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

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

DUNS Number: 001425594

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National Energy Technology Laboratory

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Ruben Juanes

Digitally signed by Ruben Juanes
DN: cn=Ruben Juanes, o=MIT, ou, email=juanes@mit.edu, c=US
Date: 2014.05.19 23:03:47 -05'00'

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

We have finalized a revised Project Management Plan, which has been agreed upon with DOE. We have also participated, via Webex, in the kick-off meeting for the project. Juanes presented an overview of the administrative aspects of the project; and Juanes, Waite and Ruppel described the technical content of the various tasks of the projects (Tasks 2, 3 and 4, respectively).

Carolyn Ruppel gave an invited keynote lecture at the Gordon Research Conference on Natural Gas Hydrates Systems in March.

MIT and UNH have staffed the project with graduate students.

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

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 2.1: Phase-field modeling of a static gas bubble

Introduction. We start by constructing a phase-field model to describe a static methane bubble dissolving in methane-free water in 2D. This is a two-phase (gas and liquid), two-component (CH_4 and H_2O) system where CH_4 and H_2O are miscible. We do not consider momentum effect for now so that mass transfer is driven by diffusion only in this system. We define C as the mass fraction of CH_4 and $C \in [0, 1]$. Initially, $C = 1$ inside the methane bubble and $C = 0$ in the water phase (figure 1a). Evidently, C is also a good indicator for fluid phase, where $C = 1$ is equivalent to the gas phase and $C < 1$ is the liquid phase. For this reason, C has become the natural choice for the phase variable in our model.

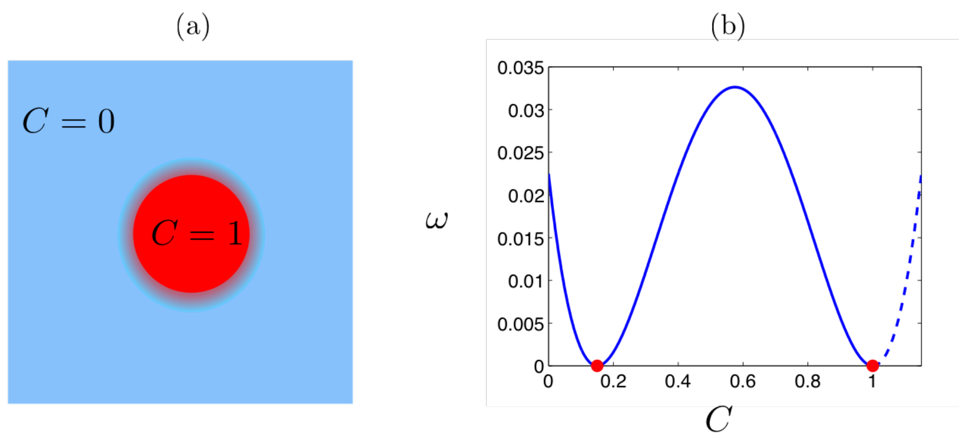

Figure 1: (a) Illustrative diagram of the 2D setup of a static methane bubble (red, $C = 1$) submerged in water (blue, $C = 0$). (b) the double-well potential for bulk energy.

We adopt the van der Waals free energy (F) description of a two-phase system van der Waals [1979]:

$$F = \beta\omega(C) + \frac{1}{2}\alpha|\nabla C|^2 \tag{1}$$

The first term in Eq.(1) is the bulk energy associated with each fluid phase, often described using a double-well potential:

$$\omega(C) = (C_{\text{sat}} - C)^2(1 - C)^2, \tag{2}$$

where C_{sat} is the saturation mass fraction of CH_4 in water, which we take here as $C_{\text{sat}} = 0.15$. At thermodynamic equilibrium, the free energy of the system should be minimized, which is why ω reaches its local minima at $C = 0.15$, indicating full saturation of gas in the liquid phase, and at $C = 1$, indicating pure gas phase equilibrium (Figure 1b). The second term in Eq.(1) is the gradient energy term, describing the interfacial energy associated with the liquid-gas phase boundary. The chemical potential, ψ, is the rate of change, computed as a variational derivative, of F with respect to the phase variable C :

$$\begin{aligned}\psi &= \frac{\delta F}{\delta C} = \frac{\partial F}{\partial C} - \nabla \cdot \left(\frac{\partial F}{\partial (\nabla C)} \right) \\ &= -2\beta (C_{\text{sat}} - C)(1 - C)(1 - 2C + C_{\text{sat}}) - \alpha \nabla^2 C\end{aligned} \tag{3}$$

