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You will not hear audio until we begin.





Geochemical Effects of CO₂ Saturated Brine on Reservoir and Seal Rocks

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15 June 2023





Outline



- General Comments on CO₂ Changes to Rock and Fluids
- Methods to Investigate Changes to Formation Rocks
- Fluid-Fluid and Rock-Fluid Modeling Software
- Static CO₂ Saturated Brine Exposure for Low K Rocks
- Dynamic CO₂ Saturated Brine Injectivity Testing



CO₂ Effects on Seal and Target Zone



- CO₂ Saturated brine can reach a pH as low as approximately 3.5 in relatively fresh waters.
- The pH will be less affected as the brine salinity increases and as pressure and temperature increase.
- These acidic effects could be important in both the target and seal layers
- Geochemical Reactions of the rock minerals should be investigated by modeling and various testing methods



Thoughts to Consider for CO₂ Injection



- Carbonic acid is formed when CO₂ contacts water/brine
- Approximately 2 mole percent CO₂ is the maximum CO₂ water can carry
- Dry CO₂ injection will vaporize some fraction of contacted water, which will increase salinity (lowers CO₂ content and raises pH)
- Acids begin to react (spend) as soon as they contact minerals
- Reaction will depend on mineral (most reactive minerals are calcite, potassium feldspars, and high surface area clays)
- Water saturation fraction will reduce near injection well with CO₂ injection
- Reservoir Pressure will increase with CO₂ injection



Determining CO₂ Effects on Seal and Target Zone



After periods of CO₂ saturated brine exposure carbonic acid effects can be investigated by various standard core analysis methods

- Visual inspection
 - CT or MicroCT Scan
 - Petrographic Description (Thin Section and SEM)
- Porosity and Permeability Determination
- Formation Damage – Permeability vs Throughput Testing
- Mercury Injection Capillary Pressure – Including Threshold Entry Pressure
- Geomechanics Testing for Rock Strength



USGS Sponsored Geochemical Software Example



- Z. Duan et al., "An improved model for the calculation of CO₂ solubility in aqueous solutions containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻", Marine Chemistry (Elsevier) February 2006
- CO₂-H₂O mixtures in the geological sequestration of CO₂. I. Assessment and Calculation of mutual solubilities from 12 to 100°C and up to 600 bar, N Spycher et al., Geochemica et Cosmochimica Acta, Volume 67, Issue 16, August 2003, Pages 3015-3031.

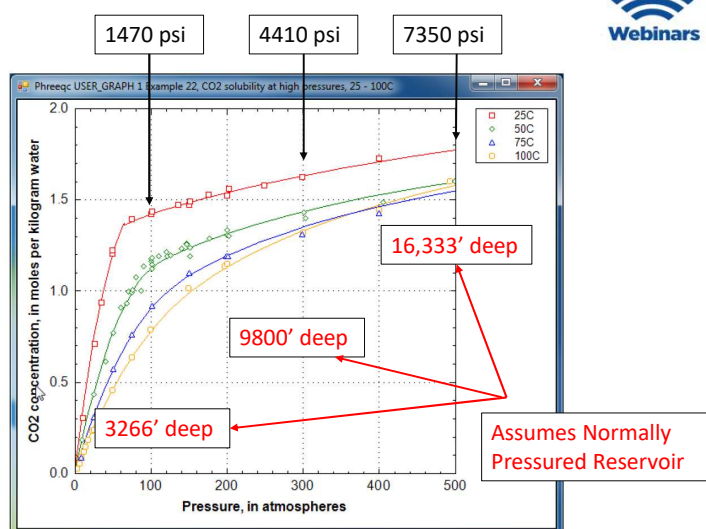


Figure 27. Solubility of CO₂ gas as a function of gas pressure at 25, 50, 75 and 100 °C. Data points are from compilations by Duan and others (2006) and Spycher and others (2003); lines are calculated with PHREEQC.

