

# Wellbore Leakage Mitigation Using Advanced Mineral Precipitation Strategies

Project Number DE-FE0026513

Adrienne Phillips, Al Cunningham, Robin Gerlach and  
Lee Spangler  
Montana State University

---

U.S. Department of Energy  
National Energy Technology Laboratory  
Mastering the Subsurface Through Technology, Innovation and Collaboration:  
Carbon Storage and Oil and Natural Gas Technologies Review Meeting  
August 16-18, 2016

# Presentation Outline

---

- Project Benefits
- Goals and Objectives
- Methodology
- Accomplishments to date
- Synergy opportunities
- Summary
- Organization chart
- Gantt Chart
- Bibliography

# Benefit to the Program

---

- Program Goal Addressed:
  - (1) Develop and validate technologies to ensure 99 percent storage permanence;
  - *“Develop and/or field-validate next-generation materials or methods for preventing or mitigating wellbore leakage in existing wells under a variety of pressure, temperature, and chemical conditions, and in the presence of CO<sub>2</sub>-saturated brine.”*

# Benefit to the Program

---

**The mineralization technologies here use low viscosity fluids to promote sealing allowing flow through small apertures, narrow leakage channels, and porous media. Promote sealing of fracture networks, mechanical components, cement gaps, and potentially the rock formation surrounding the wellbore.**

- Active enzyme as well as direct thermal hydrolysis of urea drive mineralization precipitation developing **engineered mineralization sealing at greater depths and higher temperatures** to “*prevent or remediate detected leaks in complicated environments under a variety of pressure, temperature, and chemical conditions*”.

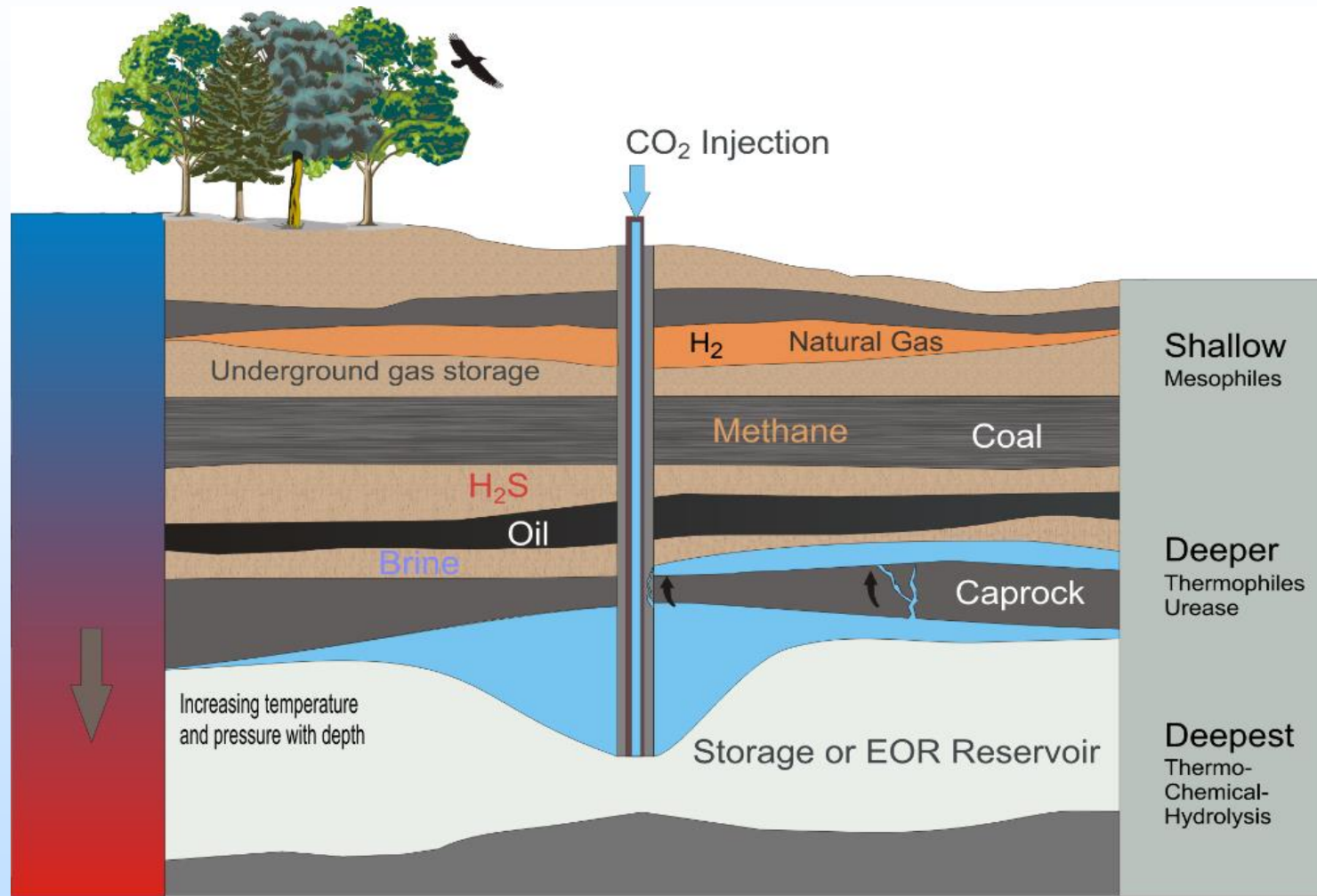
# Project Overview: Objectives

---

## Objectives

1. Develop robust urea hydrolysis-based mineral precipitation strategies for mitigating wellbore leakage.
2. Assess the resistance of precipitated mineral seals to challenges with CO<sub>2</sub> and brine.
3. Refine the existing Stuttgart Biomineralization Model to predict mineral precipitation resulting from advanced mineral precipitation strategies.
4. Perform field validation of the most appropriate mineral sealing technology in a well.

