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 14, 2018

Presentation Outline

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

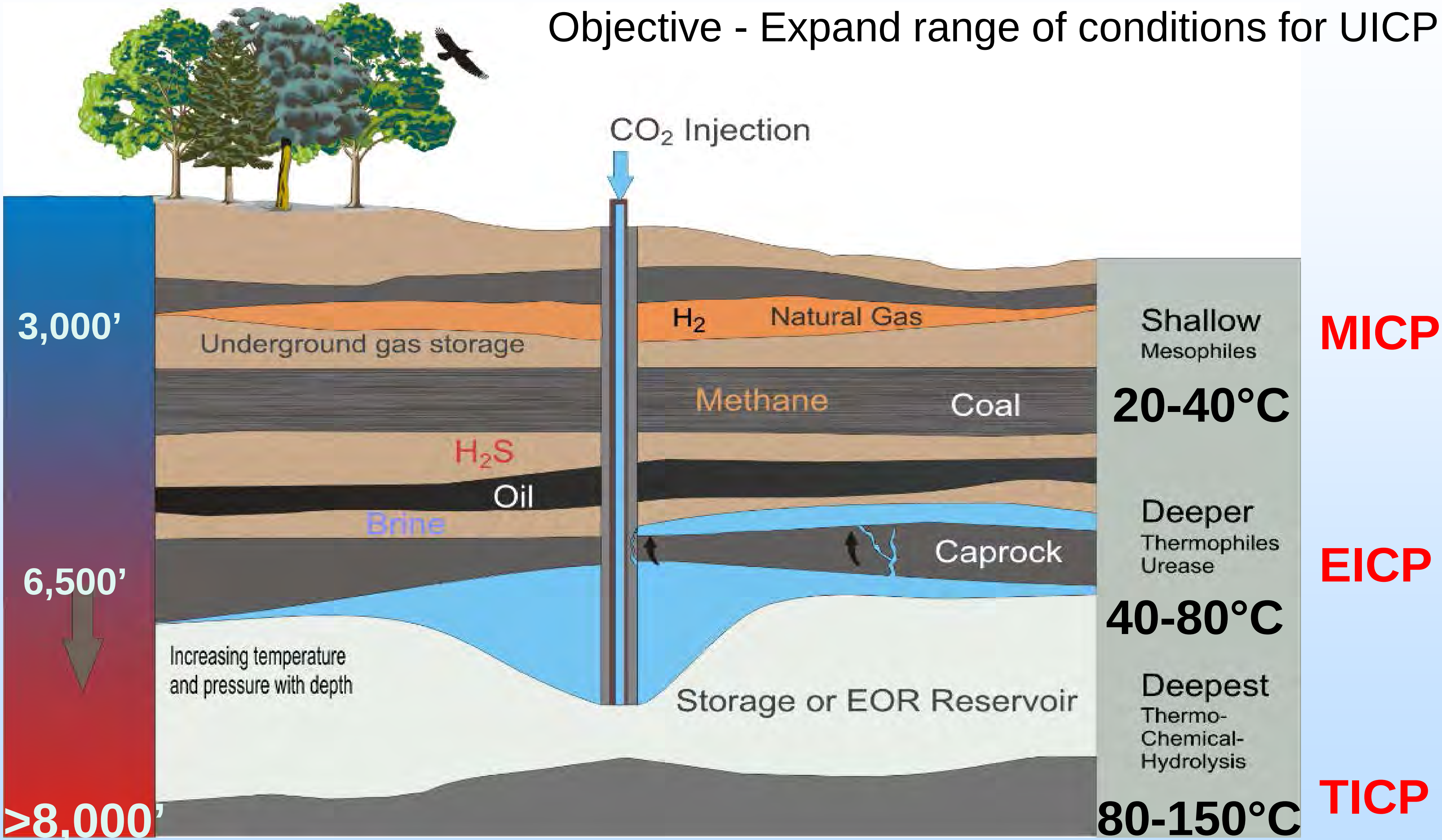
Project Overview: Objectives

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_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

Objective - Expand range of conditions for UICP



Advancing technologies for mitigating subsurface gas leakage

Mineralization

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

- The **e**nzyme urease hydrolyzes urea to form ammonium and carbonates, which increases alkalinity
- **T**hermal hydrolysis of urea can result in the same chemistry
- In the presence of Ca^{2+}, saturation can be exceeded and calcium carbonate (calcite) precipitates- EICP and TICP

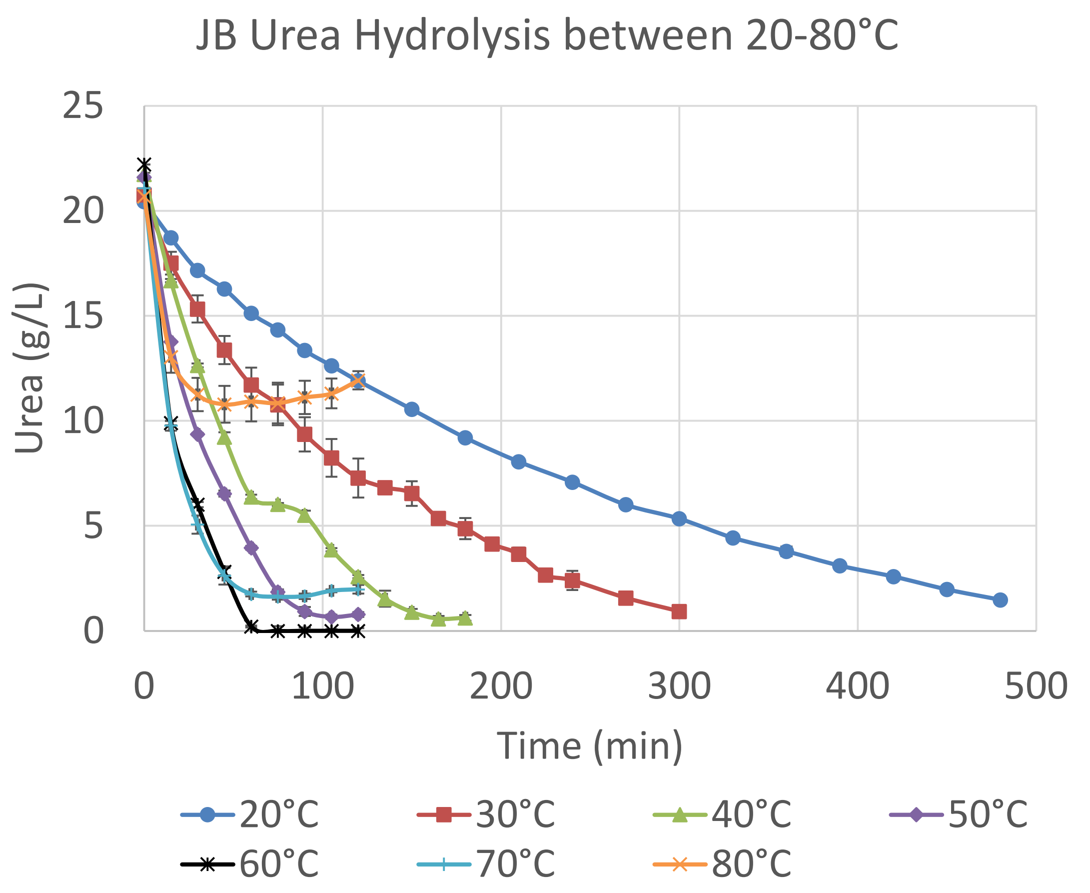
Accomplishments: Objective 1

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

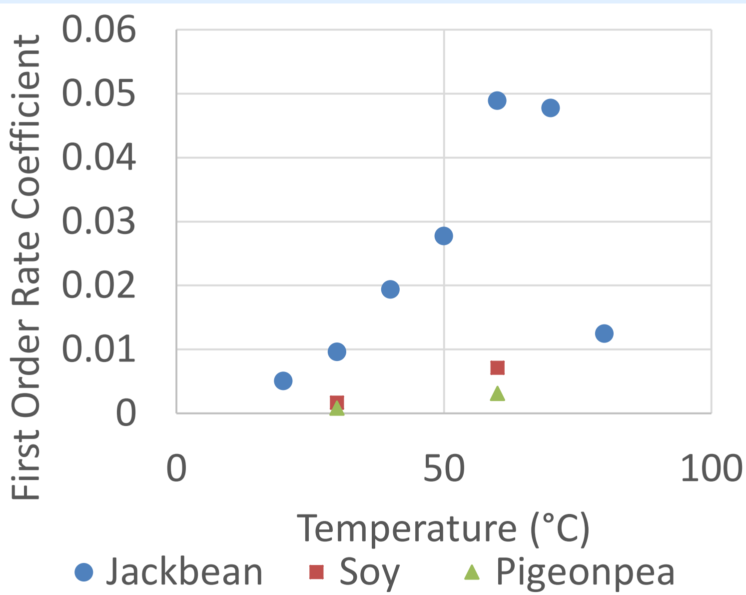
Experiments to date:

- Kinetics of urea hydrolysis under temperature, pressure and chemical conditions congruent with subsurface applications
- Model: urea hydrolysis and enzyme inactivation rates
- Immobilization of enzyme to protect from denaturation
- Develop injection strategies to control mineral precipitation
    - Seal fractured core, sand columns
- 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

