LANL Sequestration Activities:
Long-term Wellbore and Caprock Seal Integrity
FWP FE-715-16-FY17

U.S. Department of Energy National Energy Technology Laboratory
Mastering the Subsurface Through Technology Innovation,
Partnerships and Collaboration: Carbon Storage and Oil and Natural Gas Technologies Review Meeting

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Earth & Environmental Sciences
Los Alamos National Laboratory

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Traci Rodosta for guidance and support

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Outline/Motivation

- **Project goal: Quantify possible leakage processes of CO_2 through wellbore and caprock seals**
- **Numerical and experimental study of geochemical self-sealing processes in wellbore systems**
  - Self-sealing in cemented wellbores: Mechanisms, dynamics, and implications
  - How much cement is needed to ensure self-sealing?
  - What is a CO_2-compatible cement?
- **Geomechanical model of injection-induced damage in wellbore systems**
  - Injection/production results in expansion/contraction of the reservoir
  - Shear stress has the potential to damage the well-formation interface
- **Geomechanical experiments on fracture-permeability behavior of caprock**
  - Results on shale, dolomite and anhydrite

Self sealing in cemented wellbores: Mechanisms, dynamics, and implications

EPA (2010) — *Federal Register*, **75(237):**77251

- "EPA proposed that all materials used in the construction of Class VI wells must be compatible with fluids with which the materials may be expected to come into contact, and that **cement and cement additives must be compatible with the CO_2 stream and formation fluids** and of **sufficient quality and quantity to maintain integrity** over the design life of the project."

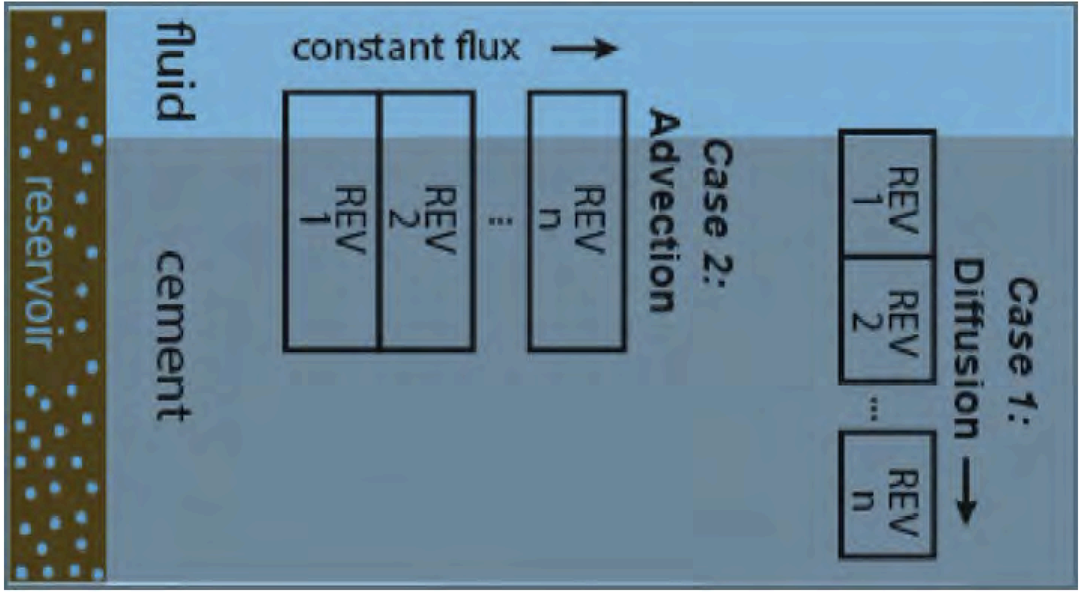
Project Goals:

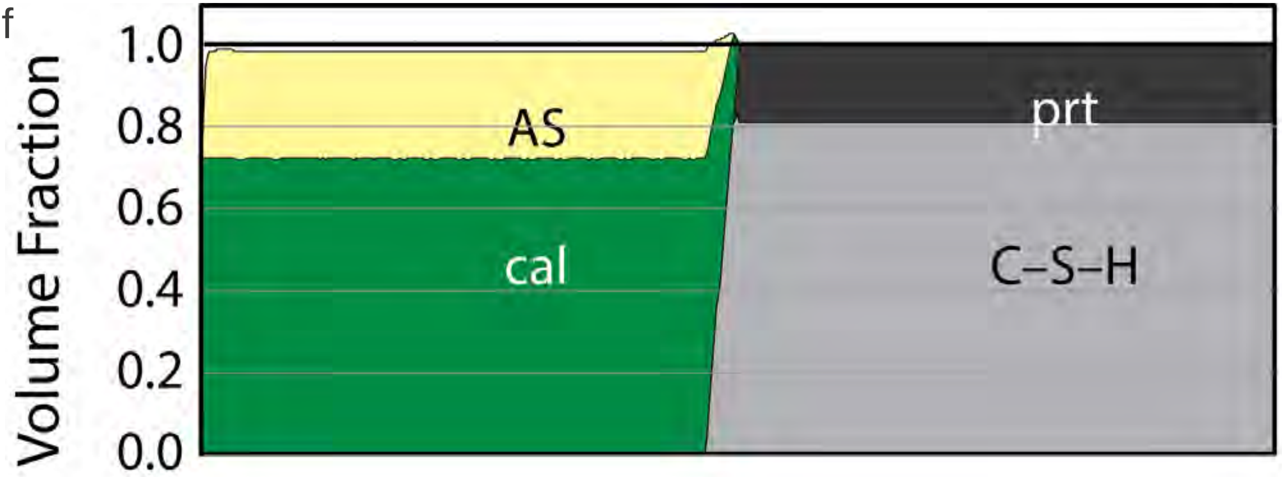
- Develop an easily used model to evaluate the spatial and temporal distribution of self-sealing in cement
- Address the question of just what is a "compatible cement"

Simulation of Self-Sealing

Setup

- 1-D reactive transport model of simplified cement chemistry (portlandite + calcium silica hydrate [CSH])
- Constant flow conditions
- Determine sensitivity to thermodynamics, kinetics, Ca/Si ratio of CSH
- Rather than residence time, formulate results in terms of rate of fluid movement and distance along the well for sealing to occur
- Sealing determined by net porosity reduction due to calcite precipitation

