Characterization of Coupled Chemical-Mechanical Alteration in CO_2-Storage Reservoir Rocks through Scratch Testing

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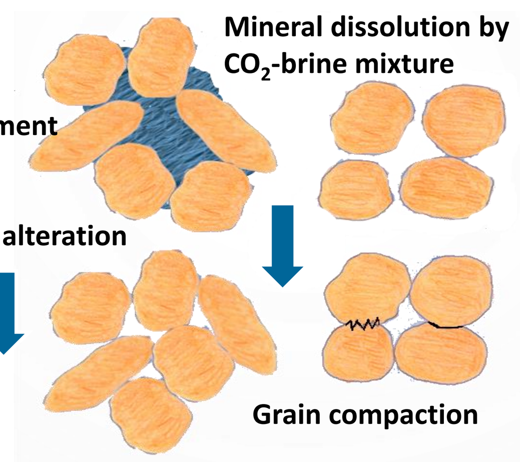
Introduction

Injection of large volumes of CO_2 into geologic formations can help reduce the atmospheric CO_2 concentration and lower the impact of burning fossil fuels. The injection of CO_2 into geologic reservoirs shifts the chemical equilibrium between the mineral assemblage and the pore fluid. Field and laboratory experiments have shown that this shift will situationally facilitate dissolution and re-precipitation of load carrying mineral phases and affect the long term mechanical stability of the host formation [Lu et al., 2012; Carroll et al., 2011; Carroll et al., 2013; Major et al., 2014].



Schematic of how mineral dissolution by CO_2-brine mixture could cause formation compaction [Railsback, 2006].

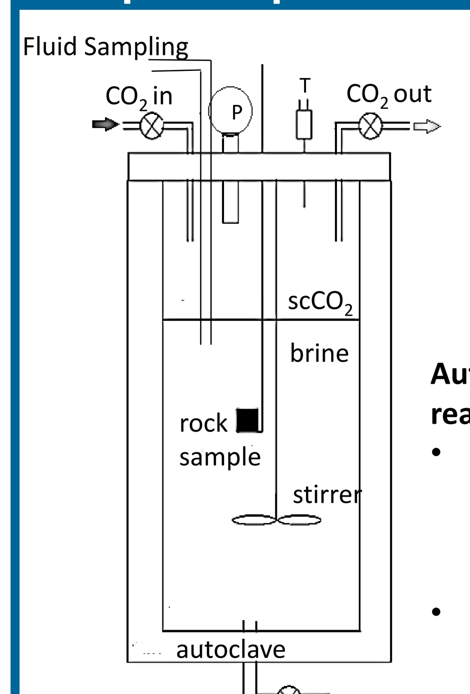
Degradation of mechanical properties can facilitate reservoir compaction and caprock bending above the affected reservoir zones [Kim & Santamarina, 2014].

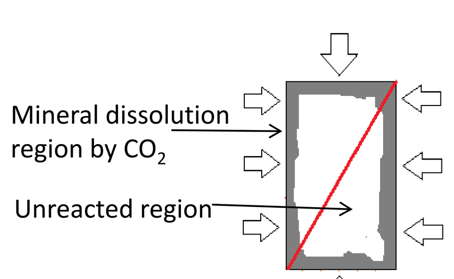
We show chemical and micro-mechanical testing results on Entrada sandstone and Summerville siltstone (Crystal Geyser, Utah) altered due to exposure to natural CO_2-brine environments as well as on analogous samples altered in controlled laboratory experiments at high pressure, temperature, and in the presence of dissolved CO_2

Objectives

- Quantify variation of elastic and strength mechanical parameters of silicic and carbonate reservoir rocks exposed to CO_2-water mixtures to predict emergent chemo-mechanical behavior in CO_2 storage reservoirs
- Identify time scales of the coupled chemical-mechanical reservoir response through experimental evidence
- Determine constitutive parameters from time-dependent experimental data to fit with geochemical modeling

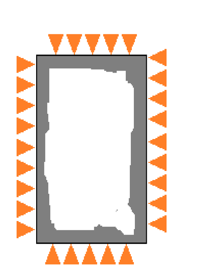
Sample Preparation





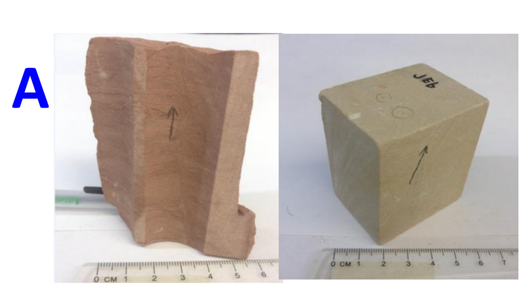
Traditional core test:
- Relatively large sample size.
- Difficult to determine reacted region properties.

