Montana Emergent Technologies

Wellbore Leakage Mitigation Using Advanced Mineral Precipitation Strategies

Project Number DE-FE0026513

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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
August 1-3, 2017

Presentation Outline

- Objectives of the project
- Technical Status
- Methodology
- Accomplishments to date
- Synergy opportunities
- Summary

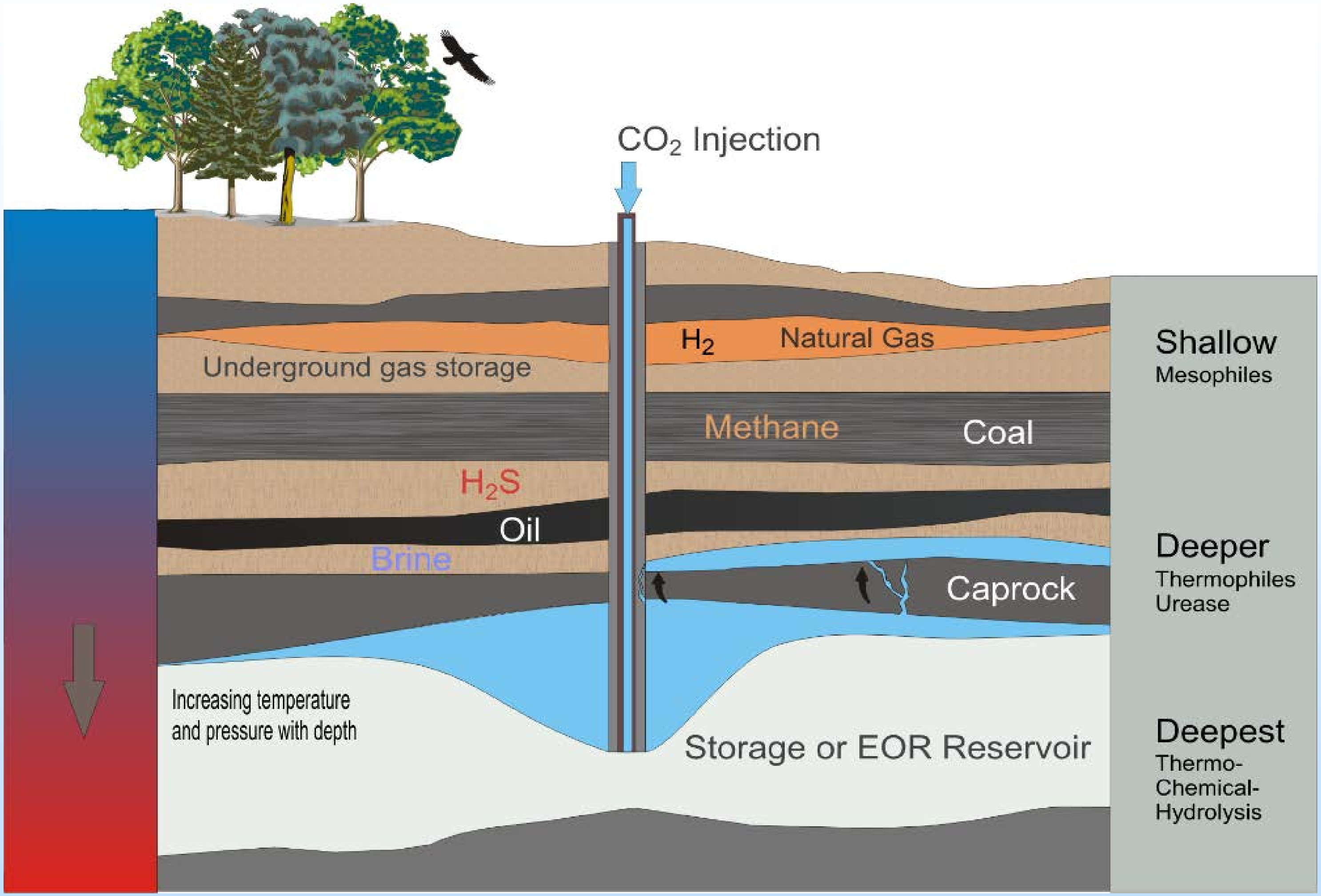
Project Overview: Objectives

MONTANA STATE UNIVERSITY Mountains & Minds
CENTER FOR BIOFILM ENGINEERING

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_2 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: <u>Wellbore</u> or caprock- chemicals, fugitive methane, CO_2, stored gas

Mineralization Technology Application

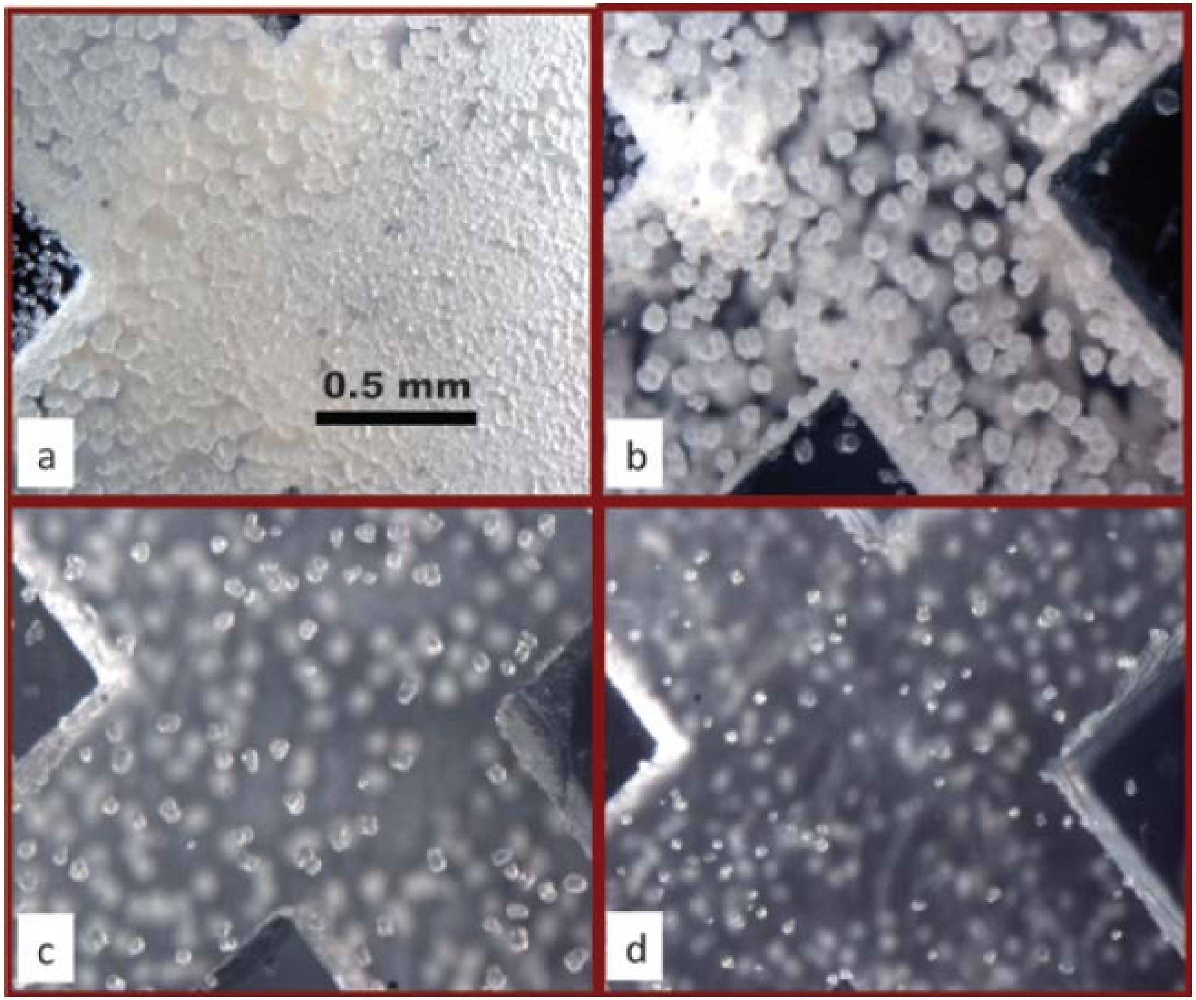
Approx. Temperature Range		**Urea Hydrolysis Mechanism**	**Typical Depth feet and (m)**
20-45°C	68-113°F	Microbes **(MICP)**	Less than 3,000 (<914 m)
30-80°C	86-158°F	Enzyme **(EICP)**	Less than 6,500 (<1,981 m)
90-140°C	194-284°F	Thermal hydrolysis **(TICP)**	8,000 to 13,000 (2,438 to 3,962 m)

Mineralization

$$(NH_2)_2CO + 2H_2O + Ca^{2+} \rightarrow 2NH_4^+ + CaCO_3$$

- 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 Ca^{2+}, saturation can be exceeded and calcium carbonate (calcite) precipitates

