DEPARTMENT OF
Chemical Engineering
COLLEGE OF ENGINEERING | THE UNIVERSITY OF UTAH

Reactive Transport Models with Geomechanics to Mitigate Risks of CO_2 Utilization and Storage

Project: DE-FE009773

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Objectives

- Experiments to study pore level and petrophysical property changes in experiments of carbon dioxide and brine with different rock types
- Validation of models using experimental results
- Coupling of geomechanical models with flow

Experimental Strategy

Experimental systems and reactive transport model

Core flooding system

CO_2 injection rate

Petrophysical changes

Mineralogical changes

Batch reactor system

Petrophysical changes

Mineralogical changes

Changes with time

Modeling

Evaluate experimental data

Geomechanics and Flow

Comprehensive measurements

BET, He Porosimeter, and Micro-CT

Analyze porosity changes, surface area and pore structure

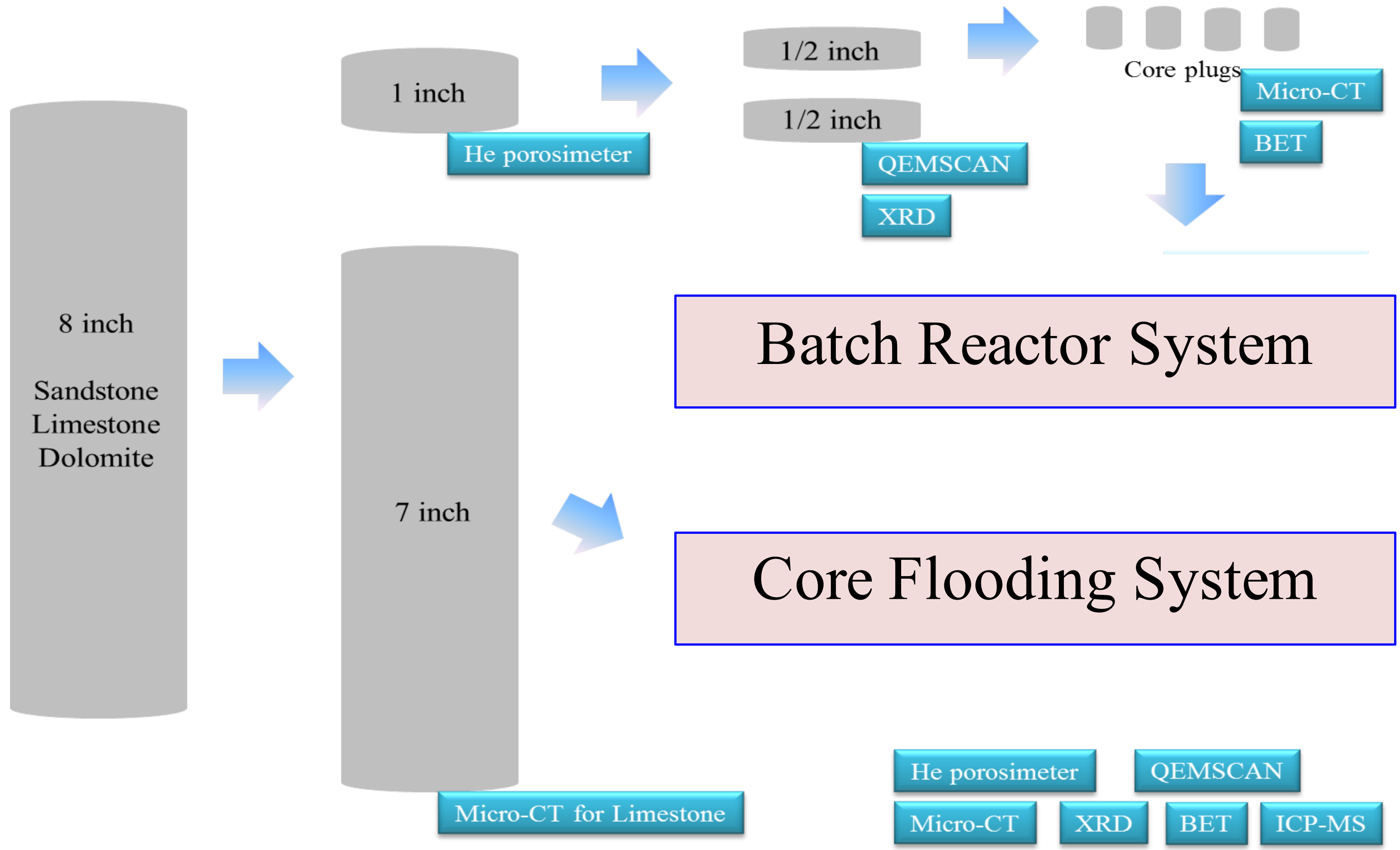
ICP-MS and pH meter

Measure pH and cation concentration of the effluent

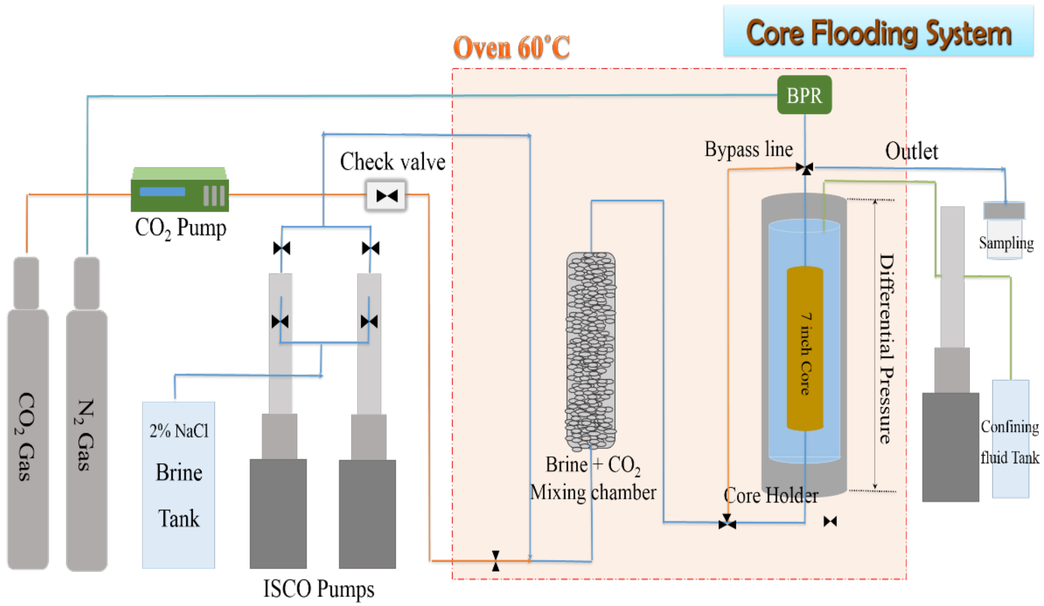
XRD and QEMSCAN

Mineralogical analysis of core samples

Sample Preparation



Experimental System

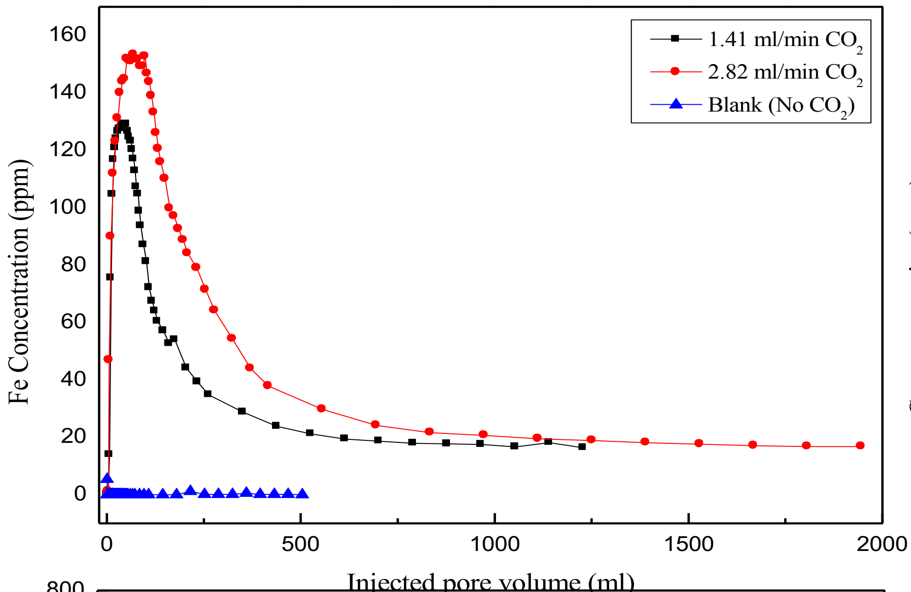


Core flooding system conditions

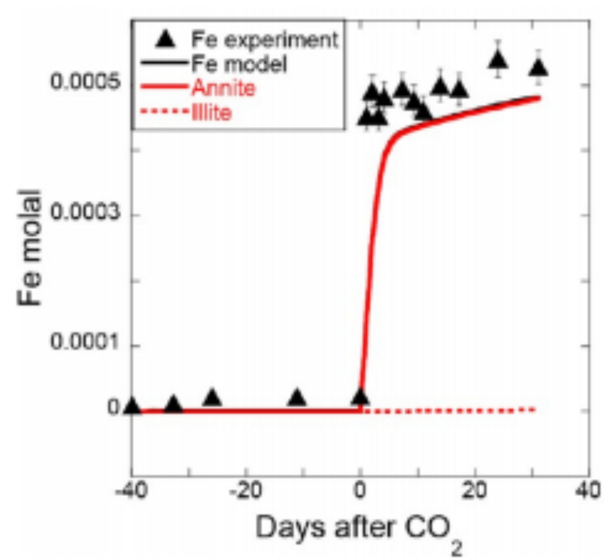
- Core pressure: 2,000 psi
- Confining pressure: 3,000 psi
- Reaction temperature: 60 C
- Reaction time : 14 days
- Cores: sandstone, limestone, and dolomite
- CO_2 : Brine ratio: Variable
- (1.5 inch diameter, 7 inch length)