# Technical Status: Methodology



Advancing technologies for mitigating subsurface gas leakage

Risks: Wellbore or caprock- chemicals, fugitive methane, CO<sub>2</sub>, stored gas 6

# Mineralization Technology Application

Approx. Temperature Range		Urea Hydrolysis Mechanism	Typical Depth feet and (m)
20-45°C	68-113°F	Microbes ( <b>MICP</b> )	Less than 3,000 (<914 m)
30-80°C	86-158°F	Enzyme ( <b>EICP</b> )	Less than 6,500 (<1,981 m)
90-140°C	194-284°F	Thermal hydrolysis ( <b>TICP</b> )	8,000 to 13,000 (2,438 to 3,962 m)

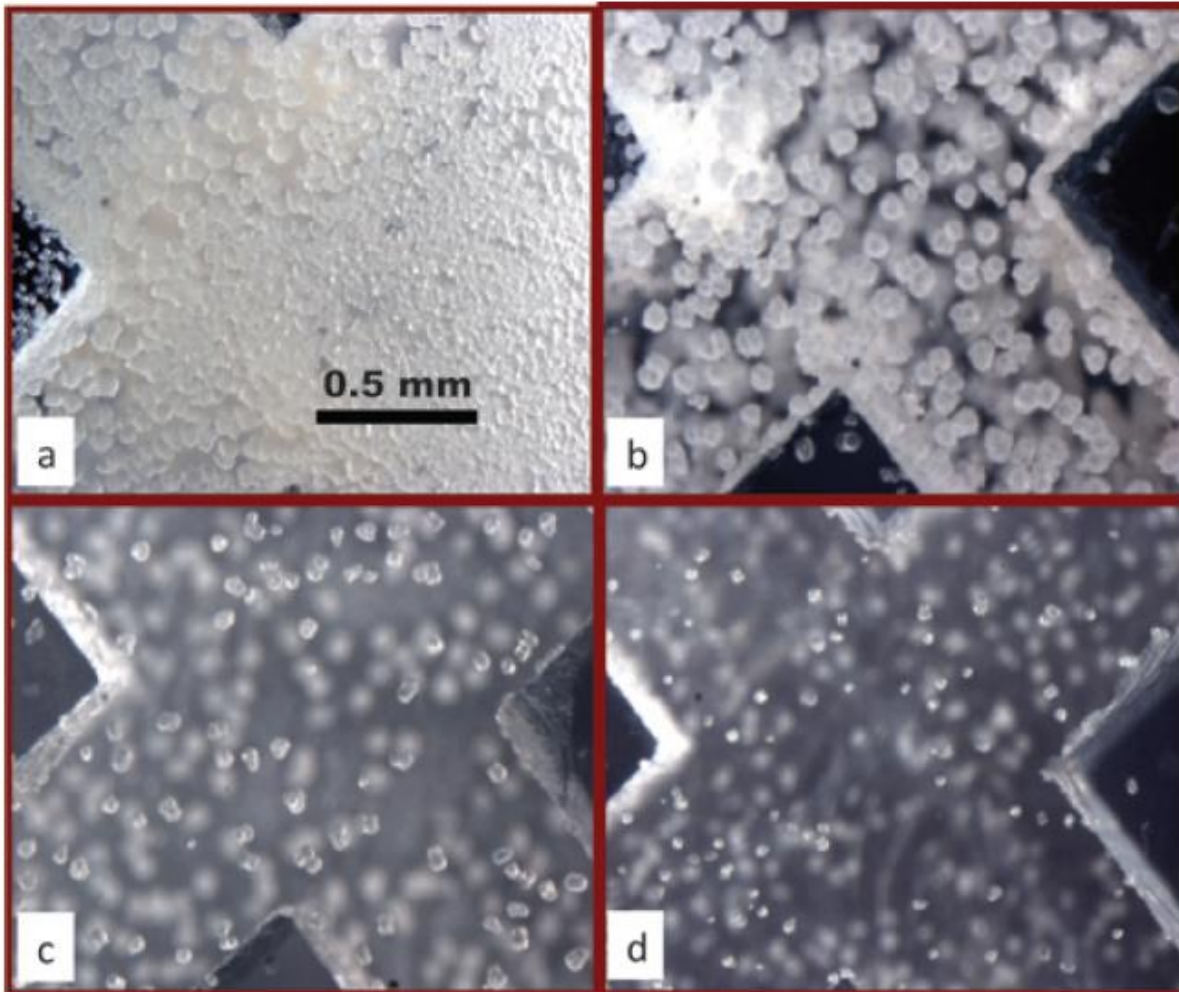
# Mineralization



- The enzyme **urease** hydrolyzes urea to form ammonium and carbonates, which increases alkalinity
- Thermal hydrolysis of urea can result in the same chemistry
- In the presence of  $\text{Ca}^{2+}$ , saturation can be exceeded and **calcium carbonate (calcite)** precipitates



# CaCO<sub>3</sub> in Pore Space



SCHULTZ, L.; PITTS, B.; MITCHELL, A.C.; CUNNINGHAM, A.B.;  
GERLACH, R. (2011). *Microscopy Today*. September 2011:10-13.

# Accomplishments to date: Objective 1,3

---

*Objective 1. Develop robust urea hydrolysis-based mineral precipitation strategies for mitigating wellbore leakage.*

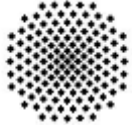
*Objective 3. Refine the existing Stuttgart Biomineralization Model to predict mineral precipitation resulting from advanced mineral precipitation strategies.*

Experiments to date:

