
8	53:47 vol% hydrate:sand	ice	impedance spectra
9	53:47 vol% hydrate:beads	hydrate	impedance spectra
10	10:90 vol% hydrate:sand	ice	mpedance spectra

The previous quarterly reports discussed the Arrhenius plots for Runs 1 to 7. Run 7 the 53:47 vol% hydrate:glass bead sample melted during loading which may have incorporated impurities. The run (7) also leaked methane, and left the hydrate stability field so we repeated the experiment in Run 9 paying careful attention to the loading of the cell, and obtained more reliable results. Figure 1 compares cryo-SEM images of the remaining ice from Run 7 and of the hydrate from Run 9.

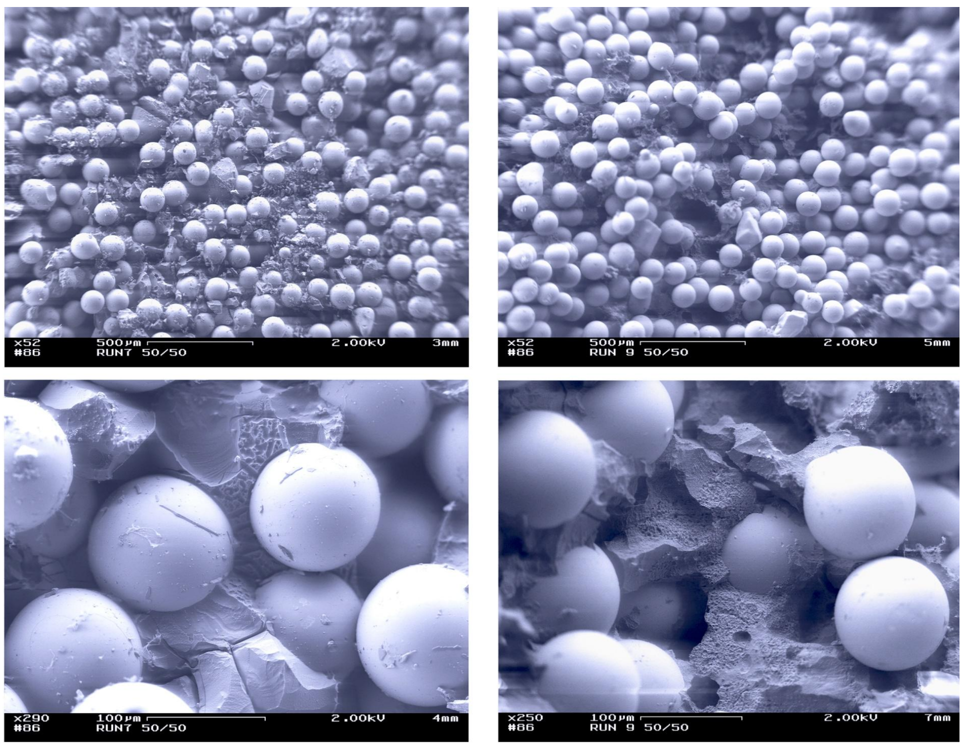

Figure 1: Low and high magnification images of Run 7 (50/50 ice + glass beads; left column) and Run 9 (50/50 ice + methane hydrate, right column.) Rapid sublimation of methane hydrate results in the appearance of a higher percentage of beads in the upper right image and in the pitted/spongy surface topology displayed in the lower right image.

Figure 2 shows cryo-SEM images of 50:50 hydrate:sand for Run 4 as hydrate and for Run 8 as dissociated ice, as well as Run 6 (70:30 ice:sand). The ice grains anneal after dissociation, but there is no significant migration of the sand grains during dissociation. There is a higher porosity in the Run 8 cryo-SEM image because of the volume reduction to the H2O phase.

Figure 3 shows cryo-SEM images of dissociated ice for two end members of 90% hydrate to 10% sand (Run 5) and 10% hydrate to 90% sand (Run 10) where we observe similar grain contacts and in Run 10 we notice the presence of connecting ice.

