Advanced CO_2 Sequestration Studies

Project Number 58159 Task 2

Utilization and Storage of CO_2 in Unconventional Reservoirs

B. Peter McGrail

Pacific Northwest National Laboratory

U.S. Department of Energy

National Energy Technology Laboratory
Carbon Storage R&D Project Review Meeting
Developing the Technologies and Building the
Infrastructure for CO_2 Storage

August 20-22, 2013

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 CO_2 storage capacity and enhanced hydrocarbon recovery in unconventional reservoirs
  - Demonstrate fate of injected CO_2 and contaminants
- <u>Project benefits statement</u>: Modeling and laboratory studies conducted on this project will lower cost and advance understanding of using CO_2 and mixed gas streams produced from post- and oxy-combustion power plants for enhanced hydrocarbon recovery and permanent storage in unconventional reservoirs. Findings from this project will advance understanding of preferred CO_2 storage opportunities and capacity in these unconventional geologic formations.

Project Overview:
Goals and Objectives

- Goal: Develop improved understanding of geologic storage opportunities in unconventional reservoirs using CO_2 and mixed gas streams
- Objective: Utilize CO_2 to enhance hydrocarbon production and minimize environmental impacts
  - Conduct experiments to examine reaction products, and mechanisms occurring in mixed gas systems.
  - Reservoir modeling to predict fate and transport of mixed gases and to optimize system efficiency.
  - Atomistic simulations to gain mechanistic insights

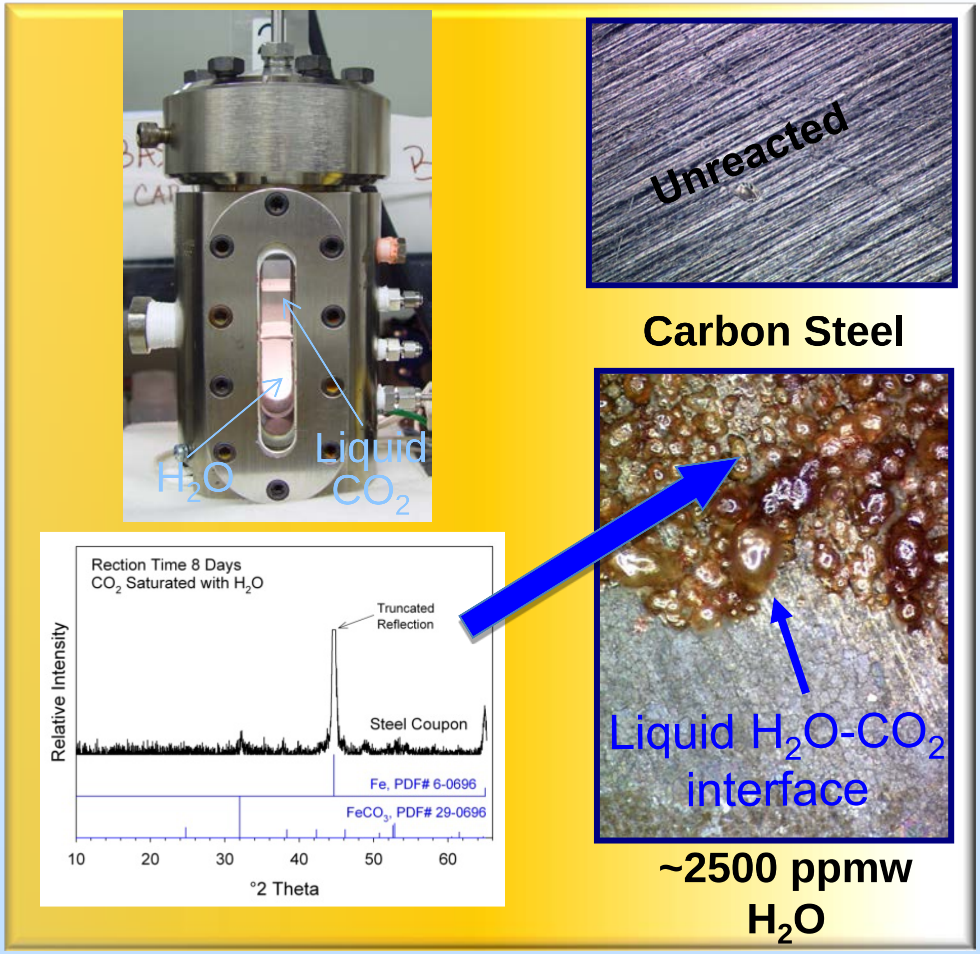
Project Overview: Scope of work

- Task 1 – Pipeline and Casing Steel Corrosion Studies
  - Evaluate corrosion behavior of pipeline steels in CO_2 mixtures containing trace contaminates (i.e. SO_2,O_2,H_2S)
  - Evaluate impact of connate water uptake in $scCO_2$ with mixed gases on corrosion resistance of well construction materials
- Task 2 – CO_2 Utilization and Storage

  Co-sequestration through in situ reactions
  - Evaluate reaction products, mechanisms, and rate of reactions in the CO_2-SO_2-O_2-H_2O system in carbonate reservoirs
  - Assess critical role of water solvated in the $scCO_2$ phase in catalyzing reactions that strip these contaminants from the $scCO_2$

  Enhanced methane production and sequestration in shale gas formations
  - Conduct fundamental measurements of CO_2 and mixed gas interactions with key minerals and organics in shales
  - Predict fate and transport to optimize hydrocarbon recovery efficiency
  - Utilize atomistic simulations to gain mechanistic insight of the reactivity between $scCO_2$ and water with various shale minerals

Mixed-Gas Transportation and Injection



McGrail, B. P.; Schaef, H. T.; Glezakou, V. A.; Dang, L. X.; Owen, A. T., Water Reactivity in the Liquid and Supercritical CO_2 Phase: Has Half the Story Been Neglected? IGGCT, 2009; Vol. 1, pp 3415-3419.

Key Issues

- Pipeline specifications for mixed gases lack industry experience
  - CO_2-SO_2 mixtures not commercially transported
  - Adequacy of current water content specifications unknown
- Evaluate stability of wellbore casing steels exposed to mixed-gases containing water

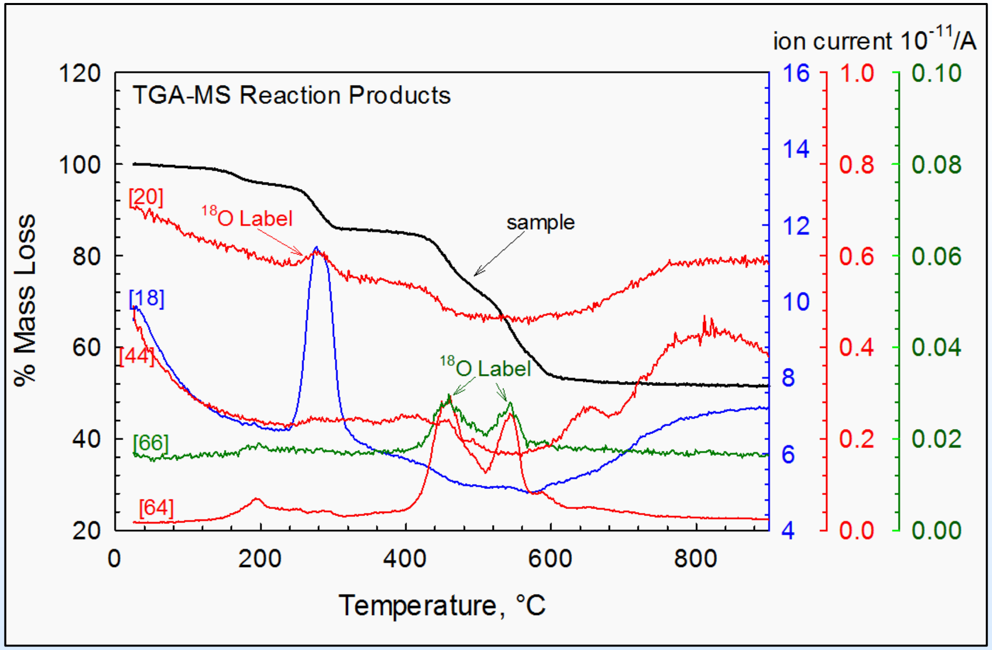
Approach

- Conduct laboratory experiments to examine reactivity of CO_2-SO_2-O_2-H_2O mixtures on steel surfaces
- Determine role of water in reaction steps and impact of steel additives (such as Mn and Mo) on corrosion

