

CO₂ Utilization in Unconventional Reservoirs

Project Number 70066

Task 2

H. Todd Schaef

B. Pete McGrail

Pacific Northwest National Laboratory

U.S. Department of Energy
National Energy Technology Laboratory
Mastering the Subsurface through Technology Innovation,
& Collaboration: Carbon Storage and Oil & Natural Gas Technologies Review Meeting
August 13-16, 2018

Presentation Outline

- Program Focus Area and DOE Connections
- Goals and Objectives
- Scope of Work
- Technical Discussion
- Accomplishments to Date
- Project Wrap-up
- Appendix (Organization Chart, Gantt Chart, and Bibliography)

Benefit to the Program

- Program goals addressed:
 - Technology development to predict CO₂ storage capacity
 - Demonstrate fate of injected CO₂
- Project benefits statement: This research project conducts modeling and laboratory studies to lower cost and to advance understanding of storing pure CO₂ and mixed gas emissions produced from post- and oxy-combustion flue gas in unconventional geologic reservoirs.

Project Overview:

Goals and Objectives

- Goal: Development of geologic storage technology with a near zero cost penalty goal – a grand challenge with enormous economic benefits.
- Objective: Employ a multidisciplinary approach for identifying key sequestration opportunities and for pursuing major research needs in:
 - Identifying R&D needs and pursuing R&D on promising low-cost technologies for utilizing CO₂ and CO₂ containing other constituents in depleted shale gas and shale oil reservoirs.
 - phase behavior and fate and transport of supercritical gas mixtures in fractured geologic formations.

Project Overview:

Scope of work

➤ Task 2 – Utilization in Unconventional Reservoirs

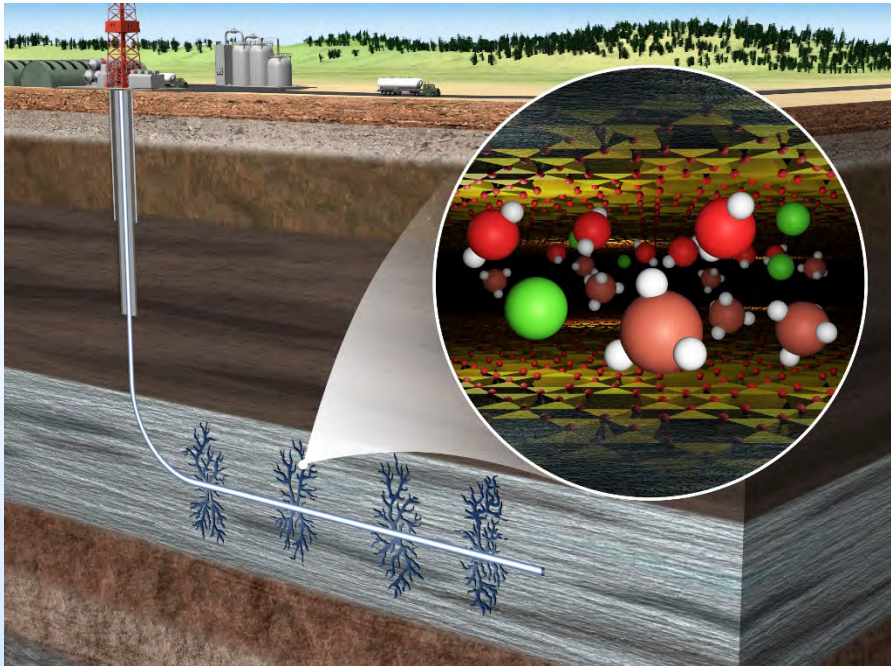
▪ 2.1 *Laboratory Based Experiments*

- Model mineral systems
- Supercritical fluids and clay interactions
 - ❖ Modification to clay structure tracked as a function of CH₄-CO₂-H₂O concentration
 - ❖ Changes to the CO₂, CH₄, H₂O chemical environments
 - ❖ Perturbations to the CO₂, CH₄ molecules

▪ 2.2 *Data Analysis and Manuscript Preparation*

- Pure CO₂ and CH₄ studies
- CO₂-CH₄ supercritical fluid mixtures
- MD simulations to support lab efforts

Clay Interactions with Supercritical Fluids



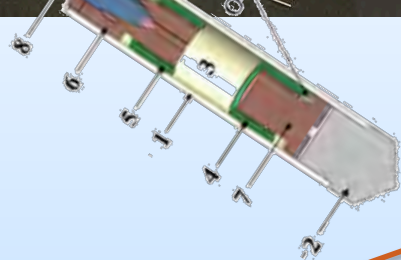
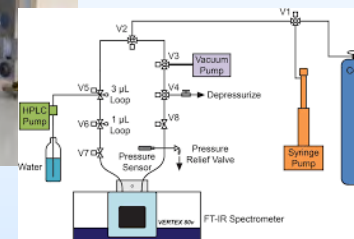
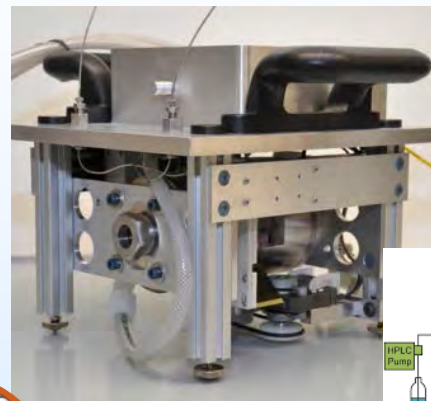
➤ Enhanced Gas Recovery with CO₂

