Experimental Determination of the Effects of Supercritical CO_2 on Saline Aquifer Host Rocks and Well Plugging Cements

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Fifth Annual Conference on Carbon Capture & Sequestration

May, 2006

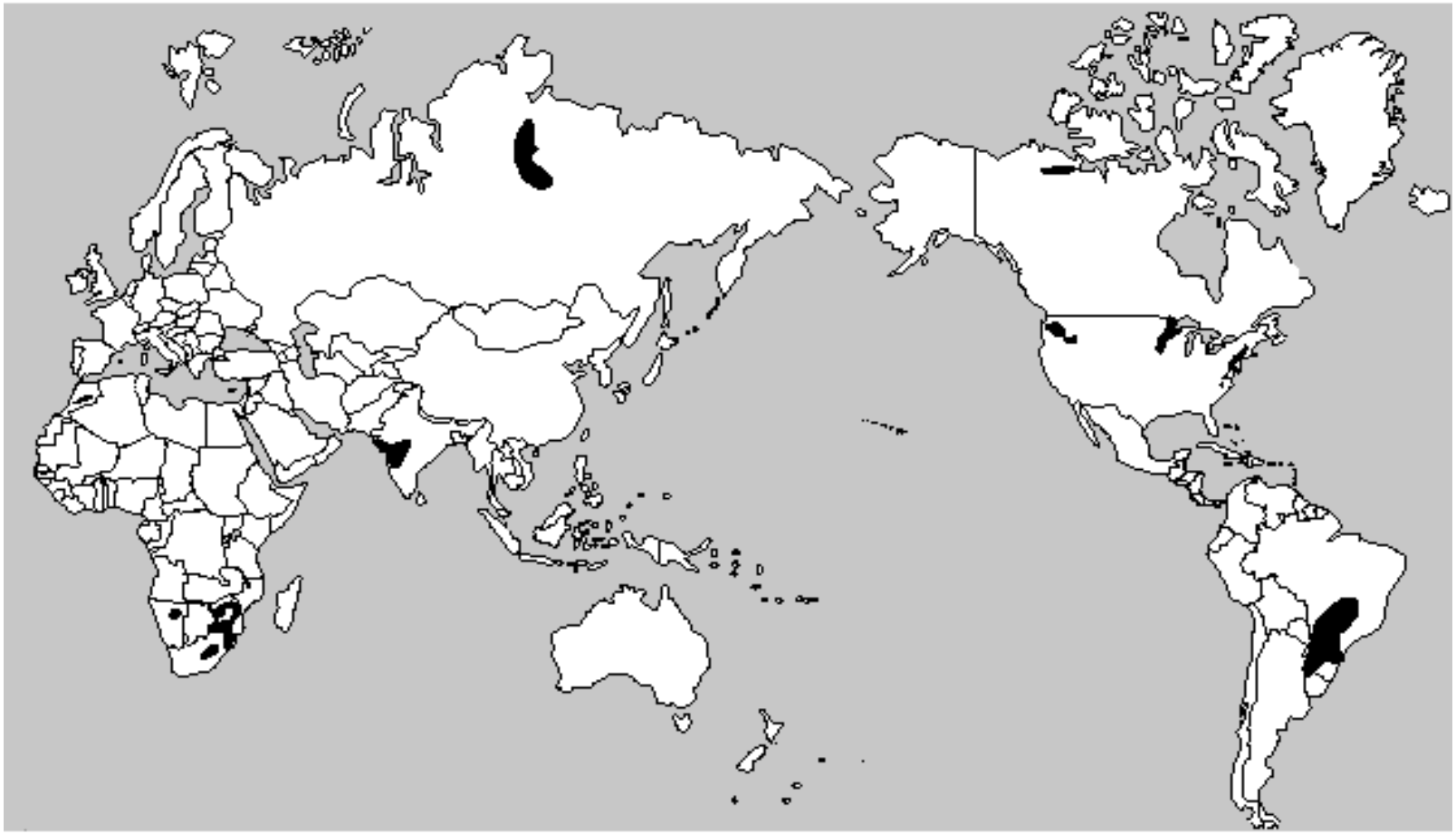
National Energy Technology Laboratory

Office of Fossil Energy

Whole Core Analysis

- **Development of core analysis system**
  - Physical & chemical impact of CO_2 flood on reservoir rock & plugging materials
  - Porosity, permeability, compressive strength
- **Baseline studies**
  - Saline aquifer host rock
    - Basalts
    - Sandstones
  - Well-plugging cements
    - Legacy wells (pre-CO_2 injection)
    - CO_2 injection wells

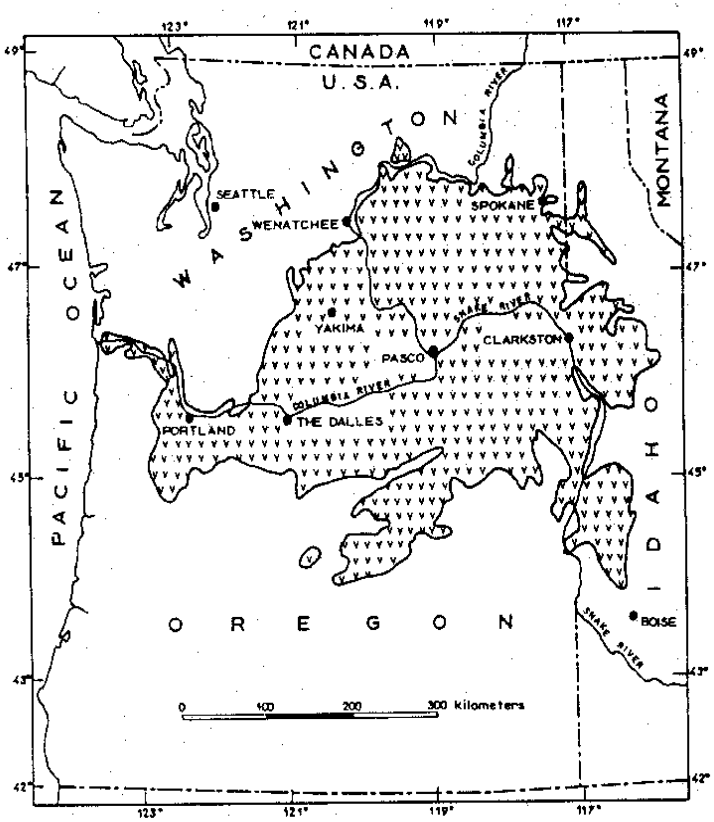
Continental Flood Basalts



Antarctica not shown here

Columbia River Basalt Group (CRBG)

- **Flood basalt province**
  - Area over 200,000 km^2
  - Average thickness of 1 km
- **Multi-flow structure**
  - Numerous aquifers
  - Isolated stratigraphically
- **Aquifer horizons**
  - 10-30 m thick
  - 10-30% porosity
  - Vast storage capacity
- **PNNL (Dr. Steve Reidel)**
  - Potential natural gas storage
  - Why not CO_2?

