U.S. Department of Energy
National Energy Technology Laboratory

DOE Award No.: DE-FE0013999

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

Principal Investigator:
Prof. Ruben Juanes
Tel: (617)253-7191
Email: juanes@mit.edu

DUNS Number: 001425594

Recipient Organization:
U.S. Department of Energy
National Energy Technology Laboratory

Project Period: October 1, 2013 – September 30, 2016

Reporting Period: October 1, 2015 – December 31, 2015

Report Frequency: Quarterly

Submission date: January 31, 2016

Ruben Juanes

Digitally signed by Ruben Juanes
DN: cn=Ruben Juanes, o=Massachusetts Institute of Technology, ou, email=juanes@mit.edu, c=US
Date: 2016.02.22 11:27:20 -05'00'

1 Executive summary

Work during this period has focused on the following tasks:

- Subtask 2.2: Model of buoyant hydrate-coated gas bubble
- Subtask 3.1: Laboratory experiments — flow-loop design, fabrication and construction
- Subtask 4.1: Analysis of plume data acquired by NOAA OE

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:

- Subtask 2.2: Model of buoyant hydrate-coated gas bubble
- Subtask 3.1: Laboratory experiments — flow-loop design, fabrication and construction
- Subtask 4.1: Analysis of plume data acquired by NOAA OE

A detailed Milestones Status Report is included as Appendix 1.

Task 2.0: Theoretical and computational models of coupled bubble rise and hydrate formation and dissociation

Subtask 2.2: Model of buoyant hydrate-coated gas bubble

Stability of hydrate shell in a buoyant gas bubble. This section of the report focuses on our recent progress in investigating the stability of the hydrate shell on a rising methane bubble. Here, we consider a bubble that is released within the hydrate stability zone (HSZ) and into a water column that is saturated with dissolved methane. Under this setting, it is reasonable to assume that hydrate can readily form on gas bubble upon its contact with the water column. We further assume that, upon its release, the bubble is already covered by a thin layer of uniform hydrate film that serves as nucleation sites for subsequent hydrate shell thickening.

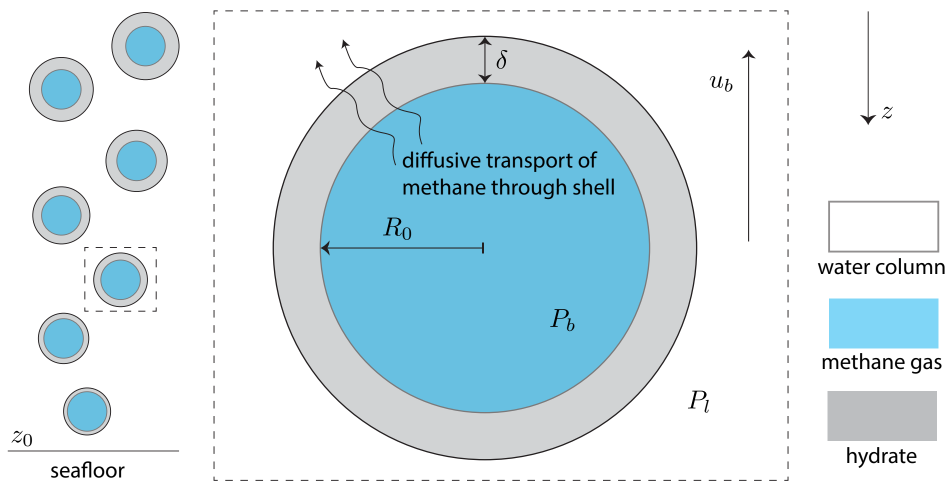

Figure 1: Diagram illustrating key parameters controlling the mechanical stability of a hydrate shell during the rise of a methane bubble.