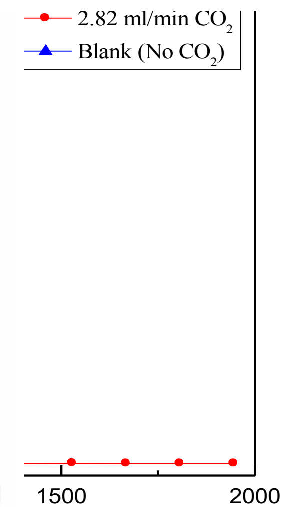
Sandstone Effluent Analysis

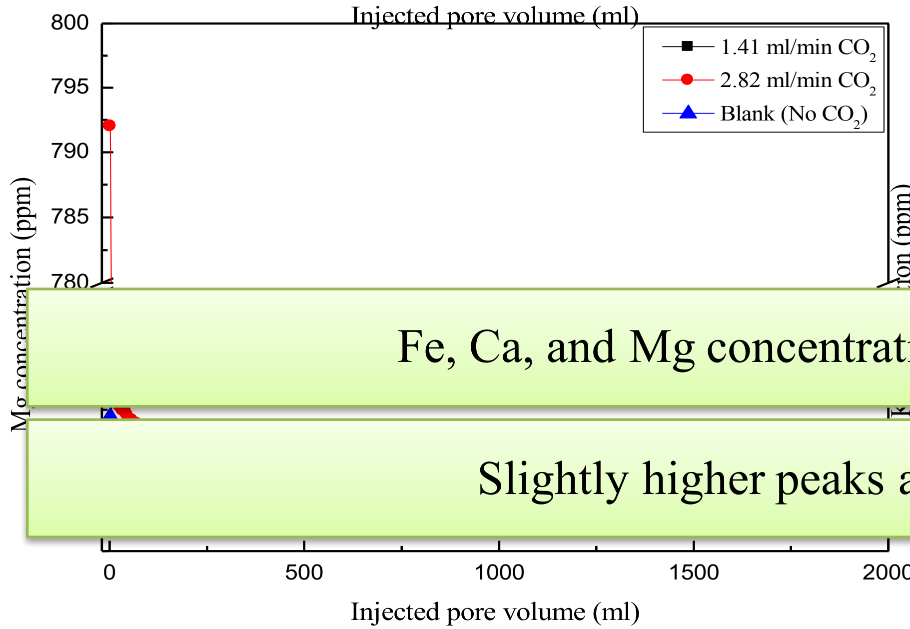
Mineralogical changes: Effluent analysis using ICP-MS, sandstone

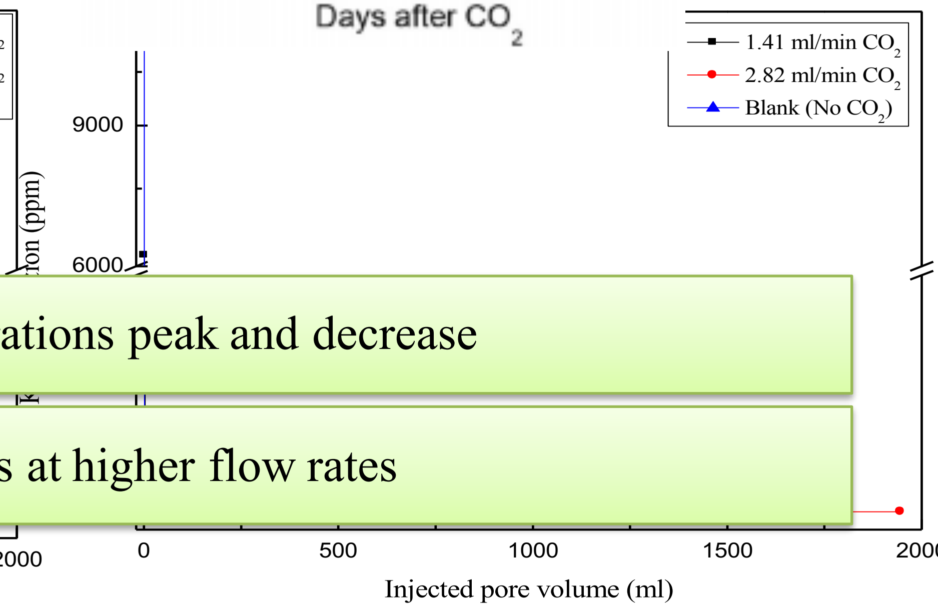


Iron involvement observed by Carroll et al.(2012)