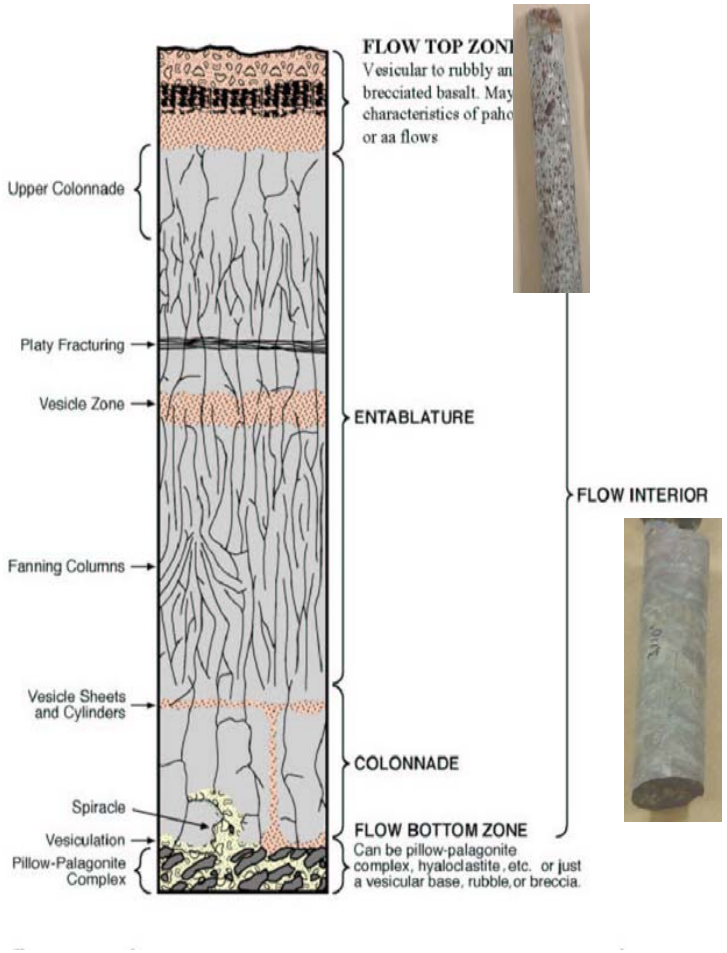


Exposures of CRBG

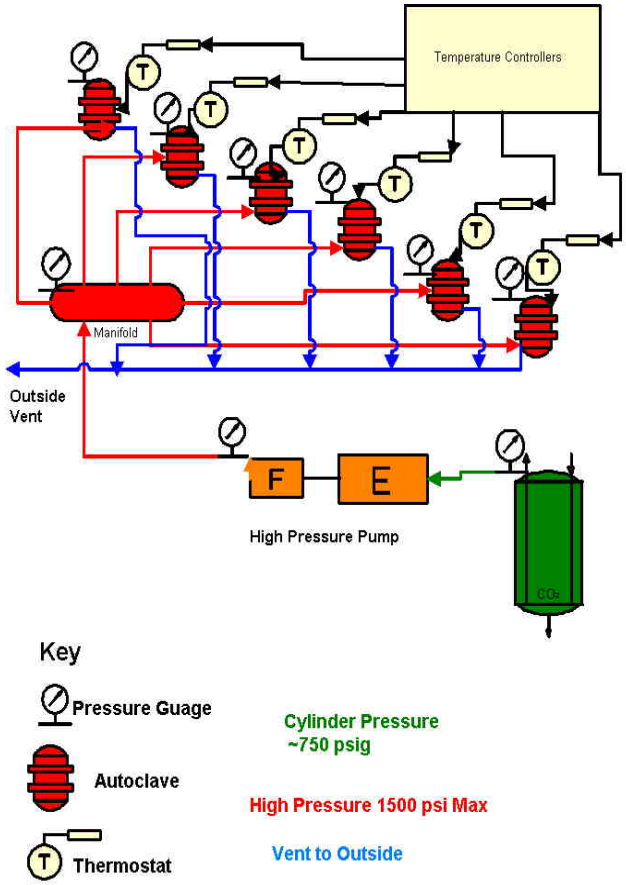
NE Oregon, Imnaha Canyon, >3,000 ft of exposures, at least 24 basalt flows

Idealized Cross-Section With Typical Core

- **Flow top**
  - Volcanic gases escape during emplacement
  - Vesicular basalt with high porosity
- **Flow bottom**
  - Pillow complex, brecciated
  - Lies above prior flow top
    - Interflow zone
- **Entabulature**
  - Massive interior section
  - Seals interflow zone
    - Cap rock
    - Bottom aquitard