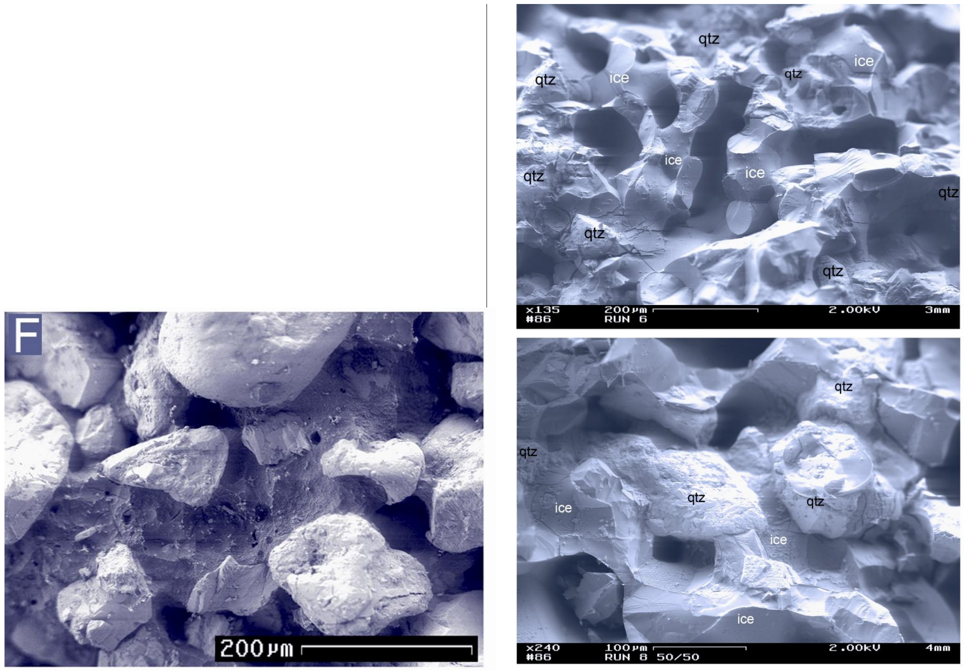

Figure 2: Run 4 50:50 hydrate:sand and Run 6 (70:30 ice:sand, top image) and Run 8 (50:50 ice:sand, bottom image) also displayed uniform mixing of phases. In both cases close examination of the ice phase showed essentially no hydrate remaining in the samples.

A summary of Arrhenius plots is shown for hydrate/sediment hydrate mixtures and the dissociated ice phase in Figure 4. The conductivity measurements of pure CH4 hydrate are shown in blue and range between 10^{-5} to 10^{-4} S/m. After dissociation to ice both conductivity and activation energy increased. The conductivity of CH4 hydrate is less than seawater (10^{-1} to 10^{1} S/m) and greater than quartz (< 10^{-18} S/m). In determining the conductivity of mixtures the cyro-SEM images allow us to consider the connectivity, angularity, and vol% of multiphase assemblages, however, we also need to consider the chemical interaction between hydrate and sediments.

To evaluate the effects of sediments we measured the conductivity of CH4 hydrate mixed with either sand (OK#1) or glass beads. We immediately noticed that samples containing both hydrate and sand had higher conductivity than unmixed samples, which is counterintuitive considering that the quartz sand by itself is highly resistive. Increased concentrations of sand up to 47 vol% resulted in increased conductivity and decreased activation energy (Ea) (green, purple, yellow, orange). Sand resulted in similar increase in the conductivity of samples with dissociated ice. The run with 10vol% hydrate and 90vol% sand (red) exceeded the percolation threshold (i.e. poorly connected hydrate) causing a dramatic decrease in conductivity magnitude, indicating that the majority of electrical current conducts through the hydrate/ice phases. Fine particles on the weathered surfaces of the sand likely increased the concentrations of impurities and charge carriers in the surfaces of hydrate/ice grains leading to increased surface conductivity. To evaluate this mechanism further we performed a run mixed with 53vol% hydrate and 47vol% glass beads (shown in pink). The synthetic glass beads are significantly less weathered and have higher purity than the natural quartz sand, and hence we observed a less pronounced surface conductivity contribution. A full report of results to-date is currently being prepared and a brief article will appear in the NETL Fire in the Ice Newsletter.

