

# Oil & Natural Gas Technology

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Quarterly Research Performance Progress Report (Period ending 09/30/2014)

## THCM Coupled Model For Hydrate-Bearing Sediments: Data Analysis and Design of New Field Experiments (Marine and Permafrost Settings)

Project Period (10/1/2013 to 09/30/2015)

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Office of Fossil Energy

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## ACCOMPLISHMENTS

*The experimental study of hydrate bearing sediments has been hindered by the very low solubility of methane in water (lab testing), and inherent sampling difficulties associated with depressurization and thermal changes during core extraction. This situation has prompted more decisive developments in numerical modeling in order to advance the current understanding of hydrate bearing sediments, and to investigate/optimize production strategies and implications. The goals of this research is to addresses the complex thermo-hydro-chemo-mechanical THCM coupled phenomena in hydrate-bearing sediments, using a truly coupled numerical model that incorporates sound and proven constitutive relations, satisfies fundamental conservation principles. This tool will allow us to better analyze available data and to further enhance our understanding of hydrate bearing sediments in view of future field experiments and the development of production technology.*

## ACCOMPLISHED

The project management plan (PMP, Task 1) and the selection of the PhD Students working during the 1<sup>st</sup> year of the project were competed and informed in the first quarterly report. The main accomplishments for this first period address Tasks 2, 3 and 4 of the original research plan, and include:

- Student training.
- Literature review.
- Update of constitutive equations.
- Update of THCM-Hydrate.
- Close-form analytical solutions.
- Numerical analyses

### **Training**

The training of the two PhD students working in this project has continued during this period. As for Mr. Xuerui (Gary) Gai (i.e. the Ph.D. student at TAMU), he is progressing in the understanding and modeling of problems involving has hydrate sediments. As for Mr. Zhonghao Sun (the Ph.D. student at GT), he has continued with the implementation of analytical solutions in MATLAB and other pieces of software. Both students have progressed positively with their coursework at their respective universities.

### **Literature review**

The literature review (Task 2a) was completed during the previous period.

### **Update of constitutive equations**

The update of the constitutive laws for hydrate-bearing marine sediments (Task 2b–ongoing) and HBS in the permafrost (Task 2c – ongoing) were completed during this period.

The section below (page 6) entitled: “IT Tool for HBS” briefly presents a tool that has been developed in the Mathcad computer software to assist numerical and analytical analyses involving gas hydrates sediments.

### **Update of THCM-Hydrate**

The update of the numerical code “THCM-Hydrate” was completed during this reporting period. The main following activities for the different subtasks are highlighted:

- Validation of implemented functions (Task 3a – completed), including
  - The implementation and validation of constitutive equations and phase relationships for the different phases contemplated in the proposed HBS formulation was completed during this period.
- Synthetic numerical tests (Task 3b – completed), including
  - Synthetic numerical tests looking at the validation of the proposed numerical approach have been performed. One case involving depressurization of the HBS is presented in this report (page 11).
- Code comparison analyses (Task 3c – ongoing), including
  - We have continued with the simulations aimed at comparing our code against other ones developed to model the behavior of HBS.

### **Close-form analytical solutions**

The review on the main governing evolution laws, parameters, dimensionless ratios and simplifying assumptions for HBS dissociation has been continued during this period.

### **Numerical analyses**

The numerical analyses solving field production experiments as boundary value problems have been started in this period.

### **Plan - Next reporting period**

We will advance analytical and numerical fronts to enhance our code to solve coupled THCM problems involving with HBS, with renewed emphasis on simulating the natural processes under *in-situ* conditions and gas production.

Milestones for each budget period of the project are tabulated next. These milestones are selected to show progression towards project goals.

	Milestone Title Planned Date and Verification Method	Actual Completion Date	Comments
Title Related Task / Sub- tasks Planned Date Verification method	Complete literature review 2.0 / 2.a March 2014 Report	March 2014	Completed
Title Related Task / Sub- tasks Planned Date Verification method	Complete updated Constitutive Equations 2.0 / 2.b & 2.c June 2014 Report (with preliminary validation data)	July 2014	Completed
Title Related Task / Sub- tasks Planned Date Verification method	Validate new THCM constitutive equations 3.0 / 3.a, 3.b & 3.c September 2014 Report (with first comparisons between experimental and numerical results)	September 2014	Completed
Title Related Task / Sub- tasks Planned Date Verification method	Complete close-form analytical solutions 4.0 / 4.a & 4.b February 2015 Report (with analytical data)	February 2015	Progress- ing as planned
Title Related Task / Sub- tasks Planned Date Verification method	Complete numerical analyses 5.0 / 5.a, 5.b & 5.c July 2015 Report (with analytical and numerical data)	July 2015	Progress- ing as planned
Title Related Task / Sub- tasks Planned Date Verification method	Complete THCM-Hydrate code modifica- tions 6.0 / 6.a June 2015 Report (with numerical data)	June 2015	Progress- ing as planned
Title Related Task / Sub- tasks Planned Date Verification method	Complete production optimization 7.0 / 7.a, 7.b, 7.c, 7.d & 7.e September 2015 Report (with numerical data)	September 2015	Progress- ing as planned

