Advanced Co-Sequestration Studies

Project Number 58159 Task 2

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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 21-23, 2012

Presentation Outline

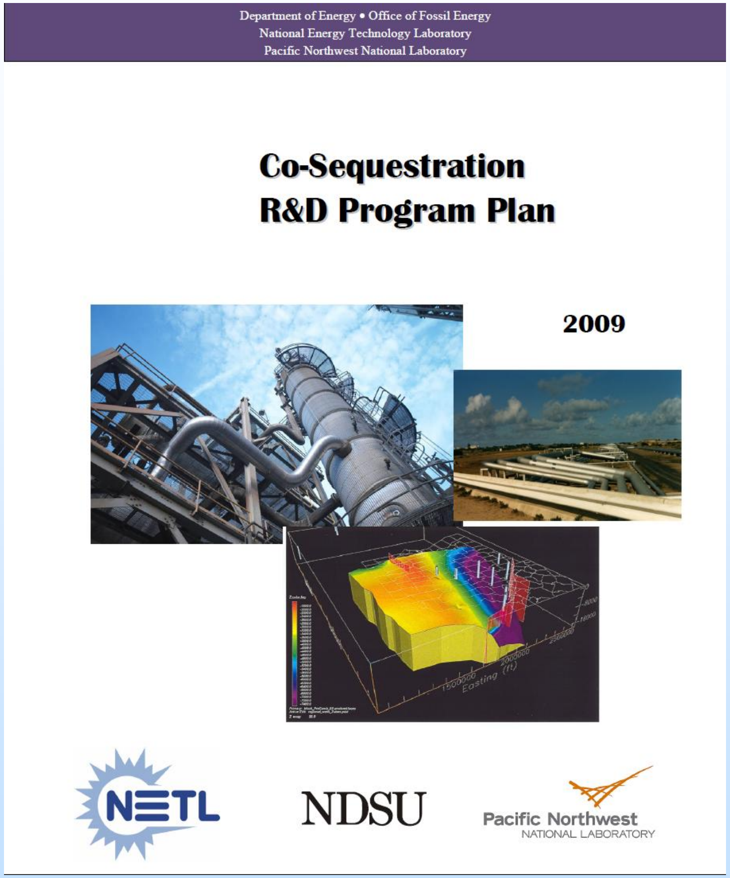
- Program Focus Area and DOE Connections
- Goals and Objectives
- Scope of Work
- Technical Discussion
- Accomplishments to Date
- Project Wrap-up
- Appendix (Organization Chart, Gantt Chart, and Bibliography

Benefit to the Program

- Program goals addressed:
  - Technology development to predict CO_2 and mixed gas storage capacity in various geologic settings
  - Demonstrate fate of injected mixed gases
- <u>Project benefits statement</u>:
  - This research project conducts laboratory studies and modeling to advance fundamental understanding of sequestering mixed gas emissions produced from post- and oxy-combustion coal fired power plants
  - Provides scientific basis for framing sensible regulatory requirements around sequestration of mixed gas streams
  - Lower overall cost of CCUS through an emissions management strategy integrating surface and subsurface

Project Overview: Goals and Objectives

- Goal: Develop geologic storage paradigm around mixed-gas streams to lower cost and energy penalty of integrated CCUS
- Objective: Utilization of CO_2 to enhance hydrocarbon production and minimize environmental impacts
  - Conduct experiments to examine reaction products, and mechanisms occurring in mixed gas systems
  - Advance reservoir modeling to predict fate and transport of mixed gases to optimize system efficiency
  - Implement connections between atomistic simulations and reservoir simulators to advance mechanistic insights for co-sequestration systems



Project Overview:
Scope of work

- Task 1 – Pipeline and Casing (Transport) Materials Studies
  - Evaluate corrosion behavior of casing materials in CO_2-H_2O mixtures containing trace contaminates (i.e. SO_2,O_2,H_2S)
  - Evaluate impact of connate water uptake in $scCO_2$ mixtures on corrosion resistance of well construction materials
- Task 2 – Mixed Gas Utilization and Storage

  2.1 Exploiting 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 $scCO_2$

  2.2 Co-sequestration reservoir modeling

  - Predict fate and transport of mixed gas systems and optimize system efficiency

  2.3 Molecular dynamics modeling

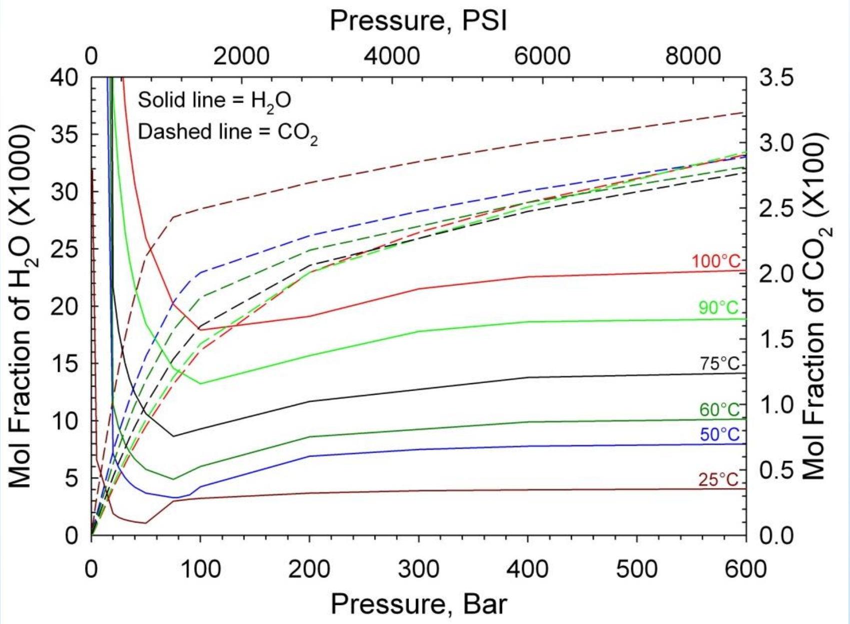
  - Utilization of atomistic simulations to gain mechanistic insight of the reactivity between $scCO_2$, water, and various components of a sequestration system
  - Identify possible reactive products and the barriers to such transformations guided by experiments
  - Formulate and incorporate new rate laws for $scCO_2$ phase chemical reactions