Commercial Software Example of CaCO₃ Solubility/Deposition

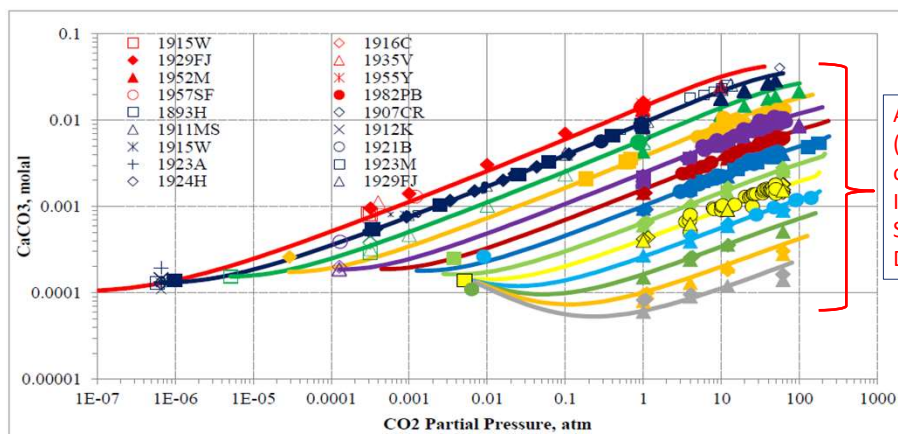


Figure 11 – Predicted solubility of calcite scale as a function of temperature, pressure, and CO₂. Symbols are the measured values and lines are OLI predictions



Graph Source: OLI software marketing correspondence

CO₂ Extended Exposure Methodology

- Samples drilled from whole core material if possible and trimmed to 1.5-inch diameter right cylinders (horizontal and vertical). Test samples can vary from right cylinder plugs to small chunks of rock.
- Synthetic formation brine was prepared based on the provided analysis using deionized water and reagent grade chemicals. The brine was filtered to 0.45 microns and degassed.
- Each sample was placed in a labeled bag and loaded into a stainless-steel vessel filled with test brine.
- The vessel was capped and pressurized to 100 psi with carbon dioxide (CO₂).
- The vessel was heated to 150°F while monitoring pressure. Pressure was not allowed to exceed 1500 psi during this process.
- Once temperature stabilized at 150°F, pressure was maintained at 1500 psi using CO₂.
- Exposure time (1 month, 6 months, ??) for each of the samples.
- Upon completion, samples were slowly depressurized, unloaded and dried in a convection oven.

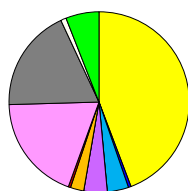


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Silty Mudrock Seal

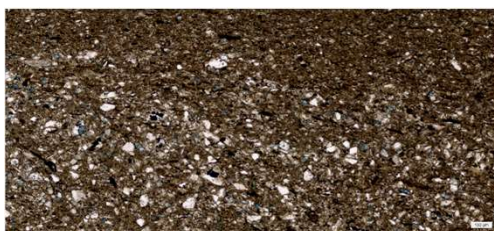


$\phi = 5.3\%$; $K_{\text{Swanson}} = 6.47\text{E-}05 \text{ mD}$; $\text{GD}_{\text{900}} = 2.664 \text{ g/cc}$; $\text{Pd}_{\text{CO}_2} = 972 \text{ psi}$

