Methane Recovery from Hydrate-bearing Sediments

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ABSTRACT

Gas hydrates are crystalline compounds made of gas and water molecules. Methane hydrates are found in marine sediments and permafrost regions; extensive amounts of methane are trapped in the form of hydrates. Methane hydrate can be an energy resource, contribute to global warming, or cause seafloor instability. This study placed emphasis on gas recovery from hydrate bearing sediments and related phenomena. The unique behavior of hydrate-bearing sediments required the development of special research tools, including new numerical algorithms (tube- and pore-network models) and experimental devices (high pressure chambers and micromodels). Therefore, the research methodology combined experimental studies, particle-scale numerical simulations, and macro-scale analyses of coupled processes. Research conducted as part of this project started with hydrate formation in sediment pores and extended to production methods and emergent phenomena. In particular, the scope of the work addressed: (1) hydrate formation and growth in pores, the assessment of formation rate, tensile/adhesive strength and their impact on sediment-scale properties, including volume change during hydrate formation and dissociation; (2) the effect of physical properties such as gas solubility, salinity, pore size, and mixed gas conditions on hydrate formation and dissociation, and it implications such as oscillatory transient hydrate formation, dissolution within the hydrate stability field, initial hydrate lens formation, and phase boundary changes in real field situations; (3) fluid conductivity in relation to pore size distribution and spatial correlation and the emergence of phenomena such as flow focusing; (4) mixed fluid flow, with special emphasis on differences between invading gas and nucleating gas, implications on relative gas conductivity for reservoir simulations, and gas recovery efficiency; (5) identification of advantages and limitations in different gas production strategies with emphasis; (6) detailed study of CH4-CO2 exchange as a unique alternative to recover CH4 gas while sequestering CO2; (7) the relevance of fines in otherwise clean sand sediments on gas recovery and related phenomena such as fines migration and clogging, vuggy structure formation, and gas-driven fracture formation during gas production by depressurization.

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EXECUTIVE SUMMARY

Gas hydrates are crystalline compounds made of gas and water molecules. Methane hydrates are found in marine sediments and permafrost regions; extensive amounts of methane are trapped in the form of hydrates. Methane hydrate can be an energy resource, contribute to global warming, or cause seafloor instability. This study placed emphasis on gas recovery from hydrate bearing sediments and related phenomena.

The scope of the work included: hydrate formation and growth in pores, hydrate tensile and bonding strengths, the mechanical response of hydrate bearing sediments during loading and dissociation, the effect of pore size distribution on hydraulic conductivity, pressure dependent interfacial tension and contact angle the effect of gas generation methods on the soil water characteristic curves, the evolution of relative permeabilities with unsaturation, geomechanical phenomena during gas production from hydrate-bearing sediments, CH_4-CO_2 replacement in hydrate-bearing sediments, gas recovery efficiency, and emergent phenomena during gas production.

Unique experimental studies were implemented using unprecedented high-pressure chambers that allowed for the observation of processes in micromodels and in effective stress controlled cells, including the measurement of mechanical and electrical properties during hydrate formation, dissociation and exchange reactions.

Experimental results were analyzed using physical, chemical and mechanical concepts and were complemented with analytical solutions and numerical simulations. Two types of network models (tube-network and pore-network) allowed upscaling pore-scale properties, while discrete element simulations were used to upscale grain-scale phenomena in order to analyze and anticipate macro- sediment-scale behavior. A selection of important observations follows.

- Initial hydrate formation is fast and consumes gas dissolved in water during the induction time. Faster than anticipated growth rates suggest the presence of discontinuities in the hydrate shell, probably due to liquid-to-hydrate volume expansion. The solubility of hydrate-forming gas in water in the presence or absence of hydrate affects hydrate formation and dissolution; dissolved gas in the pore water contributes to hydrate lenses in fine-grained sediments (lens-to-sediment ratio 4/1000).

- A hydrate-mineral system fails in tension either through the tensile failure of the hydrate mass, or by hydrate debonding from the mineral substrate. The adhesive/tensile strengths of CH_4 and CO_2 hydrates range between 150- and-200 kPa. Hydrate may dissociate during tensile loading. The tensile/debonding strength determines the Mohr-Coulomb cohesive intercept. Sediments with patchy hydrate saturation exhibit delayed dilation during shear.

- As few as 10 percent of the pores may be responsible for 50 percent of the total fluid flow in sediments. Spatially correlated sediments show higher focused channeling.

- The gas-water interfacial tension is pressure dependent. The contact angle changes as interfacial tension changes. The topology of gas distributions during gas nucleation leads to lower gas permeability for gas nucleation than for gas invasion. Existing relative permeability equations can be used to simulate gas production in hydrate bearing sediments but with caution.

- A self-sustaining CH4-CO2 replacement reaction using the excess heat that is liberated is expected as far as ~3K inside the stability field. Replacement rates increase near the CH4 hydrate phase boundary, with increasing pore fluid, and when CH4 hydrate masses are small so the surface available for CO2 exchange is high.

- While CH4-CO2 replacement requires the opening of the hydrate cage (i.e. a solid-liquid-solid transformation), both electrical and mechanical measurements suggest that CH4-CO2 replacement occurs locally and gradually so that the overall hydrate mass remains solid. In fact, CH4-CO2 replacement within the stability field occurs without a appreciable loss of sediment stiffness. We anticipate various reservoir scale phenomena during CH4-CO2 replacement, including: potential decrease in water saturation, decrease in the liquid relative permeability, pronounced increase in fluid volume when a CH4 gas phase is formed, CO2 hydrate clogging when the velocity of the invading front is low and there is enough water to supersaturate the CO2. The viscosity difference between gas-water or liquid CO2-water systems can cause viscous fingering. This will affect the efficiency of CH4-CO2 replacement and the possibility of CH4 hydrate occlusion within the reservoir.

- Excess-gas methane hydrate reservoirs should be more amenable to CH4-CO2 replacement because of high permeability to CO2, large interface between CH4 hydrate and CO2, and no early CO2 hydrate clogging. Volume-pressure changes associated to CH4-CO2 replacement in excess-water reservoirs may cause increase in fluid pressure, decrease in effective stress and strength loss, volume expansion, and gas-driven fractures if a CH4 gas phase develops and the permeability is low enough to prevent pressure dissipation.

- Gas fingering and high residual water saturation are expected from the depressurization of hydrate-bearing sediments. There is a pronounced hydrate-to-fluid volume expansion during hydrate dissociation. The gas recovery efficiency is very low, even under a high expansion condition where the initial hydrate saturation is less than Sh=5%. The pore size effect on the gas recovery efficiency vanishes when the mean pore size is larger than $\mu(Rp)$=1μm.

- The energy needed to dissociate hydrate is equivalent to the energy needed to increase the temperature of water up to $\Delta T \approx 96°C$. Hydrate in a sediment with porosity n=0.4 can be dissociated without causing ice formation when the initial hydrate saturation is lower than Sh=0.09 (for Ti=5°C) to Sh=0.32 (for Ti=20°C). Hydrate dissociation in sediments with high hydrate saturations from Sh~0.78 (for Ti=5°C) to Sh~0.94 (for Ti=20°C) requires all water to convert into ice in order to supply the energy needed for dissociation.

- The presence of fines in otherwise clean sands can lead to fines migration and clogging. During dissociation, gas bubbles grow and displace fines. The fines content on the bubble surface gradually increases; eventually fines clog pore throats. The expanding gas bubble may push away the skeletal particles, creating a vuggy structure, eventually leading to gas-driven fracture formation.

INTRODUCTION - METHODOLOGY

Gas hydrates are crystalline compounds made of gas and water molecules. Methane hydrates are found in marine sediments and permafrost regions; extensive amounts of methane are trapped in the form of hydrates. Methane hydrate can be an energy resource, contribute to global warming, or cause seafloor instability. This study placed emphasis on gas recovery from hydrate bearing sediments and related phenomena.

The scope of the work included: hydrate formation and growth in pores, hydrate tensile and bonding strengths, the mechanical response of hydrate bearing sediments during loading and dissociation, the effect of pore size distribution on hydraulic conductivity, pressure dependent interfacial tension and contact angle the effect of gas generation methods on the soil water characteristic curves, the evolution of relative permeabilities with unsaturation, geomechanical phenomena during gas production from hydrate-bearing sediments, CH4-CO2 replacement in hydrate-bearing sediments, gas recovery efficiency, and emergent phenomena during gas production.