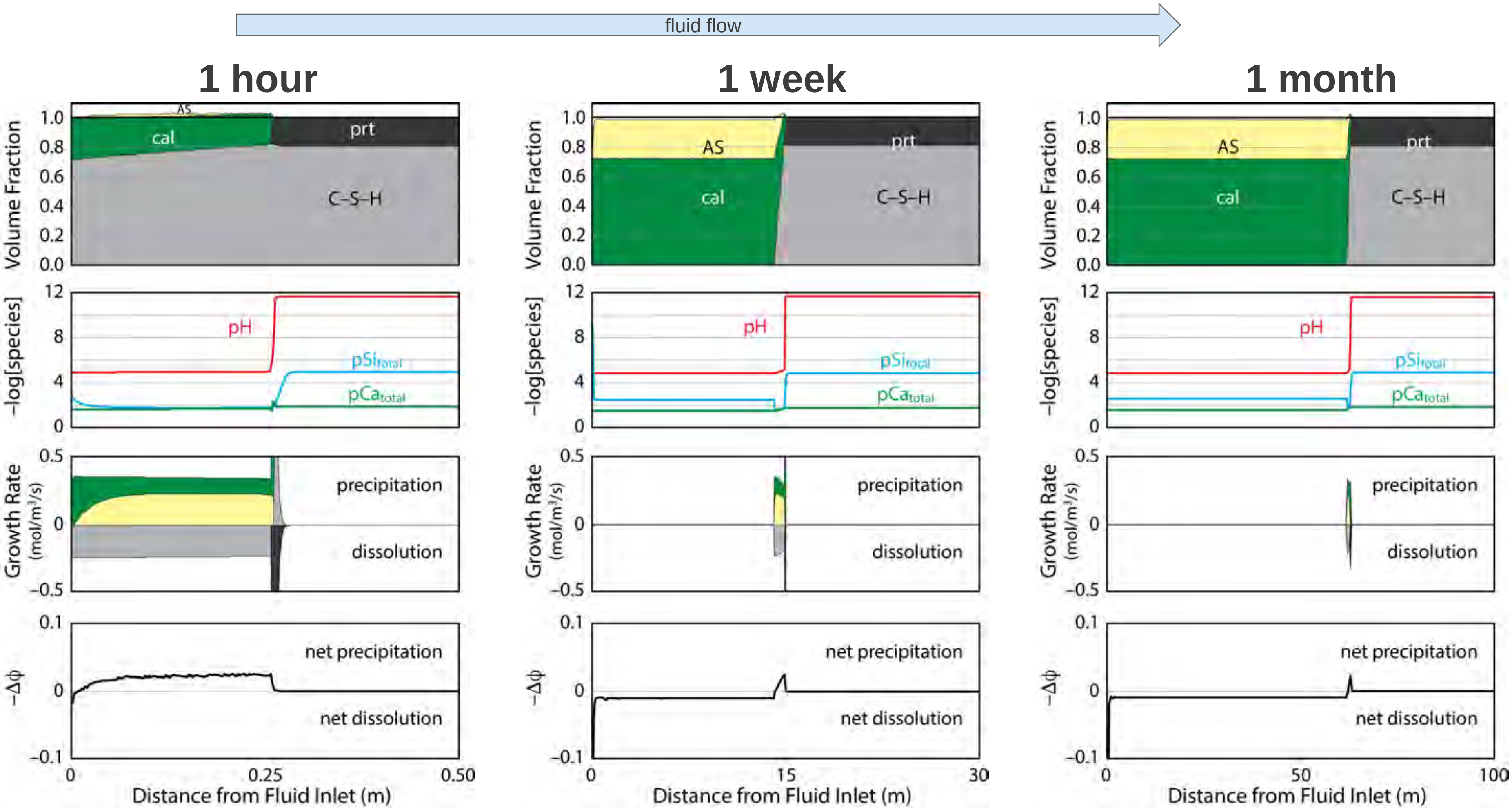




Guthrie et al. (2018) IJGGC

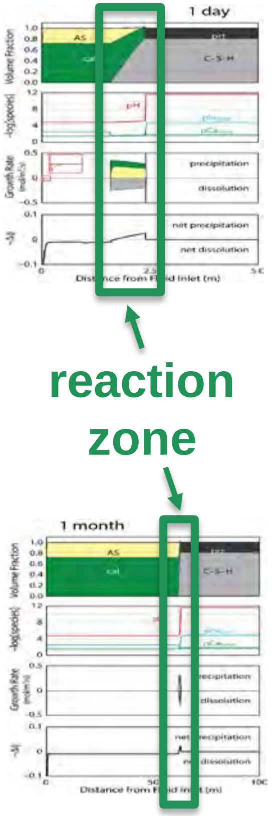
Results (Migration of Reaction Zone):

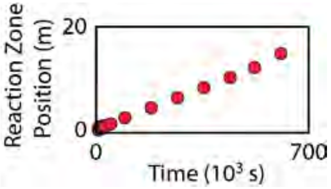
Reaction zone migrates over time in direction of fluid flow

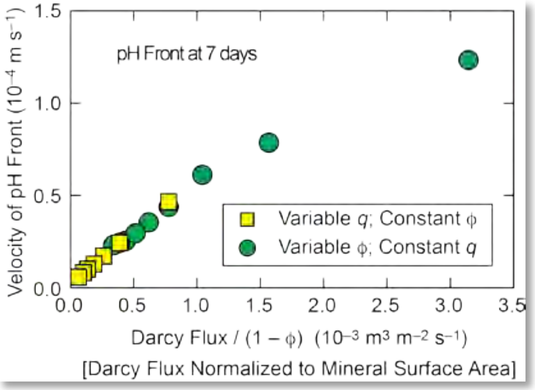


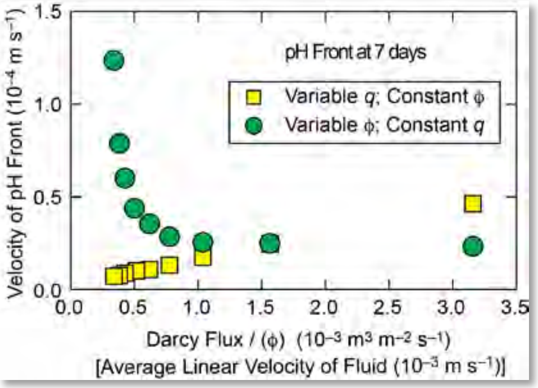
- ***Note:*** **x-axis range increases for plots moving left to right.**
- **Simulations are 1D and consider advection-only.**

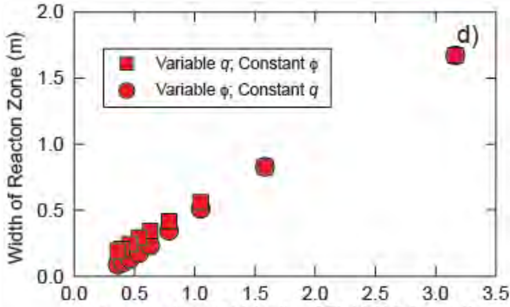
Results (Reaction-Migration):
Reaction front progresses proportional to Darcy flux











Reaction zone moves over time in the direction of fluid flow

- pH front position/velocity can be used to track reaction front

Reaction zone moves proportional to Darcy flux

- Velocity of the pH front moves nearly linearly with Darcy flux normalized to (1 – ϕ) at a small fraction of the fluid velocity
- Velocity of the pH front is not directly tied to velocity of fluid, as shown by plot with Darcy flux normalized to porosity (ϕ)

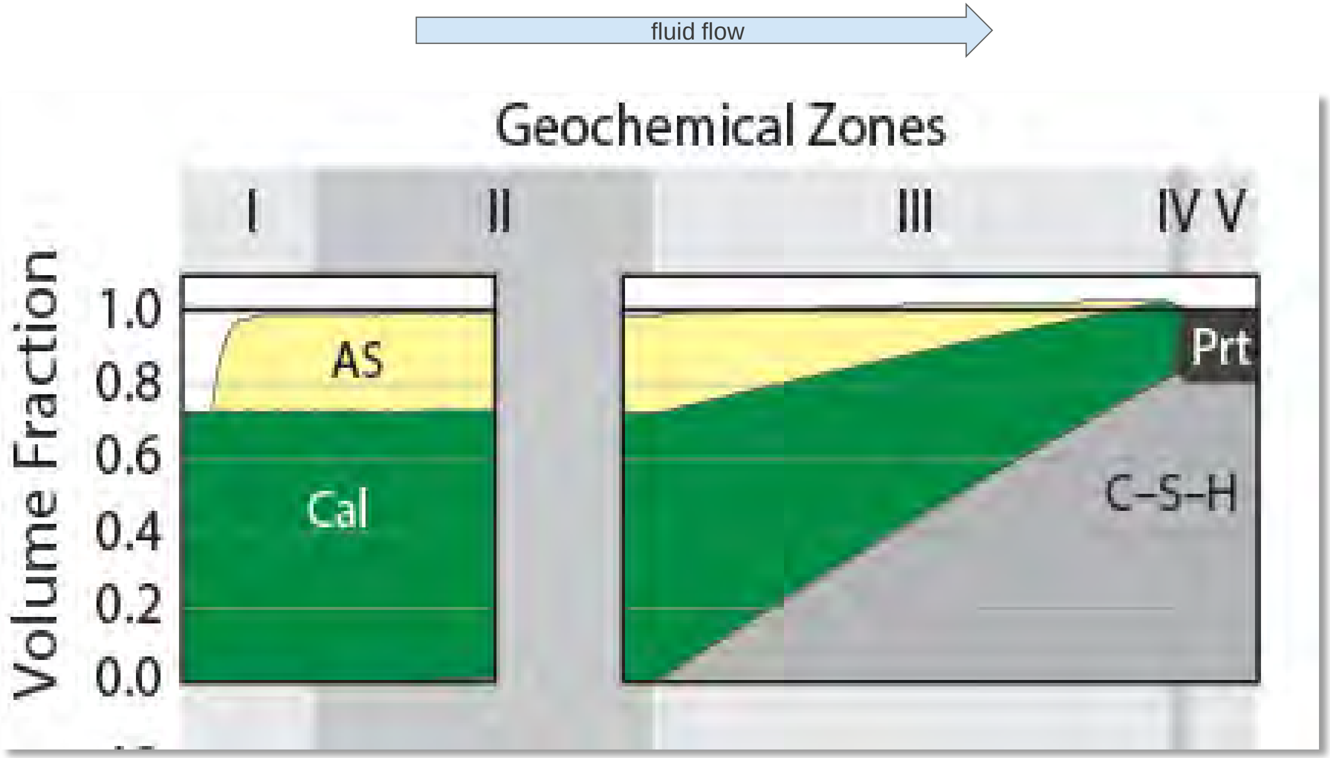
Reaction zone spreads proportional to average linear velocity of the fluid

- Reaction zone gets wider over time in response fluid flow

Guthrie et al. (2018) IJGGC

Results (Reaction Mechanisms):

Five distinct geochemical zones result from reactive flow



I — **Dissolution—porosity increase**

II — **Equilibrium of carbonated cement**

III — Loss of C-S-H with calcite precipitation—porosity decrease

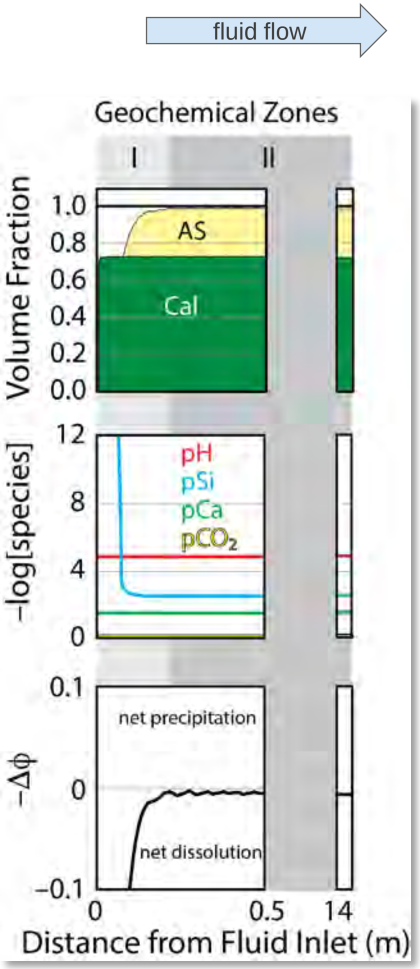
IV — Loss of portlandite and precipitation of C-S-H and calcite—porosity decrease