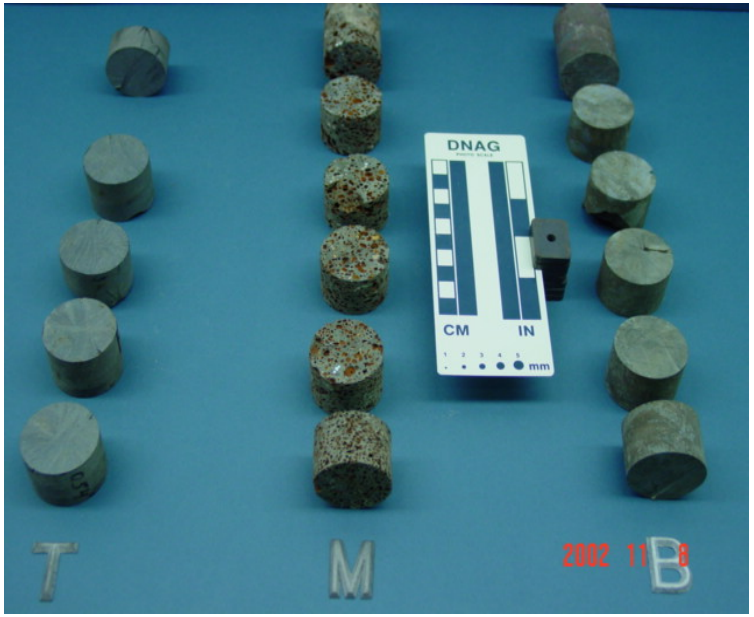


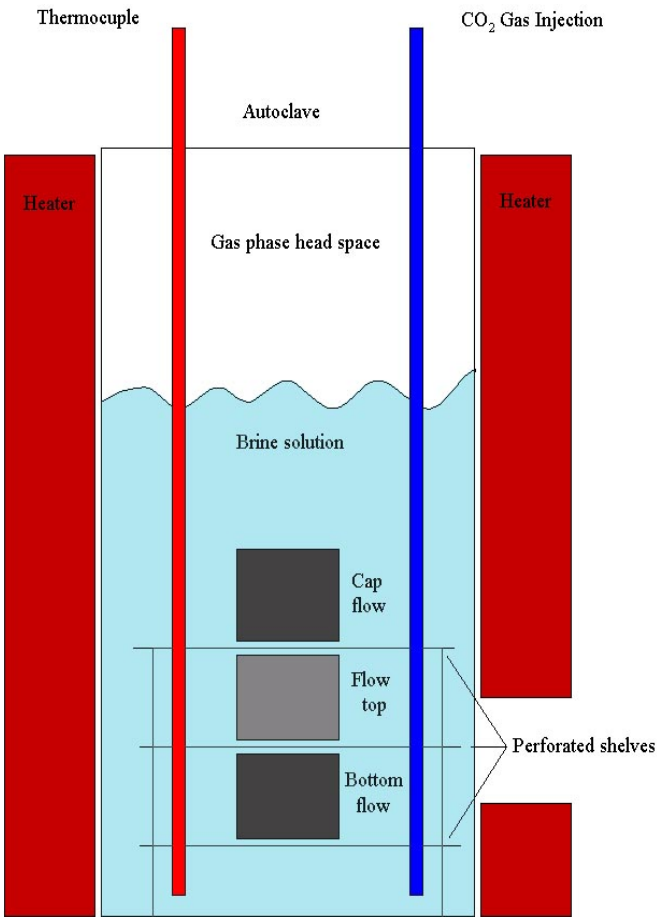
Experimental Apparatus



Core pressure leach laboratory

Core Sectioning and Autoclave Placement



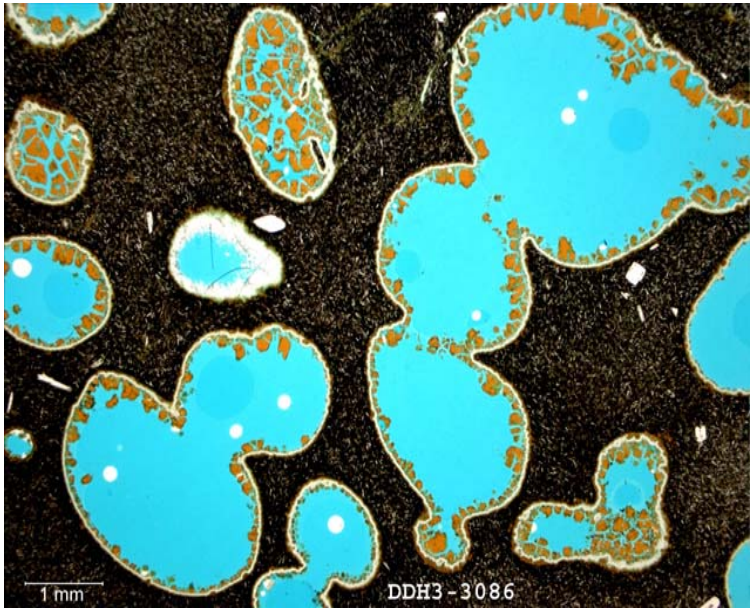


Sectioned cores, nominal 1-inch diameter, 1-inch high

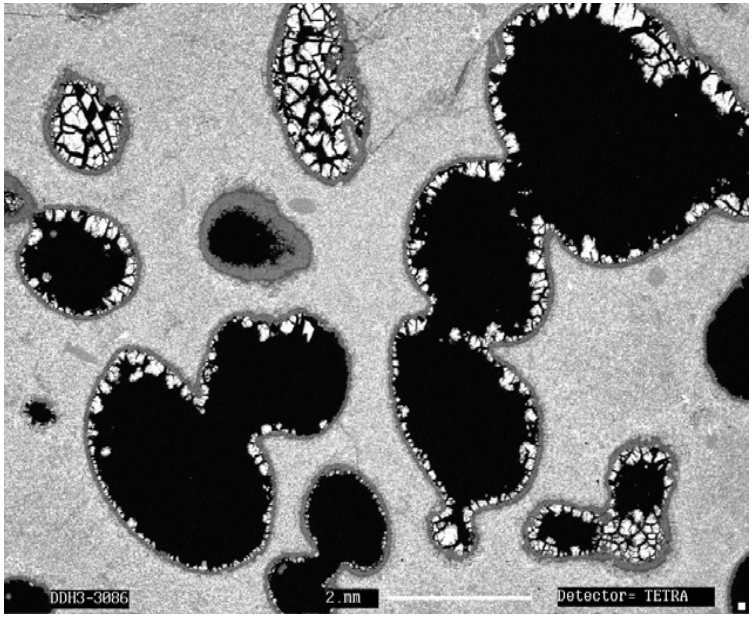
Test Conditions

- **Simulate in-situ conditions**
  - Brackish solution (pH ~9.24)
    - Cl: 240 mg/l; F: 40 mg/l
    - Na: 260 mg/l; HCO_3: 120 mg/l
  - 35°C temperature
  - Typical injection pressure
    - P_{CO2}= 1,500 psig (100 atm)
- **FT core porosity: ~30% @ 3086 ft depth interval**
- **Time series 100, 500, 1,000, 1,500, & 2,000 h**

Pre-Test Core Porosity: Microscopic View



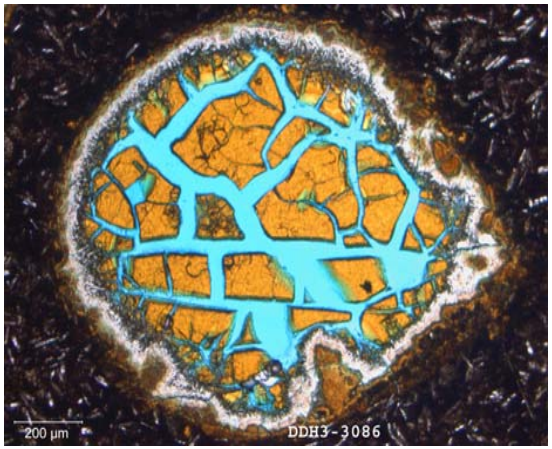
TLP: blue dye added to epoxy to accentuate porosity, pores lined with secondary minerals; basalt matrix

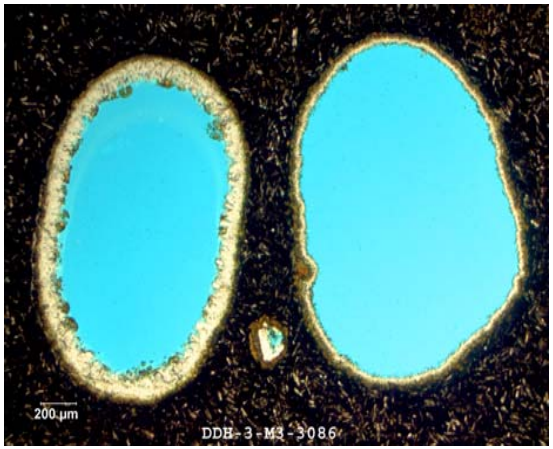


SEM-BSE photomicrograph: brighter zones – higher atomic number; innermost secondary mineral (Fe-rich)

