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Workshop on Clean Utilization of Coal

Daniel Giammar¹, Wei Xiong¹, Fei Wang¹, Sophia Hayes², Jeremy Moore², J. Andrew Surface², Catherine Peters³, Bin Guo³, Anurag Mehra⁴

¹Washington University Dept. Energy, Environmental, and Chemical Engineering
²Washington University Department of Chemistry
³Princeton University Department of Civil and Environmental Engineering
⁴Indian Institute of Technology Bombay Department of Chemical Engineering

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Jill Pasteris
Mark Conradi
Dustin Crandall, Grant Bromhal, Bryan Tennant, Johnathan Moore (NETL)
Carbon Sequestration

The IPCC Special Report on Carbon dioxide Capture and Storage, 2005
Sequestration in Magnesium-Rich Formations

Most target formations are sandstones, but mafic (Fe- and Mg-rich) rocks are alternative formations with high mineral trapping capacity.

Continued fracturing of the rock may be promoted by temperature and volume changes from reactions.

Pilot-scale tests in magnesium-rich basalts in Washington State and Iceland.

Also applicable to \textit{ex situ} mineral carbonation in engineered reactors.
When and where do carbonate minerals precipitate in systems with high solid:water ratios and with mass transfer limitations? How does precipitation affect transport properties?
Aquifers have high water-rock ratios and pores of varying sizes.
Conditions in diffusion-limited zones may be much different than in the bulk.
Tubular Reactor Experiments

Tube packed with forsterite particles is open to well-mixed CO$_2$-rich solution at the top.

Experimental Parameters
- Tube length = 5 cm
- Tube diameter = 1 cm
- Porosity = 0.48
- Volume of batch reactor = 200 cm$^3$
- Particle diameters = 5-40 µm
Extent of carbonate formation is spatially localized.

Carbonate minerals continue to form even below the zone of maximum carbonate precipitation.

• Magnesite (MgCO$_3$) forms in the forsterite bed just below the interface with the well-mixed CO$_2$-rich solution.

• Hydromagnesite (Mg$_2$(CO$_3$)(OH)$_2$) forms deeper in the bed.
Progress of Carbonate Mineral Formation

- Magnesite (MgCO₃) becomes the dominant product.
- Extent of carbonate formation is spatially localized.
In Situ Monitoring with $^{13}$C NMR

High pressure zirconia reaction vessel for in situ $^{13}$C NMR measurements of mineral-water-CO$_2$ reactions.

In Situ Monitoring of Reactions

- $^{13}$C NMR can track the in-growth of magnesium carbonate.
- Spatially-resolved NMR found solid carbonates predominantly at a depth of ~1 cm into the bed of forsterite.

80 °C, 105-120 bar CO$_2$-forsterite-water

**In Situ Monitoring: X-ray CT**

**In situ X-ray Computed Tomography (CT)**
- Industrial CT scanner at the National Energy Technology Laboratory (NETL) in Morgantown
- Voxel resolution 14.7 μm
- Tube scanned before and during reaction.
- San Carlos olivine reacted for 60 days at 100°C and 100 bar CO$_2$.

The reconstructed image for the bed has 1978 slices.
Reactive Transport Modeling

Tubular Reactor

\[
\frac{\partial c_{Mg,t}}{\partial t} = D_{Mg} \frac{\partial^2 c_{Mg,t}}{\partial z^2} + R_{Mg, Fo}
\]

accumulation diffusion dissolution

\[
r_{diss, Fo} = k_0 e^{-\frac{E_a}{RT}} \times \left\{ H^+ \right\}^{nH^+} \left( 1 - \frac{IAP}{K_{sp}} \right) = \frac{1}{2} r_{Mg, Fo}
\]

\[
R_{Mg, Fo} = r_{Mg, Fo} \cdot \frac{\text{surface area}}{\text{volume}}
\]

Boundary conditions (BCs)

At \( z = L \), \(- D_{Mg} \frac{\partial c_{Mg,t}}{\partial z} = 0 \)

At \( z = 0 \), \( c_{Mg,t} = c_{Mg,b} \)

Initial condition (IC)

At \( t = 0 \), \( c_{Mg,t} = c_{Mg,b} = 0 \)

- Similar mole balance for dissolved inorganic carbon (DIC).
- Determine pH at each time and location based on charge balance.
- Dissolution rate affected by pH.
Evolution of Composition in Tube

• Gradients develop in pH, dissolved Mg, and dissolved inorganic carbon.
• The saturation index calculated for the region of maximum magnesite precipitation provides information on the necessary conditions for carbonate mineral formation.

\[ SI_{\text{magnesite}} = \log \left( \frac{Mg^{2+} \cdot CO_{3}^{2-}}{K_{sp}} \right) \]
Conclusions and Implications

• Carbonate precipitation is spatially localized.
• Geochemical gradients lead to local reaction rates and products much different from volume-averaged properties.
• Carbonate-rich zone did not block access of dissolved carbon to react with forsterite deeper in the bed.

Remaining Questions

• How do reactions proceed in fractured rocks?
• What volume of a mafic rock is available for sequestration?
• Will carbonate mineral precipitation impede or accelerate sequestration?
New DOE Project on Fractured Basalts

Impact of microstructure on the containment and migration of CO₂ in fractured basalts

- Dan Giammar
- Sophia Hayes
- Phil Skemer
- Mark Conradi
- Brian Ellis (Michigan)

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Cost-sharing provided by the Consortium for Clean Coal Utilization was critical.

Post-reaction X-ray μCT imaging
Localized Mineral Trapping in Geologic Carbon Sequestration

Questions?
giammar@wustl.edu