Oil & Natural Gas Technology

DOE Award No.: DE-FE0013999

Quarterly Research Performance

Progress Report (Period Ending 06/30/2017)

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

Project Period (10/01/2013 – 09/30/2017)

Submitted by:
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U.S. DEPARTMENT OF ENERGY | NATIONAL ENERGY TECHNOLOGY LABORATORY

1 Executive summary

Work during this period has focused on the following tasks:

- Subtask 2.4: Phase-field modeling validation with experimental observations
- Subtask 3.2: Laboratory experiments — Quantify pressure and dissolved Xe saturation in the water column for hydrate formation on a rising bubble
- Subtask 3.3: Laboratory experiments — evolution of the bubble structure during a simulated rise through the water column
- Subtask 4.1: Analysis of plume data acquired by NOAA OE
- Subtask 4.2: Place US Atlantic margin seeps in regional and global context of gas hydrate system dynamics

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 has focused on the following tasks:

- Subtask 2.4: Phase-field modeling validation with experimental observations
- Subtask 3.2: Laboratory experiments — Quantify pressure and dissolved Xe saturation in the water column for hydrate formation on a rising bubble
- Subtask 3.3: Laboratory experiments — evolution of the bubble structure during a simulated rise through the water column
- Subtask 4.1: Analysis of plume data acquired by NOAA OE
- Subtask 4.2: Place US Atlantic margin seeps in regional and global context of gas hydrate system dynamics

In this report, we focus on the description of progress of Subtasks 3.2, 4.1 and 4.2. 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 has constructed 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 operates at pressures high enough for the gas to form xenon hydrate. Xenon was chosen for the hydrate-forming gas so hydrate could be formed at 190 psi at room temperature (21°C, 70°F), and at only 60 psi when the system is cooled to 10°C (50°F) [*Ohgaki et al.*, 2000].

Design Summary. To date, the flow loop has been used to observe hydrate shell formation and bubble rise rates. In this quarter, we began work toward an acoustic sensing capability intended to establish whether echosounder returns could be used to differentiate between hydrate-free and hydrate-coated bubbles in the field. At UNH, Weber constructed an electrical pass through for instrumenting the USGS flow loop with a UNH echosounder unit. The unit and electrical feed have been installed in the flow loop (Figure 3.1). A new gas line has also been constructed and installed (Figure 3.1), positioned now for releasing bubbles just above the echosounder. As bubbles are captured in the capture cone portion of the flow loop, the echosounder will be able to send acoustic pulses from below the bubble and record returns from the bottom face of the hydrate-free or hydrate-coated bubble.

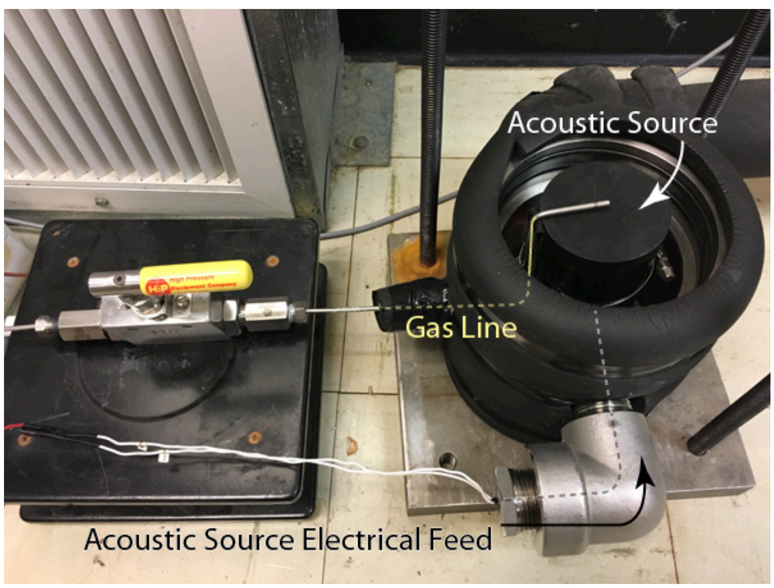

Figure 3.1. Echosounder installation into the USGS Flow Loop. An echosounder's acoustic source (black cylinder in the flow loop base) has been installed along with its electrical feeds for power and data. The gas injection line has been rerouted to now produce bubbles just above the top of the echosounder.