$CaCO_3$ in Pore Space



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

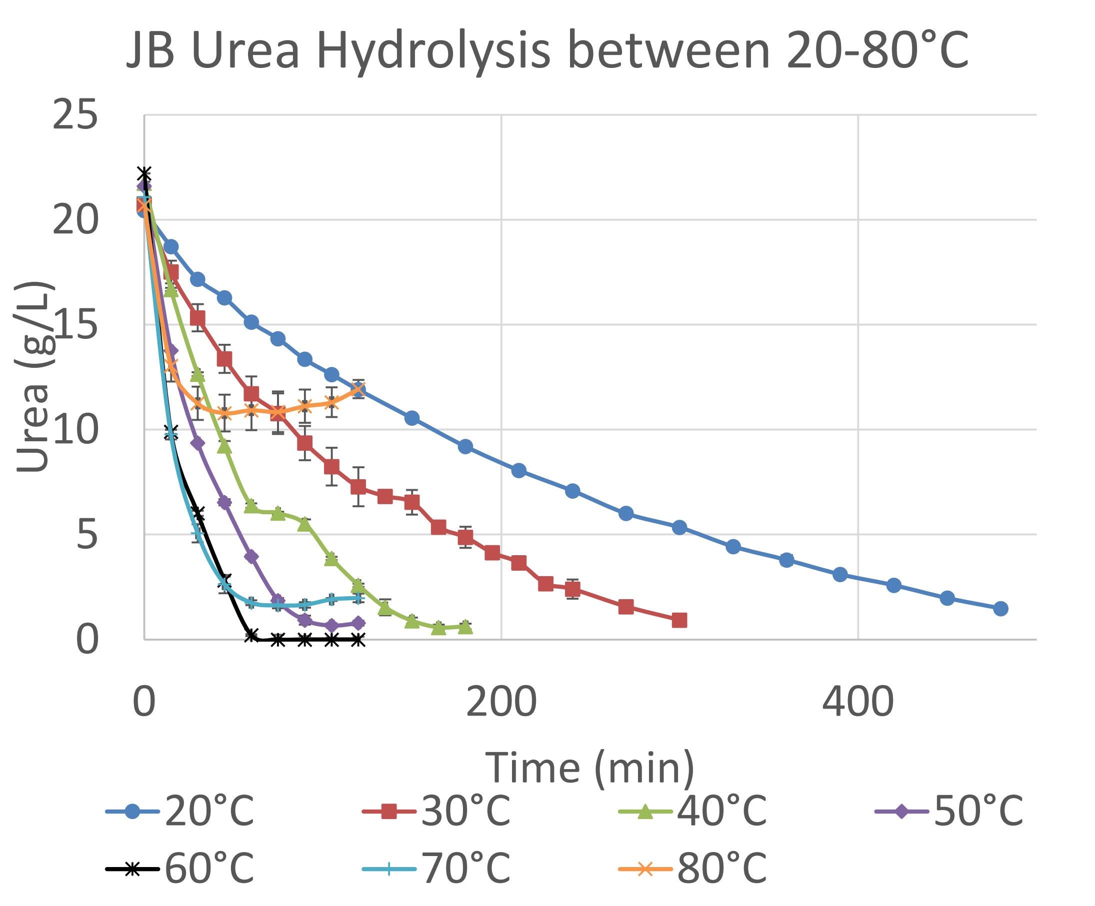
Accomplishments: Objective 1

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

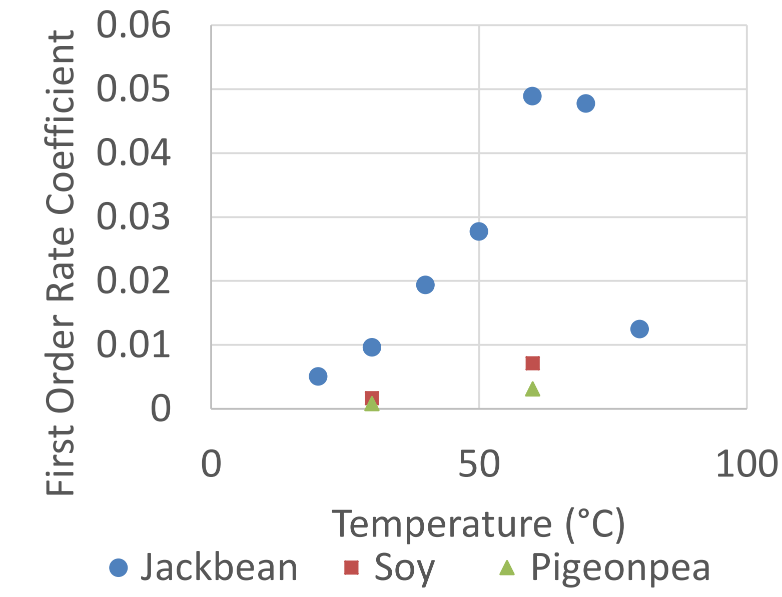
Experiments to date:

- Kinetics of urea hydrolysis under temperature, pressure and chemical conditions congruent with subsurface applications (EICP and TICP)
- Mathematical model of the urea hydrolysis rate and rate of inactivation of enzyme
- Develop injection strategies to control mineral precipitation
- Assess development of minerals other than calcite

JACK BEAN UREASE KINETICS



- Optimum JB urea hydrolysis at 60°C
  - < 60°C = longer to hydrolyze
  - > 60°C = thermal inactivation of enzyme



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

$E_N \underset{K_d}{\rightarrow} E_D$ – *First Order Inactivation*

$E_N \underset{k_1}{\rightarrow} E_I \underset{k_2}{\rightarrow} E_D$ – *Series Inactivation*

$E_N \underset{k_1}{\rightarrow} E_I$, $E_N \underset{k_3}{\searrow} E_D$, $E_I \underset{k_2}{\swarrow} E_D$ –*Series Parallel Inactivation*

E_N – *Native form*

E_I – *Active intermediate form*

E_D – *Deactivated form*

k_x – *Kinetic rate constant(s)*

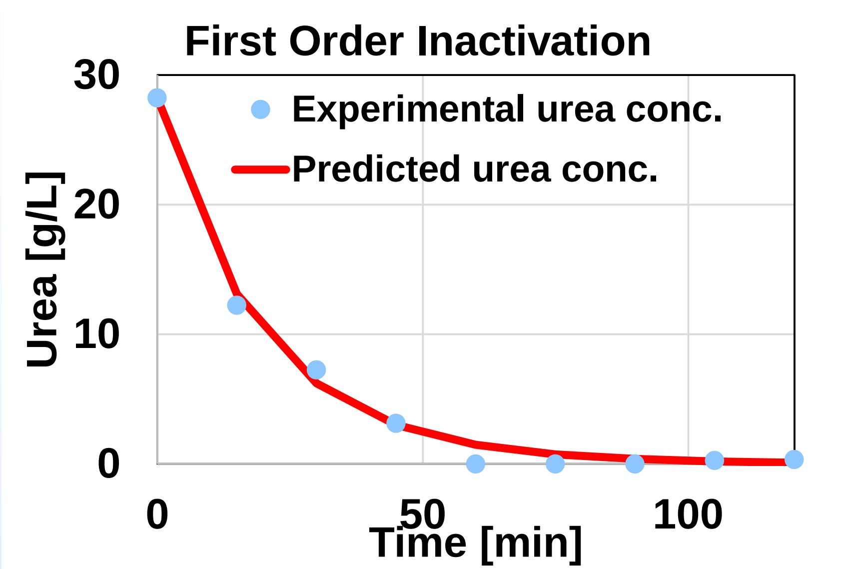
Overall rate equation: $\frac{\Delta Urea}{dt} = k_a(T) * [U_0] * [A(T)]$

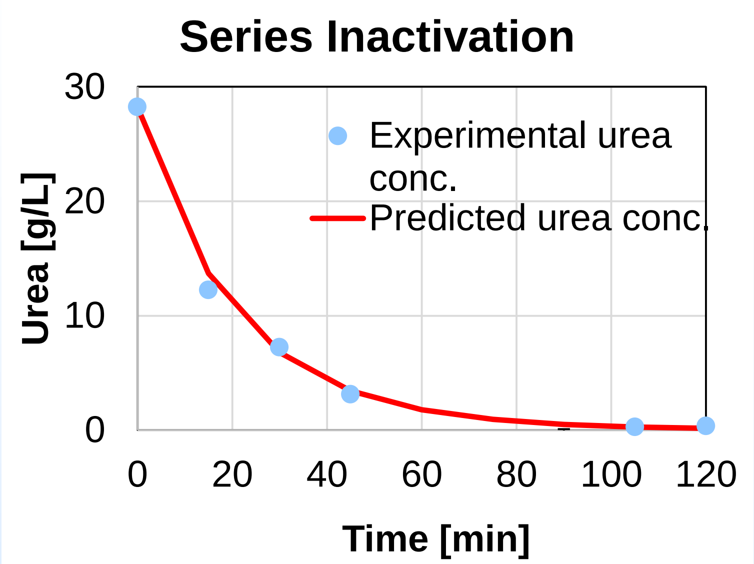
First order activity equation: $A(T) = \boldsymbol{e^{-k_d t}}$