## IT Tool for Hydrate Bearing Sediments

A database compiling the main published data related to hydrate bearing sediments was developed using the Math-cad software. This IT tool compiles the main constitutive equations proposed for the thermo, hydraulic and mechanical problems; including their dependences on temperature, fluids pressures, stresses and water chemistry. The database also incorporates the phase laws and phase boundaries (including mixed gases) associated with HBS. The main model parameters and their typical range of variation are key components of the database as well.

The IT tool plays a central role in analysis involving HBS. As shown in Figure 1, the IT tool collects the experimental information gathered from different sources, including in-situ investigation, data from Pressure Core Characterization Tools (PCCTs) and experimental information obtained in the laboratory from disturbed samples. As shown in the scheme below, the IT tool is then used to feed the models with appropriate constitutive equations, phase laws and parameters needed in the numerical/analytic simulations. The proposed IT tool is the nexus between the existing information and current knowledge about HBS and the numerical/analytic models. In summary, this is a key tool in HBS analysis because:

- Serve as a repository for constitutive equations, phase laws and parameters for HBS.
- Provide best estimation of properties given limited input
- Guide the back-analysis of test data
- Provide robust correlations
- Assist the validation of available models
- Provide consistent set of parameters for THCM simulators

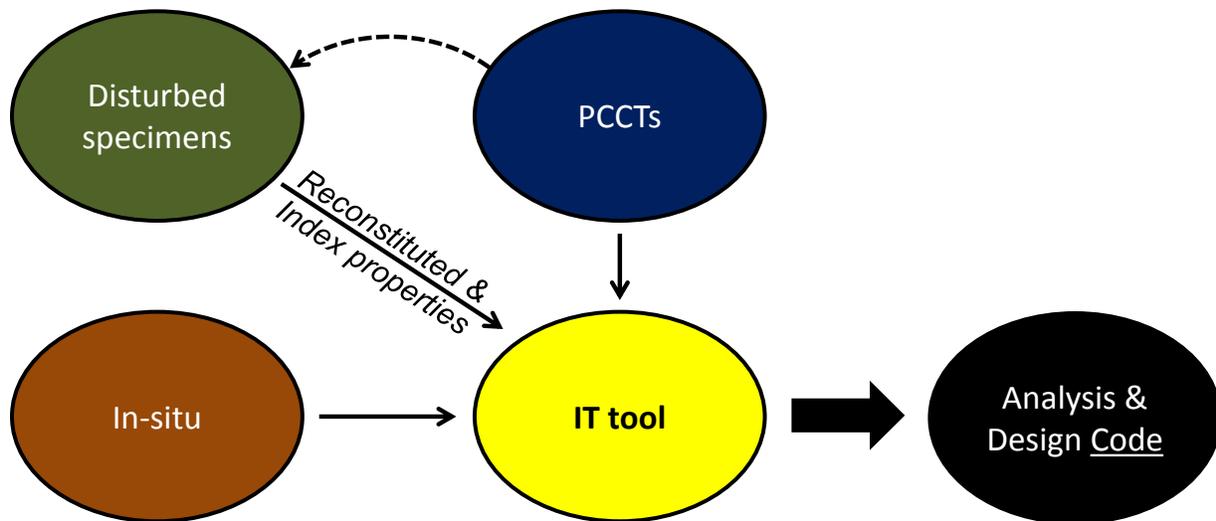


Figure 1. Scheme showing the link between the proposed IT tool, the source of data (for HBS) and the modeling.

The IT tool will be updated and upgraded as new experimental information and insight on HBS behavior become available. This task is shared/complements other projects.

Table 1 presents the list of properties contemplated in the IT tool and Table 2 shows (as an example) some of the constitutive laws contemplated for the mechanical problem. Likewise, constitutive equations for the thermal and hydraulic problems have been incorporated in the database.