INACTIVATION MODELING

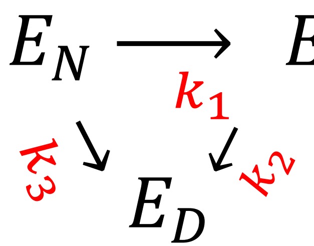
First Order Inactivation

$$E_N \xrightarrow[K_d]{} E_D$$

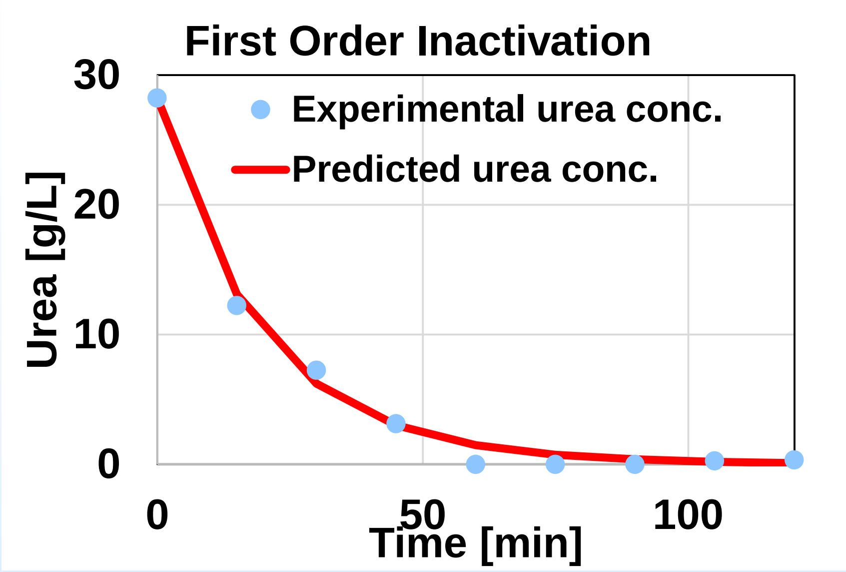
Series Inactivation

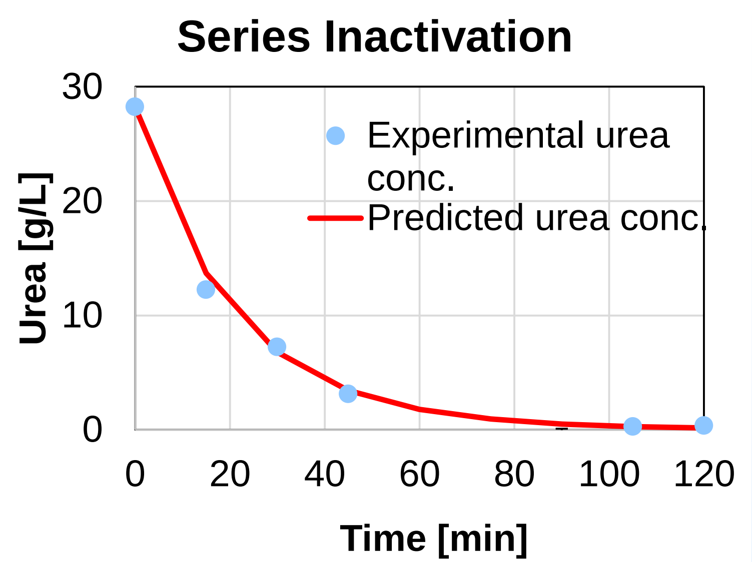
$$E_N \xrightarrow[k_1]{} E_I \xrightarrow[k_2]{} E_D$$

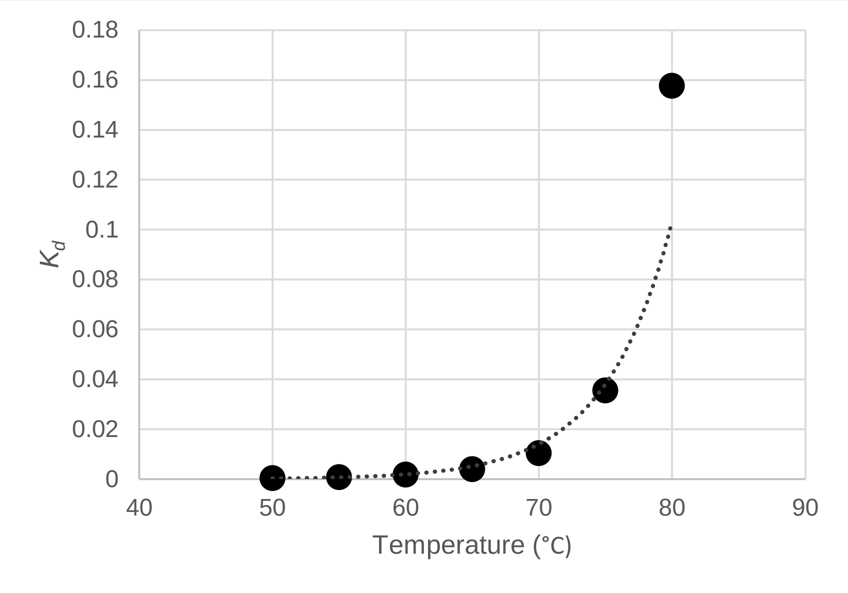
Series Parallel Inactivation

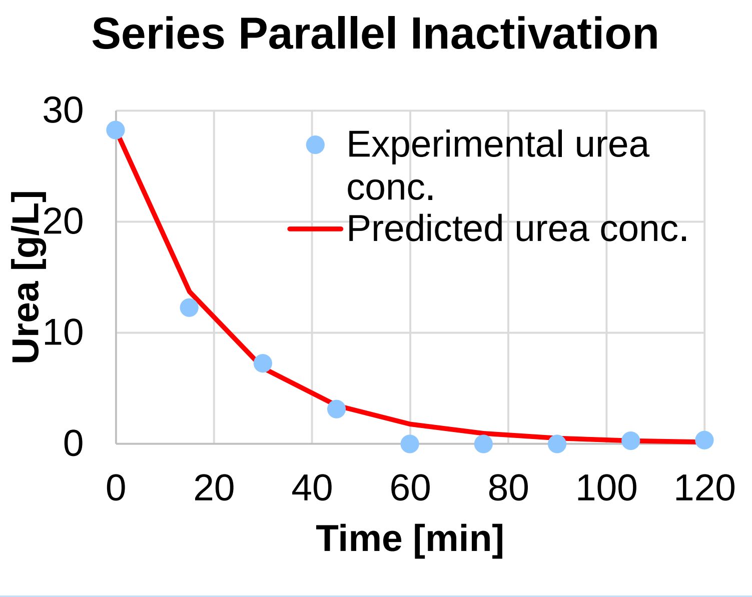


JACK BEAN UREASE KINETICS & RATES







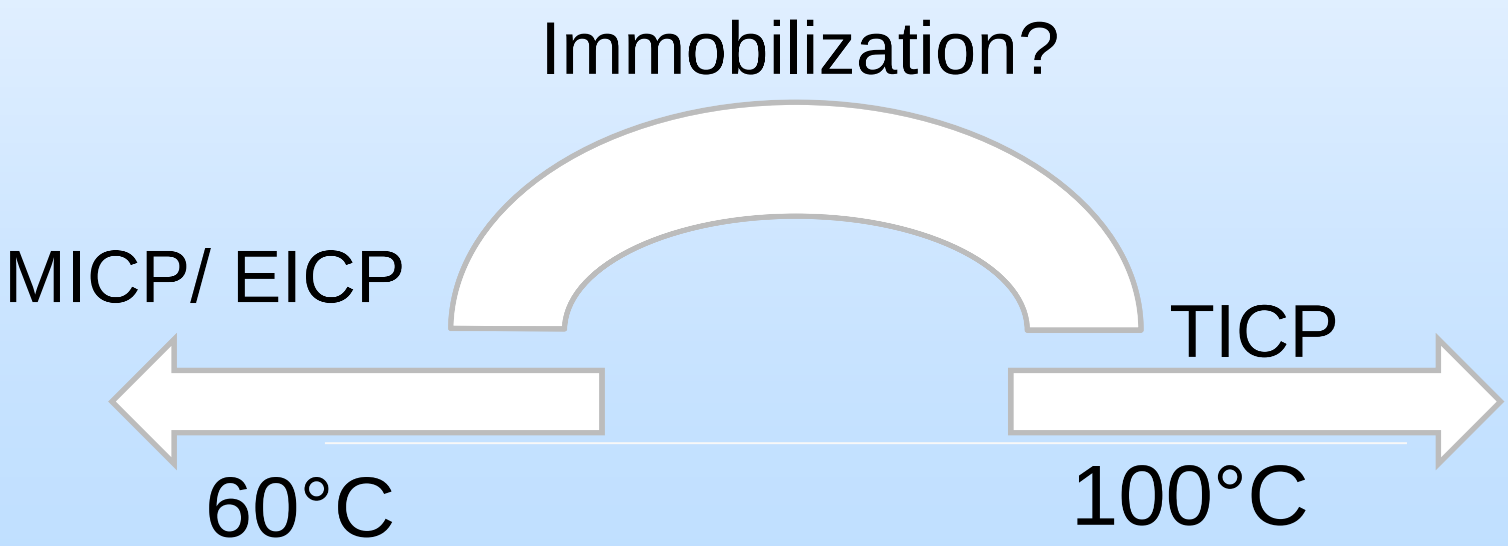


IMMOBILIZATION

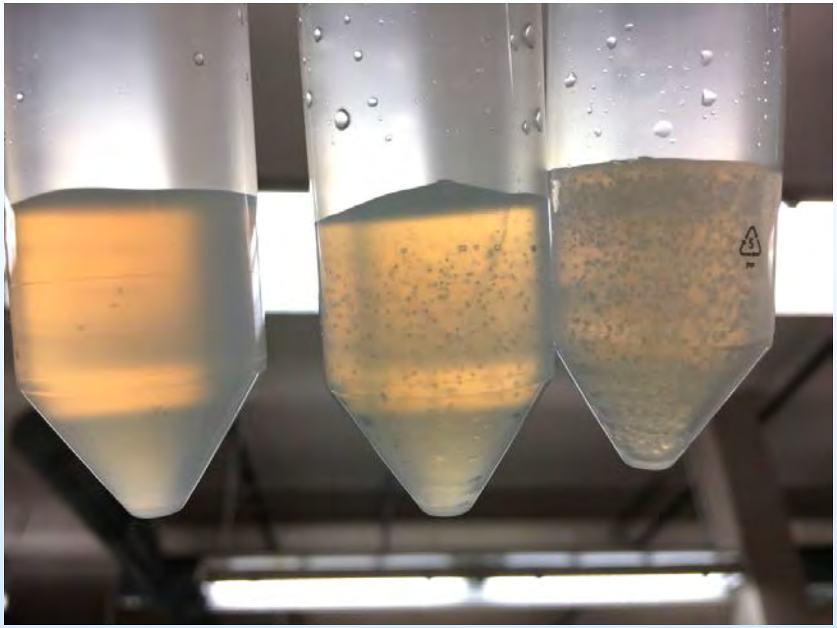
Enzyme activity decreases due to thermal inactivation