We have successfully determined the electrical conductivity of single-phase methane hydrate and have revealed general trends in the comparison of ice/sediment mixtures to hydrate/sediment mixtures. Greater investigation is required to fully understand the contributions of chemical impurities, surface conductivity,

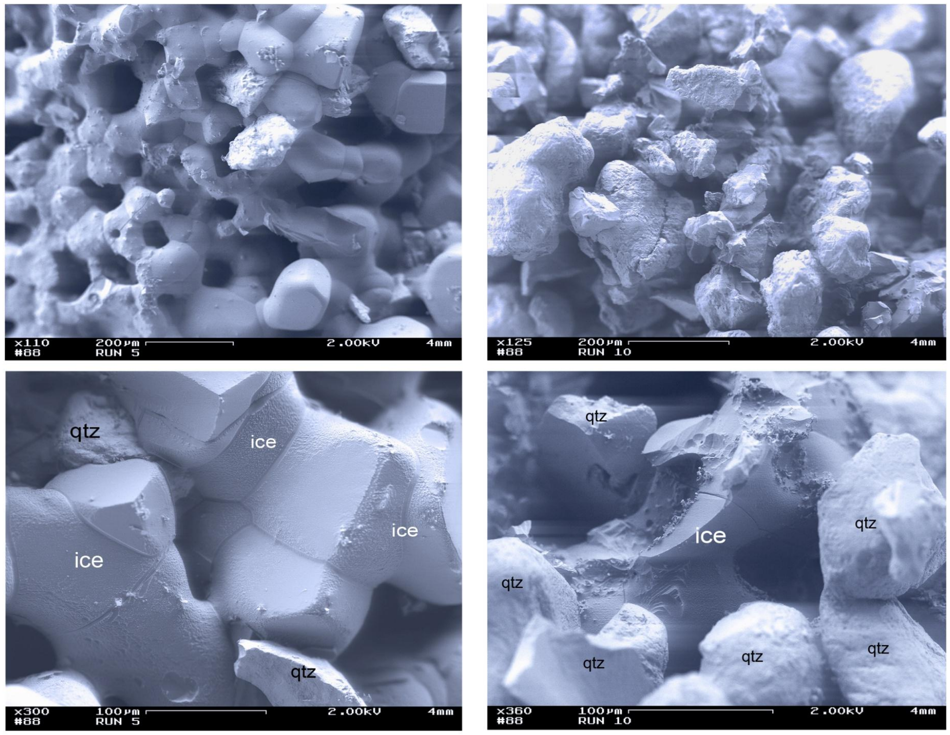

Figure 3: Comparison of Run 5 (90:10 ice:sand, left column) to Run 10 (90/10 sand:ice, right column), after full dissociation of methane hydrate back to ice. SEM imaging shows relatively equal distribution of the phases throughout both samples (i.e. very little clumping). Samples dissociated for over a week at -3° C, resulting in annealing of the ice phase after dissociation. The excess pore space in Run 5 is partly due to the volume reduction of the H2O phase that accompanies dissociation to ice (14%).

sediment surface angularity, and porosity and permeability issues and how these various mechanisms compete.

Task 7.0: Modeling and Inversion of Field Data. Initial 2D forward modeling has commenced and some general comparisons have been made with CSEM pseudosections and to the seismic data available at GC 955.

Task 8.0: Estimate Quantitative Hydrate Volumes from Field Models and Laboratory Studies. Part of this task was completed in the Year 2 Final Report.

Task 9.0: Technology Transfer. The data have been distributed to the sponsors (February, 2009) and preliminary results have been presented at the Seafloor Electromagnetics Consortium annual meetings in 2009, 2010 and 2011. Version 1.0 of the transmitter navigation was distributed to sponsors in early December 2009. Processed data were distributed to sponsors at the end of March 2010. We have undertaken a project to further develop the Vulcan technique with an industry partner. We have also started a collaboration with Carolyn Ruppel to develop a similar system to be used to map permafrost in the Beaufort sea.

Phase 3.

Task 10.0: Final Publication. Several manuscripts are in preparation. A paper on the laboratory work was published this June in *Geophysical Research Letters* .

CONCLUSION. We have made several laboratory electrical conductivity measurements on gas hydrate