Tracking Reaction Mechanisms Through Isotopic Labels

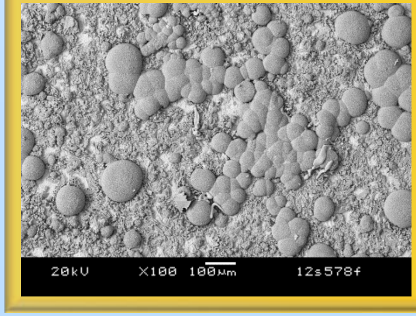
Experimental Approach

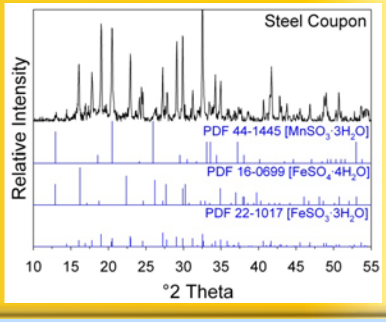
- Role of Water in Corrosion
  - How does water interact with metal surfaces during corrosion processes
  - Isotopic labels such as $H_2^{18}O$ can track dissolved water behavior
- Corrosion with X65 Pipe Steel
  - CO_2-SO_2-$H_2^{18}O$
  - Gas Chemistry show rapid consumption of SO_2
  - XRD and SEM indicate significant surface corrosion
  - TGA-MS identifies ^{18}O in reaction product, indicating no free water phase



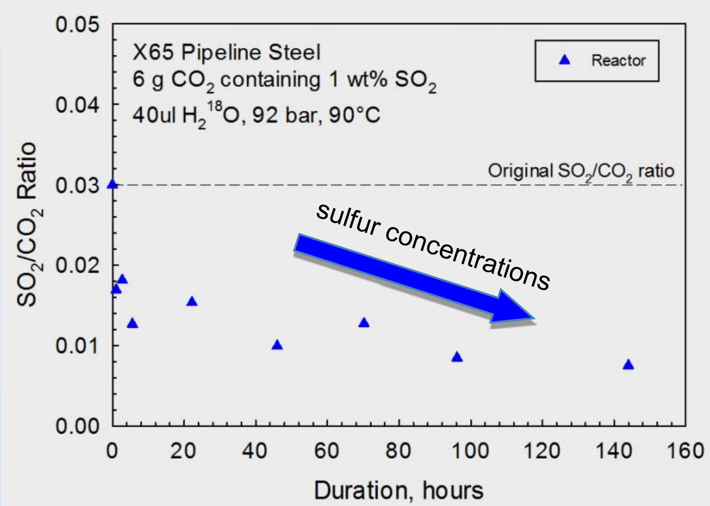
Surface Reaction Products (SEM & XRD)

CO_2 (92 bar), SO_2 (~13,000 ppmw), H_2O (7,937 ppmw), 90°C



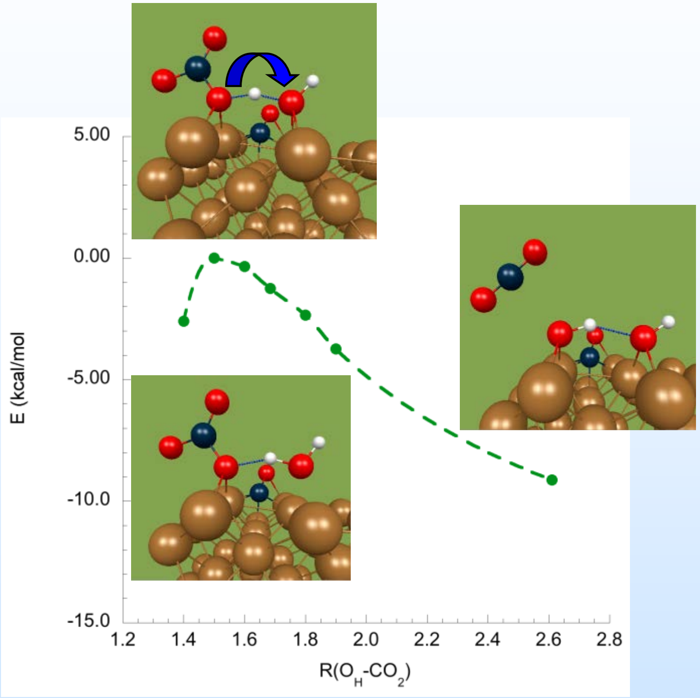


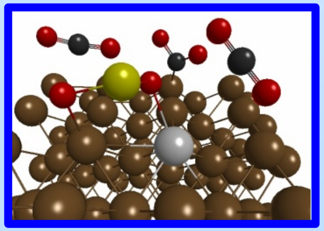
in situ Gas Chemistry Analysis

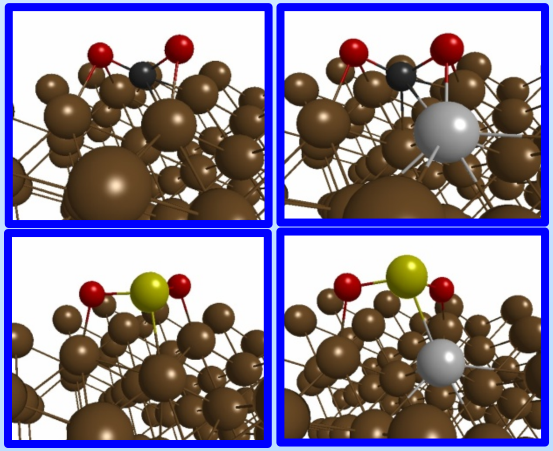


Molecular Simulations Provide Insights on Surface Interactions

- **Molecular Scale:** H_2O on metal surface remains in molecular form
  - Binds strongly in presence of absorbed oxygen
  - Inclination to hydroxylate surface
  - Reduction in barrier energies to <9.0 kcal/mol
  - Regeneration of H_2O by H transfer to nearby OH
- **DFT Calculations:** SO_2 binds more strongly on Fe or Fe/Mn surface compared to CO_2
  - Mn increases binding energy
  - SO_2 prefers Mn binding sites
  - non-equilibrium effects upon rates
  - dynamic morphology changes of catalysts
- **Current Activity**: CO_2-SO_2-O_2-H_2O experiments



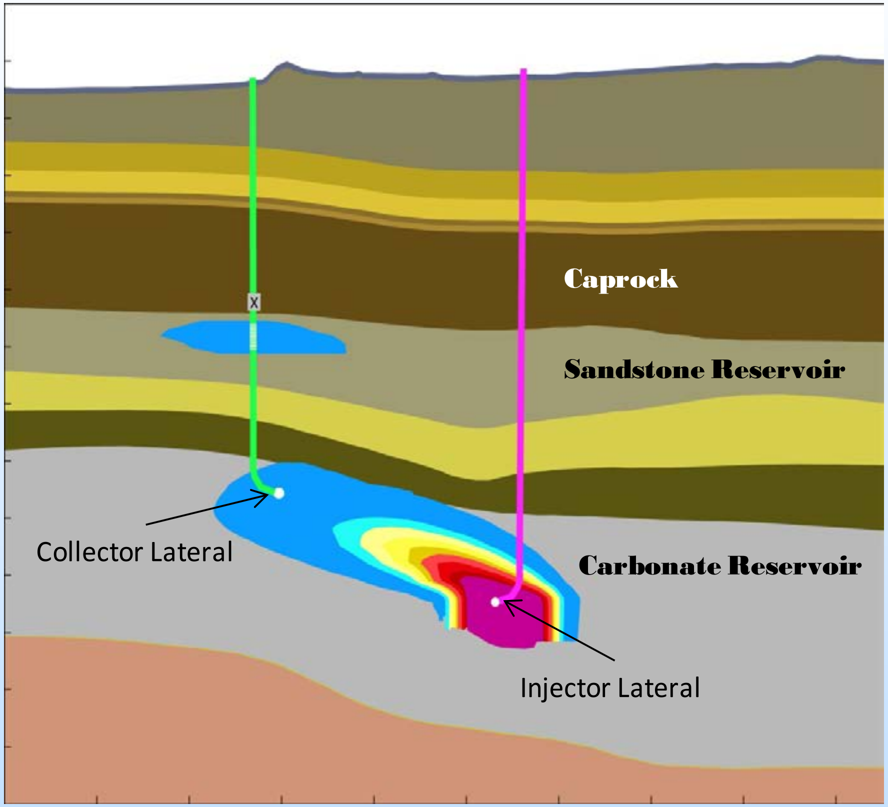




In Situ Scrubbing Concept

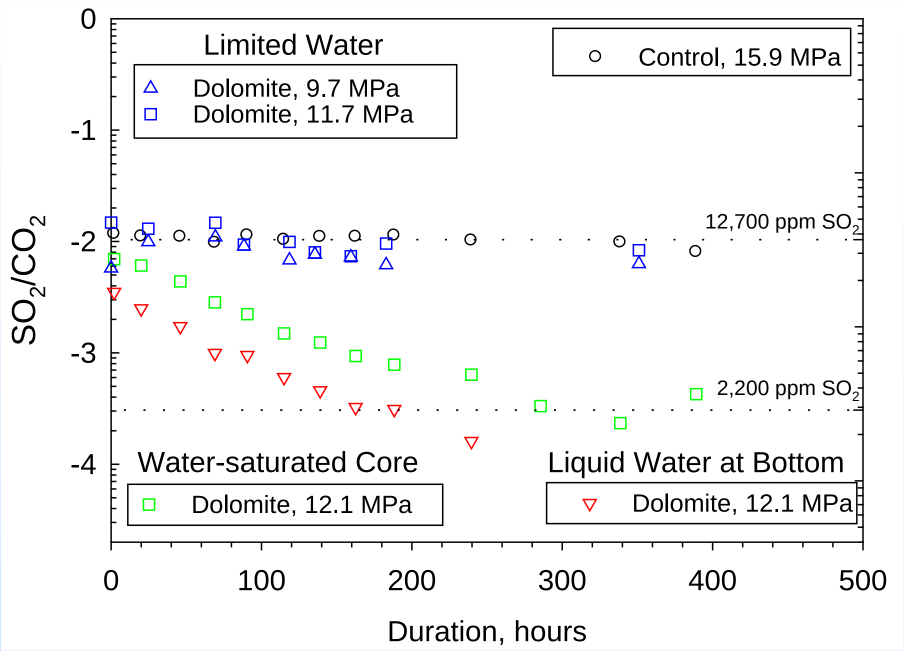
- Oxy-combustion gas streams can contain over 1% SO_2
  - Likely candidate technology for new builds or retrofits
  - Currently managed through SO_2 scrubbers
- Chemistry behind SO_2 removal
  - In wet FGD process, SO_2 becomes sulfurous acid:
    - $SO_2 + H_2O \rightarrow H_2SO_3$
  - Combines with limestone
    - $CaCO_3 + H_2SO_3 \rightarrow CaSO_3 + H_2O + CO_2$