Post-Test Core Microscopy

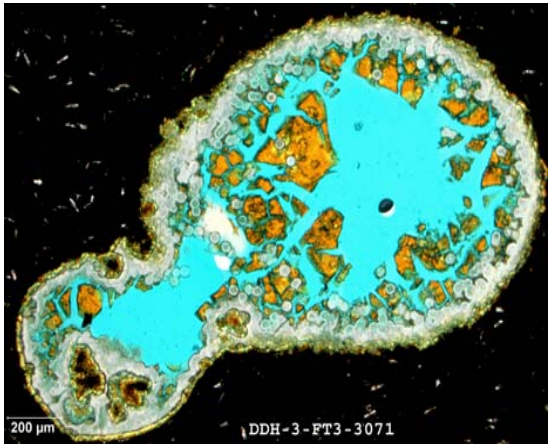
Pre-test

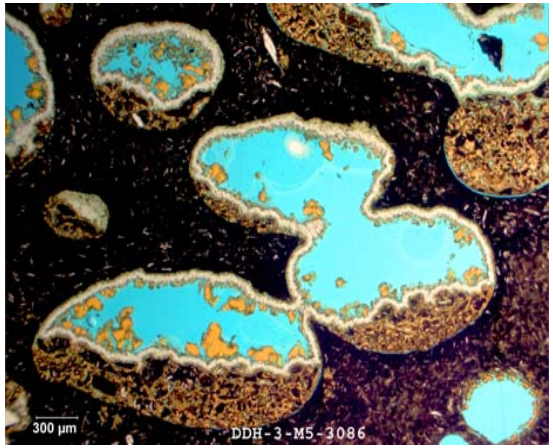




500 h

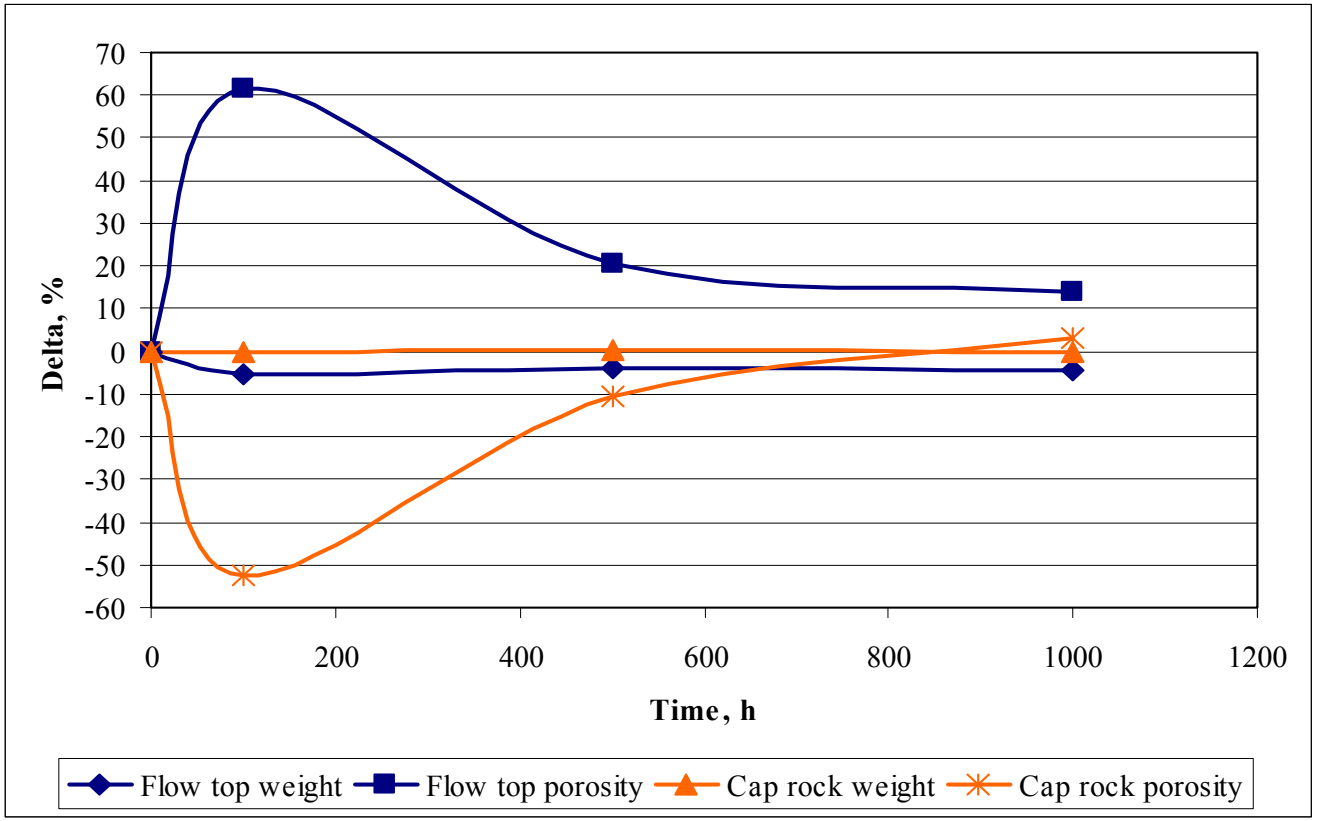
1000 h





2000 h

Core Physical Changes



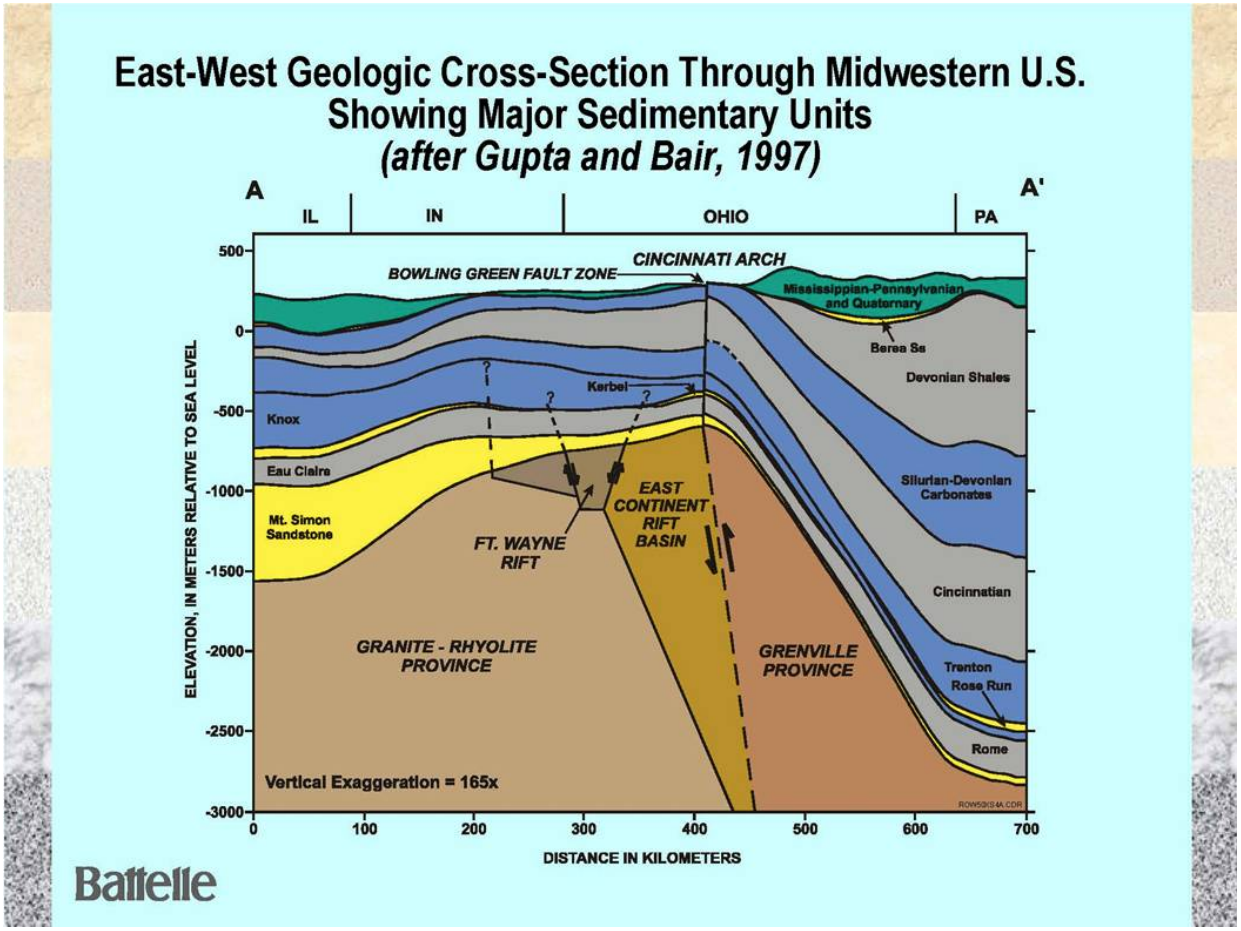
Product Core Chemistry and Mineralogy

- **XRD analysis**
  - Pre-existing secondary minerals
    - Zeolites absent from 500 h test solids
  - **Carbonate minerals**
    - **Magnesite trace phase in several test solids**
- **Microscopic analysis**
  - Amorphous silica precipitate
  - Indistinct “carbonate” precipitate
- **Chemical analysis**
  - **Up to 0.26 wt pct CO_2**

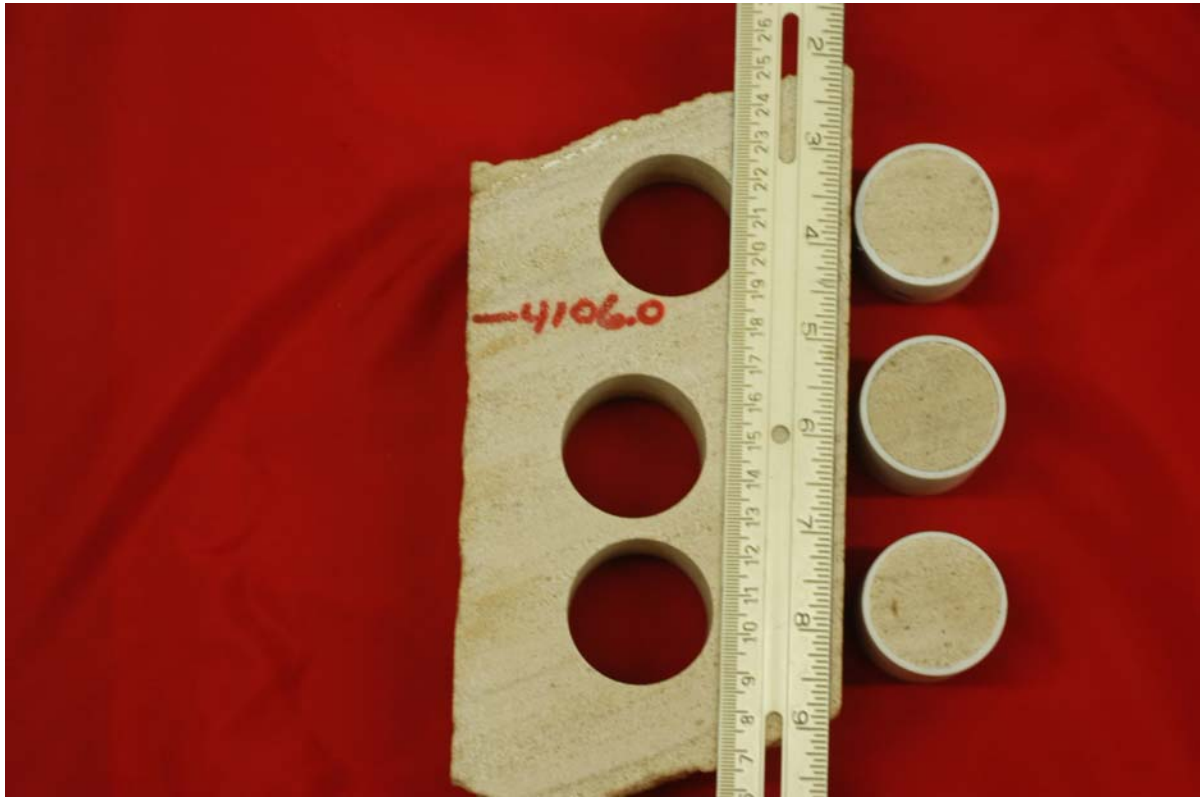
Mt. Simon Sandstone
Core Samples

- **Select appropriate saline aquifer host rock**
- **Illinois State Geological Survey (ISGS)**
  - Dr. Scott Frailey
  - David Morse
    - Selecting core samples
    - Providing aquifer solution chemistry
- **ARC conducted bulk chemistry & XRD**
  - Shared that information with the ISGS