  2.4 Methane production and co-sequestration in shale gas formations

Rational for Examining Water Bearing CO_2

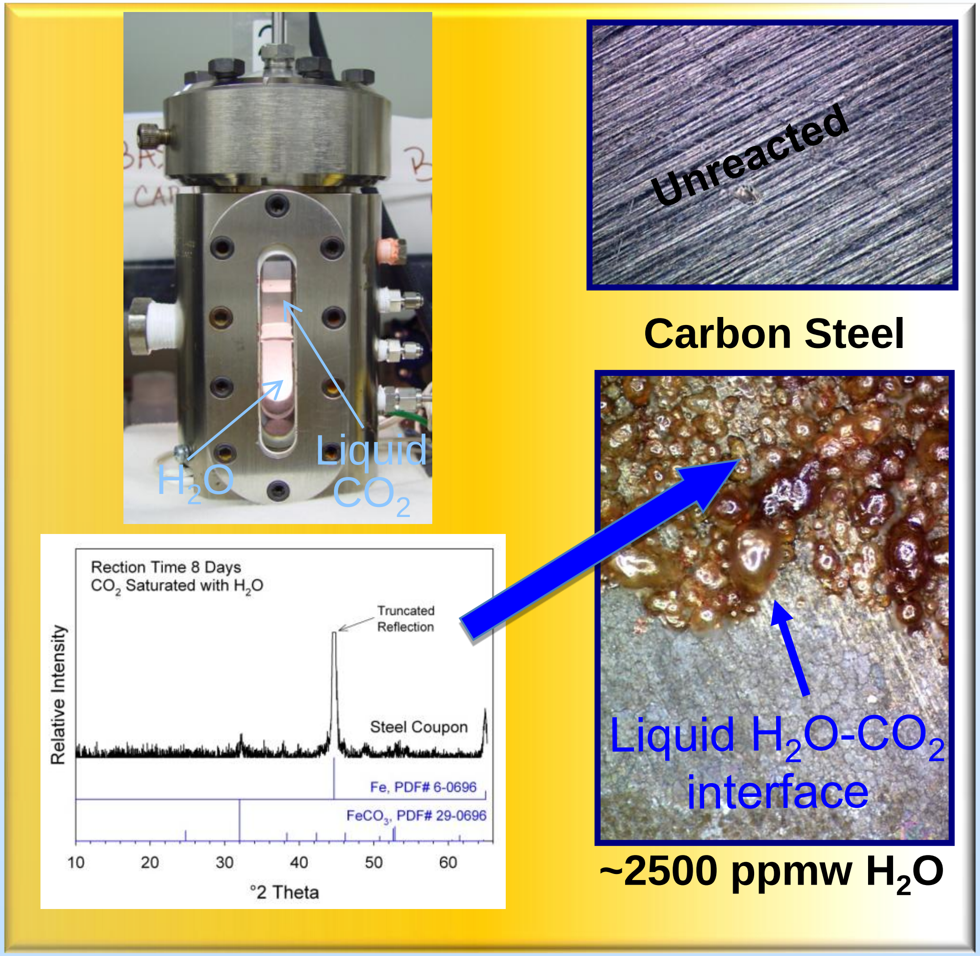
- Pipeline specifications vary and are largely related to end user application, i.e. EOR
  - Dry CO_2 and CO_2-H_2S streams are unreactive with pipeline steels
  - Knowledge gap for CO_2 streams containing intermediate water content
  - Multistage compression can be used to reduce water content in CO_2 stream and potentially eliminate dehydration system
  - Lack of industry experience with CO_2-SO_2 mixtures
- Initially dry liquid or supercritical CO_2 quickly absorbs water post-injection
- *All current reservoir simulators treat the $scCO_2$ phase as being inert*
- Only basic experimental scoping studies on rock-CO_2-water systems available
  - Regnault et al. 2005 (200°C, 105/160 bar several pure mineral phases)
  - Lin, et al. 2008 (100°C, <1 week, granite)
- No experiments or modeling with mixed gas WBSFs

Mutual Solubilities



Computed from Spycher et al. 2003 EOS

Mixed-Gas Transportation and Injection



McGrail, B. P., H. T. Schaef, V. A. Glezakou, L. X. Dang, and A. T. Owen. 2009. "Water Reactivity in the Liquid and Supercritical CO_2 Phase: Has Half the Story Been Neglected?" *Energy Procedia* ***1(1):3415-3419.***

Key Issues

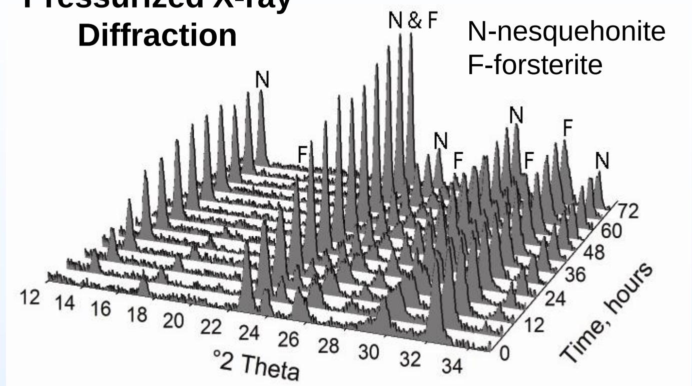
- Appropriate pipeline specifications for mixed gases lacking industry experience
  - CO_2-SO_2 mixtures
  - Water content limits
  - Dehydration requirements
- Evaluate stability of wellbore casing steels exposed to mixed-gases containing water

Approach

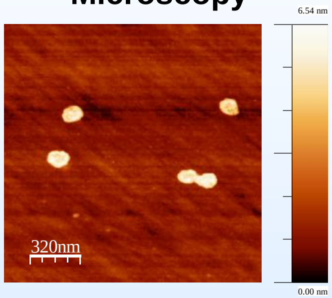
- Conduct laboratory experiments to examine reactivity of CO_2-SO_2-O_2-H_2O mixtures on steel surfaces
- Determine role of water in reaction steps and impact of steel additives (such as Mn and Mo) on corrosion