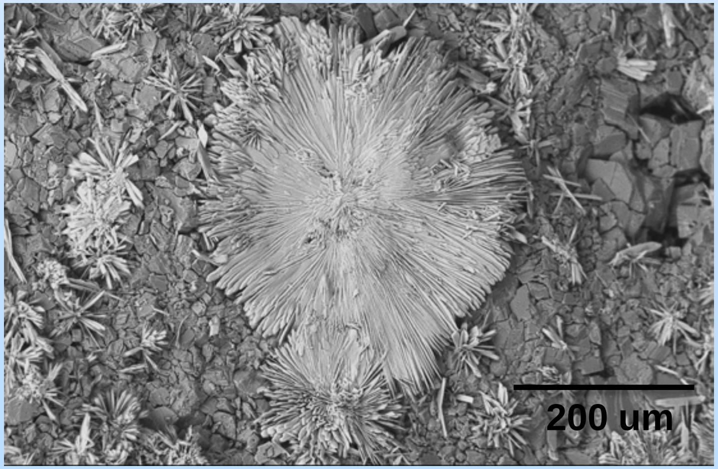
    To form sulfites, which can be oxidized to sulfates
- In situ stripping mimics FGD process but deep underground
  - More economically favorable when retrofitting existing power plants for CO_2 capture
  - Produce pipeline grade CO_2 for EOR/EGR with no additional capital or operating costs for FGD



Glezakou, V. A., B. P. McGrail, and H. T. Schaef. 2012. "Molecular Interactions of SO_2 with Carbonate Minerals under Co-Sequestration Conditions: A Combined Experimental and Theoretical Study." *Geochim. Cosmochim. Ac.* ***92:265-274.***

Low-water environments: Does SO_2 stripping occur?



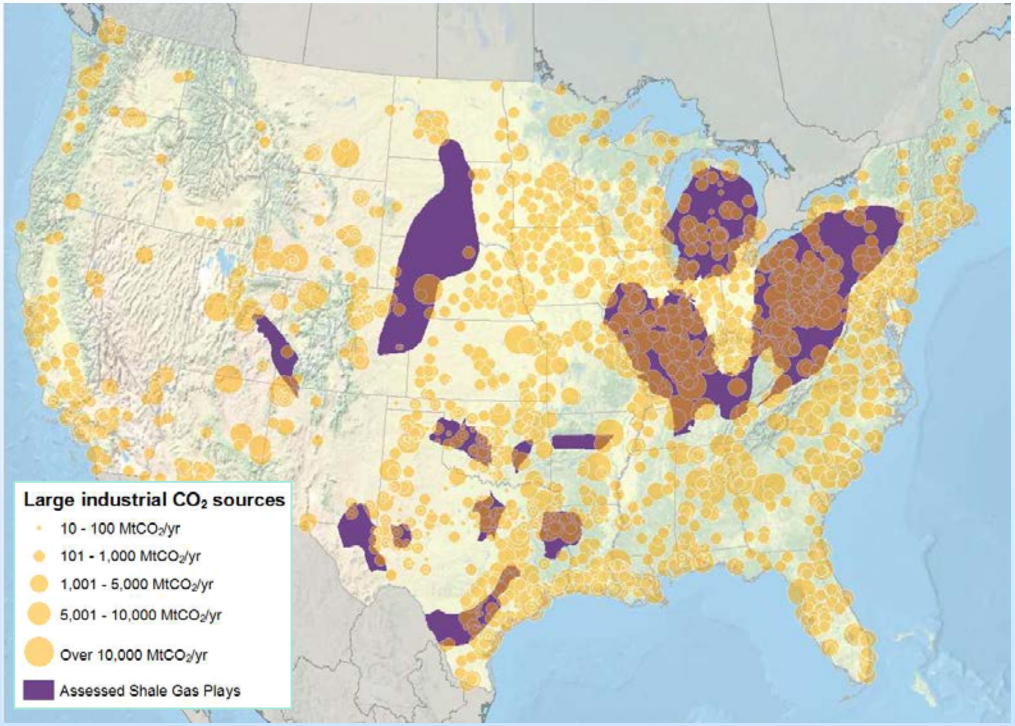


- **Results**
  - Sulfur species permanently removed from $scCO_2$ phase
  - Solid sulfur products
    - Surface coatings form very rapidly
    - Hannebachite ($CaSO_3.0.5H_2O$)
- **Utilization**
  - Carbonate reservoirs are widespread and appear well suited for accepting mixed CO_2-SO_2 gas streams
  - In situ stripping could be used for gas cleanup
    - More economically favorable when retrofitting existing power plants for CO_2 capture
    - Produce pipeline grade CO_2 for EOR with no additional capital or operating costs for FGD

Evaluating potential of CO_2 use in shales for enhanced gas recovery and storage

<u>Objective</u>: Identify early opportunities for utilization of CO_2 in secondary shale gas recovery

- **Additional gas recovery potential via CO_2-EGR**
  - 27 USGS assessment units, 10 basins
  - 96 – 390 TCF at EGR:EUR ratios of 0.25 – 0.75
  - Potential total value of $350-1500 billion
  - *Average* value of \$11-43 / tCO_2
- **CO_2 storage potential**
  - Estimated via methane mass replacement as a function of depth
  - Same 27 assessment units represent a CO_2 storage resource as large as 36,000 MMT CO_2
  - Marcellus shale accounts for 25% of this total



<u>Approach</u>

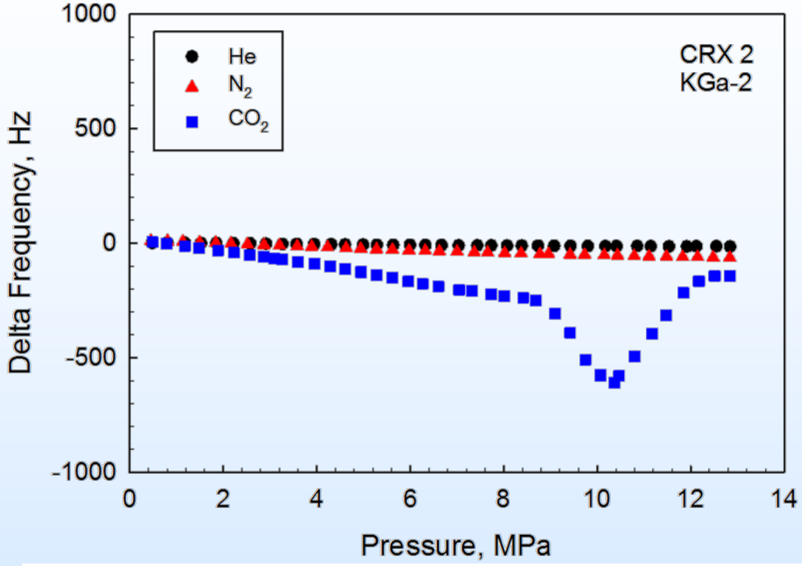
I. Improve understanding of permanent CO_2 gas trapping mechanisms in shales

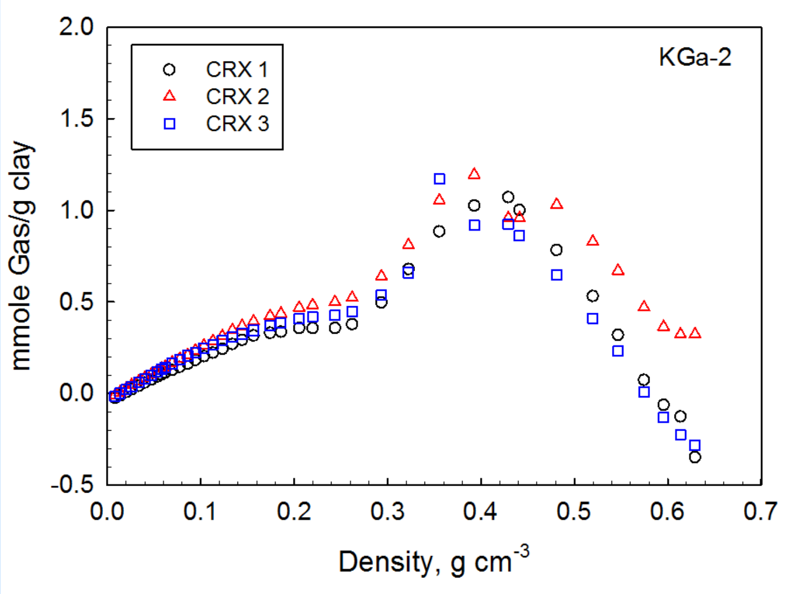
II. Conduct reservoir simulations to improve secondary recovery