Autoclave reactor:
- Slow reaction rate, long experiment time.
- Limited reaction skin depth



Indentation / scratch test:
- Small samples.
- Quick.
- Test on the surface / reacted region.

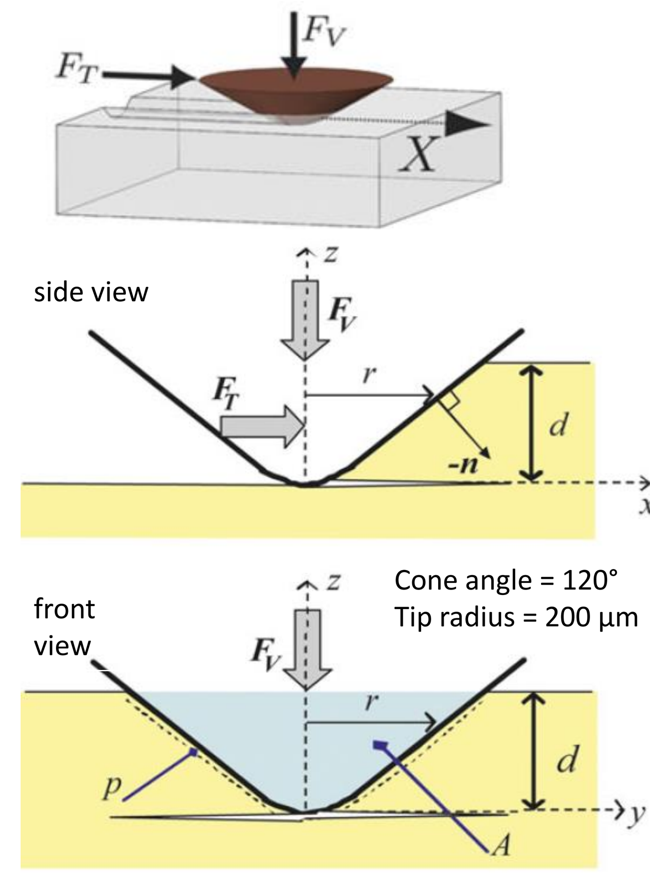
(Left) Schematics of a typical autoclave reactor for CO_2-brine on rock reaction. (Right) Comparison between traditional core-scale test and indentation & scratch tests on CO_2-reacted rock samples. (Below) Labeled picture of experimental setup



unaltered geologically altered
Entrada Sandstone

(A) Rock samples taken from the Crystal Geyser site near Green River, Utah. Samples provided by Jonathan Major from the Bureau of Economic Geology.
(B) An Entrada Sst sample after alteration in an autoclave with CO_2 and deionized water at 1350 psi and 80C for 2 weeks.

Methods - Micro Scratch Test



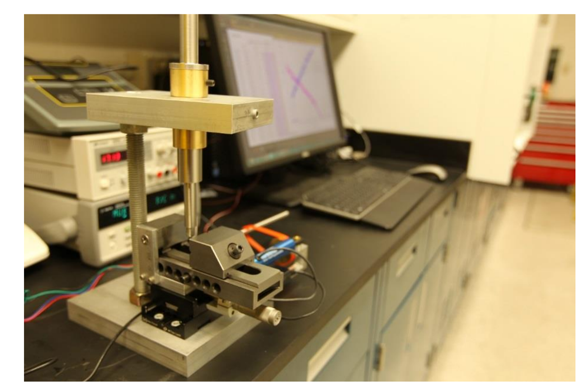
Fracture Toughness (K_c):

$$K_c = \frac{F_T}{\sqrt{2pA}}, \text{ [MPa m}^{1/2}\text{]}$$

Scratch Hardness ($H_{scratch}$):