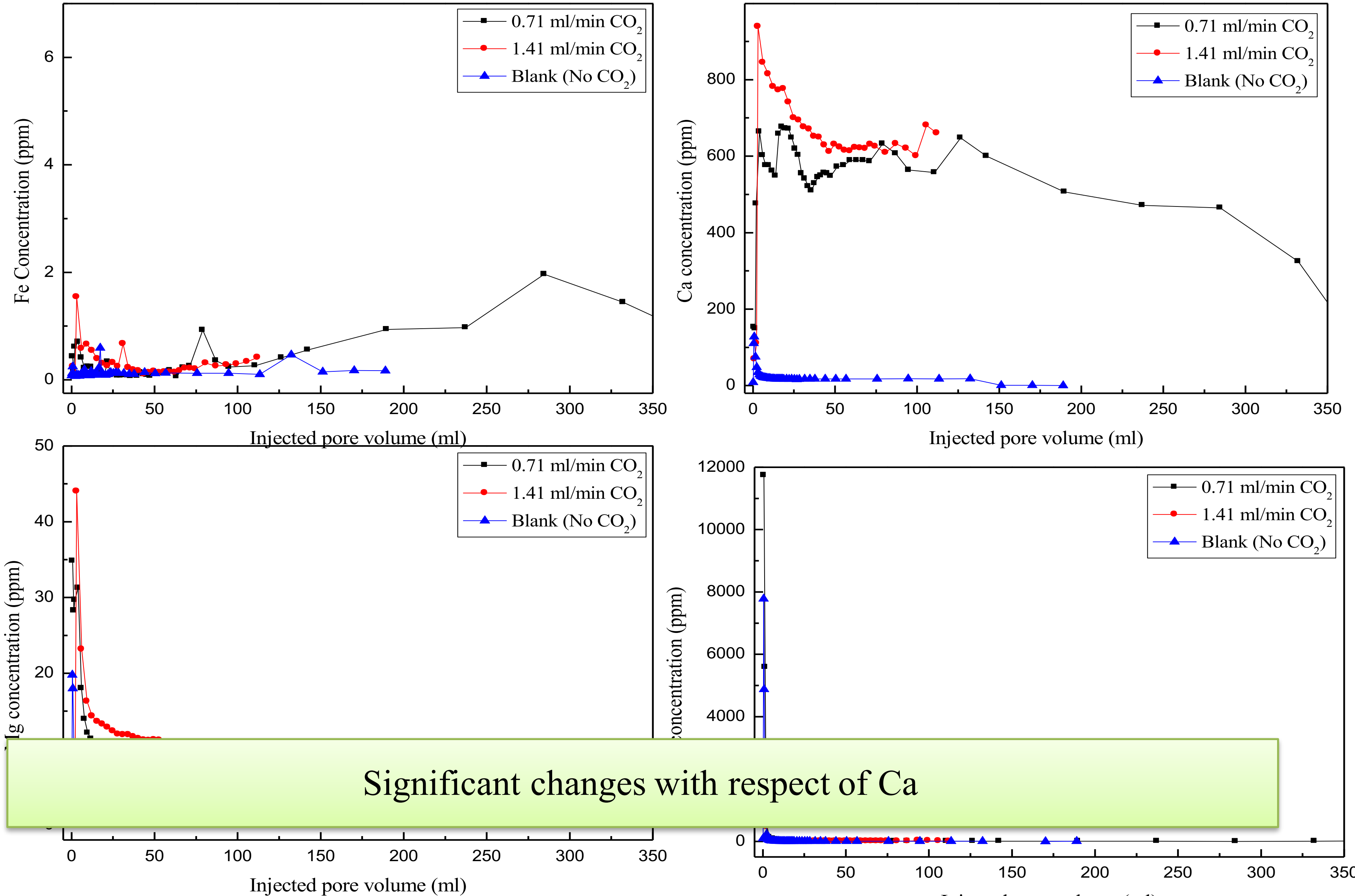


Fe, Ca, and Mg concentrations peak and decrease

Slightly higher peaks at higher flow rates

Limestone Effluent Results

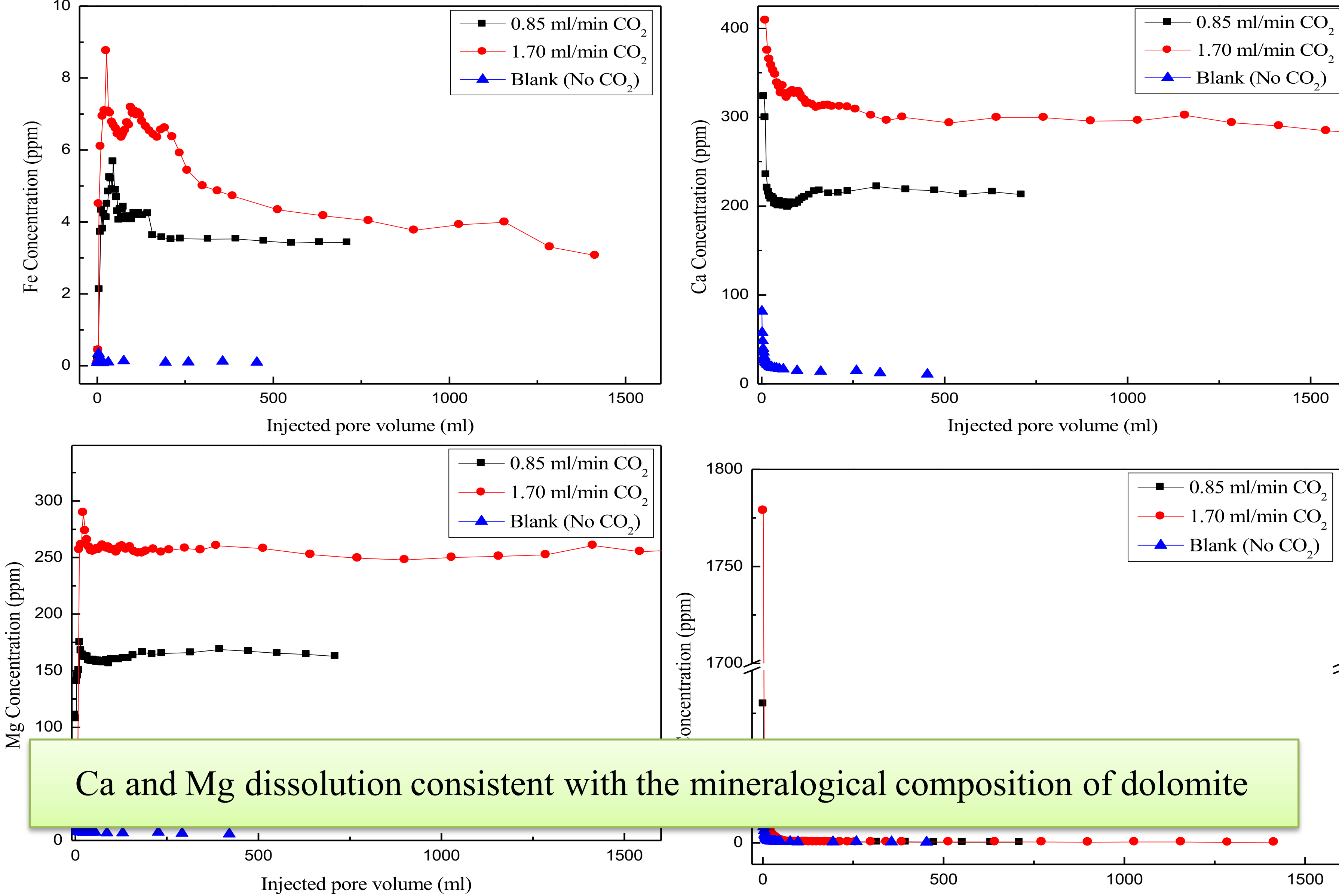
Mineralogical changes: Effluent analysis using ICP-MS, limestone



Significant changes with respect of Ca

Dolomite Effluent Results

Mineralogical changes: Effluent analysis using ICP-MS, dolomite



Ca and Mg dissolution consistent with the mineralogical composition of dolomite

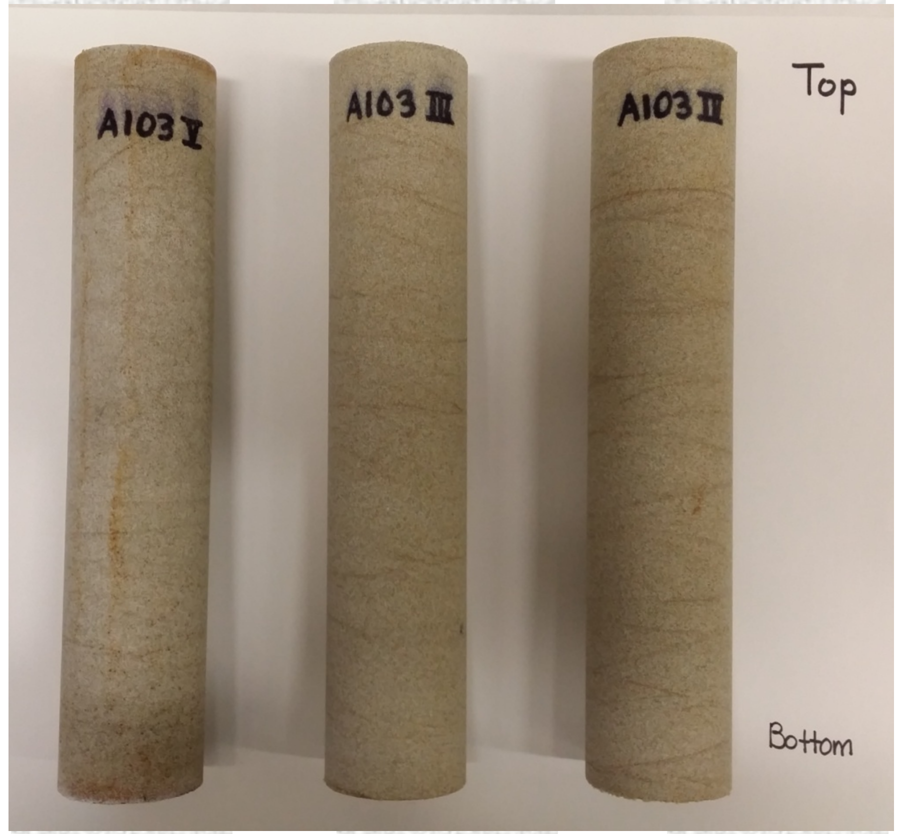
Effluent Analysis

- Core flooding conducted at sequestration conditions shows effluent peaks of key cations – Fe, Ca and Mg
- The level of iron dissolution in sandstone – even over short durations was higher than expected – may have major implications in practical sequestration scenarios
- Ankerite and siderite are the main iron bearing reactive minerals in sandstone and they dissolve almost completely in the two-week experiment
- In XRD spectra, differences were observed in sandstone, but not in limestone or in dolomite
- Higher flow rates led to higher levels of mineral dissolutions

Porosity Changes - Sandstone

Petrophysical changes: Porosity measurement using helium porosimeter, sandstone

Unreacted Sandstone	Brine: 1 ml/min CO_2: None	Brine: Initially saturated CO_2: 1.41 ml/min	Brine: 1 ml/min CO_2: 1.41 ml/min	Brine: 1 ml/min CO_2: 2.82 ml/min
Outlet	21.263 %			
	21.307 %			
	21.110 %			
Average porosity of sandstone 21.234 %	21.175 %			
	21.739 %			
	21.634 %			
Inlet	21.706 %	21.462 %	22.822 %	22.650 %
Porosity changes:	0.18 %	0.12 %	0.60 %	1.01%



Limestone Porosity Changes

Petrophysical changes: Porosity measurement using helium porosimeter, limestone

Unreacted Sandstone

Outlet

Average porosity Of limestone

19.973%

Inlet

	Brine: 0.5 ml/min CO_2: None	Brine: Initially saturated CO_2: 0.71 ml/min	Brine: 0.5 ml/min CO_2: 0.71 ml/min	Brine: 0.5 ml/min CO_2: 1.41 ml/min	Brine: 1 ml/min CO_2: 1.41 ml/min
Outlet	20.812 %	20.321 %	20.349 %	20.349 %	20.390 %
	20.704 %	20.402 %	20.403 %	20.715 %	22.320 %
	20.822 %	20.314 %	20.680 %	20.650 %	23.589 %
				20.646 %	
Inlet	20.619 %	20.619 %	29.847 %	25.720 %	23.772 %
Porosity changes:	0.70%	0.55 %	1.12(5.46) %	1.59 %	2.79 %