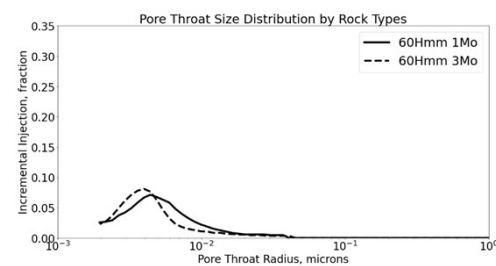
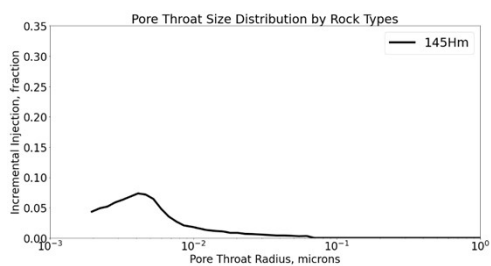
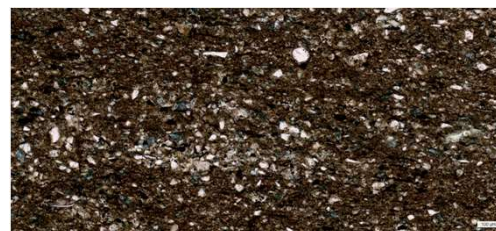


■ Quartz
 ■ K-Feldspar
 ■ Plagioclase
 ■ Calcite
 ■ Dolomite
 ■ Siderite
 ■ Pyrite
 ■ Illite/Smectite
 ■ Illite & Mica
 ■ Kaolinite
 ■ Chlorite

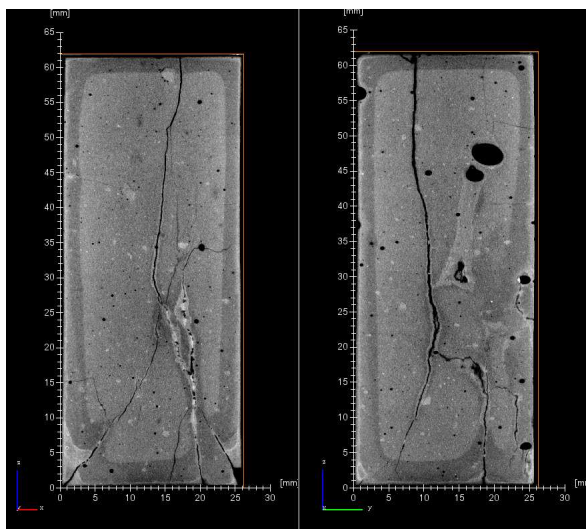
Pre-CO₂ Exposure



Month Post-CO₂ Exposure



Cement - Post Exposure CT Scan



- Cement contain approximately 60% calcite
- Areas of brine contact can be seen by darker colors around the edge of the sample and near fractures
- Bright colors are indications of high-density material left behind after CO₂ dissolution

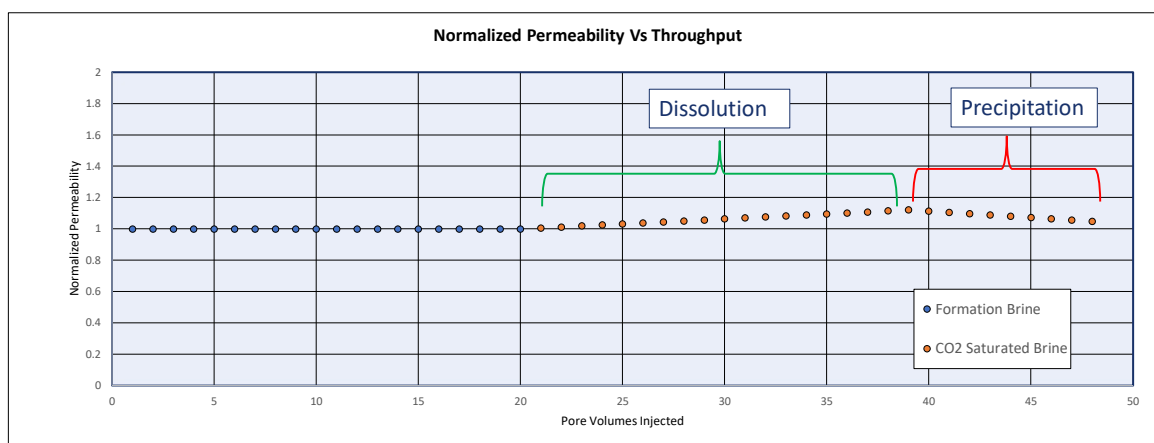
Dynamic Exposure for Higher Permeability Samples (contact to all primary flow pathways)