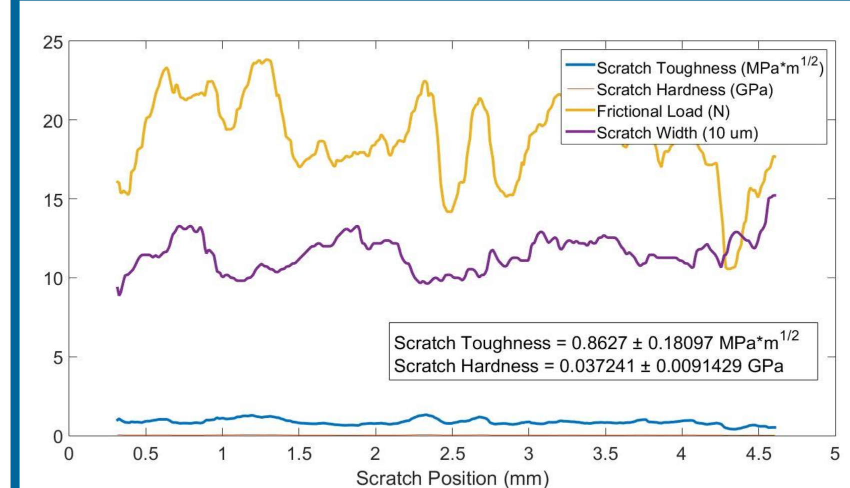
$$H_{scratch} = \frac{kF_V}{w^2}, \text{ [GPa]}$$

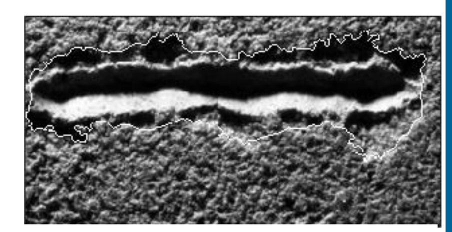
Variables:
- F_T: Horizontal force
- F_V: Vertical force (constant)
- $2pA$: Shape function of the indenter
- k: Geometric constant
- w: Scratch width
- v: Translation velocity (constant)



(Top) Diagram of scratch test showing translation direction. (Middle) Side view and (Bottom) front view of loaded axisymmetric stylus with relevant parameters. (Right) In-house scratch apparatus setup [Figures, equations from Akono et al., 2012, ASTM G171]