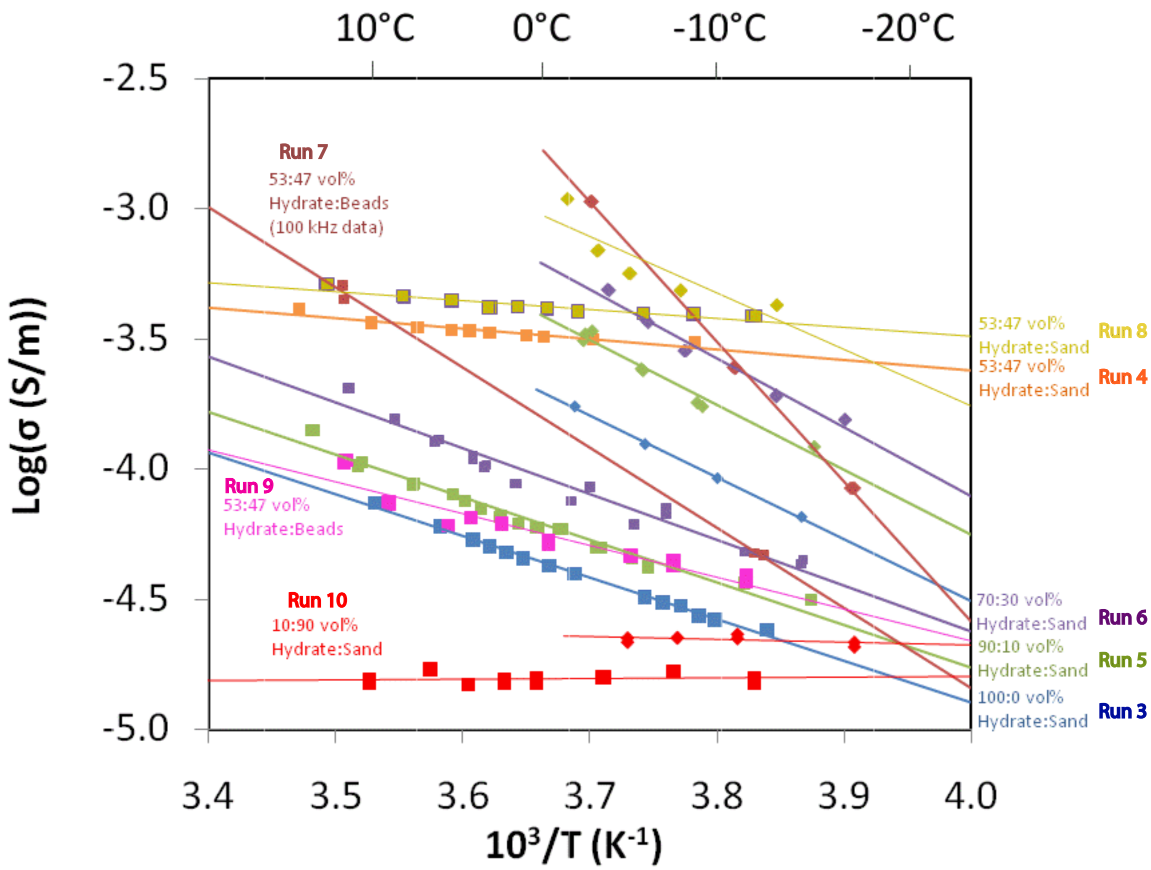

Figure 4: Summary of Arrhenius plots for all hydrate and sediment hydrate mixtures.

sediment mixtures. Publication of the work is on track. We received an oral slot at the 2011 Fall AGU meeting.

MILESTONE STATUS

Milestone log for Budget Period 3.

Milestone 22 Fall AGU abstracts submitted. Task 9.0,10.0 Submitted a 2011 Fall AGU abstract, August 2011.

Milestone 23 Papers submitted for publication Task 10.0, in progress.

Milestone 24 Industry workshop to be held Task 9.0, to be completed later this budget period.

Milestone 25 Papers revised in final form Task 10.0, scheduled for later this year. One paper has been published.

Milestone 26 Web page updated Task 9.0, scheduled for later this budget period.

Milestone 27 Produced Phase 3 report Task 9,10 to be completed later this budget period.

ACCOMPLISHMENTS

• Collection of the Marine CSEM Field Data

• Conductivity cell completed.

• Processing of the data is completed.

• Raw data and processed data have been distributed to sponsors (2009, 2010).

• Generated merged transmitter navigation with the CSEM data using the Total field navigation program and distributed this version to the sponsors in early December 2009 and March 2010.

• Generated pseudosections for the 0.5 Hz and 6.5 Hz CSEM data transmissions for all 14 tows of the 4 surveyed areas in the Gulf of Mexico 2010.

• Generated pseudosections for Vulcan at MC 118, GC 955, AC 818, and WR 313 and preliminary interpretations of the data, 2010.

• Completed calibration tests of cell using water standard.

• Installed the cell in Menlo Park, formed hydrate in the cell and produced SEM images of this sample.

• Made three hydrate samples in the cell and have measured activation energies and produced Arrhenius plots.