III. Address long term impacts to U.S. CO_2 storage capacity

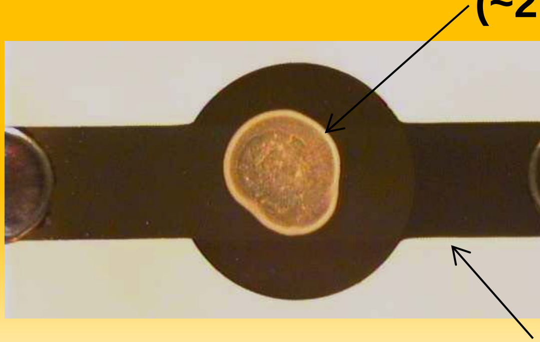
Fundamental Gas Adsorption Studies

- Quartz Crystal Microbalance
  - High mass sensitivity for micro weighing in pressurized environments
  - Excellent for studying mineral-fluid interfaces including adsorption and chemical processes
- Gas adsorption on Kaolinite
  - N_2 ~0.1-0.2 mmol/g clay
  - $scCO_2$ adsorption reaches a max near 0.4 g/cm³ (50º C)





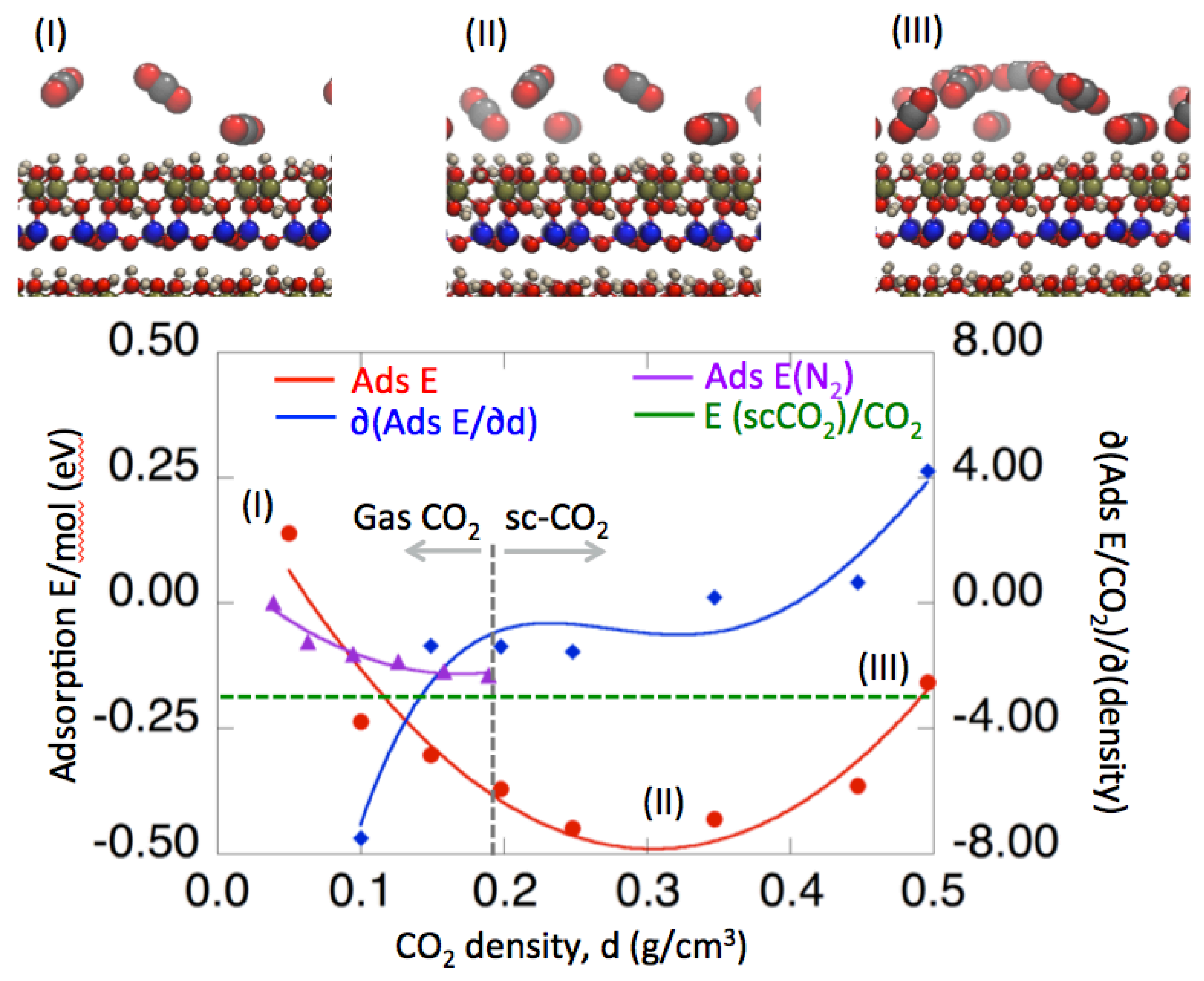
10 MHz ATR Quartz Crystal



kaolinite (~2,868 ng)

gold electrode

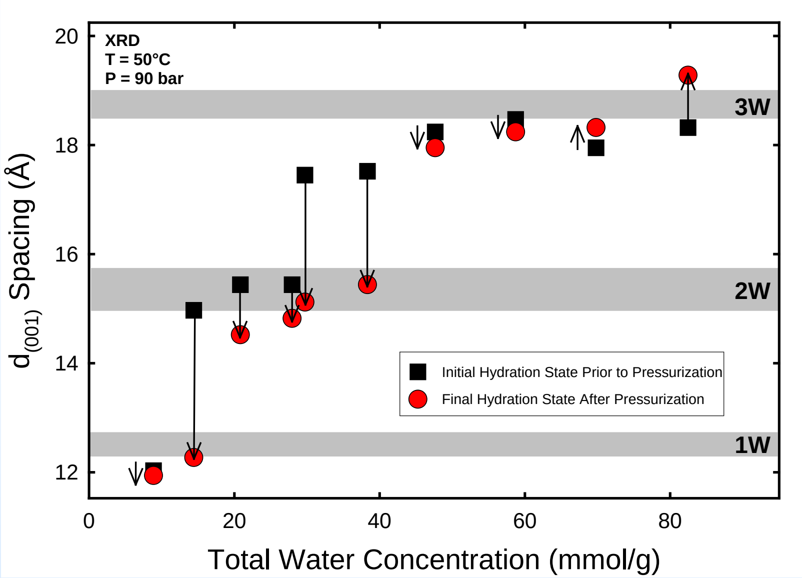
Computational Studies of CO_2/N_2 Adsorption on Kaolinite

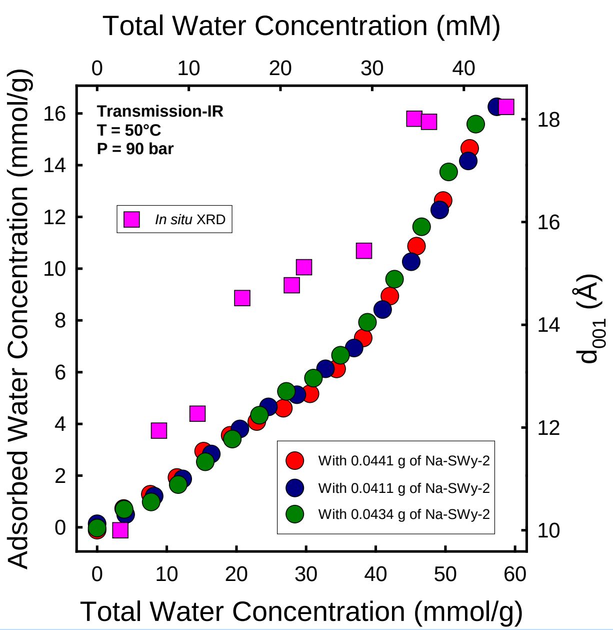


- (I) CO_2 molecules adsorb almost parallel to the kaolinite surface
- (II) CO_2 aggregation in characteristic distorted T-shaped orientation (max ~0.35-0.4 g/ml)
- (III) Desorption occurs after the crossover point (~0.2 eV, green line)