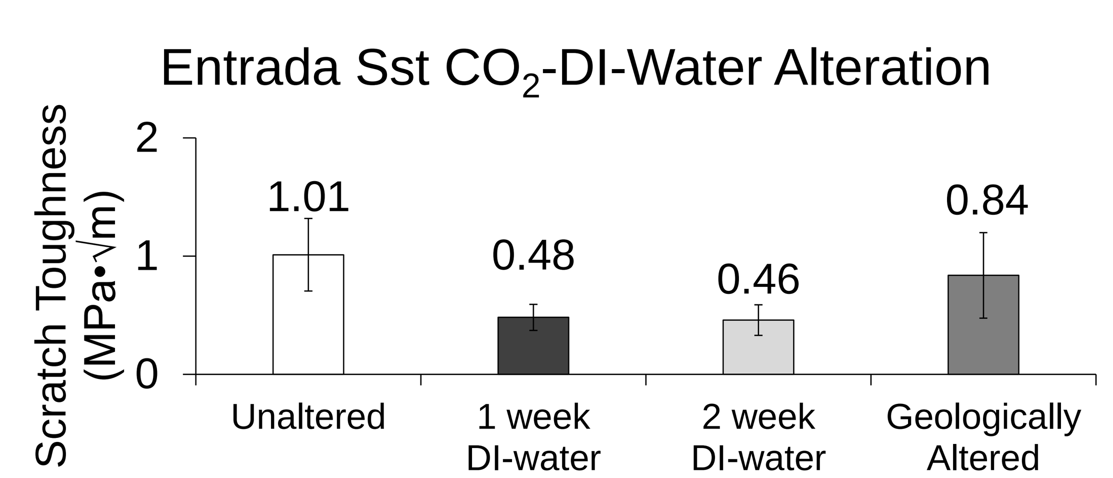
Results - Micro Scratch Test

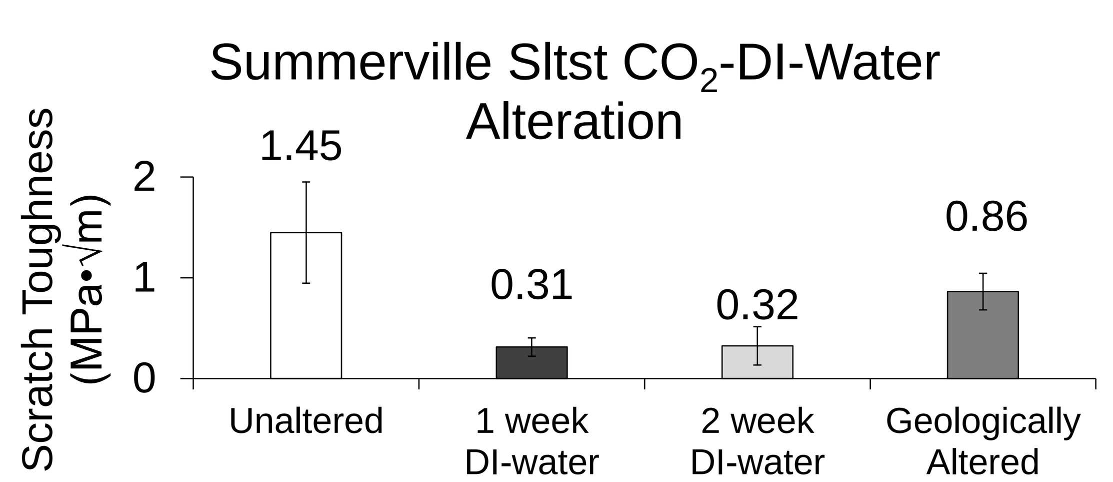




Residuals of a 49 N (F_V) scratch on a geologically altered (bleached) field sample of Summerville Sltst. Residuals were