Results. The Task benefitted from two unplanned group meetings in this quarter. In late April, Waite travelled to UNH to give an invited talk for the CCOM Seminar Series (Methane gas hydrates: A tale of bubbles great and small). The visit was an opportunity to present our results to date, and discuss implications during a question and answer session. A key question was about the bubble's hydrate shell thickness. Because the volume change between hydrate and the entrapped gas at standard temperature and pressure is ~164, the bubble's hydrate shell thickness needs to be quite thin, or creating the hydrate shell would consume most or all of the bubble's gas. We currently do not have an accurate means of measuring bubble thicknesses in the flow loop, but going forward we may be able to provide thickness estimates based on volume changes during hydrate formation or breakdown.

In early May, Waite travelled to MIT for an AAPG lecture provided by Collett (USGS). Juanes and Fu were able to meet with Waite to discuss modeling and experimental results. A key issue was understanding the connection between gas saturation in the water, and hydrate formation on a gas bubble's surface. A 3-Zone concept was developed for understanding the pressure-temperature-gas concentration space in terms of the dominant gas consumption mechanisms.

- *Zone 1* describes a region in phase space where the system is only slightly within the hydrate's pressure-temperature stability zone and the methane concentration is low. In Zone 1, the dominant methane consumption mechanism is dissolution: gas dissolves out of the bubble too rapidly for a hydrate shell to develop. This type of behavior was observed in the USGS flow loop as we first began introducing hydrate-forming gas into the chilled, pressurized flow loop water. We know dissolution is occurring because the gas bubbles shrink and eventually disappear (Figure 3.2a).

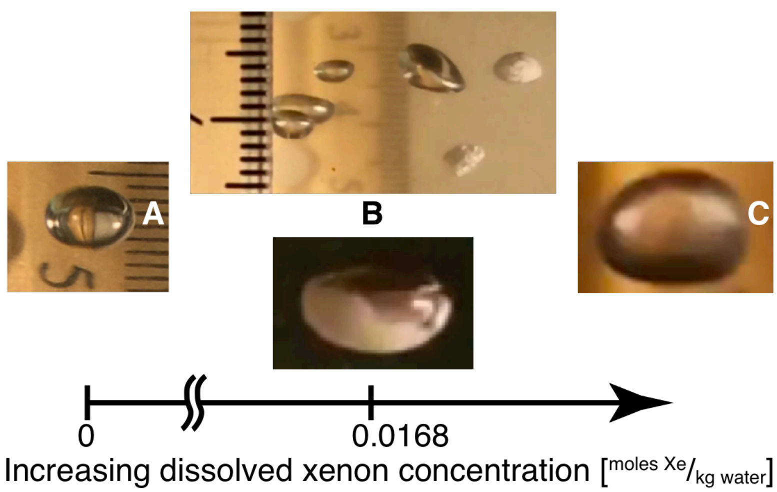

Figure 3.2. Bubble morphology with increasing dissolved-phase xenon content. (A) Initially shiny, transparent bubbles that do not form hydrate shells because of extremely low xenon concentrations in the water (Zone 1) give way to bubbles that are (B) fully or partially coated in a white, frosty hydrate shell at 9.7 °C, ~1 MPa when the dissolved phase xenon concentration reaches 0.0168 moles Xe/kg water (transition from Zone 1 to Zone 2). (C) Subsequent bubbles form uniform, gray shells even before the bubbles themselves are observable in the chamber (Zone 2).

