U.S. Department of Energy
National Energy Technology Laboratory

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Fate of Methane Emitted from Dissociating Marine Hydrates: Modeling, Laboratory, and Field Constraints

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1 Executive summary

Work during this period focused on the following tasks:

- Task 1.0: Project Management, Planning and Reporting
- Subtask 2.1: Phase-field modeling of a static gas bubble
- Subtask 3.1: Laboratory experiments — flow-loop design, fabrication and construction
- Subtask 4.1: Quantitative analysis of newly-discovered US Atlantic margin methane plumes

2 Accomplishments

2.1 Major goals and objectives of the project

The overall goals of this research are: (1) to determine the physical fate of single and multiple methane bubbles emitted to the water column by dissociating gas hydrates at seep sites deep within the hydrate stability zone or at the updip limit of gas hydrate stability, and (2) to quantitatively link theoretical and laboratory findings on methane transport to the analysis of real-world field-scale methane plume data placed within the context of the degrading methane hydrate province on the US Atlantic margin.

The project is arranged to advance on three interrelated fronts (numerical modeling, laboratory experiments, and analysis of field-based plume data) simultaneously. The fundamental objectives of each component are the following:

1. Numerical modeling: Constraining the conditions under which rising bubbles become armored with hydrate, the impact of hydrate armoring on the eventual fate of a bubbles methane, and the role of multiple bubble interactions in survival of methane plumes to very shallow depths in the water column.

2. Laboratory experiments: Exploring the parameter space (e.g., bubble size, gas saturation in the liquid phase, "proximity" to the stability boundary) for formation of a hydrate shell around a free bubble in water, the rise rate of such bubbles, and the bubbles acoustic characteristics using field-scale frequencies.

3. Field component: Extending the results of numerical modeling and laboratory experiments to the field-scale using brand new, existing, public-domain, state-of-the-art real world data on US Atlantic margin methane seeps, without acquiring new field data in the course of this particular project. This component will quantitatively analyze data on Atlantic margin methane plumes and place those new plumes and their corresponding seeps within the context of gas hydrate degradation processes on this margin.

2.2 Accomplishments in this reporting period

Work during this period focused on the following tasks:

- Task 1.0: Project Management, Planning and Reporting
- Subtask 2.1: Phase-field modeling of a static gas bubble
- Subtask 3.1: Laboratory experiments — flow-loop design, fabrication and construction
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A detailed Milestones Status Report is included as Appendix 1.

Task 3.0: Laboratory experiments on hydrate armoring, rise rate, and gas loss from ascending bubbles

Subtask 3.1: Flow-loop design, fabrication and construction

Introduction. The USGS is constructing a high-pressure flow loop designed to "capture" gas bubbles for subsequent visual and acoustic imaging studies as well as bubble evolution and rise-rate measurements. The apparatus must be able to operate at pressures high enough for the gas to form hydrate. Xenon was chosen for the hydrate-forming gas, meaning hydrate can be formed at ~1.3 MPa (190 psi) at room temperature (21°C, 70°F), and at lower pressures when the system is cooled [*Ohgaki et al.*, 2000].

Design Summary. A key requirement for the bubble-capture chamber described by *Maini & Bishnoi* [1981] is establishing a low-fluid-velocity "well" along the vertical axis of the cone (see also figure 3 in *Warzinski et al*. [2008]). During a one-day meeting at the University of New Hampshire (UNH), the variable-length straw approach favored by *Maini & Bishnoi* [1981] and *Warzinski et al*. [2008] was demonstrated in the UNH low-pressure bubble capture system. Several additional fluid-flow-regulating designs were considered for additional testing to increase the velocity contrast, or "depth" of the low-velocity well in the capture zone. The more dramatically the downward fluid-flow velocity increases with radius in the capture cone, the more axially-confined the captured bubble will be. This axial confinement enhances the bubble's accessibility for acoustic testing, enhances video records of the bubble's evolution, and prevents contamination or hydrate nucleation due to contact with the chamber walls.

Fabrication Activities.