measured using image processing techniques.

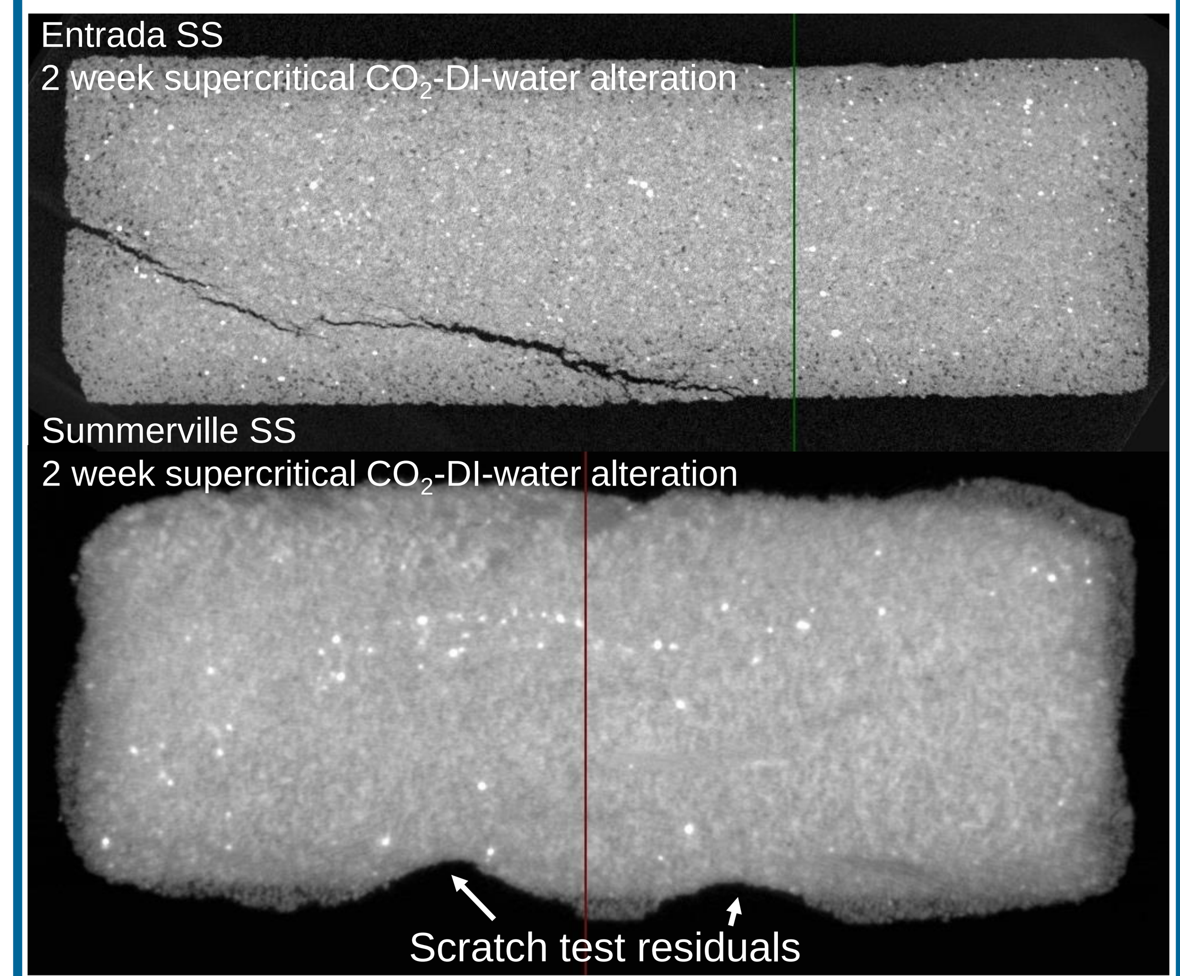
Scratch toughness trends for a bleached sample of Summerville Sltst. Frictional load in yellow; scratch width in purple; scratch toughness in blue.