V — **Equilibrium of original cement**

Guthrie et al. (2018) IJGGC

Results (Reaction Mechanisms):

Zone I: Dissolution; Zone II: Static (Equilibrium)



Zone I

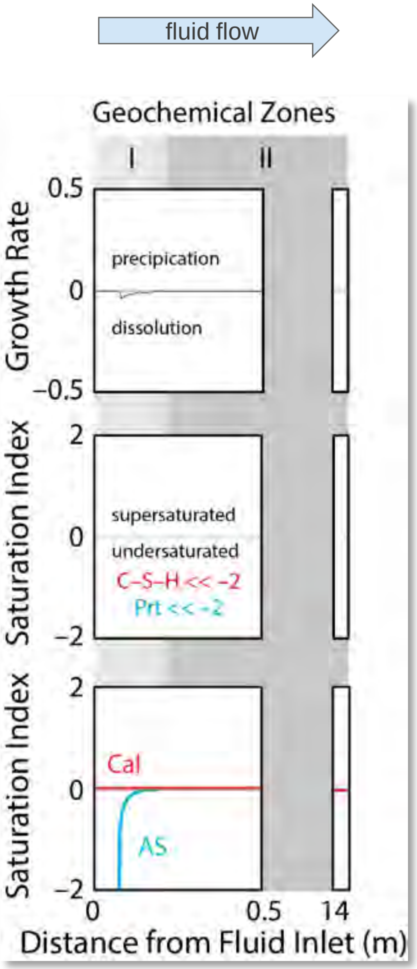
$$SiO_{2\,(am)}\ (+\ CaCO_{3\,(s)} + H^{+}) \rightarrow SiO_{2\,(aq)}\ (+\ Ca^{2+} + HCO_3^{-})$$

- Dissolution of silica+calcite, depending on incoming brine (shown in ”Volume Fraction” and “–$\Delta\phi$” and “Growth Rate”)
- Undersaturated in all phases except reservoir mineralogy (shown in “Saturation Index”)
- Aqueous chemistry initially reflects reservoir equilibrium (shown in “–log[species]”)

Zone II

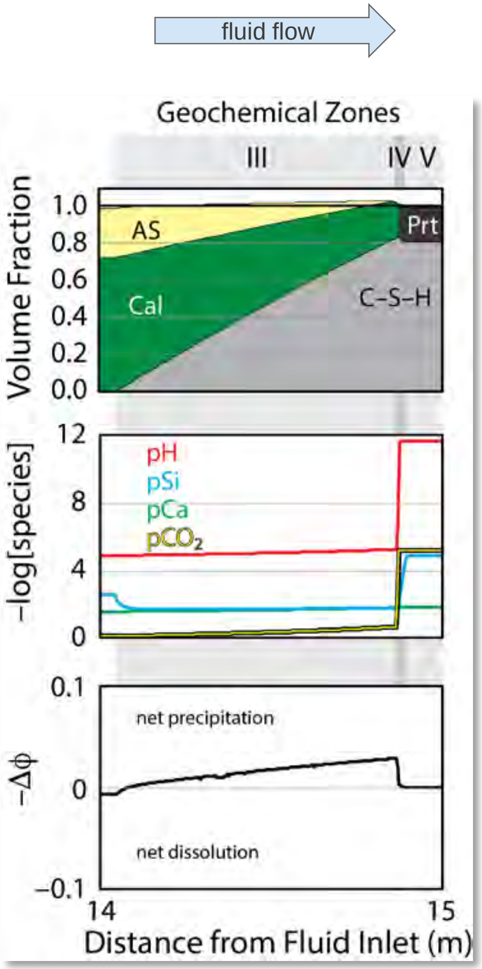
$$SiO_{2\,(am)} + CaCO_{3\,(s)} + H^{+} \leftrightarrow SiO_{2\,(aq)} + Ca^{2+} + HCO_3^{-}$$

- No net dissolution or precipitation (shown in ”Volume Fraction” and “–□ ” and “Growth Rate”)
- Equilibrium between fluid and carbonated cement (silica+calcite) (shown in “Saturation Index”)
- Aqueous chemistry exhibits low pH and low pCO_2 (i.e., high $[CO_2]$) (shown in “–log[species]”) (i.e., silica+calcite is in equilibrium with a carbonated acidic brine)



Guthrie et al. (2018) IJGGC

Results (Reaction Mechanisms):
Zones III & IV: Self-Sealing Reaction Zone



Zone III

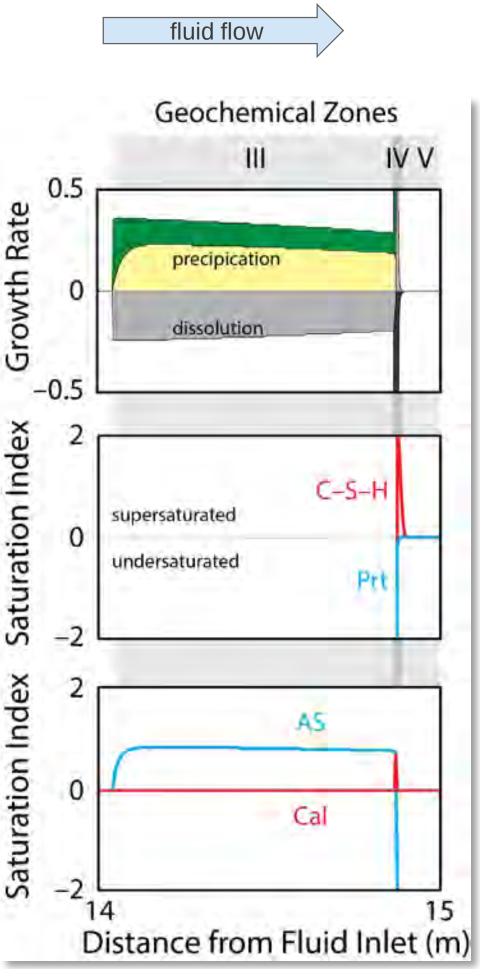
$\text{C–S–H} + H^{+} + HCO_3^{-} \rightarrow CaCO_{3\,(s)} + SiO_{2\,(am)}\ SiO_{2\,(aq)}$

- Net increase in volume of solids
  Dissolution of C–S–H and precipitation of calcite and silica
  (shown in ”Volume Fraction” and “–Δϕ” and “Growth Rate”)
- Undersaturated in C–S–H and portlandite;
  saturated in calcite; supersaturated in amorphous silica
  (shown in “Saturation Index”)
- Aqueous chemistry shows slight raising of pH and pCO_2,
  but a decrease in pSi (i.e., an increase in dissolved silica)
  (shown in “–log[species]”)

Zone IV

$Ca(OH)_{2\,(s)} + H^{+} + HCO_3^{-} + SiO_{2\,(aq)} \rightarrow \text{C–S–H} + CaCO_{3\,(s)}$

- Net increase in volume of solids
  Dissolution of portlandite; precipitation of C–S–H and calcite
  (C–S–H could be a proxy for any Ca-rich silicate)
  (shown in ”Volume Fraction” and “–Δϕ” and “Growth Rate”)
- Undersaturated in portlandite & silica;
  supersaturated in calcite & C–S–H
  (shown in “Saturation Index”)
- Aqueous chemistry shows rapid rise in pH, pCO2, and pSi
  (shown in “–log[species]”)



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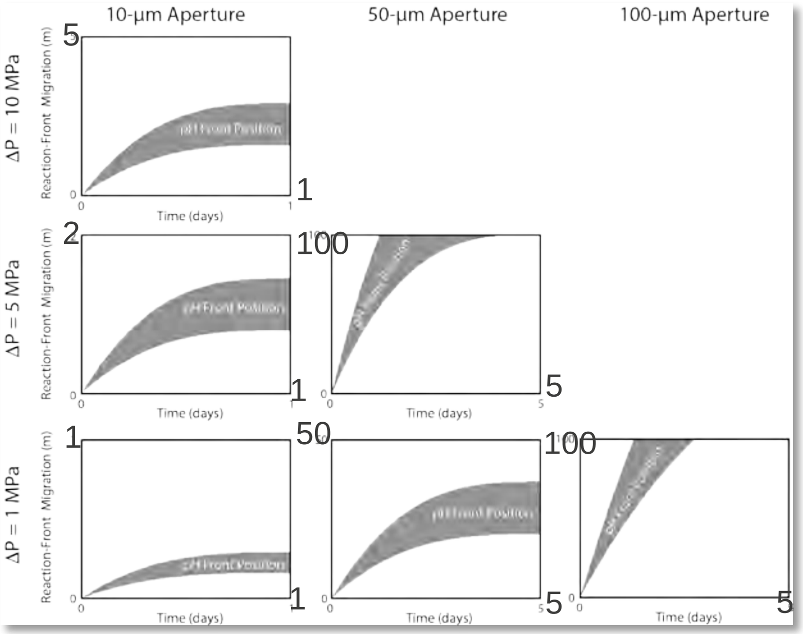
Results (Dynamics of Self Sealing): What conditions should self-seal?