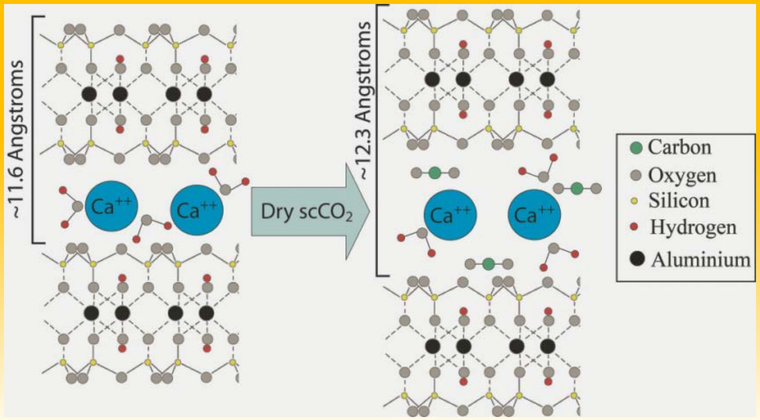
Clay Expansion/Contraction

- **Experiments**: Exposing variable hydrated Na^+ montmorillonite (Na-SWy-2) to anhydrous $scCO_2$ (90 bar and 50°C)
  - Structural changes (XRD)
  - H_2O concentrations in $scCO_2$ or on clay
- Dehydration processes dominate when clay is in a ~1W or 2W hydration state
  - Water partitioning from clay into $scCO_2$
  - $scCO_2$ entering /exiting interlayer
- Mineral volume changes



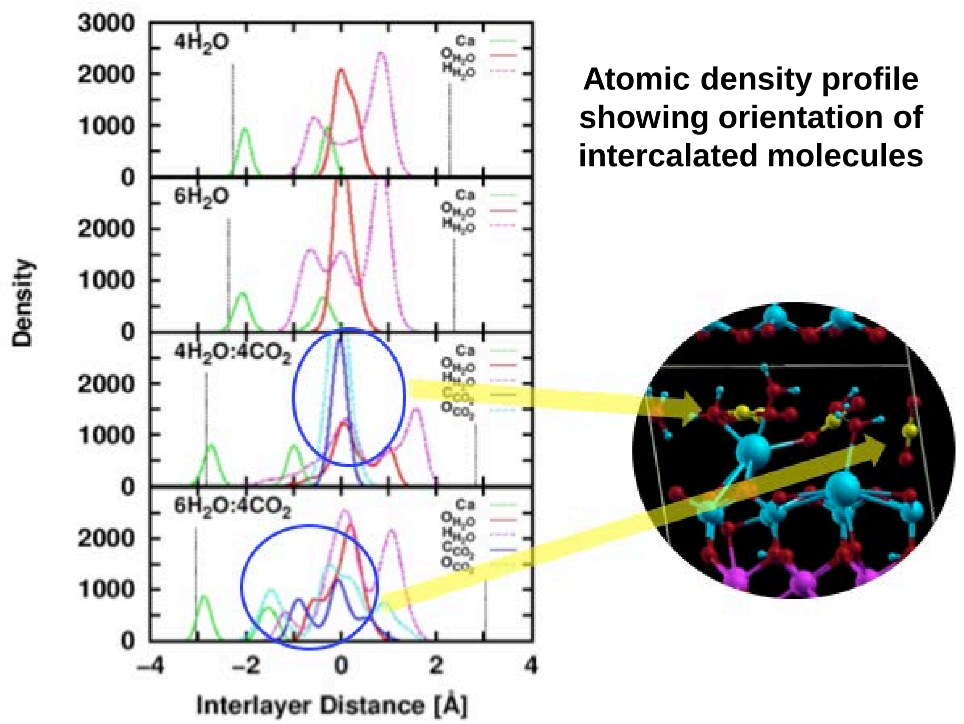


Application: Clay expansion due to CO_2 and water intercalation could reduce reservoir permeability and limit injectivity/recovery



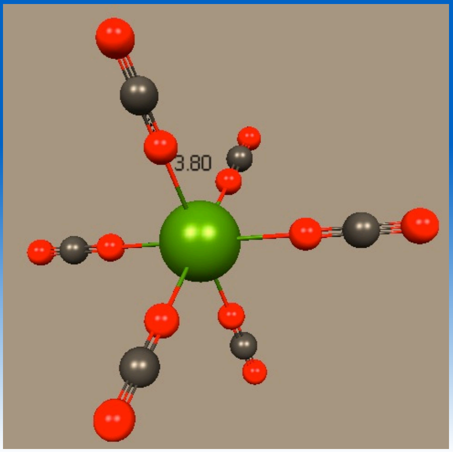
Molecular Modeling: interactions of CO_2 with Montmorillonites

- **Objective**: Estimate relative abundance of H_2O/CO_2 intercalated in montmorillonites
  - 1W ~4-6 H_2O and 4 CO_2 per interlayer Ca^{2+} cation
  - CO_2 coordinates with the interlayer cation and organizes into layers
  - Higher CO_2 concentrations produce preferred distorted T-shaped orientation
- Enhance gas recovery implications



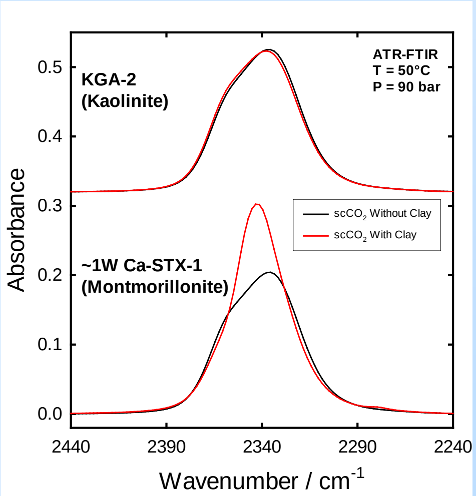
Atomic density profile showing orientation of intercalated molecules

Findings: Calculations show bonding interactions of M^{n+}/CO_2 (about 30% less than M^{n+}/H_2O)



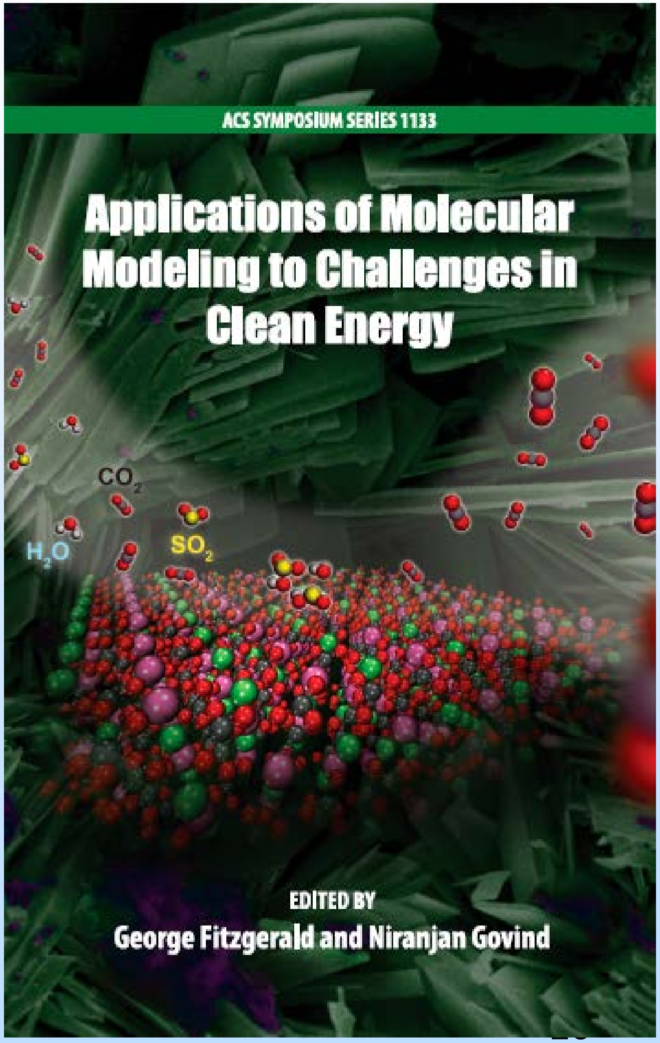
Experimental in situ IR Data:

- Montmorillonite: ATR-IR spectrum narrowed, indicating <u>rotationally constrained</u> CO_2.
- Kaolinite: No Change.