Scratch toughness K_S results for Entrada sandstone and Summerville siltstone. K_S values are calculated across 2-5mm length scratches and averaged. Error bars represent 1σ. For a linearly elastic isotropic material, the scratch toughness is equivalent to fracture toughness in the fracture driven regime (Akono & Kabir, 2016).

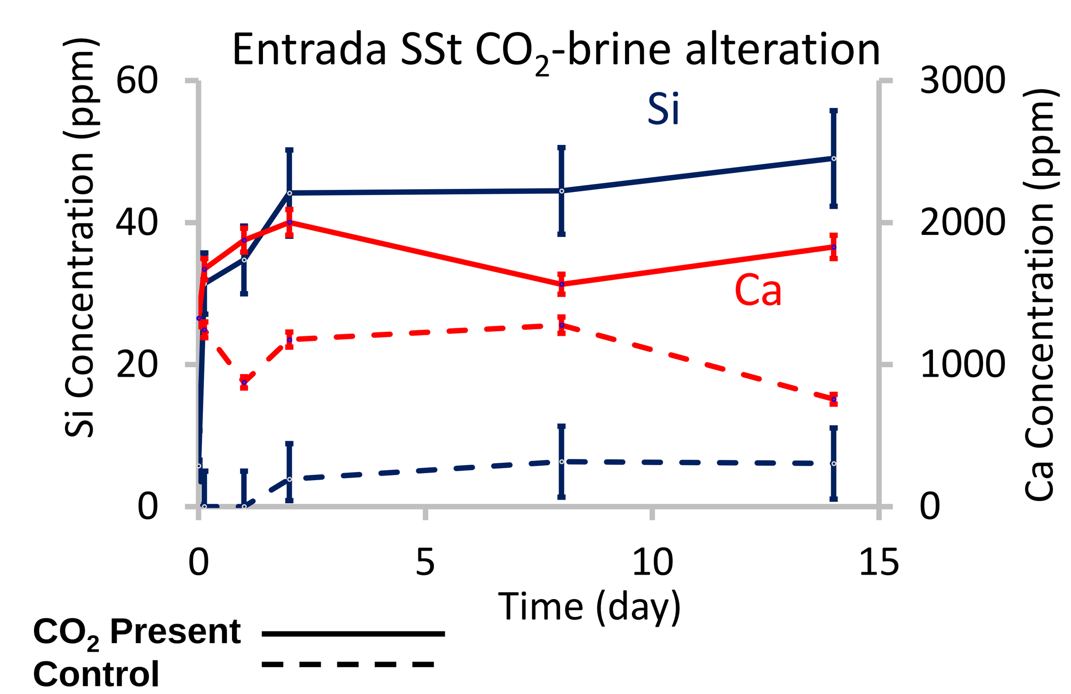
Results – X-ray Microscopy

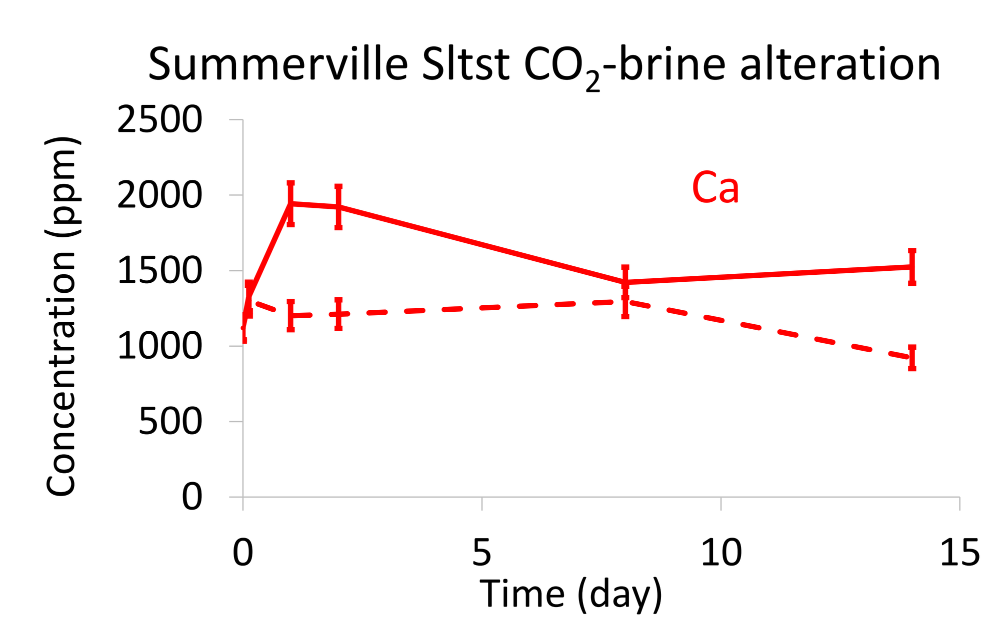


µCT images of Entrada Sst (top) and Summerville Sltst (bottom) samples after 2 weeks alteration at 1350 psi CO_2 and 80°C with deionized water. Darker periphery regions show porosity increase. Alteration induced dissolution was the likely cause for the crack in the Entrada sample.

Results – Analytical Geochemistry

Aqueous samples were collected at intervals of reaction time, preserved, diluted to 1000-1500x depending on the analysis method, and analyzed with ICP-MS using a Nexion 350D and for cations and anions with a Dionex ICS-1100.

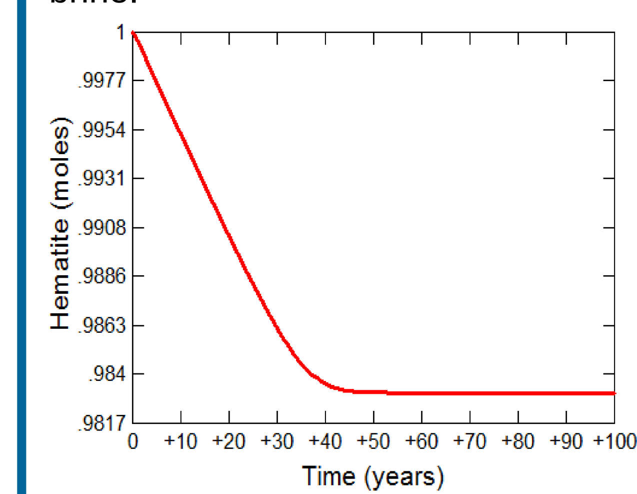




Ion concentrations of Ca^{2+}, analyzed by ion chromatography, and Si 28, analyzed by ICP-MS, for supercritical CO_2-brine alteration reactions with powdered Entrada Sst (top) and Summerville Sltst (bottom). Solid lines represent experiments with CO_2 present and dashed lines represent control water baths with no CO_2 and all other conditions held constant. Error bars represent cumulative uncertainty from dilution, calibration, and analysis. Additional analyses were completed for Na, K, Mg, Li, Cl, SO_4, and PO_3; no significant differences from the control reactions were observed. Initial synthetic brine concentrations followed the table displayed in the Geochemical Modeling section.