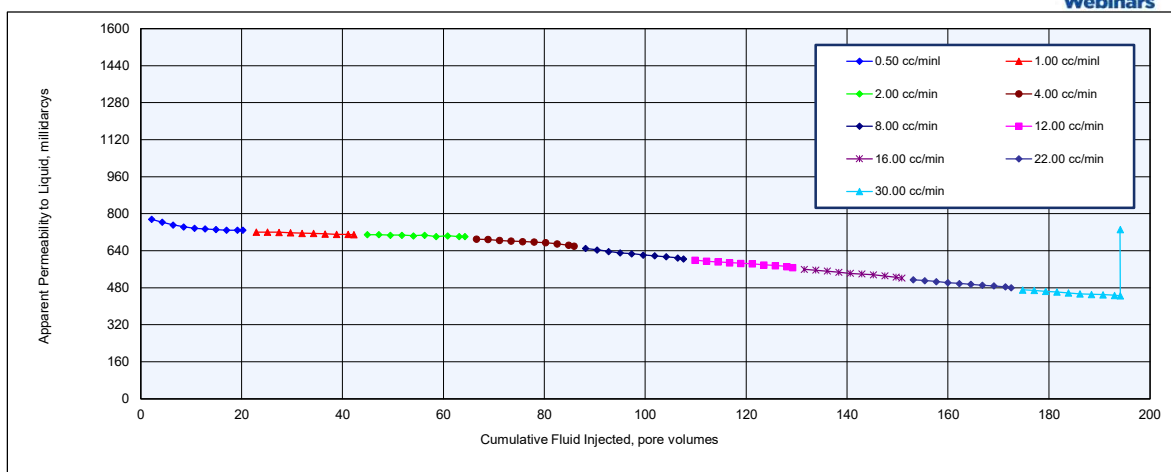
- Measure Grain Volume and Sample Weight
- Saturate Sample with Reservoir Formation Brine
- Measure Baseline Permeability to Reservoir Brine (Reservoir Temperature)
- Inject CO₂ Saturated Brine and Monitor Permeability Changes vs Pore Volumes of Throughput (Reservoir Temperature)
- Slowly Reduce Test to Ambient Conditions
- Dry Sample
- Measure Grain Volume and Sample Weight



Permeability Vs Throughput



Critical Velocity from Liberated Fines



CO₂ and Brine Co-Injection on Inlet Face



10 PV of Injection



56 PV of Injection



155 PV of Injection



Pore Volume Increased from 56.74 to 66.9 cc (24.8% Increase)

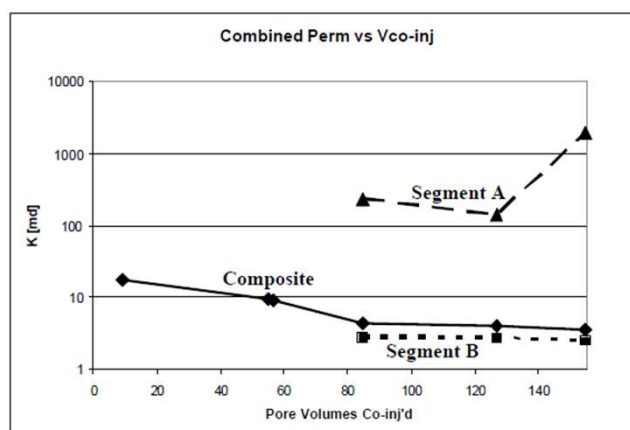


SCA2003-19: CO-INJECTED CO₂-BRINE INTERACTIONS WITH INDIANA LIMESTONE
Reid B. Grigg and Robert K. Svec, New Mexico Petroleum Recovery Research Center