Thermal ureolysis beyond 100-110°C- starts at 80°C- days to weeks

Fill the gap



IMMOBILIZATION

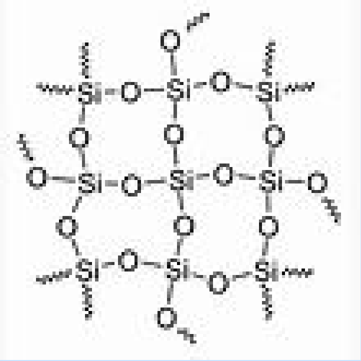


Ludox® gel with mineral precipitation

Ludox® colloidal silica gel or proppant (sand) used

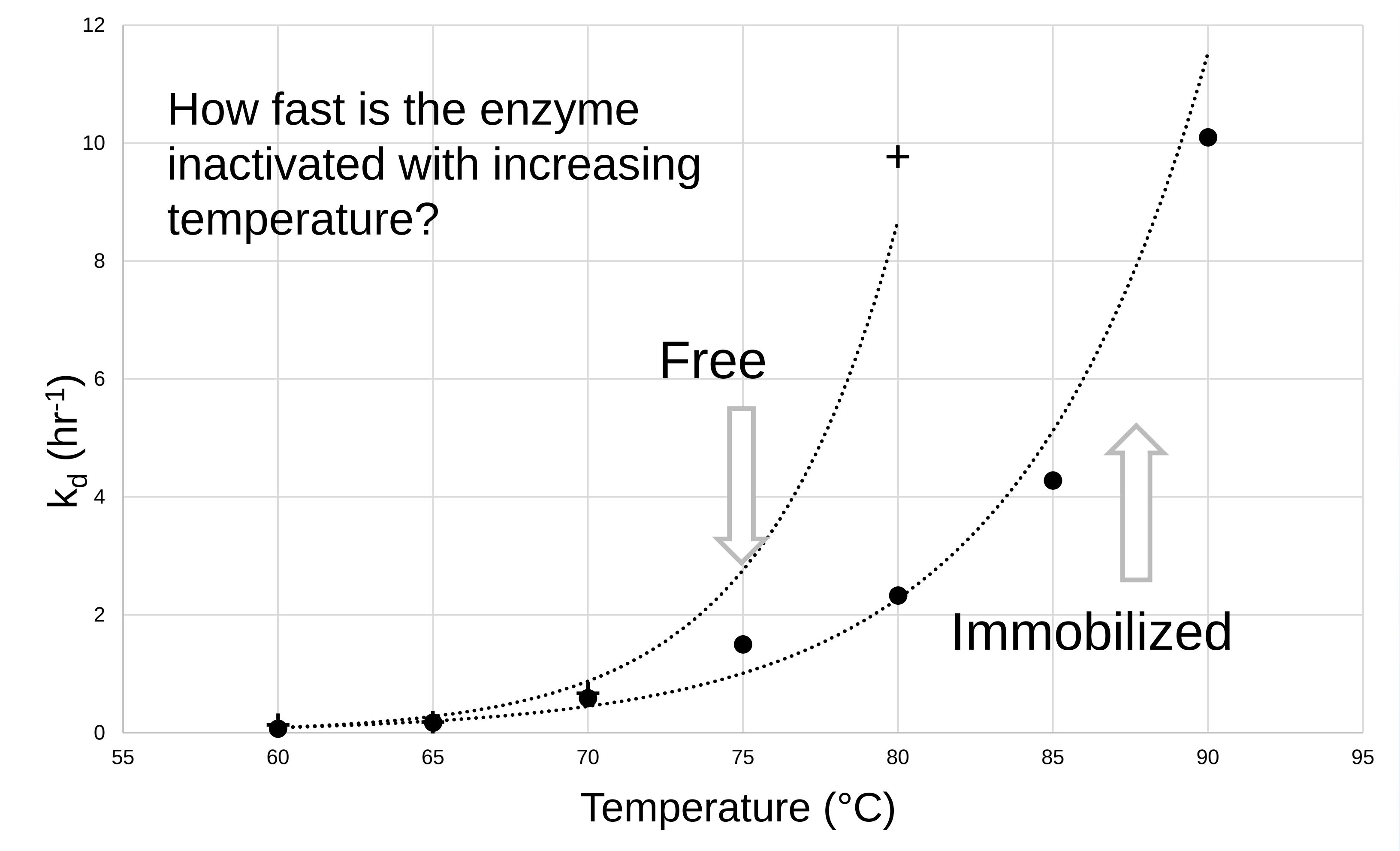
Gel-Enzymes trapped in polymer matrix

Gel becomes enzymatically active



Silicon dioxide particles polymerize in the presence of cations or low pH creating gel

IMMOBILIZATION



The first order thermal inactivation rate constant (k_d) for immobilized cells is lower than free enzyme.

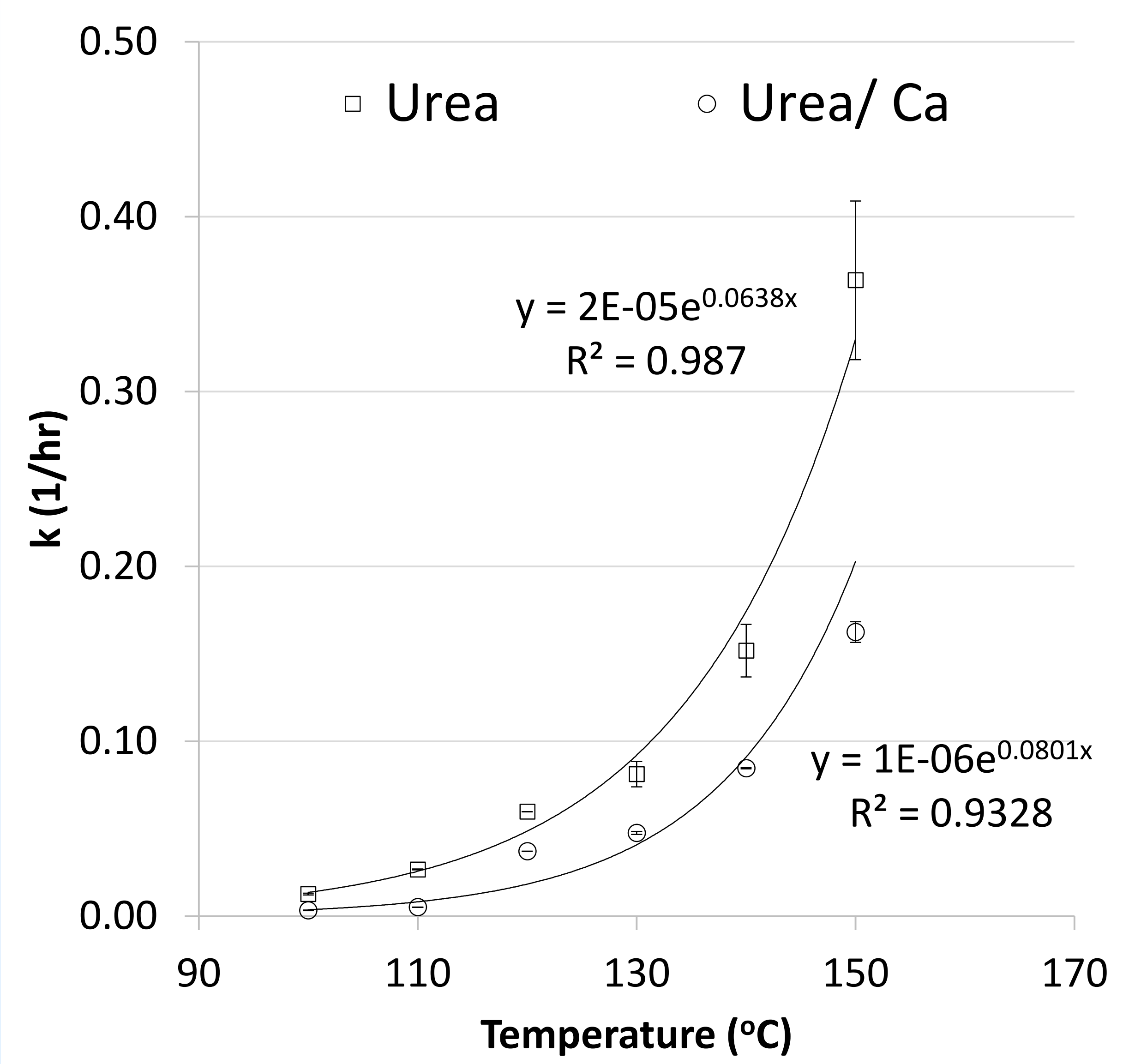
IMMOBILIZATION- HALF LIFE

Temperature (°C)	Immobilized Half Life (hr)	Free Half Life (hr)
60	10	5.3
65	4.1	3.8
70	1.2	1.0
75	0.5	0.2
80	0.3	0.07
85	0.2	-----
90	0.07	-----

$$t_{1/2} = \frac{\ln 2}{k_d}$$

↑ half life= active longer

THERMAL UREOLYSIS- TICP



Enzyme may be limited to Temps < 80-90°C

Direct thermal heat used to drive mineral precipitation > 80°C (tested to 150°C)

Hours instead of days

Difference between rates of urea alone and urea/calcium

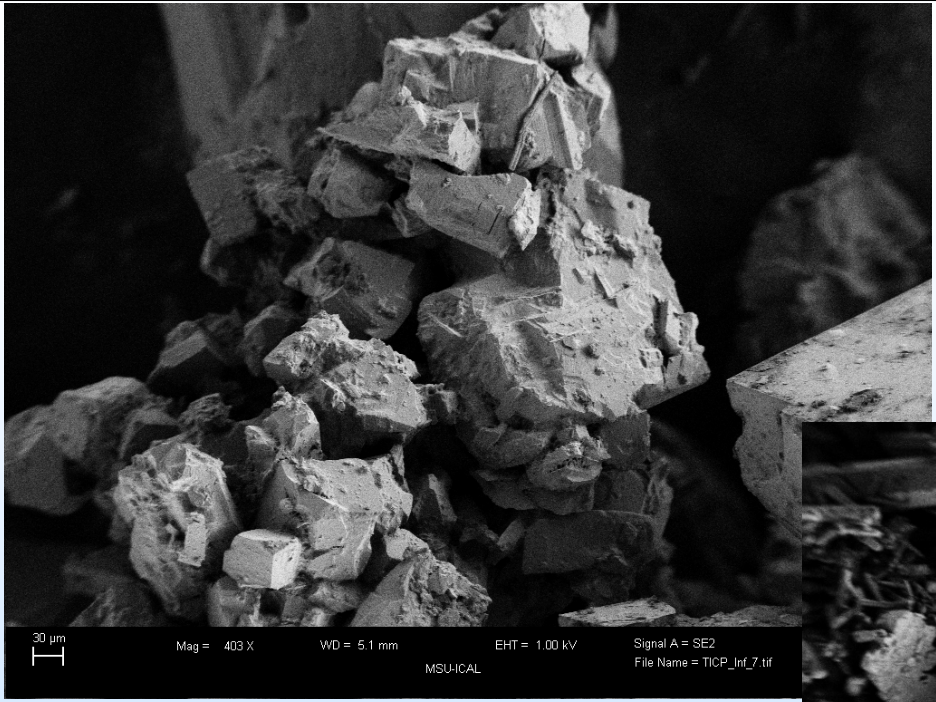
Increase U/Ca concentrations for increased precipitation

