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The Effects of Hydrous Supercritical Carbon Dioxide on Reservoir Rock Integrity over Various Time Scales

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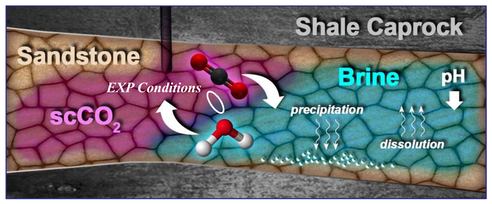
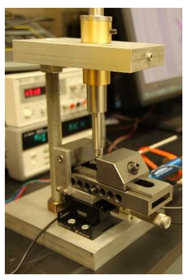
Introduction

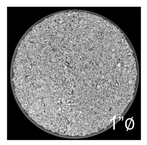
Experimental rock deformation was used to quantify the relationship between supercritical carbon dioxide ($scCO_2$), water vapor, failure strength, and fracture toughness in an analog for Tertiary sandstone saline formation reservoirs. Storing large volumes of carbon dioxide in depleted petroleum reservoirs and deep saline aquifers over geologic time is an important tool in mitigating effects of climate change. Carbon dioxide is injected as a supercritical phase, where it forms a buoyant plume. At brine-plume interfaces, $scCO_2$ dissolves over time into the brine, lowering pH and perturbing the local chemical environment. Previous work has shown that the resulting geochemical changes at mineral-fluid interfaces can alter rock mechanical properties, generally causing a decrease in strength. Additionally, water from the native brine can dissolve into the $scCO_2$ plume where it is present as humidity. This study investigates the effect of hydrous $scCO_2$ on the failure of Boise sandstone on two different time scales: in situ fracture toughness experiments investigated short term chemical effects on strength, and triaxial compression experiments investigated the effects of long term chemical reactions on strength. Reductions in failure strength seen in this study could be important in predicting reservoir response to injection, reservoir caprock integrity, and borehole stability of injection wells.



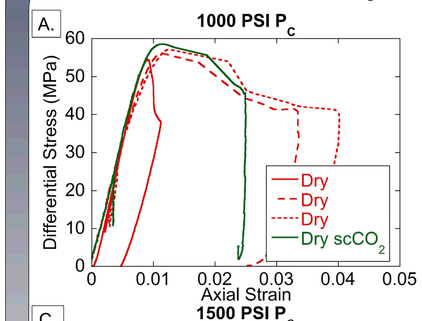
Methods

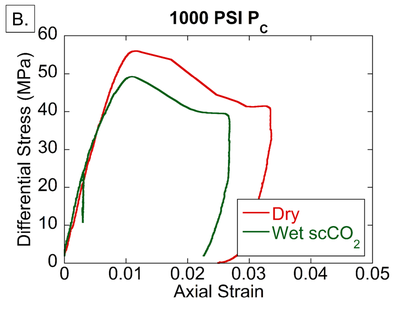
- All experiments were conducted on Boise Sandstone
  - Quartz 31 wt%, Albite 28 wt%, Microcline 17 wt%, Illite-smectite 15 wt%, Calcite 9 wt%
  - ~29% porosity
  - Analog for Gulf of Mexico Tertiary sandstones
- Hydrous $scCO_2$ was generated using a Thar 2.5L pressure vessel at 70C, 9.6 MPa.
  - Deionized water was added via a Rheodyne injector valve and recirculating pump Batches were prepared with increasing amounts of water, from 0 to 40mL in 5mL increments, corresponding to relative humidities of 0, 14, 28, 42, 56, 70, 84, 98, and 100%.
  - Additional batches were prepared with excessive water to ensure saturation.
- Samples of Boise sandstone were reacted in the presence of $scCO_2$ with varying amounts of water, and later deformed dry to investigate long term effects
  - Samples consisted of a Boise sandstone core 25mm in diameter and 50mm long, and a Boise sandstone disc 25mm in diameter, 5mm thick
  - Samples were loaded in a separate hydrostatic vessel, jacketed with nickel foil and teflon, heated to 70C and pressurized to 10.6 MPa.
  - Hydrous $scCO_2$ was flowed through the sample stack for a period of 24 hours using the Thar and the recirculating pump.
  - After reaction, the Boise cores were tested in a triaxial load frame at 2.3, 4.7, and 7.1 MPa confining pressure (P_C) at strain rates of 10^{-5} sec^{-1} at room temperature, or scratch tested
  - Residual water remaining in Thar after cooling and depressurization was collected and acidified with nitric acid for analysis of cations and anions via an ICPMS.
- Fracture toughness experiments were conducted at in situ conditions in the presence of $scCO_2$ with varying amounts of water
  - Samples consisted of a Boise sandstone core 25mm in diameter and 75mm long
  - A 60° notch was cut into the sample using a 0.4mm blade, and a 5mm groove was machined at the top of the saw cut for loading
  - The sample was loaded onto the jaws of the tester, and placed inside the Thar pressure vessel
  - The Thar is filled with CO_2, heated to 70C, and pressurized to 9.6 MPa. Water is added and allowed to equilibrate for 1 hour
  - The tester is controlled by a hydraulic ram, powered by an Isco syringe pump, and displacement is measured by an LVDT
  - Ram pressure is used to calculated load on the sample, and fracture toughness
  - 3 tests per condition
  - Crack tips imaged using 3D surface profilometer