Bubble-capture chamber:

- The stainless-steel load frame and chamber support pieces for the optically-clear pressure housing and capture cone have been machined and assembled.
- Stainless steel pieces designed to mate with the optically clear chambers and provide pressure seals for the flow loop are being machined.

Water circulation through the flow loop:

- A high-pressure pump capable of delivering the high flow rates necessary to counter the rise rate of a gas bubble has been delivered, mounted, and connected to a three-phase, variable-frequency drive.
- Building modifications necessary to supply the power required by the water-circulation pump have been completed. The three-phase-transformer required for the water-circulation pump has been installed.
- A high-pressure flow meter suitable for our expected flow rates has been delivered.

References.

Maini, B. B., and P. R. Bishnoi (1981), Experimental investigation of hydrate formation behaviour of a natural gas bubble in a simulated deep sea environment, Chemical Engineering Science, 36, 183-189.

Ohgaki, K., T. Sugahara, M. Suzuki, and H. Jindai (2000), Phase behavior of xenon hydrate system, Fluid Phase Equilibria, 175(1-2), 1-6.
Warzinski, R. P., D. E. Riestenberg, J. Gabitto, I. V. Haljasmaa, R. J. Lynn, and C. Tsouris (2008), Formation and behavior of composite CO2 hydrate particles in a high-pressure water tunnel facility, Chemical Engineering Science, 63(12), 3235-3248.

Task 4.0: Field data analysis to link models and laboratory data to real world gas hydrate dynamics.

Subtask 4.1: Quantitative analysis of newly-discovered US Atlantic margin methane plumes

Raw split-beam echosounder (SBES) and multibeam echosounder (MBES) acoustic data collected by the NOAA Ship *Okeanos Explorer* over several hundred seeps of free gas on the US Atlantic margin [Ruppel et al., in press] is currently being QA/QC'd and processed to extract metrics that are relevant to the evolution and fate of the gas bubbles as they rise. Approximately 70 of the seeps observed within this dataset were simultaneously observed with the SBES, and both the MBES and SBES have undergone an initial analysis to examine the height and least-depth of each seep within this subset (Figure 1). It is important to note that some of the seep-height observations cease because the bubbles have exited the SBES/MBES field of view. Within the ~70-seep data set, about half originate in depths greater than the top of the water column gas hydrate stability zone (WC-GHSZ), with the other half originating in water depths significantly shallower than the WC-GHSZ. The SBES data are currently being processed to extract profiles of their acoustic scattering strength. For seeps that are considered discrete (small compared to the beamwidth), the seeps are extended along the direction of the beam but are constrained horizontally. Accordingly, these data are being normalized in the vertical (or z) direction, and profiles of the acoustic scattering strength per unit depth, S_z, are being extracted from the SBES data (Figure 2). The shape of these profiles (i.e., how S_z changes with depth) will later be used to help constrain/ground-truth models for the fate and evolution of the rising free gas within these seeps.