We consider a methane bubble of initial radius R_0 [mm] released at a depth z_0 [km]. Initially, the bubble is covered by a thin hydrate layer of thickness $\delta_0 = 15\mu m$, typical of experimental observations [Taylor et al., 2007]. The ensuing fate of this bubble is a complex interplay of four fundamental mechanisms. In the simplest form, this can be summarized as follows (see Figure 1 for illustration):

Hydrodynamics: the bubble is rising at a terminal velocity u_b [m/s]. The terminal velocity of a hydrate covered bubble has been the subject of previous experimental studies. Field measurements suggests $u_b \approx 0.12$m/s for bubbles of radius less than 3mm [Sauter et al., 2006]. In a recent paper, $u_b = 0.23$m/s is used [Warzinski et al., 2014]. In a controlled laboratory experiment, a dependence of u_b on the bubble radius R_0 is shown and it is reported that for hydrate-coated bubble $u_b \approx 0.1$m/s for $R_0 = 0.5$mm and $u_b \approx 0.18$m/s for $R_0 = 2$mm[Bigalke et al., 2010]. Here we adopt the measurements by Bigalke et al. [2010] and assume a linear relation between u_b and R_0:

$$u_b = 0.054 * (R_0 - 0.5) + 0.1[\text{m/s}]. \quad (1)$$

As a result of bubble rising, the water column pressure (P_l) will decrease hydrostatically:

$$P_l = \rho_s g(z_0 - u_b t)/(10^6) \text{ [MPa]}, \tag{2}$$

where $\rho_s = 1029\text{kg/m}^3$ is the density of seawater, $g = 9.8\text{m/s}^2$ is the standard gravity, and t is time since release in *seconds*.

Thermodynamics: the thickness of hydrate shell (δ [mm]) grows linearly at a rate r_H [mm/min]:

$$\delta = \delta_0 + r_H \frac{t}{60\text{s/min}} \text{ [mm]}. \tag{3}$$

Under ideal hydrate forming conditions, a few experimental studies have reported the rate of hydrate growth on a *flat* interface between a methane gas reservoir and liquid pool of water supersaturated with methane. Specifically, $r_H \approx 3.6\text{mm/min}$ is reported [Taylor et al., 2007]. Depending on the subcooling of the system, this rate can fluctuate over a wide range, between 0.005 and 10mm/min [Saito et al., 2010].

Transport: methane gas diffuses into the water column through the porous shell at a diffusive rate $D[\text{mm}^2/\text{s}]$. Such diffusion is driven by a gradient in methane molar concentration (partial pressure), denoted c, directed from the gas bubble to the pores within the porous hydrate shell. We assume that all methane is depleted in the pore fluid of the hydrate shell so that pore volume methane concentration is always zero: $c_{\text{pore}} = 0$ mol/mm^3. We approximate the diffusive transport of methane out of the bubble with a simple diffusion equation:

$$\frac{dc}{dt} = -D\frac{c - c_{\text{shell}}}{\delta_0^2} \text{ [mol/mm}^3\text{]}. \tag{4}$$

We assume that bubble volume is kept constant due to the support from the hydrate layer: $V_b = \frac{4}{3}\pi R_0^3$. As a result, gas pressure inside the bubble (P_b) is inversely related to c:

$$P_b = \frac{RT}{cV_b} \text{ [mol/mm}^3\text{]}. \tag{5}$$

Methane transport out of the bubble results in a depression in bubble pressure. We assume that initially $P_b(t = 0) = P_l(t = 0)$ and compute the initial methane concentration inside the bubble as:

$$c(t = 0) = \frac{P_l(t = 0)}{RT} \text{ [mol/mm}^3\text{]}. \tag{6}$$

Here $R = 8.314\text{cm}^3\text{MPa/K/mol}$ is the gas constant, $T = 277\text{K}$ is the water column temperature.