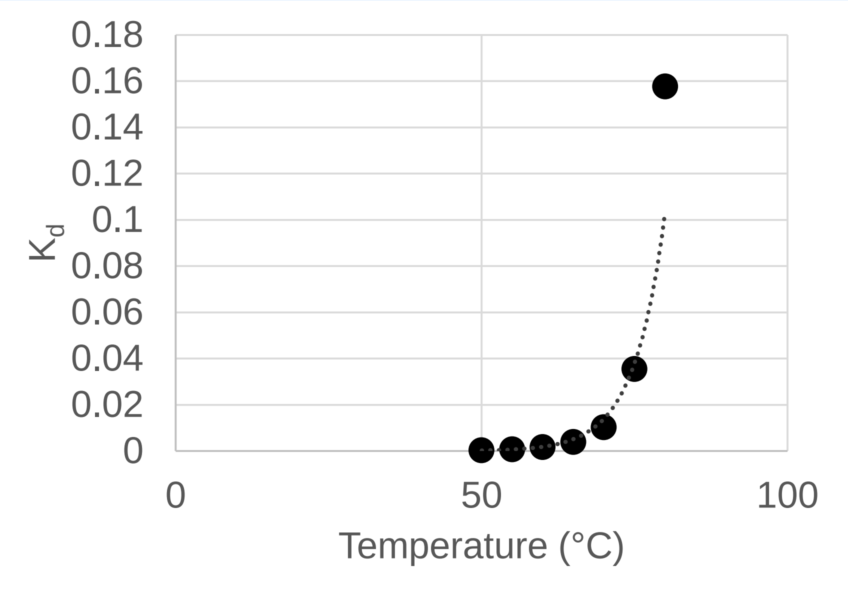
Series: $A(T) = \left(1 + \frac{\boldsymbol{\beta_1 k_1}}{\boldsymbol{k_2 - k_1}}\right) \boldsymbol{e^{-k_1 t}} - \frac{\boldsymbol{k_1 \beta_1}}{\boldsymbol{k_2 - k_1}} \boldsymbol{e^{-k_2 t}}$

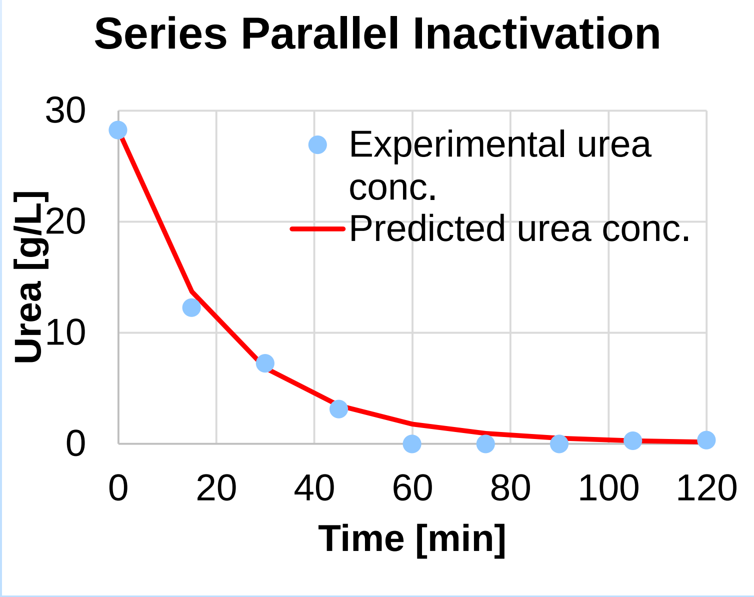
Series-parallel: $A(T) = \left(1 + \frac{\boldsymbol{\beta_1 k_1}}{\boldsymbol{k_2 - k_1 - k_3}}\right) \boldsymbol{e^{-(k_1 + k_3) t}} - \frac{\boldsymbol{k_1 \beta_1}}{\boldsymbol{k_2 - k_1 - k_3}} \boldsymbol{e^{-k_2 t}}$

JACK BEAN UREASE KINETICS & RATES

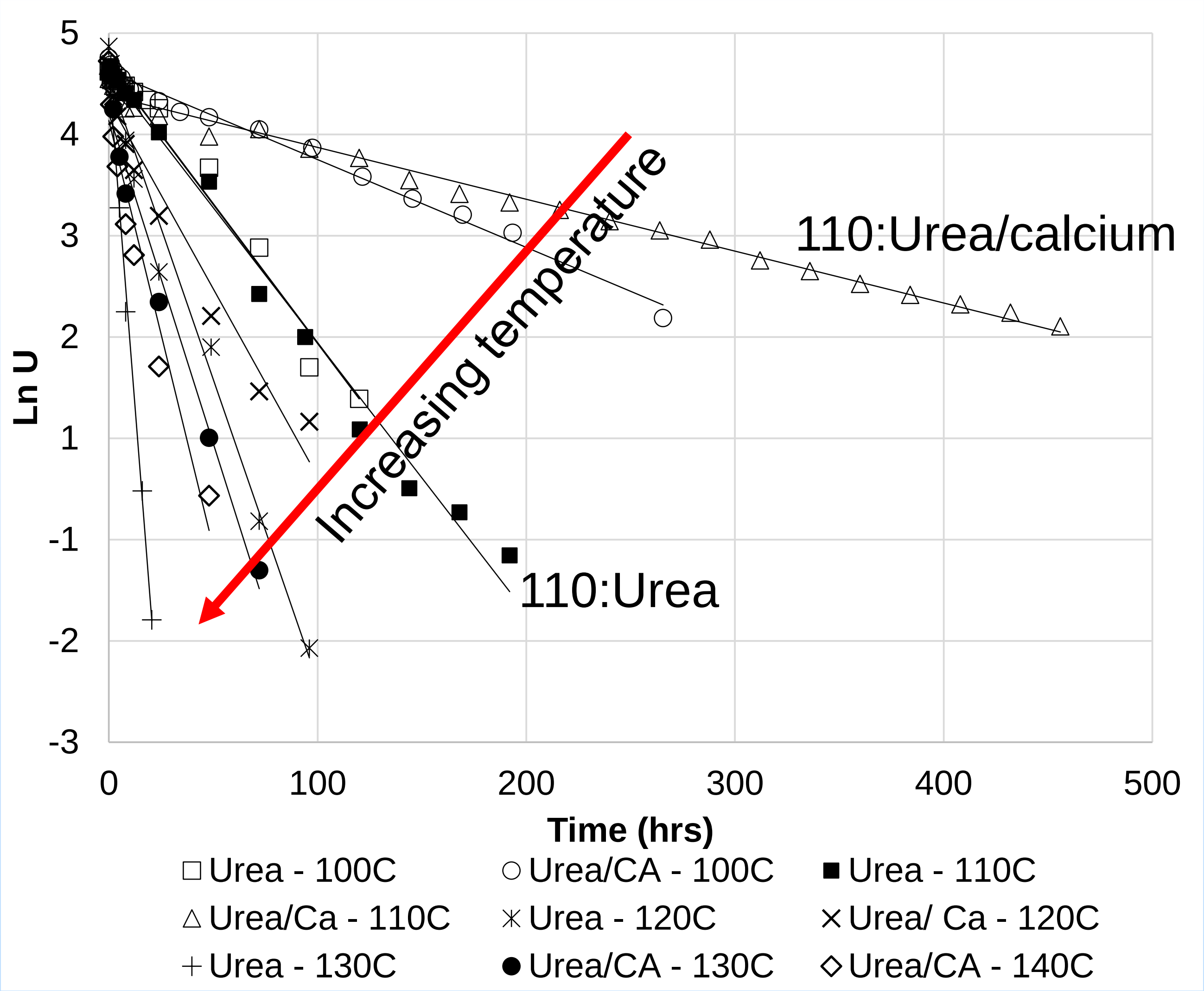








THERMAL UREOLYSIS- TICP



Enzyme < 80°C

Direct thermal heat = mineral precipitation (tested to 140°C)