- Replacing current fracking fluids with CO₂ or modified fluids requires we understand the CH₄/CO₂/surface interactions on a molecular scale
- Focus on expandable clays

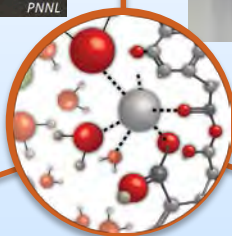
Key Findings and Outcomes:

- Swelling by CO₂ depends mostly on strength of interaction between cation and clay basal surfaces
- CH₄ sorbs via passive space filling but does not cause swelling
- Increasing fluid CO₂ concentrations leads to expansion of Na saturated clays to 1W state at lower RH
- Measured water solubility for CH₄-CO₂ mixtures and benchmarked against models

In Situ High Pressure Instrumentation

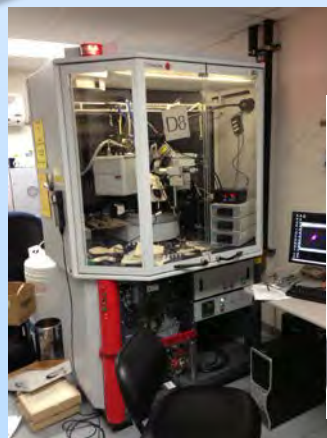


NMR



IR

XRD



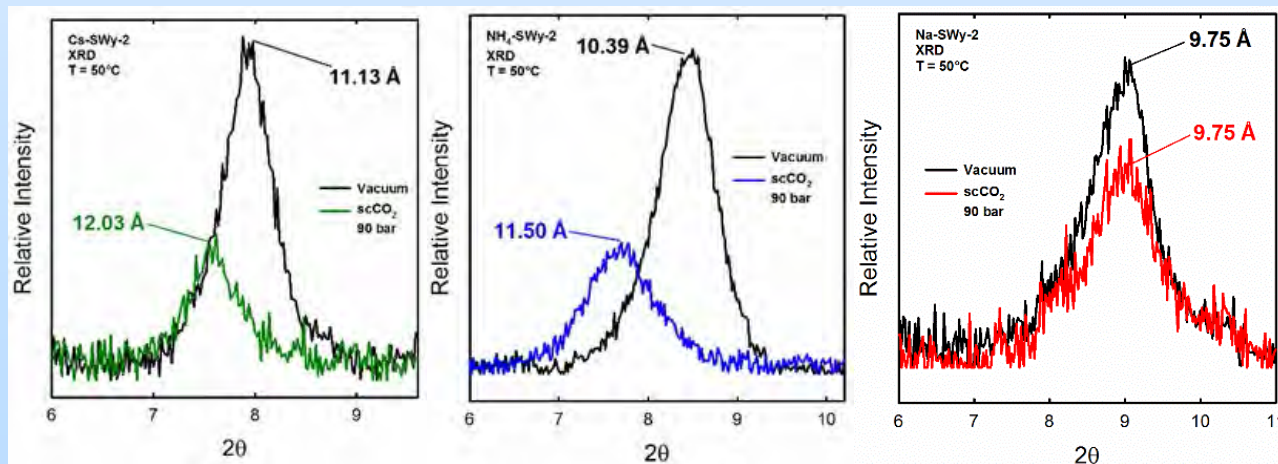
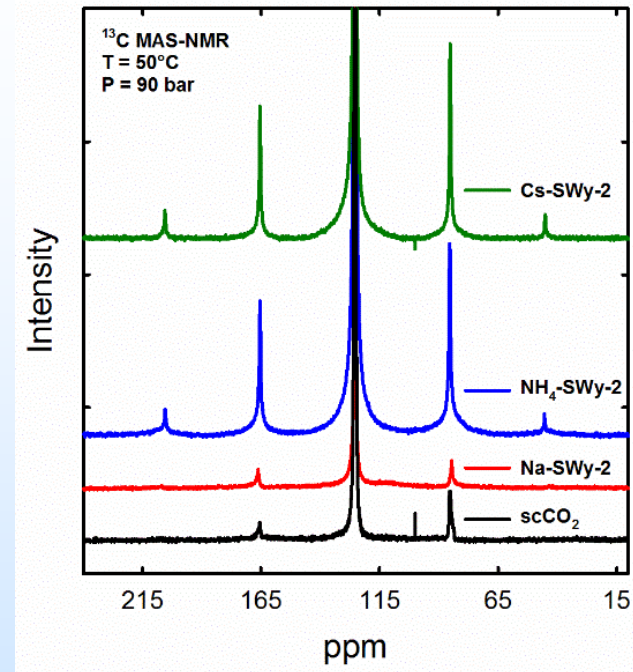
Cation and Dry CO₂ interactions: What is happening in the clay interlayer?