Table 1. List of Properties

	Properties
Phase Boundaries	Hydrate phase
	Gas mixtures
	Liquid chemistry
Mechanical	Strength
	Stiffness
	Wave velocities
Hydraulic	Soil water characteristic curve
	Hydraulic conductivity
	Permeability of HBS
	Relative permeability
Thermal	Thermal conductivity
	Heat capacity

Table 2. Mechanical properties

Properties	Formulation	Reference
Strength	$q = \frac{\sin \phi'}{1 - \sin \phi'} \sigma_3' + \frac{\cos \phi'}{1 - \sin \phi'} c' + \alpha S^\beta$	Santamarina and Ruppel (2008)
	$q = a\sigma_3' + bq_h \left(\frac{S_h}{n}\right)^2$	Miyazaki et al. (2012)
Stiffness	$E_{50} = a \left(\frac{\sigma_3'}{1kPa}\right)^b + cE_{50} S_h^d$	Jung et al. (2012)
S-wave velocity	$V_s = \sqrt{\left(\frac{V_h S_h^2}{n}\right)^2 \theta + \left[\alpha \left(\frac{\sigma_v' + \sigma_h'}{2kPa}\right)^\beta\right]^2}$	Santamarina and Ruppel (2008)
	Effective medium model	Helgend et al. (1999), Ecker et al. (1998)
P-wave velocity	$V_p^2 = V_s^2 \left[ \frac{4}{3} + \frac{2(1 + \nu_{sk})}{3(1 - 2\nu_{sk})} \right] + \frac{1}{\rho_{HBS}} \left[ \frac{n(1 - S_h)}{B_w} + \frac{nS_h}{B_h} + \frac{1 - n}{B_m} \right]$	Santamarina and Ruppel (2008)
	Effective medium model	Helgend et al. (1999), Ecker et al. (1998)

Figures 2a) and 2b) presents examples of comparisons between experimental data and results from proposed constitutive equations for mechanical properties. Figure 2a) is related to predicted strength by Santamarina and Ruppel (2008) and measured strength; while Figure 2b) is associated with the predicted strength by Miyazaki et al. (2012) and measured strength.

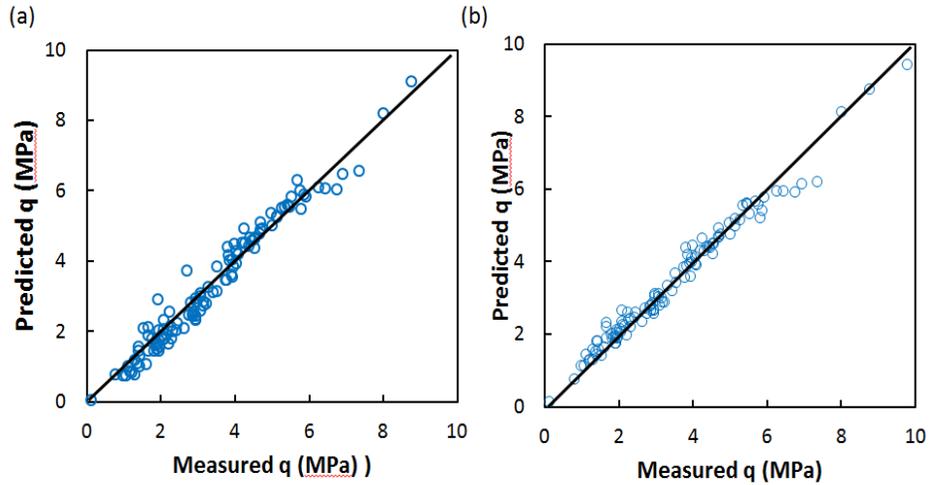


Figure 2. Examples of data and formulations for mechanical properties: a) comparison of predicted strength by Santamarina and Ruppel (2008) and measured strength; and b) comparison of predicted strength by Miyazaki et al. (2012) and measured strength.

Table 3 shows some typical phase properties incorporated in the database. Figures 3a) and 3b) present the functions for hydrate phase equilibrium in seawater and freezing point of seawater respectively.

Table 3. Phase properties

Properties	Formulation	Reference
Hydrate phase equilibrium	$P [MPa] = 1MPa \times e^{\frac{a+b}{T/1K}}$	Sloan and Koh (2008)
	Equation considering effect of salinity	Tishchenko et al. (2005)
Gas density Liquid density	Van der Waals Equation of State	Beyer (2005)
	Peng-Robinson Equation of State	Peng and Robinson (1976)
	Duan's Equation of State	Duan et al. (1992)
Gas viscosity	$\mu_g [Pa \cdot s] = 1.03 \times 10^{-5} [Pa \cdot s] \left[ 1 + 0.053 \frac{P}{MPa} \left( \frac{280K}{T} \right)^3 \right]$	Younglove and Ely (1987)
Liquid viscosity	$\mu_w [Pa \cdot s] = 2.1 \times 10^{-6} [Pa \cdot s] e^{\frac{1808.5K}{T}}$	Sanchez and Santamarina
Freezing point of seawater	$T_f = -0.0575S(\%) + 1.710523 \times 10^{-3} S(\%)^{3/2} - 2.154996 \times 10^{-4} S(\%)^2 - 0.0753P$	Fofonoff and Millard (1983)