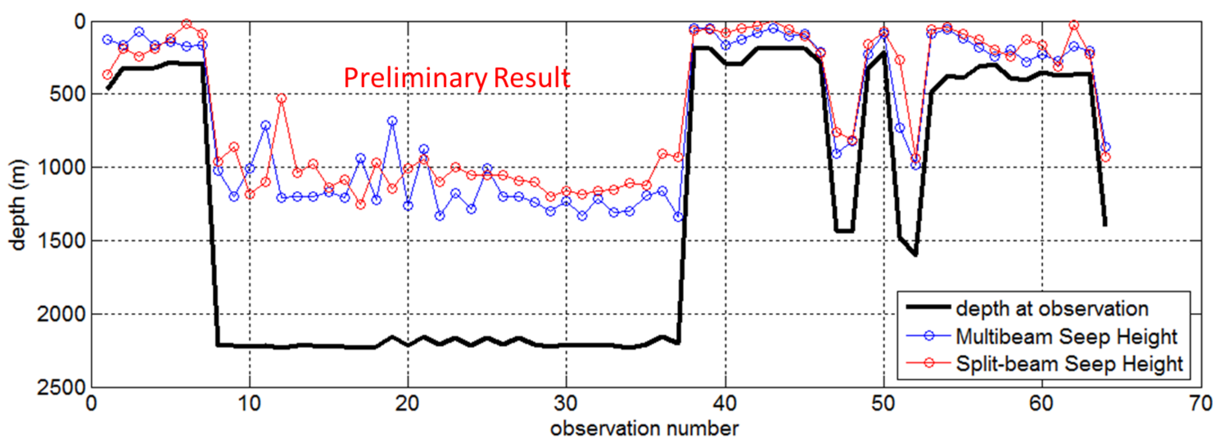

Figure 1. Minimum observed depth of seeps of free gas simultaneously observed with the MBES (blue) and SBES (red). The water depth at the observation is shown as the black line.

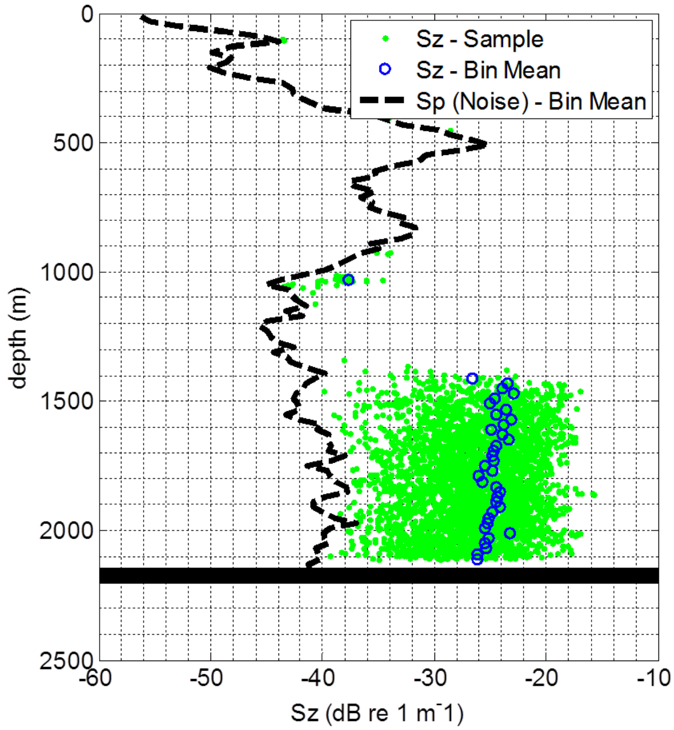

Figure 2. An example profile of the acoustic scattering strength per unit depth, S_z, for a seep observed in deep water on the US Atlantic margin. In this case, the seep exhibits a very high signal-to-noise ratio but rises outside the beam footprint, and is no longer observable, above a water depth of approximately 1400 m.

Subtask 4.2 Place US Atlantic margin seeps in regional and global context of gas hydrate system dynamics.

Progress on this task during the reporting period focused on starting a compilation of known global upper slope seep systems and on tracking down alternate measures of bottom water temperature fluctuations on the Atlantic margin. We also undertook preparations for an early July 2014 cruise of opportunity on the US Atlantic margin.

The newly-discovered pervasive seepage on the northern US Atlantic margin hints that many more such seeps may exist, but remain undiscovered, in upper slope settings worldwide. As noted by earlier publications (e.g., Ruppel, Nature Knowledge, 2011), upper slope gas hydrate degradation should be a global phenomenon, not merely an Arctic one, as intermediate waters warm. While many such upper slope areas have never been surveyed with tools appropriate for the identification of seeps, other locations have not been properly analyzed in terms of the genetic link between seepage and other processes. Where data do exist, upper slope seepage does seem widespread, but not evenly distributed. The seepage seems to be correlated with areas of known downslope gas hydrate occurrences, but this observation is preliminary.