Mechanics: the structural stability of the growing hydrate shell is challenged by the pressure variations inside and outside the shell. We can simply compute such pressure difference (ΔP) as:

$$\Delta P = P_l - P_b \text{ [MPa]}, \tag{7}$$

and test ΔP against the critical buckling pressure of a thin shell. If the thin shell is perfectly uniform in thickness, one can compute its buckling pressure as [Hutchinson, 1967]:

$$P_{\text{buckle}}^{uniform} = \frac{2E}{[3(1-\nu^2)]^{0.5}} \left(\frac{\delta}{R_0 + \delta/2}\right)^2 \text{ [MPa]}. \tag{8}$$

The Young modulus (E) and Poisson ratio (ν) of hydrate are measured in detail in Helgerud et al. [2009]. The proposed formula for E and ν of methane hydrate as a function of temperature and pressure are:

$$E = 8.39 + (-1.09 \times 10^{-2})T + 3.8 \times 10^{-3} P_l \text{ [GPa]}, \tag{9}$$

$$\nu = 0.3151 + (-9 \times 10^{-5})T + 6.6 \times 10^{-5} P_l. \tag{10}$$

At $T = 277\text{K}$ and $P_l = 10\text{MPa}$, we compute that:

$$E = 8.4 \text{ GPa}, \quad \nu = 0.32. \tag{11}$$

After rising for 100 meters, the change in water pressure is about 1MPa; assuming changes in temperature is small, then the resulting change in E and ν is approximately 3.8×10^{-3}GPa and 6.6×10^{-5} respectively. This is small compared the the absolute value of E and ν. Therefore, we assume that E and ν are constant throughout the rising process.

Meanwhile, imperfections in shell thickness can drastically reduce the required buckling pressure, to as low as only 30 percent of the theoretical value [Hutchinson, 1967]. Here we assume that the hydrate shell formed are rough and non-uniform and has a much lower buckling pressure:

$$P_{\text{buckle}} = 0.35 P_{\text{buckle}}^{\text{uniform}}. \tag{12}$$

The hydrate shell buckles if $\Delta P > P_{\text{buckle}}$.

Preliminary model analysis. Figure 2 shows a sample run of the above model for the following parameters: $R0 = 3\text{mm}$, $z_0 = 1\text{km}$, $D = 7 * 10^{-7}\text{mm}^2/\text{s}$ and $r_H = 0.05$ mm/min. As shown, the two pressure profiles (ΔP and P_{buckle}) crosses at $t_{\text{buckle}} \approx 5\text{s}$. We compute the buckle height (z_{buckle}), as the length the bubble has traveled since its release, at the time of buckling: $z_{\text{buckle}} = u_b(R_0) \times t_{\text{buckle}} \approx 1.17\text{m}$.

Next, we probe different parameters in the model and investigate how they impact the buckle time of a bubble. For each set of parameter study, we also simulate the model for different R_0. For example, in figure 3, we fix r_H and D, but change the release depth z_0 and do so for a wide range of bubble sizes (R_0). It is not surprising to see that smaller bubbles are mechanically more stable during its rising process. This is because smaller bubbles have a larger δ/R_0 ratio, increasing the buckling pressure as calculated in Eq. 8. From figure 3, we also observe that bubbles released at a deeper depth have a shorter life span before buckling. This could be explained by the high water column pressure in deep ocean.

In figure 4, we fix z_0 and D, but change the hydrate growth rate r_H. Here we observe that a fast hydrate growth rate can greatly enhance the rigidity of the shell and protects it

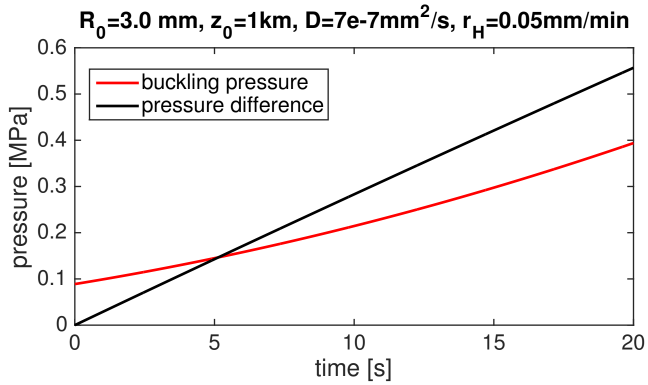

Figure 2: The buckling time, t_b is defined as the cross-over time of the two temporal pressure profiles: the pressure difference cross the hydrate shell (dark), and the theoretical shell buckling pressure based on shallow shell theory [Hutchinson, 1967].