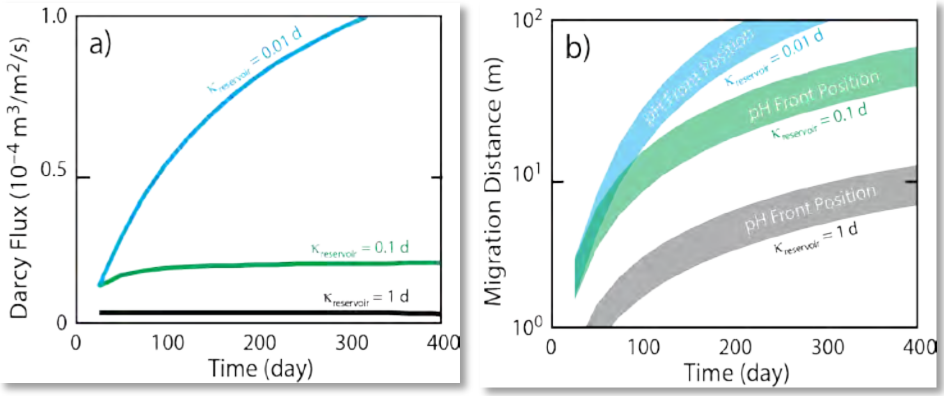
Fracture-Controlled Flow



Small fractures should self-seal

- Conservatively, fractures <10 µm will self seal (calcite-only precipitation; cubic law flow)
- Significantly larger fractures are likely to be inherently self-sealing for realistic scenarios (calcite and silica precipitation; etc.)

Pressure-Controlled Flow

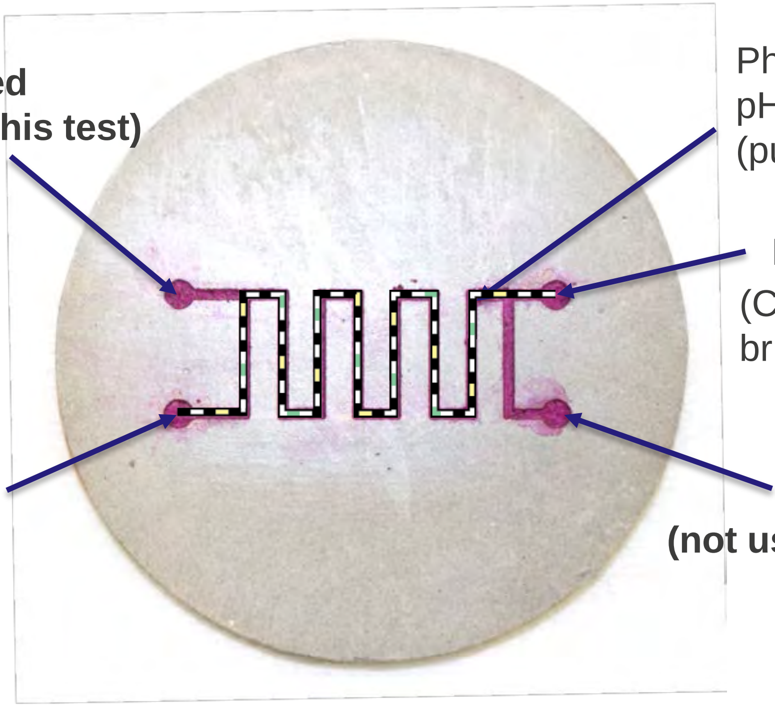


Pressure-management should limit self-sealing conditions to within 10s of meters of cemented sections, even for large fractures

- High permeability reservoirs maintain low pressures during injection phase, limiting the migration of the self-sealing reaction zone
- Other pressure management strategies (e.g., water co-production) could maintain favorable conditions even for lower permeability reservoirs

Guthrie et al. (2018) IJGGC

Experimental Study of Self-Sealing



Plugged (not used in this test)

Phenolphthalein pH indicator (purple is basic)

Inlet

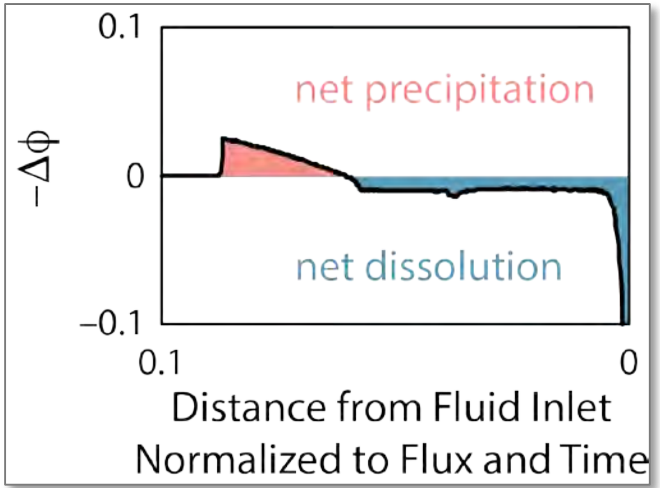
(CO_2 saturated brine injection)

Outlet

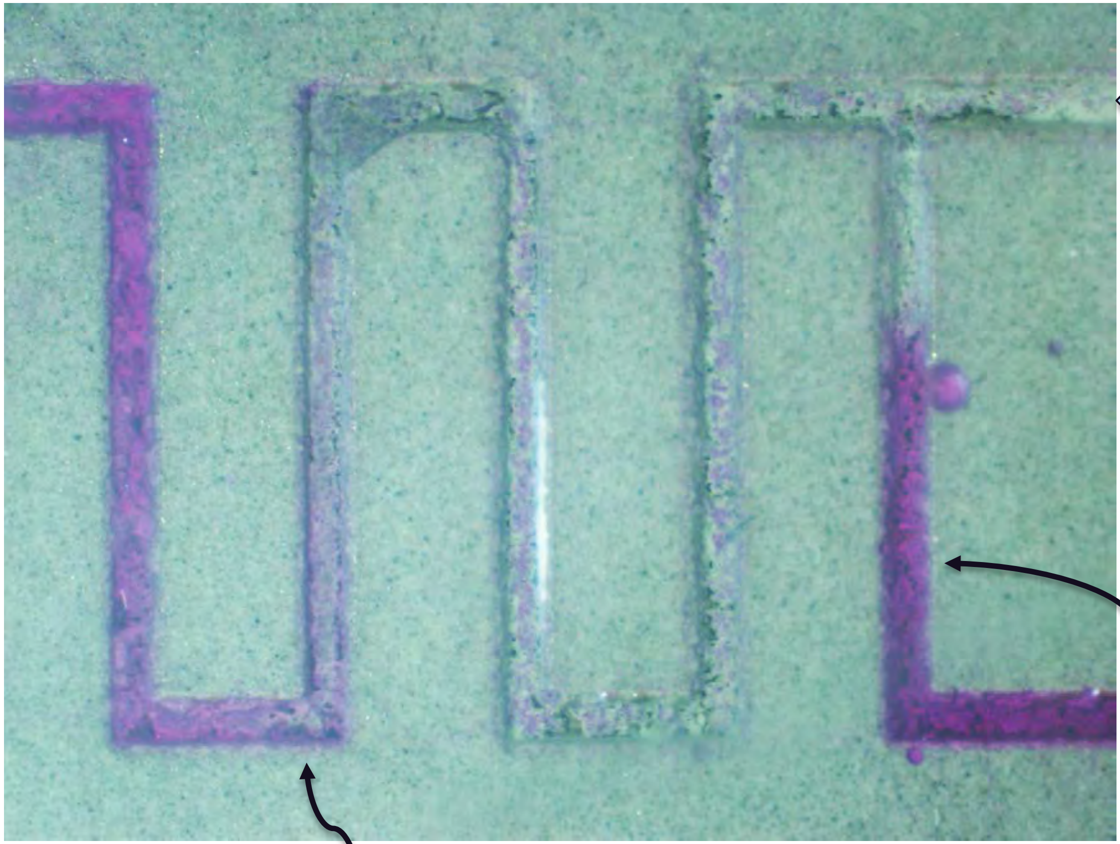
Plugged (not used in this test)

- Type G Portland Cement with etched channel system
- Inject CO_2-bearing deionized water
- 5 µL per min for 33 minutes
- Experimental conditions: P = 8 MPa, T = 50 ^{o}C
- Channel system is 500 µm deep, 500 µm wide and 50 mm in length