Location of Mt. Simon Core Samples - Illinois Basin

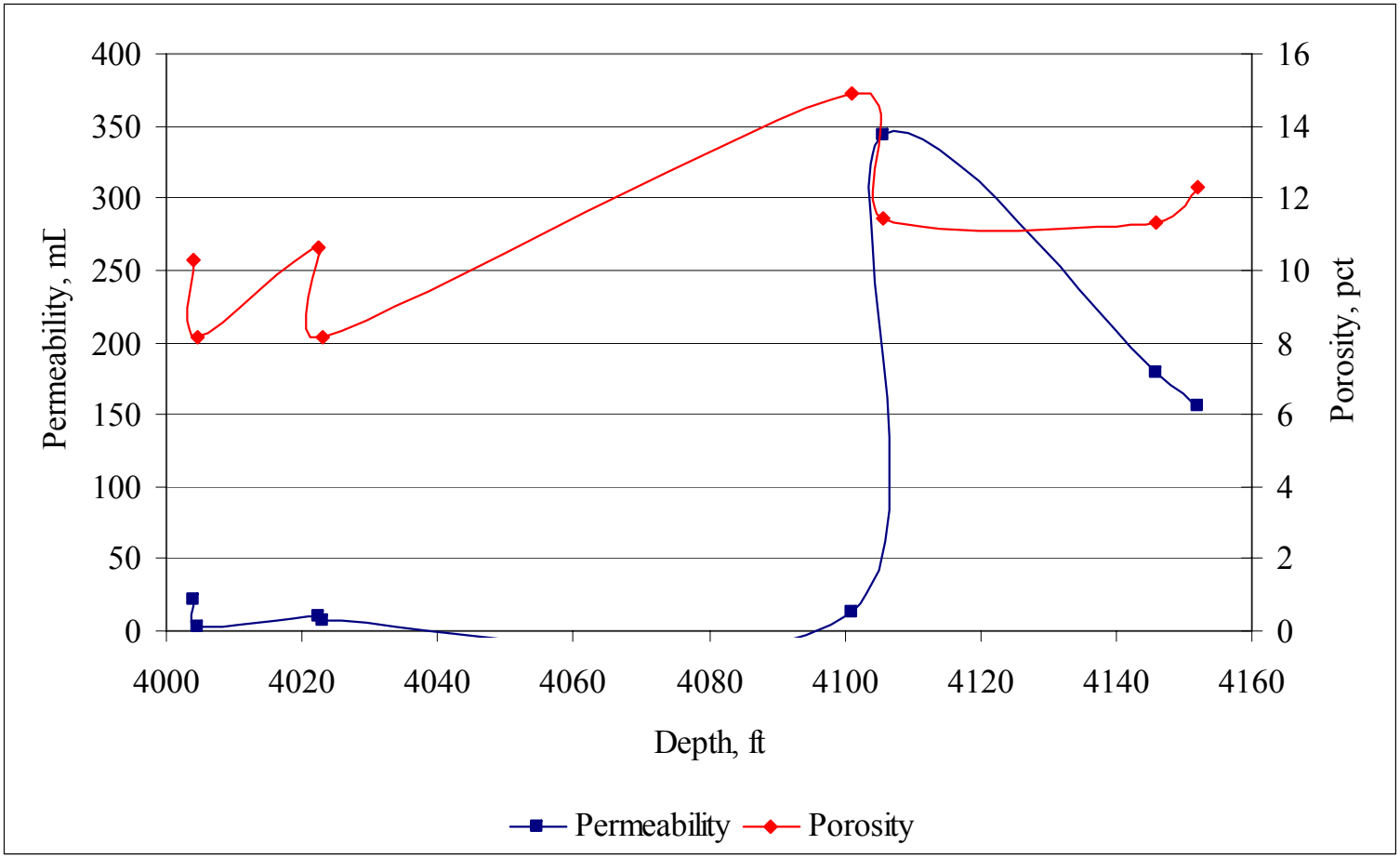


Mt. Simon Sandstone Whole Core Samples



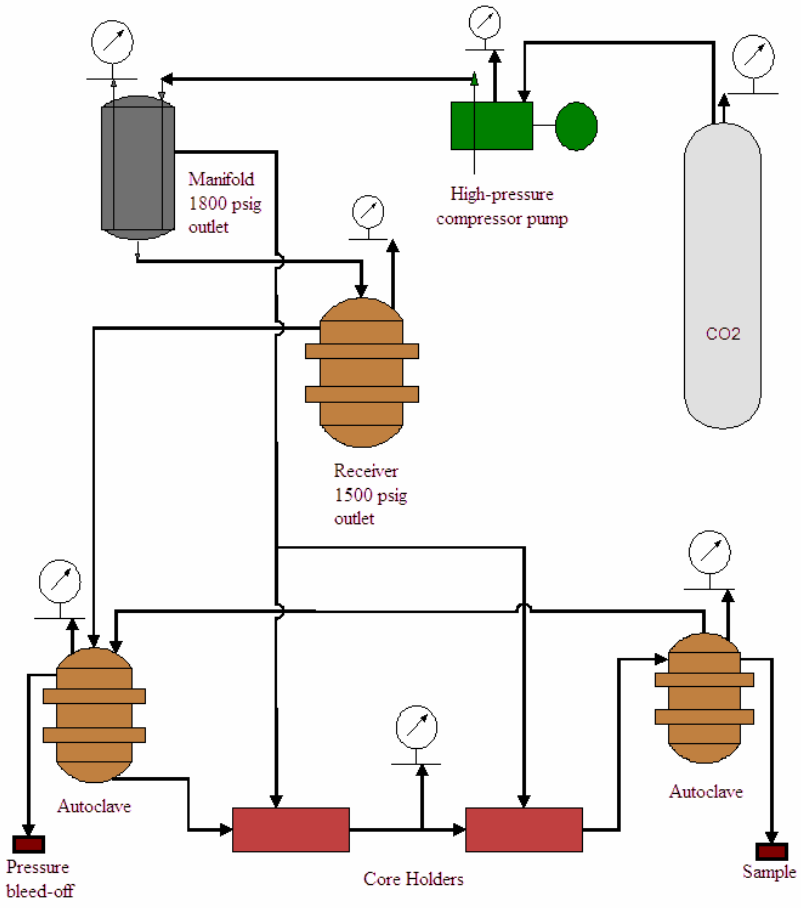
Mt. Simon sandstone half core, re-cored for CO_2 flood tests