In Situ Supercritical Suite: An $8M Laboratory Investment

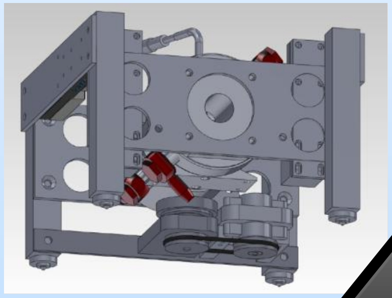
Pressurized X-ray Diffraction



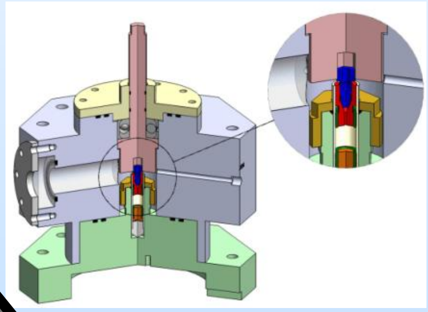
In situ Atomic Force Microscopy



Novel reactors for in situ IR ATR spectroscopy



High Pressure MAS NMR Reactor



Structural data on intermediate phases during mineral transformation processes

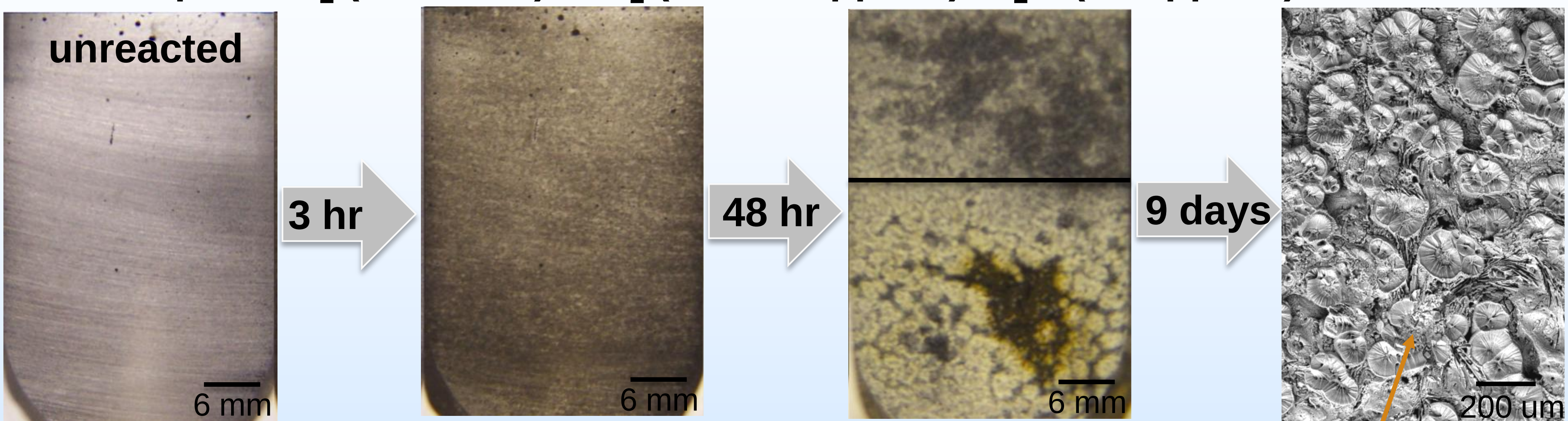
Rate equations and parameters for reactions occurring between water dissolved into $scCO_2$ and primary silicate minerals in basalts

Spectroscopic and microscopic probes of interfacial structure and processes

Identification of chemical species, amorphous silica, and detection of carbonation

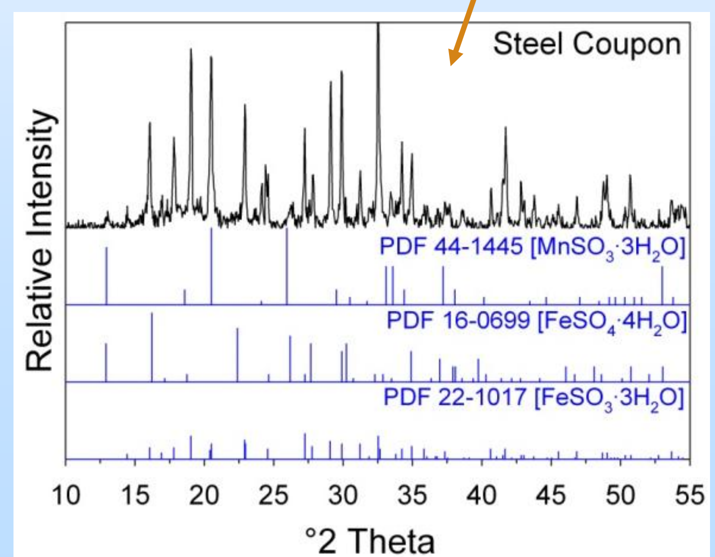
X65 Steel Corrosion with Mixed Gases

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



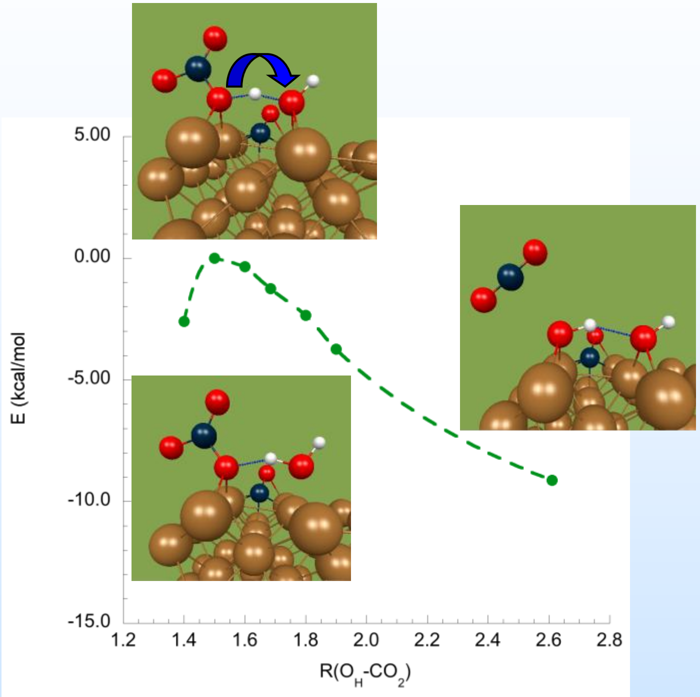
Mixed Gas Chemistry

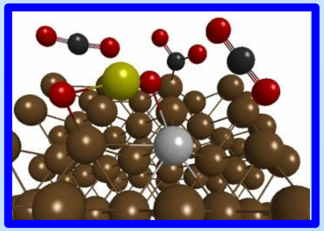
- Surface corrosion products develop after 3 hours
  - Different surface corrosion products form including an unexpected Mn sulfite phase
- Water threshold
  - Tests with less water (300 ppmw) indicate a much lower threshold for onset of visible surface corrosion versus CO_2-H_2O
  - Increases in H_2O content produce more corrosion