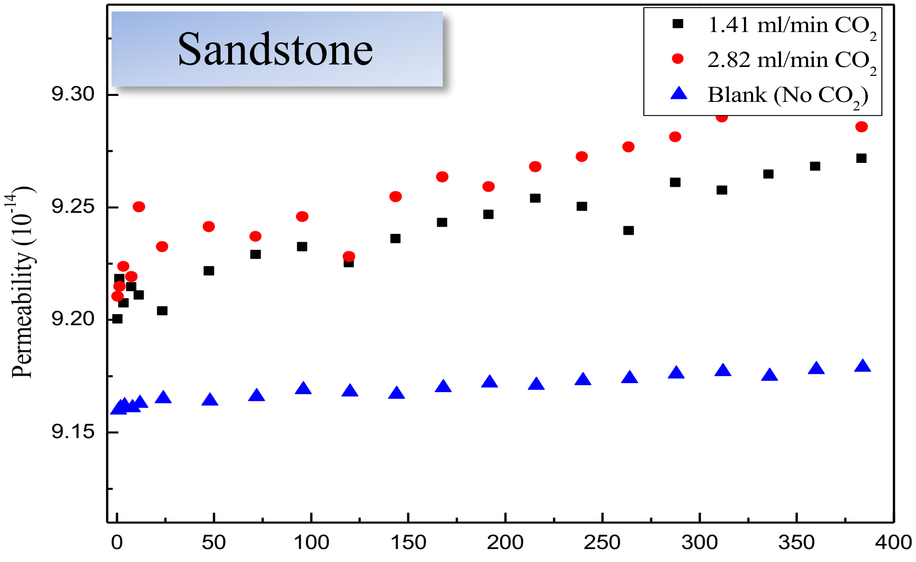
Dolomite Porosity Changes

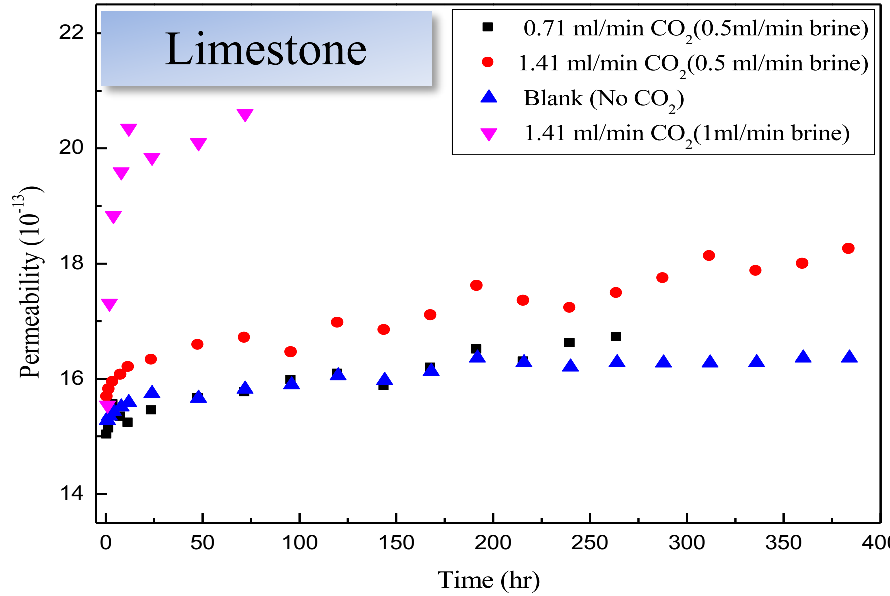
Petrophysical changes: Porosity measurement using helium porosimeter, dolomite

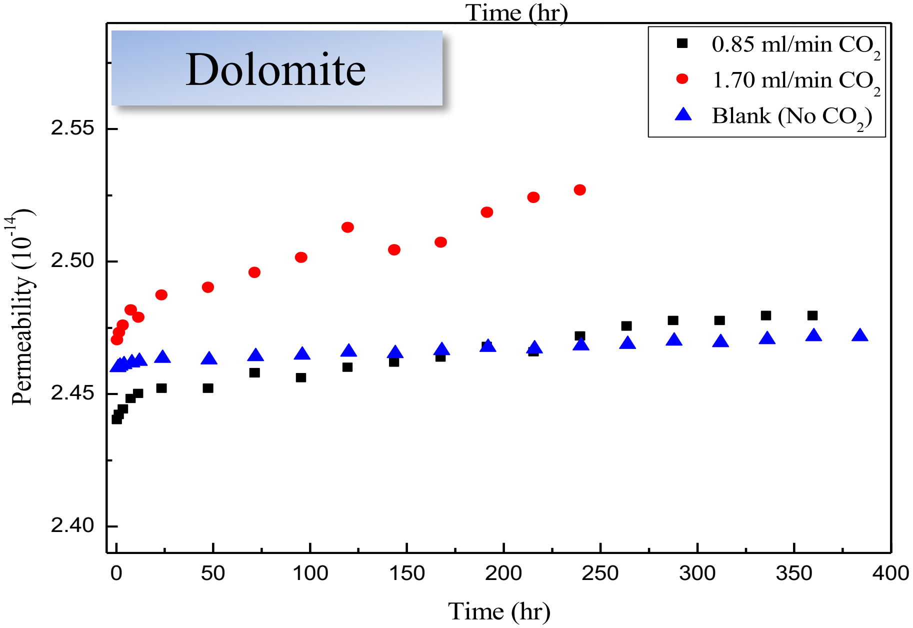
Unreacted Sandstone	Brine: 0.6 ml/min CO_2: None	Brine:0.6 ml/min CO_2: 0.85 ml/min	Brine: 0.6 ml/min CO_2: 1.70 ml/min
Outlet	14.264 %	14.235 %	14.362 %
Average porosity of sandstone 14.016 %			
Inlet	14.662 %	19.754 %	24.846 %
Porosity changes:	0.42%	1.58 %	2.52 %

Permeability Changes

Petrophysical changes: Permeability calculation







Permeability change ranges

Sandstone: from 0.21 % to 1.43 %

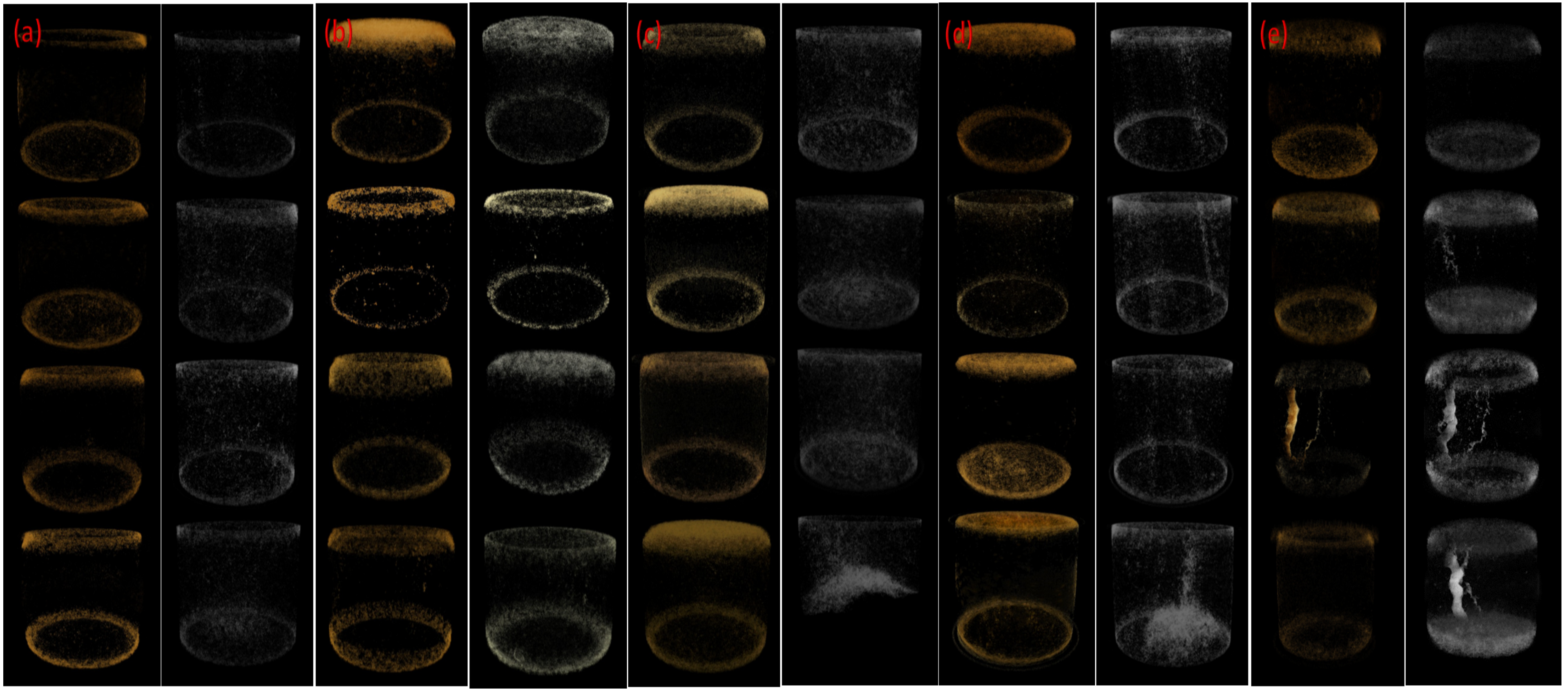
Limestone: from 1.06 % to 3.42 %

Limestone: from 0.51 % to 2.41 %

Micro-CT Imaging

Petrophysical changes: Limestone core analysis using Micro-CT

Images of different sections of limestone core using Micro-CT Pre- (left, orange color) images and post (right, gray color) flooding experiments