The original bottom water temperature (BWT) database compiled for this project relied on a set of 35,000 CTDs culled from a far more complete database that had been acquired on the US Atlantic margin over several decades. Only CTDs that provided site-specific constraints on BWT were used in the our Atlantic margin database. Having looked at a range of XBTs collected on this margin and had concerns about the reliability of some of the data, we having started looking at other potential BWT sources, particularly for the upper slope. Records from submersible dives have proved unavailable or too sparse. To date, the most useful records we have found are not available in digital form and will require significant work to digitize. If no other sources are found, we will build a BWT database supplement with these measurements by typing them in from analog records.

During the performance period, we also undertook preparations for a short cruise of opportunity funded by NSF on the R/V Endeavor for early July 2014. This cruise will visit Hudson Canyon, where 50 seeps were discovered for the first time by Skarke et al. (Fall AGU Meeting, 2013). Weber and Ruppel both have berths on this cruise, and they will oversee the acquisition of split-beam water column data and subbottom profiling data in the areas of gas seepage. In addition, the cruise will acquire new CTDs, which should closely constrain BWT variations in the canyon's thalweg over the seep sites.

2.3 Opportunities for training and professional development

The project has offered opportunities for training of our graduate students Christos Nicolaides (MIT) and Xiaojing Fu (MIT). Graduate student Liam Pillsbury at UNH has also joined the project.

2.4 Dissemination of results to communities of interest

Several PIs and graduate students participated in the Gordon Research Conference on Natural Gas Hydrate Systems, held in March 23-28, 2014, in Galveston, TX. PI Ruppel gave one of the keynote talks, titled "Investigating climate-sensitive marine gas hydrates to evaluate late Pleistocene to contemporary climate change".

2.5 Plans for the next reporting period

The project is progressing according to the anticipated plan. In the next reporting period we will continue to work on the following tasks:

- Subtask 2.1: Phase-field modeling of a static gas bubble
- Subtask 3.1: Laboratory experiments — flow-loop design, fabrication and construction
- Subtask 4.1: Quantitative analysis of newly-discovered US Atlantic margin methane plumes

3 Products

3.1 Journal publications, conference papers, and presentations

3.1.1 Journal publications

- L. Cueto-Felgueroso and R. Juanes. A phase-field model of two-phase Hele-Shaw flow. *J. Fluid Mech.*, 2014. Submitted for publication.

- Weber, T., Mayer, L., Jerram, K., Beaudoin, J., Rzhanov, Y. and Lovalvo, D., 2014. Acoustic estimates of methane gas flux from the seabed in a 6000 km2 region in the Northern Gulf of Mexico. *G-cubed*, 2014. Submitted for publication.

3.1.2 Conference papers

Nothing to report.

3.1.3 Presentations

- Skarke, A., Ruppel, C.D., Kodis, M., Lobecker, E., and Malik, M., 2013, Geologic significance of newly-discovered methane seeps on the Northern US Atlantic Margin, EOS Trans. Amer. Geophys. Union, Fall Meeting, OS21A-1613.

- Kodis, M., Skarke, A.D., Ruppel, C.D., Weber, T., Lobecker, E., and Malik, M., 2013, US Atlantic Margin methane plumes identified from water column backscatter data acquired by NOAA ship Okeanos Explorer, EOS Trans. Amer. Geophys. Union, Fall Meeting, OS21A-1612

- Ruppel, C.D., 2014, Investigating climate-sensitive marine gas hydrates to evaluate late pleistocene to contemporary climate change, Invited lecture, Gordon Research Conference on Natural Gas Hydrate Systems, Galveston, TX.

3.2 Website(s) or other Internet site(s)

Nothing to report.

3.3 Technologies or techniques

Nothing to report.

3.4 Inventions, patent applications, and/or licenses

Nothing to report.

3.5 Other products

(such as data or databases, physical collections, audio or video products, software or NetWare, models, educational aids or curricula, instruments, or equipment)

Nothing to report.