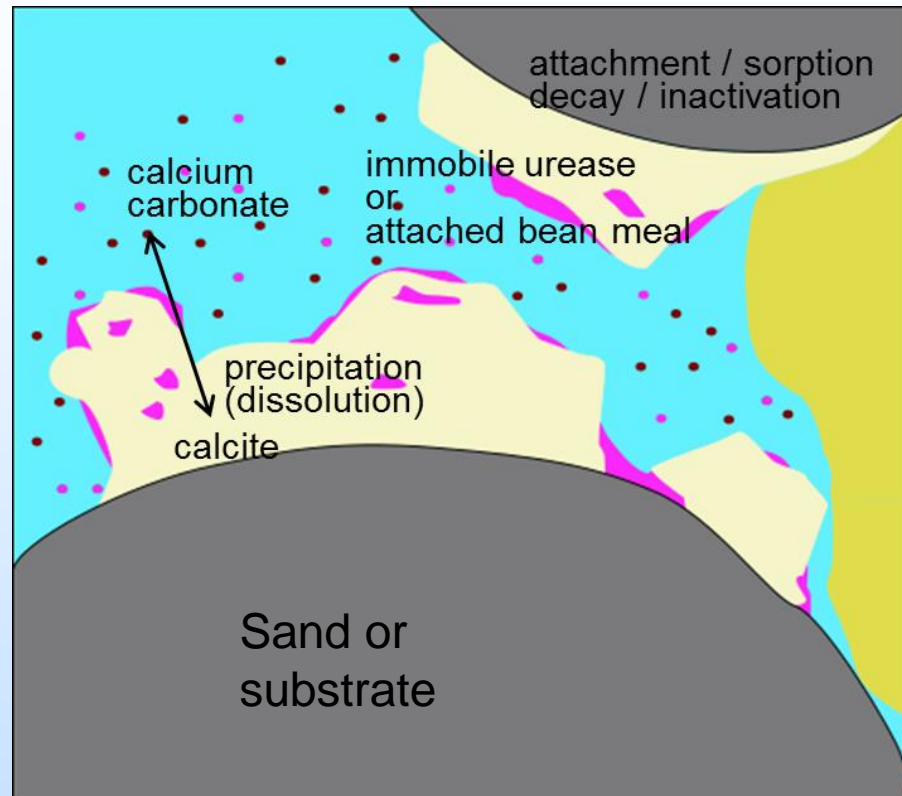
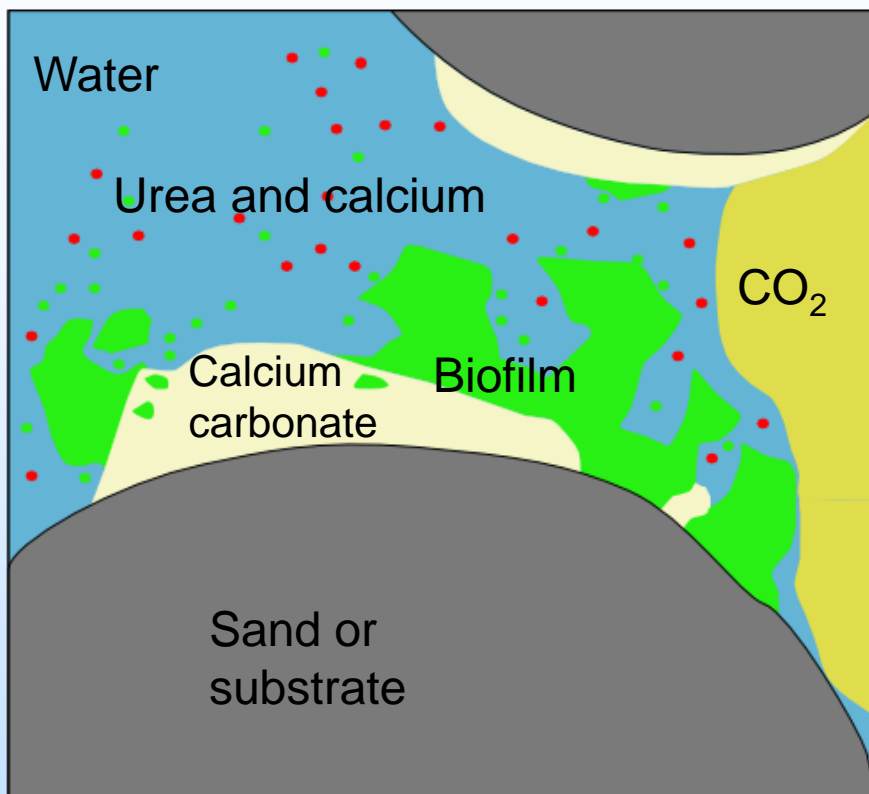
- Kinetics of urea hydrolysis under temperature, pressure and chemical conditions congruent with subsurface applications (EICP and TICP)
- Develop injection strategies to control mineral precipitation

Model to date:

- Update code to utilize kinetic parameters



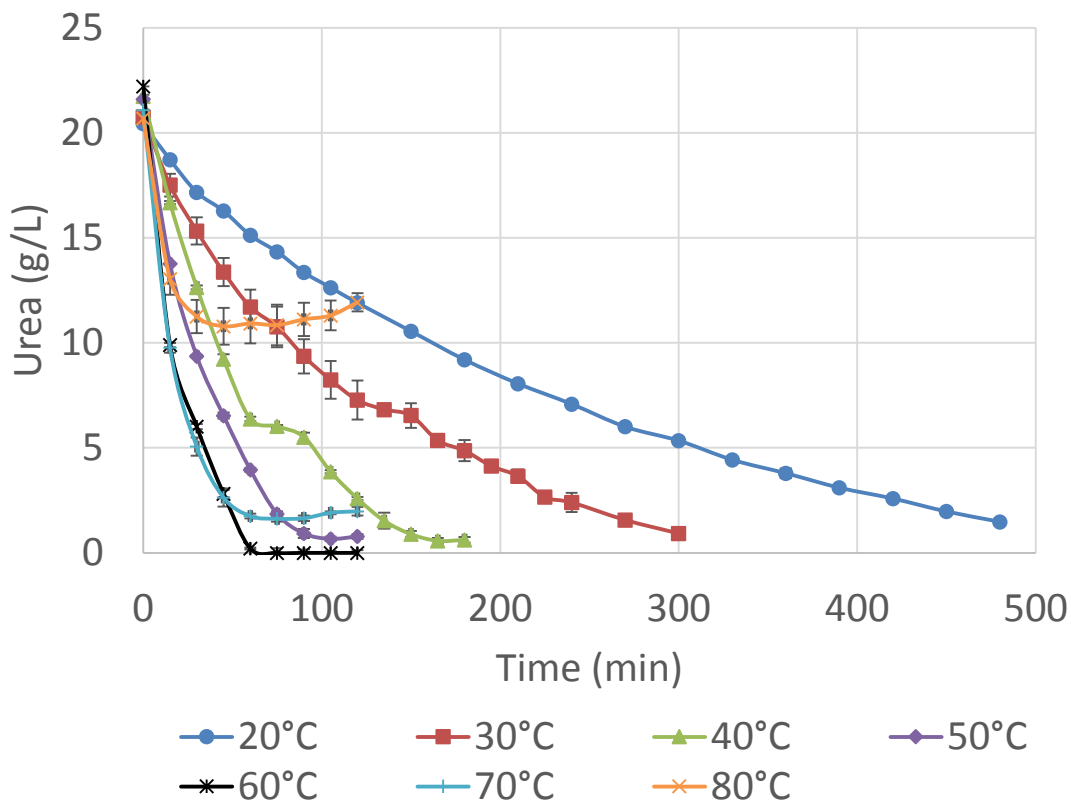
# MICP to EICP Model



- Ebigbo A.; Phillips, A.; Gerlach, R.; Helmig, R.; Cunningham, A.B.; Class, H.; Spangler, L. (2012): Darcy-scale modeling of microbially induced carbonate mineral precipitation in sand columns. *Water Resources Research*. 48, W07519, doi:[10.1029/2011WR011714](https://doi.org/10.1029/2011WR011714).
- Hommel, J.; Lauchnor, E.; Phillips, A.J.; Gerlach, R.; Cunningham, A.B.; Helmig, R.; Ebigbo, A.; Class, H. (2015): A revised model for microbially induced calcite precipitation - improvements and new insights based on recent experiments. *Water Resources Research*. 51(5):3695–3715. doi:[10.1002/2014WR016503](https://doi.org/10.1002/2014WR016503)