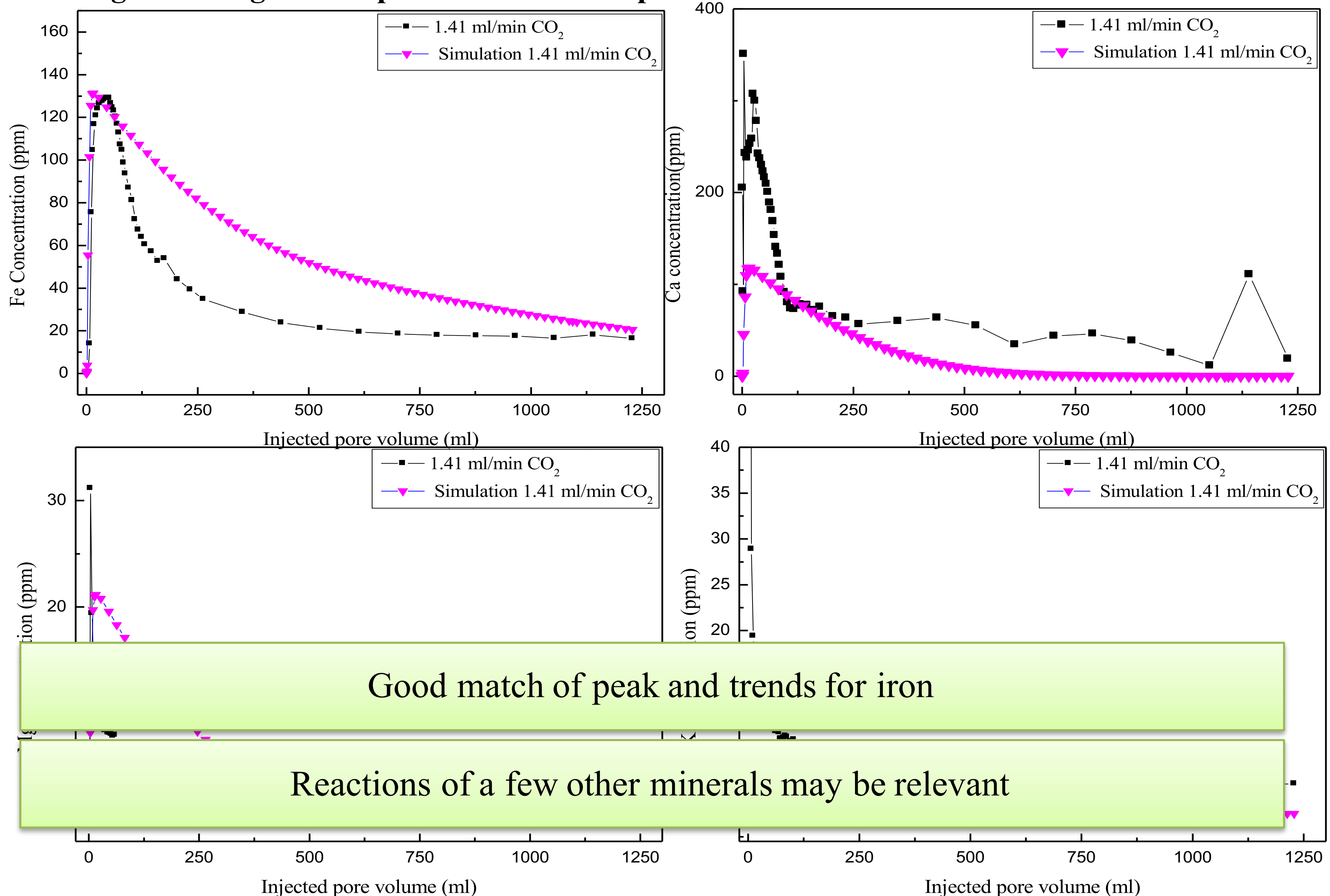
Brine: 0.5 ml/min CO_2: None	Brine: Initially saturated CO_2: 0.71 ml/min	Brine: 0.5 ml/min CO_2: 0.71 ml/min	Brine: 0.5 ml/min CO_2: 1.41 ml/min	Brine: 1 ml/min CO_2: 1.41 ml/min

Summary of Petrophysical Changes

- Changes in porosity and permeability were quantified.
- Porosity changes were measured by helium porosimeter. In the sandstone, limestone, and dolomite the porosity change ranged from 0.12 % to 1.01 %, from 0.55 % to 2.79 %, and from 0.42 % to 2.52 %, respectively.
- In sandstone, permeability change ranged from 0.21 % to 1.43 %. Also limestone and dolomite showed increase, from 1.06 % to 3.42 % and from 0.51 % to 2.41 %, respectively.
- Higher flow rates led to larger changes.
- Pore morphology changes were found in limestone using Micro-CT. At lower flow rates beginnings of wormhole type structures were observed, and higher flow rates fully developed wormhole was shown.

ToughReact Simulations

Mineralogical changes: Comparison between experiment and simulation results



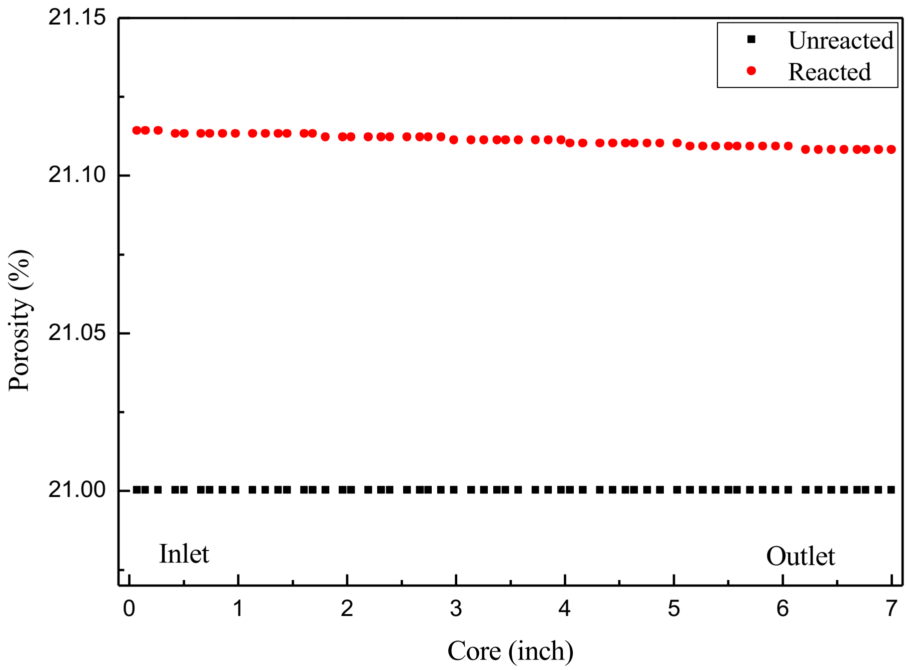
Good match of peak and trends for iron

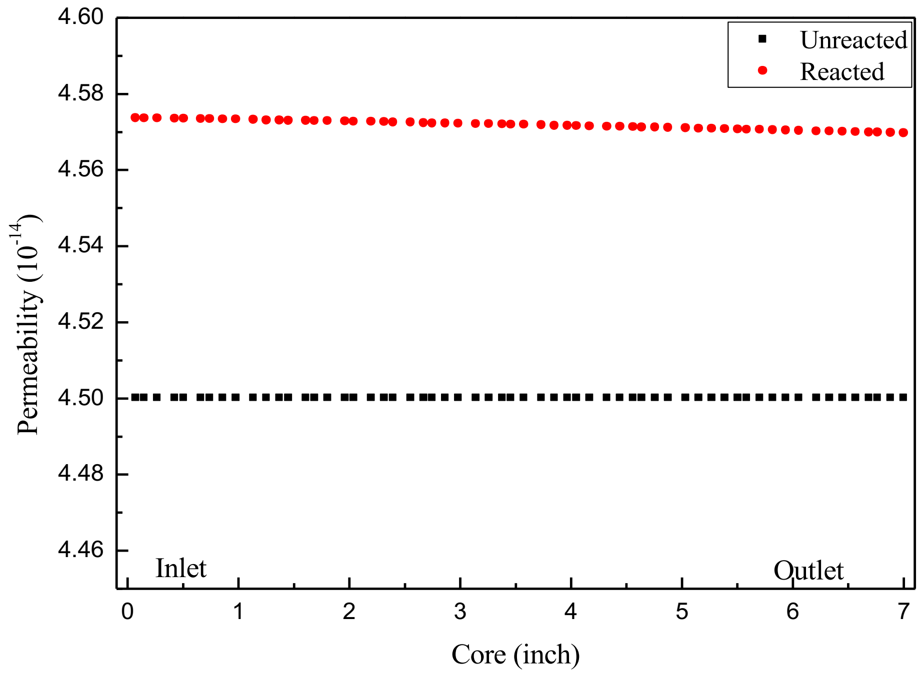
Reactions of a few other minerals may be relevant

Petrophysical Changes

Petrophysical changes: Porosity and permeability changes

Figures show the comparison between pre-experiment and post-experiment values of porosity and permeability distribution in the core.





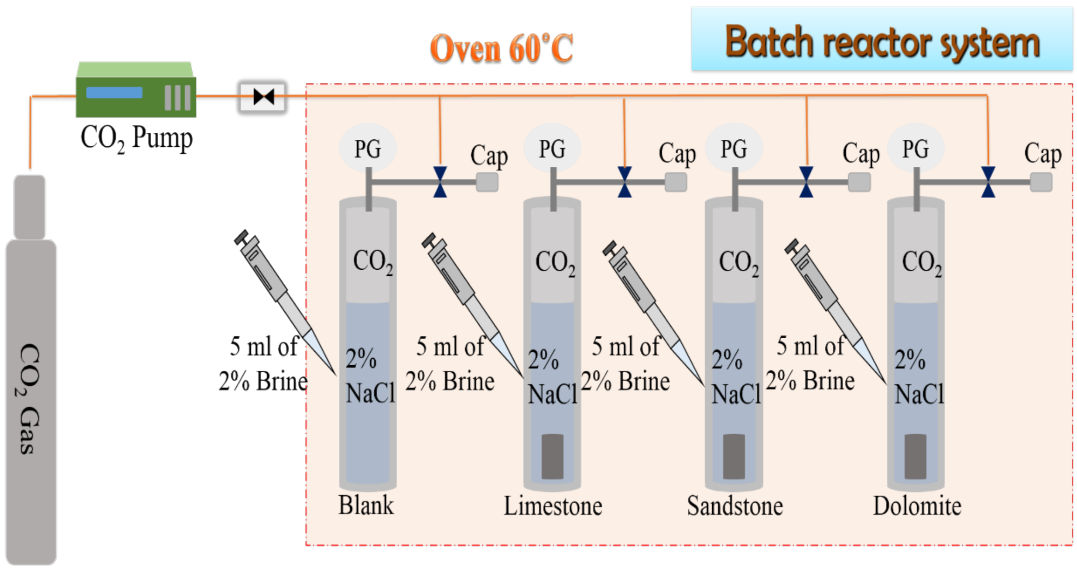
Slightly larger changes at the inlet. Maximum amount is predicted to be 0.5 % and 1.4 % for porosity and permeability, respectively. This is consistent with experimental data.