4 Participants and collaborating organizations

4.1 Individuals working on the Project

- Name: Ruben Juanes
  Project Role: Principal Investigator / Project Director
  Nearest person month worked: 1
  Contribution to Project: Ruben Juanes, as project director, is responsible for overall coordination of the effort and for the technology transfer activities, including progress and topical reports, and project review presentations. He takes the lead in the modeling and simulation of hydrate formation and dissociation in rising methane bubbles (Task 2.0), and advises the MIT graduate student responsible for doing the modeling. He also serves as primary advisor to the MIT student who conducts the laboratory experiments of bubble rise and hydrate formation with analogue multiphase fluids (Task 3.0), in collaboration with Waite (USGS).
  Funding Support: MIT academic-year salary / DOE summer salary
  Collaborated with individual in foreign country: No
  Country(ies) of foreign collaborator: Not applicable
  Travelled to foreign country: Not applicable
  Duration of stay in foreign country(ies): Not applicable

- Name: Thomas Weber
  Project Role: Co-Principal Investigator
  Nearest person month worked: 1
  Contribution to Project: Thomas Weber leads the field component of the project (Task 4.0), particularly the quantitative analysis of existing public domain data for northeast Atlantic margin bubble plumes. He also advises a graduate student at UNH. Weber also assists with the acoustics aspects of the laboratory experiments (Task 3.0), both in design of the acoustic component and the interpretation of the resulting data.
  Funding Support: MIT academic-year salary / DOE summer salary
  Collaborated with individual in foreign country: No
  Country(ies) of foreign collaborator: Not applicable
  Travelled to foreign country: Not applicable
  Duration of stay in foreign country(ies): Not applicable

- Name: Carolyn Ruppel
  Project Role: Co-Principal Investigator
  Nearest person month worked: 1
  Contribution to Project: Carolyn Ruppel has responsibility for keeping the project grounded in natural gas hydrates systems and in the issues of greatest relevance for the US gas hydrates research community, particularly the part of the community focused on the environmental impact of methane emissions from gas hydrate deposits. She is also responsible for ensuring that appropriate resources (salary support) are allocated to herself, Waite, and the USGS engineers supporting this project and interacts frequently with Juanes and his students at MIT, where she maintains a second office. She is also responsible for regional analysis and integration of observational data related to

hydrate-derived seeps and plumes on the U.S. Atlantic margin and for linking the newly emerging observational data to other existing data sets (e.g., BOEMs gas hydrates assessment of the Atlantic margin) in this area and in other areas worldwide (Task 4.0).
Funding Support: USGS salary
Collaborated with individual in foreign country: No
Country(ies) of foreign collaborator: Not applicable
Travelled to foreign country: Not applicable
Duration of stay in foreign country(ies): Not applicable

- Name: William Waite
  Project Role: Co-Principal Investigator
  Nearest person month worked: 1
  Contribution to Project: William Waite leads the lab component of the project (Task 3.0) and has primary responsibility for design and construction oversight of the xenon hydrate lab apparatus. He interacts with the USGS engineers, visits UNH to see existing devices at Webers lab, and meets with MIT staff to understand the parameters for the cell installation at MIT. After completion of the testing phase of the laboratory work at the USGS, Waite is responsible for moving the apparatus to MIT. Waite takes on primary responsibility for developing the collaboration among MIT, UNH, and the USGS for the multifaceted lab experiments and working directly with the MIT graduate student on the experiments at MIT.
  Funding Support: USGS salary
  Collaborated with individual in foreign country: No
  Country(ies) of foreign collaborator: Not applicable
  Travelled to foreign country: Not applicable
  Duration of stay in foreign country(ies): Not applicable

- Name: Christos Nicolaides
  Project Role: Graduate Student at MIT
  Nearest person month worked: 3
  Contribution to Project: Christos Nicolaides works on Task 2.0: Theoretical and computational models of coupled bubble rise and hydrate formation and dissociation.
  Funding Support: Vergottis Fellowship (MIT cost-share)
  Collaborated with individual in foreign country: No
  Country(ies) of foreign collaborator: Not applicable
  Travelled to foreign country: Not applicable
  Duration of stay in foreign country(ies): Not applicable

- Name: Xiaojing Fu
  Project Role: Graduate Student at MIT
  Nearest person month worked: 0
  Contribution to Project: Xiaojing Fu works on Task 2.0: Theoretical and computational models of coupled bubble rise and hydrate formation and dissociation.
  Funding Support: DOE
  Collaborated with individual in foreign country: No

Country(ies) of foreign collaborator: Not applicable
Travelled to foreign country: Not applicable
Duration of stay in foreign country(ies): Not applicable

4.2 Other organizations involved as partners

Nothing to report.