• Made several hydrate sediment mixtures and measured activation energies and produced Arrhenius plots.

PROBLEMS OR DELAYS Determining the navigational parameters for the transmitter have taken longer then anticipated and at this stage the navigational parameters are as good as is possible.

PRODUCTS

• Revised Project Management Plan.

• A project website was set up:

http://marineemlab.ucsd.edu/Projects/GoMHydrate/index.html

Cruise Report is available for download.

• Project Summary:

project summary outlining project goals and objectives on the NETL project Web site.

• Collection of Marine CSEM data in the Gulf of Mexico:

Data distributed to sponsors early February.

• NETL kick off meeting, Morgantown, WV - January 6, 2009

The PI delivered a project overview presentation.

• Fire in the Ice article published in 2009.

• Participated in a "Spot Light on Research" article for Fire in the Ice in 2009.

• Talk given at the 2009 MARELEC Meeting - Stockholm, Sweden - July 7-9 2009

Steve Constable presented *Applying marine EM methods to gas hydrate mapping*

•Steve Constable gave an invited talk at LLNL mid march 2009 called:

Marine Electromagnetic Methods for Mapping Gas Hydrate

• SIO Seafloor Electromagnetics Consortium annual meeting, La Jolla, CA - March 18-19, 2009

Karen Weitemeyer delivered two presentations:

Marine EM for gas hydrate studies, with first results from the Gulf of Mexico

Using Near field data to navigate controlled source electromagnetic data

• Karen Weitemeyer gave two invited talks in Australia

Marine EM for gas hydrate studies, with first results from the Gulf of Mexico

Steven Constable delivered a presentation in Japan:

Marine Electromagnetic Methods for Mapping Gas Hydrate

• Submitted the Phase 1 report October 2009.

• AGU Poster presentation December 2009 by Karen Weitemeyer and Steven Constable

Marine EM for gas hydrate studies, with first results from the Gulf of Mexico

• DoE Atlanta Hydrate Meeting January 25-29, 2010. A talk and Poster presented by KW and SC

Applying Marine EM Methods the Gas Hydrate Mapping

• Fire in the Ice article published March 2010.

Test of a new marine EM survey method at Mississippi Canyon 118, Gulf of Mexico

• SIO Seafloor Electromagnetics Consortium annual meeting, La Jolla, CA - March 17-18, 2010

Karen Weitemeyer and Steven Constable delivered a presentation:

Results from the GoM gas hydrate studies

• Processed data distributed to sponsors late March, 2010 and early April, 2010.

• First Break Article published this June (2010).

Mapping shallow geology and gas hydrate with marine CSEM surveys

• Attended the 20th Electromagnetic Induction Workshop in Giza, Egypt September 18-25, 2010, and presented a poster.

Mapping gas hydrates and shallow sedimentary structure in the Gulf of Mexico using marine CSEM

• Geophysics paper published this Fall (2010).

• SIO Seafloor Electromagnetics Consortium annual meeting, La Jolla, CA - March 9-10, 2011

Karen Weitemeyer delivered a presentation:

Updates on marine CSEM for hydrate mapping

• *submitted Phase 2 Report May 1 2011.*

• *Oral presentation at the 2011 MARELEC Meeting - San Diego, USA - June 20-23 2011*

• Geophysical Research Letters paper published this June (2011). Electrical Properties of Pure, Polycrystalline Methane Hydrate Wyatt L. Du Frane, Laura A. Stern, Karen A. Weitemeyer, Steven C. Constable, John C. Pinkston, Jeffrey J. Roberts

• Two abstracts to the 7th International Conference on Gas Hydrates (ICGH7), were presented in July 2011.

a poster by Du Frane, Stern, Weitemeyer, Constable, Pinkston, Roberts, on

Electrical resistivity of laboratory-synthesized methane hydrate

The second by Weitemeyer and Constable on

The development of marine electromagnetic methods for gas hydrate mapping

• *Geophysics Journal International* paper published (2011): 'A marine electromagnetic survey to detect gas hydrate at Hydrate Ridge, Oregon.' by Weitemeyer, Constable and Tréhu

• 2011 Fall AGU abstract submitted: 'Electrical properties of methane hydrate + sediment mixtures'. by Du Frane, Stern, Weitemeyer, Constable, Roberts

• Fire in the Ice article submitted for November 2011.

Electrical properties of methane hydrate (+sediment) by Du Frane, Stern, Weitemeyer, Constable, Roberts

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