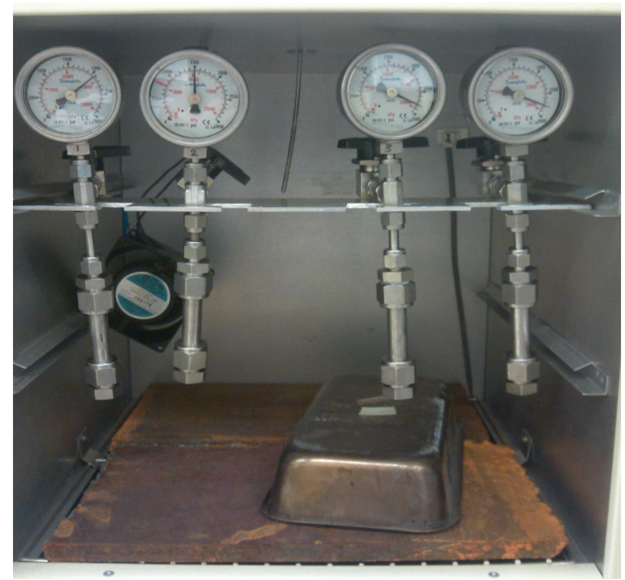
Core Flood Modeling Summary

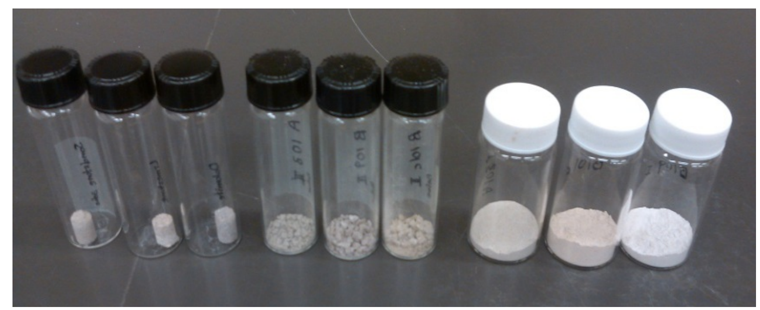
- Trends and peaks of effluent ion concentrations (particularly, Fe) were matched by the simulations.
- Simulations showed that ankerite dissolution was fast relative to siderite leading to the characteristic iron effluent peak observed in the experiments.
- Porosity and permeability changes predicted in the simulation were reasonably close to the experimental values.

Batch Reactors

Schematic diagram of the batch reactor system







Batch reactor system conditions

- Reaction pressure: 2,400 psi
- Reaction temperature: 60 *C*
- Reaction time: 14 days
- Core samples: sandstone, limestone, and dolomite
- (Powder, fractures, and 0.5 inch core plug)

Batch Systems – Main Results

Mineralogy changes with different surface area: Effluent analysis using ICP-MS

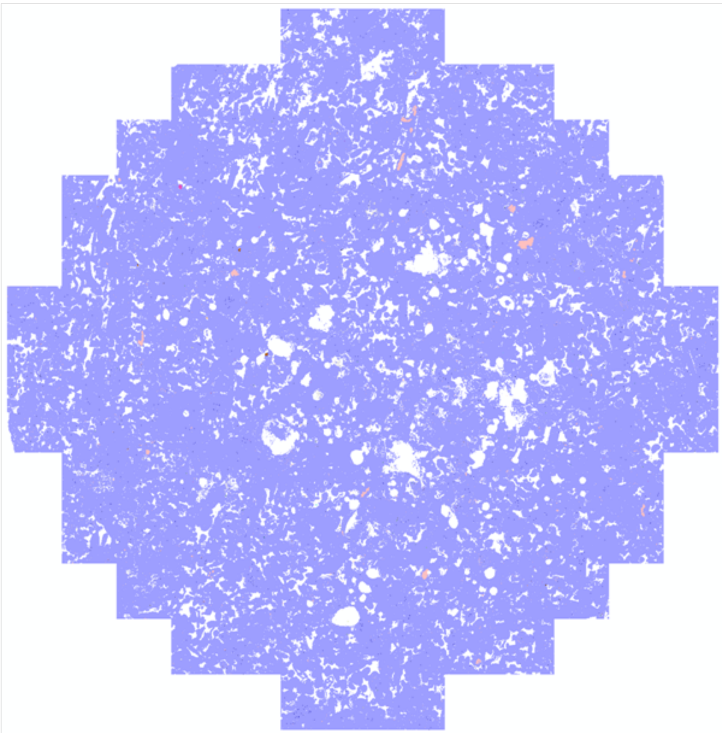
Table 7. ICP-MS results for core plug, fractured core, and powdered core after two week

	Na (mg/kg)	Mg (mg/kg)	Al (mg/kg)	Si (mg/kg)	K (mg/kg)	Ca (mg/kg)	Fe (mg/kg)
LOD	2	0.004	0.06	0.06	7	13	0.05
Core plug samples							
Blank	7024	0.68	0.64	0.22	<7	<13	1.92
Sandstone	7108	60.2	27.2	3.8	72	154	126
Limestone	7024	24	2.43	1.16	64	571	0.08
Dolomite	7188	302	0.87	5.04	80	428	0.08
Fracture samples							
Blank	7096	0.82	<0.06	0.25	<7	<13	1.14
Sandstone	7103	109	64.9	8.4	140	204	192.1
Limestone	7028	29	1.39	3.07	96	708	0.07
Dolomite	7097	444	0.15	2.37	137	543	0.08
Powder samples							
Blank	7018	0.74	0.32	1.68	<7	<13	1.53
Sandstone	6904	167.2	98.5	17.2	211	384	271.44

Enhanced changes are observed as we go from core plugs to fracture samples to powders

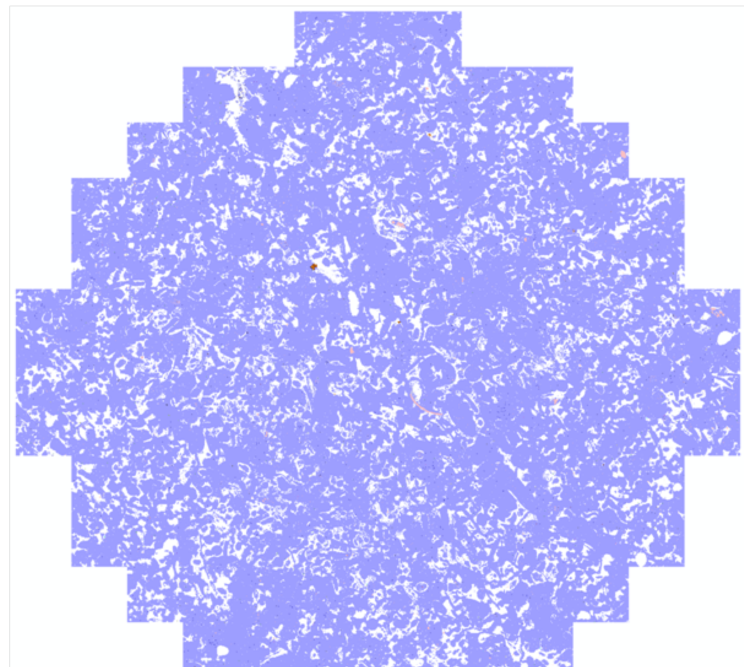
Limestone – QEM Scan

Mineralogical changes: Limestone core plug analysis using QEMSCAN



Mineral Name	
Calcite	99.08
Background	14.58
Quartz	0.34
Particle Rims	0.29
Micrite	0.19
Dolomite	0.05
Ankerite	0.03
Apatite	0.01