4.3 Other collaborators or contacts

We have established a collaboration with Luis Cueto-Felgueroso, formerly a research scientists in Juanes's group and currently a researcher at the Technical University of Madrid, and with Hector Gomez, a professor at the University of La Coruña and who has visited MIT on several occasions and has published joint papers with Juanes. Both researchers are experts in phase-field modeling, and the collaboration will bring new perspectives on the mathematical aspects of multiphase–multicomponent flows.

We have also established contact with Carolyn Koh's group at Colorado School of Mines, where they have built an experimental system that is related to the one proposed in our project. William Waite has already visited their group and we anticipate that this contact will be very beneficial for the experimental aspects of the project.

Ruppel continues to make plans to visit some of the deepwater Nantucket seeps on the R/V Endeavor in July 2014 as part of a NSF cruise funded to J. Kessler (U. Rochester).

5 Impact

5.1 Impact on the principal discipline of the Project

No impact to report yet.

5.2 Impact on other disciplines

No impact to report yet.

5.3 Impact on the development of human resources

The project is supporting the training of graduate students.

5.4 Impact on physical, institutional, and information resources that form infrastructure

Nothing to report yet.

5.5 Impact on technology transfer

Nothing to report yet.

5.6 Impact on society beyond science and technology

No impact to report yet.

5.7 Dollar amount of the awards budget spent in foreign country(ies)

Zero.

6 Changes and problems

Nothing to report.

7 Special reporting requirements

Nothing to report.

8 Budgetary information

The Cost Plan is included as Appendix 2.

MILESTONE STATUS REPORT

Milestone	Task/ Subtask	Project Milestone Description	Year 1 Q1	Year 1 Q2	Year 1 Q3	Year 1 Q4	Year 2 Q1	Year 2 Q2	Year 2 Q3	Year 2 Q4	Year 3 Q1	Year 3 Q2	Year 3 Q3	Year 3 Q4	Planned Start date	Planned End date	Actual Start date	Actual End date	Comments (notes, explanation of deviation from plan)
1	1.0	Revise PMP	X												1-Oct-13	31-Dec-13	1-Oct-13	3-Dec-13	Revised PMP sent by email on Dec 3, 2013
2	1.0	Kick-off meeting	X												1-Oct-13	31-Dec-13	1-Oct-13	14-Nov-13	Webex meeting on Nov 14, 2013
3	2.1	Model of static gas bubble in 3D				X									1-Oct-13	30-Sep-14	1-Oct-13		
4	3.1	Verify flow-loop				X									1-Oct-13	30-Sep-14	1-Oct-13		
5	4.1	Extract MBES/SBES seep parameters				X									1-Oct-13	30-Sep-14	1-Oct-13		
6	3.2	Acoustic signature due to hydrate formation							X						1-Oct-14	31-Jul-15			
7	4.2	Estimate of methane flux from Atlantic							X						1-Oct-14	31-Jul-15			
8	2.2	Model of buoyant hydrate-coated gas bubble								X					1-Oct-14	30-Sep-15			
9	3.3	Measure gas-loss rate at low initial pressures								X					1-Jul-15	30-Sep-15			
10	4.1	Analyze plume data acquired by NOAA OE								X					1-Oct-14	30-Sep-15			
11	2.3	Model of bubble-bubble interactions										X			1-Apr-15	31-Mar-16			
12	3.3	Measure gas-loss rate at high initial pressures										X			1-Oct-15	31-Mar-16			
13	4.2	Extend bottom water temperature database										X			1-Jun-15	31-Mar-16			
14	2.4	Model formulation and comparison with field observations												X	1-Oct-15	30-Sep-16			
15	all	Manuscripts submitted / Final project synthesis and report												X	1-Oct-14	30-Sep-16			

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