



Center for Frontiers of Subsurface Energy Security

Molecular to Pore-Scale Processes Associated with Geological Carbon Storage

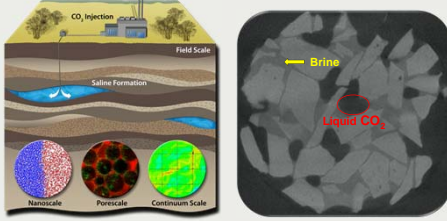
Randall T. Cygan¹, Craig M. Tenney¹, Louise J. Criscenti¹, Kuldeep Chaudhary², Philip C. Bennett², Wen Deng², Kimberly D. Gilbert², William Wolfe², and Bayani Cardenas²

¹Sandia National Laboratories

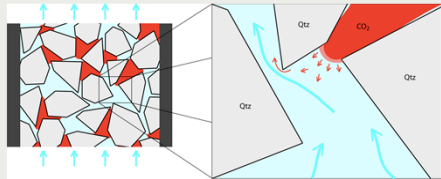
²Jackson School of Geosciences, University of Texas at Austin



Informing continuum models

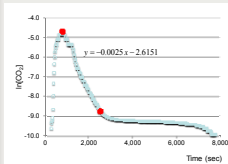


- | Relevant Processes | Relevant Parameters | Relevant Equations |
|--|---|---|
| <ul style="list-style-type: none"> Mineral solubility CO₂ solubility Bioclogging Mineral trapping Solubility trapping Enhanced element mobility | <ul style="list-style-type: none"> Density Viscosity Solubility Diffusion coefficient Dispersion coefficient Contact angles Permeability | $\frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x}$ <p>Advective diffusion</p> $q = -\frac{k \partial P}{\mu \partial x}$ <p>Darcy flow</p> $P_c = \frac{2\gamma \cos \theta}{r}$ <p>Capillary pressure</p> |

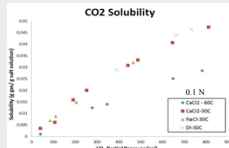


CO₂ dissolution and solubility

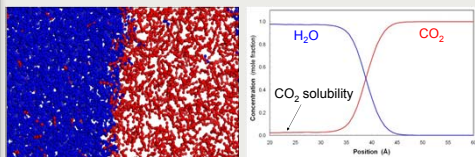
Experiment



- Dissolution is first order, slow, with two different rate periods.
- Surface area and dissolution rate vary with residual saturation.
- Solubility in Na:Cl follows closely predictions by primary EOS at 0.1 N.



Molecular dynamics simulation



- A fully flexible force field for modeling the dissolution of scCO₂ in pure water, and water into CO₂, has been developed.

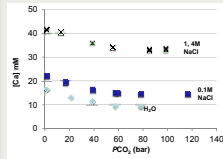
Mineral solubility

Experiment

Decreasing pH should protonate sulfate forming bisulfate:
 $SO_4^{2-} + H^+ \leftrightarrow HSO_4^-$

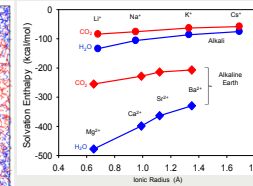
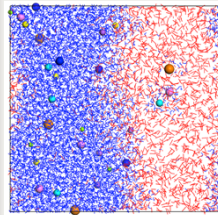
Decreasing sulfate means more gypsum dissolves.
 $CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$

Solubility should increase with increasing CO₂...



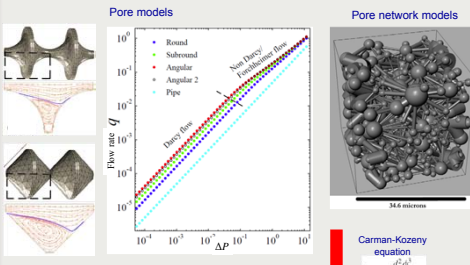
- Solubility decreases ~50% at the CP, in conflict with model predictions.
- Gypsum can clog pore throats and change permeability.
- Future work includes column permeability experiments, molecular modeling of water activity, and modeling of gypsum precipitation in porous media.

MD simulation

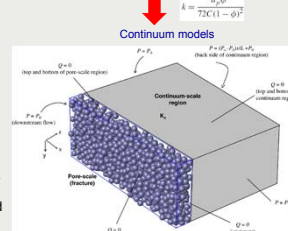


- MD results in water are consistent with experiment.
- MD results suggest solvation of some cations into scCO₂. We are designing experiments to test this hypothesis.

Pore modeling and scale-up



Pore models are used to determine the foundation for continuum concepts and parameters like Darcy's Law, Forchheimer Laws, and (apparent) permeability. Models constructed for different pore geometries (grain angularity/roundness) describe flow through throats/necks on pore network models, which are coupled to continuum models developed by Focus Area 4.

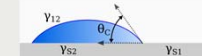


Contact angle measurement

Contact angle indicates the degree of wettability of a surface for a fluid and influences capillary pressure.

Young's Equation
 $\gamma_{S1} = \gamma_{S2} + \gamma_{12} \cos \theta_c$

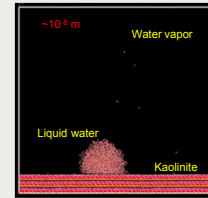
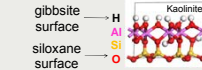
Young-Laplace Equation
 $\Delta P_c = (2\gamma_{12} \cos \theta_c) / r$



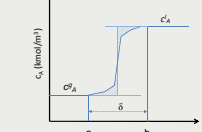
θ_c = contact angle
 γ = surface free energy (interfacial tension)
 ΔP_c = capillary pressure



MD simulation – water and CO₂ on kaolinite



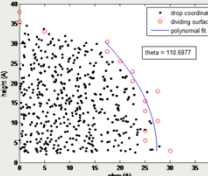
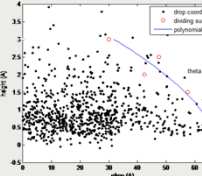
Equimolar dividing surface



- 214 Å x 205 Å x 200 Å (3-d periodic)
- 1700 H₂O molecules

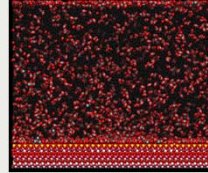
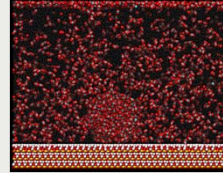
Water on gibbsite (hydrophilic) surface

Water on siloxane (hydrophobic) surface



CO₂ in water on gibbsite surface (non-wetting)

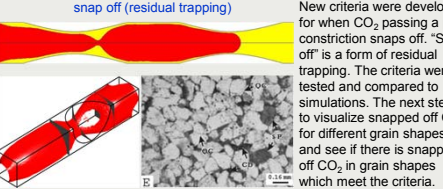
CO₂ in water on siloxane surface (wetting)



- 196 Å x 197 Å x 152 Å PBC cell
- 3000 CO₂ molecules
- 160,000 H₂O molecules (transparent)

State-of-the-art large-scale MD simulations

CO₂ snap-off/residual trapping



New criteria were developed for when CO₂ passing a pore constriction snaps off. "Snap off" is a form of residual trapping. The criteria were tested and compared to simulations. The next step is to visualize snapped off CO₂ for different grain shapes and see if there is snapped off CO₂ in grain shapes which meet the criteria.

Acknowledgements

This material is based upon work supported as part of the Center for Frontiers of Subsurface Energy Security, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC001114. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-04OR21400.