- *Zone 2* describes a region in phase space where the system is modestly in the hydrate pressure-temperature stability zone, and the dissolved gas concentration is below the solubility limit. In this zone, the rate of gas dissolution from the bubble is slow enough for a hydrate shell to form. In Zone 2, the hydrate shell is both dissolving (increasing the gas concentration in the surrounding water) and forming (from gas within the bubble itself). This type of behavior is observed in the USGS flow loop as the threshold dissolved gas saturation is exceeded (Figure 3.2b, c). This behavior is also observed by *Chen et al*. [2014] at high pressure in their methane hydrate bubble tests, where they demonstrate that gas supersaturation of the fluid is not necessary so long as the system is far enough inside the hydrate stability field for hydrate to form fast enough to keep up with the rate of dissolution. This Zone 2 behavior likely also explains why hydrates only formed on bubble surfaces for *Maini and Bishnoi* [1981] only after their system was pressurized ~4 MPa beyond the minimum pressure for hydrate stability. Bubbles observed in nature (e.g. Rehder et al. [2009]; Wang et al. [2016]), which are within the hydrate pressure-temperature stability field but do not initially form a hydrate shell, are observed to form a shell some second or minutes later. It is possible these bubbles are dissolving, raising the dissolved gas concentration in their immediate vicinity to levels which allow hydrate formation and gas dissolution to occur simultaneously.
- *Zone 3* describes a region in phase space where hydrate are stable with regard to temperature and pressure, and the dissolved gas concentration in the surrounding water is above the solubility limit (supersaturated). In Zone 3, net dissolution does not occur because water surrounding the bubble is already supersaturated. In Zone 3, hydrate shell formation can occur using gas molecules from the bubble and from the surrounding water. This situation was created by Warzinski et al. [2014] for their methane hydrate-coated bubble experiments and by Chen et al. [2014] for the lower-pressure portion of their methane hydrate-coated bubble experiments.

These results are incorporated into the poster presentation given at the 9th International Conference on Gas Hydrates, June 25-30, 2016, Denver, CO (Waite, W.F., Weber, T., Fu, X., Juanes, R., Ruppel, C., Laboratory observations of the evolution and rise rate of bubbles with and without hydrate shells).

References.

Chen, L. T., E. D. Sloan, C. A. Koh, and A. K. Sum (2014), Methane Hydrate Formation and Dissociation on Suspended Gas Bubbles in Water, Journal of Chemical and Engineering Data, 59(4), 1045-1051.

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.

Rehder, G., I. Leifer, P. G. Brewer, G. Friederich, and E. T. Peltzer (2009), Controls on methane bubble dissolution inside and outside the hydrate stability field from open ocean field experiments and numerical modeling, Marine Chemistry, 114(1-2), 19-30.

Wang, B. B., S. A. Socolofsky, J. A. Breier, and J. S. Seewald (2016), Observations of bubbles in natural seep flares at MC 118 and GC 600 using in situ quantitative imaging, J. Geophys. Res.-Oceans, 121(4), 2203-2230.
Warzinski, R. P., R. Lynn, I. Haljasmaa, I. Leifer, F. Shaffer, B. J. Anderson, and J. S. Levine (2014), Dynamic morphology of gas hydrate on a methane bubble in water: Observations and new insights for hydrate film models, Geophysical Research Letters, 41(19), 6841-6847.

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

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

Model-data comparisons have returned to a more detailed analysis of seeps observed in 2012 at Blake Ridge. At this site, during a single cruise, 10's of measurements were collected at offset-spacing over a site with multiple plume locations (Figure 4.1). Data were collected with both a 30 kHz multibeam echo sounder (MBES) and an 18 kHz split-beam echo sounder (SBES). The advantage of this data set is that the number of independent observations, and the dense coverage of the survey, creates high confidence that the 'observable top' of the seep was imaged. That is, the rising bubbles were observed as high as possible in the water column, until they were masked by background reverberation or other noise (as opposed to advecting sideways out of the beam). SBES observations show the gas bubbles rise to 1000 m water depth (1200 m rise height), prior to decay or masking from reverberation (in this case, the deep scattering layer; see Figure 4.2). Observations with the higher-frequency MBES show the bubbles rising 200 m higher in the water column. As previously described, our approach is to compare these to modeled bubbles using typical release sizes (1-10 mm diameter). Our model had previously been based on the McGinnis 2006 model, but we have recently adopted the TAMOC model (from Scott Socolofsky's group at Texas A&M) due to its faster run time and more extensive testing (than our own version of the McGinnis 2006 model). As we refine/upgrade our modeling approach, we have also re-examined our data inputs. This has included a discovery of archived faulty dissolved oxygen data, which we have replaced with non-faulty archival data from a different cruise; we are also working to refine the gas composition at the bubble source. The uncertainty surrounding these model input parameters has necessitated a sensitivity study as we bring this model-data comparison to conclusion.