XRD spectra of Cs, NH₄, and Na-clay in contact with scCO₂

- Structural changes to Cs⁺ and NH₄⁺
- No shift in the Na⁺

¹³C MAS-NMR of CO₂ sorbed to Cs, NH₄, Na-clay

- Resonance for scCO₂ and Na⁺-clay + scCO₂ at ~124 ppm are similar
- Centerbands for Cs⁺ and NH₄⁺-clays have increased fwhh (more restrictive CO₂ environment), double sets of SSB



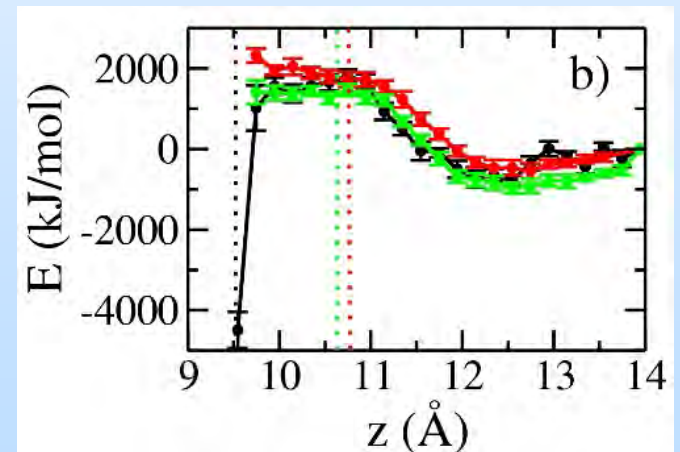
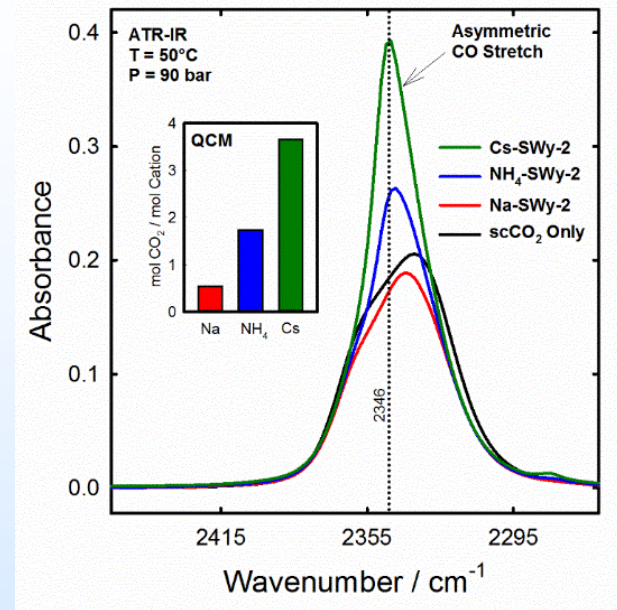
Cation and Dry CO₂ interactions: What is happening in the clay interlayer?

IR and QCM Measurements

- Asymmetrical CO stretching at 2335 cm⁻¹ changes intensity and shape for Cs and NH₄ clay
- Na-clay similar to bulk scCO₂
- QCM captures external and internal CO₂
- CO₂ concentrations trend with IR

MD Simulations

- Immersion energy increases for Na⁺ clay, from 9.5 to 10.7Å, indicating collapsed state is stable
- Little or no barrier for Cs⁺ and NH₄⁺ clays
- CO₂ induced swelling depends on interaction between clay basal surface and cation



