

Quarterly Report: March 2007

Methane Recovery from Hydrate-bearing Sediments

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Submitted By:

J. Carlos Santamarina
Georgia Institute of Technology
School of Civil and Environmental Engineering
Atlanta, GA 30332-0355
Phone: (404)-894.7605
Fax: (404)-894.2278
E-mail: jcs@gatech.edu

Costas Tsouris
Oak Ridge National Laboratory
Georgia Institute of Technology
School of Civil and Environmental Engineering
Atlanta, GA 30332-0373
E-mail: costas.tsouris@ce.gatech.edu

SUMMARY:

Task 1.0 Research Management Plan
Done

Task 2.0 Technology Status Assessment
Done

Task 3.0 Continuous Literature
In Progress

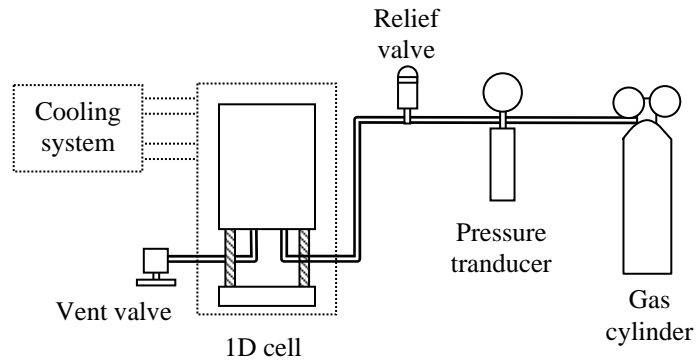
Task 4.0 Studies at the Mineral Surface Scale (1D-interface phenomena)
In progress

Task 5.0 Studies at the Mineral Surface Scale (2D-interface phenomena)
In progress: Cell design

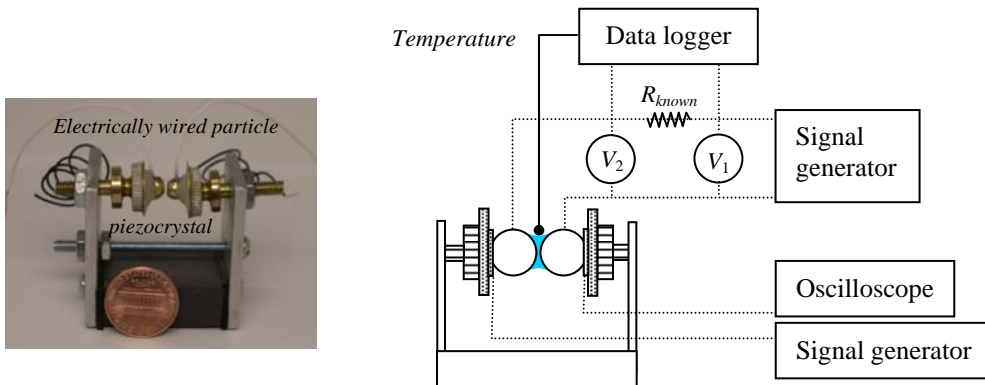
Details on the progress of Task 4 follow.

Subtask 4.1 Experimental studies – Phenomena and properties

Devices. The designed and built pressure system, cooling system, 1D cell and electrical devices are shown below. The cooling system provides a T-range from -10°C to ambient temperature. The temperature control of the 1D cell is achieved through the circulation of coolant through copper tube wrapping the 1D cell.



Instrumentation and peripheral electronics have been built and calibrated to measure mechanical impedance and electrical resistance of hydrate forming at the contact between two particles. The 1D model and the instrumentation are placed inside the pressure cell and electrical signals travel via electrical feed-through under pressure.