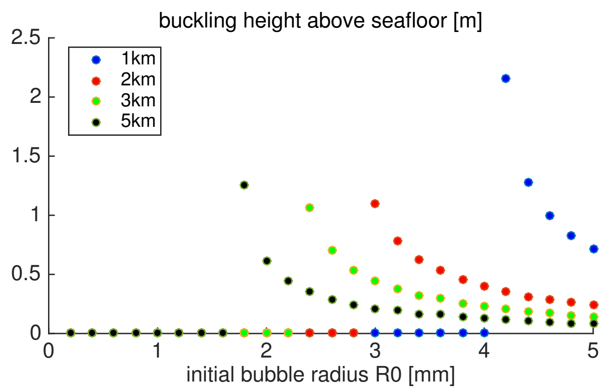

Figure 3: The buckling heights ([m]) against initial bubble radii ([mm]) are plotted here for four different release depth (z_0 [km]). Here we fix other parameters in the model as: $r_H = 0.1\text{mm/min}$, $D = 4.95 \times 10^{-7}\text{mm}^2/\text{s}$.

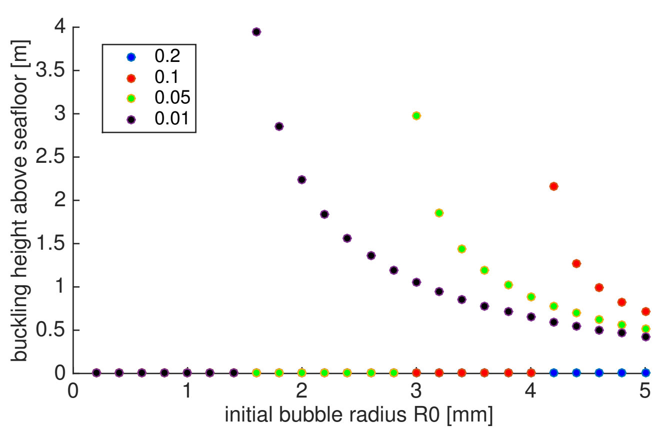

Figure 4: The buckling heights ([m]) against initial bubble radii ([mm]) are plotted here for four different hydrate growth rates (r_H [mm/min]). Here we fix other parameters in the model as: $z_0 = 1\text{km}$, $D = 4.95 \times 10^{-7}\text{mm}^2/\text{s}$.

against the diffusive pressure depression inside. When r_H is as high as 0.2mm/min, we do not observe buckling for any bubble size.

In figure 5, we fix z_0 and r_H, but change the rate of methane diffusion through shell D. Here we observe that a faster diffusion rate can threaten the stability of the shelled bubble. This is intuitive because a higher D indicates a faster rate of pressure depression inside the bubble.

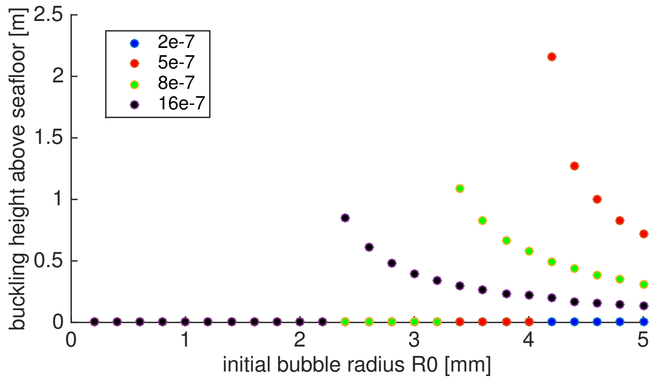

Figure 5: The buckling heights ([m]) against initial bubble radii ([mm]) are plotted here for four different rates of diffusion (D [mm^2/s]). Here we fix other parameters in the model as: $z_0 = 1\mathrm{km}$, $r_H = 0.1\mathrm{mm/min}$.