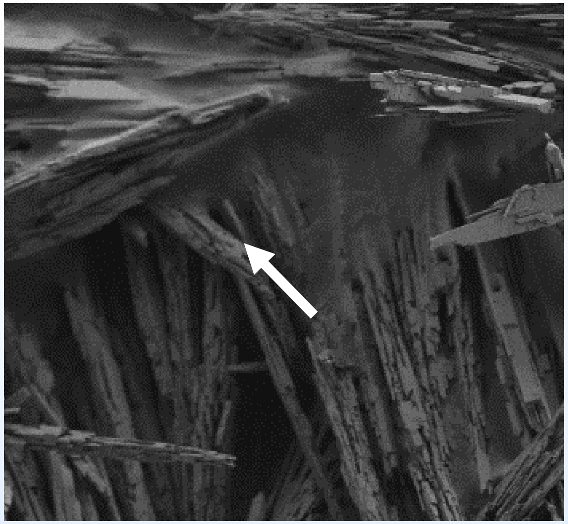
Hours instead of days

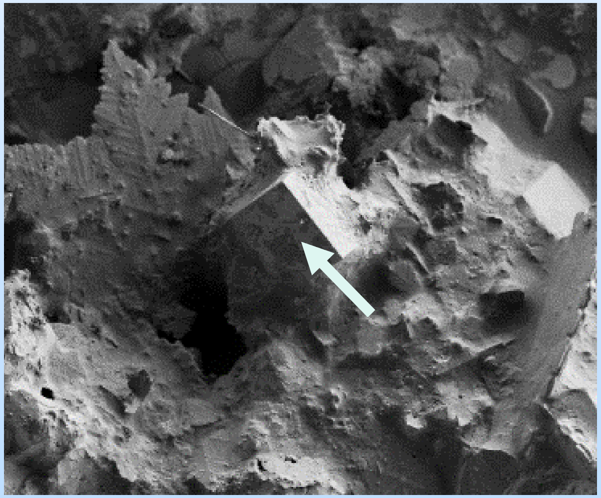
Rates of U vs. U/Ca

Increase [U/Ca] for increased precipitation

Injection Strategies

TICP- Column Systems





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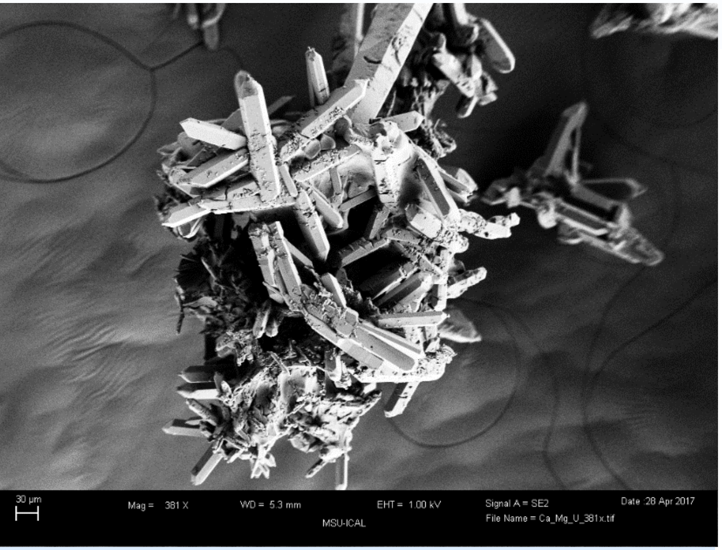
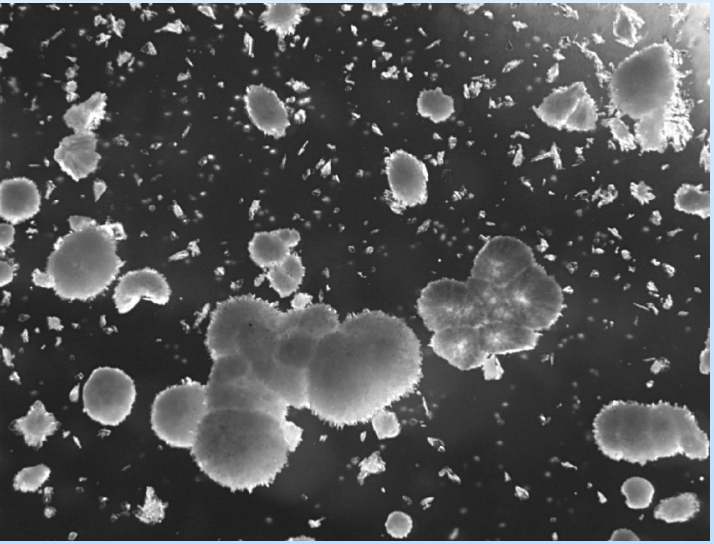
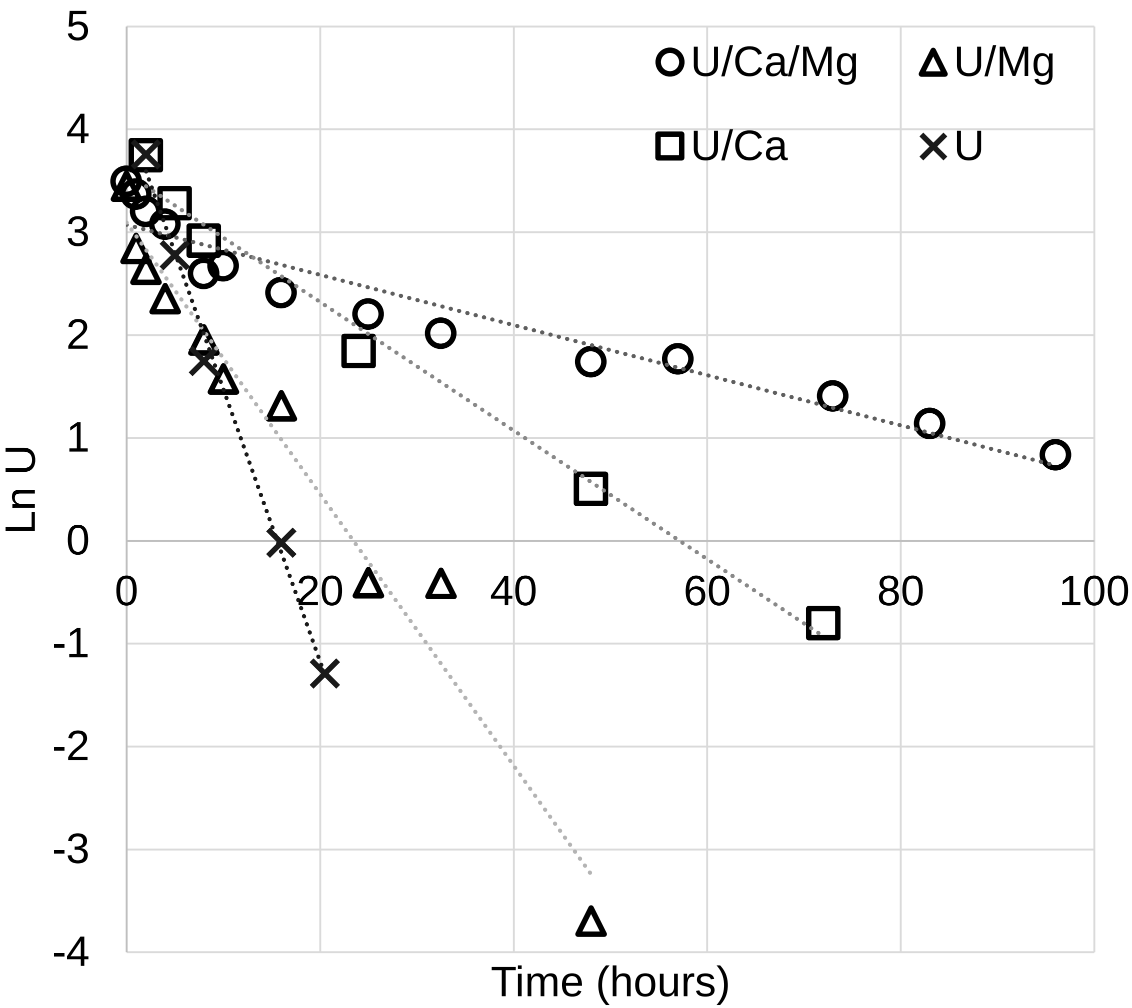
ALTERNATIVE MINERALS-TICP