# JACK BEAN UREASE KINETICS & RATES

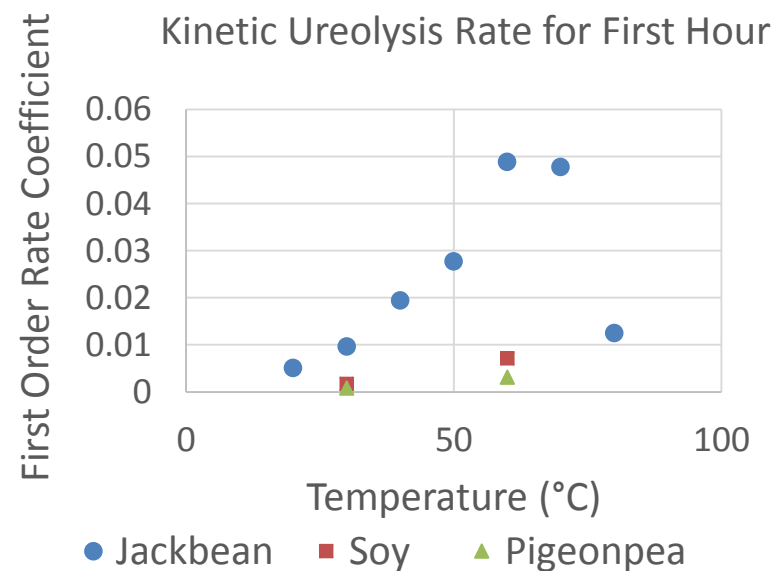
JB Urea Hydrolysis between 20-80°C



❖ Optimum JB urea hydrolysis at 60°C

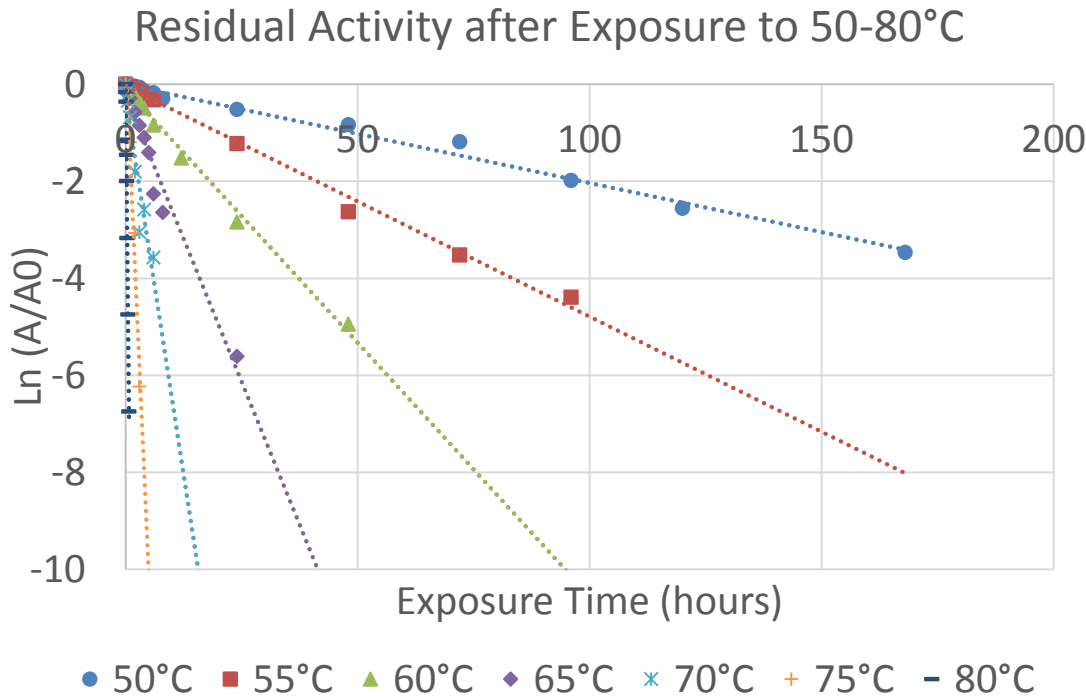
- < 60°C = longer to hydrolyze
- > 50°C = thermal inactivation of enzyme

Kinetic Ureolysis Rate for First Hour



Marnie Feder, Adrienne Phillips, Vincent Morasko, Robin Gerlach (In Prep) Plant-based ureolysis kinetics and urease inactivation at elevated temperatures for use in engineered mineralization applications

# JB UREASE INACTIVATION



$$\ln \left( \frac{A}{A_0} \right) = k_d t_{exp}$$

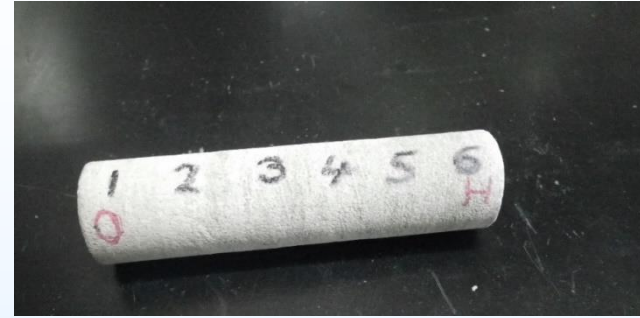
JB urease thermal inactivation > 50°C, with > 97% inactivation occurring after:

- 168 hours at 50°C
- 48 hours at 60°C
- 5 hours at 70°C
- 3 hours at 75°C

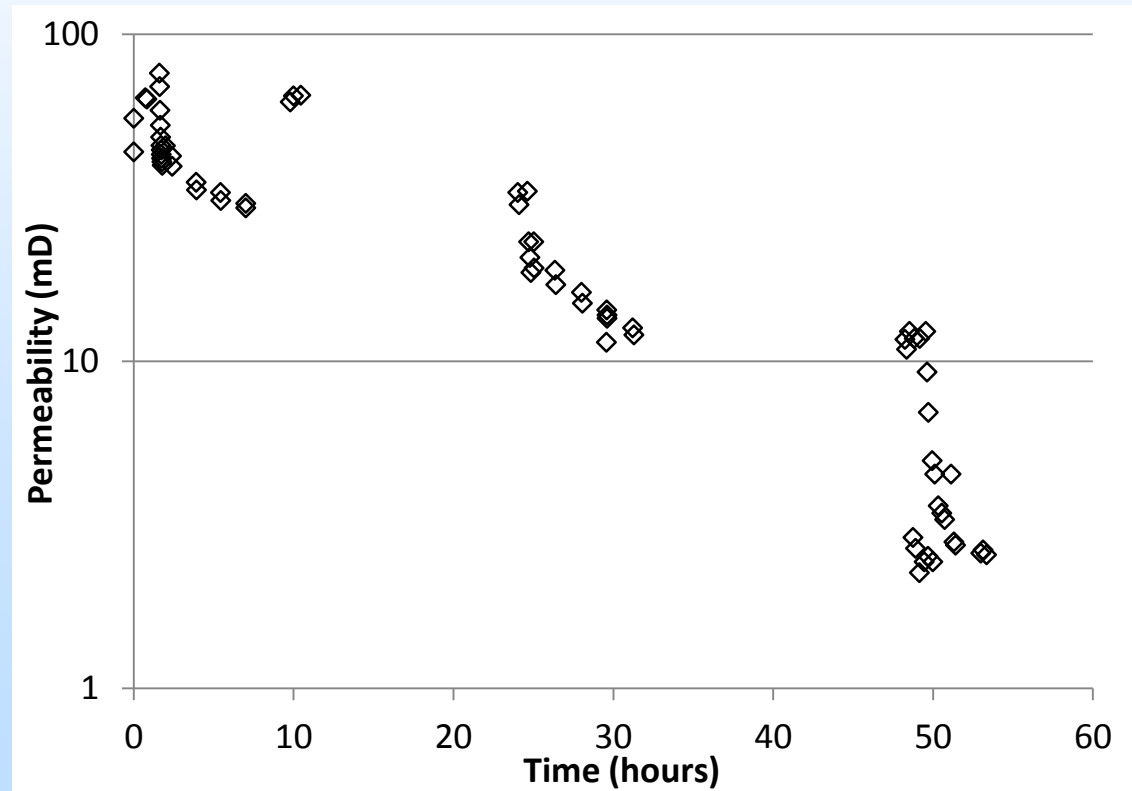
Point to need to control temperature during injection