Unique experimental studies were implemented using unprecedented high-pressure chambers that allowed for the observation of processes in micromodels and in effective stress controlled cells, including the measurement of mechanical and electrical properties during hydrate formation, dissociation and exchange reactions. Experimental results were analyzed using physical, chemical and mechanical concepts and were complemented with analytical solutions and numerical simulations. Two types of network models (tube-network and pore-network) allowed upscaling pore-scale properties, while discrete element simulations were used to upscale grain-scale phenomena in order to analyze and anticipate macro- sediment-scale behavior. The methodology is summarized in the following figure. Salient observations follow.
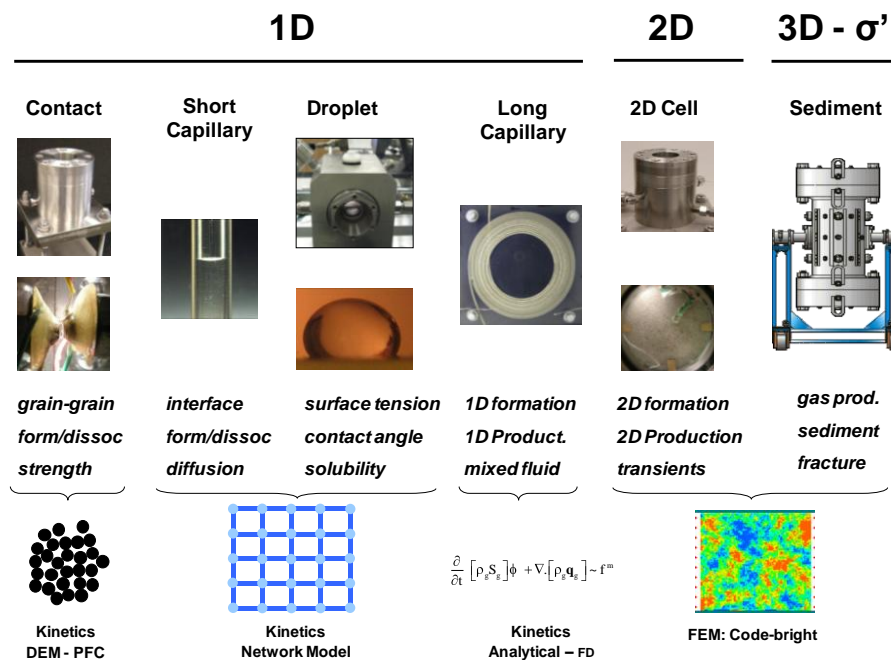
PHYSICAL PROCESSES

Hydrate formation and growth in pores [1] - Lenses

We use optical, mechanical and electrical measurements to monitor hydrate formation and growth in small pores to better understand the hydrate pore habit in hydrate-bearing sediments. Results show that the hydrate mass does not grow homogeneously but advances in the form of lobes that invade the water phase. Hydrate formation in capillary tubes shows that hydrate growth involves the complex and dynamic interaction between diffusion and solubility. During hydrate formation, water flows out of menisci and spreads on the surface forming a thin hydrate sheet when water-wet substrates are involved; however, water does not flow away from menisci when oil-wet substrates are involved. Gas diffuses very slowly through a continuum hydrate mass, therefore, gas must flow through cracks in the hydrate shell to justify the relatively fast growth rate observed in the experiments. Hydrate formation is accompanied by ion exclusion, yet, there is an overall increase in electrical resistance during hydrate formation. Hydrate growth may become salt-limited in trapped water conditions; in this case, liquid brine and gas CH_4 may be separated by a thin hydrate shell and the three-phase system may remain stable within the pore space of sediments. Changes in contact stiffness readily reflect the evolution of three pore-scale processes.
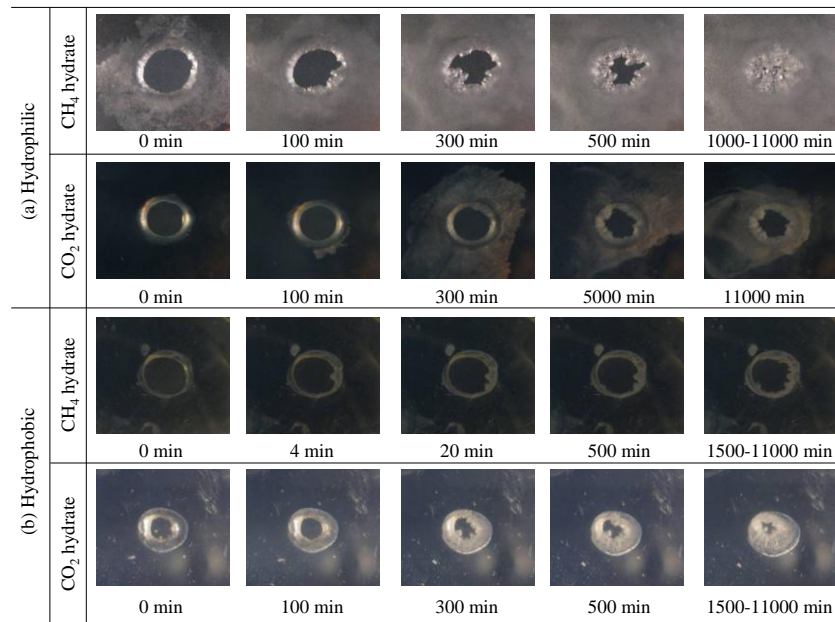

The solubility of hydrate-forming gas in water in the presence or absence of hydrate affects hydrate formation and dissolution. Solubility changes associated with temperature changes within the hydrate stability zone and the presence/absence of a hydrate phase can

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[1] Jung, JW., Santamarina, JC., Hydrate Formation and Growth in Pores (under review – Available from the PI).

trigger oscillating hydrate formation and dissolution cycles during early stage of hydrate formation. Dissolved gas in the pore water of fine grained sediments can be used to form hydrate lenses. The methane hydrate lens density can reach 4/1000.

Hydrate adhesive and tensile strengths[2]

The physical properties of hydrate-bearing sediments depend on the interaction between hydrates and minerals. In particular, hydrates prefer to nucleate on mineral surfaces, therefore, the hydrate-mineral adhesive strength and the tensile strength of the hydrate mass itself affect the mechanical response of hydrate-bearing sediments. In this study, ice and hydrates made with various guest molecules (CO_2, CH_4, and THF) are formed between mica and calcite substrates. Adhesive and tensile strengths are measured by applying an external pull-out force. Results show that tensile failure occurs in CO_2 and CH_4 hydrates when calcite is the substrate, while ice and all hydrates exhibit adhesive failure on mica. The debonding strength is higher when calcite substrates are involved rather than mica substrates. A nominal pull-out strength of 0.15 ± 0.03 MPa can be adopted for mechanical analyses of hydrate-bearing sediments. Numerical FEM simulation results show the possibility of local hydrate dissociation during tensile loading. Micromechanical analyses show that the tensile/debonding strength determines the Mohr-Coulomb cohesive intercept.

(a)   (b)   (c)

7.8mm

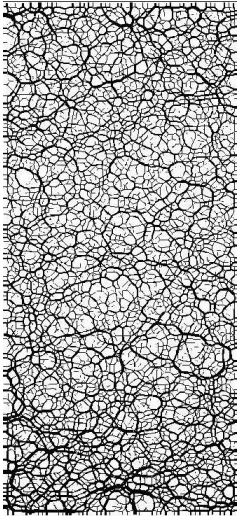Water CH_4 hydrate

(d)   (e)   (f)
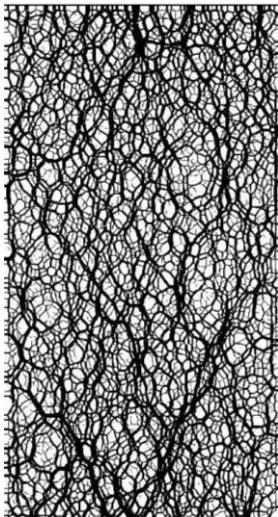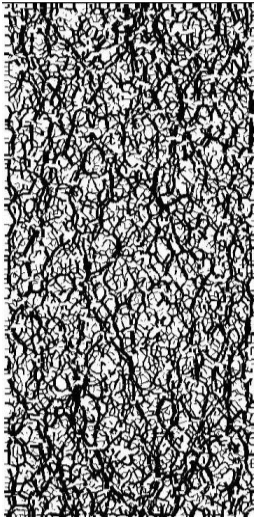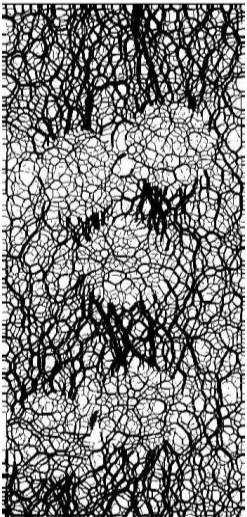
8.4mm

Water CH_4 hydrate

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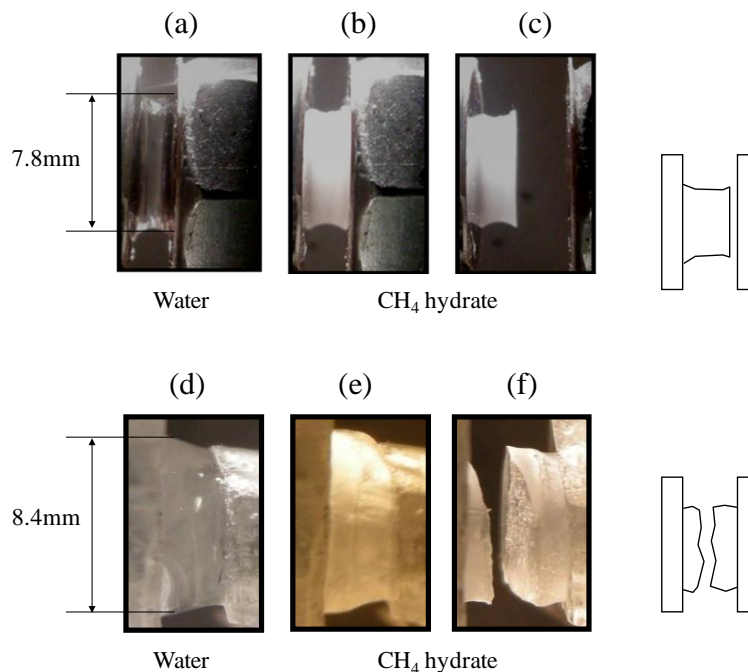
[2] Jung, JW., Santamarina, JC. (2012), Hydrate Adhesive and Tensile Strength, G-Cubed Geochemistry, Geophysics and Geosystems (in print).