Results – Geochemical Modeling

The Geochemist's Work Bench (GWB) Path of Reaction Modeling (Bethke, 1998), is used to predict the changes in mineralogical composition in Entrada sandstone during its alteration by CO_2-charged brine.



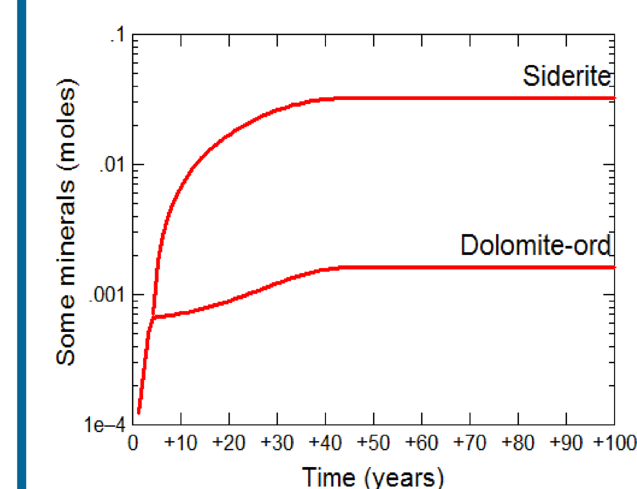


Fig.8. Numerical model: alteration of Entrada sandstone by CO_2-charged brine. Hematite dissolution (top), and siderite and dolomite precipitation (bottom) are predicted.

Table 1. Input for the path of reaction models: initial composition of Entrada sandstone brine, and amounts of reacting carbon dioxide and methane.

Input		
pH	8.1	
Eh	0	
Na^+	24200	mg/l
K^+	1	mg/l
Mg^{++}	315	mg/l
Ca^{++}	1455	mg/l
Fe^{++}	1	mg/l
Cl^-	37950	mg/l
HCO_3^-	762.5	mg/l
SO_4^{--}	3250	mg/l
$SiO_2(aq)$	Equilibrium with quartz	
Reactants		
30 mmol of $CO_2(aq)$		
5 mmol of $CH_4(aq)$		

Table 2. Input for the path of reaction models: mineral assemblage, reactive surface areas, and kinetic rate constants.

Mineral	Specific surface area, cm^2/g	Kinetic rate constant log (mol/cm^2 sec)
Quartz	10	-16
K-feldspar	10	-15
Hematite	10	-14
Calcite	10	-8

The initial brine composition is based on the compilation of ground-water chemistry for the Green River Formation (Wanty et al., 1991). This brine was reacted with CO_2 and CH_4, and minerals quartz, K-feldspar, calcite, and hematite. The concentrations of CO_2 and CH_4 in the reactive fluid are chosen based on Wigley et al., 2012.

Conclusions & Ongoing Work

- Exposure of Entrada Sst and Summerville Sltst to reactive CO_2-brine mixtures over geological time frames resulted in mechanical degradation as shown by decreases in fracture toughness.
- Mechanical property trends determined from scratch tests validate previous double torsion fracture tests performed on same-source rock samples.
- Brine-CO_2 alteration of Entrada Sst and Summerville Sltst result in measurable dissolution of calcareous and silicate minerals, based on increases in Ca^{2+} and Si^{4-} across laboratory time scales with respect to brine-only control alteration.
- Further validation is required to determine whether geological heterogeneity, measurement error, and calibration inaccuracies are possible sources for variations in scratch toughness.
- Ongoing alteration experiments and corresponding micromechanical tests will investigate the alteration of Entrada Sst, Summerville Sltst, Mancos and Woodford shales, and Castlegate and Cranfield Sst with brine and deionized water autoclave fluids.

Acknowledgements

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