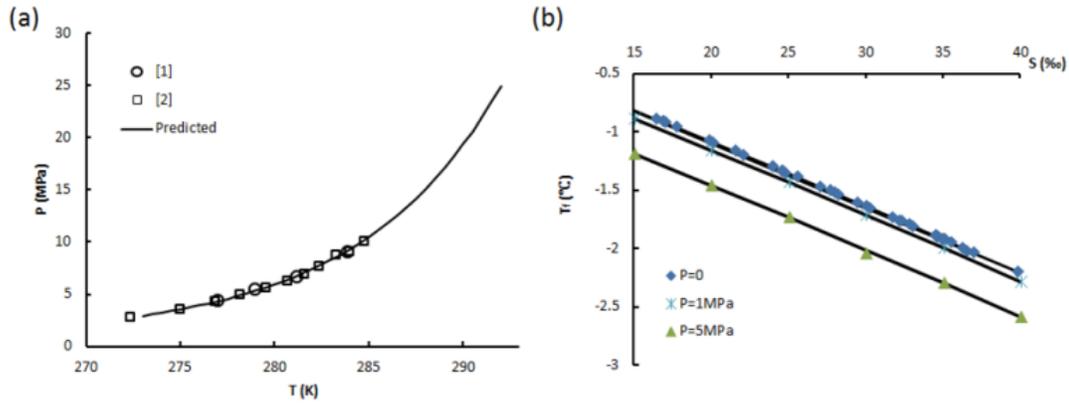


Figure 3. Phase boundaries: a) hydrate phase equilibrium in seawater; and b) freezing point of seawater

The user interface allows a readable introduction for each property; including: “Descriptions”, “Definitions and parameters”, “Functions/ scripts”, and “Calculations/examples”. Figure 4 shows a Mathcad based IT tool prototype.

<b>PHASE BOUNDARIES</b>
Descriptions _____
Definitions and parameters _____
functions/scripts _____
Calculations/examples _____
<b>SMALL STRAIN PROPERTIES</b>
Description _____
Definitions and parameters _____
Functions/scripts _____
Calculations/examples _____
<b>LARGE STRAIN PROPERTIES</b>
Description _____
Definitions and parameters _____
Functions/scripts _____
Calculations/examples _____
<b>HYDRAULIC PROPERTIES</b>
Descriptions _____
Definitions/parameters _____
Functions/scripts _____
Calculations/examples _____
<b>THERMAL PROPERTIES</b>

Figure 4. Mathcad based IT tool prototype.

Input, feature, and reference of functions were introduced in “Descriptions”, while parameters in functions were defined in “Definitions and parameters”, scripts can be found in “Functions/scripts”, and a simple example of application of functions can be found in “Calculations/examples”.

Model predictions can be made by providing input and choosing proper parameters. Also recommended parameters are listed in the “Parameters to choose” section. Figures 5 show examples of the Mathcad based IT tool interfaces for parameter input/selection.

Input		Parameters to choose	
Seawater properties	Pressure	$P := 1\text{MPa}$	Density $\text{opt\_density} := 1$  (opt==1, Van der Waals equation; opt==2, Peng-Robenson equation; opt==3, correlation from Sanchez and Santamarina)
	Temperature	$T_w := 273\text{K}$	
	Salinity	$S_w := 35$	
Sediment pore fluid	Water saturation	$S_w := 0.7$	Recommended values for parameters (Lee et al., 2010)
	Hydrate saturation	$S_h := 0.2$	
	Gas saturation	$S_g := 0.1$	
	Ice saturation	$S_i := 1 - S_w - S_h - S_g = 0$	
Sediment properties	Porosity	$n := 0.4$	Soil type $\alpha$ (m/s) $\beta$ $\theta$
	Void ratio	$e := \frac{n}{1-n} = 0.667$	
	Specific surface	$S_s := 1000 \frac{\text{m}^2}{\text{kg}}$	
	Poisson's ratio	$\nu_{sk} := 0.15$	
Sediment grain	Specific gravity	$G_s := 2.7$	Recommended values Soil type    a    b
	Density	$\rho_m := 1000 \frac{\text{kg}}{\text{m}^3}; G_s = 2.7 \times 10^3 \frac{\text{kg}}{\text{m}^3}$	
	Bulk stiffness	$B_{hbs} := 45\text{GPa}$	
	Thermal conductivity	$\lambda_m := 0.73 \frac{\text{W}}{\text{m}\cdot\text{K}}$	
	Heat capacity	$c_m := 2500 \frac{\text{J}}{\text{kg}\cdot\text{K}}$	
Hydraulic conductivity		$b_k := 3$	Recommended values Soil type $b_k$