*Other decay models (biexponential) being explored*

# ENZYME MINERALIZATION- EICP

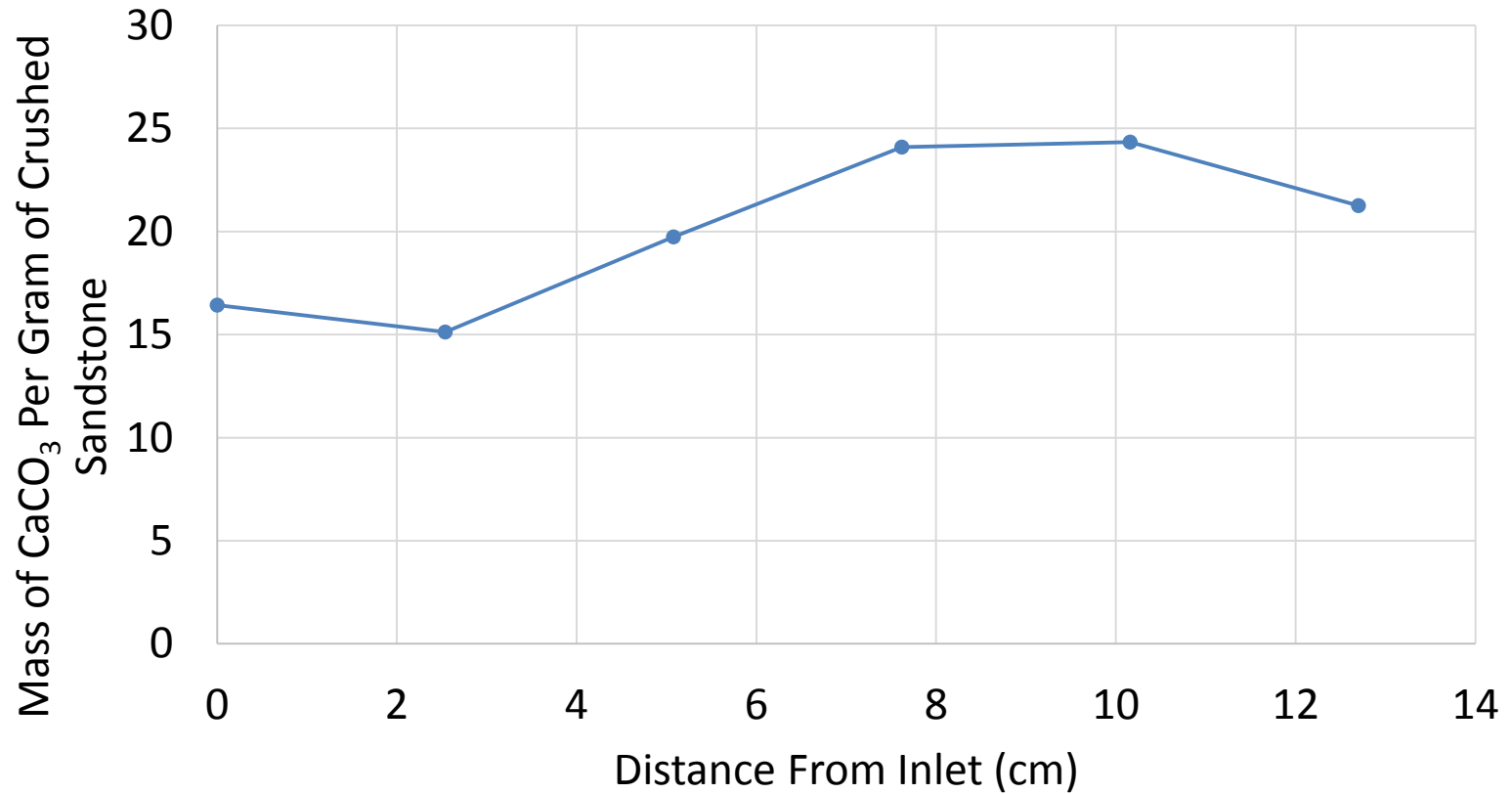


63 to 2.4 mD in  
three days  
100 g/L NaCl  
200 psi  
60°C



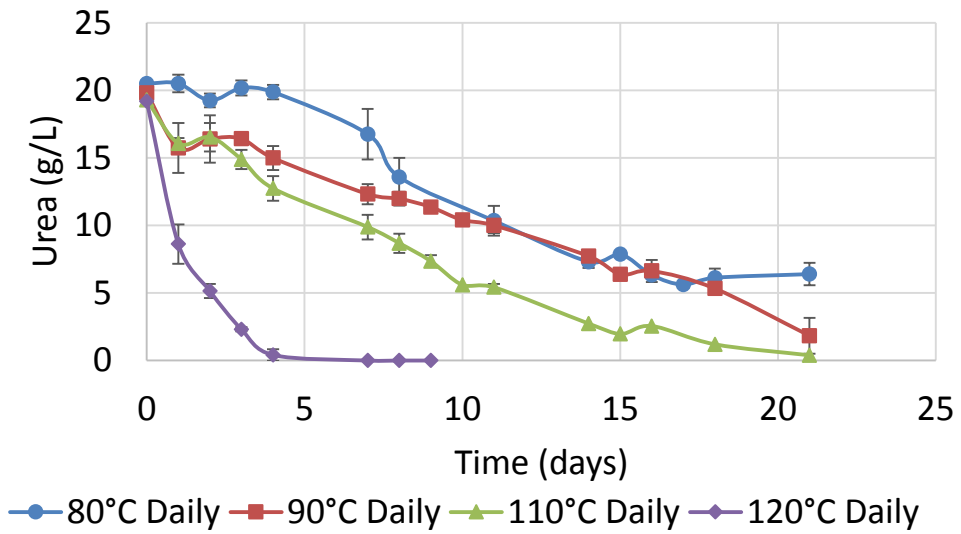
# ENZYME MINERALIZATION- EICP

## Distribution of $\text{CaCO}_3$ Along Core Length



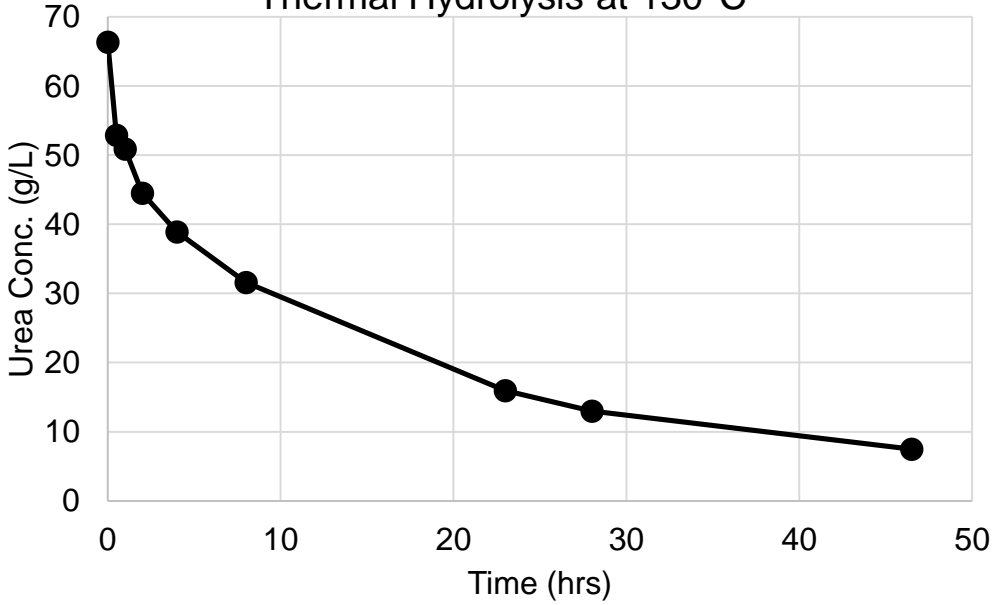
# THERMAL UREOLYSIS- TICP

### Thermal Ureolysis between 80-120°C



- ❖ Enzyme limited to Temps < 80°C
- ❖ Direct thermal heat used to drive mineral precipitation > 80°C
  - 120°C hydrolyzes 20 g/L urea in 6 days
  - 80-110°C hydrolyzes urea in ~ 21 days
  - 130°C hours instead of days

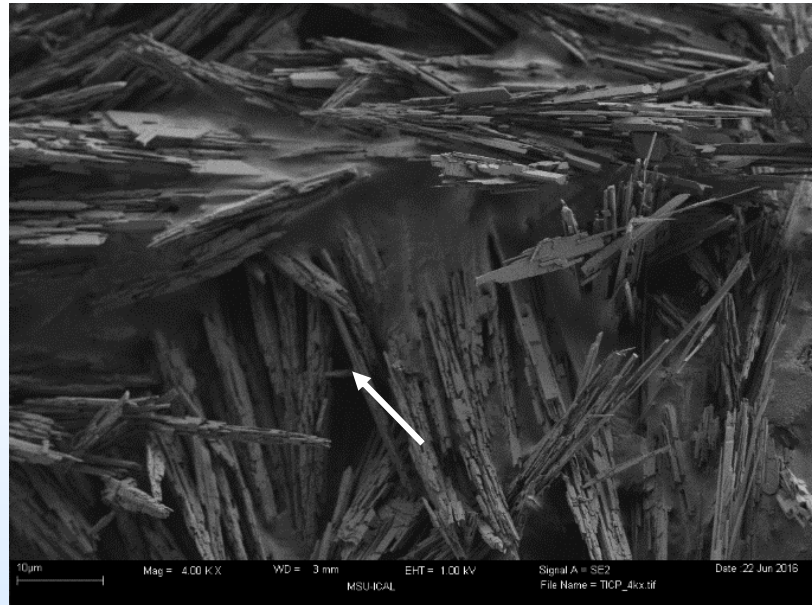
### Thermal Hydrolysis at 130°C



Increase urea and calcium concentrations for increased precipitation



# THERMAL HYDROLYSIS- TICP



# Synergy Opportunities

Mesoscale high pressure vessel for scale up work – radial flow, samples up to ~70 cm diameter, ~50 cm height