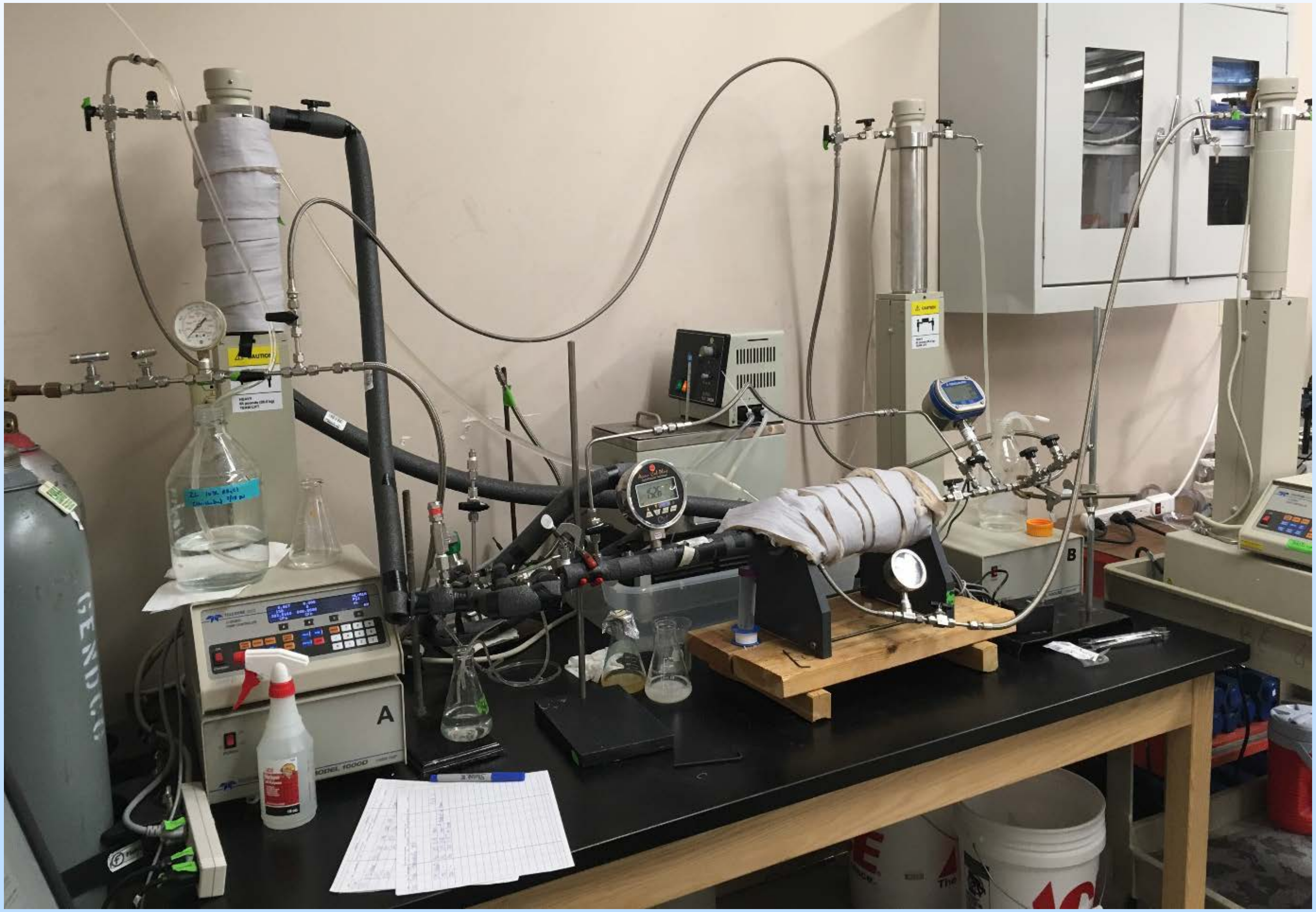




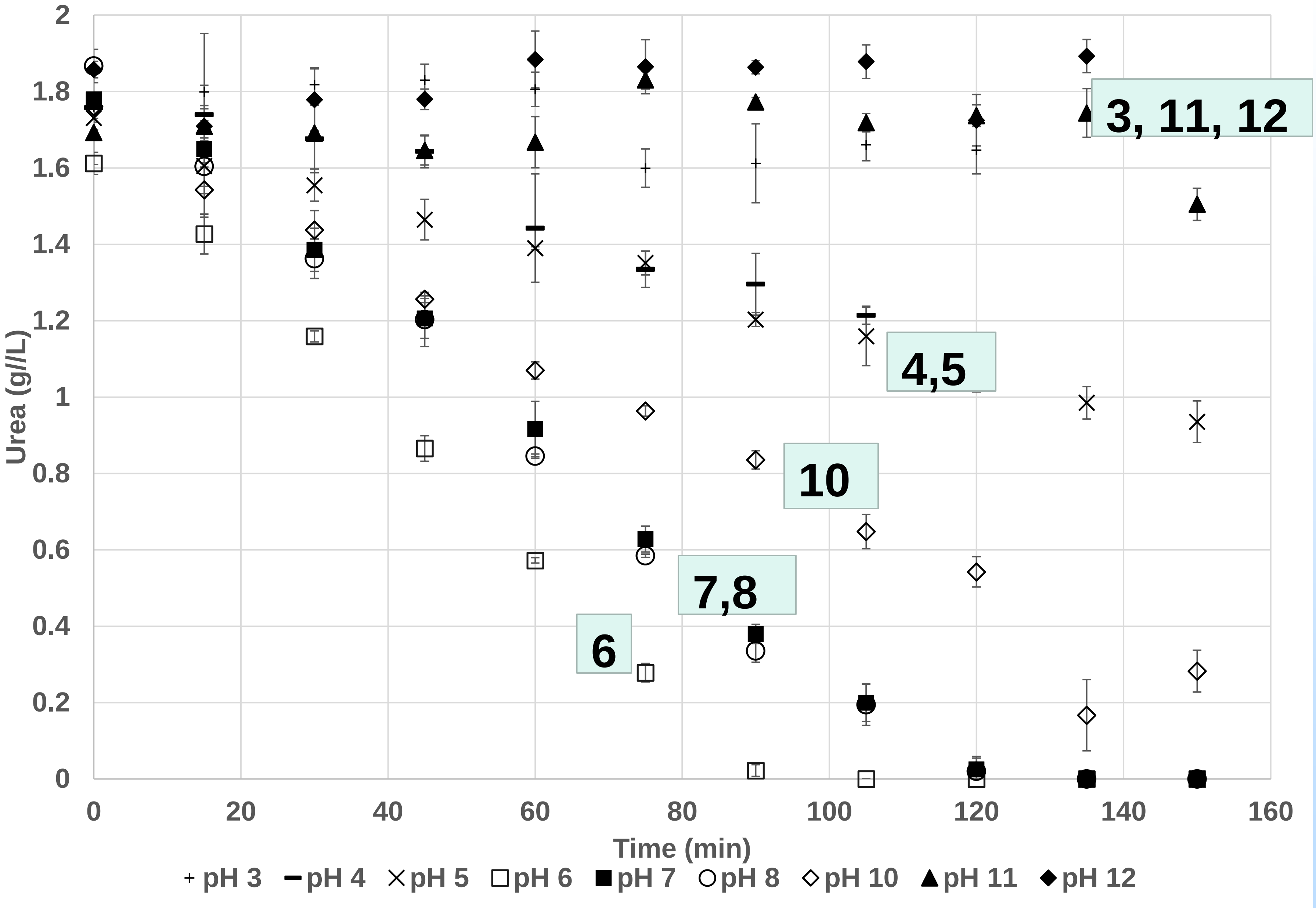
Accomplishments: Objective 2

Objective 2: Assess the resistance of precipitated mineral seals to challenges with CO_2 and brine.

Two core experiments- permeability and porosity reduction



Kinetics of ureolysis- JBM

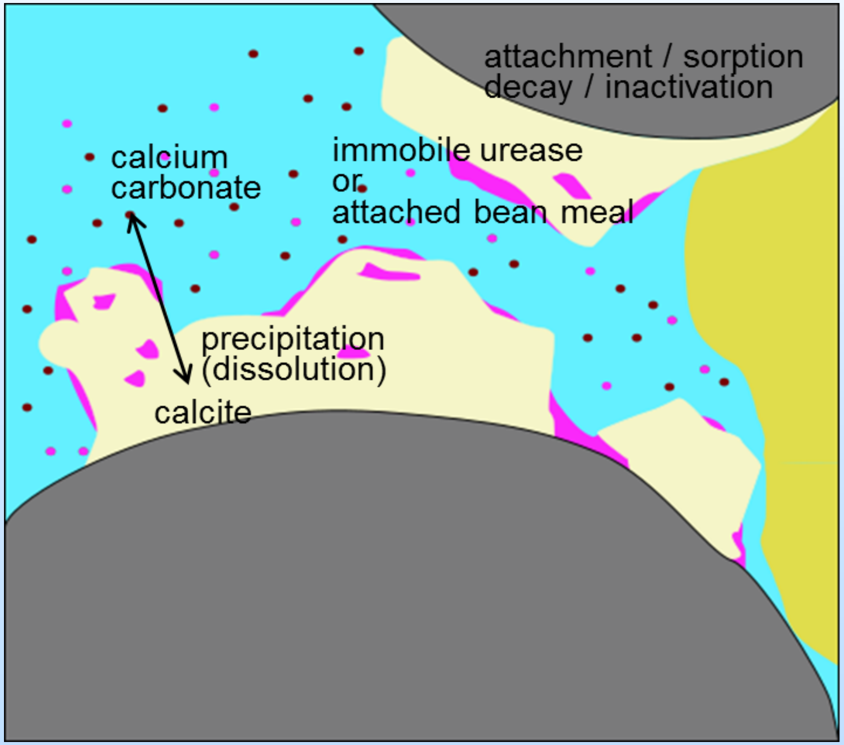


Accomplishments: Objective 3

Objective 3. Refine the existing biomineralization model to predict mineral precipitation resulting from advanced mineral precipitation strategies.