Output	
Density	Gas density $\rho_g := \rho_g(P, T, \text{opt\_density}) = 7.255 \frac{\text{kg}}{\text{m}^3}$
	HBS density $\rho_{hbs} := \rho_{hbs}(n, S_w, S_i, S_g, S_h, \rho_m, P, T, \text{opt\_density}) = 1.973 \times 10^3 \frac{\text{kg}}{\text{m}^3}$
Phase boundary	Dissociation pressure $P_{dis} := P_{dis}(T, S) = 2.935 \times 10^6 \text{Pa}$
	Freezing point $T_f := T_f(P, S) = 271.152 \text{K}$
Wave velocity	S-wave velocity $v_s := v_{s\_sr}(S_h, n, \alpha, \beta, \theta, \nu_{sk}, \sigma_h) = 425.072 \frac{\text{m}}{\text{s}}$
	P-wave velocity $v_p := v_{p\_sr}(v_s, \nu_{sk}, \rho_{hbs}, n, S_h, B_m) = 1.835 \times 10^3 \frac{\text{m}}{\text{s}}$
Stiffness	Small-strain stiffness $G := \rho_{hbs} \cdot v_s^2 = 3.565 \times 10^8 \text{Pa}$
Strength	Max q $q := S_u(S_h, n, \sigma_h, a, b) = 1.055 \times 10^6 \text{Pa}$
	Hydraulic conductivity

Figure 5. Example of Mathcad based IT tool interfaces for parameter input/selection.

## NUMERICAL ANALYSIS - CODE VALIDATION

The validation of the *THCM-hydrate* code has continued during this period. In this section we present the validation of the code against experimental data gathered in the lab from a ventilation test. A pressure core recovered from hydrate bearing sediments in the Krishna-Godavari Basin was depressurized while measuring the internal temperature in the sediment at the center of the core (Yun et al., 2010). The main goal of this exercise is to check if the mathematical formulation and associated for gas hydrates (presented in previous reports) is able to capture the main features observed in the depressurization test.

The samples used in the experiment were part of the first Indian National Gas Hydrate Program expedition (NGHP expedition 01) which took place in the spring and summer of 2006 across the Indian Ocean shoreline. The samples were recovered in water depths ranging between 907 and 2674 m. It included 6 geophysical studies, drilling at 21 sites, logging while drilling of 12 boreholes, and the recovery of both standard and pressure cores. Five pressure cores were recovered at site NGHP-01-21, transferred into storage chambers under hydrostatic pressure, and kept at 4 °C and 13 MPa fluid pressure for subsequent characterization and analysis.

Three pressure cores were tested at an onshore facility in Singapore. The test program included the measurement of elastic wave velocity, shear strength, and electrical conductivity, followed by fast depressurization of the sub-sampled core round. A specially designed “instrumented pressure testing chamber” (IPTC) was used to characterize the cores. The IPTC permits obtaining small-strain P-wave (using p-inducers) and S-wave (using bender elements) velocities, large-strain undrained shear strength (using a cone-shaped penetrometer), electrical conductivity profile (using an electrical needle probe), and internal core temperature (using a thermocouple). The IPTC device along with the peripheral electronics horizontal displacement manipulator and X ray imaging system was housed in a 6.1 m long refrigerated container.

The IPTC was used in previous studies to inspect Gulf of Mexico samples and further details are available in Yun et al. (2006). The IPTC chamber was filled with chilled water (~4 °C) and 13 MPa of fluid pressure was maintained. After conducting initial X-ray imaging, controlled depressurization tests were conducted on the samples. The instrumentation of the sample during the test was conducted at intervals along the length of the samples based on the points of interest ascertained through the X-ray images. The location of the instrumentation for one such sample is shown in **Error! Reference source not found.**