Stress-strain response of hydrate-bearing sediments [3]

While the presence of hydrates can have a profound affect on sediment properties, the stress-strain behavior of hydrate-bearing sediments is poorly understood due to inherent limitations in laboratory testing. In this study, we use numerical simulations to improve our understanding of the mechanical behavior of hydrate-bearing sediments. Initially, hydrate crystal prefers to form in pores and onto mineral surface in laboratory-scale time. A concentration gradient between the water that surrounds a small crystal and a nearby large one leads to the growth of large hydrate crystals at the expense of small ones. Therefore, the hydrate mass is simulated as either small randomly distributed bonded grains or as "patchy saturation" whereby sediment clusters with 100% pore space hydrate saturation are distributed within a hydrate-free sediment. Simulation results reveal that either reducing the sediment porosity or increasing the degree of hydrate saturation causes an increase in stiffness, strength and dilative tendency. The strength of sediments with patchy hydrate distribution is slightly lower and it appears at higher strain levels than when hydrate is evenly distributed. The combined effects on strength and dilation causes a shift in the critical state line toward higher void ratios and higher mean effective stress p' deviatoric stress q values. Finally, hydrate dissociation under the draining condition of sand leads to volume contraction and/or stress relaxation, and pronounced shear strains develop if the hydrate-bearing sediment is subjected to deviatoric loading during dissociation.

| (a) Isotropic load $(\sigma_o=1MPa, \sigma_d=0MPa)$	Under deviatoric load $(\sigma_o=1MPa, \sigma_d=1.2MPa)$		
	(b) Hydrate-free sediments	(c) Distributed hydrate $(S_h=20\%)$	(d) Patchy saturated hydrate $(S_h=20\%)$

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[3] Jung, JW., Santamarina, JC., Soga, K., Stress-Strain Response of Hydrate Bearing Sediments – Numerical Study Using DEM Simulations, Journal of Geophysical Research (in print).

Hydraulic conductivity in spatially varying media [4]

The hydraulic conductivity can control geotechnical design, resource recovery, and waste disposal related to gas recovery. We investigate the effect of pore-scale spatial variability on flow patterns and hydraulic conductivity using network models realized with various tube size distributions, coordination number, coefficient of variation, correlation and anisotropy. In addition, we analyze flow patterns to understand observed trends in hydraulic conductivity.

In most cases, hydraulic conductivity decreases as the variance in pore size increases because flow becomes gradually localized along fewer flow paths. As few as 10 percent of the pores may be responsible for 50 percent of the total flow in sediments with high pore-size variability. Spatial correlation reduces the probability that small pores will plug highly conductive flow paths. Spatially correlated networks show a higher focused channeling of fluid flow than uncorrelated networks with the same pore size distribution. Hydraulic conductivity increases with increased correlation length. The hydraulic conductivity in anisotropic uncorrelated pore networks is bounded by the two extreme 'parallel-of-series' and 'series-of-parallel' tube configurations. Anisotropic correlated networks show increased hydraulic conductivity with an increasing correlation length parallel to the flow direction.

These results highlight the relevance of grain size and formation history dependent pore size distribution and spatial variability on hydraulic conductivity, related geo-process, and engineering applications.

① COV(R^2)=0.49 ② COV(R^2)=1.26 ③ COV(R^2)=1.95

(a) Uncorrelated network (Fig. 4 and 6)
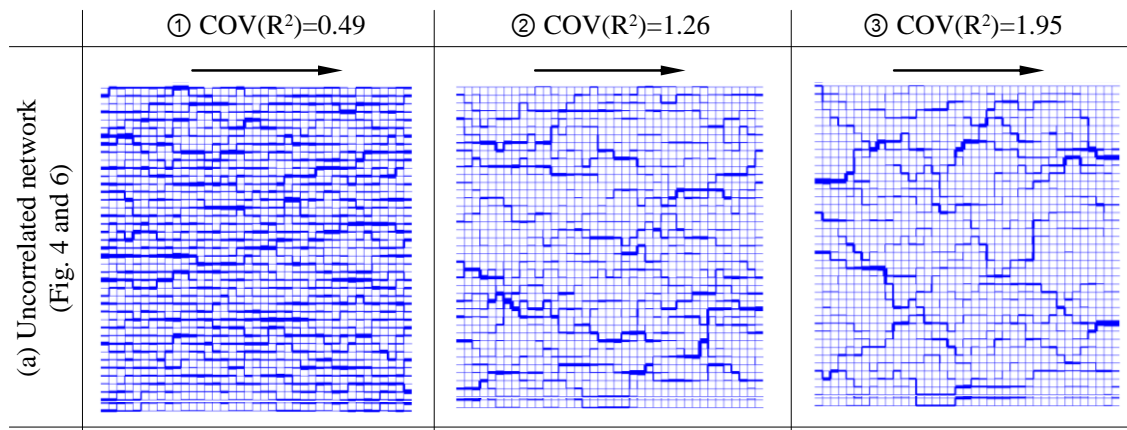
Water-CH4-mineral systems: interfacial tension and contact angle [5]

Gas-water interfacial tension is pressure dependent. The contact angle changes as interfacial tension changes. CH4-water interfacial tension decreases up to 20mN/m from atmospheric pressure to high pressure relevant to reservoir conditions. Minor changes in

[4] Jang, J., Narsilio, G. and Santamarina, J.C. (2011), Hydraulic Conductivity in Spatially Varying Media -A Pore-Scale Investigation, Geophysical Journal International, vol. 184, pp. 1167-1179
[5] Espinoza, D.N. and Santamarina J.C., Water-CH_4-mineral systems: interfacial tension and contact angle. Under review (available from the PI)

contact angle are measured upon CH4 pressurization. Quartz, calcite, coal, and PTFE substrates show receding contact angles θ<90° (waterwet); calcite, coal and PTFE show advancing contact angles θ>90° (gas-wet). While stable displacement is expected during gas recovery from natural gas conventional reservoirs, gas fingering and high residual water saturation are expected from the depressurization of hydrate-bearing sediments.
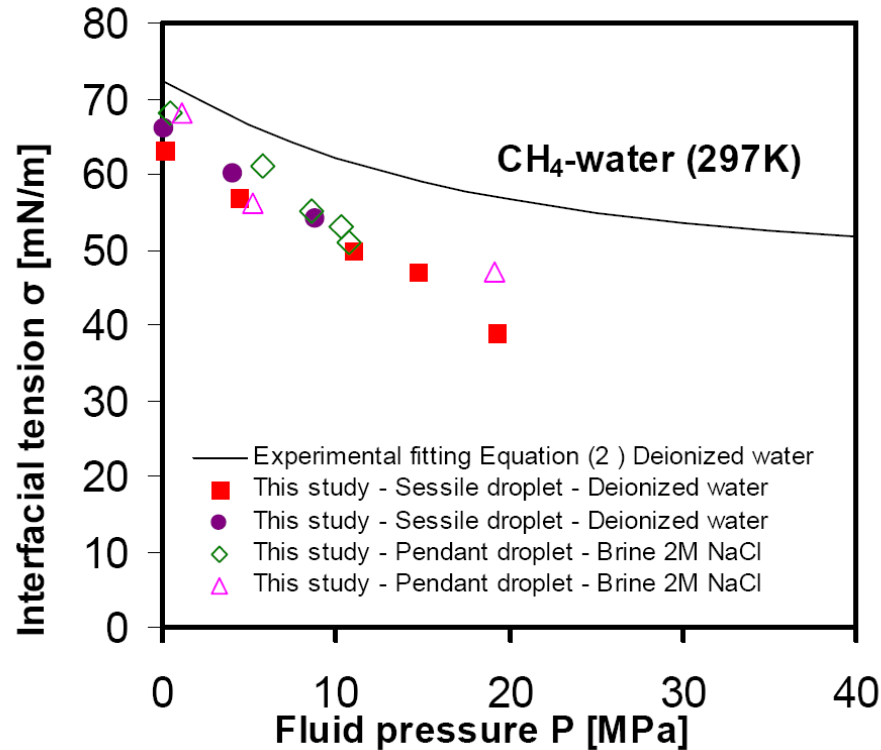
Evolution of gas saturation during gas nucleation - Relative permeability [6]

Gas and water permeabilities control gas recovery efficiency and determine the economic development of hydrate bearing sediments. While it would appear that gas and water permeabilities during hydrate dissociation should depend on initial hydrate distributions, there is no laboratory data or numerical simulation result to guide the selection of adequate parameters for reservoir simulations. The study of unsaturated soil behavior has led to the development of expressions for degree of saturation S and permeability kr as a function of capillary pressure Pc. These Pc-S expressions can be used to investigate similar conditions in resource recovery.