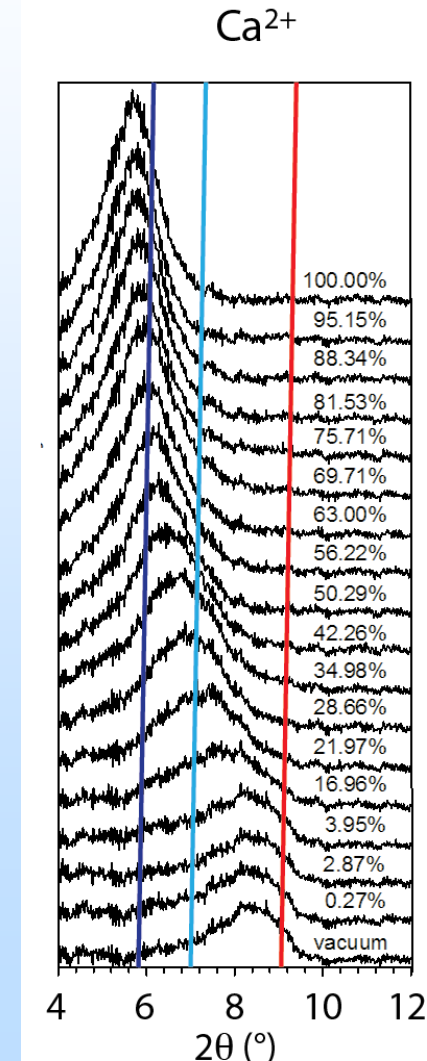
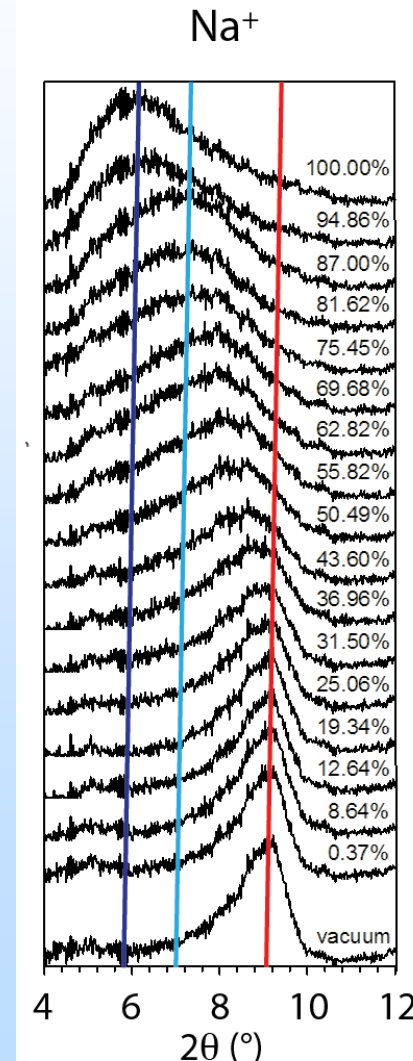
Interactions of scCH₄ with Clays under Reservoir Conditions

Cation exchanged smectites (Ca²⁺, Pb²⁺, Na⁺, Cs⁺) exposed to variable wet scCH₄ give insight into gas/clay interactions.

Pressurized XRD Experiments

- Variable wet scCH₄, 50°C
- No expansion when exposed to dry scCH₄
- Clays expand with increasing RH
- Na-clay ranges from 9.8 Å to 15.0 Å

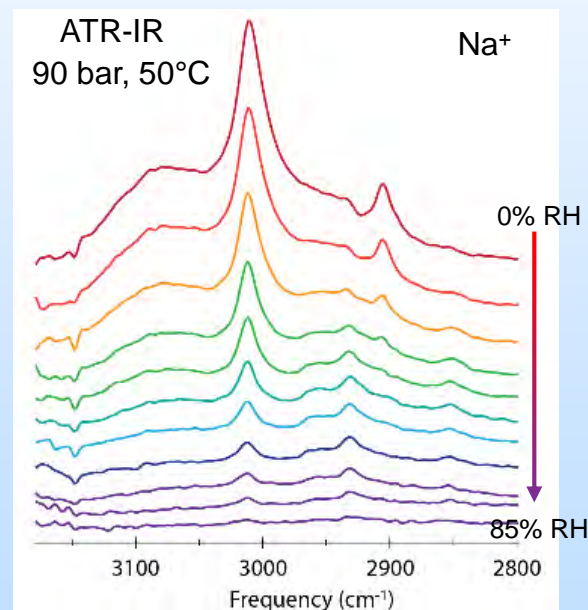
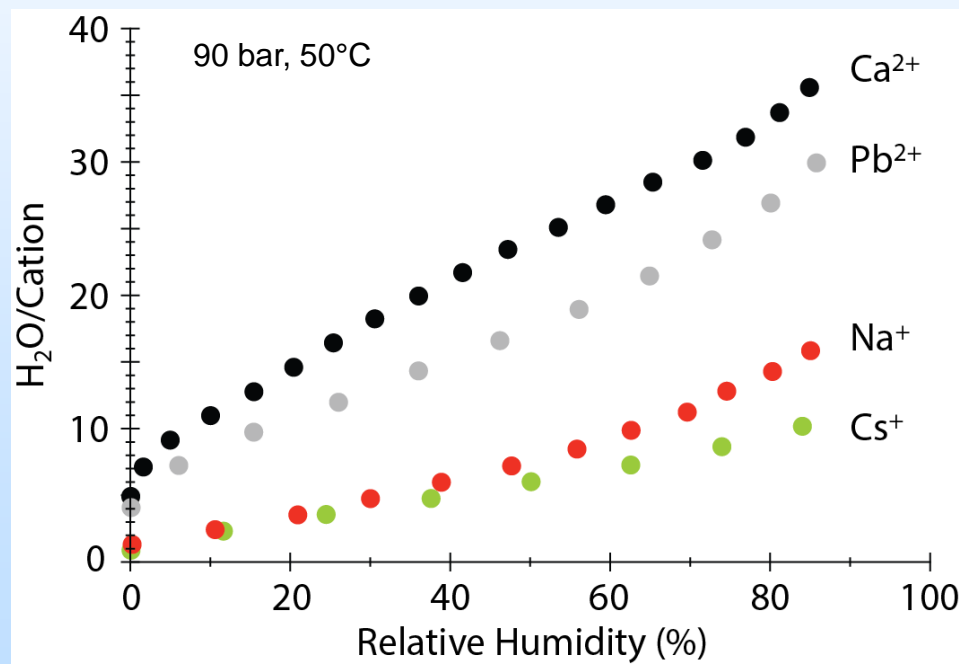
Cation	Vacuum (10 ⁻³ Torr)	scCH ₄ 90 Bar
Na ⁺	9.8	9.8
Cs ⁺	11.2	11.1
Pb ²⁺	10.8	11.00
Ca ²⁺	10.6	10.8