Future work. The next stage of the modeling effort will entail:

1. Modeling the rheology of hydrate phase in a way that is consistent with the phase-field framework.

2. Incorporating hydrodynamics in the ambient fluid, first in a Darcy framework and then in a Navier-Stokes framework.

References

N. K. Bigalke, L. I. Enstad, G. Rehder, and G. Alendal. Terminal velocities of pure and hydrate coated CO2 droplets and CH4 bubbles rising in a simulated oceanic environment. *Deep-Sea Research I*, 57(9):1102–1110, 2010.

M. B. Helgerud, W. F. Waite, S. H. Kirby, and A. Nur. Elastic wave speeds and moduli in polycrystalline ice Ih, sI methane hydrate, and sII methane-ethane hydrate. *J. Geophys. Res.*, 114(2):1–11, 2009.

J. W. Hutchinson. Imperfection sensitivity of externally pressurized spherical shells. *J. Appl. Mech.*, 34:49–55, 1967.

Kota Saito, Amadeu K. Sum, and Ryo Ohmura. Correlation of hydrate-film growth rate at the guest/liquid-water interface to mass transfer resistance. *Ind. Eng. Chem. Res.*, 49(15): 7102–7103, 2010.

Eberhard J. Sauter, Sergey I. Muyakshin, Jean-Luc Charlou, Michael Schlüter, Antje Boetius, Kerstin Jerosch, Ellen Damm, Jean-Paul Foucher, and Michael Klages. Methane discharge from a deep-sea submarine mud volcano into the upper water column by gas hydrate-coated methane bubbles. *Earth Planet. Sci. Lett.*, 243(3-4):354–365, 2006.

Craig J. Taylor, Kelly T. Miller, Carolyn A. Koh, and E. Dendy Sloan. Macroscopic investigation of hydrate film growth at the hydrocarbon/water interface. *Chem. Eng. Sci.*, 62 (23):6524–6533, 2007.

Robert P. Warzinski, Ronald Lynn, Igor Haljasmaa, Ira Leifer, Frank Shaffer, Brian J. Anderson, and Jonathan S. Levine. Dynamic morphology of gas hydrate on a methane bubble in water: Observations and new insights for hydrate film models. *Geophys. Res. Lett.*, 41:6841–6847, 2014.

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. An inverted, conical “bubble capture” element is in place (Figure 3.1, cone enclosed in lower acrylic cylinder), but repeated testing at UNH by Prof. Weber’s group repeated showed the instability of bubbles in such a chamber. Contact with the chamber walls, which could significantly alter the behavior of hydrate formation and coherence on bubble surfaces, occurred frequently. UNH testing of a “vortexer” unit ahead of the bubble capture chamber showed through video tracking that adding a rotational component to the fluid flow was effective in holding relatively dense water at the sides of the chamber while restricting relatively low-density bubbles to the chamber’s central axis. UNH shared the plans for one of these 3D-printed devices with the USGS, which has had the device built and installed in the counterflow system (Figure 3.1, white insert enclosed in upper acrylic cylinder).

Fabrication Activities.

- *Data acquisition*: all sensors, as well as the water pressure and gas injection pumps, have been tied into a computerized control and data acquisition system.

- *Temperature control*: A cooling bath has been installed, utilizing direct-contact cooling of the counterflow circulatory pump. The circulatory pump and cooling coils have now been insulated as well.

- *Water pressure control*: pump system has been tested and shown to maintain 700 psi (200 psi above maximum operational pressure), leak-free up to the connection with the counterflow device.

- *Water circulation*: In the course of assessing pipe connections, we have simplified the fluid flow return from the chamber to the circulatory pump, reducing both the number of pipe connections and the number of bends in the flow path. Failed fittings are being identified and replaced as we build toward the system’s peak operational pressure of ~500 psi.