Background area increased
From 14.58% to 23.54%

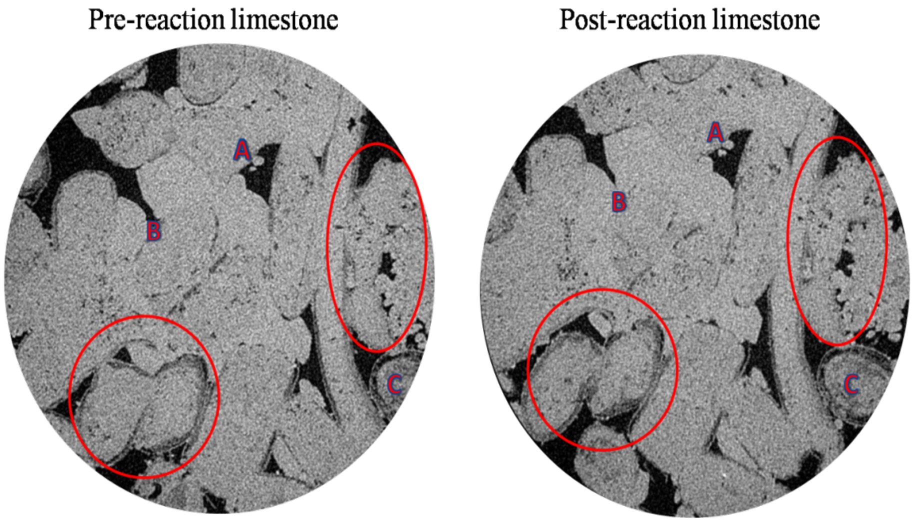


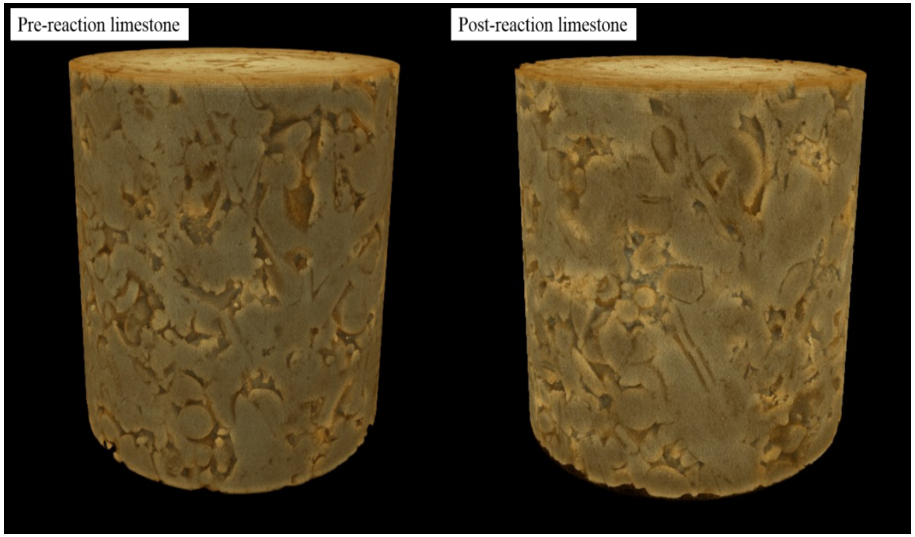
Mineral Name
Calcite
Background
Particle Rims
Quartz
Micrite
Dolomite
Ankerite
Alkali Feldspar
Illite
Plagioclase
Other Silicates
Apatite

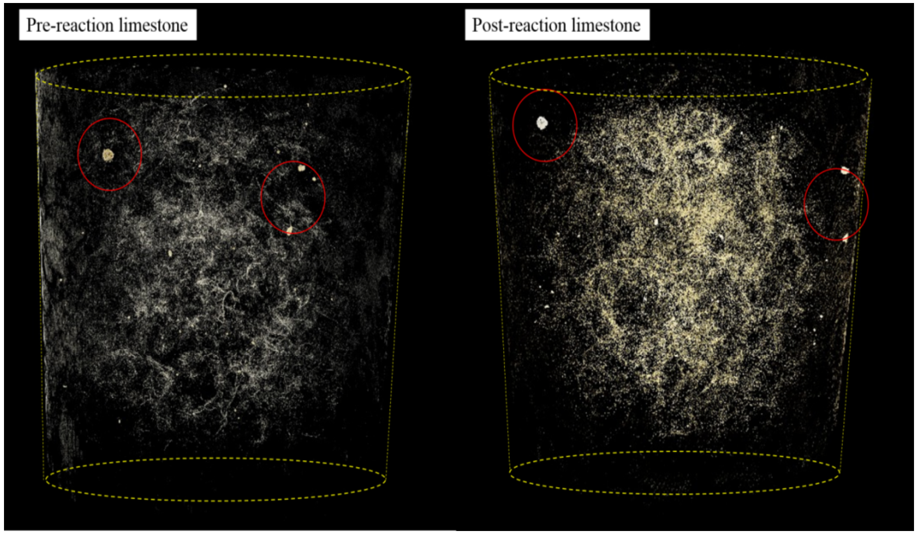
Widespread dissolution including internally

Limestone – Micro CT

Petrophysical changes: Limestone core plug analysis using Micro-CT







- The cross sectional 2D images the pore morphology change is easily recognized
- The 3D solid image there are many pore changes on the surface of the core plug
- The 3D negative image is cloudier after the batch experiment reaction

Batch Reactor Observations

- Mineral dissolution caused the growth and expansion of pores in all mineralogies.
- The 2D cross section Micro-CT results showed pore expansion within the sandstone and limestone core plugs.
- The 3D solid images showed pore changes on the surface of sandstone, limestone, and dolomite. The 3D negative images displayed removed particles and increased porosity.
- Surface area changes were measured by BET instruments. Increased surface area in sandstone, limestone, and dolomite ranged from 24.30 % to 35.47 %, 9.98 % to 19.58 %, and 7.45 % to 40.94 %, respectively.

Experimental Conclusions

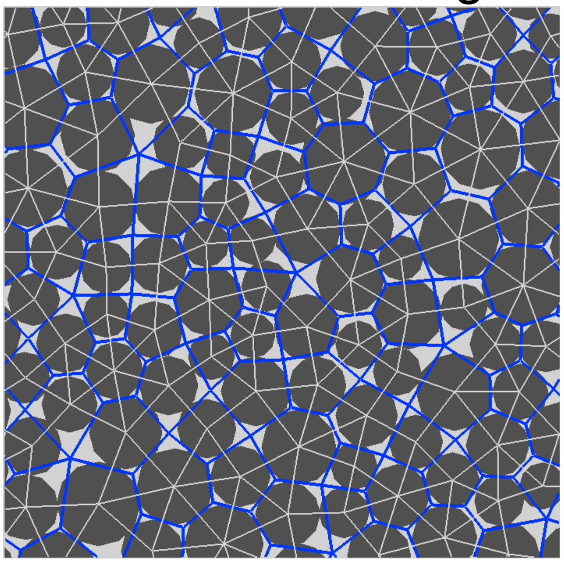
- Mineralogical changes after two weeks of injection have the potential to cause significant petrophysical and subsequent structural changes in sandstone, limestone and dolomite formations under carbon dioxide sequestration conditions. This was the original hypothesis that was validated using high-pressure core floods in this work.
- Iron chemistry plays an unexpectedly larger role in sequestration in sandstone formations. Dissolution of ankerite and siderite lead to large iron effluent concentrations. A reactive transport model such as TOUGHREACT may be used to explain the complex interconnected reactions with flow. However, some of the flow rate effects observed in the experiments could not be reproduced in the model.
- In limestone and dolomite, calcium and magnesium bearing minerals dissolve leading to formation of large dissolution zones, including wormholes.

Conclusions (continued)

- Porosity and permeability changes are small – of the order of 1-2% and similar values result from TOUGHREACT.
- Batch experiments showed similar trends in iron in sandstones, and calcium and magnesium in limestone and dolomite. As the surface areas increase by using rock chips and then powders, reactivities increase leading to larger cationic concentrations in brine.
- Approximate morphology of the reacted volume is viewed using QEMSCAN and Micro-CT for batch samples. Reactions appear to be uniform throughout the volume for limestone and dolomite, whereas they appear to be limited more to the surface in sandstone.

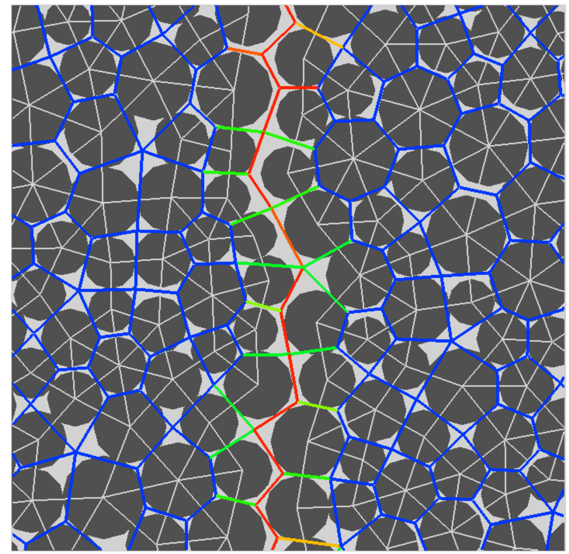
Method: Coupling DEM with Conjugate Network Flow Model (INL)

Prior to fracturing



$$q_{ij} = \frac{k_0 \cdot A_{ij}}{\mu} \frac{(P_i - P_j)}{l_{ij}}$$

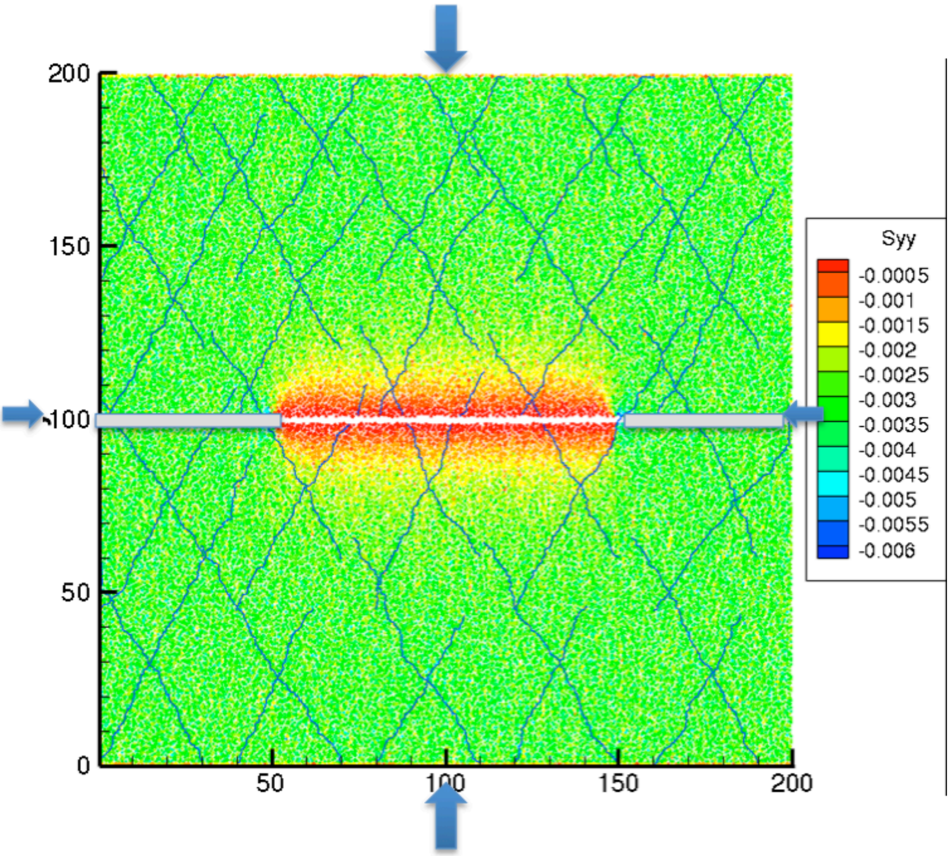
After fracturing



$$q_{ij} = \frac{k_{ij} \cdot b_{ij}}{\mu} \frac{(P_i - P_j)}{l_{ij}}, \quad with\ k_{ij} \approx b_{ij}^2 / 12$$