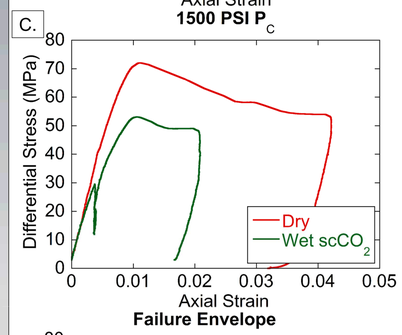


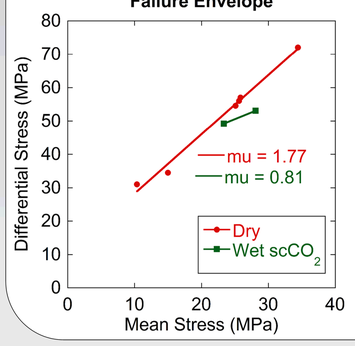


Hydrous $scCO_2$





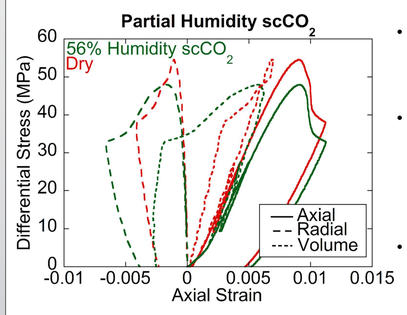




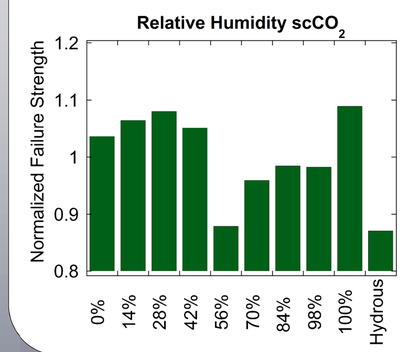
Boise cores were flooded with fully saturated $scCO_2$ with excess water present in the system. Tests were conducted dry, at room temperature, and at a strain rate of 10^{-5} sec^{-1}.
A. The sample reacted with dry $scCO_2$ shows no change in strength beyond natural variation.
B. Core reacted with saturated $scCO_2$ shows a 13% reduction in failure strength compared to dry experiments.
C. At higher confining pressures, dramatic weakening is seen as failure strength is reduced by 26% due to exposure to saturated $scCO_2$.

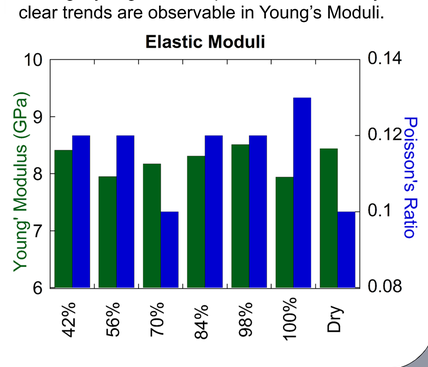
- Dry $scCO_2$ does not have any effect on the strength of Boise sandstone
- Fully saturated $scCO_2$ weakens Boise sandstone
- Water does not affect strength of Boise sandstone
- Triaxial experiments are performed later, dry, at room temperature; decreases in strength due to chemical reaction of Boise sandstone with humidity
- Water present as humidity in $scCO_2$ must cause disassociation of CO_2 to create an acidic phase to cause chemical reactions, similar to observations of CO_2 dissolved in liquid water
- Weakening exacerbates at higher confining pressure, suggests chemical reactions could be targeting cement phases