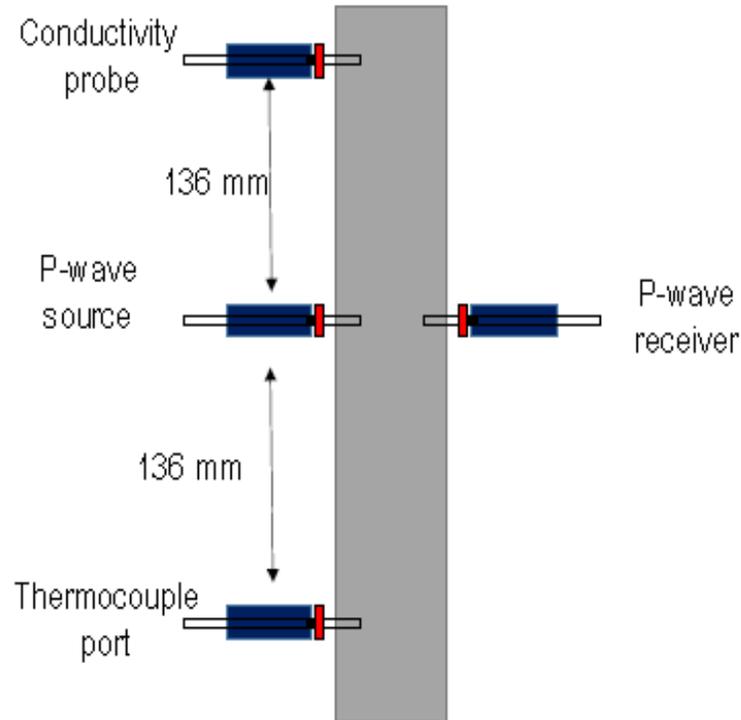


Figure 6. Instrumentation of the tests for sample 21C-02E (modified after Yun et al., 2010)

The total length of the sample used in the depressurization was 380 mm (**Error! Reference source not found.6**). The fluid pressure of the IPTC chamber was slowly reduced until the fluid pressure dropped to 0. Figure 7 shows the path in the P-T plane followed during the depressurization experiment.

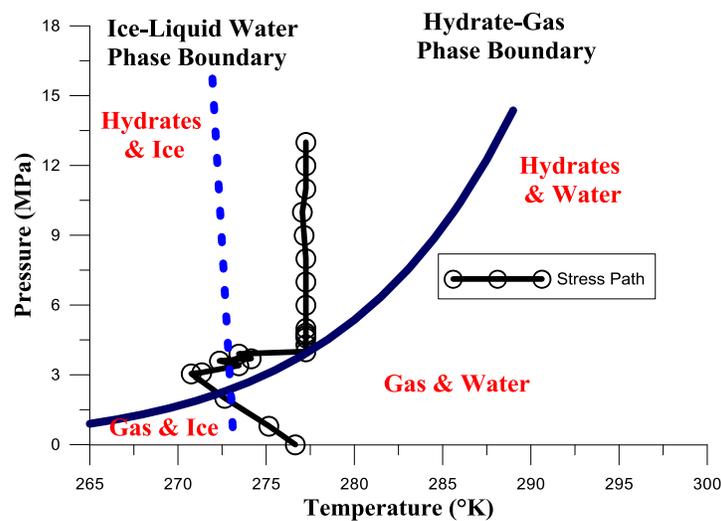


Figure 7. Path in the P-T plane followed during of a pressure core gathered from the Krishna-Godavari Basin (reported by Yun et al., 2009).

It can be observed that the decrease of pressure in the stability zone was almost vertical. Once the P-T path reached the phase boundary dissociation started. Because of the endothermic character of the hydrate dissociation, the sample cooled down during depressurization (as recorded by thermocouples, Fig. 7). This induced that the P-T path moved towards the water-to-ice transformation line, reaching freezing temperatures and leading to ice formation.

The change in the temperature, p-wave velocity, electrical conductivity and the amount of gas generated was recorded during the experiment. The relevant results of these tests are shown in Figures 8a) and 8b). As expected, no gas was produced during the depressurization in the stability zone. However, as soon as the P-T path reached the phase boundary (i.e. for a fluid pressure around 4 MPa), the production of gas started, and it continued until all the hydrate dissociated.