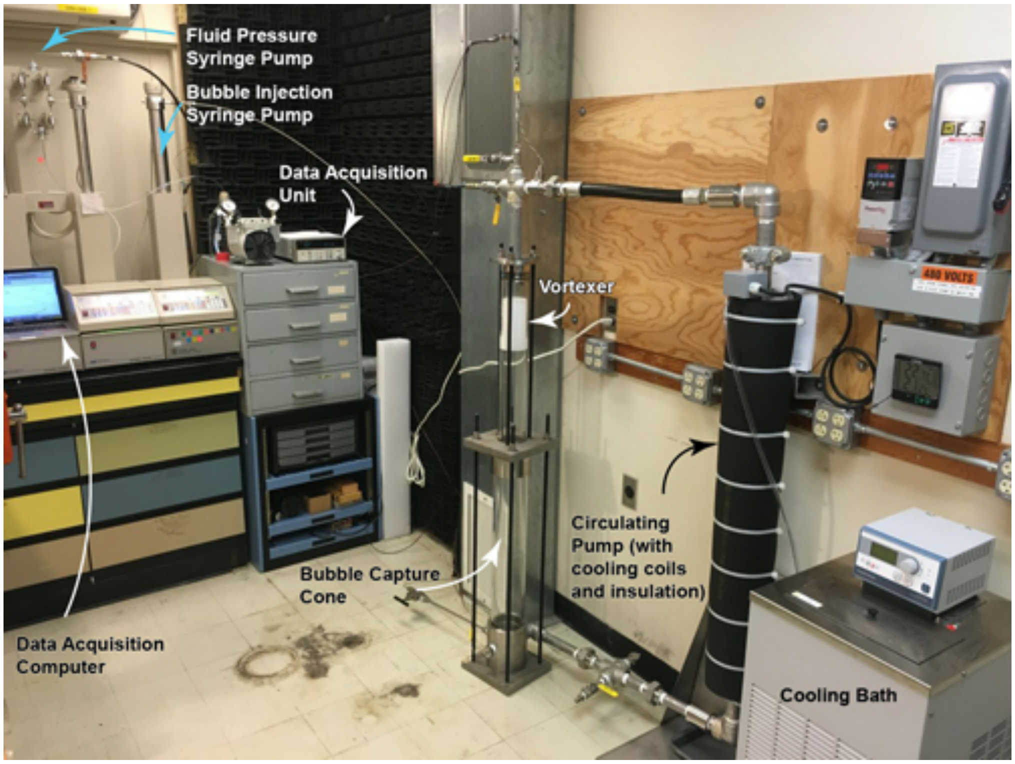

Figure 3.1: Current flow loop configuration. Data acquisition, fluid pressure and gas injection systems (back left), are all connected to the flow loop (center-right). Flow loop now includes a vortexer (center) to impart a rotation to the circulating water that UNH has shown helps to confine bubbles to the central axis of flow. Circulating pump is now wrapped in cooling coils, insulated (black vertical cylinder) and connected to a cooling bath (lower right).

References.

Ohgaki, K., T. Sugahara, M. Suzuki, and H. Jindai (2000), Phase behavior of xenon hydrate system, Fluid Phase Equilibria, 175(1-2), 1-6.

2.3 Opportunities for training and professional development

The project has offered opportunities for training of our graduate students Amir Pahlavan (MIT), Xiaojing Fu (MIT), Ben Scandella (MIT), and Liam Pillsbury (UNH).

2.4 Dissemination of results to communities of interest

See the *Products* section (Section 3.1.3).

2.5 Plans for the next reporting period

The project is progressing according to the anticipated plan, with the exception of the construction and validation of the flow loop for hydrate formation using Xenon as hydrate former. We are currently addressing some of the fabrication issues. In the next reporting period we will continue to work on the following tasks:

- Subtask 2.3: Phase-field modeling of multiple buoyant bubbles within the HSZ.
- Subtask 3.1: Laboratory experiments — flow-loop design, fabrication and construction
- Subtask 3.2: Laboratory experiments — acoustic signature due to hydrate formation
- Subtask 4.2: Estimate of methane flux from Atlantic margin