Phillips, AJ, Eldring, J, Hiebert, R, Lauchnor, E, Mitchell, AC, Gerlach, R, Cunningham, A, and Spangler, L. High pressure test vessel for the examination of biogeochemical processes. *J. Petrol. Sci. Eng.* 126, February 2015:55-62, DOI: [10.1016/j.petrol.2014.12.008](https://doi.org/10.1016/j.petrol.2014.12.008)

Designed and built by Joe Eldring & Alaskan Copper, Seattle, WA, USA

# Synergies (and Synergy Opportunities)

- Additional R&D projects:
  - Methods to enhance well bore cement integrity with microbially-induced calcite precipitation (MICP) – Montana State University et al. (DE-FE0024296)
- Possible synergies with other NETL & FE projects, e.g.
  - Wellbore Seal Repair Using Nanocomposite Materials - University of New Mexico - John Stormont (DE- FE0009562)
  - Programmable Sealant-Loaded Mesoporous Nanoparticles for Gas/Liquid Leakage Mitigation - C-Crete Technologies, LLC – Rice University Rouzbah Shasavari (DE-FE0026511)
  - Bill Carey (LANL) - Wellbore and Seal Integrity
  - Others

# SUMMARY & FUTURE

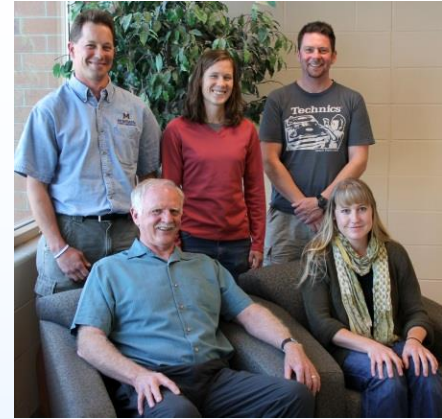
## Summary

- JB urease kinetics determined between 20-80°C, 60°C optimum temperature
- JB urease determined to become thermally inactivated: 75°C within a few hours to over a week at 50°C
- Permeability reduction, Ca in EICP mineralized core
- Thermal hydrolysis of urea > 80°C

## Current efforts: EICP and TICP

- Modelling- modifying code
- Mineralization strength
- Challenges to CO<sub>2</sub> and brine- in progress
- Field characterization and plan

# Acknowledgements



## Collaborators

Robin Gerlach, Al Cunningham, Ellen Lauchnor, Lee Spangler, Joe Eldring, James Connolly, Logan Schultz, Marnie Feder, Laura Dobeck, Montana State University  
Randy Hiebert, Montana Emergent Technologies  
Jim Kirksey, Wayne Rowe, Schlumberger  
Bart Lomans, Joe Westrich, Shell  
Richard Esposito, Southern Company  
Pete Walsh, University of Alabama Birmingham  
Anozie Ebigo, Johannes Hommel, Holger Class, and Rainer Helmig, University of Stuttgart  
Andrew Mitchell, Aberystwyth University

## Supporters

Dayla Topp, Josh Stringam, Adam Rothman, John Barnick, Neerja Zambare, Eric Troyer, Abby Thane, Cody West, Sam Zanetti, Brooke Filanoski, Drew Norton, CBE, ERI



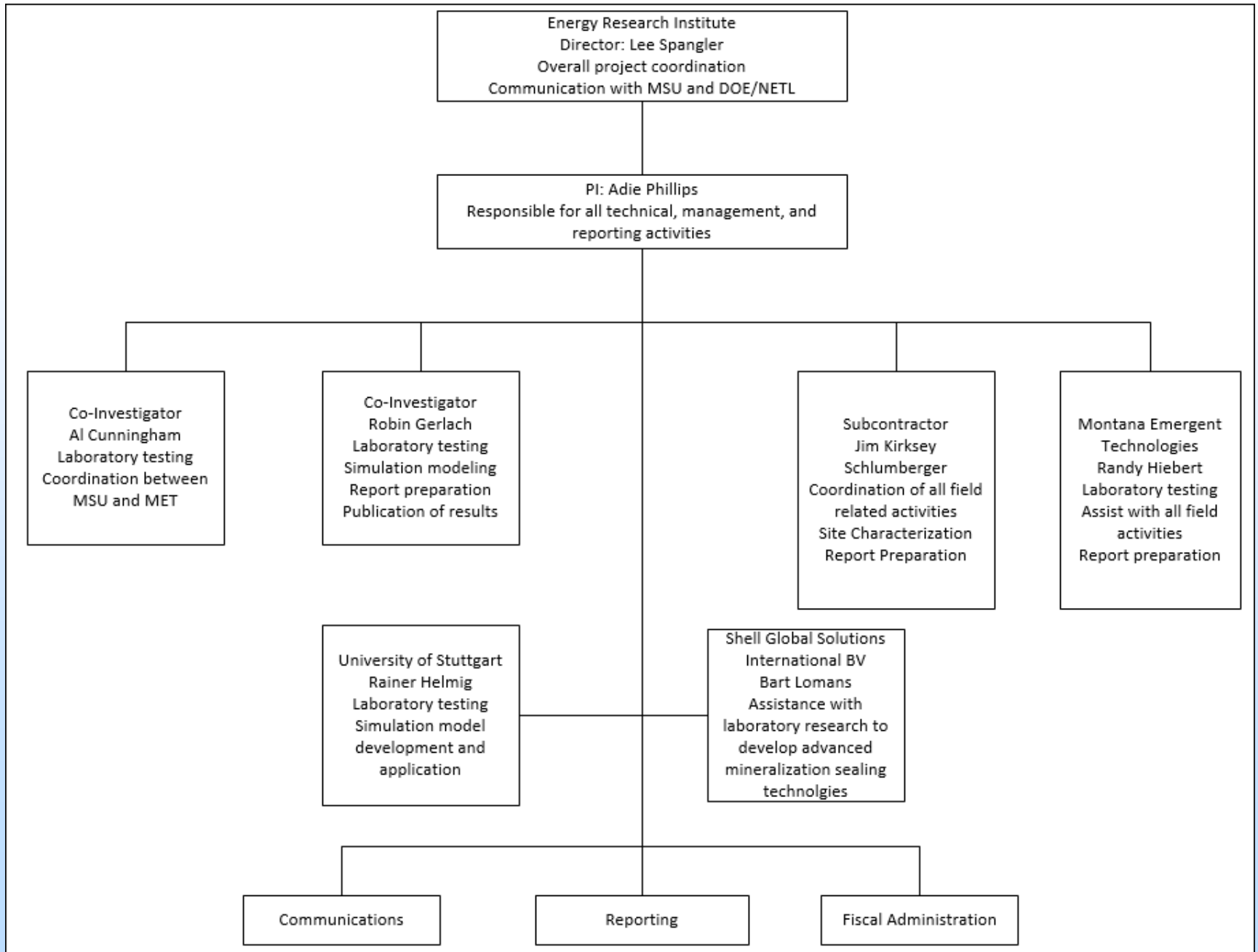
[adrienne.phillips@montana.edu](mailto:adrienne.phillips@montana.edu)