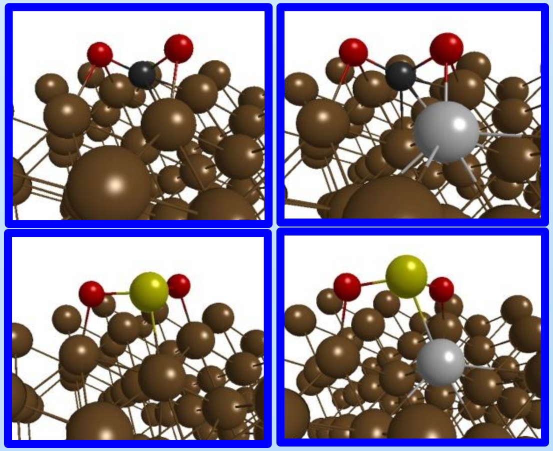


Molecular Simulations Provide Insights on Surface Interactions

- **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:**
  - Catalytic activity of H_2O
  - H_2CO_3/H_2SO_3 formation is not necessary
  - SO_2 binds more strongly on Fe or Fe/Mn surface compared to CO_2, SO_2 prefers Mn binding sites, scavenges O from ads CO
  - non-equilibrium effects upon rates
- **Current Activity**: CO_2-SO_2-O_2-H_2O experiments

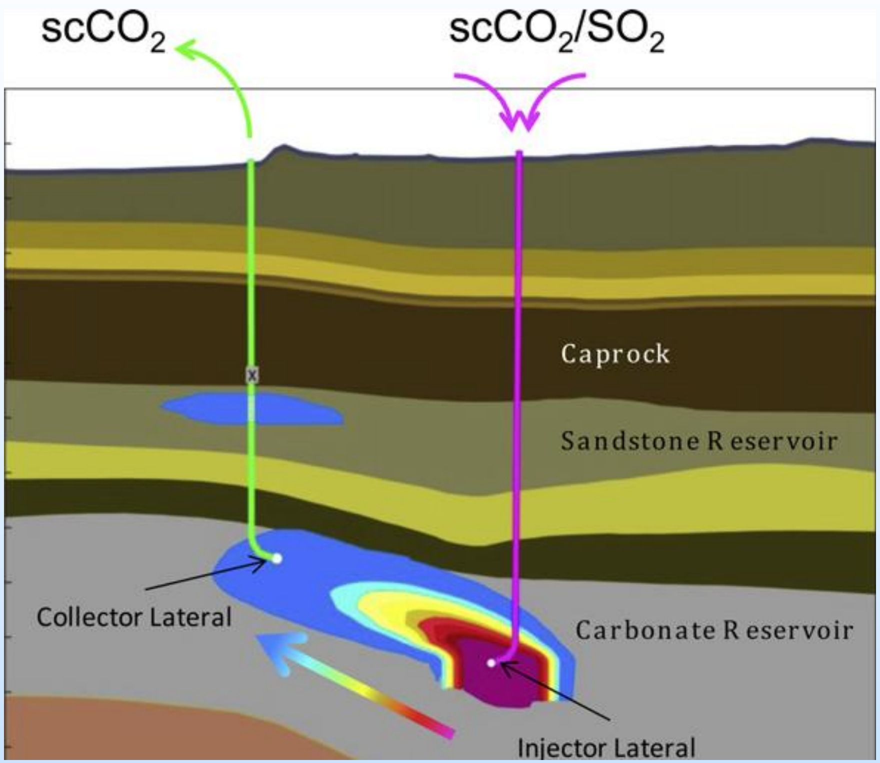






In Situ Scrubbing Concept

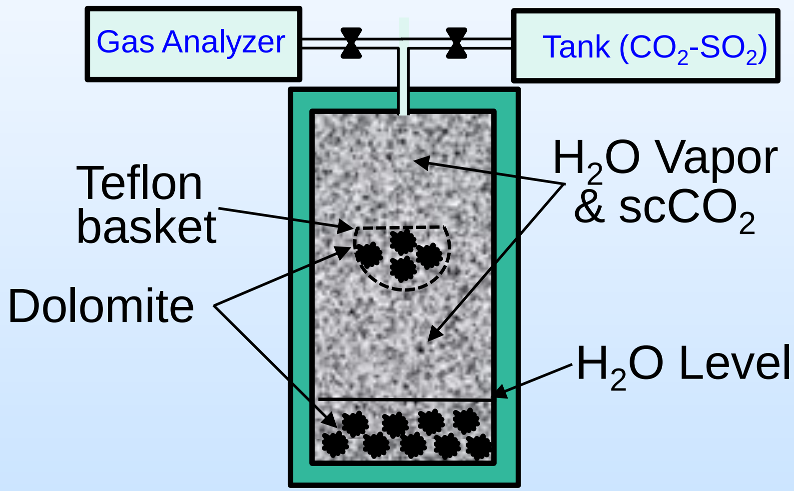
- Oxy-combustion gas streams can contain over 1% SO_2
  - Likely candidate technology for new builds or retrofits
  - Currently managed through SO_2 scrubbers
- In situ stripping could be used for gas cleanup
  - More economically favorable when retrofitting existing power plants for CO_2 capture
  - Produce pipeline grade CO_2 for EOR/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.***

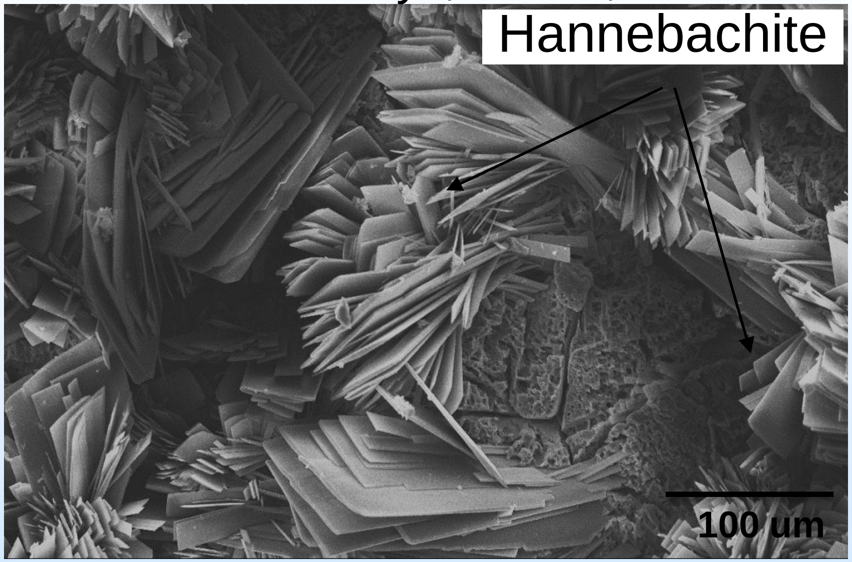
Co-sequestration in Carbonate Reservoirs