Baseline Porosity & Permeability



Porosity & permeability versus depth for the Mt. Simon sandstone

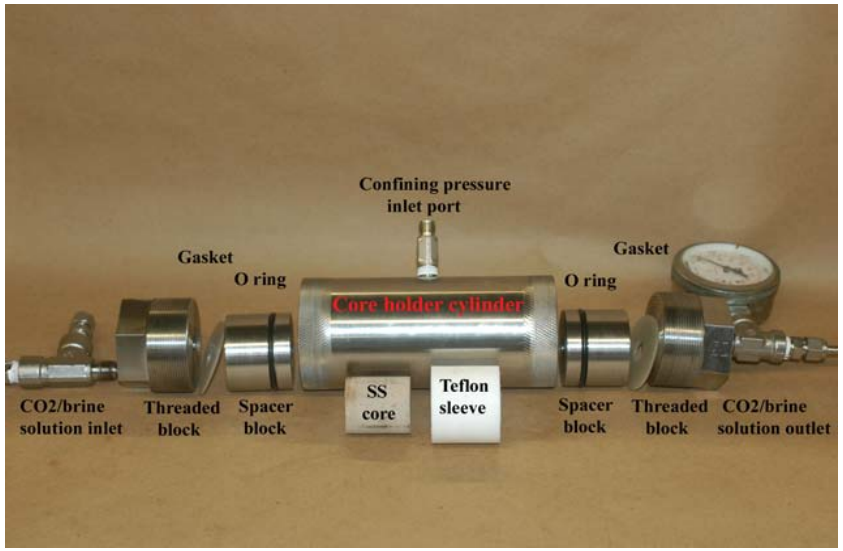
CO_2 Flood Test Apparatus



Simplified Flow Chart

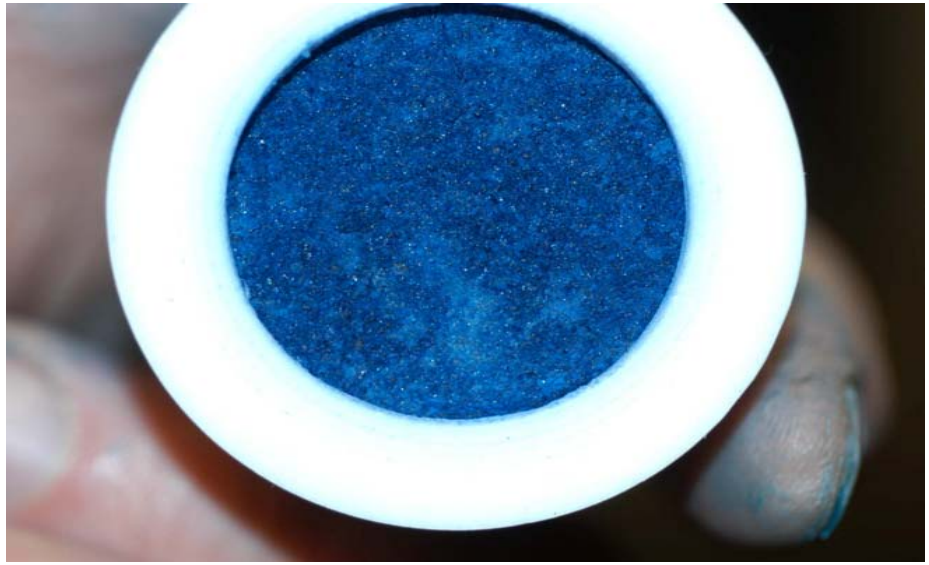
Core Holders

Core holder

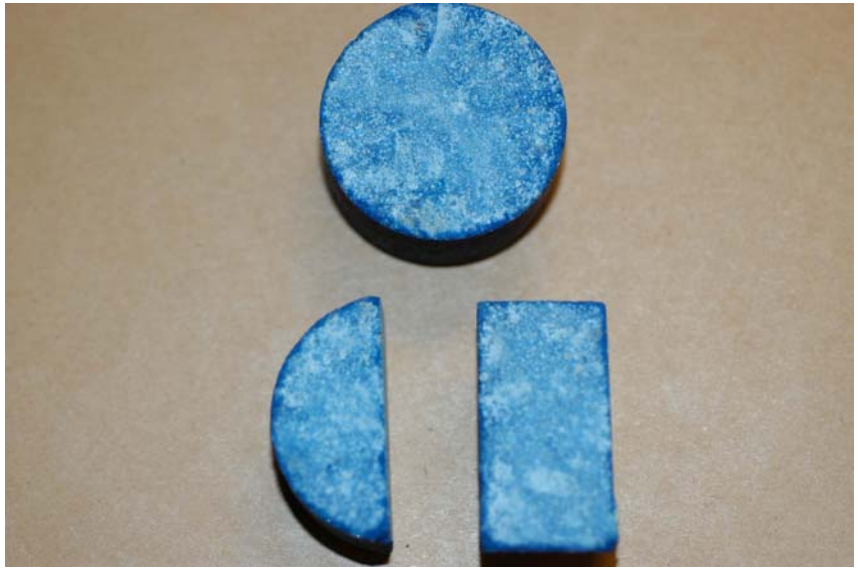


Exploded view

Core Holder Seal



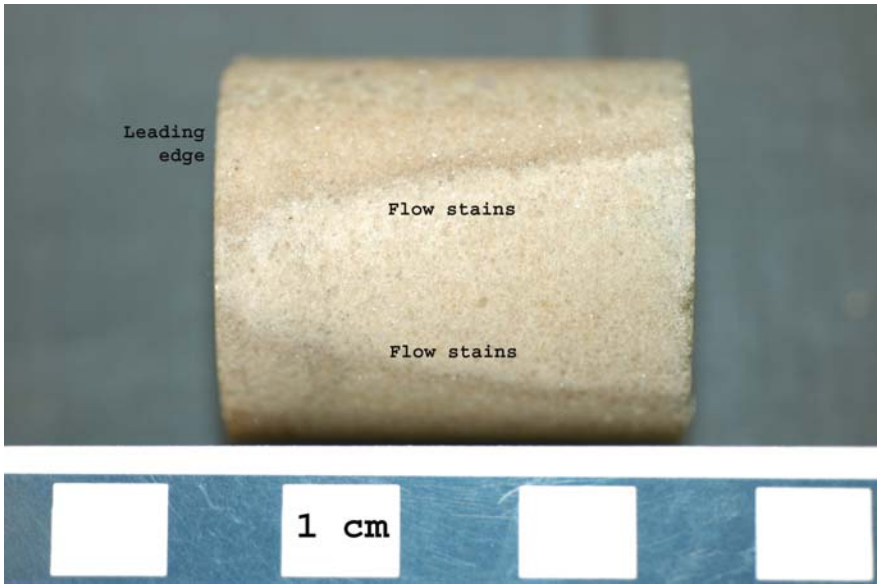
Dyed core in teflon ring



Core sectioned to reveal interior staining

Impact of the CO_2 Flood on Mt. Simon Sandstone

- **Geochemistry**
  - No carbonate phases identified by XRD
  - No CO_2 pick-up identified by bulk chemistry
- **Definite impact on cement matrix**
  - Strength
  - Solution chemistry (Ca & Si increase)



Impact of the CO_2 Flood on the Mt. Simon Sandstone

- Physical Properties

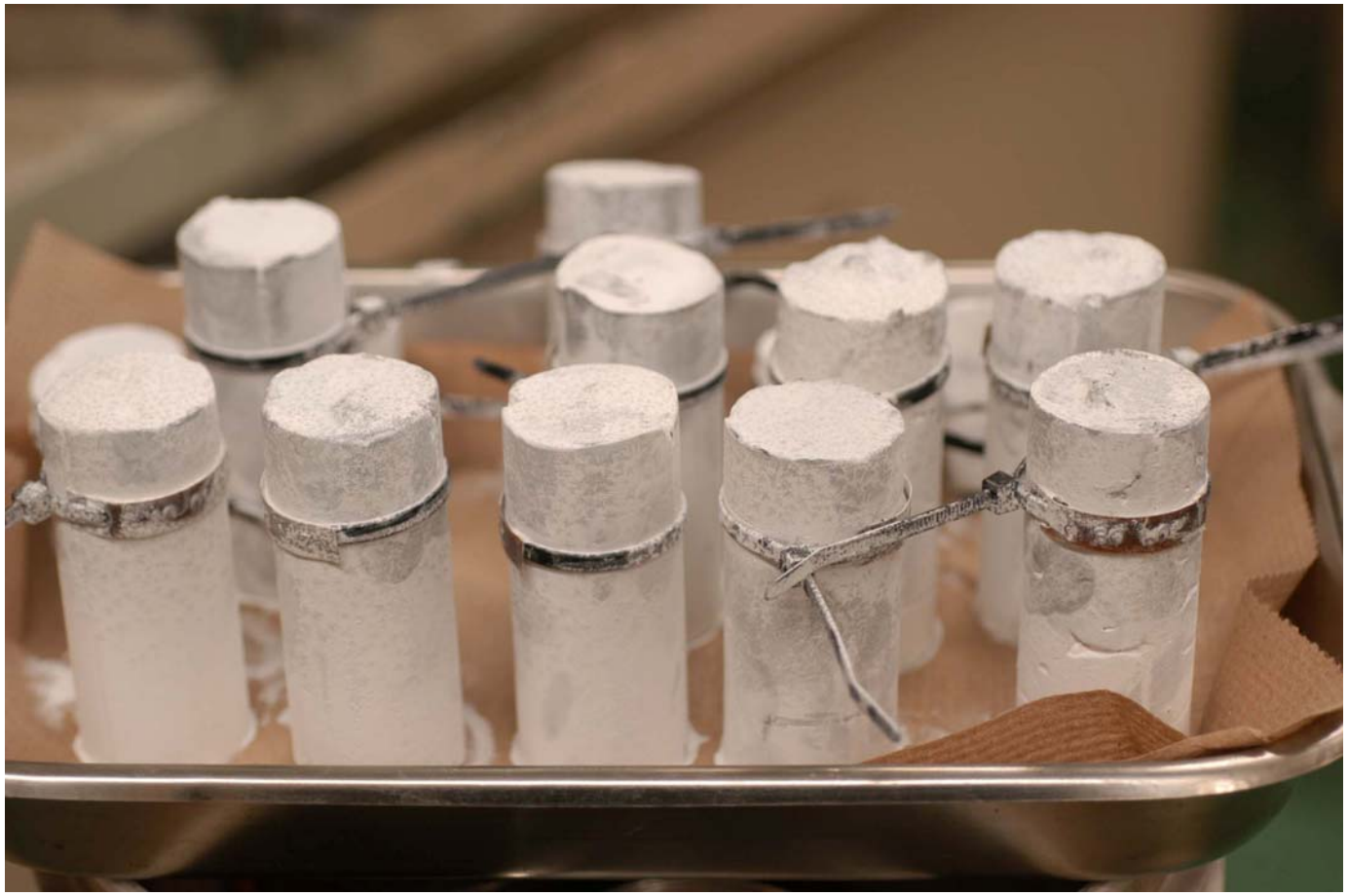
	Porosity, pct			Permeability, mD		
Core depth	Pre	Post	Diff., %	Pre	Post	Diff., %
4101.0	7.9	8.3	4.7	8.9	8.0	-10.1
4105.5	11.5	13.0	13.0	344.5	351.4	2.0
4106.0	13.3	na	nc	288.9	na	nc

	Compressive strength, kpsi			Double shear strength , kpsi		
Core depth	Pre	Post	Diff., %	Pre	Post	Diff., %
4101.0	na	na	nc	5.6	5.2	-5.6
4105.5	12.2	4.8	-61.0	na	na	nc
4106.0	10.8	4.2	-61.6	na	na	nc

Well Plugging Cements
Simulate Plugging of Legacy Wells

- **LaFarge Class H cement (Portland cement)**
- **Baseline cement core**
  - Olivine, serpentine, wollastonite additives
- **Cured for 28 days in Illinois Basin brine**
  - 35˚C, 1 atm
- **Removed cores from brine bath, placed in autoclave for 2000 h CO_2 flood test**
  - 35˚C, 1,500 psig CO_2