Interactions of scCH₄ with Clays under Reservoir Conditions

Pressurized IR data collected from cation exchanged smectites exposed to variable wet scCH₄ highlight gas/clay interactions at reservoir conditions.

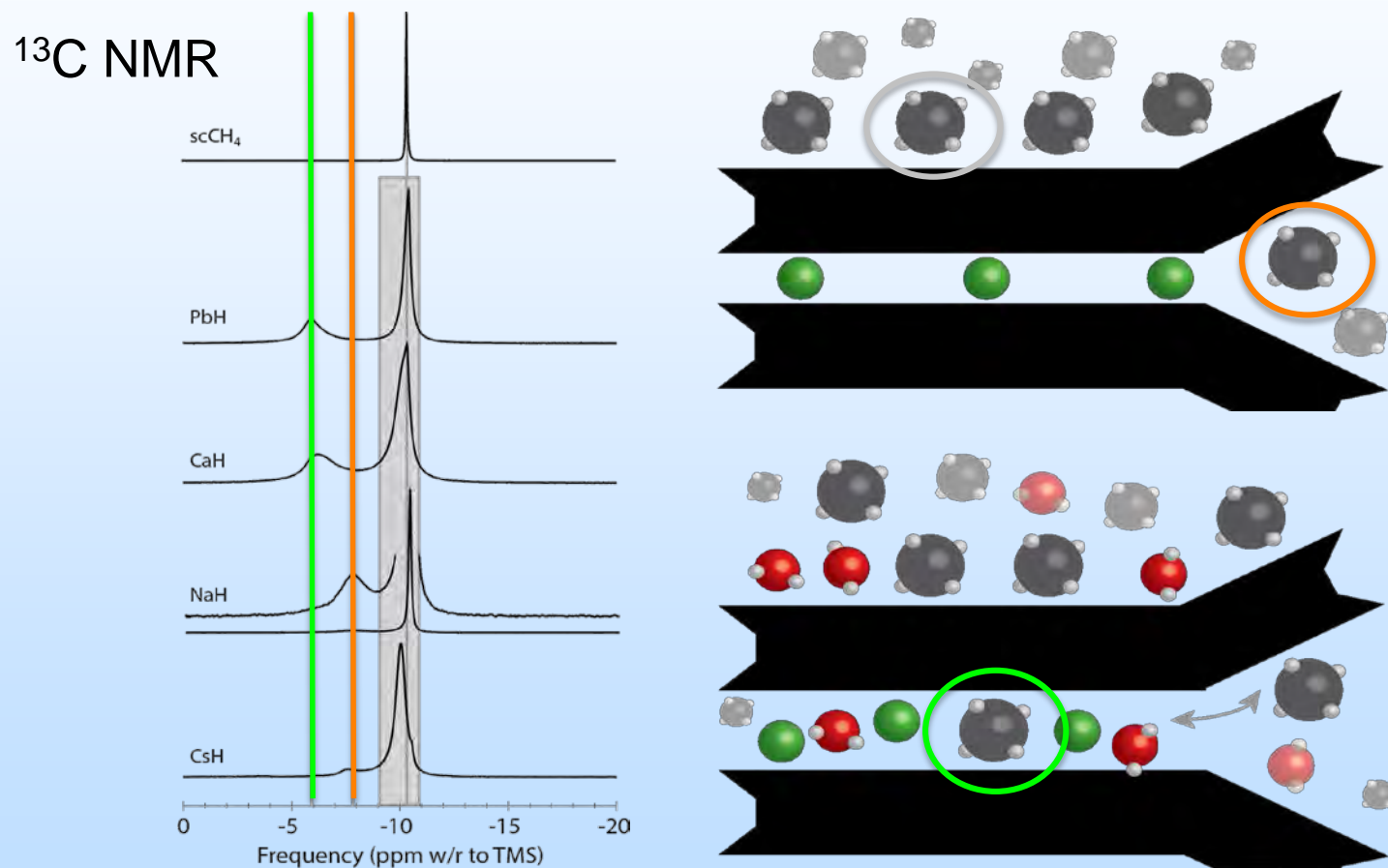
- Ca²⁺, Pb²⁺ clays sorb more water than Na⁺, Cs⁺ (Transmission IR) during exposure to scCH₄
- Sorbed CH₄ decreases with increasing RH (ATR-IR) for all clays