# Appendix

---

- These slides will not be discussed during the presentation, **but are mandatory**

# Organization Chart



# Gantt Chart

Project Title: Wellbore Leakage Mitigation Using Advanced Mineral Precipitation Strategies																																																									
Task Description	FY2016, Q1			FY2016, Q2			FY2016, Q3			FY2016, Q4			FY2017, Q1			FY2017, Q2			FY2017, Q3			FY2017, Q4			FY2018, Q1			FY2018, Q2			FY2018, Q3			FY2018, Q4			FY2019, Q1			FY2019, Q2			FY2019, Q3			FY2019, Q4											
	Oct-15	Nov-15	Dec-15	Jan-16	Feb-16	Mar-16	Apr-16	May-16	Jun-16	Jul-16	Aug-16	Sep-16	Oct-16	Nov-16	Dec-16	Jan-17	Feb-17	Mar-17	Apr-17	May-17	Jun-17	Jul-17	Aug-17	Sep-17	Oct-17	Nov-17	Dec-17	Jan-18	Feb-18	Mar-18	Apr-18	May-18	Jun-18	Jul-18	Aug-18	Sep-18	Oct-18	Nov-18	Dec-18	Jan-19	Feb-19	Mar-19	Apr-19	May-19	Jun-19	Jul-19	Aug-19	Sep-19									
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48										
<b>1.0 Project Management and Planning</b>																																																									
Milestone 1 Updated Management Plan		①																																																							
Milestone 2 Kickoff Meeting		②																																																							
<b>2.0 Laboratory investigation to develop and evaluate enhanced mineral sealing</b>																																																									
Milestone 3 Complete modification of the high pressure systems				③																																																					
Milestone 5 Complete development of field test protocol																																																									
Milestone 6 Complete field test																																																									
2.1 Develop and test laboratory systems for performing mineral sealing experiments																																																									
2.2 Develop protocols for forming mineral seals in rock cores																																																									
2.3 Assess the resistance of precipitated mineral seals to challenges with supercritical CO2-saturated brine																																																									
<b>3.0 Refine the existing Stuttgart Biomineralization Model to predict mineral precipitation resulting from alternative mineral precipitation strategies</b>																																																									
3.1 Modify the existing code to simulate mineral precipitation																																																									
3.2 Use the model to make field predictions of mineralization sealing scenarios at the Danielson well site																																																									
<b>4.0 Perform field test and evaluation of appropriate mineral sealing technology at the Danielson well site</b>																																																									
Milestone 4 Complete well characterization and preparation																																																									
Milestone 7 Conduct field test to evaluate mineralization seal																																																									
Milestone 8 Complete evaluation of all field and laboratory test results																																																									
4.1 Conduct initial field characterization activities at the Danielson well site																																																									
4.2 Design the field injection strategy based on laboratory results and simulation																																																									
4.3 Perform mineralization sealing test at the Danielson well and evaluate results																																																									
4.4 Evaluate the integrity of the mineralization seal																																																									

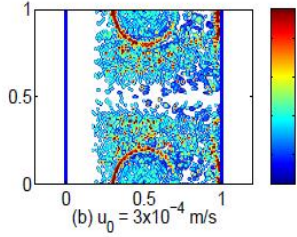


# Bibliography

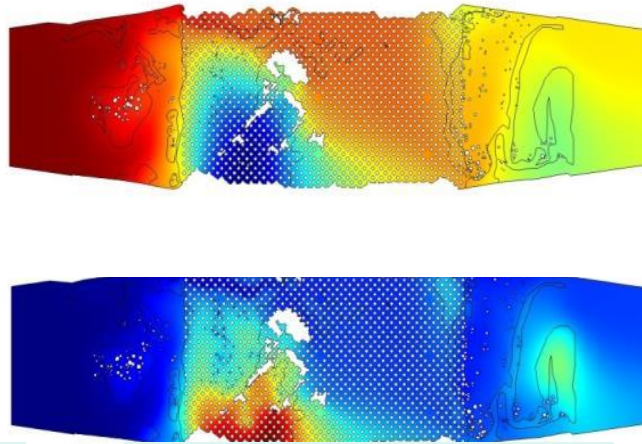
---

- Feder, M, Morasko, V, Gerlach, R, Phillips, AJ. Plant-based ureolysis kinetics and urease inactivation at elevated temperatures for use in engineered mineralization applications (*In preparation*)

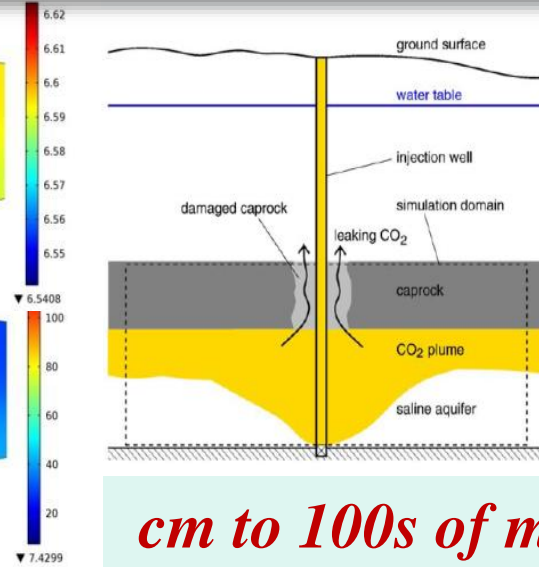
# Scale Up



*nm to cm*



*$\mu\text{m}$  to dm*



*cm to 100s of m*