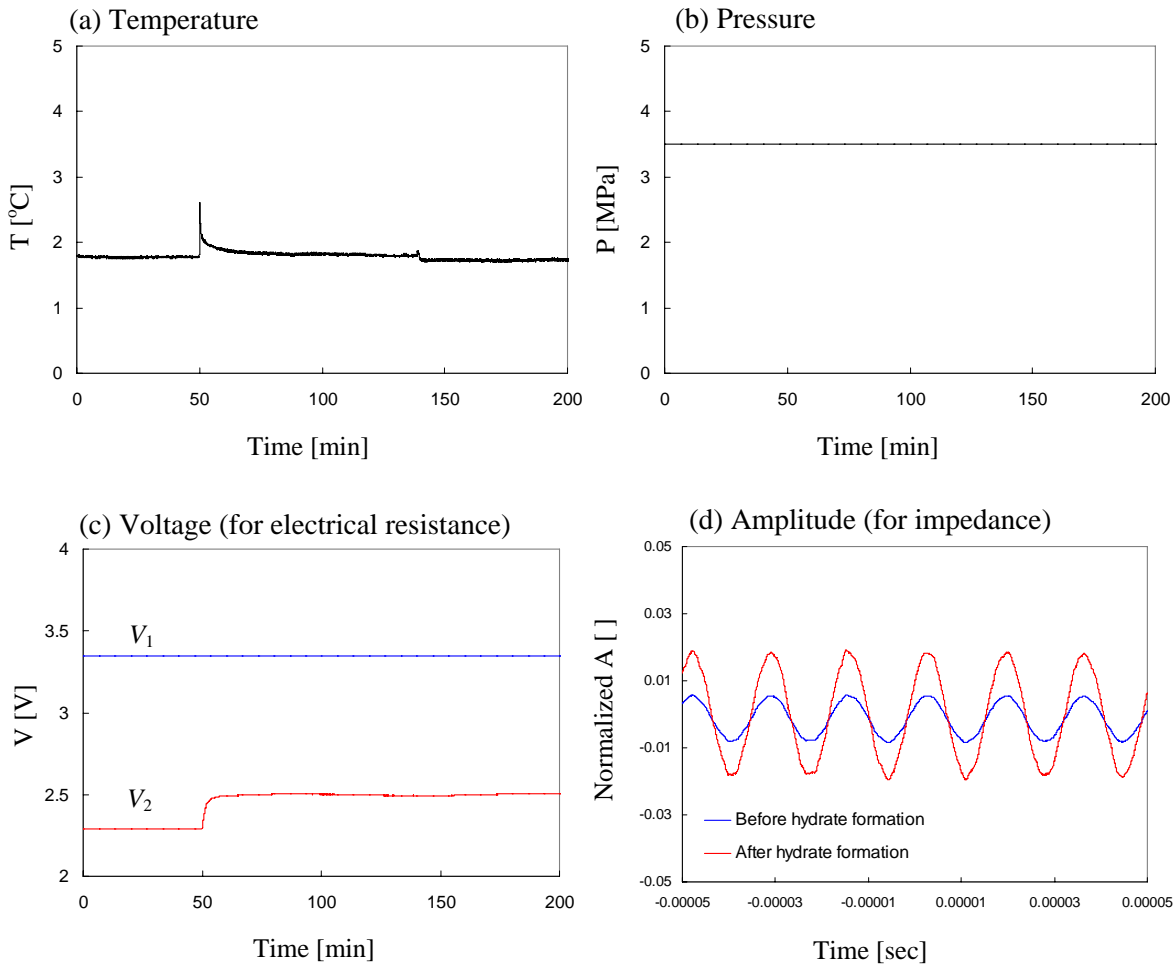
Test Procedure

The preliminary tests conducted so far have involved sequential sets of studies using various pore fluids to simulate fresh to saline water (deionized, 1.5%, 2.5% and 3.5% concentration). The electrical resistance and mechanical impedance evolution are measured during hydrate formation and dissociation. A simplified test sequence follows:

1. Place the instrumented 2-particle micro-model on the cell base.
2. Add a water droplet between the particles to form a fluid meniscus
3. Place the thermocouple partially touching the meniscus
4. Seal cell and increase gas pressure (current tests: CO₂ at ~ 3.8MPa)
5. Gradually decrease the temperature.
6. Log pressure and temperature every 2 seconds.
7. Once 5C is reached, close the gas pressure and continue decreasing the temperature to ~ 1°C.
8. A 60kHz signal is used to monitor the evolution of the mechanical impedance of the droplet (this frequency is selected from previous exploratory tests to obtain the maximum change). The output voltage is logged every 2 seconds.
9. Electrical resistance is evaluated using a 50kHz sinusoidal wave to avoid electrode polarization effects. Voltage is logged every 2 seconds.