Bowers, GM, JS Loring, HT Schaefer, et al., 2018. "Interaction of Hydrocarbons with Clays under Reservoir Conditions: In situ Infrared and Nuclear Magnetic Resonance Spectroscopy and X-ray Diffraction for Expandable Clays with Variable Wet Supercritical Methane, ACS Earth and Space Chemistry, 2, 640-652.

Interactions of scCH_4 with Clays under Reservoir Conditions

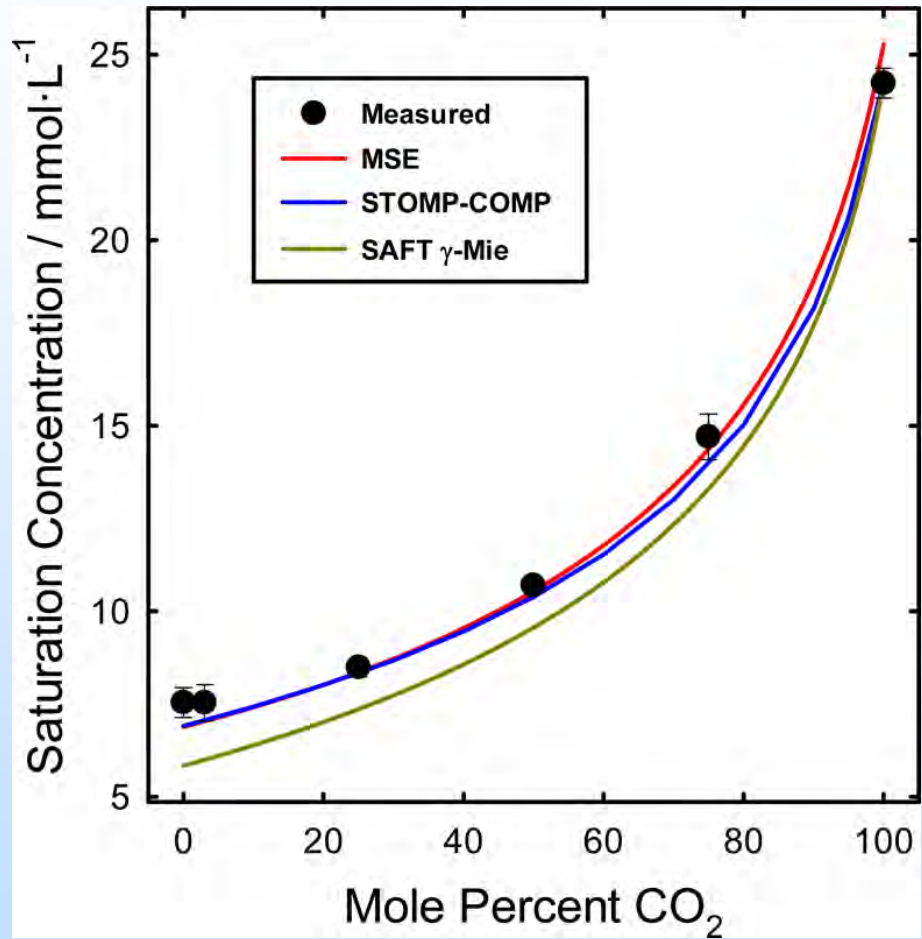
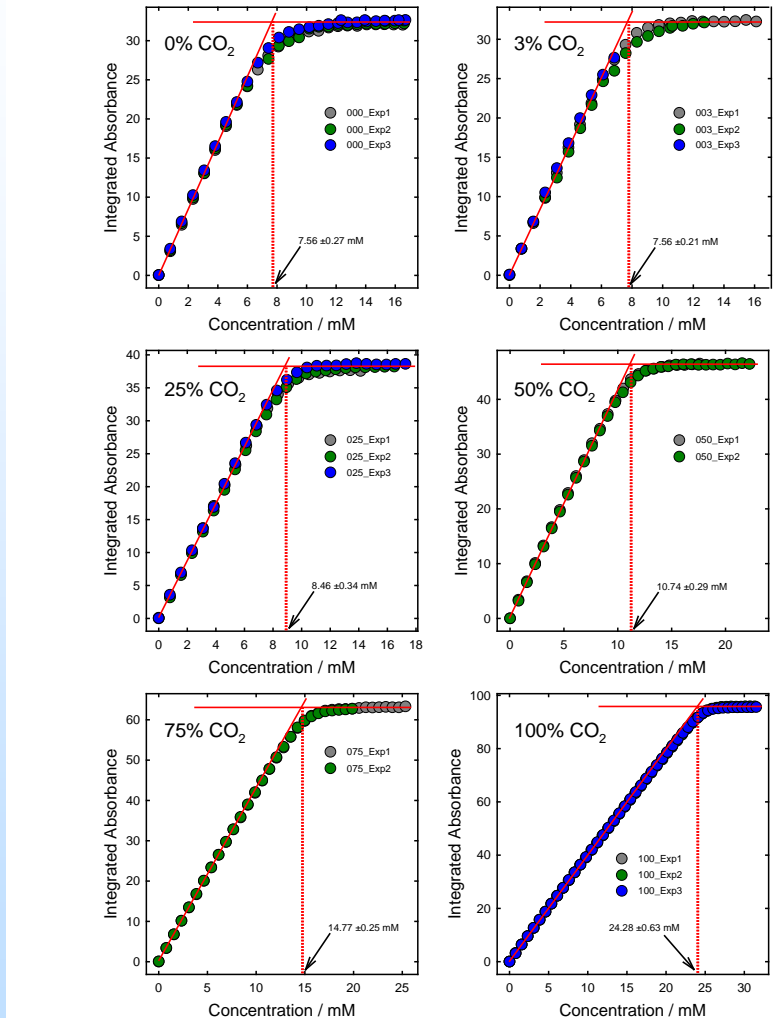
Pressurized ^{13}C MAS NMR of scCH_4 in contact with smectite indicated different chemical environments