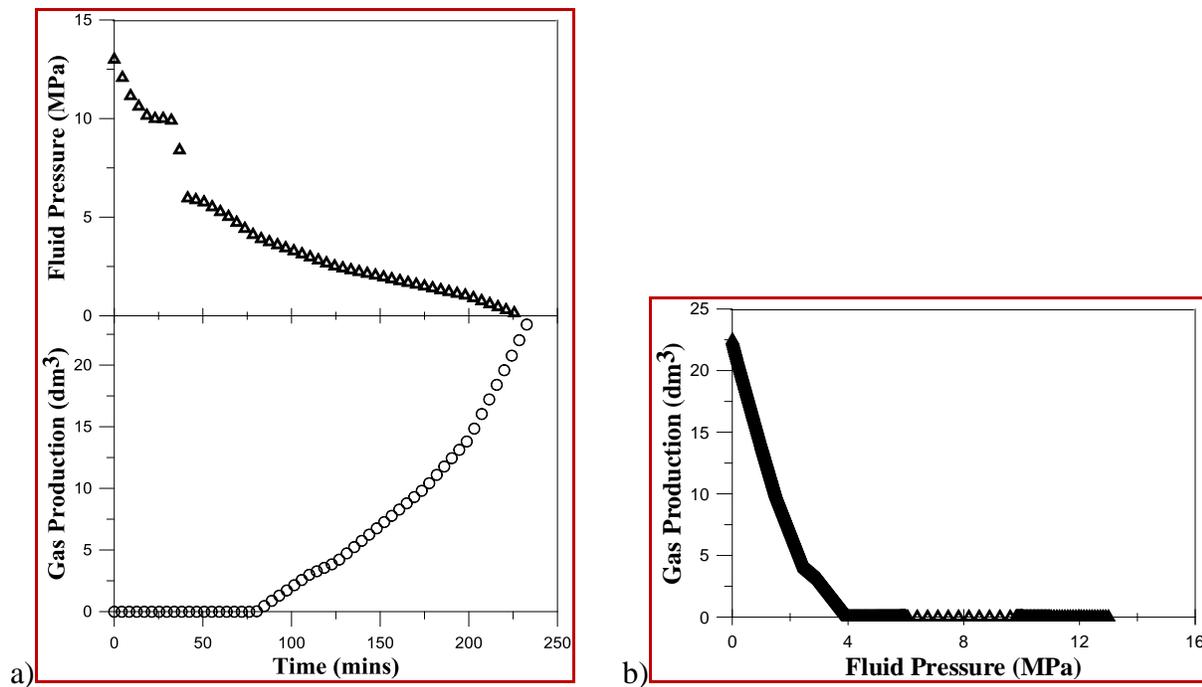


Figure 8. Evolution of the main variables recorded during the experiment: a) time evolution of pressure and gas production; and b) gas production versus fluid pressure (data gathered from the Krishna-Godavari Basin, Yun et al., 2009).

This test has been initially modeled using ‘a point level’ simulation. The main model results are presented in Figure 9. It can be seen that the model captures quite well the main pattern of HBS behavior and features observed during the experiment. Figure 9a) shows schematically the P-T imposed in the model. Figure 9b) present the P-T path predicted by the model. The model reproduces satisfactorily the cool down of the sample. The P-T paths remained on the phase boundary during gas dissociation. As in the experiment, gas started to produce when the P-T path reached the phase boundary, around 4 MPa. The model also predicts the formation of secondary ice during depressurization.