Accomplishments to Date

- **Multicomponent mixed gas transportation in pipelines and wellbores**
  - Water content thresholds established for corrosion initiation in CO_2-SO_2 mixtures
  - MD simulations illustrate reaction paths and reaction products
  - High impact publications (2nd most cited paper in *Energy Procedia*) and new programs
- **CO_2 storage in unconventional reservoirs**
  - Demonstrated feasibility of in situ scrubbing of SO_2 from gas phase in carbonate reservoirs
  - Advancing understanding of CO_2 trapping mechanisms in shales
    - In situ techniques allow separation of mechanisms (adsorption, intercalation, chemical reaction)
    - DFT simulations providing critical mechanistic understanding necessary for implementation in reservoir simulations



Summary

- Key Findings
  - Pipeline and wellbore construction materials are susceptible to corrosion processes in mixed gas systems containing small amounts of water
  - Mixed gases can be stripped of contaminants in suitable subsurface reservoirs eliminating need for surface scrubbers when doing CO_2 capture retrofits
- FY13 Activity Summary
  - Transition initial carbon steel corrosion work into casing materials of importance for constructing co-sequestration injection wells
  - Initiate new activity in mixed gas storage and utilization in shale gas formations
    - Distinguish among trapping mechanisms through
    - Apply MD simulations to understand reaction mechanisms
    - Construct first principles based model for fate and transport of multicomponent gas mixtures in fractured shale gas reservoirs

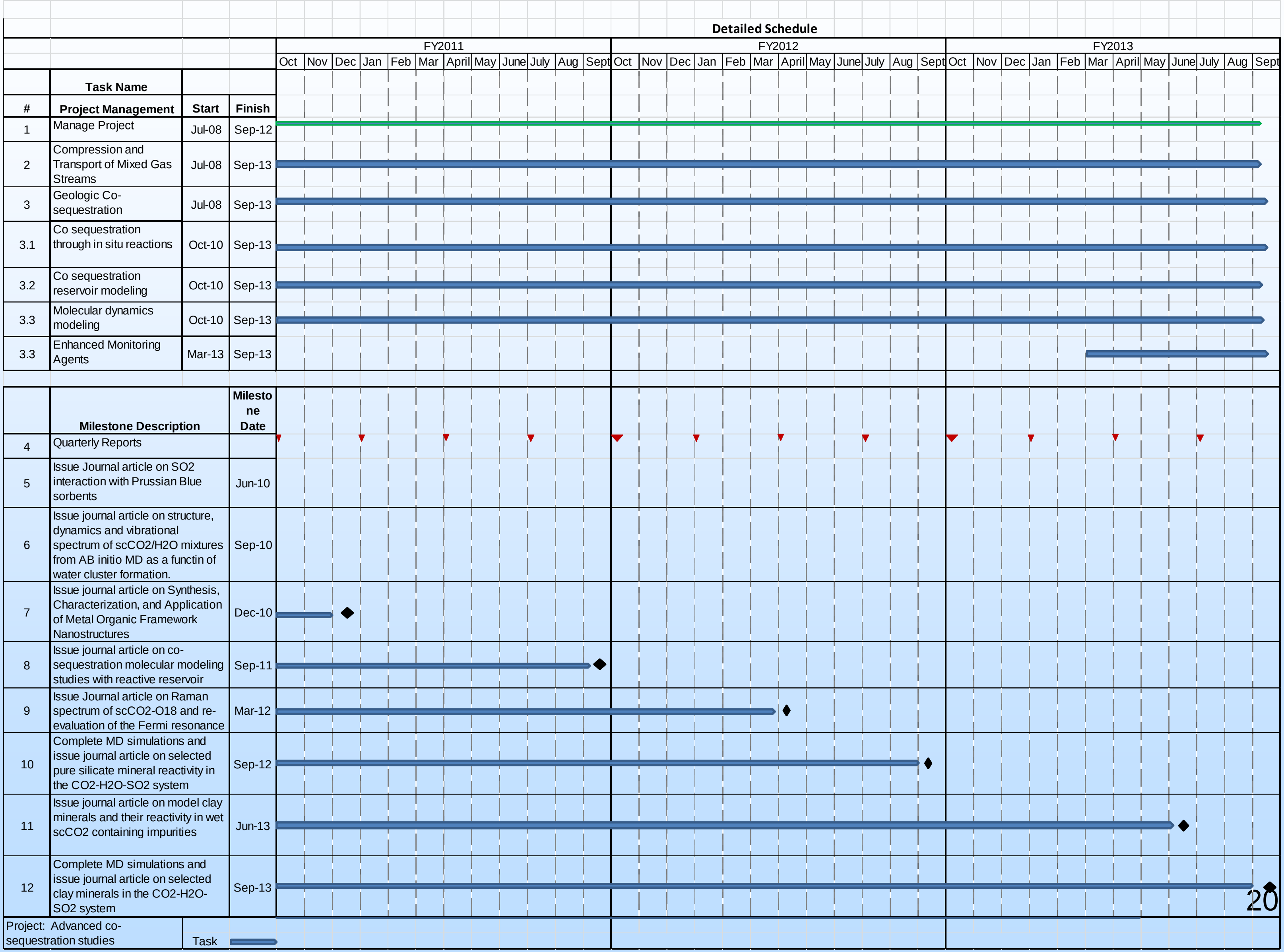
Appendix

- 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

Gantt Chart



#	Task Name Project Management	Start	Finish
1	Manage Project	Jul-08	Sep-12
2	Compression and Transport of Mixed Gas Streams	Jul-08	Sep-13
3	Geologic Co-sequestration	Jul-08	Sep-13
3.1	Co sequestration through in situ reactions	Oct-10	Sep-13
3.2	Co sequestration reservoir modeling	Oct-10	Sep-13
3.3	Molecular dynamics modeling	Oct-10	Sep-13
3.3	Enhanced Monitoring Agents	Mar-13	Sep-13

#	Milestone Description	Milestone Date
4	Quarterly Reports	
5	Issue Journal article on SO2 interaction with Prussian Blue sorbents	Jun-10
6	Issue journal article on structure, dynamics and vibrational spectrum of scCO2/H2O mixtures from AB initio MD as a functin of water cluster formation.	Sep-10
7	Issue journal article on Synthesis, Characterization, and Application of Metal Organic Framework Nanostructures	Dec-10
8	Issue journal article on co-sequestration molecular modeling studies with reactive reservoir	Sep-11
9	Issue Journal article on Raman spectrum of scCO2-O18 and re-evaluation of the Fermi resonance	Mar-12
10	Complete MD simulations and issue journal article on selected pure silicate mineral reactivity in the CO2-H2O-SO2 system	Sep-12
11	Issue journal article on model clay minerals and their reactivity in wet scCO2 containing impurities	Jun-13
12	Complete MD simulations and issue journal article on selected clay minerals in the CO2-H2O-SO2 system	Sep-13

Project: Advanced co-sequestration studies

Task ▬

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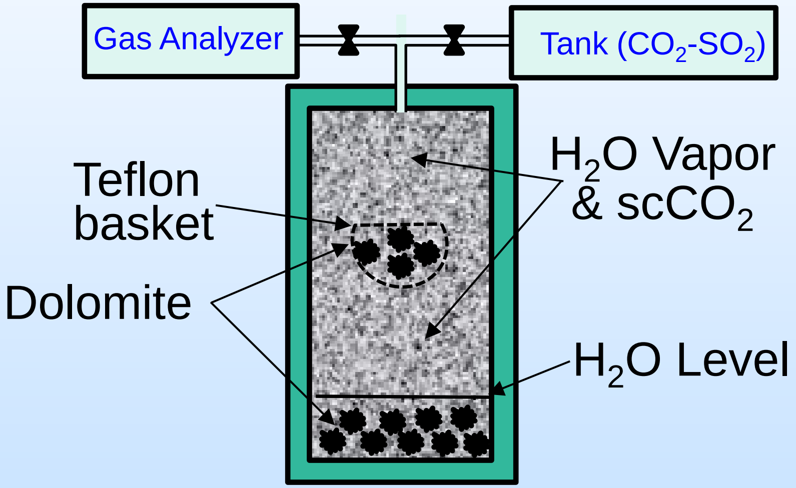
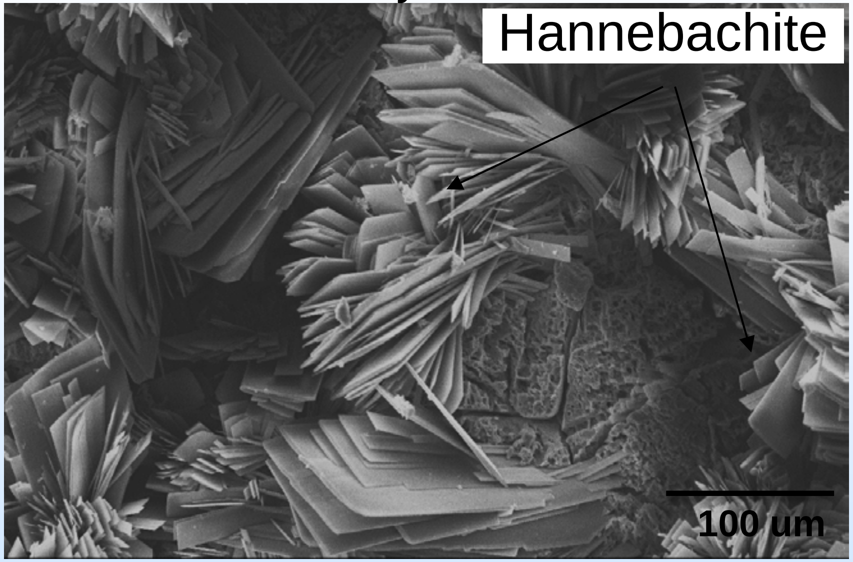
Co-sequestration in carbonate reservoirs

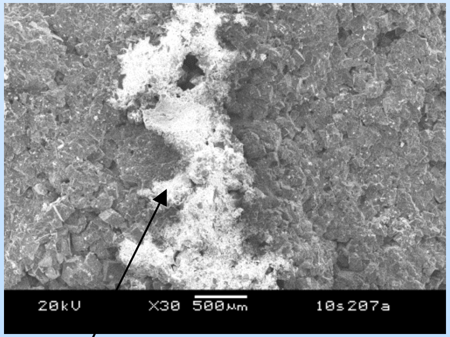
- **Goal**: Designing laboratory tests to simulate subsurface conditions
- **Experimental Approach**:



- **Results**: Carbonate reservoirs are reactive and strip aqueous dissolved gaseous SO_2 from solution to precipitate solid sulfur bearing minerals

Dolomite 30 days, 100°C, 10.3 MPa



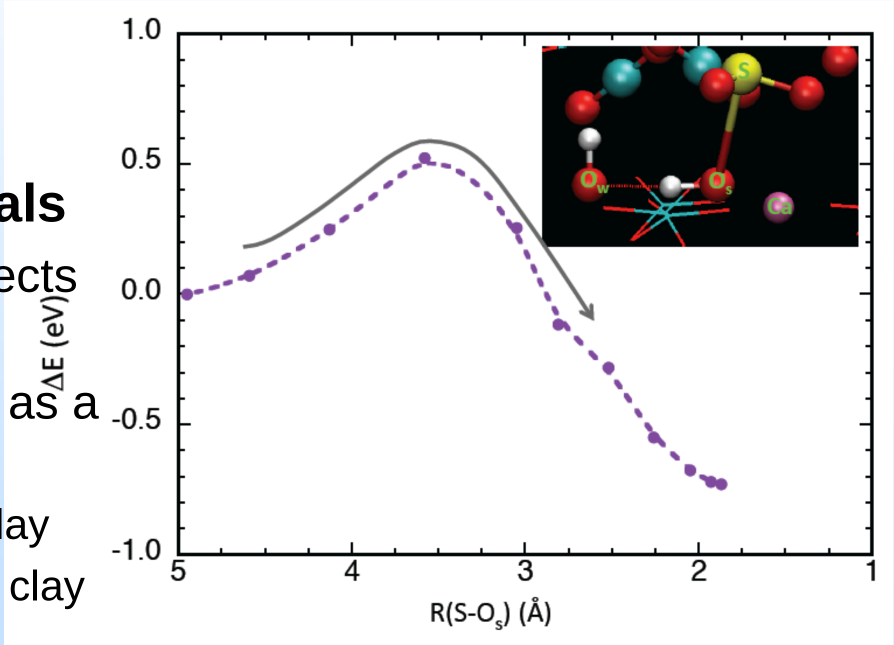


Dolomite suspended above H_2O line contained no sulfur bearing reaction products

Energy profile for initial steps of sulfation reactions: Surface defects do the trick!

- Surface defects radically change the energy profile of sulfation reaction
- Formation of SO_3 proceeds with small barrier, ~0.5 eV
- Estimated rates ~ $10\text{-}10^4\ s^{-1}$

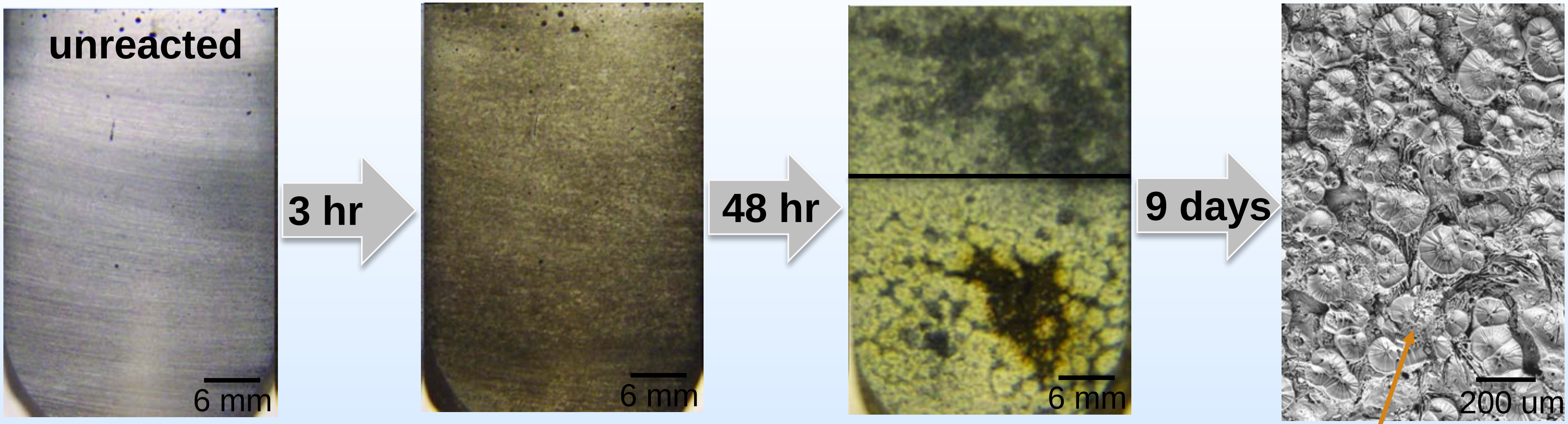
- **Application to clay minerals**
  - Pressure and viscosity effects accurately removed
  - Gas adsorption measured as a function of pressure
    - N_2 uptake ~3.1 mmol/g clay
    - CO_2 update ~7.1 mmol/g clay
- **Utilization**
  - Measure adsorbed gas concentrations on shales

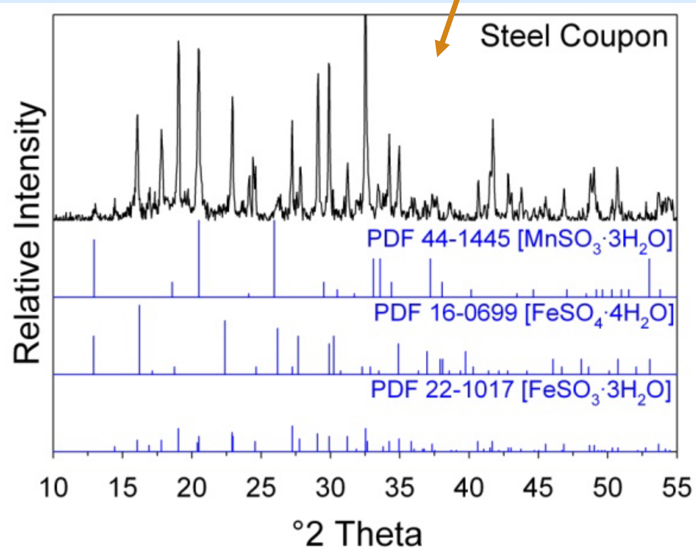


V-A Glezakou, BP McGrail, HT Schaef, 2012. “Molecular interactions of SO_2 with carbonate minerals under co-sequestration conditions: a combined experimental and theoretical study”, Geochimica et Cosmochimica Acta, 92, 265-274.

Steel Corrosion with Mixed Gases

Liquid CO_2 (6.14 MPa), SO_2 (~13,000 ppmw), H_2O (760 ppmw), 25°C





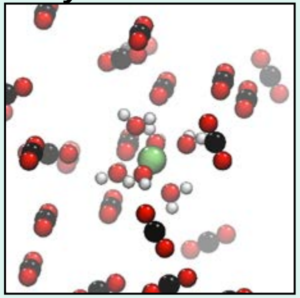
Mixed Gas Chemistry

- Surface corrosion products develop after 3 hours
  - Different surface corrosion products form including an unexpected Mn sulfite phase
- Water threshold
  - Tests with less water (300 ppmw) indicate a delay in onset of visible surface corrosion
  - Increases in H_2O content produce more corrosion

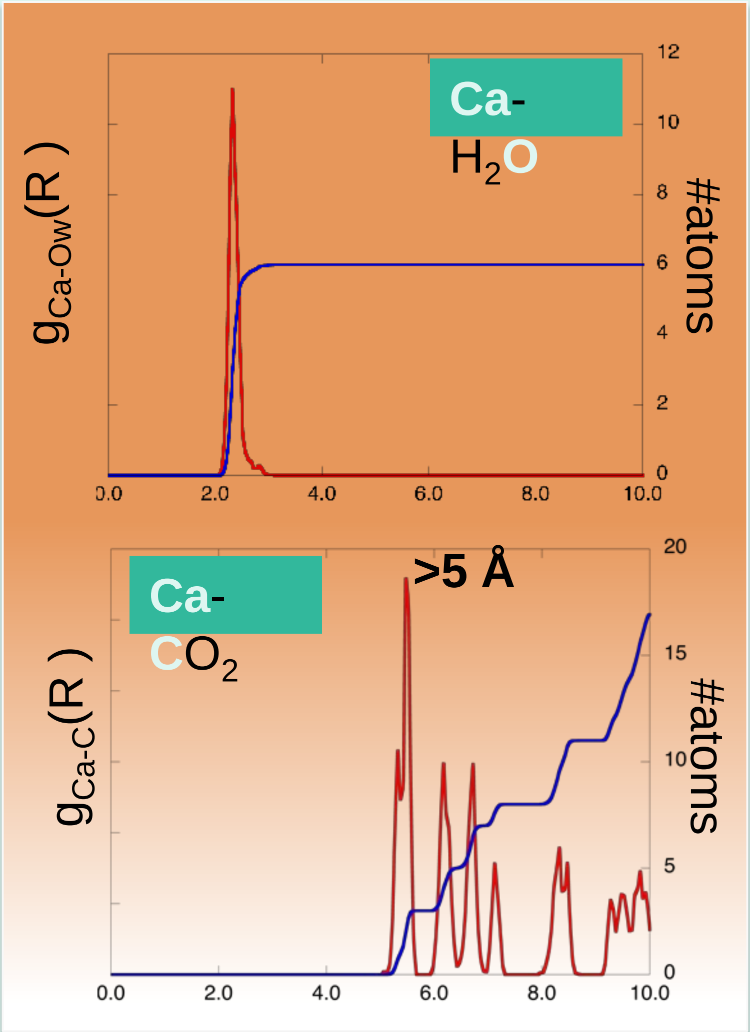
Molecular Modeling: interactions of CO_2 with H_2O and Ca^{2+}