THERMAL UREOLYSIS- TICP

Aragonite vs Calcite

Mineral material properties

Use of organics



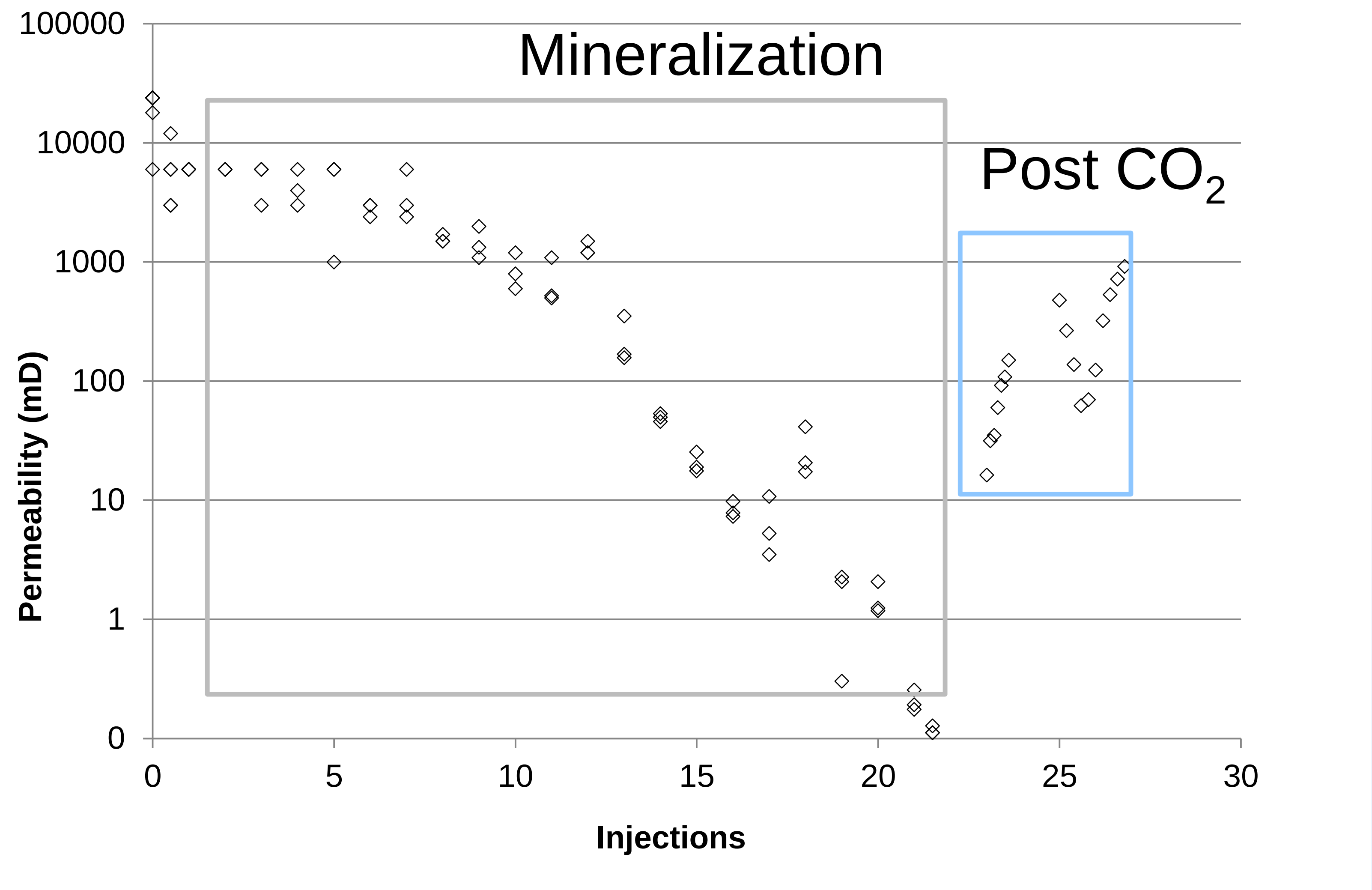
Accomplishments: Objective 2

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

CO_2 EXPERIMENT

- 1in. X 2in. sandstone and cement core
- Soaked core with CO_2 saturated brine
- Mineralization pulses
- Challenged core with CO_2 saturated brine
- Scanned the core with X-ray-CT and NMR rock core analyzer
  - pre-mineralization
  - post-mineralization
  - post- CO_2 challenge

CO_2 EXPERIMENT

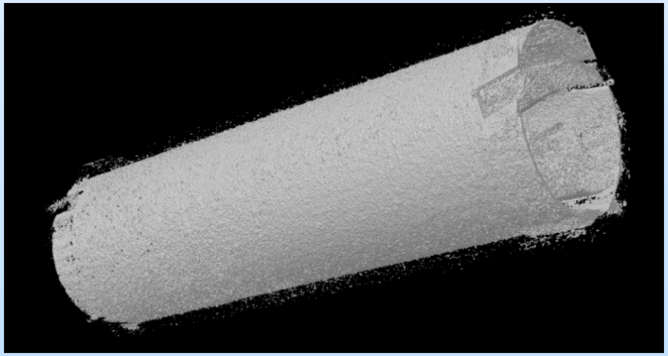


CO_2 EXPERIMENT

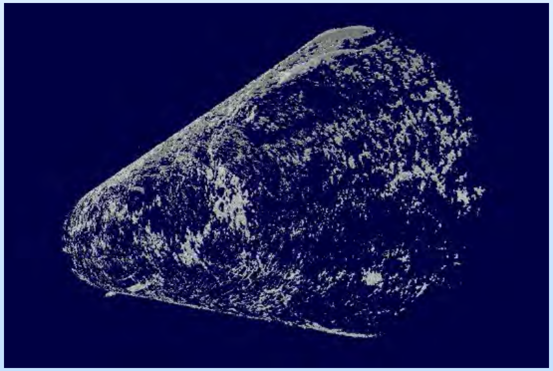
NMR and CT

Sample	Porosity	Volume (Liquid)
Pre-mineralization	13.3%	3.5 mL
Post-mineralization	7.0%	1.9 mL
Post CO_2 challenge	7.4%	2.0 mL

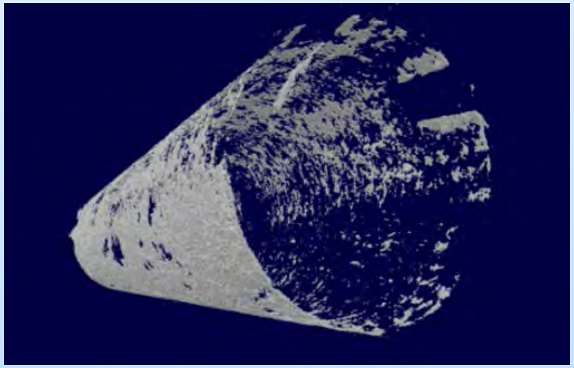
Pre-Mineralization



Post-Mineralization



Post CO_2



Ryanne Daily, Linn Thrane, Sarah Codd, Olivia Firth

Accomplishments: Objective 3

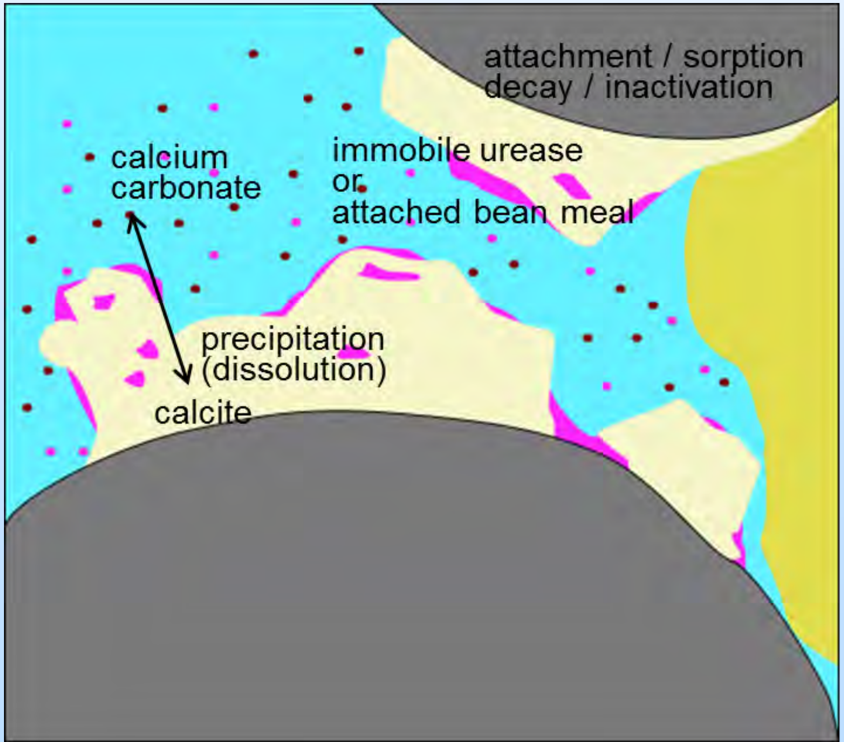
Objective 3. Refine the existing Stuttgart Biomineralization Model to predict mineral precipitation resulting from advanced mineral precipitation strategies.