Humid $scCO_2$

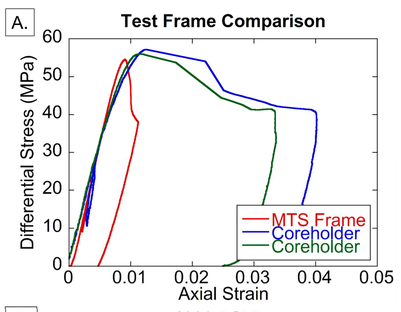


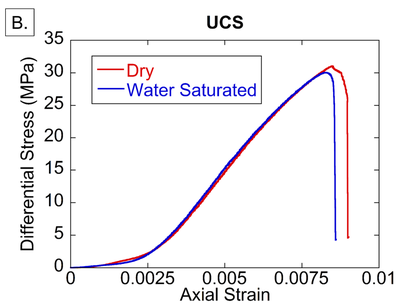
- Boise cores were flooded with at different humidities of $scCO_2$. Tests were conducted dry, at room temperature, at a strain rate of 10^{-5} sec^{-1}, in coreholders and servo-hydraulic frames.
- Samples reacted at 56% relative humidity (+20mL H_2O) show weakening compared to unaltered samples. The reduction in strength at this humidity is comparable to fully saturated experiments. All other humidities, even 100%, do not show significant changes in strength.
- Elastic moduli for relative humidity sample do not show significant variation. Poisson's ratio tends to be slightly higher, except for 70% humidity. No clear trends are observable in Young's Moduli.

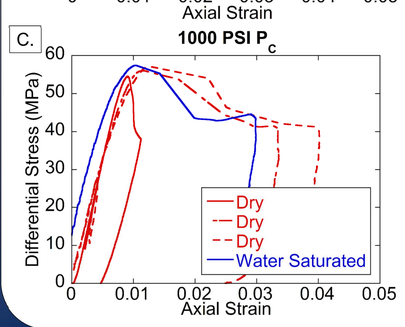




Boise Control Experiments



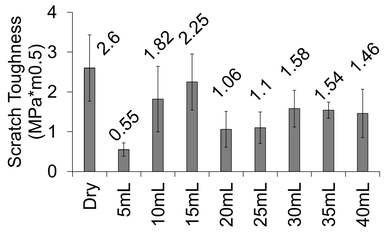


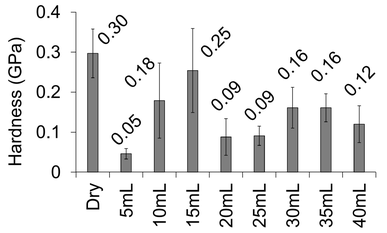


A. Two different load frames were used in this study, a Temco triaxial coreholder and a MTS 220kN servo-hydraulic frame. The MTS frame is stiffer, but negligible difference in strength
B. UCS tests on dry and water saturated cores were performed on a MTS servo-hydraulic load frame. Water saturated samples are weaker, but not significantly so.
C. Water saturated experiment conducted at 70C under constant flow at an effective pressure of 1000 PSI. Failure strength is with natural variation of dry experiments.

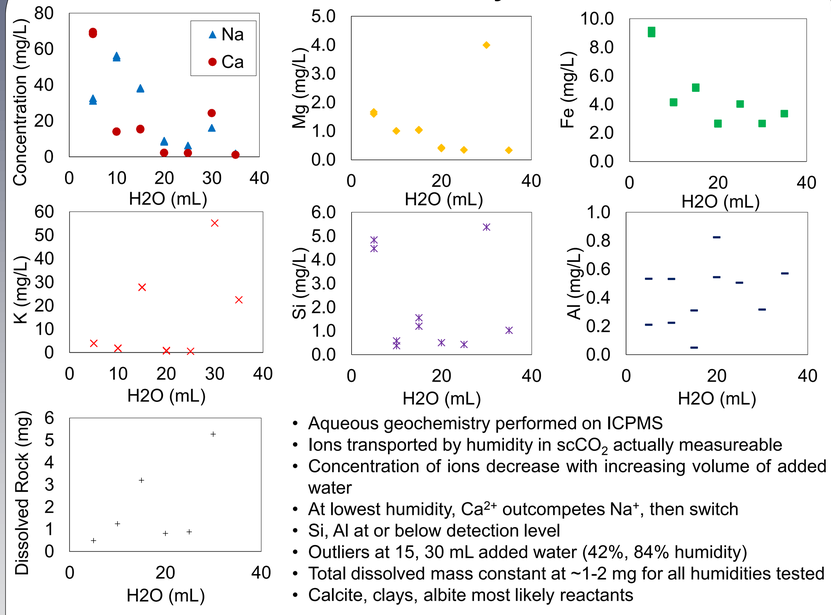
Scratch Testing

- Lowered scratch toughness and hardness values in altered samples compared to dry $scCO_2$
  - Variation greater than differences
- Maximum vertical load same order as surface roughness
  - Can't differentiate between surface roughness, natural heterogeneity, and alteration