Predicted Change in Volume



Microfluidics Experiments:
Phenolphthalein used to track pH front



Fluid outflow

Fluid inflow

1-cm

pH front

Dead-end fracture

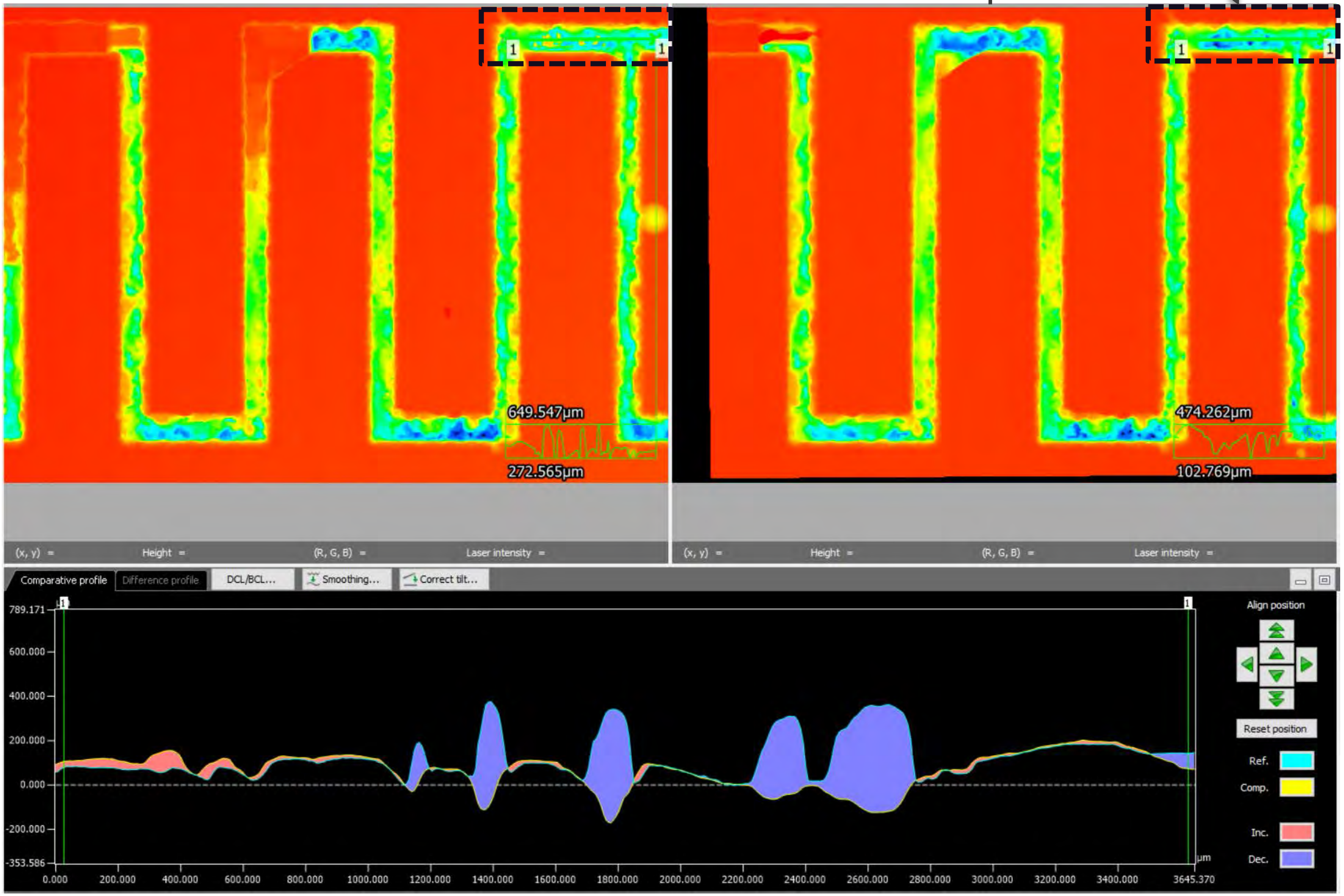
Nguyen, Carey, Guthrie

- CO_2+brine
- 8 MPa; 50 °C
- 0.5x0.5 mm^2 cross section
- 5.0 µl/min

Inlet region: average 58 µm dissolution

Comparison area

← Inlet

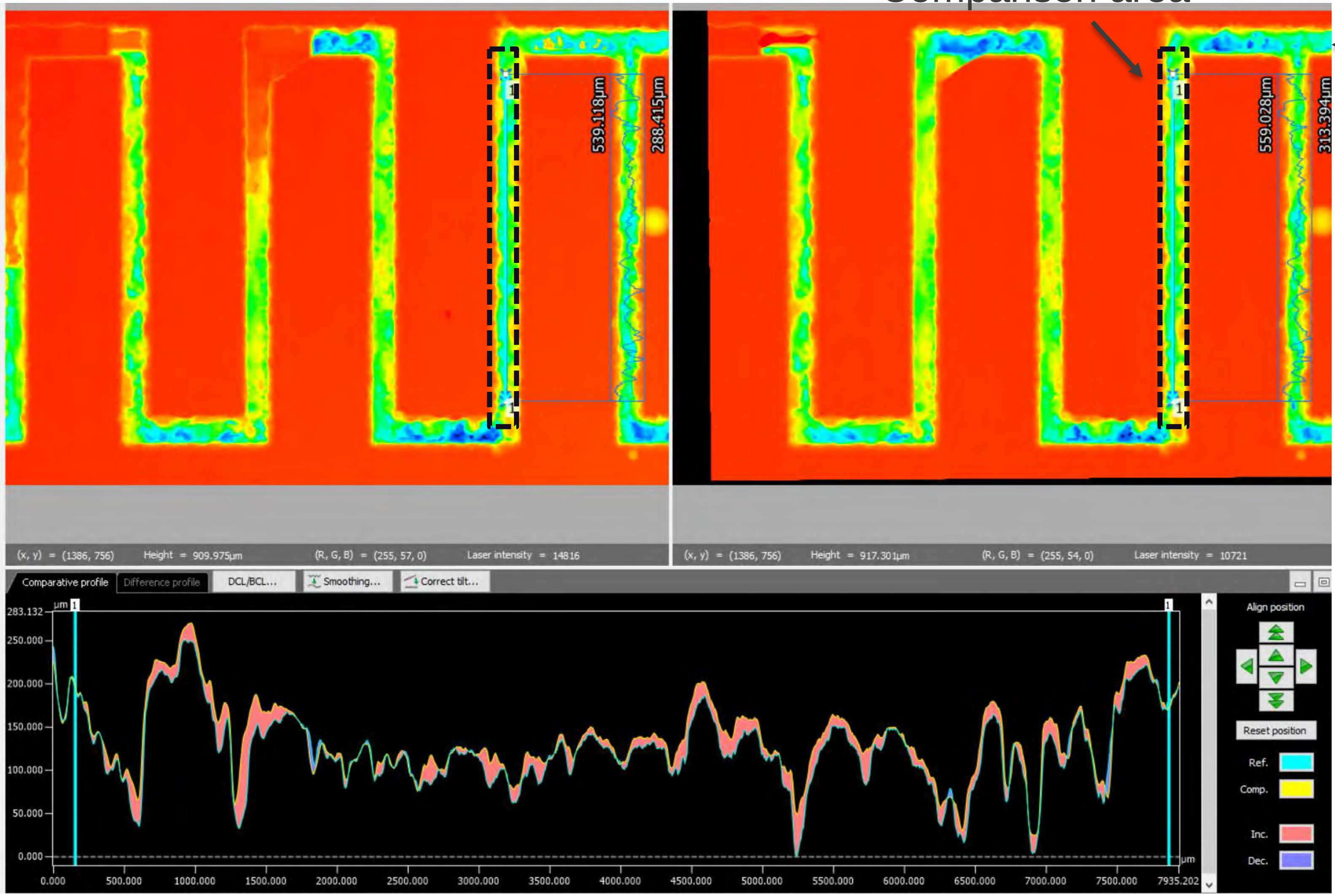


🟦 Dissolution
🟥 Precipitation

First long leg: average 13 µm precipitation

Comparison area

Inlet



(x, y) = (1386, 756) Height = 909.975µm (R, G, B) = (255, 57, 0) Laser intensity = 14816