The air-vapor phase is continuous in unsaturated soils, where the gas-vapor phase invades the medium from a boundary, i.e., "external gas drive process". However, gas comes out of solution and bubbles grow within the sediment in methane production from hydrate bearing sediments, i.e., "internal gas drive process" (Note: this situation also takes place in

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[6]Jang, J. and Santamarina, J.C. (2011), Gas saturation during gas invasion and gas nucleation. (Under review – Available from the PI)

seepage conditions downstream of earth dams). These two cases are referred to as "internal gas drive process" for the case of nucleation and gas liberation during depressurization, and "external gas drive process" or gas injection, for the case of forced invasion. We use a micromodel to gather unprecedented experimental data, and tube-network models for numerical simulations that explore differences between gas invasion and gas nucleation on the evolution of the soil water saturation and relative permeabilities.

The topology of gas distributions during gas invasion and gas nucleation are fundamentally different: Invading gas forms a percolating path, while nucleating gas forms isolated gas-filled lacunae. Tube-network model simulation results show that the soil water characteristic curve and relative water permeability are similar for both gas invasion and nucleation. However, gas permeability is lower for gas nucleation than it is for gas invasion because some of the gas-filled tubes remain isolated without contributing to the global gas conductivity. Existing relative permeability equations can be used to simulate gas production in hydrate bearing sediments. However, special attention must be devoted to determine appropriate parameters for relative gas permeability as a function of saturation.

Water-CO2-mineral systems: Interfacial tension, contact angle and diffusion [7]

Previous studies have shown that the interfacial tension and contact angle in CO_2-water-mineral systems change noticeably with fluid pressure. We compile previous results and extend the scope of available data to include saline water, different substrates (quartz, calcite, oil-wet quartz, and PTFE) and a wide pressure range (up-to-20MPa at 298K). Data analysis provides interfacial tension and contact angle as a function of fluid pressure; in addition we recover the diffusion coefficient of water in liquid CO_2 from long-term observations. Results show that CO_2-water interfacial tension decreases significantly as pressure increases in agreement with previous studies. Contact angle varies with CO_2 pressure in all experiments in response to changes in CO_2-water interfacial tension: it increases on non-wetting surfaces such as PTFE and oil-wet quartz; and slightly decreases in water-wet quartz and calcite surfaces. Water solubility and its high diffusivity (from $D=20\times10^{-9}m^2/s$ to $200\times10^{-9}m^2/s$) in liquid CO_2 govern the evolution of inter-particle pendular water. CO_2-derived ionic species interaction with the substrate leads to surface modification if reactions are favorable, e.g. calcite dissolution by carbonic acid and precipitation as water diffuses out of the droplet. Pressure-dependent interfacial tension and contact angle affect injection patterns and breakthrough mechanisms, in other words, the performance of geological formations that act as either reservoirs or seals.

(1) Increasing Pressure

σ
θ

(2) Increasing Time (constant pressure)

D
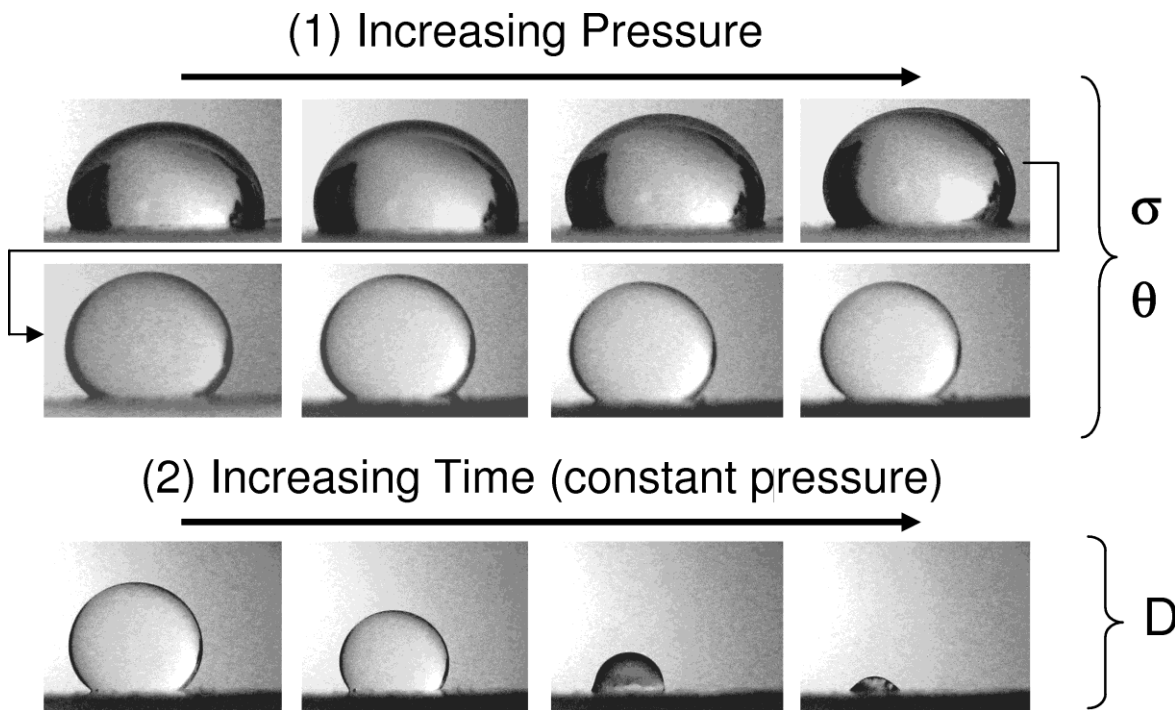
[7] Espinoza, D.N. and Santamarina J.C. (2010), Water-CO2-mineral systems: interfacial tension, contact angle and diffusion – Implications to CO2 geological storage, Water Resources Research, vol. 46, DOI: 10.1029/2009WR008634.

Gas Production by CH$_4$-CO$_2$ replacement [8]

The injection of carbon dioxide CO$_2$ into methane hydrate bearing sediments causes the release of methane CH$_4$ and the formation of carbon dioxide hydrate, even if global pressure-temperature conditions remain within the CH$_4$ hydrate stability field. This phenomenon, known as CH$_4$-CO$_2$ exchange or CH$_4$-CO$_2$ replacement, creates a unique opportunity to recover an energy resource, methane, while entrapping a greenhouse gas, carbon dioxide. Multiple coexisting processes are involved during CH$_4$-CO$_2$ replacement, including heat liberation, mass transport, volume change, and gas production among others. Therefore, the comprehensive analysis of CH$_4$-CO$_2$ related phenomena involves physico-chemical parameters such as diffusivities, mutual solubilities, thermal properties and pressure-temperature dependent phase conditions. We combine new experimental results with published studies to generate a dataset we use to evaluate reaction rates, to analyze underlying phenomena, to explore the pressure-temperature region for optimal exchange, and to anticipate potential geomechanical implications for CH$_4$-CO$_2$ replacement in hydrate-bearing sediments.

The hydrate phase boundary is affected by pore size, salinity, and gas mixtures. Small pores and salts in water lower the activity of water, which shifts the phase boundary to lower temperature and higher pressure conditions. Methane and carbon dioxide gas mixtures have intermediate phase boundaries between the boundaries for pure methane and pure carbon dioxide hydrates, depending on the mass ratio of each component in the mixture. These complex conditions are found in in-situ hydrate reservoirs, they determine the lower bound of the hydrate stability zone, and affect gas recovery.

Results show that the CH4 hydrate cage must separate to release the CH4 molecule and trap the CO2 molecule. A self-sustaining CH4-CO2 replacement reaction using the excess heat that is liberated is expected as far as ~3K inside the stability field when minerals, water, and excess gas are present. While CH4-CO2 replacement requires the opening of the hydrate cage (i.e. a solid-liquid-solid transformation), both electrical resistance and relative stiffness measurement suggest that CH4-CO2 replacement occurs locally and gradually so that the overall hydrate mass remains solid. Therefore, no stiffness loss should be expected at the sediment scale.