CO₂ and Brine Co-Injection – Permeability Changes



- Initial Total Injection Rate was 80 cc/hour for the first 55 Pore Volumes of Injection
- Injection Rate was Reduced to 40 cc/hour from 55 Pore Volumes to 155 Pore Volumes

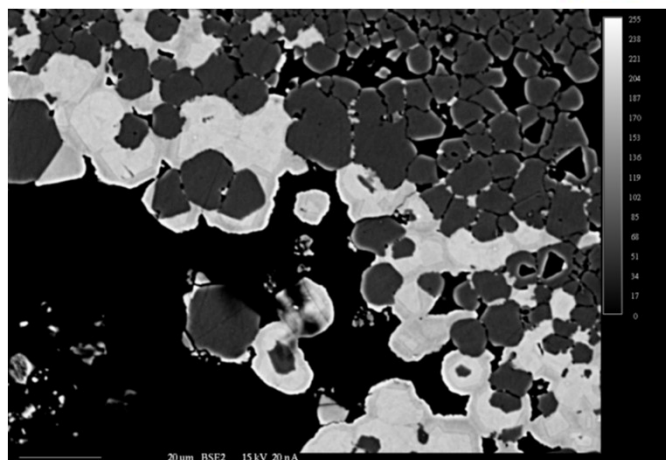


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CO₂ and Brine Co-Injection Mineral Deposition



The White Areas in Backscattered Electron Image are Rich in Strontium from the Brine (5000 ppm SrCl₂)



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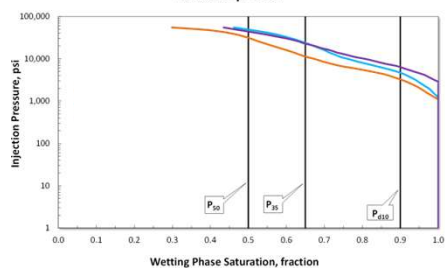
Capillary Pressure – Mercury Injection

(CO₂ Exposure)



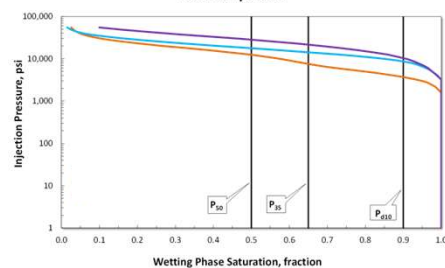
Sample #1

Data Comparison

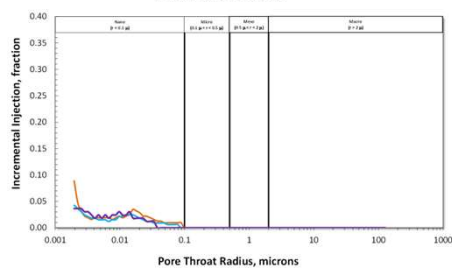


Sample #2

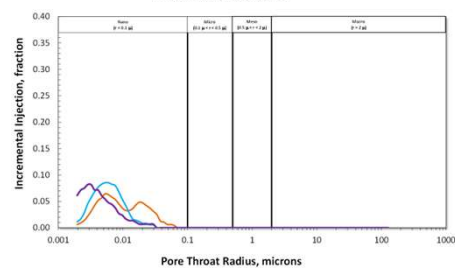
Data Comparison



Pore Size Distribution



Pore Size Distribution



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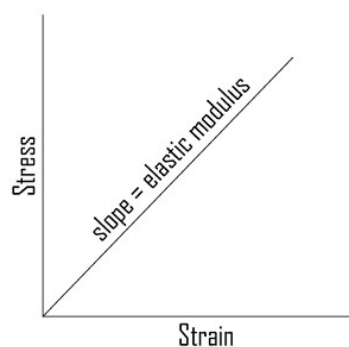
Triaxial Test



A stress-strain curve is a basic tool used to interpret rock mechanical data such as