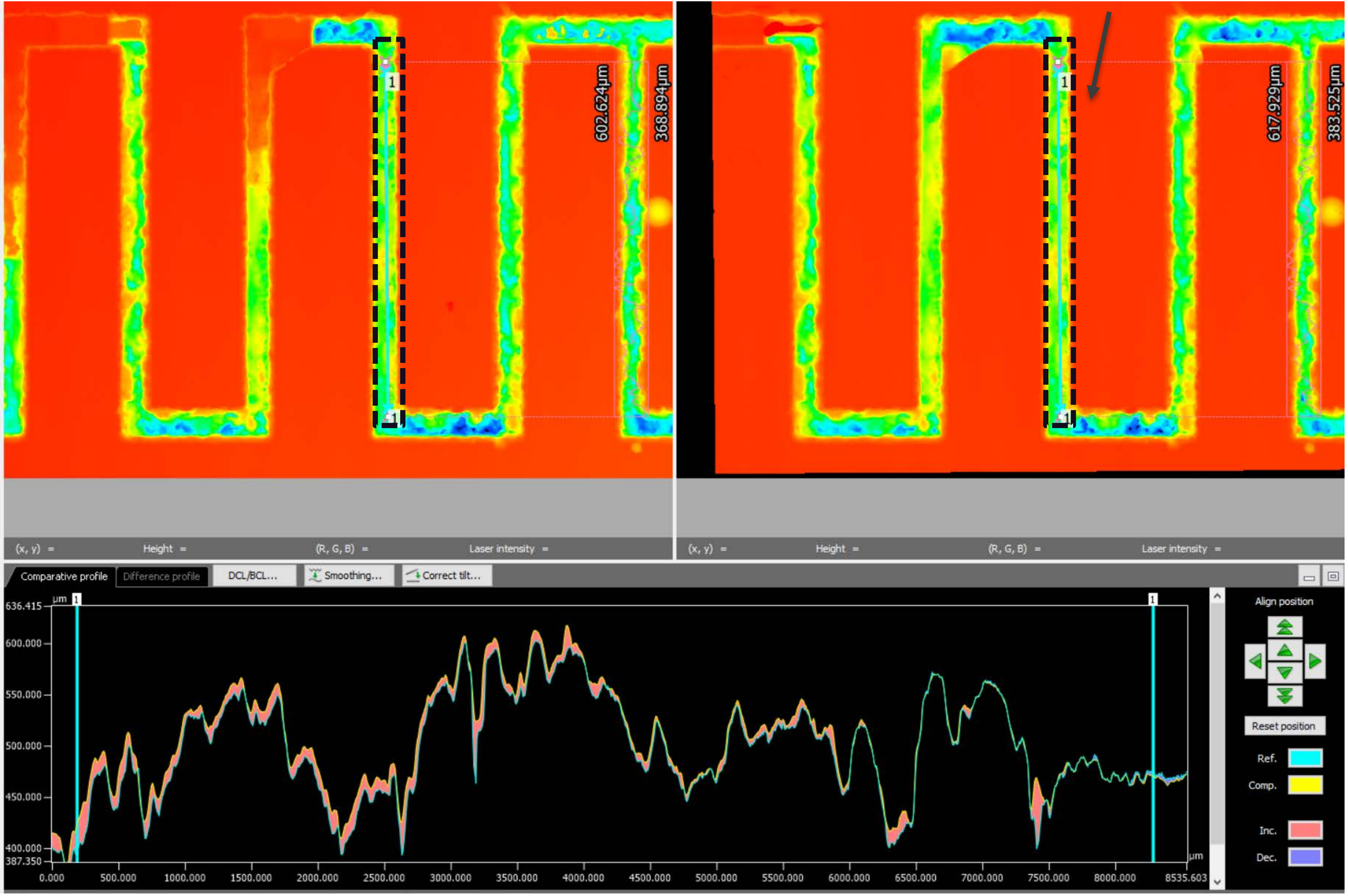
(x, y) = (1386, 756) Height = 917.301µm (R, G, B) = (255, 54, 0) Laser intensity = 10721

🟦 Dissolution

🟥 Precipitation

Second long leg: average 9 µm precipitation

Comparison area

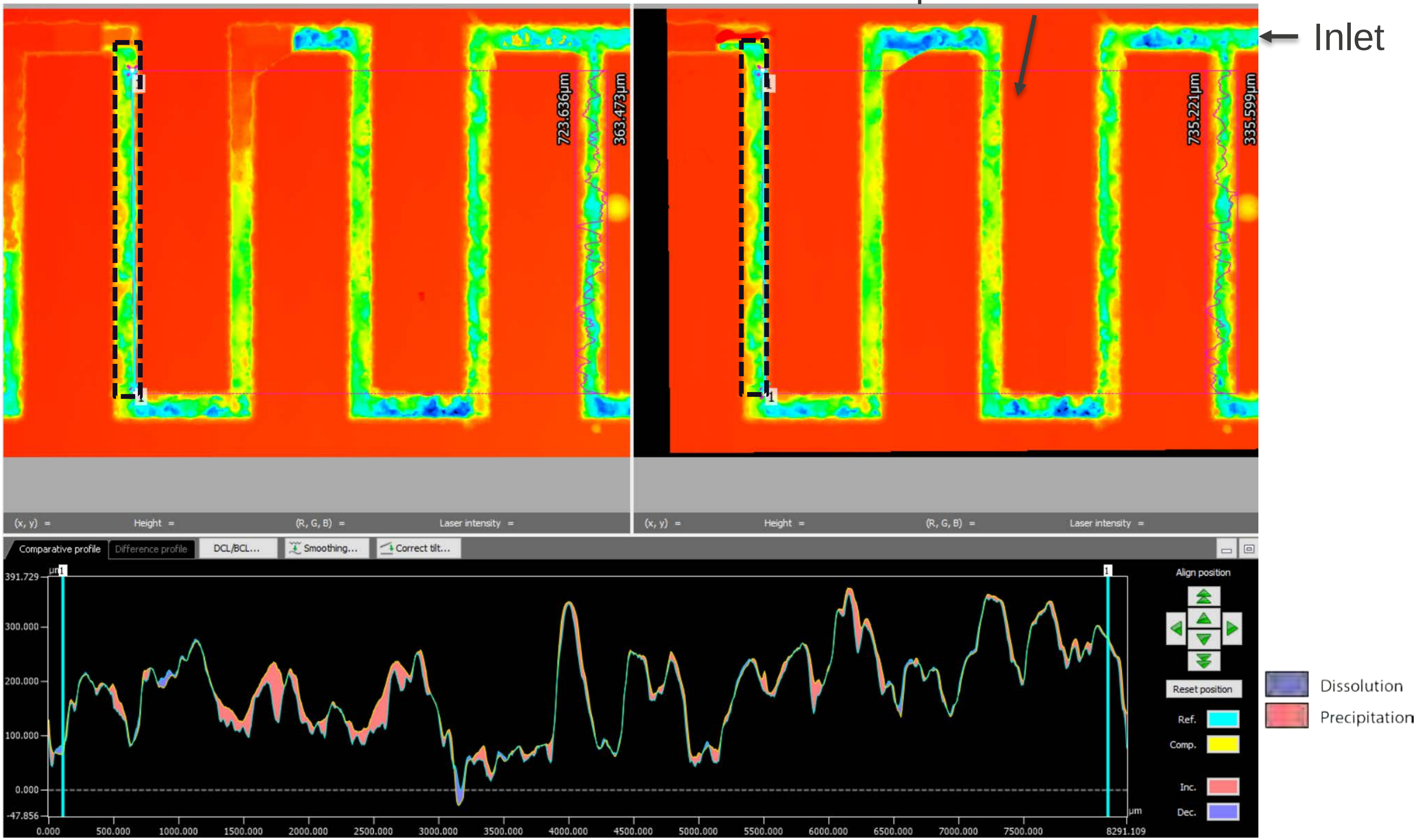


← Inlet

🟦 Dissolution

🟥 Precipitation

Fourth long leg: 11 µm average precipitation

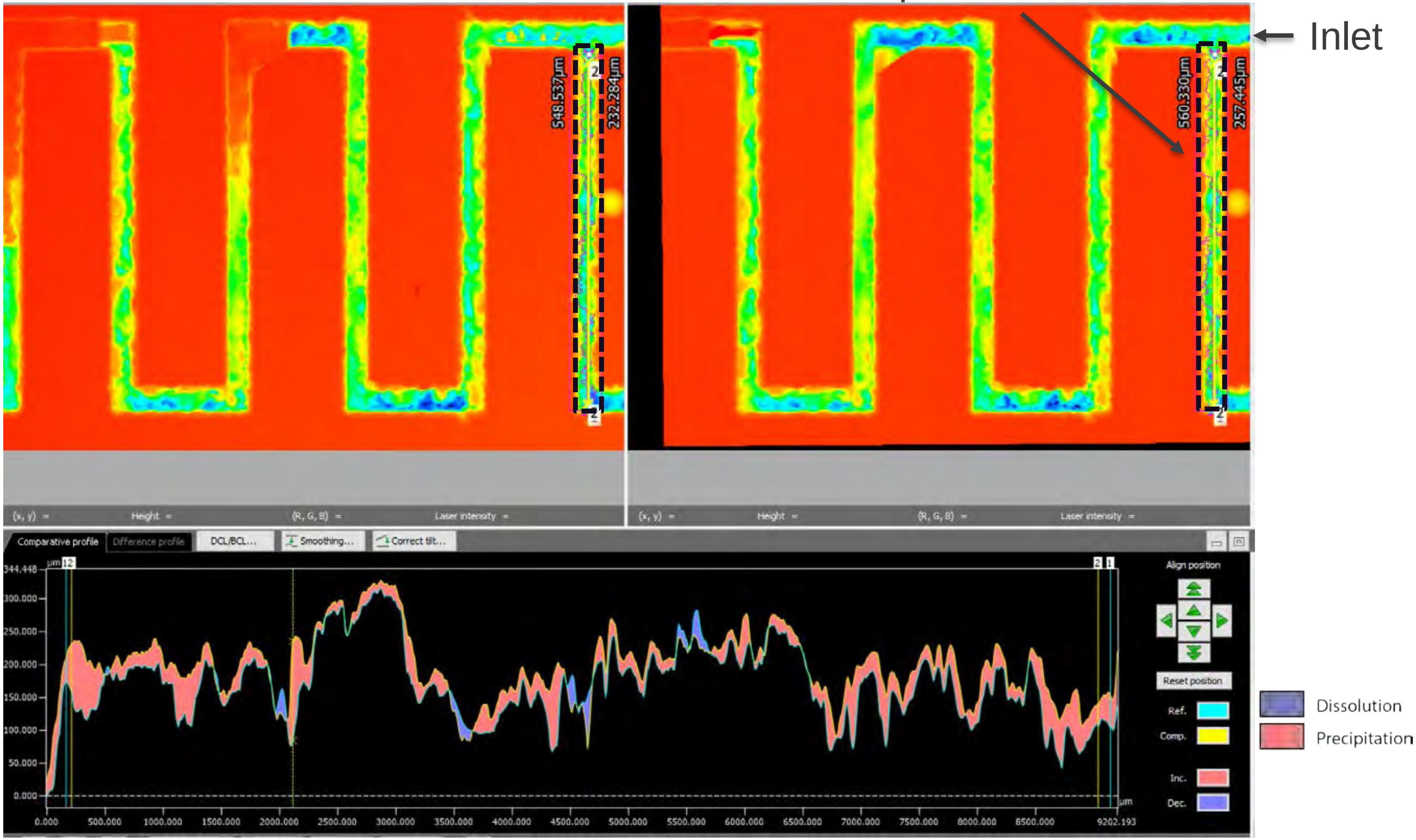


Comparison area

Inlet

Dead-end fracture: 31 µm average precipitation (151 max)