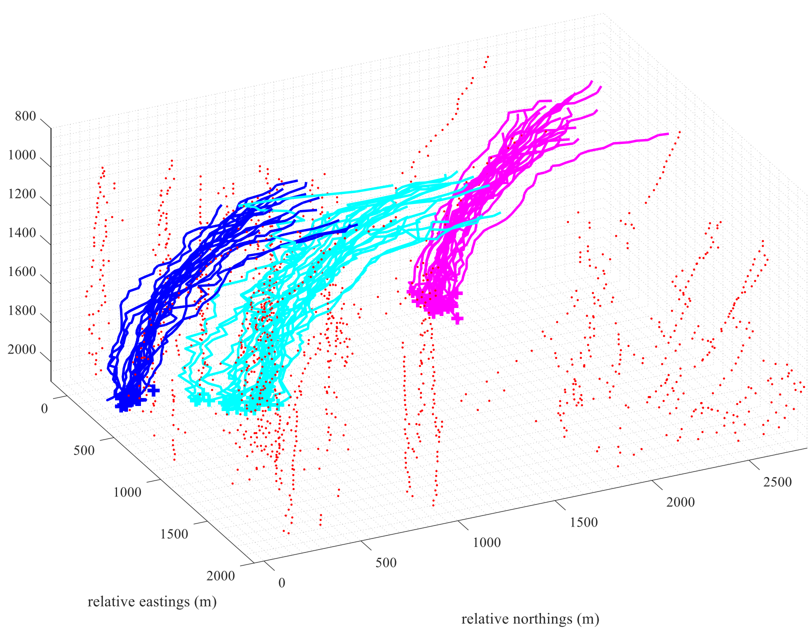

Figure 4.1. Multibeam echo sounder observations of gas seeps at Blake Ridge. Note that multiple passes are overlaid on this plot.