The newly formed CO2 hydrate shell must be either fractured or porous in order to allow for the high exchange rates that are experimentally observed Replacement rates increase near the CH4 hydrate phase boundary, with increasing pore fluid pressure until the CO2 liquefies, and, when CH4 hydrate masses are small so the surface available for CO2 exchange is high. Lower hydrate saturation is expected after CH4-CO2 replacement in water-limited reservoirs because hydrate forming water dissolves into liquid CO2.

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[8] Jung, J.W. and Santamarina, J.C. (2010), CH$_4$-CO$_2$ Replacement in Hydrate-Bearing Sediments: A Pore-Scale Study, G-Cubed Geochemistry, Geophysics and Geosystems, Vol. 11, Q0AA13, doi:10.1029/2010GC003339.

Jung, J.W., Espinoza, D.N. and Santamarina, J.C. (2010), Hydrate Bearing Sediments: CH$_4$-CO$_2$ Replacement, Journal of Geophysical Research, vol. 115, B10102, doi:10.1029/2009JB000812

We anticipate various reservoir scale phenomena during CH4-CO2 replacement, including: potential decrease in water saturation, decrease in the liquid relative permeability, pronounced increase in fluid volume when a CH4 gas phase is formed, CO2 hydrate clogging when the velocity of the invading front is low and there is enough water to supersaturate the CO2, and the possibility of CO2 fingering leading to CH4 hydrate occlusion within the reservoir. Excess-gas methane hydrate reservoirs should be more amenable to CH4-CO2 replacement because of high permeability to CO2, large interface between CH4 hydrate and CO2, and no early CO2 hydrate clogging. Volume-pressure changes associated to CH4-CO2 replacement in excess-water reservoirs may cause increase in fluid pressure, decrease in effective stress and strength loss, volume expansion, and gas-driven fractures if a CH4 gas phase develops and the permeability is low enough to prevent pressure dissipation. The fluid displacement pattern under mixed fluid flow conditions is affected by interfacial tension, contact angle, viscosity, and flow rate. The viscosity difference between gas-water or liquid CO2-water systems can cause viscous fingering. This will affect the efficiency of CH4-CO2 replacement, or the injection of liquid CO2 for geological storage.

(a) -2539min – Before replacement, in CH_4 atmosphere — CH_4 gas / CH_4-hydrate

(b) During liquid CO_2 flooding (rising from the bottom) — CH_4 gas / CH_4-hydrate

(c) 0min – Immediately after liquid CO_2 flooding — Liquid CO_2 / CH_4-hydrate

(d) 18min – In liquid CO_2

(e) 36min – In liquid CO_2

(f) 186min – In liquid CO_2

(g) 1176min – In liquid CO_2

(h) 2178min – In liquid CO_2

(i) 3768min – In liquid CO_2

1mm
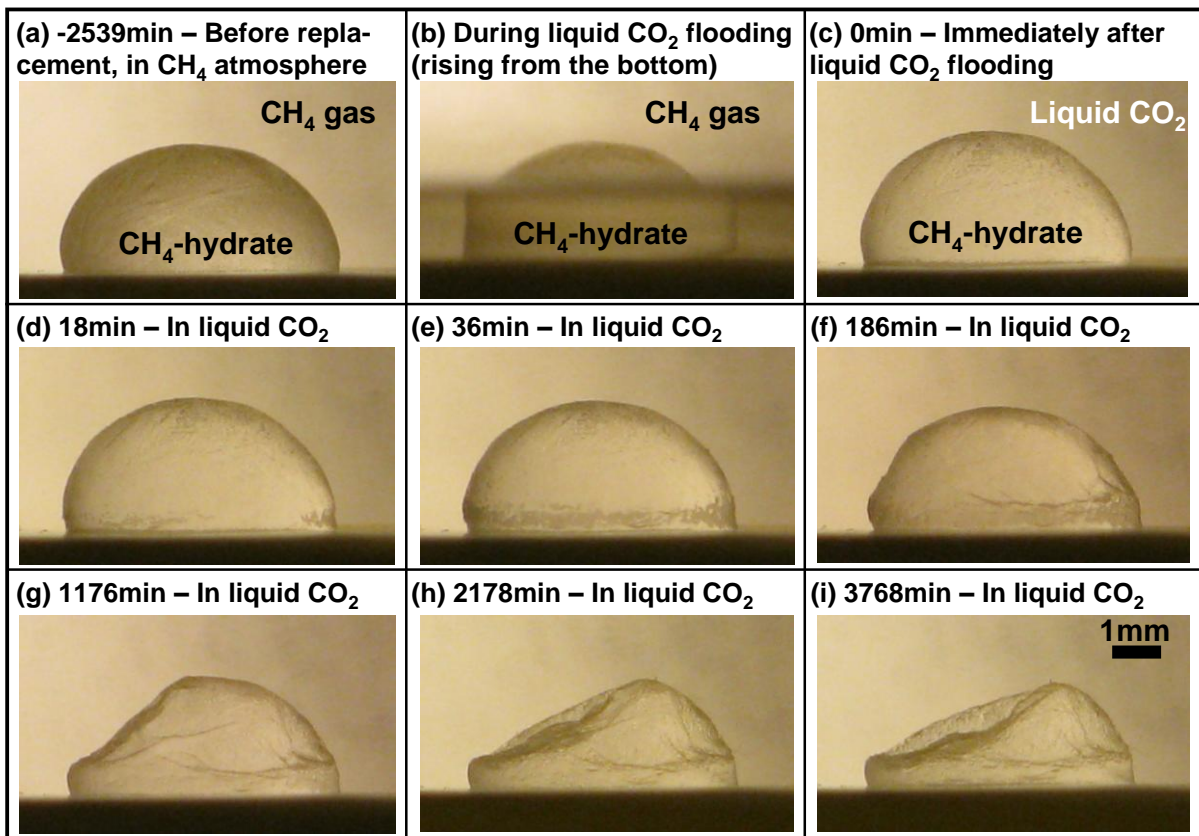
P-wave monitoring of hydrate-bearing sand during CH4-CO2 replacement [9]

While previous studies have shown successful CH_4-CO_2 replacement in hydrates, the mechanical response of hydrate-bearing sediments during CO_2 injection, CH_4-CO_2 replacement, and CH_4 production needs to be adequately understood in order to avert production problems such as borehole instability, sand production, and buckling of the casing. We take advantage of the characteristics of elastic mechanical wave propagation in sediments to monitor CH_4 hydrate-bearing sands before, during, and after CO_2 injection. Results show that CH_4-CO_2 replacement occurs without a loss of stiffness in the granular medium. This implies that CO_2-flooded sandy reservoirs can remain mechanically stable during and after CH_4 gas production. On the other hand, pure CO_2 dissolves hydrate from the pore space, and continued sediment flushing with pure CO_2 reduces the degree of hydrate saturation, opens the pore throats, and weakens the granular skeleton. This phenomenon may cause a significant loss of strength near the injection points and regions subjected to high liquid CO_2 flow rate. The results of complimentary analyses show a decrease in bulk stiffness as water is displaced by liquid CO_2, a stiffening of the granular skeleton during hydrate formation at contacts (diffusion limited), and the implications of water solubility in liquid CO_2.
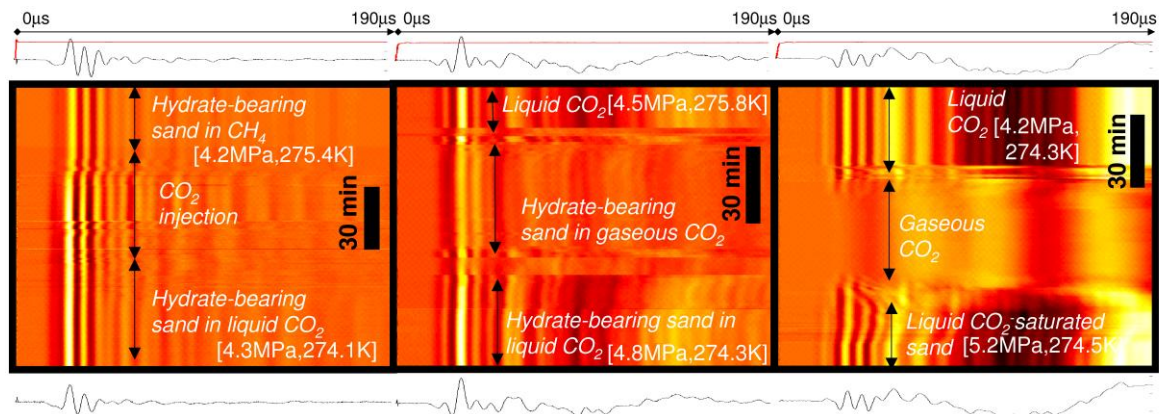
Recoverable gas from hydrate bearing sediments[10]

The volume of hydrate expands into a significantly larger volume of water and gas upon dissociation. Gas recovery and capillary-trapped residual gas saturation are investigated by simulating hydrate dissociation within pore-networks. A fluid pressure-controlled boundary condition is used to determine the amount of recovered gas as a function of volume expansion; in this form, results are applicable to gas production by either thermal

[9] Espinoza, D.N. and Santamarina, J.C., P-wave monitoring of hydrate-bearing sand during CH4-CO2 replacement (under review).