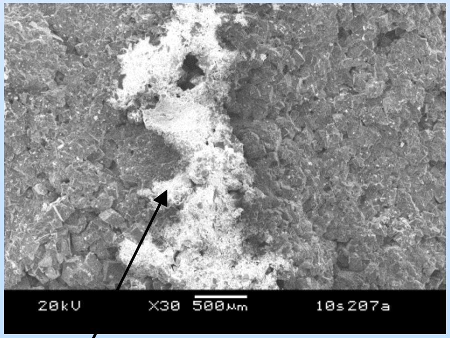
- **Goal**: Designing laboratory tests to simulate subsurface conditions
- **Experimental Approach**:



- **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

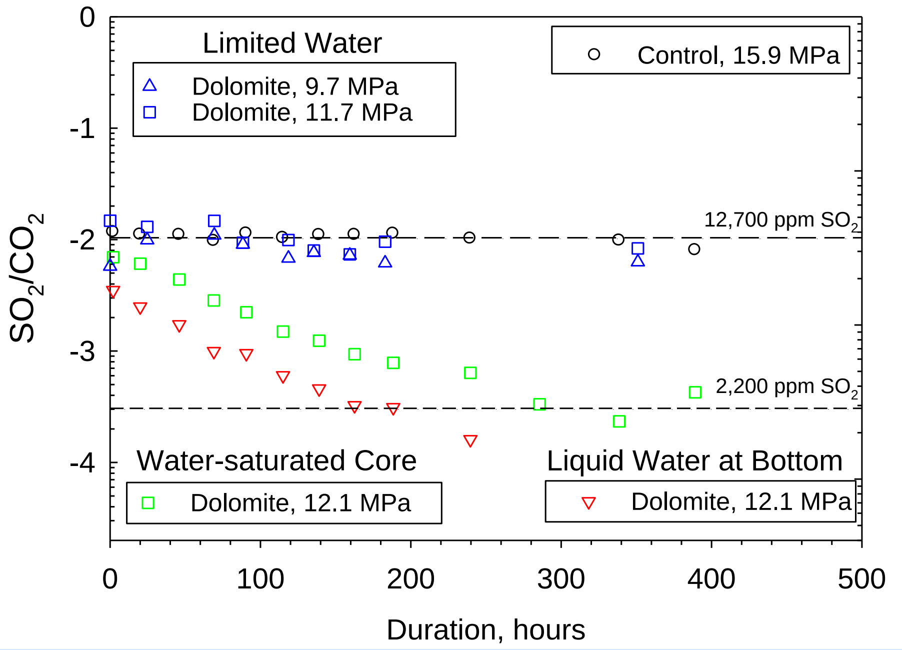


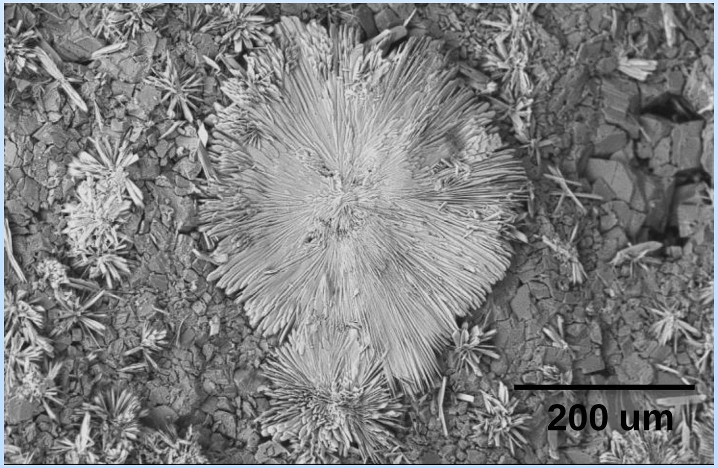


Dolomite suspended above H_2O line contained no sulfur bearing reaction products

Low-water environments: Does SO_2 stripping occur?

- **Results**
  - Sulfur species permanently and quickly removed from $scCO_2$ phase
  - Solid sulfur products
    - Surface coatings form very rapidly
    - Hannebachite ($CaSO_3 \cdot 0.5H_2O$)
- **Utilization**
  - Carbonate reservoirs are widespread and appear well suited for accepting mixed CO_2-SO_2 gas streams
  - Clean CO_2 generated via in situ scrubbing could be stored or used immediately for EOR/EGR

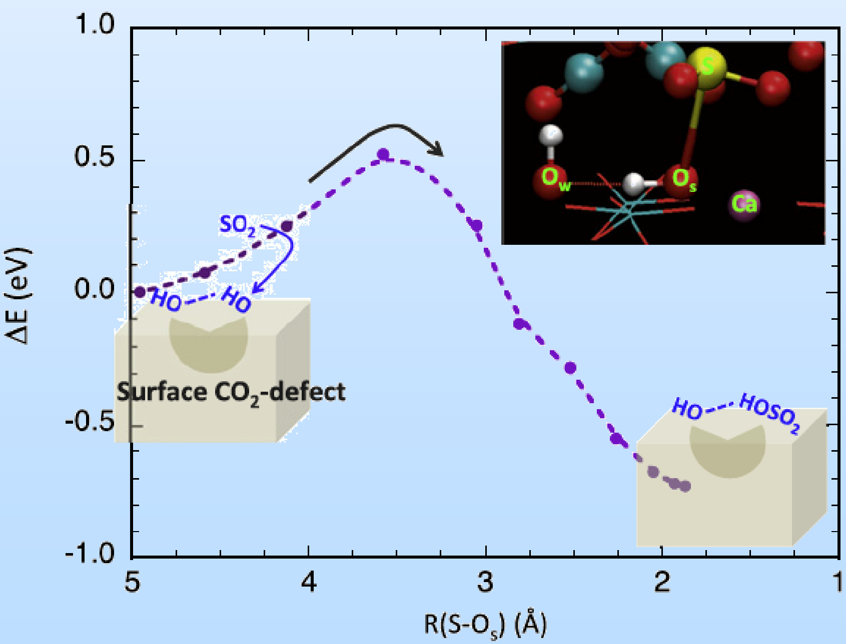




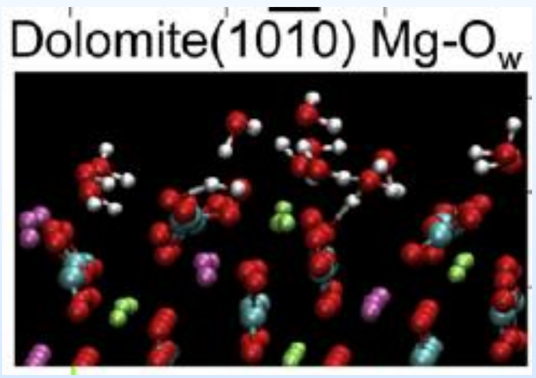
Energy profile for initial steps of sulfation reactions: Surface defects do the trick!