Universität Stuttgart

Model to date: Update code to utilize kinetic parameters- enzyme inactivation and TICP

Model CO_2 predictions

Might want to remove seal



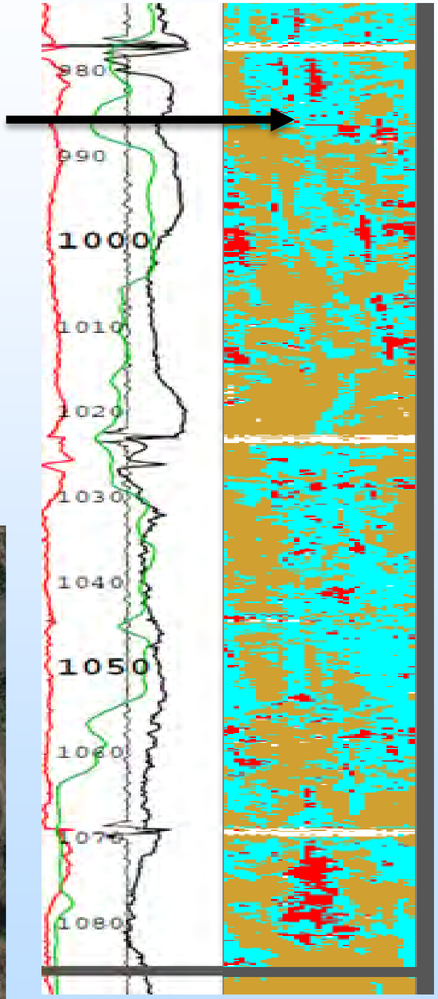
- Ebigbo A.; et al.(2012): Darcy-scale modeling of microbially induced carbonate mineral precipitation in sand columns. *Water Resources Research*. 48, W07519, doi:10.1029/2011WR011714.
- Hommel, J.; et al. (2015): A revised model for microbially induced calcite precipitation - improvements and new insights 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.

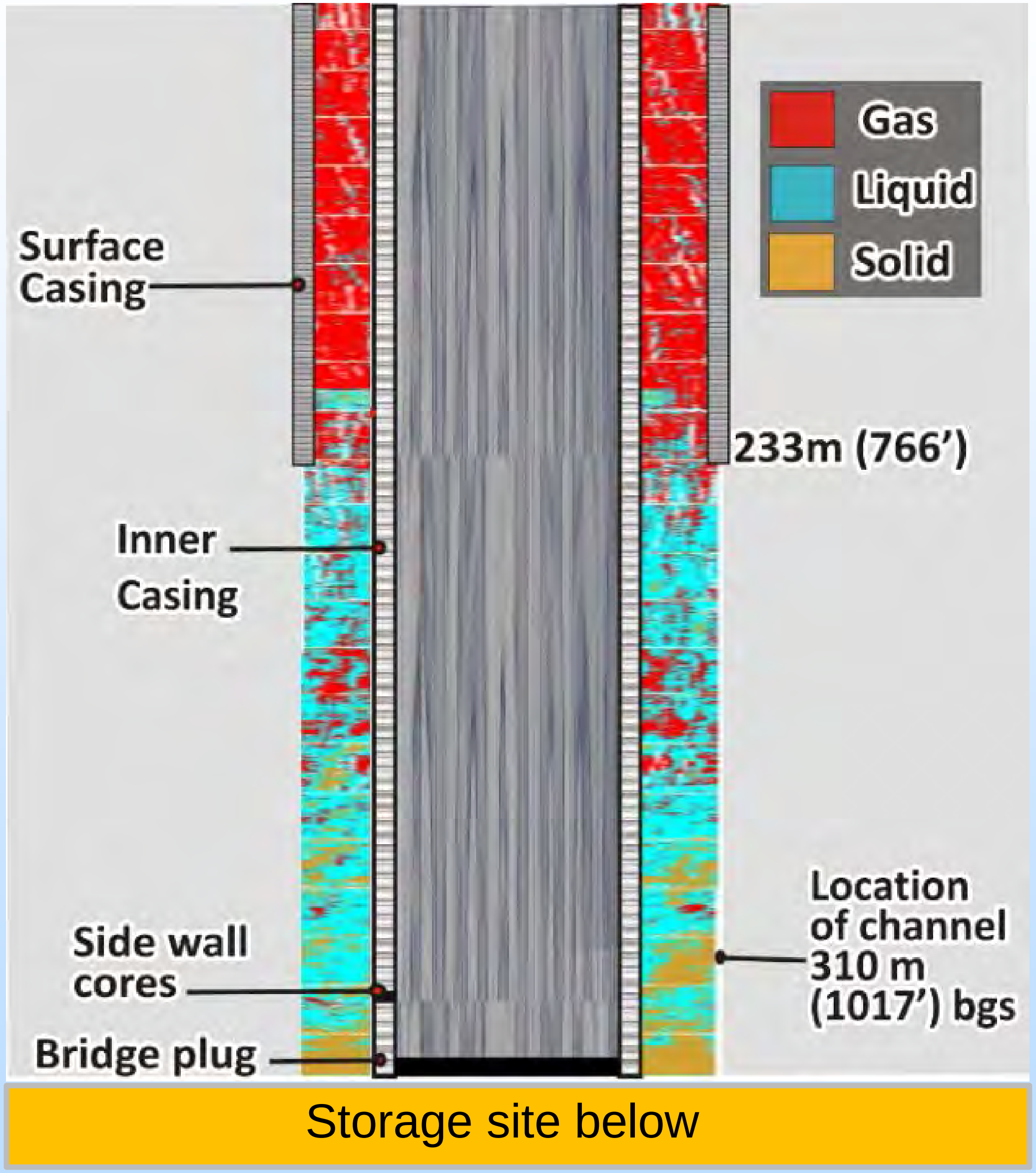
Gorgas, Alabama

EICP and CO_2



Accomplishments: Objective 4

Adding CO_2



Lessons Learned

- Mineralization expanded to higher temperature applications
  - Understand kinetics of reactions and how mineral forms
- Initial site identified- safety concerns with H_2S
  - Alternate well- now identified and characterized
  - Challenges in field work and scale up- address with modeling and laboratory work
  - CO_2 leakage pathway with targeted channel for EICP treatment

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

SUMMARY & FUTURE

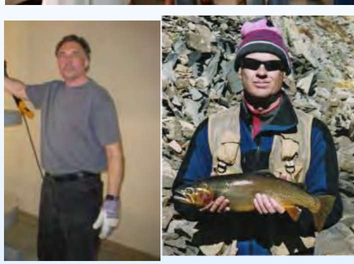
Summary

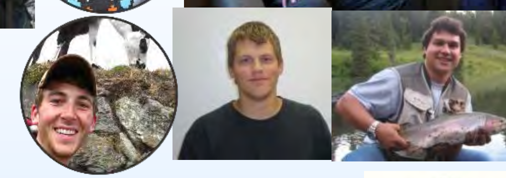
- JB urease kinetics and inactivation
- Thermal hydrolysis of urea > 80°C
- Potential for minerals other than calcite
- Model updates

Future EICP and TICP

- Mineralization strength
- Field characterization and plan – scale up

Acknowledgements





U.S. DEPARTMENT OF ENERGY

NSF

MONTANA

Schlumberger

SOUTHERN COMPANY

University of Stuttgart Germany

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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

<u>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.</u>

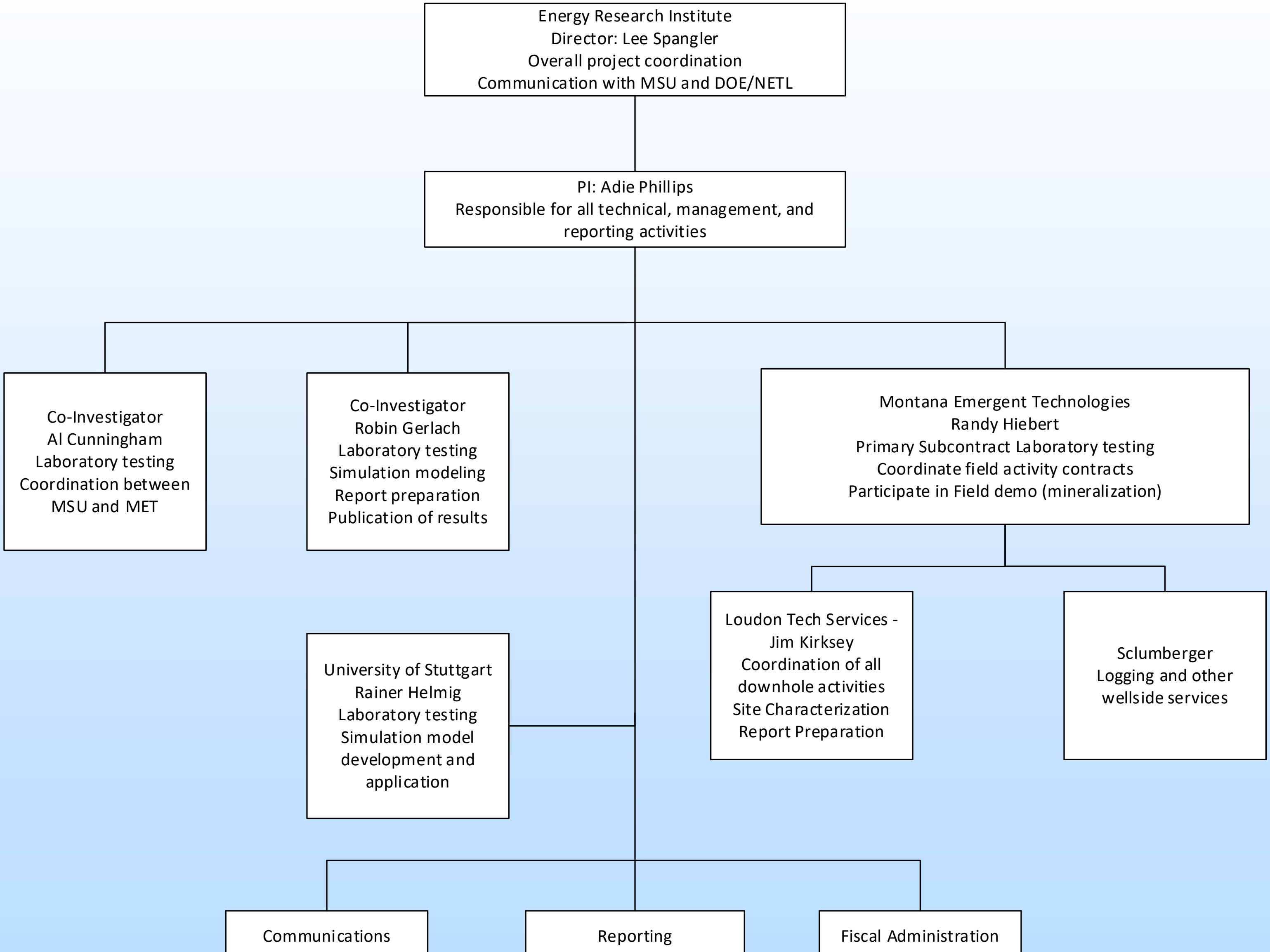
- Active enzyme as the catalyst as well as direct thermal hydrolysis of urea drive mineralization precipitation developing **engineered mineralization sealing at greater depths and higher temperatures** to address the FOA requirement to *"prevent or remediate detected leaks in complicated environments 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.
4. Perform field validation of the most appropriate mineral sealing technology in a well.