[10] Jang, J. and Santamarina J.C. (2012), Gas Production from Hydrate Bearing Sediments: Pore-Network Model Simulation and Macro-Scale Analyses, Journal of Geophysical Research - Solid Earth, (in print).

stimulation or depressurization when production rates prevent secondary hydrate or ice formation. Simulation results show that gas recovery is proportional to gas expansion, initial hydrate saturation, and the sediment pore size distribution (i.e., capillary pressure). Gas recovery is not affected by pore size in coarse grained sediments with pores larger than 1μm. Hydrate bearing sediments with low hydrate saturation yield low gas recovery. Macro-scale close-form solutions, validated using the numerical results, provide estimates for recoverable gas as a function of the initial hydrate saturation and the fluid expansion factor.
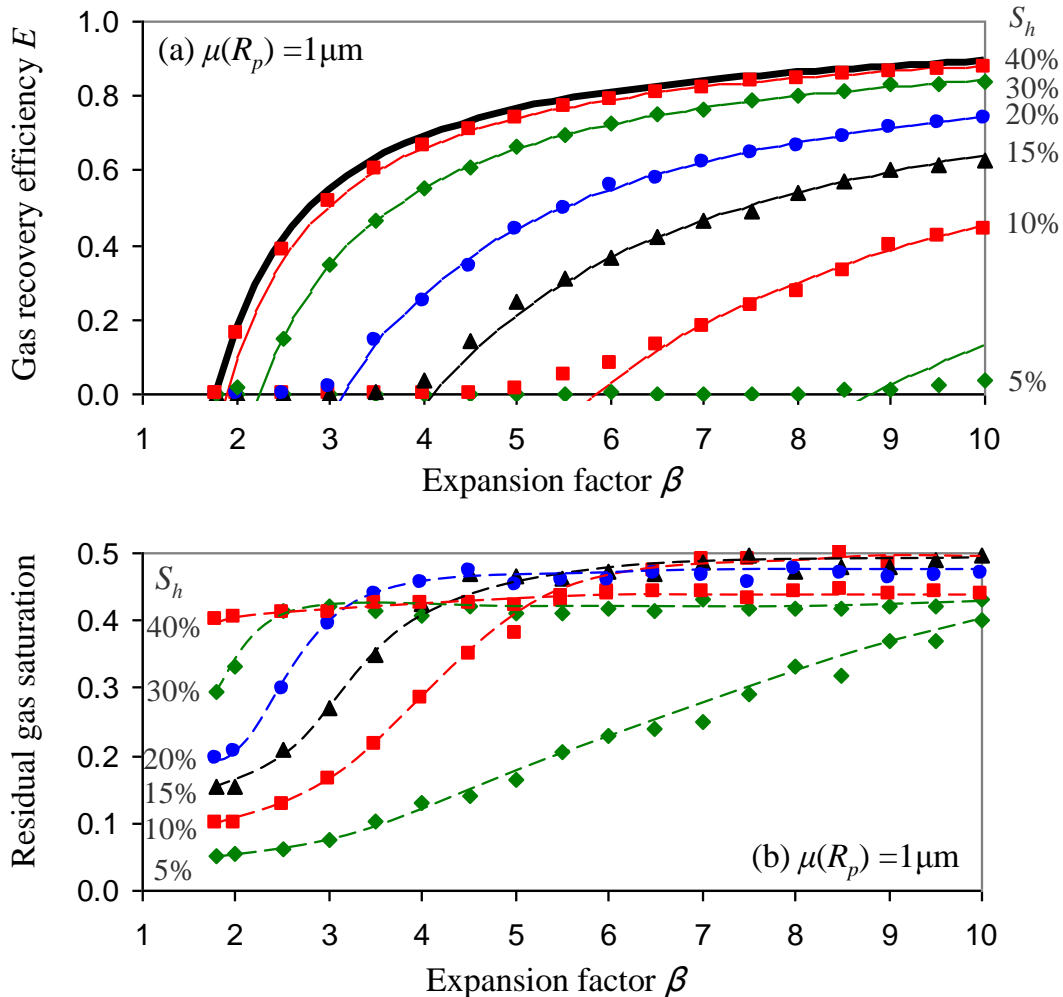
Energy required for dissociation – Ice formation

The energy needed to dissociate hydrate is equivalent to the energy needed to increase the temperature of water up to $\Delta T \approx 96°C$. Hydrate in a sediment with porosity $n=0.4$ can be dissociated without causing ice formation when the initial hydrate saturation is lower than $Sh=0.09$ (for $Ti=5°C$) to $Sh=0.32$ (for $Ti=20°C$). Hydrate dissociation in sediments with high hydrate saturations from $Sh\sim0.78$ (for $Ti=5°C$) to $Sh\sim0.94$ (for $Ti=20°C$) requires all water to convert into ice in order to supply the energy needed for dissociation.

Emergent phenomena during gas production: Fines migration [11]

Emergent phenomena may significantly affect gas production from hydrate-bearing sediments and sediment stability. The meso-scale vessel used in this study allows for the application of an effective stress to the sediment, and it is instrumented to monitor shear wave velocity, temperature, pressure and volume change during hydrate formation and gas production. The vessel sits inside the Oak Ridge National Laboratory Seafloor Process Simulator which is used to control the fluid pressure and temperature.

Depressurization and fluid flow caused fines migrated within the sediment in the direction of fluid flow. A vuggy structure formed in coarse sand containing a small fraction of fines during gas production. Vug formation was a precursor to the development of gas-driven fractures during depressurization under a constant effective stress boundary condition. Together, these results show the critical importance of fines during gas production and the development of gas-driven discontinuities at constant effective stress boundary conditions.


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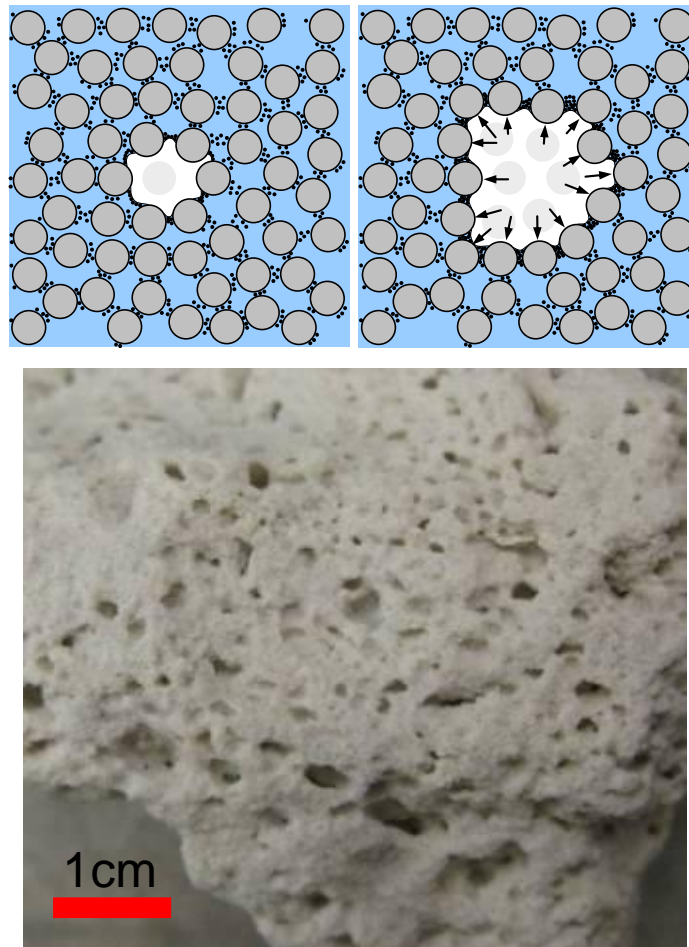
[11] Jung, JW., Jang, J., Santamarina, JC., Tsouris, C., Phelps, TJ., and Rawn, CJ., Gas Production from Hydrate-Bearing Sediments – Emergent Phenomena (under review).