Comparison area



← Inlet

🟦 Dissolution

🟥 Precipitation

Self-Sealing in Cemented Wellbores:
Major Conclusions

Self-Sealing Mechanism

→ Results from a net increase in volume of solids from two reactions tied to carbonation of hydrated cement

→ Occurs in a reaction zone between unaltered and carbonated cement, ultimately producing silica + carbonate

→ Occurs over a wide range in hydrogeochemical parameters

Self-Sealing Dynamics

→ Reaction zone migrates in the direction of flow proportional to volume of fluid moved (i.e., fluid flux) and widens proportional to speed of fluid moved (i.e., fluid velocity)

Experimental validation

→ Initial results compatible with reduced-order, 1D model showing progress of self-sealing reactions

Results (CO_2 Compatability): Hydrated Portland cement qualifies as a carbonic cement

Ordinary Portland cement (OPC) is a hydraulic cement: it sets and remains intact in the presence of water.

OPC

- Mixture of anhydrous phases (C_3S, C_2S, …)
- Phases *react* with water, forming new hydrated phases that are stable in water.
- Hydrated OPC consists of several stable phases, including C–S–H, portlandite, etc.

Hydrated OPC (HOPC) is a carbonic cement: it sets and remains intact in the presence of carbonic acid.

HOPC

- Mixture of non-carbonated phases (C–S–H and portlandite, …)
- Phases *react* with carbonic acid, forming new carbonated phases that are stable in carbonated water.
- Carbonated HOPC consists of several stable phases, including calcium carbonate and silica

Technical Status

- **Completed: Thermodynamic and kinetic model for cement self-sealing**
  - “Hydrated Portland Cement as a Carbonic Cement: The Mechanisms, Dynamics, and Implications of Self-Sealing and CO_2 Resistance in Wellbore Cements” (Guthrie et al., 2018, Int. Journal Greenhouse Gas Control)
  - Initiated microfluidics experiments on self-sealing of cement
- **Modified and enhanced a triaxial direct-shear coreflood system with simultaneous x-ray radiography/tomography**
  - Initiated experiments on mechanical-hydrologic behavior of cement-steel interfaces
- **Completed: experimental study of potential fracture leakage processes in shale as caprock**
  - Completed complementary study of anhydrite and dolomite caprock
- **Completed: “Engineering Prediction of Axial Wellbore Shear Failure due to Reservoir Uplift” (in press, SPE Journal)**

Lessons Learned

- **Portland cement is a carbonic cement with self-sealing properties; it is far more resilient than originally thought**
  - Coupled casing corrosion and cement carbonation is not yet understood
  - Experimental geomechanics of wellbore systems is just beginning
- **Caprock integrity characterization involves more than determining low permeability; fracture-permeability behavior is key to understanding risk of leakage**
  - Much work remains to understanding resilience and breakdown of caprock systems as function of lithology and subsurface conditions
- **Challenges**
  - Coupled processes are technically challenging both experimentally and computationally—proving resilience of well or caprock systems requires a coupled stress and chemistry approach
  - Field observations of well and caprock failure processes are extremely limited

Synergy Opportunities

- **Excellent opportunities to collaborate on geomechanics and induced seismicity of storage reservoir systems**
  - Penn State study of rheology of fracture slip (D. Elsworth)
  - UT-Austin study of reservoir seal geomechanics (P. Eichhubl)
  - LBL study of in situ fault slip (J. Birkholzer)
- **Excellent opportunities to collaborate on well integrity problems**
  - Clemson study of strain/stress measurement in wells (L. Murchoch)
  - LLNL study of thermal stresses in wells (J. Morris/P. Roy)
  - NETL studies of well integrity (N. Huerta/B. Kutchko)
  - LLNL studies of cement deformation and sealing (Carroll, Iyer, Walsh)
- **Many other projects are closely allied to work here (reservoir geomechanics, well integrity studies, etc.)**

Accomplishments to Date

- **Published reviews of wellbore integrity (Carey 2013; Carroll, Carey et al. (2016)**
- **Developed field evidence (Carey et al. 2007), experimental evidence (Carey et al. 2010; Newell and Carey 2013) and computational models (Guthrie et al. 2018) of self-sealing behavior**
- **Developed and demonstrated a protocol for characterizing leakage behavior in caprock as a function of stress conditions (Carey et al. 2015; Frash et al. 2016, 2017)**
- **Determined a threshold change in leakage potential in caprock as effective stress increases (Frash et al. 2016, 2017)**
- **Developed an analytical geomechanical model for analysis of stress and failure in wellbore systems (Frash and Carey, in press)**

Project Summary

- **One key to reducing risk of leakage is through observation and measurement of self-healing properties of cement and caprock**
- **We have shown that leakage is mitigated under some conditions**
  - We have developed a theoretical framework for demonstrating self-sealing and are now establishing an experimental protocol to prove this out
  - Wellbore integrity is better understood and mitigation appears to be bounded by the size and continuity of the defect
  - Understanding mitigation of caprock leakage has just started
- **Understanding fracture-permeability behavior of caprock is an effective means of addressing potential impact of induced-seismicity**
- **A complete treatment of the geomechanics of wellbore systems is limited by lack of understanding of in situ stress conditions in cement**
  - A framework for analysis has been established but awaits additional characterization of full implementation

Appendix

Benefit to Program

- Develop long-term predictive models for use in risk-based analyses of carbon storage systems

- Determine the consequences of stress-induced damage to wellbore and caprock seals?

- Develop and validate technologies to ensure 99% storage permanence.

Project Goals

- **Impact of stress (mechanical and chemical) on wellbore and caprock integrity focused on role of CO_2-water**

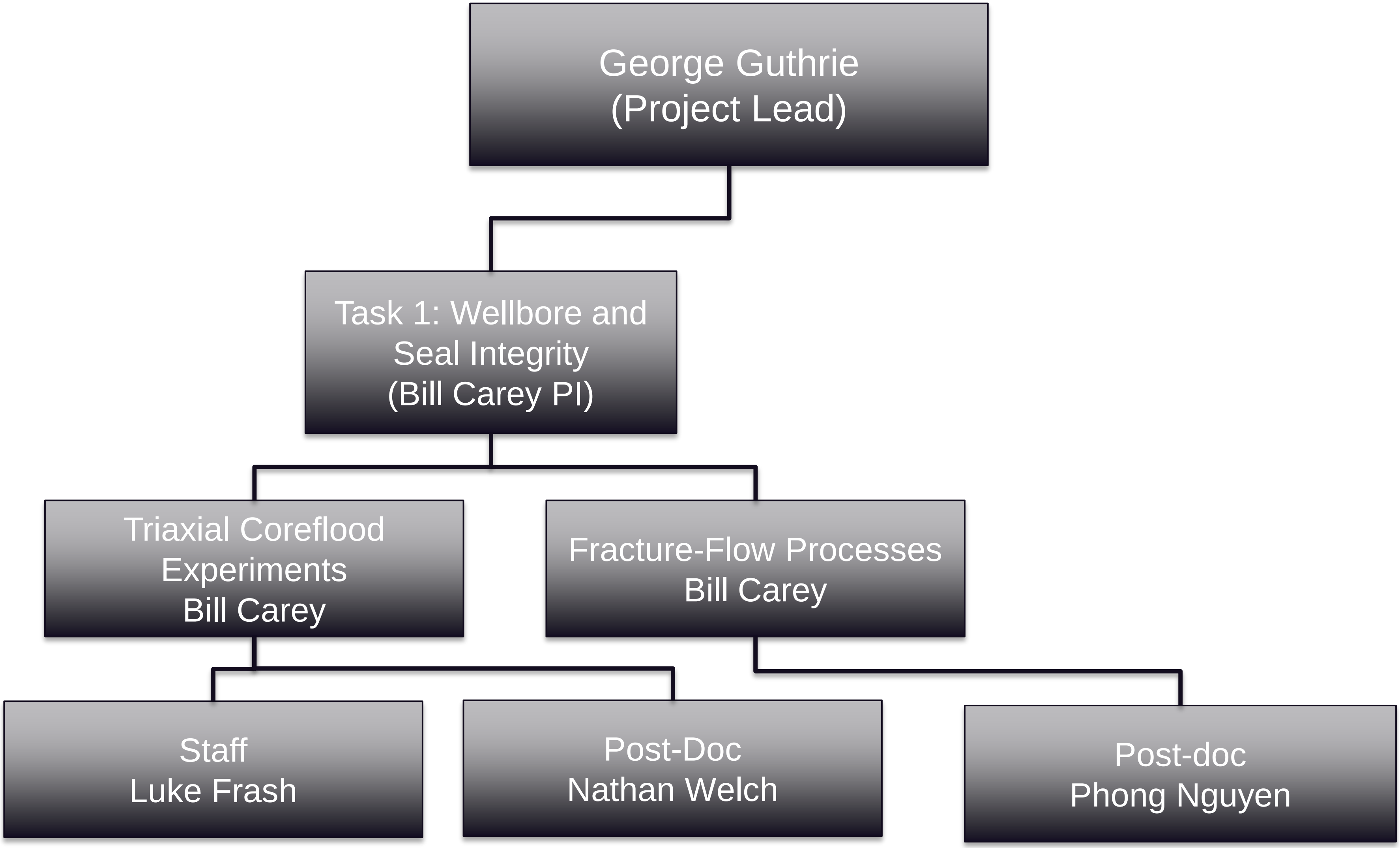
- **Experimental studies of the impact of mechanical stress on leakage processes**