- Surface defects radically change the energy profile of sulfation reaction
- Formation of SO_3 proceeds with small barrier, ~0.5 eV,
- Estimated rates

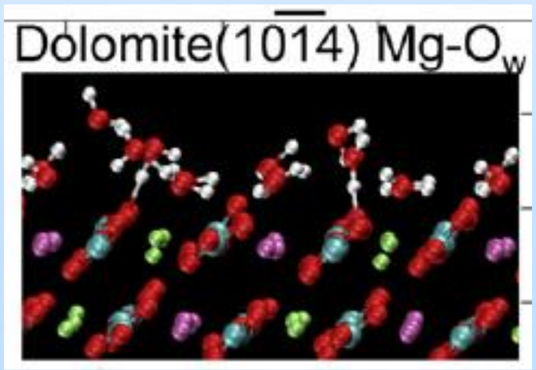
  ~ $10\text{-}10^4\ s^{-1}$



Figures from 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", *Geochim. Cosmochimi. Acta* **92**:265-274.



More reactive surface

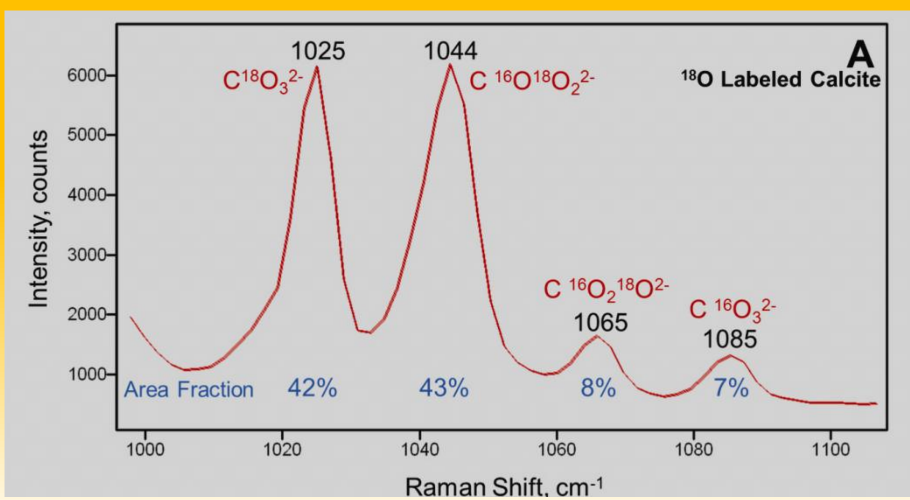


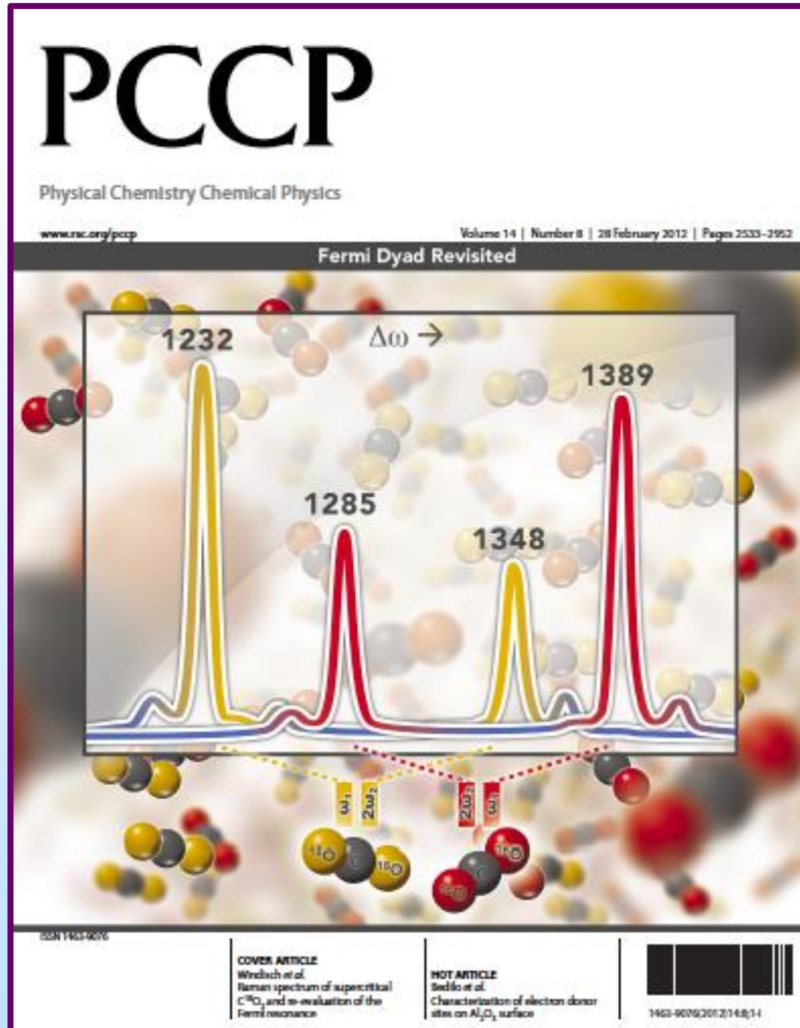
Less reactive surface

Isotopic Exchange Studies

- Raman studies of carbonate reactions under SC conditions with ^{18}O-labels for H_2O and CO_2
- First reported Raman shift for $scC^{18}O_2$ and mixed system
- Discovered unexpected swap of characteristic doublet (Fermi Dyad)

Application: Track ^{18}O uptake occurring from chemical reactions occurring in the $scCO_2$ phase using Raman spectroscopy