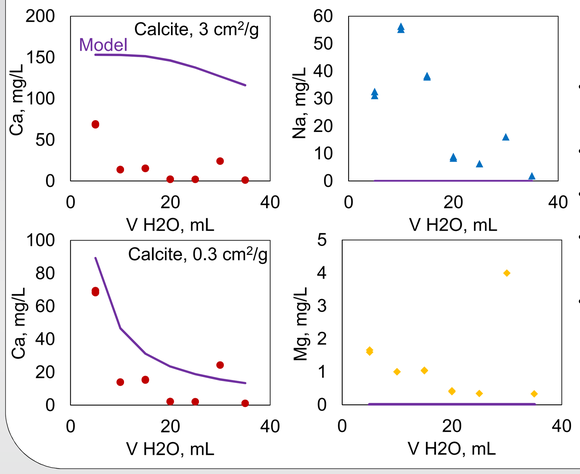




Geochemical Analysis

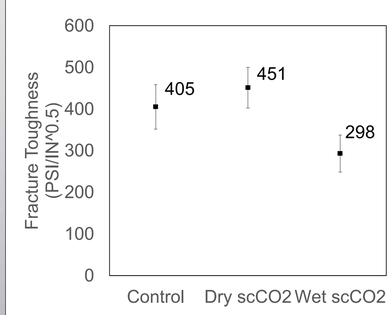


- Aqueous geochemistry performed on ICPMS
- Ions transported by humidity in $scCO_2$ actually measureable
- Concentration of ions decrease with increasing volume of added water
- At lowest humidity, Ca^{2+} outcompetes Na^+, then switch
- Si, Al at or below detection level
- Outliers at 15, 30 mL added water (42%, 84% humidity)
- Total dissolved mass constant at ~1-2 mg for all humidities tested
- Calcite, clays, albite most likely reactants

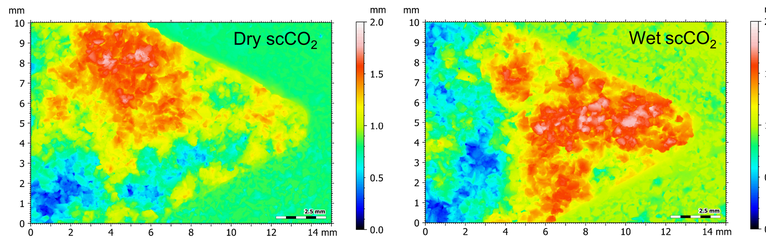


- Preliminary modeling of reactions performed in Geochemist's Workbench
- Based on mineralogy of Boise sandstone
- Water fixed by fugacity of CO_2
- Model able to match observed dissolution of calcite at lower surface area
- Model does not match observed concentrations of other ions

In Situ Fracture Toughness



- Fracture toughness tests performed at in situ conditions in the presence of hydrous $scCO_2$
- Investigating short term chemical effects on rock strength
  - 1 hour exposure
  - Subcritical, fast chemical reactions
- Slight strengthening in the presence of dry $scCO_2$, but within a standard deviation
- Weakening in the presence of wet $scCO_2$
  - 35% reduction in strength



- Rugged, higher topography crack face
- Flatter crack face

Conclusions

- Boise sandstone is generally insensitive to water, dry $scCO_2$
- Fully saturated $scCO_2$ causes weakening in Boise sandstone that is exacerbated at higher confining pressures, leading to a decrease in the slope of the failure envelope
- Partial humidities of $scCO_2$ do not show clear weakening or strengthening trends in scratch tests or triaxial tests
- Water present as humidity in $scCO_2$ does transport ions, is reactive
- Total amount of water available in partially saturated $scCO_2$ is very small, not enough to drive significant chemical reactions; but if there is sufficient amount of water available, chemical reactions can cause significant changes in strength.
- Fracture toughness is reduced in the presence of hydrous $scCO_2$
- Hydrous $scCO_2$ causes changes in strength on both the short and long term scales

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