Results for the first test sequence follow. First, typical signatures are shown. Then, key trends are summarized in the second figure.

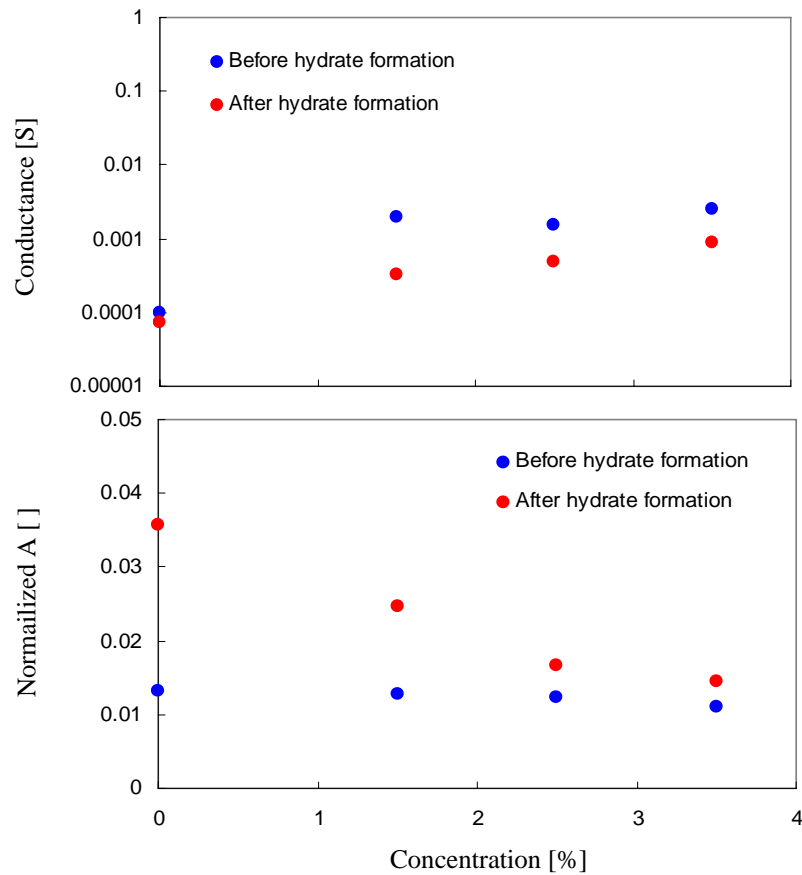
Typical signatures



Observations:

- The exothermic event marks phase transformation at ~ 50 min
- The pressure remains constant because of the small volume of hydrate (pressure drop is typically observed when hydrate forms in a close system).
- Electrical resistance: The sudden increase in voltage indicates the increase of resistance between particles during hydrate formation.
- The time for changes in temperature and voltage are the same
- Amplitude of mechanical vibrations increases after hydrate formation

Summary of main trends



Observations:

- The electrical conductance before hydrate formation increases with increasing ionic concentration. In all cases, the electrical conductance decreases after hydrate formation, however, it is higher for higher ionic concentration because ion exclusion may limit hydrate formation. This suggests incomplete hydrate formation in fluids with high initial concentration in closed systems.
- The vibration amplitude increases after hydrate formation indicating solidification. However, the improvement diminishes with increasing ionic concentration in the fluid. This confirms incomplete hydrate formation.