Extending the work by van der Waals [1979], Cahn and Hilliard proposed that the time evolution of phase variable is subject to the interfacial diffusive flux and this flux is proportional to the chemical potential gradient [Cahn and Hilliard, 1958]:

$$\frac{\partial C}{\partial t} - \nabla^2 \psi = 0 \tag{4}$$

To solve for the phase evolution equation (Eq. (4)), we assume a periodic 2D domain and compute the spatial derivative with the spectral method. We integrate in time using the backward Euler scheme and take $\alpha = \beta = 1$. In a dimensionless square of size 1×1 containing methane-free water, the methane bubble is initially centered in the domain with a radius $r_{\text{initial}} = 1/4$ (figure 2, top left). Due to undersaturation of methane in the water, the bubble starts to shrink in size as a result of CH_4 dissolution; meanwhile, C in water phase is increasing (figure 2 top right and bottom left). After some time, bubble dissolution will have introduced enough CH_4 into the water phase such that $C_{\text{liquid}} = C_{\text{sat}}$ and the system reaches the thermodynamic equilibrium; the bubble stops shrinking (figure 2 bottom right).

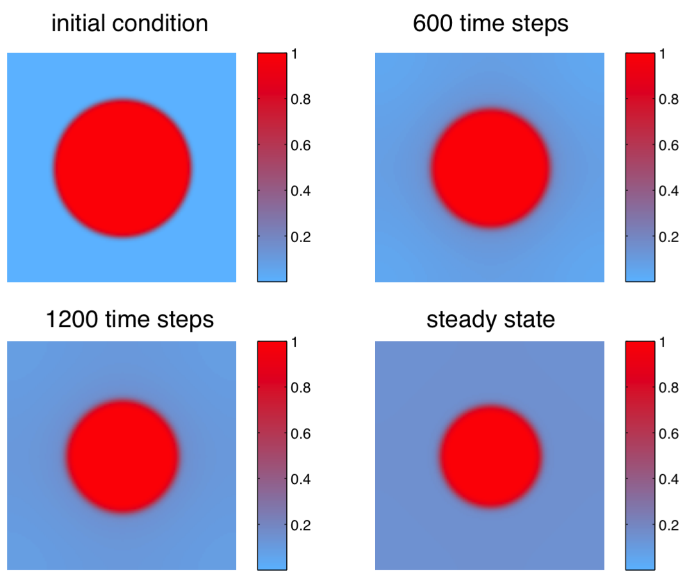

Figure 2: A single methane bubble dissolving into water. Color scale corresponds to methane mass fraction (C).

The next step to continue this modeling effort is to incorporate momentum effects into the system, so that we can consider the scenario where a bubble is rising in the water column (hydrate-free, for now). To achieve this, we plan to couple Eq.(4) with the Navier-Stokes-Korteweg (NSK) equation and assume incompressibility:

$$\nabla \cdot \mathbf{u} = 0 \tag{5}$$

$$\rho(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u}) = -\nabla p + \rho \mathbf{g} - \nabla \cdot \tau - \nabla \cdot \varsigma \tag{6}$$

$$\varsigma = \lambda \left(C\Delta C + \frac{1}{2}|\nabla C|^2 \right) \mathbf{I} - \lambda \nabla C \otimes \nabla C \tag{7}$$

The NSK equation (Eq.(6)) is similar to the original Navier-Stokes equation but with an extra term in the end, $-\nabla \cdot \varsigma$, namely the Korteweg tensor, where ς is defined in Eq.(7). The Korteweg tensor captures the momentum effect introduced in a two-phase system as a result of surface tension at the phase boundary. Future work entails solving the system of equations (Eq. (4, 5-7)) in 2D and 3D and extending the formulation to incorporate the solid phase of methane hydrate.

References

J. W. Cahn and J. E. Hilliard. Free energy of non-uniform systems. I. Interfacial free energy. *J. Chem. Phys.*, 28:258–267, 1958.

J. D. van der Waals. The thermodynamic theory of capillarity flow under the hypothesis of a continuous variation of density (1893). *J. Stat. Phys*, 1(20), 1979. (English translation by J. S. Rowlinson).

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. Following a late 2013 group meeting at the University of New Hampshire (UNH) and a site visit to see the high-pressure bubble-capture facility at the Colorado School of Mines (CSM) in action, we finalized our bubble capture chamber design. The complete bubble-capture section, as well as the water-flow-conditioning section leading into the capture chamber, will be optically clear. These sections will be linked and held together with custom-machined metal pieces.

Fabrication Activities.