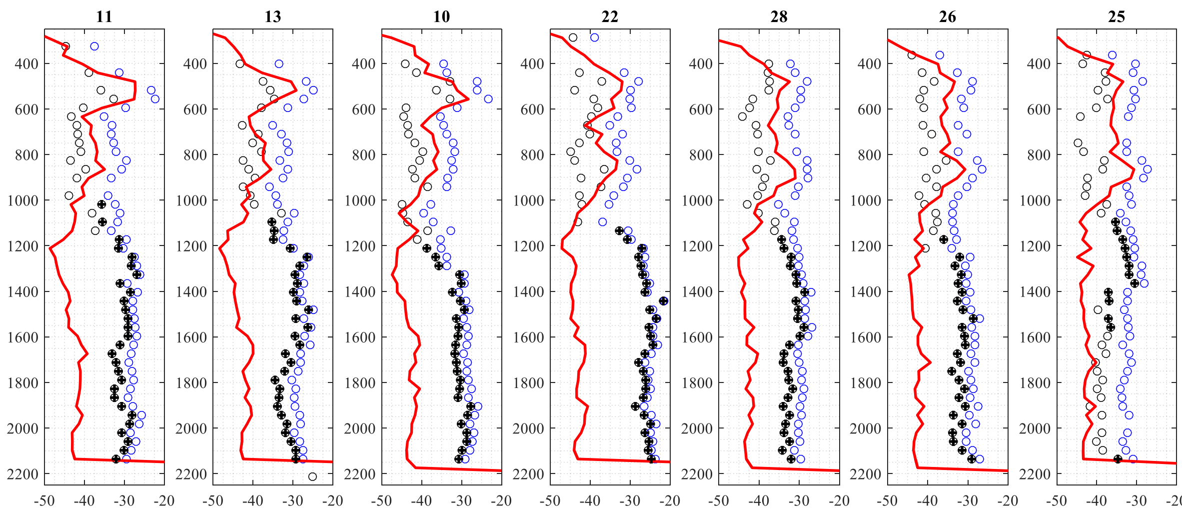

Figure 4.2. Background noise (red lines) and processed (deconvolved from noise) gas plume profiles (black circles; target strength versus depth) collected with the 18 kHz split-beam echo sounder.

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

During the reporting period, the USGS refined the empirical determinations of the landward limit of gas hydrate stability on the U.S. Pacific margin based on the analysis of the global CTD database (Figure 4.3). The USGS, in collaboration with academic colleagues and the British Geological Survey, also submitted an invited proposal to expand multidisciplinary research like that conducted on the Atlantic margin seep systems to those on the Oregon and Washington margins and to undertake new technology developments related to the character and fate of seep emissions.

The USGS has now built a database of U.S. Pacific margin seeps from publications and gray literature cruise reports and discussed the analysis of the unpublished water column data that delineates methane plumes in existing multibeam surveys with the federal group that is handling most of those data offshore the Pacific Northwest. The USGS already had access to California margin seep locations (most of which are unrelated to gas hydrate dynamics) from prior publications. Published Alaska offshore hydrocarbon seep locations identified in the 1980s and described in some USGS publications as late as 2003 have proven more elusive, but we are tracking down these reports.

The USGS is systematically re-analyzing all of the split-beam echosounder data (EK60/80) collected during its cruises on the northern US Atlantic margin since 2015 to formally update the seeps database in a peer-reviewed publication and to prepare for a DOE-sponsored August-September cruise in which Ruppel is a collaborator. Relevant seeps data and associated multibeam water column data are also being provided to other federal agencies conducting two cruises funded by NOAA and by the National Oceanographic Partnership Program (NOPP—BOEM, NOAA, and USGS) in the same timeframe.

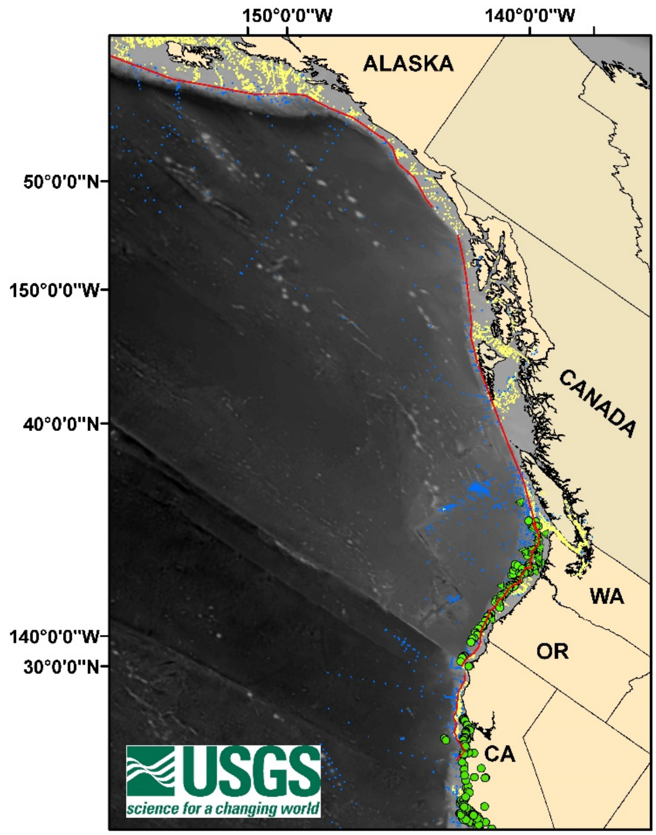

Figure 4.3. Combination of CTD bottom water database made for this project (yellow dots warmer than hydrate stability; blue dots colder), empirical landward limit of gas hydrate stability (red), and California and US Northwest Pacific margin seeps from USGS, NOAA, and other publications (green). Note that most of the California seeps are unrelated to gas hydrates, while many of those on the Oregon/Washington margins lie deeper than the landward limit of gas hydrate stability. Not shown are hydrocarbon seeps (mostly oil) on the Alaska margin, which were mapped in the 1980s by NIST and NOAA.