Bowers, GM, JS Loring, HT Schaefer, et al., 2018. "Interaction of Hydrocarbons with Clays under Reservoir Conditions: In situ Infrared and Nuclear Magnetic Resonance Spectroscopy and X-ray Diffraction for Expandable Clays with Variable Wet Supercritical Methane, ACS Earth and Space Chemistry, 2, 640-652.

CO₂/CH₄ Mixtures: Water Solubilities at Saturation

IR Titrations to determine saturation concentrations



Loring JS, DA Bacon, et al., 2017. "Water Solubility at Saturation for CO₂-CH₄ Mixtures at 323.2 K and 9.000 Mpa", J. Chem. Eng. Data, 2017, 62 (5), pp 1608-1614.

Mixed Gas Systems: CH₄/CO₂ in contact with Clays

Clays (Na, Cs, NH₄) exposed to variably hydrated supercritical fluid CO₂-CH₄ mixtures and characterized by IR and XRD.

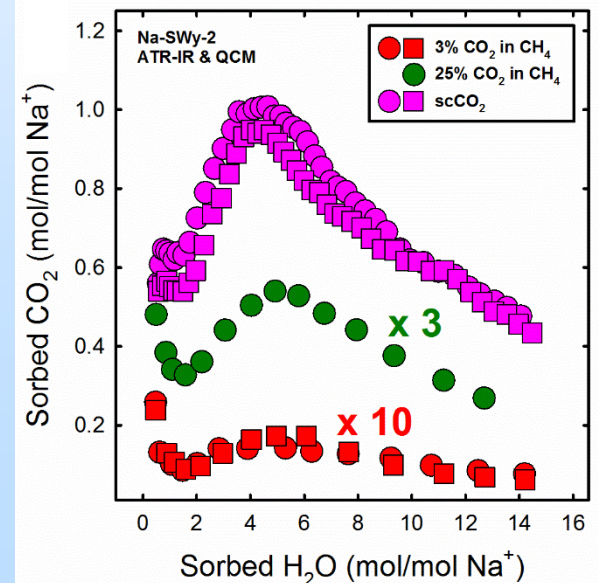
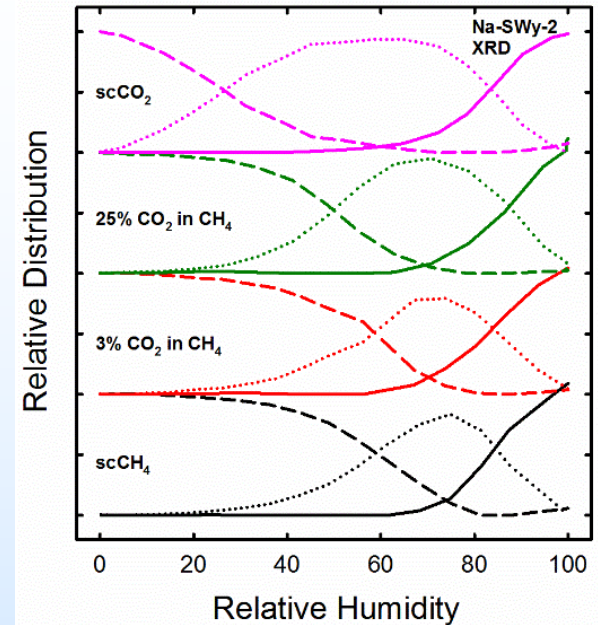
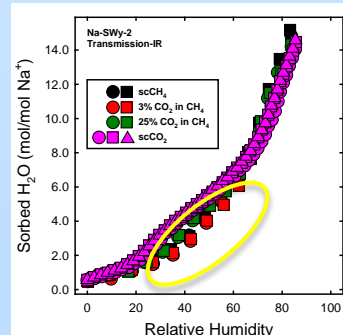
XRD of clay hydration- dashed, dotted, and solid curves correspond to relative abundance (0W, 1W, and 2W)