Emergent phenomena during gas production: Fractures [12]

Sediments subjected to fluid flow may experience fracture formation and fluid flow localization. Current explanations for hydraulic fracture in sediments fail to satisfy the inherent characteristics of granular materials: effective stress dependent cohesionless frictional strength. We apply complementary experimental and numerical techniques to identify the underlying particle-scale mechanisms. We show that the miscibility of the invading fluid with the host fluid leads to distinct localization processes that depend on the balance between particle-level skeletal forces (effective stress dependent), capillary forces (the invasion of the interfacial membrane when immiscible fluids are involved), and seepage-drag forces (associated with fluid flow velocity). The positive feedback mechanisms at surface defects and fracture tips that promote fracture initiation and sustain fracture propagation. These include increased porosity at the tip due to strains preferentially normal to the fracture alignment, either eased membrane invasion (immiscible fluids) or higher hydraulic conductivity (miscible fluids), and the emergence of particle-level forces that promote opening mode particle displacement. This effective stress compatible sequence of events helps identify the parameters that govern fluid-driven fracture formation in uncemented sediments, and explain experimental observations.

5cm
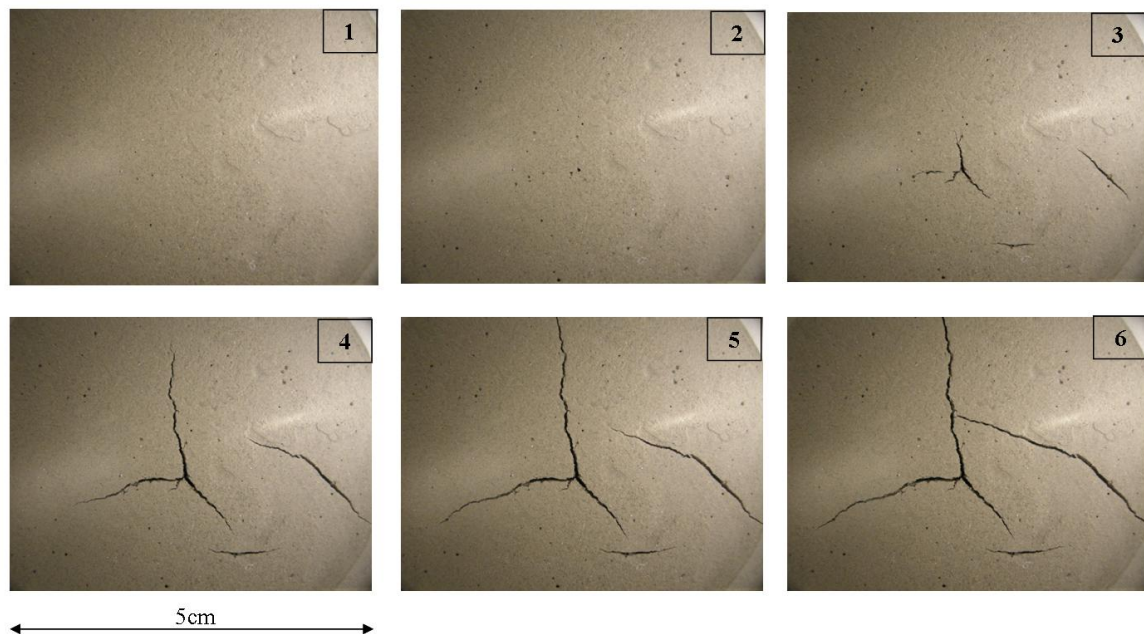
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CONCLUSIONS

The goals of this project were to identify, understand and model processes involved in methane production from hydrate-bearing sediments. The methodology involved the observation and interpretation of phenomena at multiple scales, ranging from pore-contact scale to the macro-reservoir scale, taking into consideration various possible driving forces (e.g., depressurization, thermal stimulation). Results contribute new insight to: hydrate formation and growth (with relevance to marine and permafrost environments), hydrate-mineral bonding and tensile strength with implications on the mechanical behavior of hydrate bearing sediments in view of production strategies, properties of hydrate bearing sediments including mechanical and conduction properties, interfacial tension and contact angle in mixed fluids, the evolution of unsaturation in gas production by heating and depressurization, gas production by chemo-driven methods with emphasis on the fundamental understanding of CO_2-CH_4 exchange. inherent differences between gas invasion and gas nucleation/production and implications on the evolution of degree of saturation and fluid conduction; fluid conductivity in spatially varying sediments; thermodynamic formulation; coupled thermo-hydro-chemo-mechanical analyses; production strategies in different formations; the role of effective stress and the development of gas-driven fractures; fines migration and clogging; and gas recovery efficiency. Selected observations follow.

Hydraulic conductivity in spatially varying media

- In most cases, hydraulic conductivity decreases as the variance in pore size increases because flow becomes gradually localized along fewer flow paths. As few as 10 percent of the pores may be responsible for 50 percent of the total flow in sediments with high pore-size variability.

- Spatial correlation reduces the probability that small pores will plug highly conductive flow paths. Spatially correlated networks show a higher focused channeling of fluid flow than uncorrelated networks with the same pore size distribution. Hydraulic conductivity increases with increased correlation length.

- The hydraulic conductivity in anisotropic uncorrelated pore networks is bounded by the two extreme 'parallel-of-series' and 'series-of-parallel' tube configurations.

- Anisotropic correlated networks show increased hydraulic conductivity with an increasing correlation length parallel to the flow direction.

Hydrate formation and growth in pores.

- Initial hydrate formation is fast and consumes gas dissolved in water during the induction time. Thereafter, diffusion at the tip of the hydrate mass causes hydrate dissolution. Such transient formation-dissolution cycles are readily seen during the early stages of hydrate formation.

- Hydrate growth is controlled by gas diffusion through the hydrate shell that separates water and gas. Faster than anticipated growth rates suggest the presence

of discontinuities in the hydrate shell, probably due to liquid-to-hydrate volume expansion.

- Hydrate growth in capillaries does not advance homogeneously as a planar front but in the form of lobes that invade the water phase; this topology increases surface area and favors growth in a diffusion-limited methane transport.

- Ion exclusion during hydrate formation leads to an increase in ionic concentration in trapped water and hindered hydrate growth. The resulting gas-hydrate-brine system can remain stable due to the low ion diffusion out of the trapped water through the hydrate shell.

- The solubility of hydrate-forming gas in water in the presence or absence of hydrate affects hydrate formation and dissolution. Solubility changes associated with temperature changes within the hydrate stability zone and the presence/absence of a hydrate phase can trigger oscillating hydrate formation and dissolution cycles during early stage of hydrate formation.

- Dissolved gas in the pore water of fine grained sediments can be used to form hydrate lenses. The resulting methane hydrate lens density can reach 4/1000.

Hydrate adhesive and tensile strengths.

- A hydrate-mineral system fails in tension either through the tensile failure of the hydrate mass, or by hydrate debonding from the mineral substrate. Debonding failure prevails in mica. When calcite is involved, CH4 and CO2 hydrates fail in tension while THF hydrate and ice debond.

- The adhesive/tensile strengths of CH4 and CO2 hydrates range between 150- and-200 kPa.

- Numerical FEM simulation results show the possibility of local hydrate dissociation during tensile loading.

- Micromechanical analyses show that the tensile/debonding strength determines the Mohr-Coulomb cohesive intercept.

Stress-strain response of hydrate-bearing sediments.

- The strength properties of hydrate bearing sediments depend on the hydrate pore habit.

- Distributed hydrate-bearing sediments exhibit high dilation at low confinement. A cohesive intercept that is a function of hydrate saturation is obtained when the Coulomb failure envelope is extrapolated to the origin. Yet, hydrate saturation has almost no effect on the critical state friction.

- Sediments with patchy hydrate saturation exhibit delayed dilation until a strainlevel that is comparable to the strain at peak dilation in hydrate-free sediments. There is a significant increase in critical state friction angle and there is no cohesive intercept in the p'-q projection.

- Hydrate particles bonded onto the mineral surface contribute to increased shear resistance by contiguous particles being bonded together, and by promoting rotational frustration. The strong, hydrate-saturated patches force the development of tortuous rather than planar shear planes and higher energy is required to shear the specimen, i.e. higher friction angle.

- The stiffness of hydrate-bearing sediments can be expressed using the sum of a stress-dependent hydrate-free sediments stiffness and a hydrate dependent term which is a function of hydrate saturation Sh, initial porosity n and effective confining stress $\sigma'o$.

- Hydrate dissociation under different reservoir boundary conditions leads to volume contraction and/or stress relaxation. Pronounced shear strains develop if the hydrate-bearing sediment is subjected to deviatoric loading during dissociation.

Water-CH4-mineral systems: interfacial tension and contact angle

- The gas-water interfacial tension is pressure dependent. The contact angle changes as interfacial tension changes.

- CH4-water interfacial tension decreases up to 20mN/m from atmospheric pressure to high pressure relevant to reservoir conditions.

- Minor changes in contact angle are measured upon CH4 pressurization. Quartz, calcite, coal, and PTFE substrates show receding contact angles $\theta<90°$ (waterwet); calcite, coal and PTFE show advancing contact angles $\theta>90°$ (gas-wet).