Calcium Carbonate Rind
Post 28 Day Brine Cure

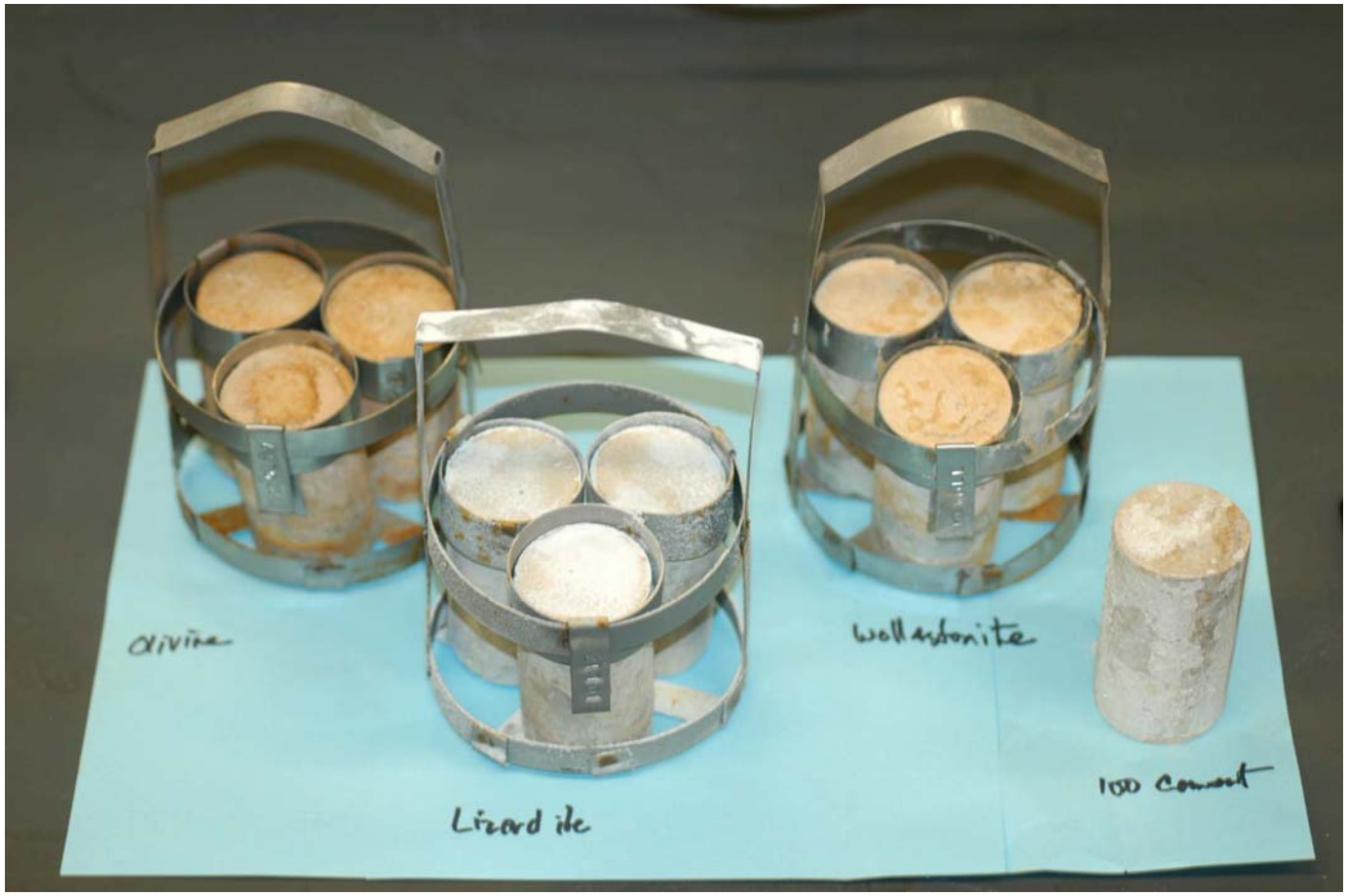


Air Versus Brine Curing

Air cured cement

Brine cured cement

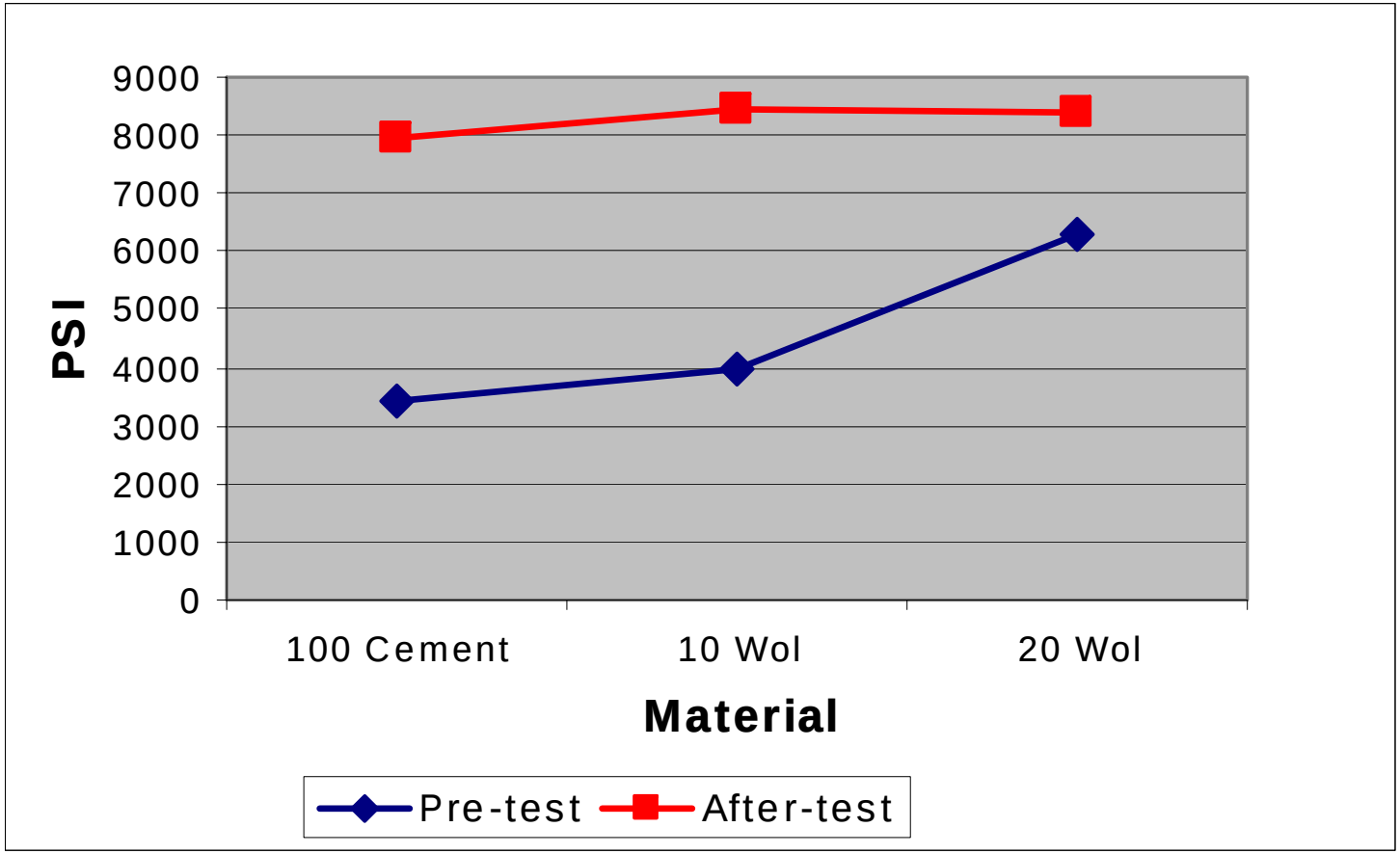
Post CO_2 Flood Test



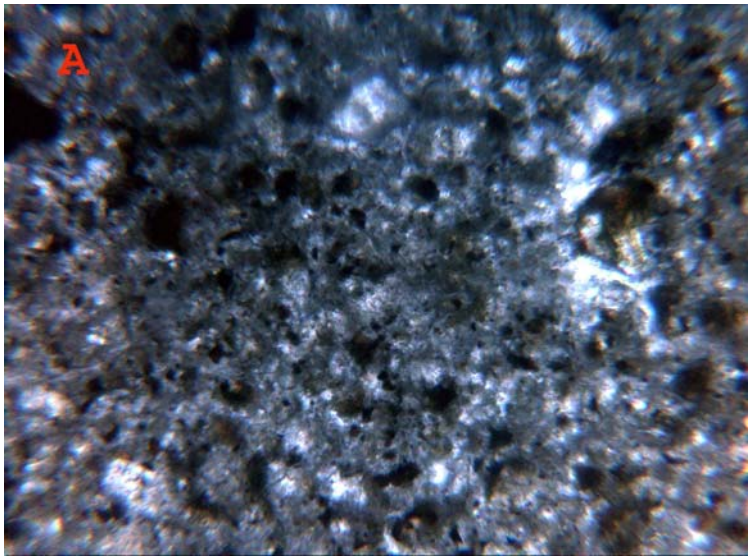
Post CO_2 Flood Carbonate Rind

- **1-3 mm rind on outer surface**
- **Calcium carbonate rind on all cores**
- **~10% CO_2 in cement bulk chemistry**
  - Head contained ~2% CO_2
  - CO_2 penetration
  - Depth (?)