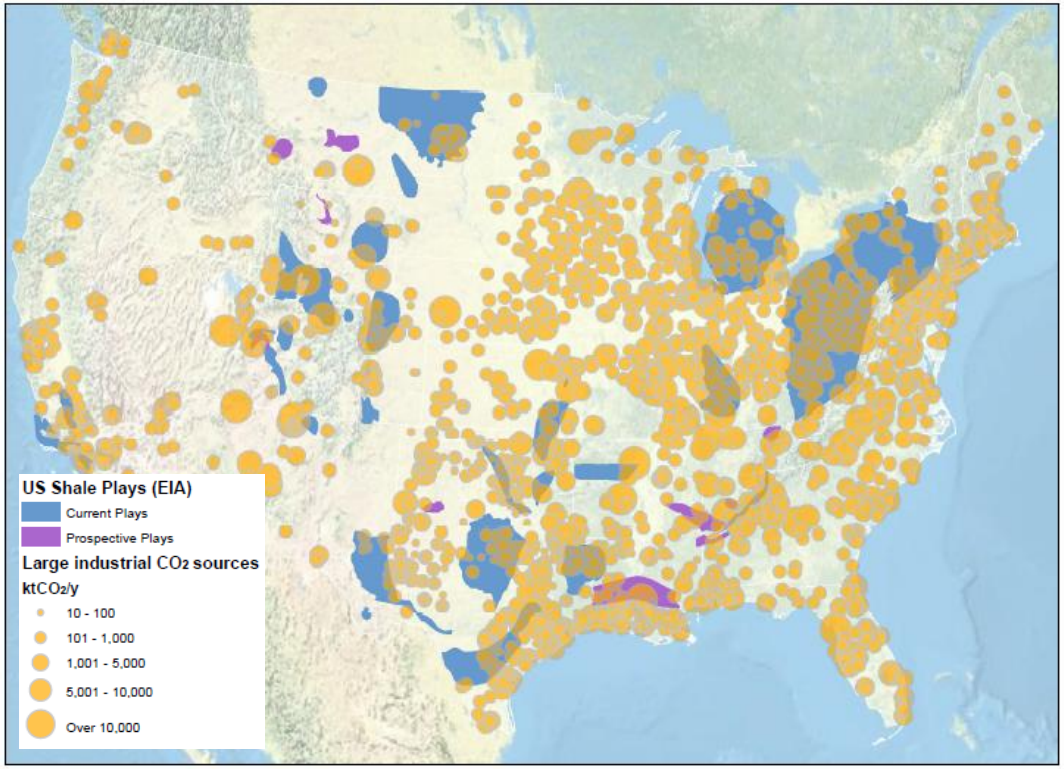




Windisch, C. F., V.-A. Glezakou, P. F. Martin, B. P. McGrail, and H. T. Schaef. 2012. "Raman Spectrum of Supercritical $C^{18}O_2$ and Re-Evaluation of the Fermi Resonance." *Phys. Chem. Chem. Phys.* ***14(8):2560-2566.***

Future Work: Mixed Gas Utilization and Storage in Shale Gas Reservoirs

- **Better understand potential opportunities for mixed gas storage and utilization in shales**
  - Assess potential for in situ chemical scrubbing in fractured shales
  - Distinguish chemical reactivity versus physisorption processes
  - Effects of solvated water and SO_2
  - Quantify impact of compositional and mineralogical variability (empirical versus first principles methods)
- **Address potential loss of U.S. CO_2 storage capacity**
  - Improve understanding of permanent CO_2 and contaminant gas trapping mechanisms in shales
  - Evaluate methods to remediate fractured shale sealing properties



Approximately half of all large stationary U.S. source emissions are located within ~50 miles of a current or prospective shale play.

Accomplishments to Date

- Multicomponent mixed gas transportation issues
  - Pipeline steel and wellbore components
    - Providing scientific basis for developing pipeline specifications for gas mixtures lacking industry experience
    - Established water thresholds necessary to initiate corrosion reactions
  - MD simulations identified reaction paths and corrosion mechanisms
- Subsurface Chemistry of Co-sequestration
  - Proved efficacy of in situ removal of sulfur from scCO_2 phase by carbonate reservoirs
    - Precipitation of sulfur based solids permanently sequestered
    - Production of pure CO_2 stream for utilization
  - Molecular understanding of mixed-gas reactivity with important minerals
  - Transferring methods to other targets such as depleted shale gas formations