- While stable displacement is expected during gas recovery from natural gas conventional reservoirs, gas fingering and high residual water saturation are expected from the depressurization of hydrate-bearing sediments.

Evolution of gas saturation during gas nucleation and production

- The topology of gas distributions during gas invasion and gas nucleation are fundamentally different. Invading gas forms a percolating path, while nucleating gas forms isolated gas-filled lacunae.

- Tube-network model simulation results show that the soil water characteristic curve and relative water permeability are similar for both gas invasion and nucleation. However, gas permeability is lower for gas nucleation than it is for gas invasion because some of the gas-filled tubes remain isolated without contributing to the global gas conductivity.

- Existing relative permeability equations can be used to simulate gas production in hydrate bearing sediments. However, special attention must be devoted to determine appropriate parameters for relative gas permeability as a function of saturation.

CH4-CO2 replacement: Water-CO2-mineral systems

- CO2-water interfacial tension decreases significantly from 72mN/m to ~25mN/m as pressure increases to reservoir pressure-temperature conditions.

- Contact angle varies with CO2 pressure in response to changes in CO2-water interfacial tension.

- Water solubility and diffusivity in liquid CO2 govern the evolution of interparticle pendular water.

- Pressure-dependent interfacial tension and contact angle affect injection patterns and breakthrough mechanisms.

CH4-CO2 replacement

- The CH4 hydrate cage must separate to release the CH4 molecule and trap the CO2 molecule.

- A self-sustaining CH4-CO2 replacement reaction using the excess heat that is liberated is expected as far as ~3K inside the stability field when minerals, water, and excess gas are present.

- While CH4-CO2 replacement requires the opening of the hydrate cage (i.e. a solid-liquid-solid transformation), both electrical resistance and relative stiffness measurement suggest that CH4-CO2 replacement occurs locally and gradually so that the overall hydrate mass remains solid. Therefore, no stiffness loss should be expected at the sediment scale.

- The newly formed CO2 hydrate shell must be either fractured or porous in order to allow for the high exchange rates that are experimentally observed

- Replacement rates increase near the CH4 hydrate phase boundary, with increasing pore fluid pressure until the CO2 liquefies, and, when CH4 hydrate masses are small so the surface available for CO2 exchange is high.

- Lower hydrate saturation is expected after CH4-CO2 replacement in water-limited reservoirs because hydrate forming water dissolves into liquid CO2.

- We anticipate various reservoir scale phenomena during CH4-CO2 replacement, including: potential decrease in water saturation, decrease in the liquid relative permeability, pronounced increase in fluid volume when a CH4 gas phase is formed, CO2 hydrate clogging when the velocity of the invading front is low and there is enough water to supersaturate the CO2, and the possibility of CO2 fingering leading to CH4 hydrate occlusion within the reservoir.

- Excess-gas methane hydrate reservoirs should be more amenable to CH4-CO2 replacement because of high permeability to CO2, large interface between CH4 hydrate and CO2, and no early CO2 hydrate clogging.

- Volume-pressure changes associated to CH4-CO2 replacement in excess-water reservoirs may cause increase in fluid pressure, decrease in effective stress and

strength loss, volume expansion, and gas-driven fractures if a CH4 gas phase develops and the permeability is low enough to prevent pressure dissipation.

- The hydrate phase boundary is affected by pore size, salinity, and gas mixtures. Small pores and salts in water lower the activity of water, which shifts the phase boundary to lower temperature and higher pressure conditions. Methane and carbon dioxide gas mixtures have intermediate phase boundaries between the boundaries for pure methane and pure carbon dioxide hydrates, depending on the mass ratio of each component in the mixture. These complex conditions are found in in-situ hydrate reservoirs, they determine the lower bound of the hydrate stability zone, and affect gas recovery.

- The fluid displacement pattern under mixed fluid flow conditions is affected by interfacial tension, contact angle, viscosity, and flow rate.

- The viscosity difference between gas-water or liquid CO2-water systems can cause viscous fingering. This will affect the efficiency of CH4-CO2 replacement, or the injection of liquid CO2 for geological storage.

P-wave monitoring of hydrate-bearing sand during CH4-CO2 replacement.

- CH4-CO2 replacement within the stability field occurs without loss of stiffness in the granular medium.

- CO2-flooded sandy reservoirs can remain mechanically stable during and after CH4 gas production.

- Continued sediment flushing with dry CO2 dissolves the hydrate, opens the pore throats, and weakens the granular skeleton.

Recoverable gas from hydrate bearing sediments.

- Hydrate distribution and saturation in sediments are determined by pore size distribution, connectivity, and spatial variability. These sediment characteristics also affect recoverable gas, the evolution of gas saturation, and the internal sediment stability during production.

- There is a pronounced hydrate-to-fluid volume expansion during hydrate dissociation. The volume expansion upon hydrate dissociation is a function of pressure and temperature.

- Pore-network model simulations show that the recoverable gas increases with gas expansion and initial hydrate saturation. The gas recovery efficiency is very low, even under a high expansion condition where the initial hydrate saturation is less than $Sh=5\%$.

- The pore size effect on the gas recovery efficiency vanishes when the mean pore size is larger than $\mu(Rp)=1\mu m$. If the mean pore size is smaller than $\mu(Rp)=1\mu m$, high capillary pressures at the pore throats inhibit gas expansion, which can cause gasdriven fractures in sediments.

Emergent phenomena during gas production from hydrate-bearing sediments.

- Phase changes: Water injection into water-limited sediments triggers hydrate nucleation. Conversely, gas-free water advection into water-saturated hydrate-bearing sediments dissolves hydrate.

- Fines: The presence of fines in otherwise clean sands can lead to fines migration and clogging. During dissociation, gas bubbles grow and displace fines. The fines content on the bubble surface gradually increases; eventually fines clog pore throats.

- Gas driven fractures: The expanding gas bubble may push away the skeletal particles, creating a vuggy structure, eventually leading to gas-driven fracture formation.

- Ice formation: The energy needed to dissociate hydrate is equivalent to the energy needed to increase the temperature of water up to $\Delta T \approx 96°C$. Hydrate in a sediment with porosity $n=0.4$ can be dissociated without causing ice formation when the initial hydrate saturation is lower than $Sh=0.09$ (for $Ti=5°C$) to $Sh=0.32$ (for $Ti=20°C$). Hydrate dissociation in sediments with high hydrate saturations from $Sh\sim0.78$ (for $Ti=5°C$) to $Sh\sim0.94$ (for $Ti=20°C$) requires all water to convert into ice in order to supply the energy needed for dissociation.

RELATED ACTIVITIES

Training Of Highly Qualified Personnel

- Dr. Tae Sup Yun (2005). Hydrate-Bearing Sediments (also obtained MSc). Sower's Award. Current Position: Assistant Professor, Yonsei University (formerly: *PC Rossin Assistant Prof.* at Lehigh U.).
- Dr. Patricia Taboada (Post Doc, 2007), Current Position: Assistant Professor, Rochester Institute of Technology.
- Dr. Changho Lee (Post-Doc, 2008 - 2010). Methane hydrates – natural formations. Current Position: Korea University.
- Dr. Hosung Shin (2009). Discontinuities (dissolution and polygonal faults, desiccation cracks, miscible and non-miscible fluid invasion). Sower's Award. Current Position: Assistant Professor, Ulsan University.
- Dr. Jong Won Jung (2010). Gas Production from Methane Hydrates. Current Position: Post Doctoral Fellow, Laurence Berkeley National Laboratory.
- Dr. Nicolas Espinoza (2011). CO_2 sequestration – Fundamental Studies. Current Position: Research Fellow, Ecole Nationale des Ponts et Chaussées, Paris.
- Dr. Jaewon Jang (2011). Gas Production from Methane Hydrates. Current Position: Assistant Professor, Wayne State University, Detroit.
- Sheng Dai (PhD Starting Fall 2008 - Current). Theme: Hydrate Bearing Sediments – Characterization.
- Jun Bong Jang (PhD Started Fall 2008 - Current). Theme: Gas production from fiine-grained sediments.
- Alessio Savioli (MSc 2011), Open Mode Discontinuities –Lenses.

Collaborations

During the implementation of this research, we developed close collaborations with researchers in the USA and abroad, including: Carolyn Ruppel (*USGS),* William Waite (*USGS),* Tommy Phelps (*ORNL),* Claudia Rawn (*ORNL*), K. Soga (*Cambridge U.)* , M. Sanchez (*Strathclyde U. in UK; moved to Texas A&M),* G.C. Cho (*KAIST, S. Korea),* C. Viggiani (*U. Joseph Fourier, Grenoble, France).*

Special Events

The following events were hosted/conducted as part of this study: Workshop on physical properties (2009), Hosted DOE Hydrates Program Review (2010), US-Japan Workshop (2010), and International Laboratory Comparison (2010-2011).

Study of Real Systems

During the course of this study, we explored real systems, including: Gulf of Mexico, Alaska North Slope, South Korea, India, Japan (in progress).

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