Bubble-capture chamber:

- Optically-clear pressure housing has been acquired. This housing material is suitable for operations at ~5 MPa (700 psi), an upper bound temperature for the xenon system because xenon reverts to a liquid state near this pressure at 10°C (50°F) [*Ohgaki et al*., 2000].
- An optically-clear bubble-capture cone (see examples in *Maini & Bishnoi* [1981], *Anderson et al*. [2012]) has been manufactured and custom-fitted into the clear-pressure housing.
- Chamber-coupling and chamber-support pieces: we have consulted the machinist, incorporated his design simplifications and given him our final plans. Stainless steel stock has been acquired, rough-cut to size, and is currently 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 purchased and is under construction.
- Building modifications necessary to supply the power required by the water-circulation pump are underway. The three-phase-transformer required for the water-circulation pump has been acquired.
- A high-pressure flow meter suitable for our expected flow rates has been identified, and the ordering process is underway.

References

Anderson, K., G. Bhatnagar, D. Crosby, G. Hatton, P. Manfield, A. Kuzmicki, N. Fenwick, J. Pontaza, M. Wicks, S. Socolofsky, C. Brady, S. Svedeman, A. K. Sum, C. Koh, J. Levine, R. P. Warzinski, and F. Shaffer (2012), Hydrates in the Ocean beneath, around, and above Production Equipment, Energy & Fuels, 26(7), 4167-4176.

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.

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

We have received raw data, previously archived on tape at the National Geophysical Database Center, corresponding to newly-discovered seeps along the US Atlantic margin [Ruppel et al., in revision]. These data, which were collected in recent years by the NOAA Ship *Okeanos Explorer*, are comprised of both split-beam echosounder (SBES) and multibeam echosounder data. Both SBES and MBES data will be examined to extract parameters related to the evolution of the bubbles as they rise through the water column (e.g., the minimum observation depth). The SBES data will also be examined to extract vertical target strength profiles building upon the techniques used by Weber et al. [2014], as well as the master's thesis work of UNH student Kevin Jerram. The first step in this process is to catalog what subset of seeps have been observed with the SBES, which has a narrower field of view than the MBES, and to gain an overall sense of the data. This initial step, which is nearing completion, involves building a visual 'scene' in which the data can be easily manipulated (an example of this is shown in Figure 1), and correlating the SBES and MBES observations.

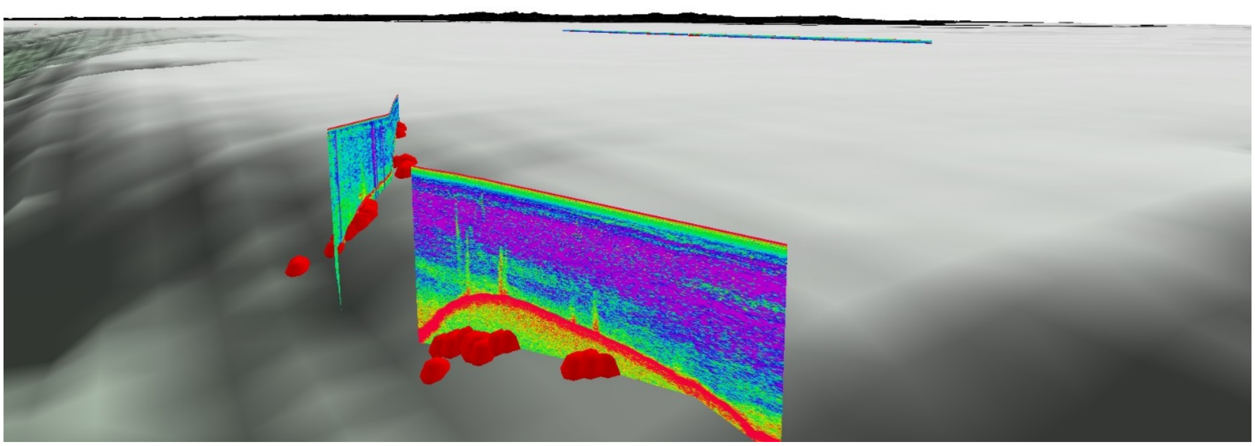

Figure 3. Methane seeps (vertical plumes) observed in the SBES data overlaid on bathymetry (ETOP02). This scene is looking from the shelf-break northward, with Cape Cod in the background. The red dots correspond to locations of methane seeps observed in the MBES data.

Weber, T. C., Mayer, L., Jerram, K., Beaudoin, J., Rzhanov, Y., & 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*.

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), who just recently started to work on the project (see section 4 of this report). A graduate student at UNH will also join the project shortly.

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			

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

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