- **Experimental studies of the impact of CO_2 flow and geochemical reactions on leakage**

- **Field studies of cement-steel-caprock samples obtained from CO_2-containing reservoirs**

- **Numerical models to predict damage and leakage in wellbore and caprock seals**

Organizational Chart



George Guthrie
(Project Lead)

Task 1: Wellbore and
Seal Integrity
(Bill Carey PI)

Triaxial Coreflood
Experiments
Bill Carey

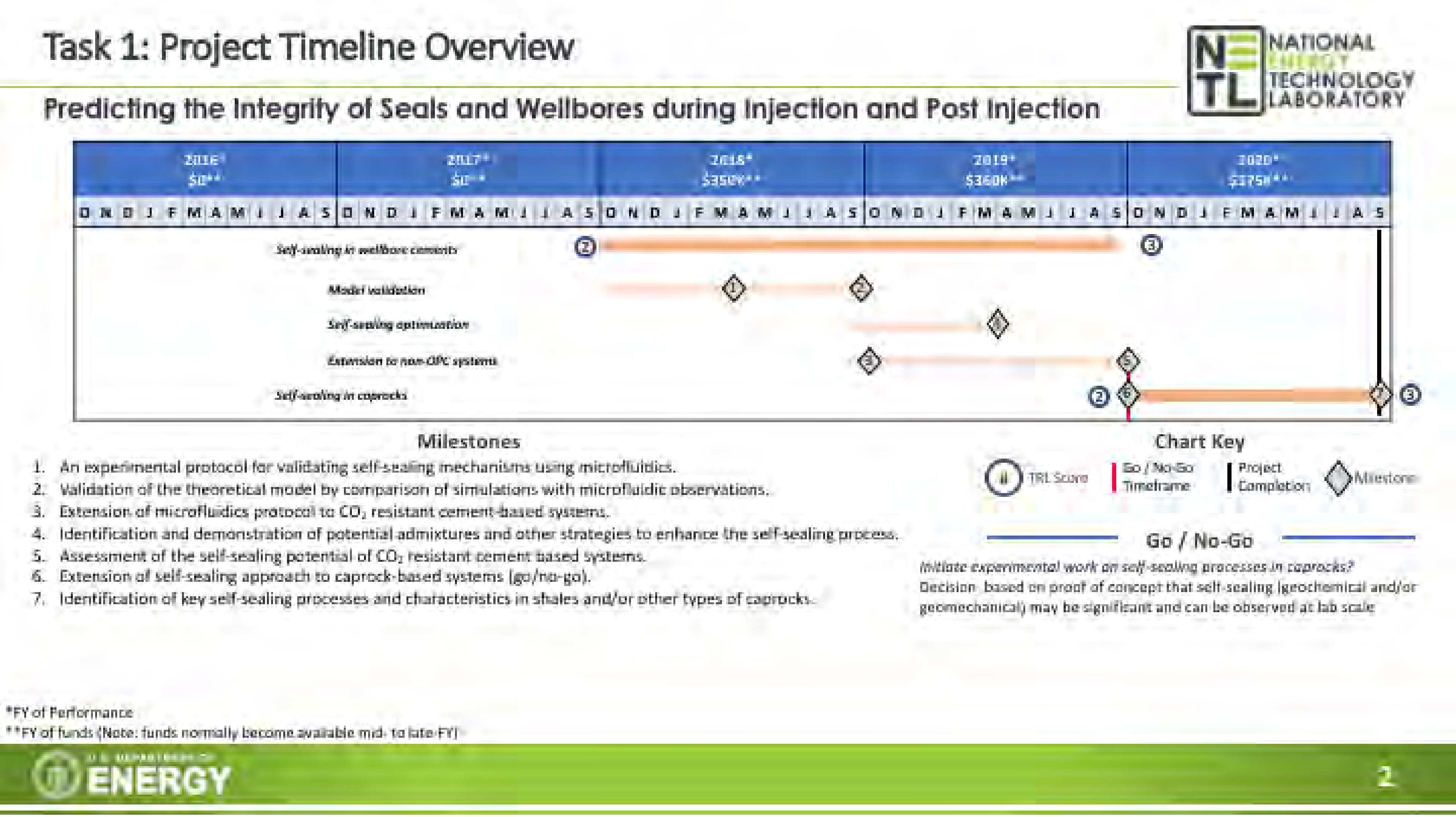
Fracture-Flow Processes
Bill Carey

Staff
Luke Frash

Post-Doc
Nathan Welch

Post-doc
Phong Nguyen

Gantt Chart



Task 1: Project Timeline Overview

Predicting the Integrity of Seals and Wellbores during Injection and Post Injection

Milestones

1. An experimental protocol for validating self-sealing mechanisms using microfluidics.
2. Validation of the theoretical model by comparison of simulations with microfluidic observations.
3. Extension of microfluidics protocol to CO_2 resistant cement-based systems.
4. Identification and demonstration of potential admixtures and other strategies to enhance the self-sealing process.
5. Assessment of the self-sealing potential of CO_2 resistant cement based systems.
6. Extension of self-sealing approach to caprock-based systems (go/no-go).
7. Identification of key self-sealing processes and characteristics in shales and/or other types of caprocks.

Chart Key

ii TRL Score | Go / No-Go Timeframe | Project Completion | Milestone

Go / No-Go

Initiate experimental work on self-sealing processes in caprocks?
Decision based on proof of concept that self-sealing (geochemical and/or geomechanical) may be significant and can be observed at lab scale

*FY of Performance
**FY of funds (Note: funds normally become available mid- to late-FY)

Publications (2015-2018)
Supported by or in part by this project

- **Guthrie, G. D., Jr., R. J. Pawar, J. W. Carey, S. Karra, D. R. Harp, and H. S. Viswanathan. (2018) The mechanisms, dynamics, and implications of self-sealing and CO_2 resistance in wellbore cements. International Journal of Greenhouse Gas Control, 75:162–179, 2018.**
- **Frash, L. P., and J. W. Carey (in press) Engineering prediction of axial wellbore shear failure due to reservoir uplift, SPE Journal.**
- **Carey, J. W. and Torsæter, M. (in press). Shale and Well Integrity. In Shale Science. John Wiley & Sons.**
- **Carey, J. W., L. P. Frash, T. Ickes, and H. S. Viswanathan (2017) Stress cycling and fracture permeability of Utica shale using triaxial direct-shear with x-ray tomography, in 51th US Rock Mechanics / Geomechanics Symposium held in San Francisco, CA, USA, 26-28 June 2017, p. 6.**
- **Frash, L. P., J. W. Carey, T. Ickes, and H. S. Viswanathan (2017) Caprock integrity susceptibility to permeable fracture creation, International Journal of Greenhouse Gas Control, 64, 60 – 72.**
- **Frash, L. P., J. W. Carey, T. Ickes, and H. S. Viswanathan, High-stress triaxial direct-shear fracturing of Utica shale and in situ x-ray microtomography with permeability measurement, Journal of Geophysical Research, 121, 5493–5508, 2016.**

Publications (2015-2018)
Supported by or in part by this project

- Carey, J. W., Frash, L. P., and Viswanathan, H. S. (2016). Dynamic Triaxial Study of Direct Shear Fracturing and Precipitation-Induced Transient Permeability Observed by In Situ X-Ray Radiography. In 50th US Rock Mechanics / Geomechanics Symposium held in Houston, Texas, USA, 26-29 June 2016.
- Carroll, S., Carey, J. W., Dzombak, D., Huerta, N., Li, L., Richards, T., Um, W., Walsh, S., and Zhang, L. (2016). Review: Role of Chemistry, Mechanics, and Transport on Well Integrity in CO2 Storage Environments. International Journal of Greenhouse Gas Control, 49:149-160.
- Carey, J. W., Lei, Z., Rougier, E., Mori, H., and Viswanathan, H. S. (2015). Fracture-permeability behavior of shale. Journal of Unconventional Oil and Gas Resources, 11:27–43. doi: 10.1016/j.juogr.2015.04.003.
- Carey, J. W., Rougier, E., Lei, Z., and Viswanathan, H. S. (2015). Experimental investigation of fracturing of shale with water. In 49th US Rock Mechanics/Geomechanics Symposium, 28 June-1 July 2015, San Francisco, CA USA.