Organization Chart



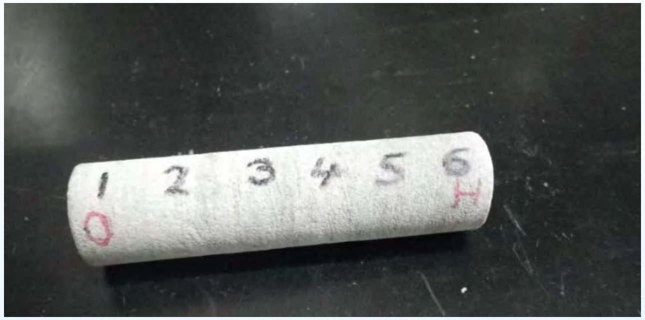
Gantt Chart

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		
	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
	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
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																																				
2.3 Assess the resistance of precipitated mineral seals to challenges with supercritical CO2-saturated brine																																				
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																																				
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																																				
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																																				

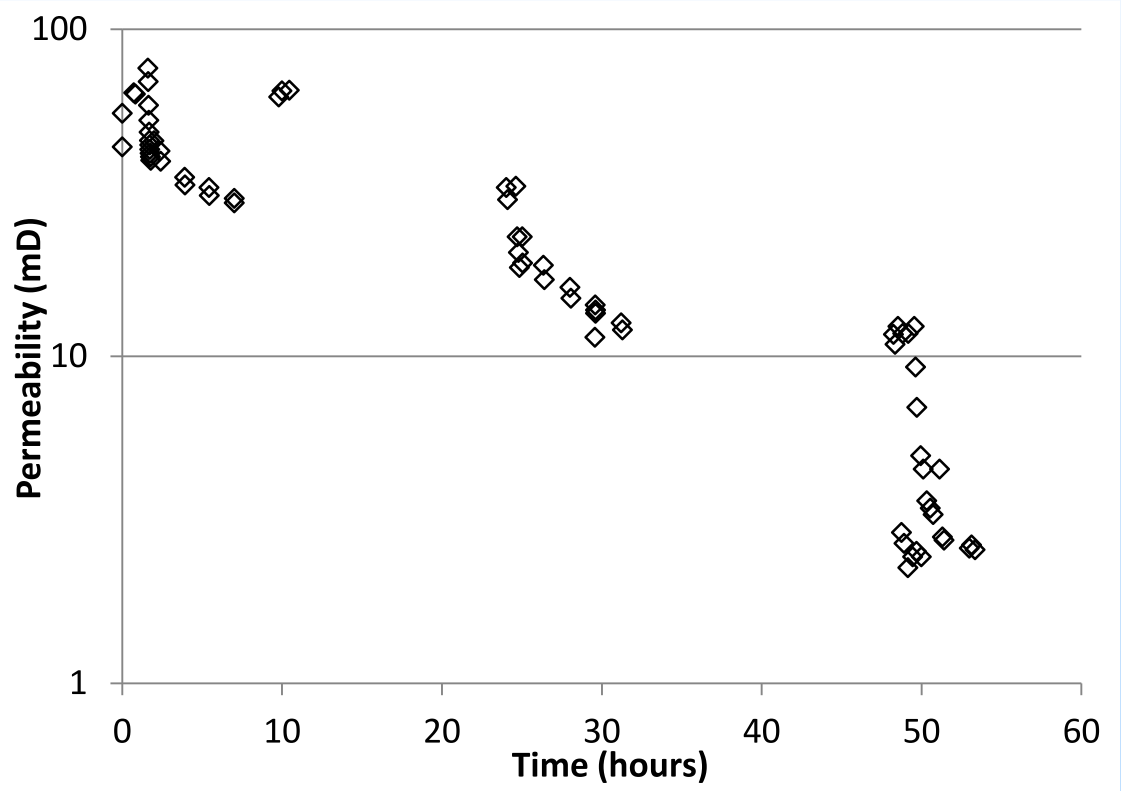
Bibliography

1. 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 for ES&T)*
2. Schultz, L, Worum, B, Deverna, K, Cunningham, A, Gerlach, R, and Phillips, AJ. Thermal hydrolysis of urea and cation inhibition in solutions at 100-150 C (*In preparation* for the International Journal of Chemical Kinetics)
3. Schultz, L, Thane, A, Worum, B, Deverna, K, Kirkland, C, Cunningham, A, Gerlach, R, and Phillips, AJ. Subsurface control of thermally-induced carbonate precipitation (TICP): Cementing fractures and altering porous media, (*In preparation* for ACS Sustainable Chemistry and Engineering)
4. Cunningham, A, Class, H, Egbibo, A, Gerlach, R, **Phillips, AJ**, Hommel, J. Field-scale modeling of microbially induced calcite precipitation, Computational Geosciences (Submitted February 2018, In revision)