Subtask 4.2 Analytical Studies – Intrinsic Kinetic Model Development

After a thorough literature review on current gas-hydrate thermodynamic models since their early development in 1957, it was concluded in our previous quarterly report that four theoretical considerations had to be incorporated into the models for a more accurate description of hydrate equilibrium in porous media. A brief description of model developments towards achieving this goal follows here.

1. *More accurate description of gas molecule – hydrate cage interactions to improve prediction of cage occupancy and gas content of hydrate phase.* An extended version of the Kihara potential with inclusion of three layers of hydrate lattice has been adapted from the literature, and will be included in the thermodynamic model. A numerical integration method will be used to calculate the energy-interaction parameters required for the description of gas-molecule occupancy of hydrate cages at constant temperature in each iteration step required during the minimization of the free energy of the system (more on thermodynamic equilibrium calculations can be found in point 4 below).
2. *Choice of different standard state for chemical potential of water to minimize the utilization of empirical expressions.* After a thorough literature review, it was concluded that the most appropriate choice for the standard state for the calculation of the chemical potential of water in the hydrate phase is the reference state (i.e., liquid water at atmospheric pressure and melting point). The chemical potential for water at the reference state will replace the standard state based on the empty hydrate lattice in the model under development. Expressions for the chemical potential change with respect to the reference state are under development. The primary variables of choice are pressure and temperature.
3. *Consideration of confinement effects in the overall thermodynamic equilibrium.* The scarce literature available on hydrate equilibrium in porous media suggests the inclusion of a capillary pressure term in the calculation of the chemical potential of water in hydrate phase to account for the fact that hydrate equilibrium takes place inside confined spaces. Although this approach may work as a first approximation, it neglects other phenomena linked to confinement. The necessity to include the effects of confinement in the criteria for equilibrium: thermal, mechanical, and chemical prompted further literature research during this quarter. Literature review on frost damage to porous solids has focused on mechanical equilibrium criteria for the description of growth of ice crystals inside porous media. Using the analysis of ice as a starting point, and assuming that ice and solid hydrate are analogous crystalline structures, we concluded that two distinct phenomena have to be included in the thermodynamic model: (1) capillary effects due to differences of wetting properties of the distinct phases present; and (2) stress imparted by the soil grains on the hydrate solid. Both capillary effects and stress define the effective pressure of each of the phases—gas, liquid, and solid—inside the porous medium. Expressions to account for capillary effects are being developed on the assumption that water is a perfectly wetting phase, while

hydrate and gas are non-wetting phases. In the case of the effects of stress, an approach analogous to the analysis of ice formation in porous media is being pursued. Additionally, a thorough review on the theoretical basis for the development of criteria for thermodynamic equilibrium has started. The goal is to include capillary and stress effects as components of the criteria for overall thermodynamic equilibrium.

4. *Application of a minimization technique to hydrate equilibrium in order to predict quantities and compositions of all phases present at equilibrium conditions.* The calculation of thermodynamic equilibrium will be performed in a similar way as that utilized in other equilibrium problems (e.g., liquid-vapor equilibrium). Basically, the idea is to minimize Gibbs energy using “partition coefficients” that describe the amount of each component present in the different phases in a procedure known as flash calculation. However, in contrast with traditional equilibrium problems, only temperature is the same for all phases in the present case. As described in point 3, each phase present has a different effective pressure. Therefore, traditional flash calculation procedures have to be adapted to allow calculations of hydrate equilibrium in porous media.

As stated in the report for the previous quarter, the slowest and most critical part of the present subtask is the development of the model itself. Special care is taken to ensure that analyses and mathematical expressions developed during this work are theoretically rigorous.

Status of Equipment Built/Purchased/Ordered for Task 4.0 (1D) and Task 5.0 (2D)

1D-interface phenomena	Pressure panel 1D cell Particle-level instrumented stand Electrical feed-through	CH ₄ and CO ₂ pressure control system Pressure chamber with viewport Electrical conductivity and impedance during hydrate formation Pressure sealed electrical wires and thermocouples (up to 20MPa)
On-going	2D cell Electronics	Design completed Multi-channel data acquisition system Microscopic video camera