3 Products

3.1 Journal publications, conference papers, and presentations

3.1.1 Journal publications

- Brothers, D.S., Ruppel, C., Kluesner, J.W., ten Brink, U.S., Chaytor, J.D., Hill, J.C., Andrews, B.D. and Flores, C., 2014, Seabed fluid expulsion along upper slope and outer shelf of the U.S. Atlantic continental margin. *Geophys. Res. Lett.*, doi: 10.1002/2013GL058048.
- Skarke, A., C. Ruppel, M. Kodis, D. Brothers, and E. Lobecker, 2014, Widespread methane leakage from the seafloor on the northern US Atlantic margin, *Nature Geoscience*, doi:10.1038/ngeo2232.
- L. Cueto-Felgueroso and R. Juanes. A phase-field model of two-phase Hele-Shaw flow. *J. Fluid Mech.*, 758, 522-552 (2014), doi:10.1017/jfm.2014.512.
- 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. *Geochemistry, Geophysics, Geosystems.* 15(5): 1911-1925 (2014), doi:10.1002/2014GC005271.
- A. Alizadeh Pahlavan, L. Cueto-Felgueroso, G. H. McKinley and R. Juanes. Thin films in partial wetting: internal selection of contact-line dynamics. *Physical Review Letters*, 115, 034502 (2015), doi:10.1103/PhysRevLett.115.034502.

3.1.2 Conference papers

Nothing to report.

3.1.3 Presentations

- Brothers, D., Ruppel, Kluesner, Chaytor, ten Brink, and Hill, 2013, Pervasive evidence for seabed fluid expulsion along upper slope of the US Atlantic continental margin, EOS Trans AGU, OS21A-1614, Fall Meeting, 2013.
- Kodis, M., Skarke, Ruppel, Weber, Lobecker, and Malik, 2013, US Atlantic margin methane plumes identified from water column backscatter data acquired by NOAA ship Okeanos Explorer, EOS Trans. AGU, OS21A-1612, Fall AGU Meeting (poster).
- Skarke, A., Ruppel, Kodis, Lobecker, and Malik, 2013, Geological significance of newly discovered methane seeps on the northern US Atlantic margin, EOS Trans. AGU, OS21A-1613, AGU Fall Meeting (poster).
- Scandella, Urban, Delwiche, Greinert, Hemond, Ruppel, and Juanes, 2013, Quantifying methane flux from lake sediments using multibeam sonar, EOS Trans AGU, B53B-0456, Fall Meeting, 2013.

- Ruppel, 2014, Gas seeps on the US Atlantic margin, NOAA Education & Outreach videotaped talk, March 2014 (invited).
- Ruppel, 2014, Exploration in the Atlantic Canyons, NOAA OER Conference and Review, Baltimore, MD, September 2014 (invited).
- Ruppel, Weber, Kessler, Pohlman, and Skarke, Methane hydrate dissociation and gas seepage on global upper continental slopes driven by intermediate ocean warming, EOS Trans. AGU, OS11C-01, AGU Fall Meeting.
- Ruppel, Skarke, Kodis, and D. Brothers, 2014, Hundreds of seeps on the northern US Atlantic margin: Evidence for warming-induced gas hydrate breakdown, US Geological Survey Santa Cruz, June 2014.
- Ruppel, Skarke, Kodis, D. Brothers, and Lobecker, 2014, Methane seepage at ~600 newly-discovered sites between Cape Hatteras and Georges Bank, URI Graduate School of Oceanography weekly seminar series, October 2014.
- Benjamin P. Scandella, Liam Pillsbury, Thomas Weber, Carolyn D. Ruppel, Harry Hemond, Ruben Juanes. Quantitative spatiotemporal characterization of methane venting from lake sediments. EOS Trans. AGU B13D-0208, AGU Fall Meeting 2014.
- Xiaojing Fu, Luis Cueto-Felgueroso, William F. Waite, Carolyn D. Ruppel, Ruben Juanes. A Phase-Field Approach to Modeling Hydrate Formation on Methane Gas Bubbles in a Water Column. EOS Trans. AGU OS21B-1119A, AGU Fall Meeting 2014.
- Benjamin P. Scandella, Liam Pillsbury, Thomas Weber, Carolyn D. Ruppel, Harry Hemond, Ruben Juanes. Spatiotemporal signature of methane venting from lake sediments: from lab to field scale. EOS Trans. AGU B51F-0485, AGU Fall Meeting 2015.
- Xiaojing Fu, Luis Cueto-Felgueroso, Ruben Juanes. Viscous fingering with partially miscible fluids. EOS Trans. AGU H41D-1356, AGU Fall Meeting 2015.