ENZYME MINERALIZATION- EICP

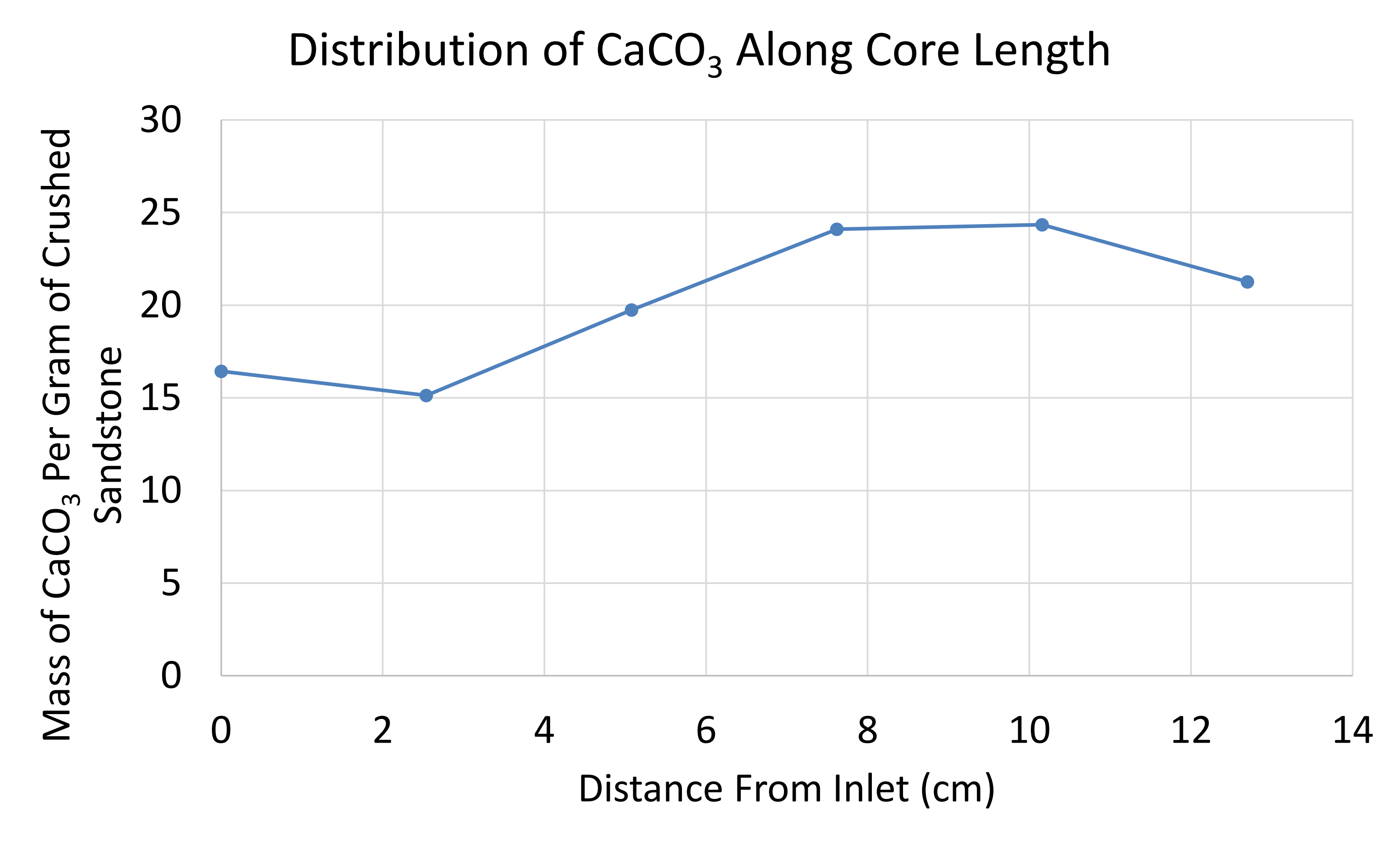


Porosity ~22%
Permeability 63 mD
Pore volume ~14 ml

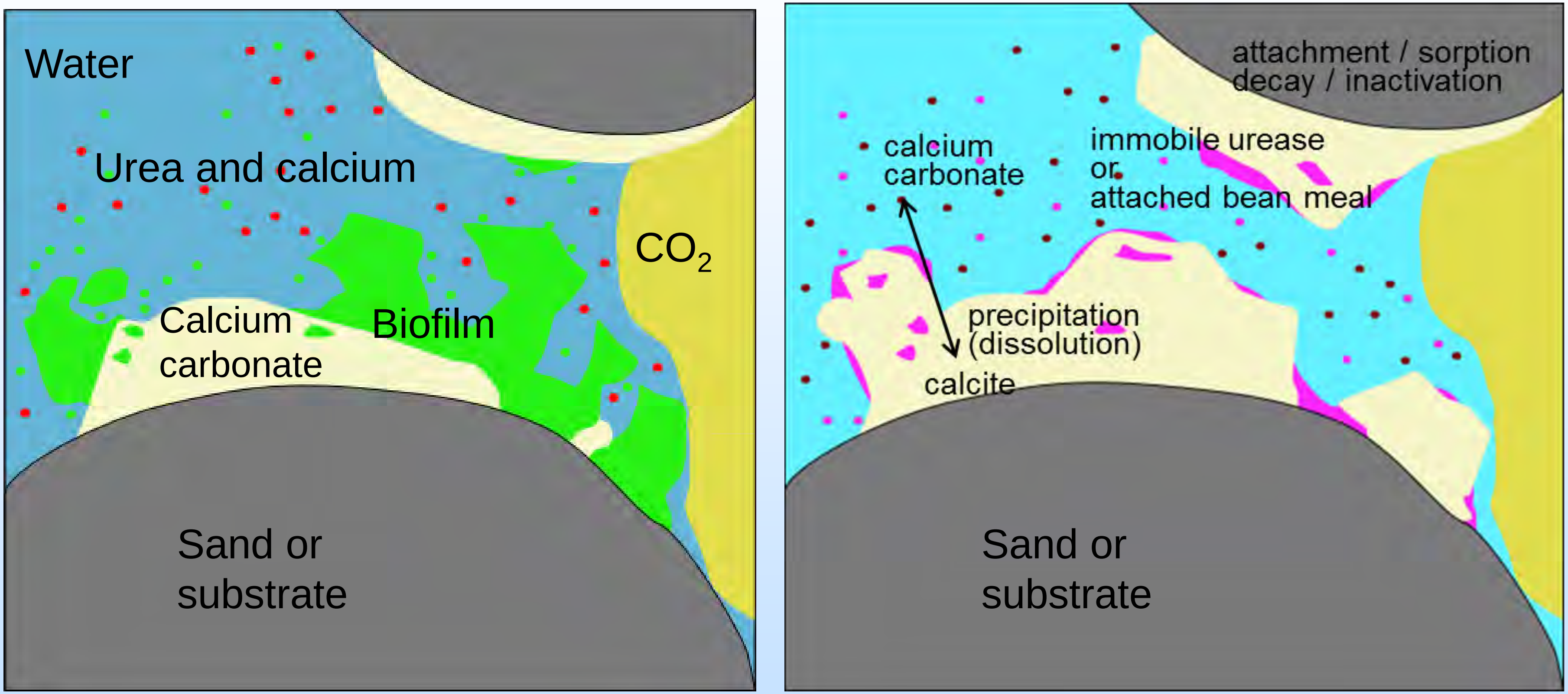


63 to 2.4 mD in three days
100 g/L NaCl
Only 200 psi
60°C

ENZYME MINERALIZATION- EICP



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.
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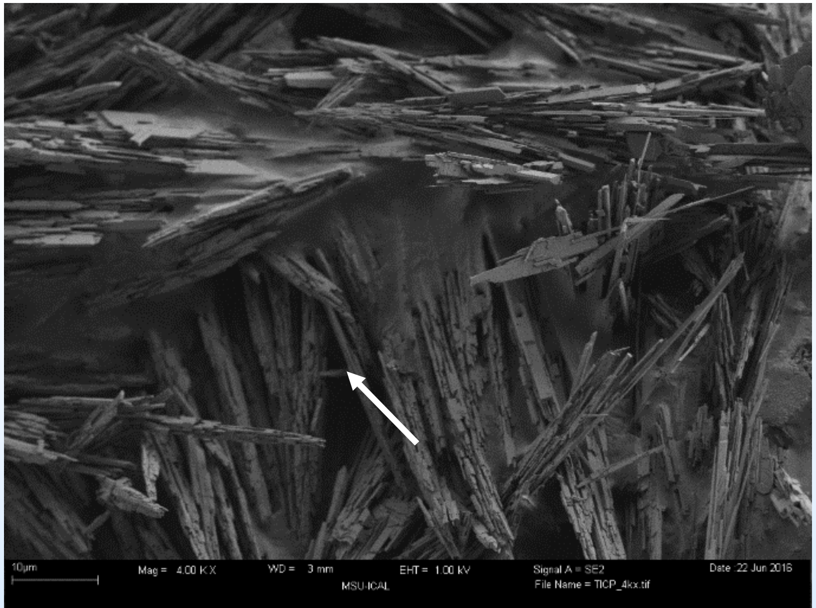
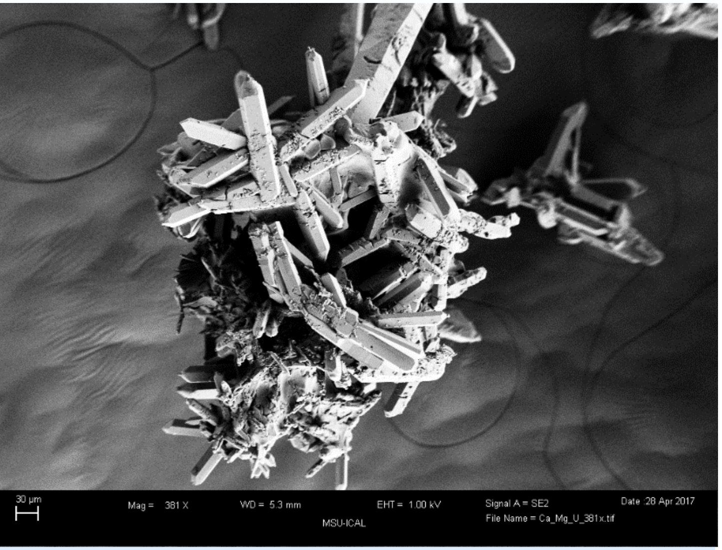
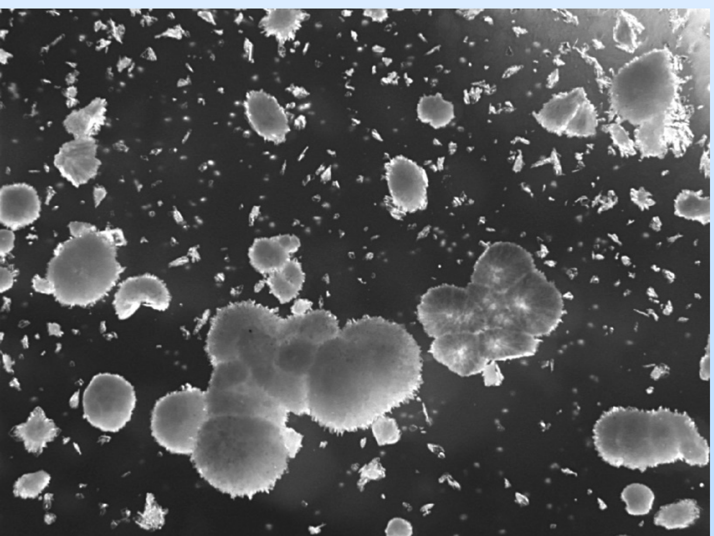
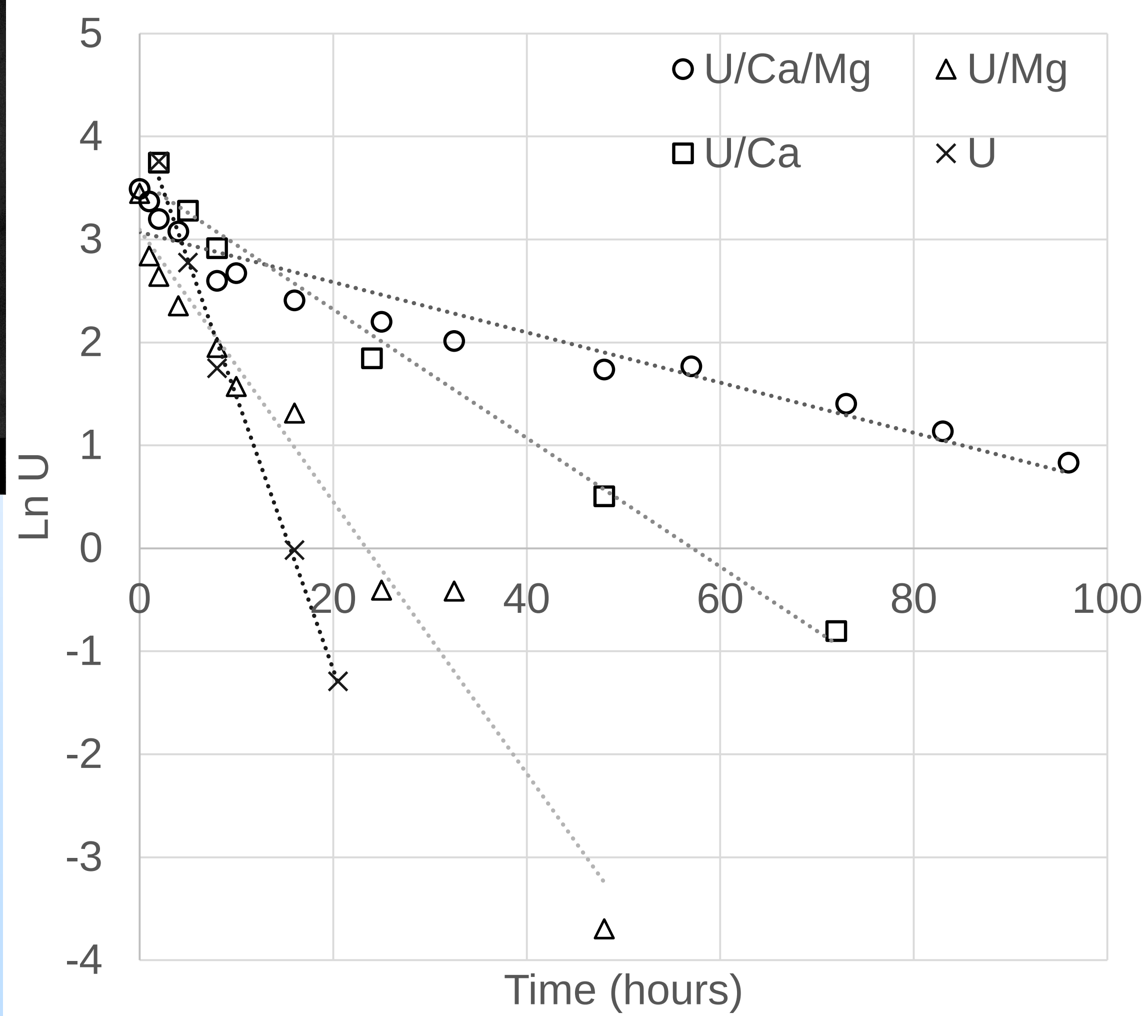
THERMAL HYDROLYSIS- TICP