Model to date:

- Update code to utilize kinetic parameters
- Previous version- predicts field
- EICP model to predict new field



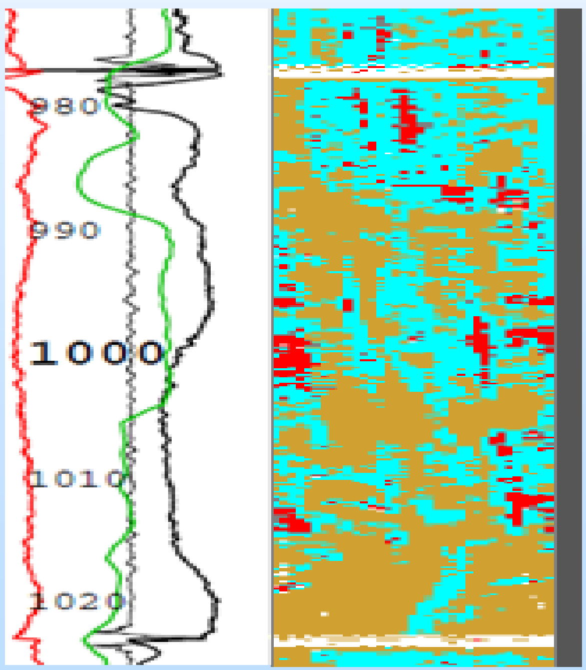
Hommel, J.; et al. (2015): A revised model for microbially induced calcite precipitation - improvements and new insights based on recent experiments. Water Resources Research. 51(5):3695–3715. doi:10.1002/2014WR016503

Accomplishments: Objective 4

Objective 4. Perform field validation of the most appropriate mineral sealing technology in a well.

Gorgas, Alabama

EICP

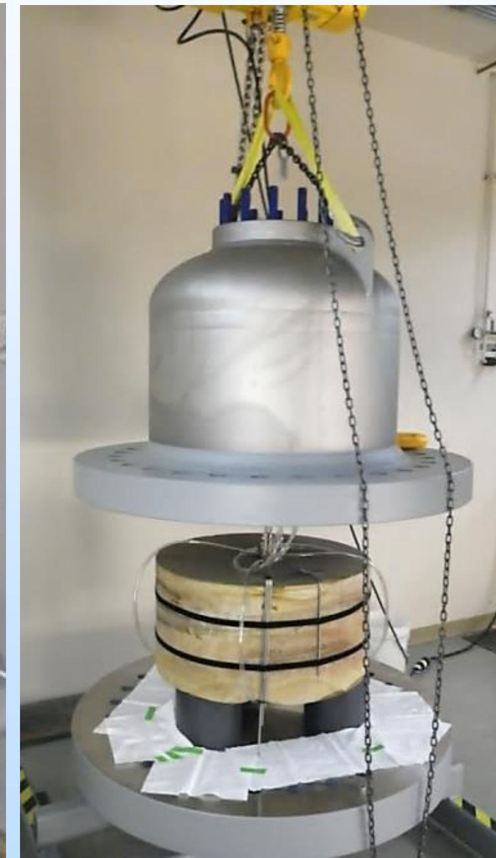


Synergies (and Synergy Opportunities)

- Additional R&D projects:
  - Methods to Enhance Wellbore Cement Integrity with Microbially-Induced Calcite Precipitation (MICP)- Montana State University DE-FE0024296
- Possible synergies with other NETL & FE projects, e.g.
  - Programmable Sealant-Loaded Mesoporous Nanoparticles for Gas/Liquid Leakage Mitigation - C-Crete Technologies, LLC – Rice University, Rouzbah Shasavari (DE-FE0026511)
  - Targeted Mineral Carbonation to Enhance Wellbore Integrity- University of Virginia, Dr. Andres Clarens (DE-FE0026582)
  - Nanoparticle Injection Technology for Remediating Leaks of CO_2 Storage Formation, University of Colorado Boulder, Yunping Xi
  - Bill Carey (LANL) - Wellbore and Seal Integrity
  - Others

Synergy Opportunities

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



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

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

Lessons Learned

- Mineralization needs to be expanded to higher temperature applications
  - Design of experiments to better understand the kinetics of reactions and how mineral forms
  - Scaling up the processes for field application

- Initial site identified- safety concerns with H_2S
  - Alternative well- now identified
  - Rely on Schlumberger for the challenges in field work, finding wells of opportunity

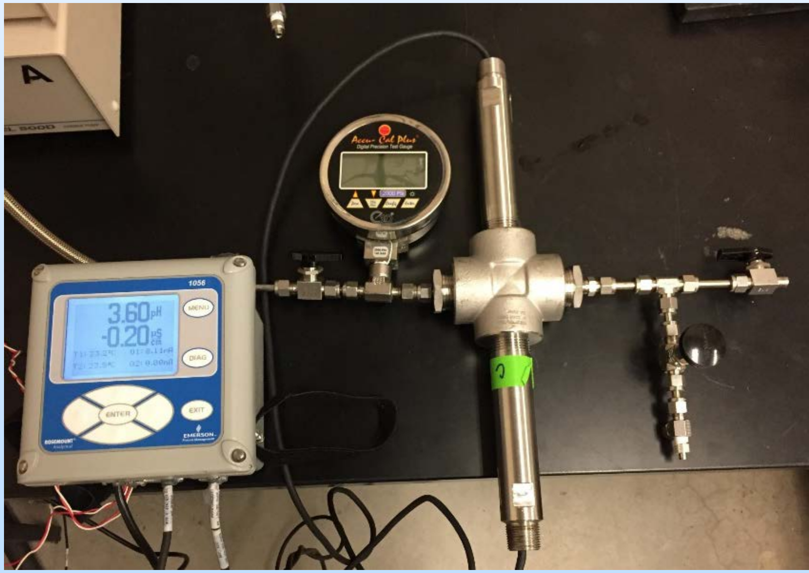
SUMMARY & FUTURE

Summary

- JB urease kinetics and inactivation
- Thermal hydrolysis of urea > 80°C
- Potential for minerals other than calcite
- Model updates- continue

Future EICP and TICP

- Mineralization material properties
  - MICP, EICP, TICP
- Challenges to CO_2 and brine
- 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**

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Richard Esposito, **Southern Company**

Pete Walsh, **University of Alabama Birmingham**

Anozie Ebigbo, Johannes Hommel, Holger Class, and Rainer Helmig, **University of Stuttgart**

Andrew Mitchell, Sara Edwards **Aberystwyth University**

Burt Todd, Leo Heath, Lee Richards**, Montana Tech**

Supporters: Dayla Topp, Josh Stringam, Adam Rothman, John Barnick, Neerja Zambare, Eric Troyer, Abby Thane, Cody West, Sam Zanetti, Brooke Filanoski, Drew Norton, Vinny Morasko, Zach Frieling, Arda Akyel, Kyle DeVerna, Dicle Beser **CBE, ERI**

Appendix

– These slides will not be discussed during the presentation, but are mandatory.

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_2-saturated brine.”*

Benefit to the Program

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

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

Project Overview: Goals and 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_2 and brine.
3. Refine the existing Stuttgart Biomineralization Model to predict mineral precipitation resulting from advanced mineral precipitation strategies.
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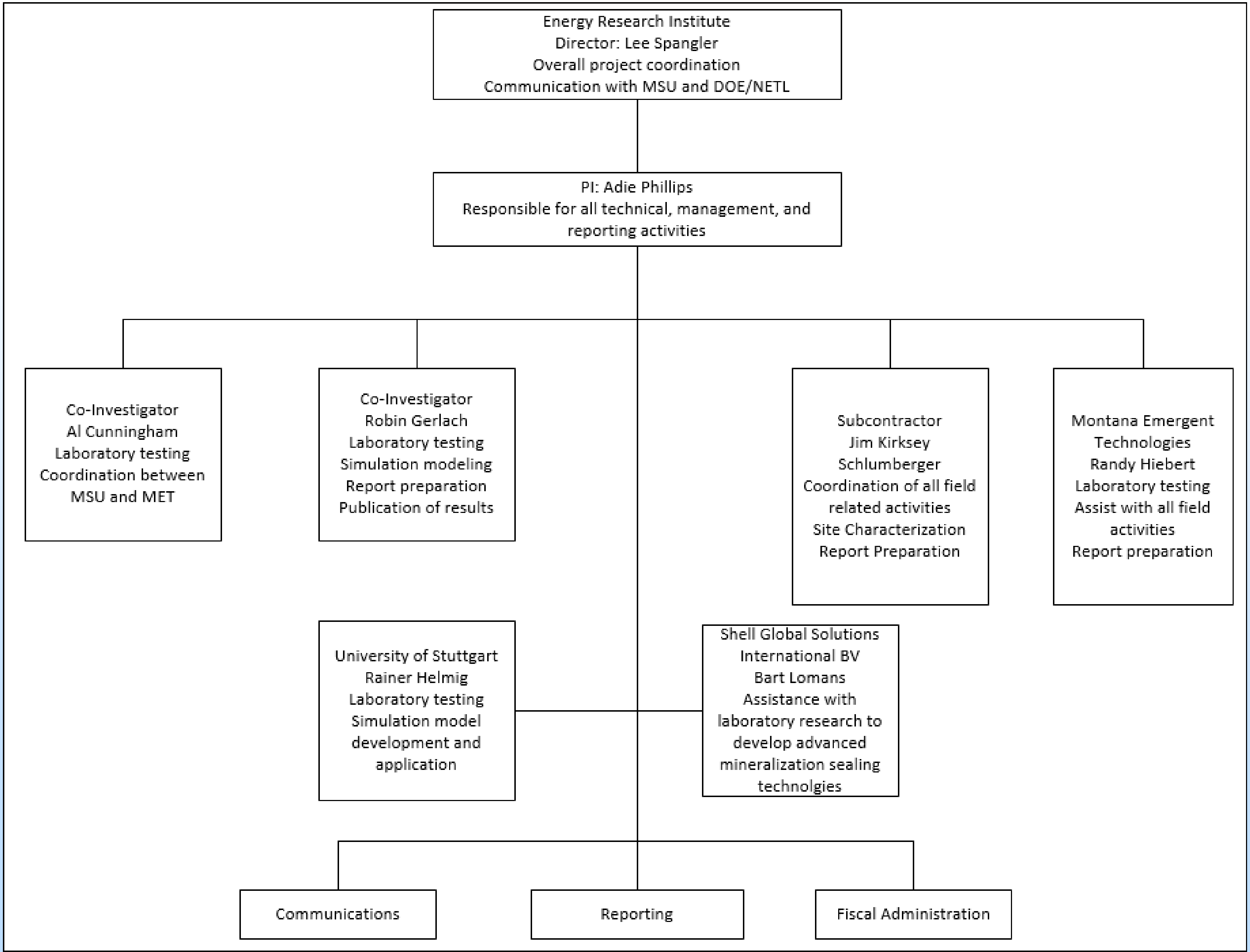
Organization Chart