The USGS has shared maps made for this project with Scott Socolofsky's group at TAMU and with a USGS group intending to write a competitive proposal for the Southeast Alaskan margin. These maps show (a) the predicted height of gas hydrate stability above the seafloor in the water column based on 1 degree global water temperature averages in the uppermost part of the oceanic water column and (b) the hydrate stable/not stable bottom water temperature conditions on US continental margins based on the CTD analyses that reach within 10% of the ocean's depth at a particular location.

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. In particular, we have made substantial progress on the construction and validation of the flow loop for hydrate formation using Xenon as hydrate former. We have addressed the fabrication issues that had slowed down this task, and the flow cell is now operational at the range of pressures and flow rates that we anticipate to use for the rest of the project. In the next reporting period we will continue to work on the following tasks:

- Subtask 2.5: Validation of phase-field model with microfluidic cell experiments.
- Subtask 3.2: Quantify pressure and dissolved Xe saturation in the water column for hydrate formation on a rising bubble.
- Subtask 3.3: Measure gas loss and evolution of the bubble structure during a simulated rise through the water column.
- Subtask 4.1: Analysis of plume data acquired by NOAA OE
- Subtask 4.2: Place US Atlantic margin seeps in regional and global context of gas hydrate system dynamics

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.

- Weinstein, A., L. Navarrete, C. Ruppel, T. C. Weber, M. Leonte, M. Y. Kellermann, E. C. Arrington, D. L. Valentine, M. I. Scranton, and J. D. Kessler. Determining the flux of methane into Hudson Canyon at the edge of methane clathrate hydrate stability, *Geochem. Geophys. Geosyst.*, 17, 3882–3892 (2016), doi:10.1002/2016GC006421.

- X. Fu, L. Cueto-Felgueroso, and R. Juanes. Thermodynamic coarsening arrested by viscous fingering in partially-miscible binary mixtures. *Physical Review E*, 94, 033111 (2016), doi:10.1103/PhysRevE.94.033111.

- X. Fu, L. Cueto-Felgueroso, and R. Juanes. Viscous fingering with partially miscible fluids. Submitted for publication.

- Ruppel, C. D., and J. D. Kessler. The interaction of climate change and methane hydrates, *Rev. Geophys.*, 54 (2016), doi:10.1002/2016RG000534.

3.1.2 Conference papers

- Waite, W.F., Weber, T., Fu, X., Juanes, R., Ruppel, C., Laboratory determination of rise rates for bubbles with and without hydrate shells, Oral presentation and conference paper to be given at the 9th International Conference on Gas Hydrates, Denver, CO, June 25-30, 2017.

- X. Fu, J. Jimenez-Martinez, M. Porter, L. Cueto-Felgueroso, R. Juanes, Experiments and phase-field modeling of hydrate growth at the interface of migrating gas fingers, Oral presentation and conference paper to be given at the 9th International Conference on Gas Hydrates, Denver, CO, June 25-30, 2017.

- J. Jimenez-Martinez, M. Porter, X. Fu, L. Cueto-Felgueroso, H. S. Viswanathan, J. W. Carey, R. Juanes, Physics of hydrate-encrusted bubbles during depressurization: Insights from 2D experiments and phase-field modeling, Oral presentation and conference paper to be given at the 9th International Conference on Gas Hydrates, Denver, CO, June 25-30, 2017.

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 $\sim$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.

- X. Fu, L. Cueto-Felgueroso, R. Juanes, Crustal fingering: solidification of a moving interface. Presentation G1.00003, APS Division of Fluid Dynamics Meeting 2016.