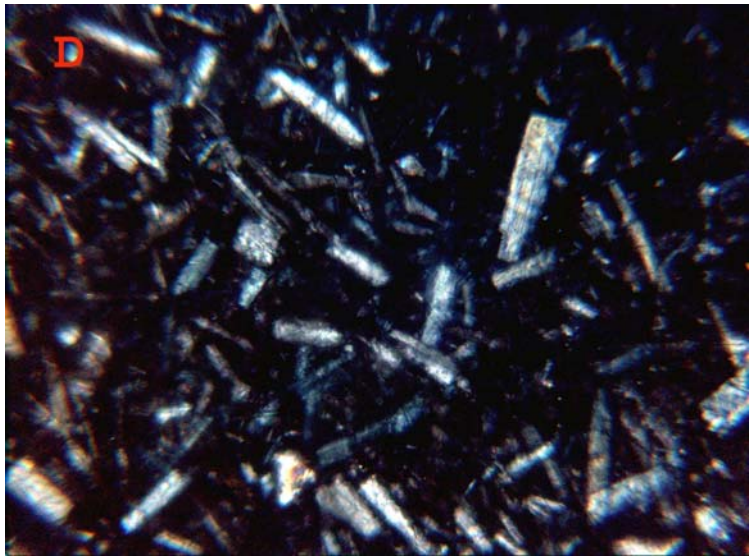
Core Compressive Strength



Cement Photomicrographs



100% cement

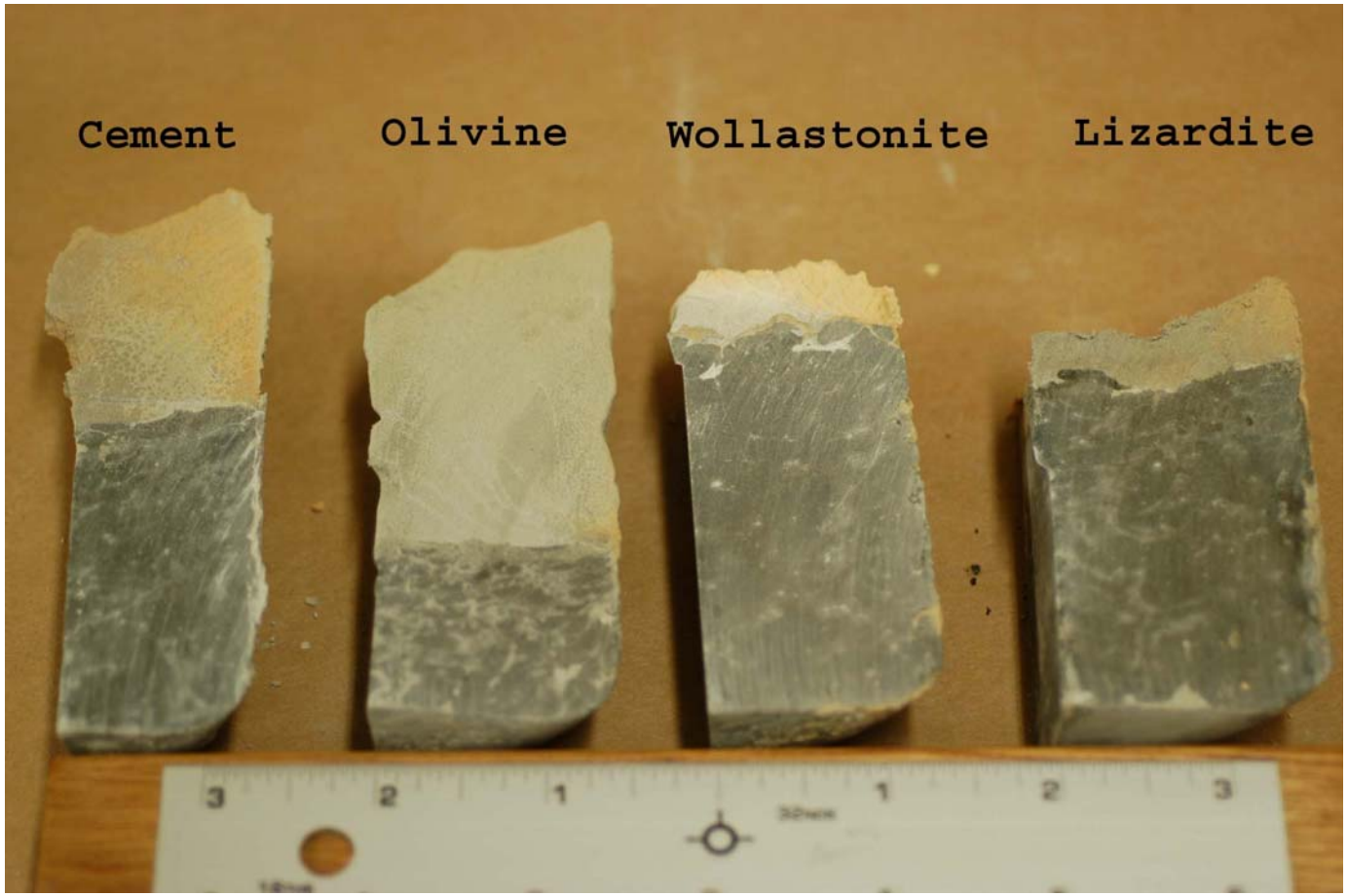


Cement with 20% wollastonite

Well Plugging Cements
Simulate Plugging CO_2 Injection Well

- **Preheat and mix brine (less Fe) to 35˚C**
- **Weigh out solids**
  - 1000 g cement @ 38% H_2O
  - 800 g cement, 200 g silicate additive @ 38% H_2O
  - Premix dry solids
- **Add 1000 ml Illinois Basin brine to teflon liner**
  - Purge with CO_2 for 1 min
  - Add Fe and purge with CO_2 for 1 min
  - Place in autoclave and cover
- **Add water to dry cement, mix for ~2 min**
- **Pour mixed cement into autoclave, seal immediately**
- **Charge with CO_2 to 1000 psig**
- **Heat to 35˚C, allow to stabilize**
- **Charge with CO_2 to 1500 psig**

Post CO_2 Flood Test



Supercritical CO_2 - cured cements

Geochemistry
Supercritical CO_2 - Cured Cements

- **Alteration zone**
  - Vaterite, calcite, halite
  - `25-30% CO_2 by weight

- **Fresh cement zone**
  - Typical cement phases
  - ~3-5% CO_2 by weight
    - Less than the brine cured cores after the CO_2 flood
    - Alteration zone “protects” the rest of the core?

Summary – Host Rock Studies

- **Basalt cores**
  - Large pore size permits observation of mineralogical trends
  - Mineral trapping indicated by XRD & chemistry
- **Sandstone cores**
  - Little or no change in bulk geochemistry
    - No mineral trapping
  - Decline in compressive strength
    - Cement alteration
    - Solution trends (Ca & Si increases)

Summary – Well Plugging Cements

- **Cement plugs in simulated legacy wells**
  - Carbonate rind on outer surface 1-3 mm thick (2000 h)
  - ~10 wt pct CO_2 in bulk core
  - Compressive strength increased for all cores post-CO_2 flood (nearly doubled for 100% cement & wollastonite additive)

- **Cement plugs in simulated CO_2 injection wells**
  - Alteration zone, greatest for 100% cement & 20% olivine
  - ~3-5 wt pct CO_2 in "fresh" cement zone
    - Lower CO_2 concentration than above
      - Alteration zone inhibiting CO_2 penetration
      - Artifact of the experimental methodology

Future Work

- **Continue reservoir host rock studies**
  - Repeat Mt. Simon tests in new system
  - Expand studies to additional sites
- **Continue examination of well plugging cements**
  - Repeat initial test series
  - Refine experimental methodology
  - Best simulation of downhole conditions