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)

- (newsletter) Chaytor, J., A. Demopoulos, and C. Ruppel, 2013, Exploring undersea terrain off the northern US Atlantic coast via telepresence-enabled research cruise, *Sound Waves*, Nov/Dec 2013.
- (newsletter) Ruppel, C. and H. Hamilton, 2014, Natural methane seepage is widespread on the US Atlantic margin, *Sound Waves*, Oct/Nov 2014.

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: Amir Pahlavan
  Project Role: Graduate Student at MIT
  Nearest person month worked: 1
  Contribution to Project: Amir Pahlavan 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

- Name: Xiaojing Fu
  Project Role: Graduate Student at MIT
  Nearest person month worked: 3
  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

- Name: Liam Pillsbury
  Project Role: Graduate Student at UNH
  Nearest person month worked: 1
  Contribution to Project: Liam Pillsbury works on Task 4.0: Field data analysis to link models and laboratory data to real world gas hydrate dynamics.
  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 Dr. Luis Cueto-Felgueroso, formerly a research scientists in Juanes's group and currently a researcher at the Technical University of Madrid, and with Prof. Hector Gomez, 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 Prof. 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 Prof. J. Kessler (U. Rochester).

We have established a collaboration with Dr. Ann Blomberg, a post-doctoral researcher at the University of Oslo. Dr. Blomberg, who has funding through the Norwegian Research Council, has an interest in acoustic detection and classification of methane gas seeps and brings an expertise in sonar signal processing. She has been working closely with us on several aspects of the data analysis for the US Atlantic margin observations as part of Task 4.1.

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

Nothing 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	30-Sep-14	
4	3.1	Verify flow-loop				X									1-Oct-13	30-Sep-14	1-Oct-13		delay in flow-loop construction -- discussed at c
5	4.1	Extract MBES/SBES seep parameters				X									1-Oct-13	30-Sep-14	1-Oct-13	30-Sep-14	
6	3.2	Acoustic signature due to hydrate formation							X						1-Oct-14	31-Jul-15	1-Oct-14		delay in flow-loop construction -- discussed at c
7	4.2	Estimate of methane flux from Atlantic							X						1-Oct-14	31-Jul-15	1-Oct-14	31-Jul-15	
8	2.2	Model of buoyant hydrate-coated gas bubble								X					1-Oct-14	30-Sep-15	1-Oct-14	30-Sep-15	
9	3.3	Measure gas-loss rate at low initial pressures								X					1-Jul-15	30-Sep-15			delay in flow-loop construction -- discussed at c
10	4.1	Analyze plume data acquired by NOAA OE								X					1-Oct-14	30-Sep-15	1-Oct-14	30-Sep-15	
11	2.3	Model of bubble-bubble interactions										X			1-Apr-15	31-Mar-16	1-Apr-15		
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-Jul-15	31-Mar-16	1-Jul-15		
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			

National Energy Technology Laboratory

626 Cochrans Mill Road
P.O. Box 10940
Pittsburgh, PA 15236-0940

3610 Collins Ferry Road
P.O. Box 880
Morgantown, WV 26507-0880

One West Third Street, Suite 1400
Tulsa, OK 74103-3519

1450 Queen Avenue SW
Albany, OR 97321-2198

2175 University Ave. South
Suite 201
Fairbanks, AK 99709

Visit the NETL website at:
www.netl.doe.gov

Customer Service:
1-800-553-7681