- Hydrated ion behavior in dry $scCO_2$
  - Segregation of hydrated Ca^{2+}
  - Average Ca^{2+} and C distance >5 Å
  - Attractive interactions between anhydrous ions and CO_2 and monomeric H_2O solvated in CO_2
  - Ca-CO_2 3.6Å

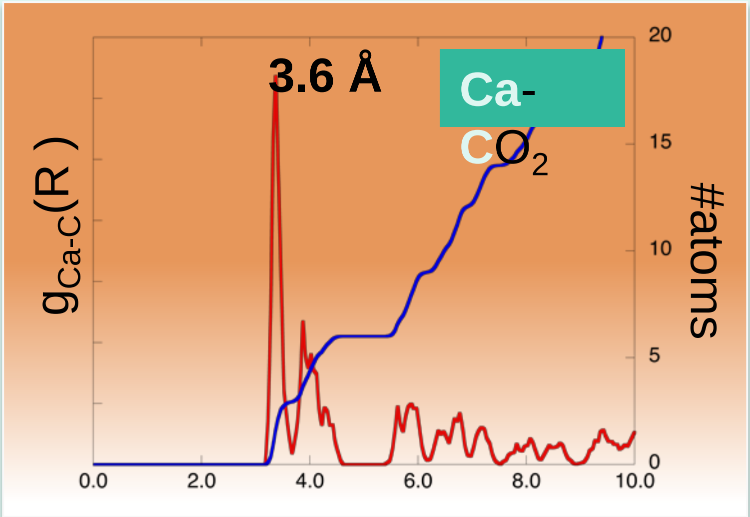
Hydrated Ca^{2+}



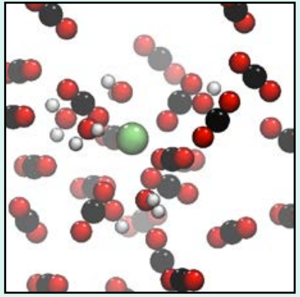
Hydrated Ca^{2+} with dry $scCO_2$



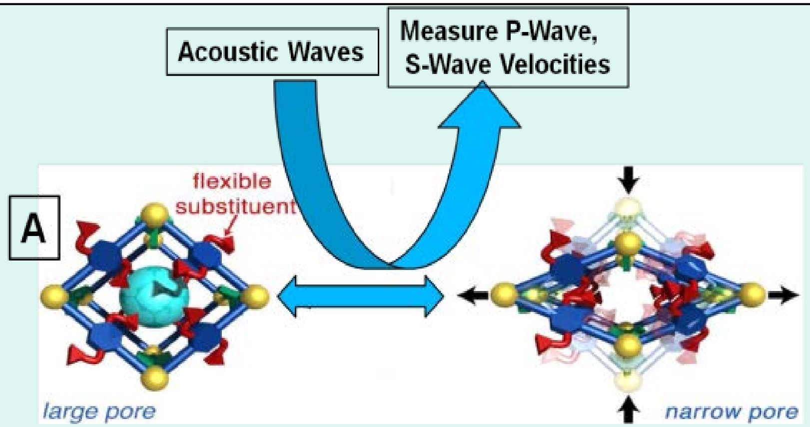
Ca^{2+} with wet $scCO_2$

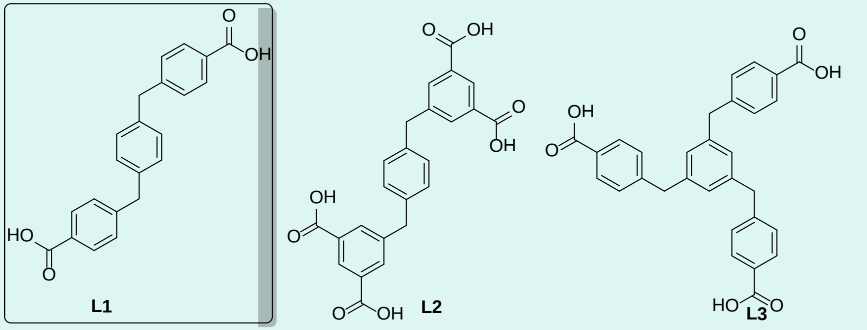


Wet $scCO_2$



Acoustically Responsive Contrast Agents for Enhanced Seismic Monitoring of Injected CO_2 in Geologic Formations





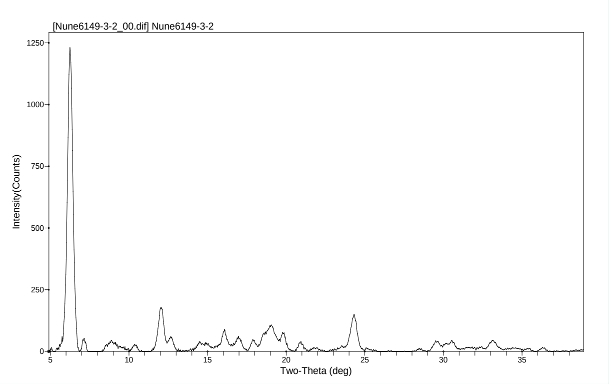
- MOF nanomaterials with high surface area and excellent porosity which respond through resonant absorption modes will be used to track injected CO_2 via conventional seismic imaging or by new laser Doppler vibrometry methods.

- The resonant modes are enabled through librational modes in the nanoparticles imparted through use of flexible organic building blocks used to construct their framework.

- Once a stable CO_2 nanofluid is formed, acoustic contrast property evaluation will be performed by velocity measurements under pressure using core flood experiments.

- Flexible ligand L1 is synthesized for making flexible MOFs

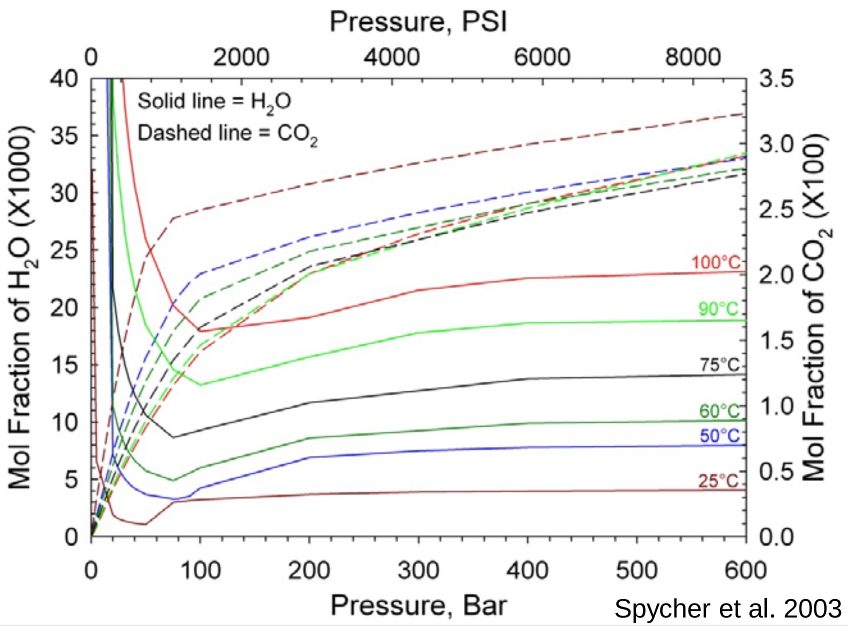
- Flexible MOF Ni-L1 synthesized using hydrothermal conditions.



Rational for Examining Water Bearing CO_2

- Pipeline specifications vary and are largely related to end user application, i.e. EOR
  - Dry CO_2 and CO_2-H_2S streams are unreactive with pipeline steels
  - Knowledge gap for CO_2 streams containing intermediate water content
  - Multistage compression can be used reduce water content in CO_2 stream and potentially eliminate dehydration system
- Initially dry liquid or supercritical CO_2 quickly absorbs water
- Reaction mechanisms of solvated water, CO_2, and contaminants in CO_2 stream are poorly understood
- Well-defined concepts in aqueous solutions do not have corresponding thermodynamic meaning
- Molecular simulations provide insights into surface interactions

Mutual Solubilities



Spycher et al. 2003

Implication to Reservoir Rocks

- Only basic experimental scoping studies on rock-CO_2-water systems available
  - Regnault et al. 2005 (200°C, 105/160 several pure mineral phases)
  - Lin, et al. 2008 (100°C, <1 week, granite)
- No experiments or modeling with mixed gas WBSFs