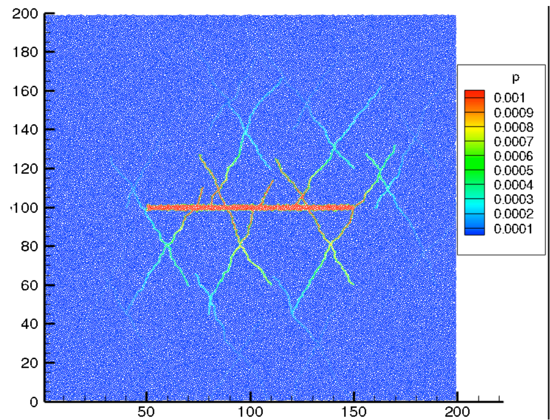
- Directly calculate apertures of micro-fractures;
- Apertures are used to as direct input for updating permeability of the flow network
- More **PHYSICS**-based hydraulic fracturing model

Mechanistic modeling of reactivations of natural fractures near injection wellbore due to CO2 injection

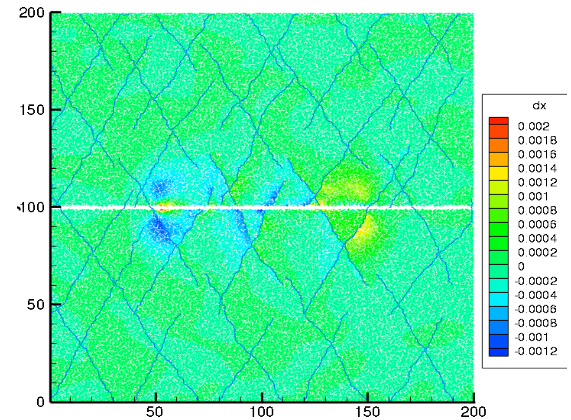


- **Cemented wellbore with open injection interval**
- **Vertical stress ~10,000psi with H/V ratio of 0.5**
- **Densely fractured reservoir**
- **Natural fractures are assumed to be mechanically closed**
- **Natural fractures have initial permeability of ~$1.4 \times 10^{-12} m^2$**
- **The reservoir matrix permeability is low,~ $1.4 \times 10^{-19} m^2$**

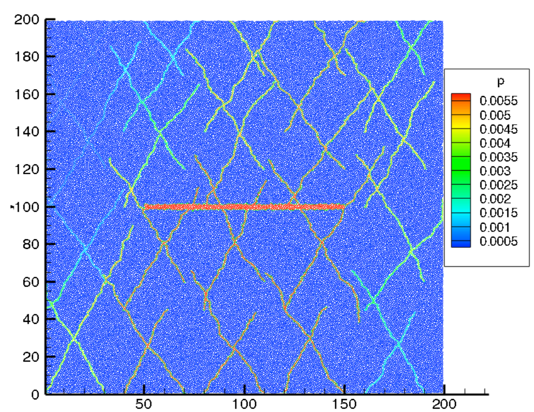
Simulations on stress and permeability changes



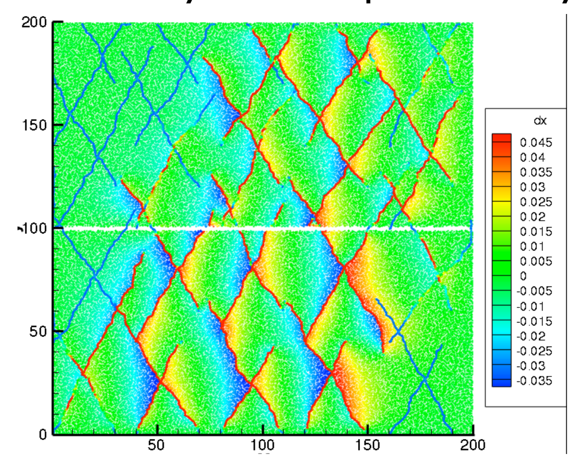
Fluid pressure distribution shortly after the injection was started



Horizontal displacement field and fracture network colored by fracture permeability

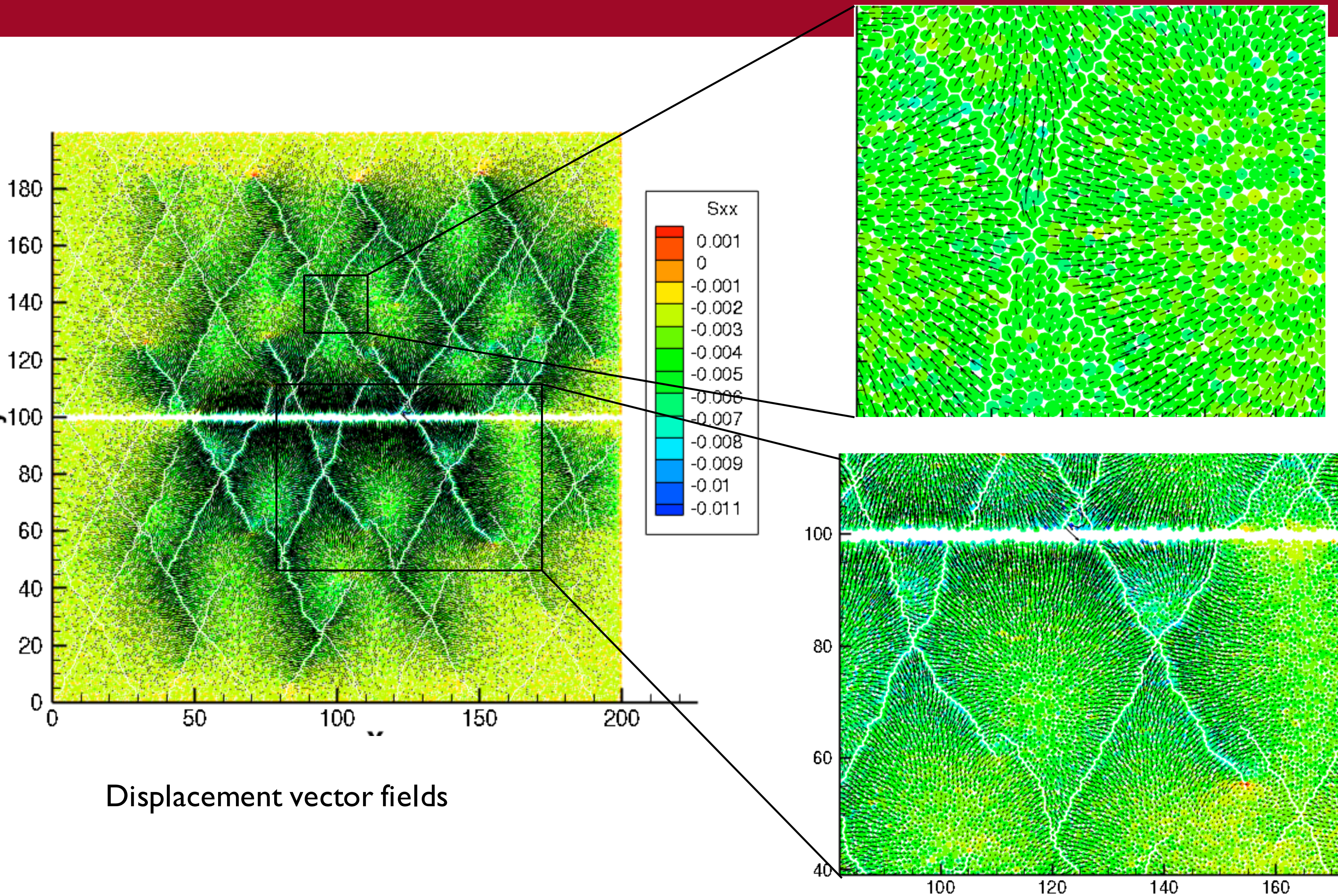


Fluid pressure distribution after flow reached steady-state



Horizontal displacement field and fracture network colored by fracture permeability

Shear slipping vs. opening?



Displacement vector fields

Geomechanics Conclusions

- DEM geomechanics model - a robust for either fractured or not-fractured reservoir
- Most natural fractures are filled with secondary minerals, and have certain tensile and shear strengths: DEM accounts for such effects in dealing with natural fractures
- We see dilational opening of fractures rather than shear failures.
- Geochemical reactions such as mineral dissolution/precipitation weaken mechanical strength natural fractures, leading to reactivation of fractures

Project Status

- Wrapping up with more data analysis on reaction rates and surface area
- Field implications
- Use of experimentally obtained parameters in INL simulations