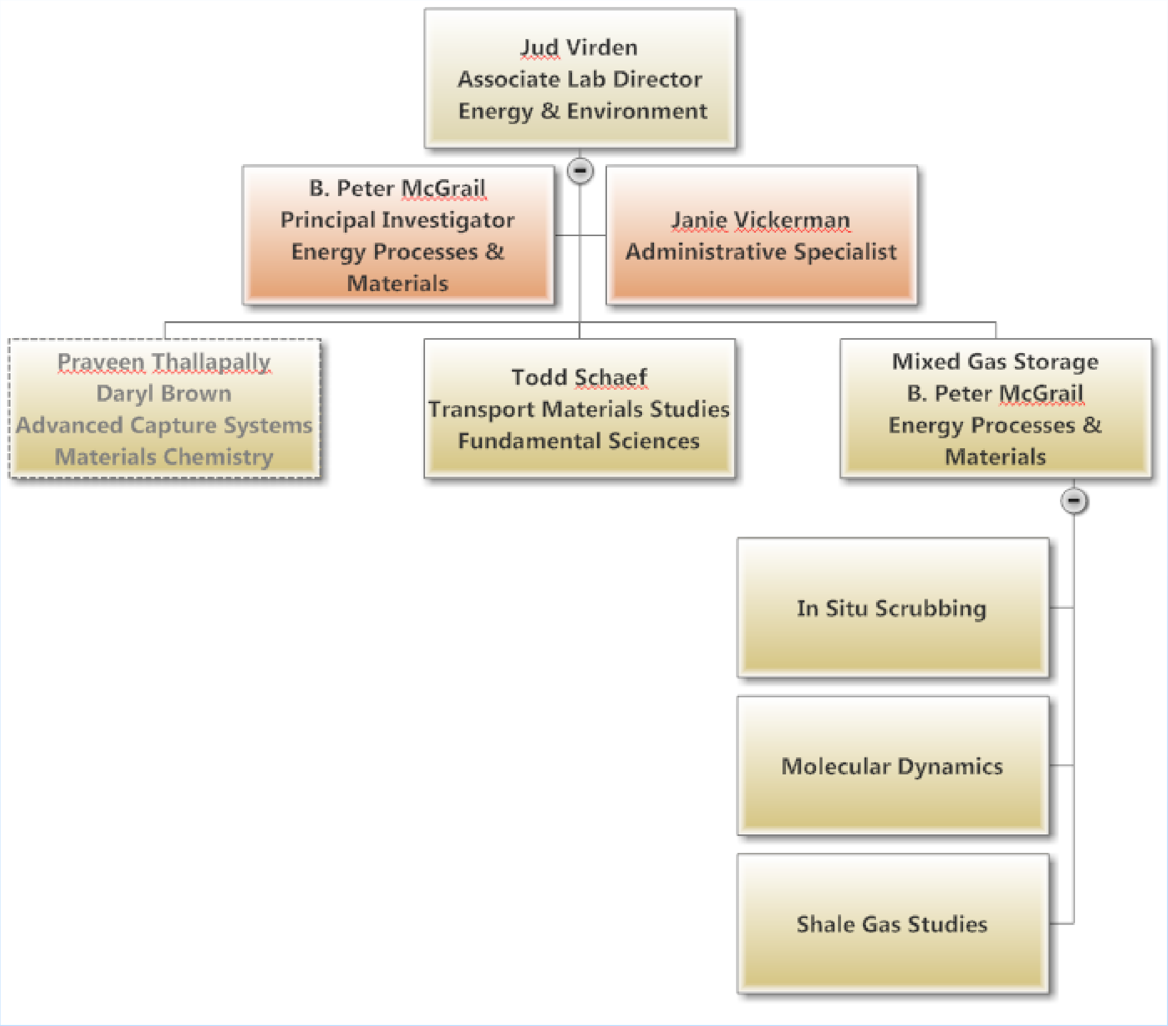
Summary

- Key Findings
  - Threshold water content for onset of corrosion in liquid CO_2 varies considerably depending on contaminant gases present
  - Industry standard pipeline steels produce unexpected corrosion products in CO_2-SO_2-H_2O mixtures
  - Carbonate reservoirs offer potential for in situ scrubbing of mixed gas streams
  - Labeled oxygen isotopes and discovery of Raman spectrum shifts in labeled $C^{18}O_2$ provide insights into reaction mechanisms of mixed-gas streams with key mineral phases
- FY13 Activity Summary
  - Extend carbon steel corrosion work into CO_2-SO_2-O_2-H_2O system and assess impacts on pipeline and 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
    - Apply MD simulations to understand reaction mechanisms
    - Assess techno-economic feasibility of EGR from 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



Gantt Chart

Detailed Schedule

Start of Integrated Master Project (58159)

FY2008: May, June, July, Aug, Sept | FY2009: Oct, Nov, Dec, Jan, Feb, Marc, April, May, June, July, Aug, Sept | FY2010: Oct, Nov, Dec, Jan, Feb, Marc, April, May, June, July, Aug, Sept | FY2011: Oct, Nov, Dec, Jan, Feb, Marc, April, May, June, July, Aug, Sept | FY2012: Oct, Nov, Dec, Jan, Feb, Marc, April, May, June, July, Aug, Sept

#	Task Name / Project Management	Start	Finish
1	Manage Project	Jul-08	Sep-12
2	Advanced capture systems	Jul-08	Sep-10
3	Compression and Transport of Mixed Gas Streams	Jul-08	Sep-13
4	Geologic Co-sequestration	Jul-08	Sep-10
4.1	Co sequestration through in situ reactions	Oct-10	Sep-13
4.2	Co sequestration reservoir modeling	Oct-10	Sep-13
4.3	Molecular dynamics modeling	Oct-10	Sep-13

#	Milestone Description	Milestone Date
5	Quarterly Reports	
6	Conducted literature review of equation of state models and data needs for co-sequestration systems	Jul-08
7	Co-sequestration workshop on compression and CO2 transport issues associated with co-sequestration. Jointly organized by NETL, PNNL, and North Dakota State	Oct-08
8	Issue PNNL report on status of development of high-temperature capable CO2 capture materials (PNNL-17-241)	Nov-08
9	Roadmap report for center for advanced capture and co-sequestration investigation	Jan-09
10	Issue Journal article on water reactivity in the Liaquid and scCO2 phase: has half the story been neglected?	Apr-09
11	Issue Journal article on SO2 interaction with Prussian Blue sorbents	Jun-10
12	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
13	Issue journal article on Synthesis, Characterization, and Application of Metal Organic Framework Nanostructures	Dec-10
14	Issue journal article on co-sequestration molecular modeling studies with reactive reservoir rocks	Sep-11
15	Issue Journal article on Raman spectrum of scCO2-O18 and re-evaluation of the Fermi resonance	Mar-12
16	Complete MD simulations and issue journal article on selected pure silicate mineral reactivity in the CO2-H2O-SO2 system	Sep-12

Project: Advanced co-sequestration studies — Task — Quarterly Report — Milestone — Phase

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<u>Legacy Capture-Related Publications</u>

- Tian, J., P. K. Thallapally, and B. P. McGrail. 2012. “Porous organic molecular materials.” *CrystEngComm* **14** (6):1909-1919.
- Liu, Jian, P. K. Thallapally, B. P. McGrail, D. R. Brown, and J. Liu. 2012. “Progress in adsorption-based CO_2 capture by metal–organic frameworks.” *Chem. Soc. Rev.* 41:2308-2322.
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Employing a multidisciplinary approach to advance co-sequestration opportunities

Identifying R&D needs

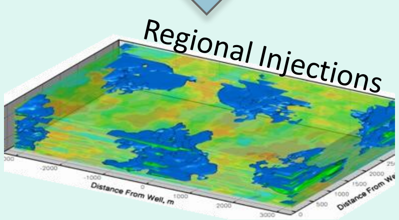
Subsurface chemistry

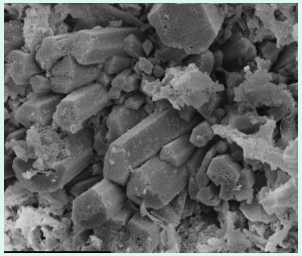
Development of low cost technologies

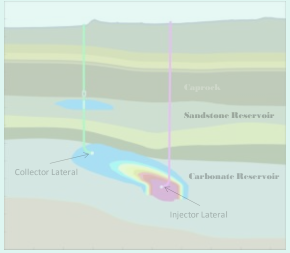
Experimental evaluation of reaction products, mechanisms, and rate of reactions in mixed gas systems

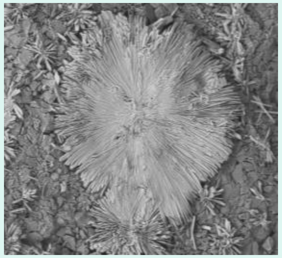
Atomistic simulations to gain mechanistic insight in a co-sequestration system

Reservoir modeling to predict fate and transport of mixed gases to optimize system efficiency

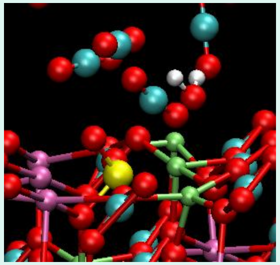








Sulfite mineral forming on dolomite



MD simulation showing initial steps of sulfation

Utilization of CO_2 to enhance energy production and minimize environmental impacts

A grand challenge with enormous economic benefits

Project goal: Develop geologic storage paradigm around mixed- gas streams to lower cost and energy penalty of integrated CCUS