- L. Cueto-Felgueroso, X. Fu, R. Juanes. Modeling multiphase, multicomponent flows at the pore scale: Wetting phenomena and non-equilibrium phase behavior. EOS Trans. AGU H44C-04, AGU Fall Meeting 2016.

- X. Fu, J. Jimenez-Martinez, M. Porter, L. Cueto-Felgueroso, R. Juanes, Experiments and phase-field modeling of hydrate growth at the interface of migrating gas fingers. EOS Trans. AGU OS54A-01, AGU Fall Meeting 2016.

- Weber, T., Acoustic observations and characterization of oceanic methane gas bubbles rising from the seabed, 172nd Meeting of the Acoustical Society of America, 28 November – 2 December, 2016, Honolulu, Hawaii. This lecture was the *Medwin Prize in Acoustical Oceanography given by ASA* (http://acousticalsociety.org/funding_resources/prizes).

- William F. Waite. Methane gas hydrates: A tale of bubbles great and small. Invited talk for the U. New Hampshire Center for Coastal and Ocean Mapping Seminar series. April 7, 2017.

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

Nothing to report.

3.3 Technologies or techniques

Phase-field models that are providing new rigorous formulations for direct numerical simulation of multiphase–multicomponent flows that account for nonequilibrium effects in phase evolution and mass transfer.

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: 0
  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 a fruitful collaboration with Joaquin Jimenez and Mark Porter from Los Alamos National Laboratory, who are conducting Hele-Shaw microfluidic experiments of controlled hydrate formation and dissociation in a water-Xenon fluid system. The direct visual observations from these experiments are proving instrumental for the validation of the phase-field models developed in this project (Tasks 2.2 and 2.3). This collaboration has already led to several joint conference presentations and conference papers, and we are working on a joint manuscript.

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 postdoctoral 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

- USGS Flow loop rise rate data sharing and concept discussions have begun with Prof. Socolofsky's NETL-supported research effort at Texas A&M (DE-FE0028895, Dynamic behavior of natural seep vents: Analysis of field and laboratory observations and modeling).
- Our phase-field models of multiphase flow and hydrate formation/dissociation are allowing interpretation of microfluidic-cell experiments in collaboration with Los Alamos National Laboratory.
- Medwin Prize in Acoustical Oceanography given by the Acoustical Society of America (http://acousticalsociety.org/funding_resources/prizes), awarded to Thomas Weber.

5.2 Impact on other disciplines

- The joint work by Carolyn Ruppel and Thomas Weber was prominently featured in a summary article written in AGUs weekly newspaper EOS in 1st quarter FY17.
- The development of phase-field models is starting to impact the Physics community (via published papers in *Physical Review* journals) and the computational mechanics community, by providing new rigorous formulations of multiphase–multicomponent flows.

5.3 Impact on the development of human resources

The project is supporting the training of graduate students, which is one of the key missions of the academic institutions in the project (MIT, UNH)

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

A medium-pressure flow loop has been constructed at the U.S. Geological Survey's Woods Hole Coastal and Marine Science Center. Flow loop has been tested and used for quantitative rise rate measurements and qualitative observations of bubble evolution with and without hydrate shells. Device development will continue with the establishment of an acoustic backscatter capacity for investigating response differences between hydrate-free and hydrate-coated bubbles. Device and data are available for collaborative research efforts. Contact William Waite (wwaite@usgs.gov).

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	31-Mar-16	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		no-cost extension: 30-sep-2017
12	3.3	Measure gas-loss rate at high initial pressures										X			1-Oct-15	31-Mar-16			no-cost extension: 30-sep-2017
13	4.2	Extend bottom water temperature database										X			1-Jul-15	31-Mar-16	1-Jul-15	31-Mar-16	
14	2.4	Model formulation and comparison with field observations												X	1-Oct-15	30-Sep-16			no-cost extension: 30-sep-2017
15	all	Manuscripts submitted / Final project synthesis and report												X	1-Oct-14	30-Sep-16			no-cost extension: 30-sep-2017

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