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
1.0 Project Management and Planning																																																
Milestone 1 Updated Management Plan		①																																														
Milestone 2 Kickoff Meeting		②																																														
2.0 Laboratory investigation to develop and evaluate enhanced mineral sealing																																																
Milestone 3 Complete modification of the high pressure systems				③																																												
Milestone 5 Complete development of field test protocol																														⑤																		
Milestone 6 Complete field test																															⑥																	
2.1 Develop and test laboratory systems for performing mineral sealing experiments																																																
2.2 Develop protocols for forming mineral seals in rock cores																								1																								
2.3 Assess the resistance of precipitated mineral seals to challenges with supercritical CO2-saturated brine																														0.5																		
3.0 Refine the existing Stuttgart Biomineralization Model to predict mineral precipitation resulting from alternative mineral precipitation strategies																																																
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																														1																		
4.0 Perform field test and evaluation of appropriate mineral sealing technology at the Danielson sell site																																																
Milestone 4 Complete well characterization and preparation																					④																											
Milestone 7 Conduct field test to evaluate mineralization seal																																											⑦					
Milestone 8 Complete evaluation of all field and laboratory test results																																															⑧	
4.1 Conduct initial field characterization activities at the Danielson well site																					0.75																											
4.2 Design the field injection strategy based on laboratory results and simulation																														1																		
4.3 Perform mineralization sealing test at the Danielson well and evaluate results																																																
4.4 Evaluate the integrity of the mineralization seal																																																

Bibliography

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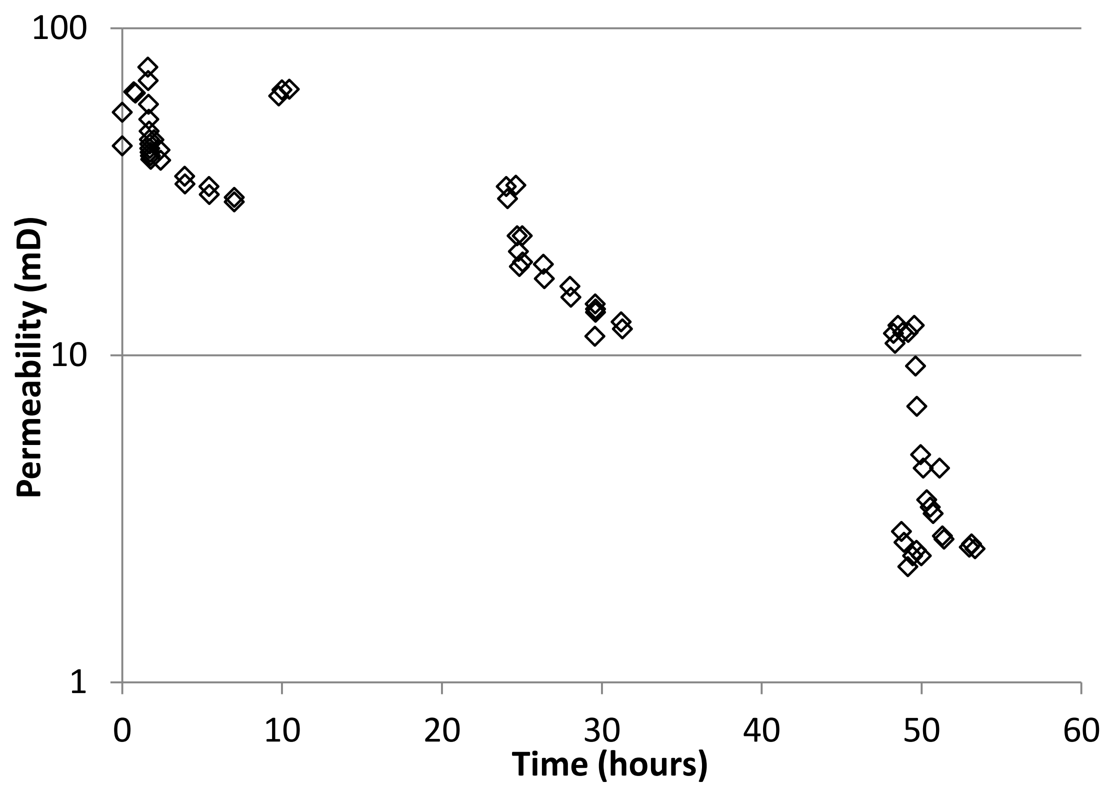
- Beser, D, West C, Daily, R, Cunningham, A, Gerlach, R, Fick, D, Spangler, L and Phillips, AJ. Assessment of ureolysis induced mineral precipitation material properties compared to oil and gas well cements. American Rock Mechanics Association 51st Annual Meeting Proceedings, June 25-28, 2017, San Francisco, CA. (Paper # 588) (Accepted)