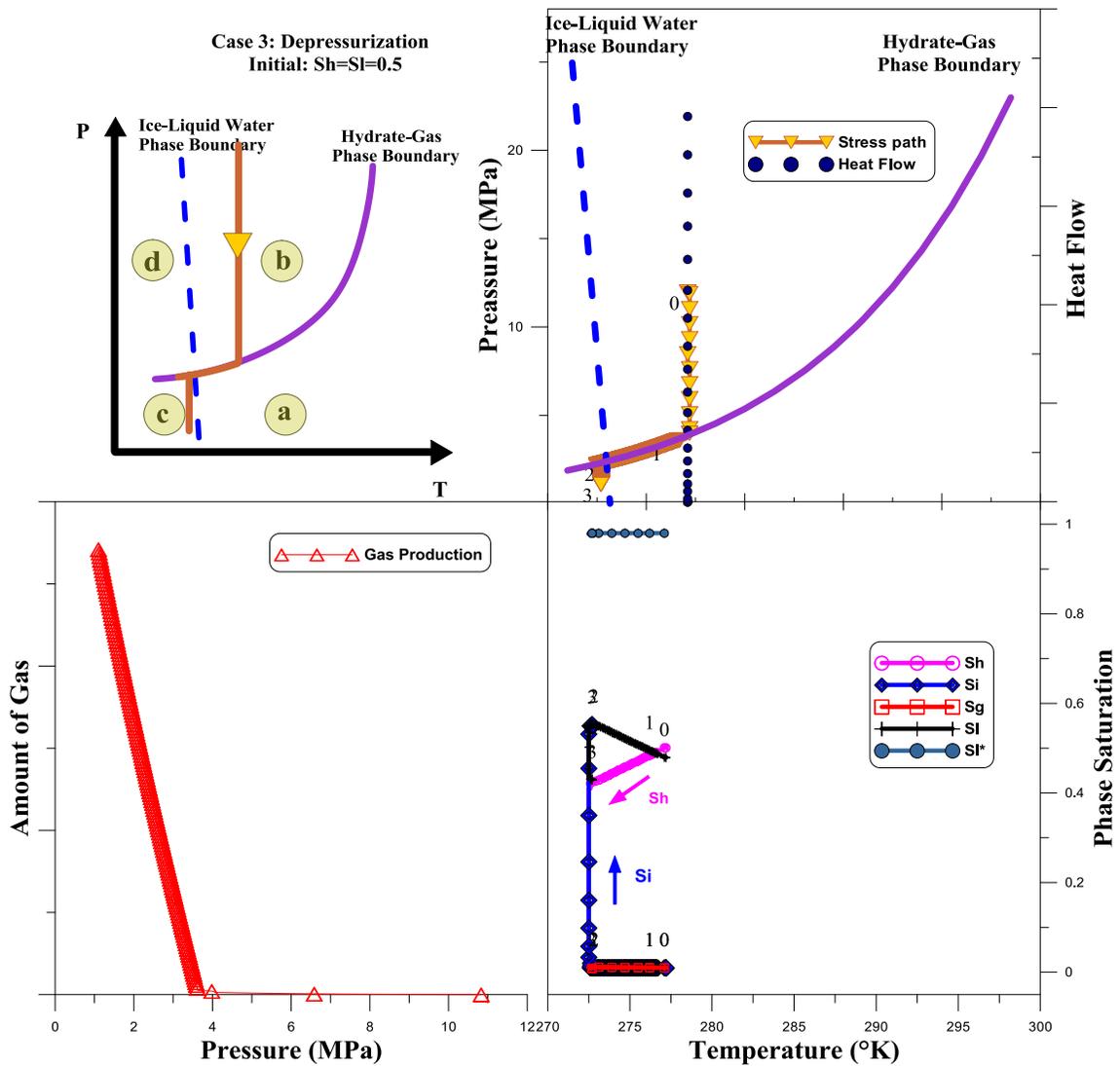


Figure 9. Results of hydrate formation by heating a) Schematic of P-T path b) P-T path plotted in the P-T plane c) Gas produced d) Phase saturation of hydrates, water (liquid), gas and ice.

A 2D simulation of this case has been started. The aim is to overcome some limitations of the point level modeling.

## References

Yun, T. S., Fratta, D., and Santamarina, J. C. (2010). "Hydrate-Bearing Sediments from the Krishna– Godavari Basin: Physical Characterization, Pressure Core Testing, and Scaled Production Monitoring." *Energy & Fuels*.

## PRODUCTS

### Publications – Presentations:

- A conference paper has been accepted for the 14<sup>th</sup> IACMAG (International Conference of the International Association for Computer Methods and Advances in Geomechanics). Kyoto Japan 22-25 September 2014 Title: “Coupled Modeling of Gas Hydrate Bearing Sediments”. Authors: M. Sanchez, J. C. Santamarina. A. Shastri & Xuerui Gai.
- A session on “Hydrate bearing soils: characterization, modeling and geomechanical implications”, has been accepted for the forthcoming AGU Fall meeting 2015, San Francisco, 15<sup>th</sup> to 19<sup>th</sup> December 2014. Marcelo Sanchez is one of the session conveners.
- Carlos Santamarina has been invited to delivered and invited lecture on hydrate bearing Sediments at AGU Fall meeting 2015.

**Website:** Publications (for academic purposes only) and key presentations are included in <http://pmrl.ce.gatech.edu/>; <http://ceprofs.civil.tamu.edu/msanchez/>

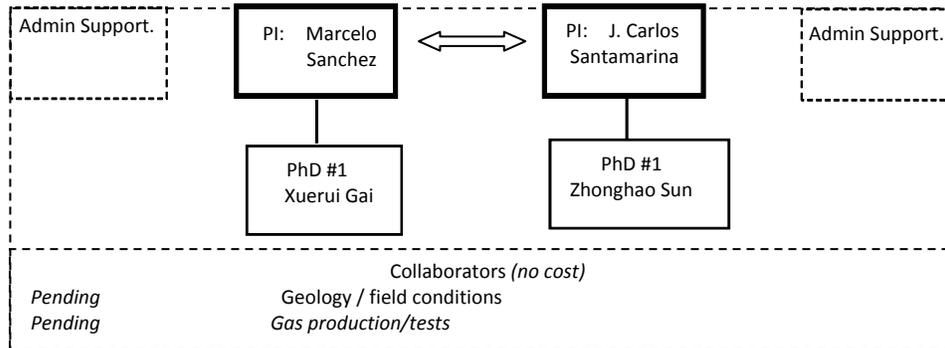
**Technologies or techniques:** None at this point.

**Inventions, patent applications, and/or licenses:** None at this point.

**Other products:** None at this point.

## PARTICIPANTS

*Research Team:* The current team is shown next.



## IMPACT

- While it is still too early to assess impact, we can already highlight the computational platform extensively validated in a wide range of coupled thermo-hydro-chemo-mechanical coupled problems (CB\_Hydrate).

## CHANGES/PROBLEMS:

None so far.

**SPECIAL REPORTING REQUIREMENTS:**

Nothing to report



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