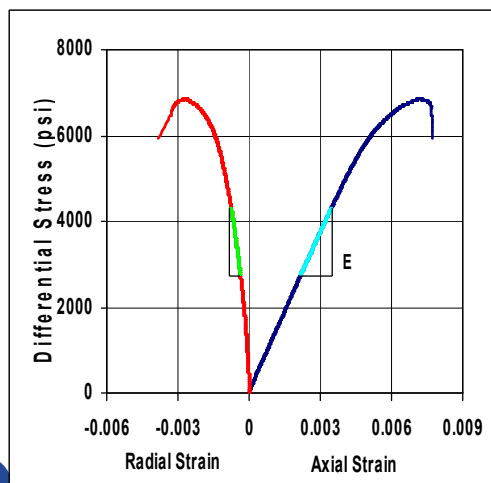
- Young's modulus (E)
- Poisson's ratio (ν)
- Compressive Strength

A Linear Elastic Stress-Strain Curve



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Young's modulus E from σ - ϵ curves



Young's modulus

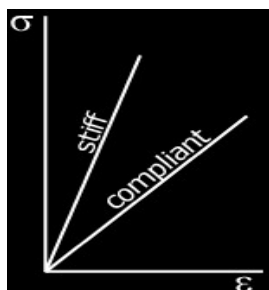
$$E = \frac{\Delta\sigma}{\Delta\epsilon_a} = 1.2 \times 10^6 \text{ psi}$$

= slope of axial curve

[slope taken at $\frac{1}{2}$ max stress]



What does Young's Modulus tell us?



Young's modulus (as well as the bulk and shear moduli) tells us about the stiffness of the rock

TABLE 3.1—TYPICAL ELASTIC PROPERTIES OF ROCK ³		
Rock Type	Young's Modulus (10 ⁶ psi)	Poisson's Ratio
Granite	3.7 to 10.0	0.125 to 0.250
Dolomite	2.8 to 11.9	0.08 to 0.20
Limestone	1.4 to 11.4	0.10 to 0.23
Sandstone	0.7 to 12.2	0.066 to 0.30
Shale	1.1 to 4.3	0.1 to 0.50



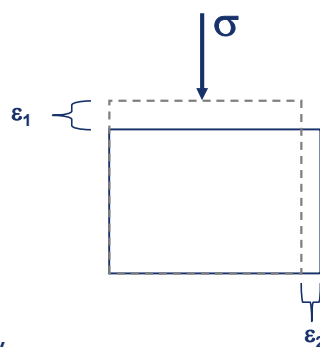
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Poisson's Ratio (ν)

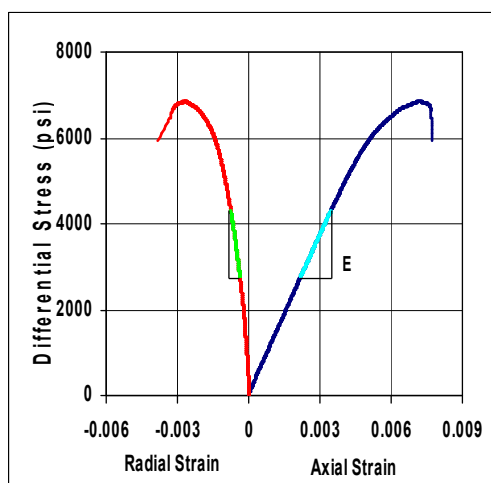
Ratio of lateral expansion to longitudinal contraction.