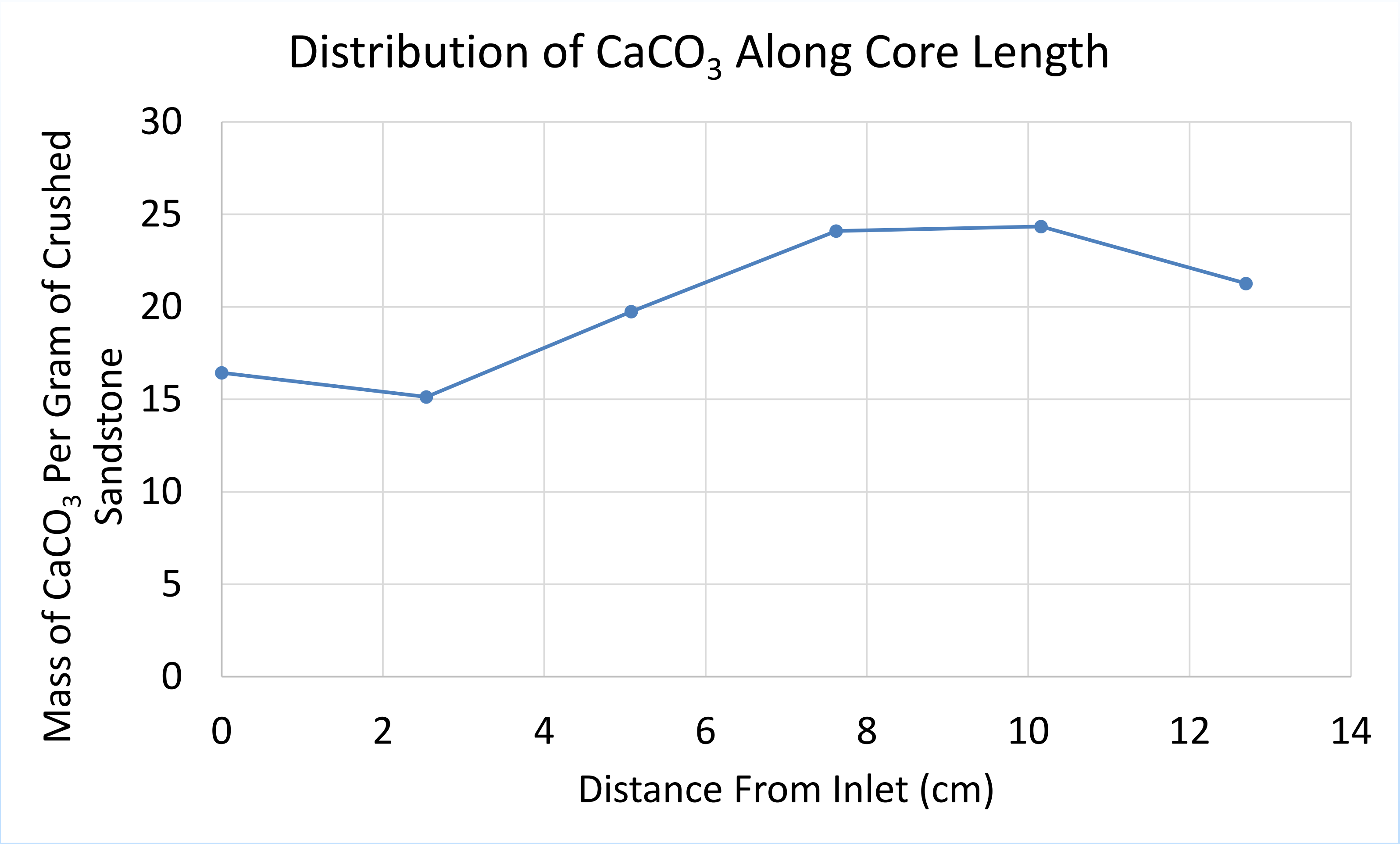
ENZYME MINERALIZATION- EICP

Porosity ~22%
Permeability 63 mD
Pore volume ~14 ml

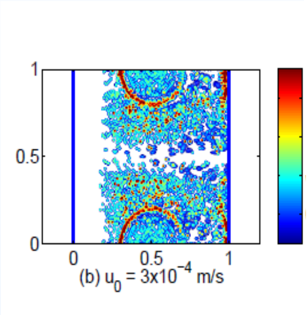
63 to 2.4 mD in three days
100 g/L NaCl
Only 200 psi
60°C

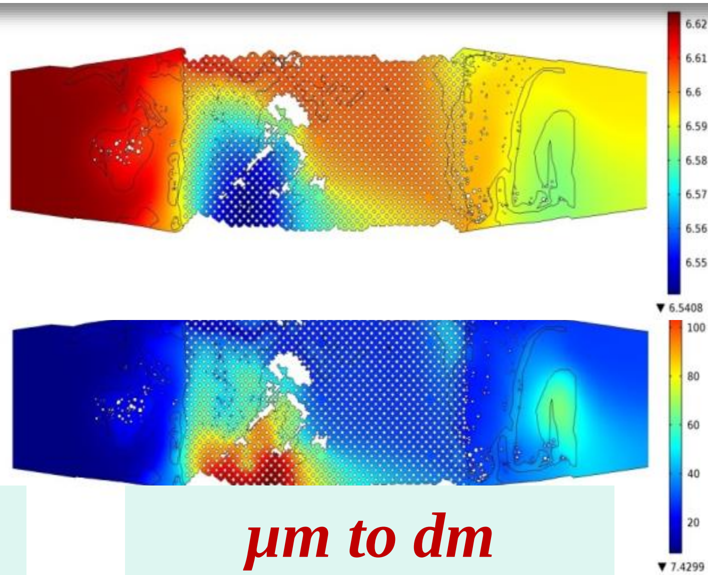


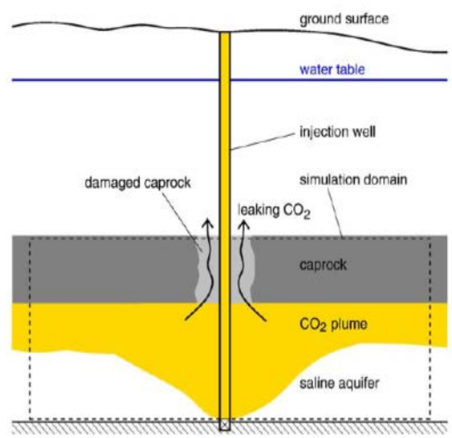
ENZYME MINERALIZATION- EICP

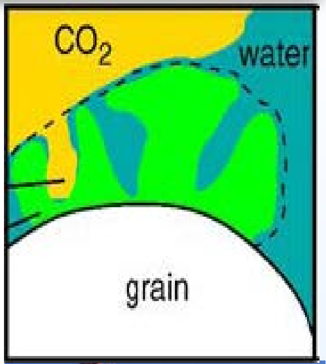


Scale Up







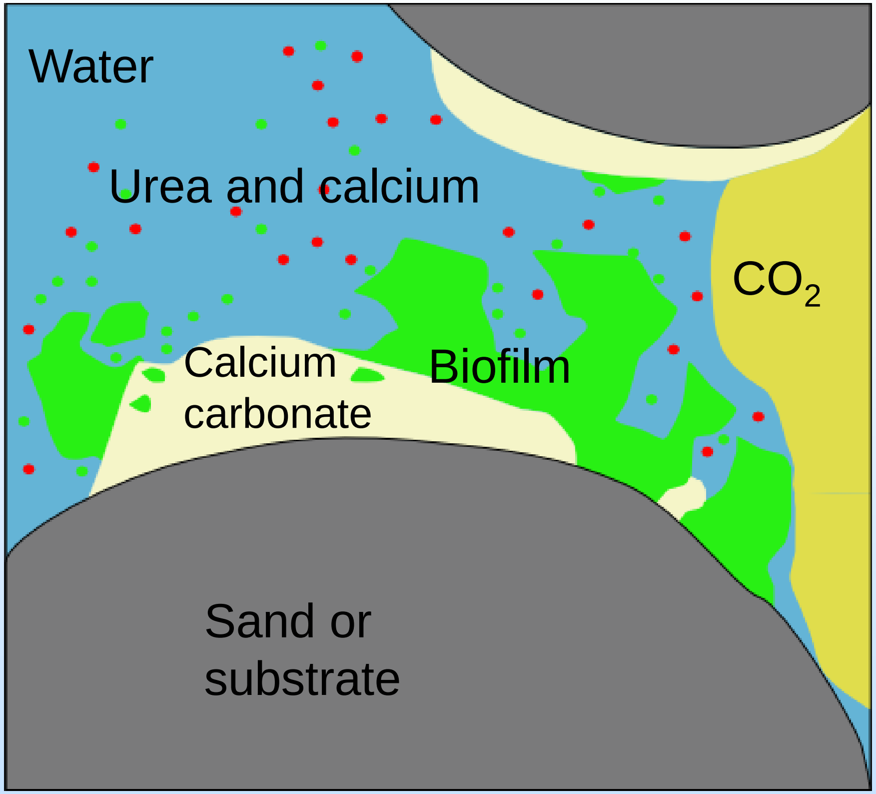


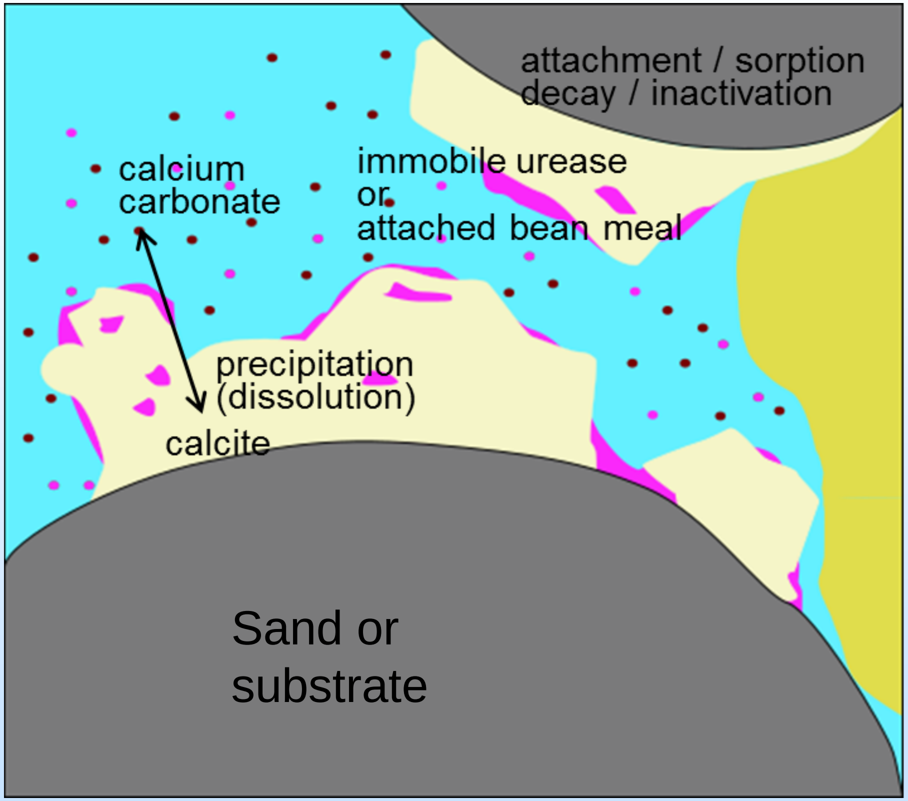
nm to cm

µm to dm

cm to 100s of m

MICP to EICP Model





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- 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