ALTERNATIVE MINERALS-TICP







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)

JB UREASE INACTIVATION

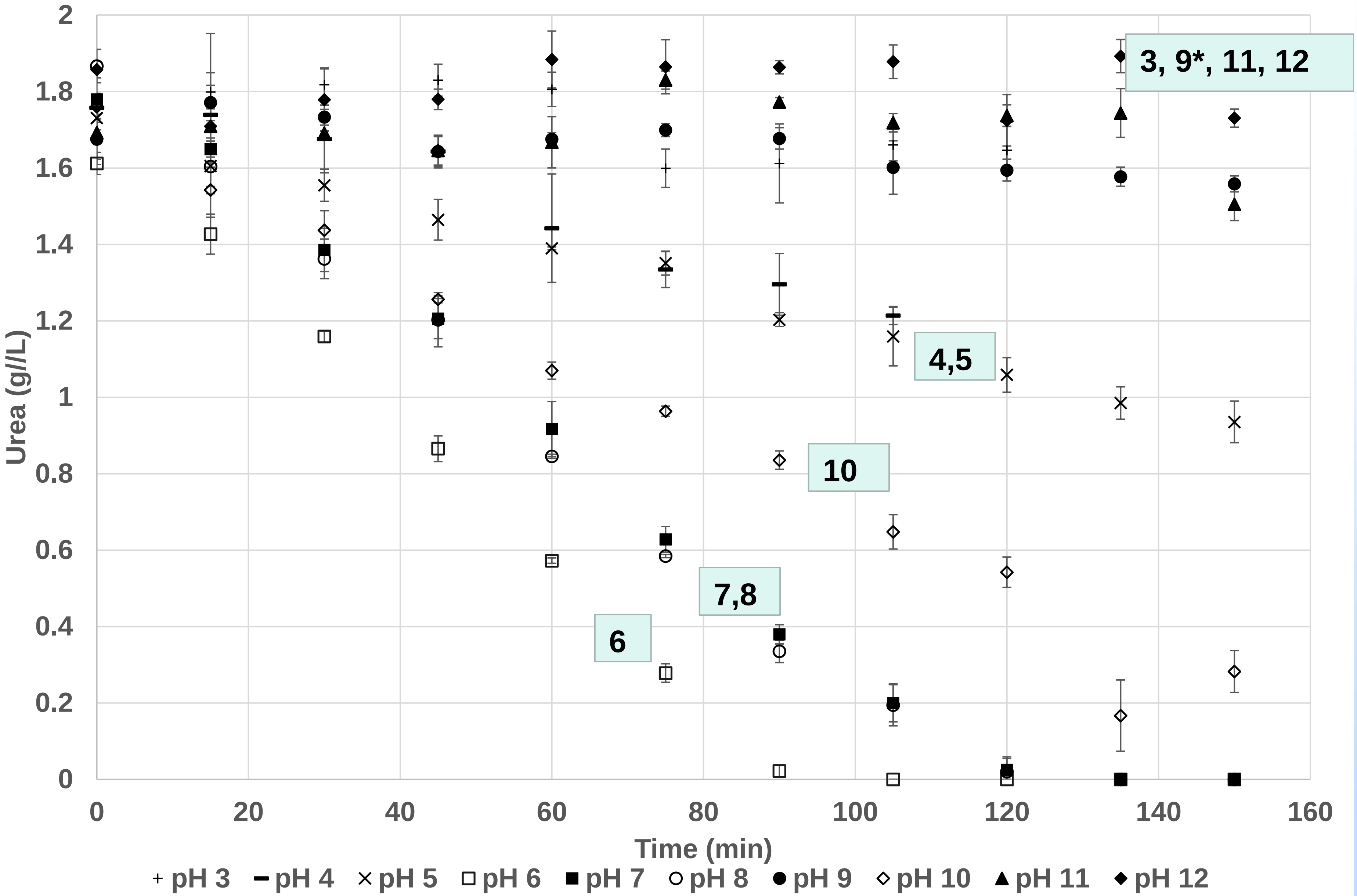
Rate equation: $\frac{dU}{dt} = k_a(T) * [U] * [A(T)]$

First order : $A(T) = \boldsymbol{e^{-k_{\mathrm{d}}t}}$

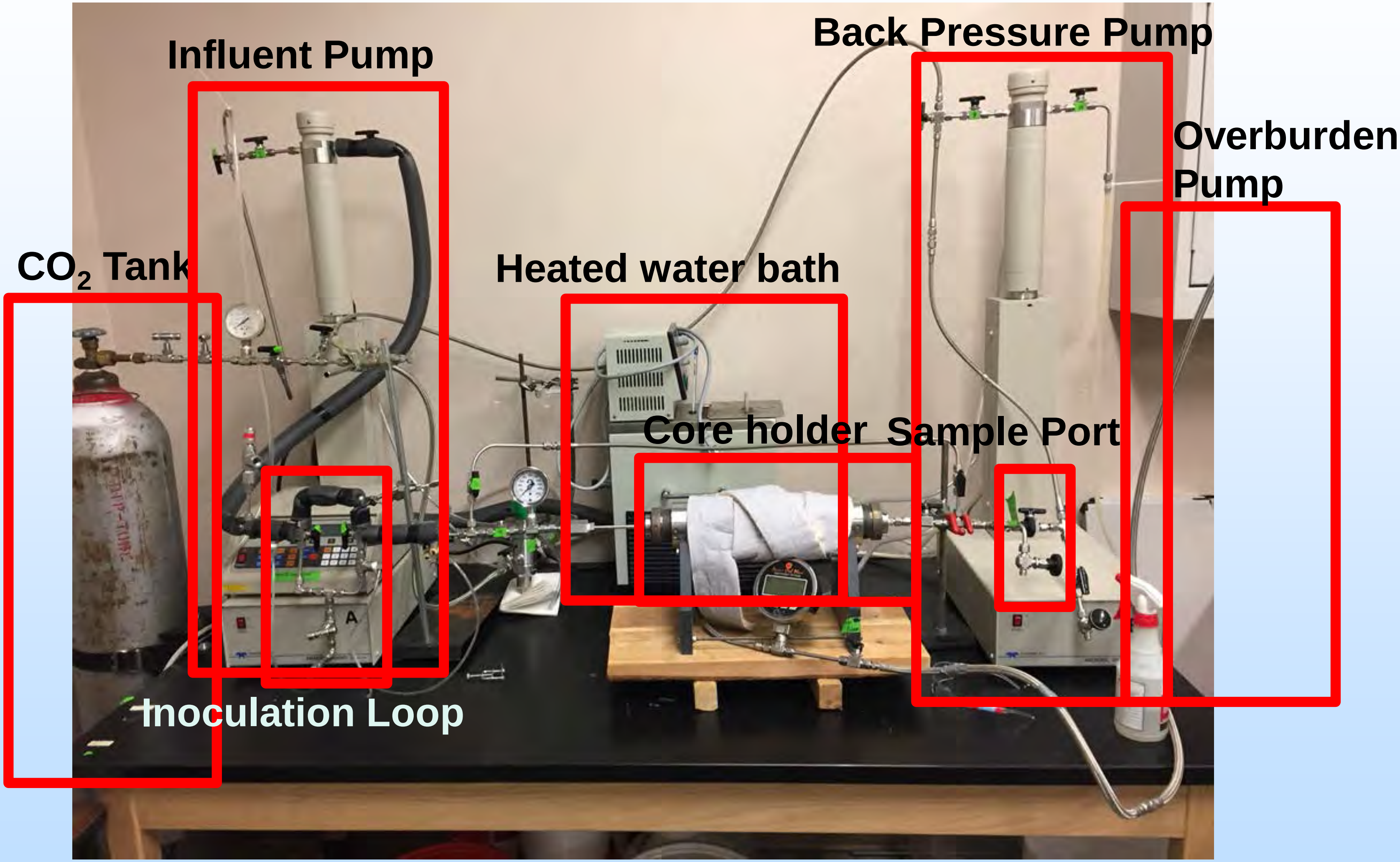
Series: $A(T) = \left(1 + \frac{\boldsymbol{\beta_1 k_1}}{\boldsymbol{k_2 - k_1}}\right)\boldsymbol{e^{-k_1 t}} - \frac{\boldsymbol{k_1\beta_1}}{\boldsymbol{k_2 - k_1}}\boldsymbol{e^{-k_2 t}}$

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

Kinetics of ureolysis- JBM



CO_2 EXPERIMENT

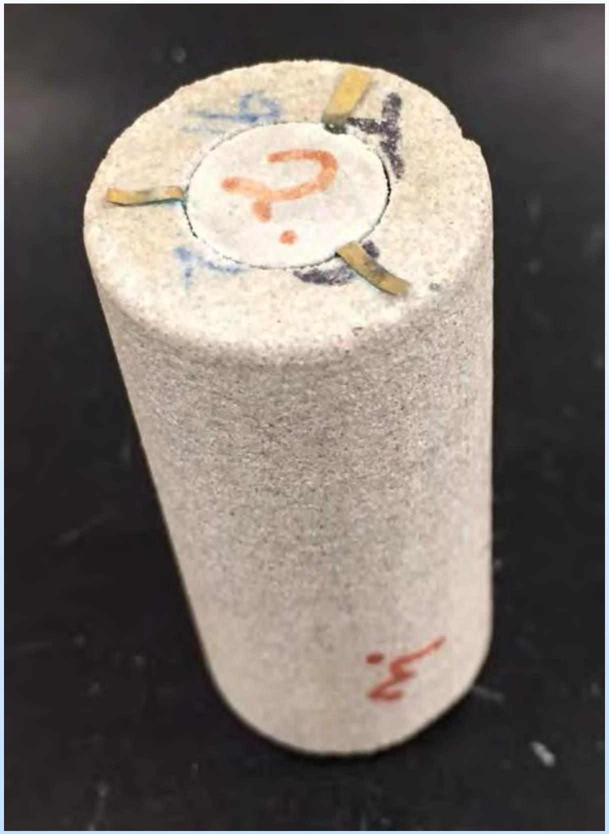


CO_2 EXPERIMENT

MONTANA STATE UNIVERSITY Mountains & Minds

CENTER FOR BIOFILM ENGINEERING

Pre-Mineralization



Post-Minera

Pre-CO_2 cha