$$\nu = -\epsilon_2 / \epsilon_1$$

The measure of the rocks tendency to expand radially as it is compressed axially



Poisson's Ratio ν from σ - ϵ curves



Poisson's ratio

$$\nu = - \frac{\frac{\Delta\sigma}{\Delta\epsilon_a}}{\frac{\Delta\sigma}{\Delta\epsilon_r}}$$

$$= - \frac{\text{slope of axial curve}}{\text{slope of radial curve}}$$

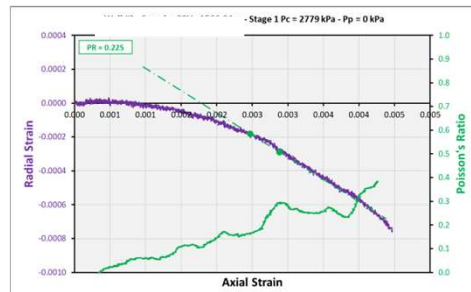
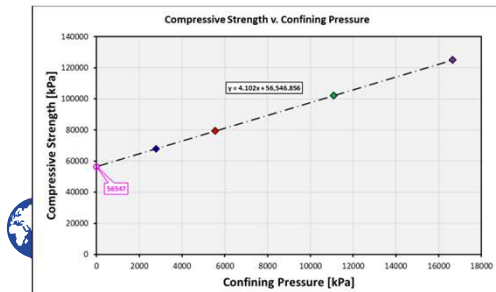
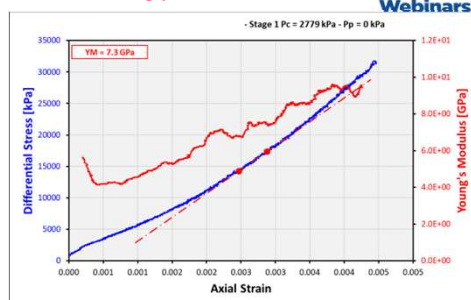
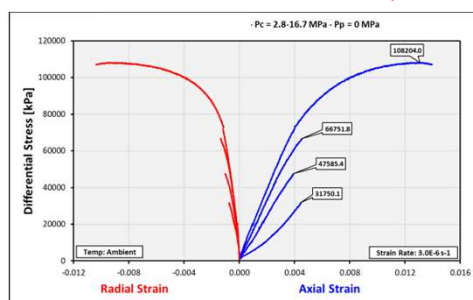
$$= 0.30$$



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Triaxial Test Data

For these example data graphs, P_c is defined as confining pressure



Triaxial Test Comparison (Shell Peterhead data)



- 2-3% Calcite cement was dissolved (confirmed by MicroCT, SEM, XRD and effluent analysis)
- No significant change in rock mechanical properties (Young's modulus, Poisson's ratio, bulk modulus, and velocities)
- Possibly indicating the loss of calcite did not alter the grain-to-grain contact strength of the sand

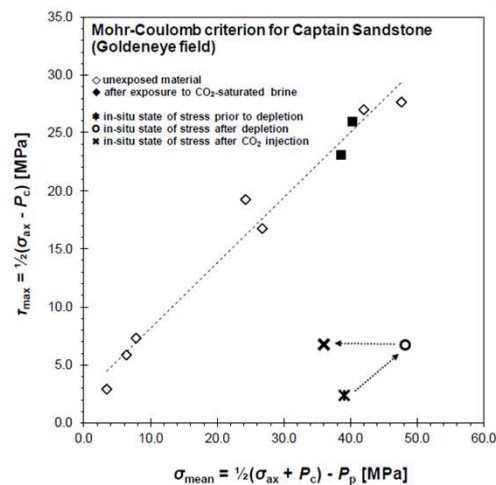


Fig. 3-12—Failure envelope for Captain Sandstone in P'-Q stress space obtained using data from a previous study⁴, as well as data obtained in this study.

Peterhead CCS Project (Shell), Special Core Analysis (SCAL) Report and Geomech / Reactive Transport Modelling (RTM) Core Analysis Reports, Doc No. PCCS-05-PTD-ZP-9034-00001 Rev-KO2

Summary



- Various freeware and commercial software packages are available to predict dissolution and potential precipitation of rock minerals due to lowering of pH caused by CO₂ injection
- The Geochem software packages are fairly-robust, but usually don't use laboratory measured data to constrain the data
- Static and/or Dynamic exposure testing should be conducted on reservoir rocks (and cement) to constrain the modeled and upscaled data