- Na-Clay: vacuum and at 50°C, collapsed d₀₀₁ value of 9.69 Å
- Exposure to four supercritical dry fluid CO₂-CH₄ mixtures resulted in no expansion
- Clay expansion starts at progressively lower RH with increasing CO₂ concentrations
- Increasing CO₂ concentrations leads to expansion of Na clay to 1W state at lower RH

ATR-IR sorbed CO₂ as a function of sorbed H₂O

- Sorbed H₂O concentrations increased with RH for all fluid compositions
- 2343 cm⁻¹ attribute to sorbed CO₂ that is rotationally constrained
- Sorbed CO₂ decreases with increasing H₂O
- CO₂ facilitates intercalation of H₂O and swelling at lower RH compared to CH₄

Loring, JS, HT Schaefer, et al., 2018. "Synergistic coupling of CO₂ and H₂O during expansion of clays in super critical fluids", in prep.



Accomplishments to Date

- ▶ Published a series of manuscripts demonstrating clay/fluid behavior at reservoir conditions
- ▶ Completed experiments relating volume changes to swelling clays in variable hydrated supercritical mixed gas fluids.
- ▶ Developed strong collaborations
 - Michigan State University
 - St Mary's College
- ▶ Acquired samples from producing basins
 - Woodford Shale from Grady County Oklahoma
 - Eastern Venezuela Basin
- ▶ Discussing with industry to identify problems and future partnerships

Appendix

- These slides will not be discussed during the presentation, but are mandatory

Organization Chart

- Project team has participants that cut across the Energy & Environment and Fundamental Sciences Directorates at PNNL
- Pacific Northwest National Laboratory is Operated by Battelle Memorial Institute for the Department of Energy

Milestone Table

#	Type	Regular or Stretch	Expected Completion Date	Description
1	<i>Progress measure</i>	Regular	09/30/2018	Coordinate experimental activities with collaborators to complete gas sorption measurements on smectite clays
2	SMART Milestone	Regular	09/30/2019	Assemble and analyze experimental data to determine optimal pressure, temperature, and water content of supercritical fluid that provides >90% exchange of CH ₄ for CO ₂ on a prototypical clay.
3	<i>Progress measure</i>	Regular	09/30/2020	Assemble and analyze basin specific experimental data for incorporation into simulator for benchmarking against actual production data. The results will also be assembled into a manuscript for publication in a peer reviewed journal.

Bibliography

- Bowers, GM, JS Loring, HT Schaef, ED Walter, SD Burton, DW Hoyt, SS Cuniff, N Loganathan, and RJ Kirkpatrick, **(2018)**. “Interaction of Hydrocarbons with Clays under Reservoir Conditions: In situ Infrared and Nuclear Magnetic Resonance Spectroscopy and X-ray Diffraction for Expandable Clays with Variable Wet Supercritical Methane”, ACS Earth and Space Chemistry, 2, 640-652.
- Loganathan, N, GM Bowers, AO Yazaydin, HT Schaef, JS Loring , AG Kalinichev, and RJ Kirkpatrick, **(2018)**, “Clay Swelling in Dry scCO₂: Effects of interlayer Cation on the Structure, Dynamics, and Energetics of CO₂ Intercalation Probed by XRD, NMR, and GCMD Simulations”, Journal of Physical Chemistry C, 122, 4391-4402.
- Schaef, HT, N Loganathan, G Bowers, RJ Kirkpatrick, AO Yazydin, SD Burton, DW Hoyt, KS Thanthiriwatte, DA Dixon, BP McGrail, KM Rosso, ES Ilton, and JS Loring. **(2017)** “Tipping Point of Expansion of Layered Aluminosilicates in Weakly Polar solvents: Supercritical CO₂”, Applied Materials and Interfaces, 9, 36783-36791.
- Loring, JS, KH Bacon, RD Spring, A Anderko, S Gopinanth, CM Yonkofski, CJ Thompson, BP McGrail, KM Rosso, and HT Schaef. **(2017)**, “Water Solubility at Saturation for CO₂–CH₄ Mixtures at 323.2 K and 9.000 Mpa”, Journal of Chemical and Engineering, 62, 1608-1614.
- Bowers, GM, HT Schaef, JS Loring, DW Hoyt, SD Burton, ED Walter, and RJ Kirkpatrick, **(2016)**. “Role of Cations in CO₂ Adsorption, Dynamics, and Hydration in Smectite Clays under in situ Supercritical CO₂ Conditions”, Journal of Physical Chemistry C, 121, 577-592.