MONTANA STATE UNIVERSITY
Energy Research Institute

U.S. DEPARTMENT OF ENERGY

Schlumberger

CENTER FOR BIOFILM ENGINEERING

SOUTHERN COMPANY

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Universität Stuttgart

Loudon Technical Services

# Wellbore Leakage Mitigation Using Advanced Mineral Precipitation Strategies

Project Number DE-FE0026513


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Montana State University



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 29, 2019

# 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

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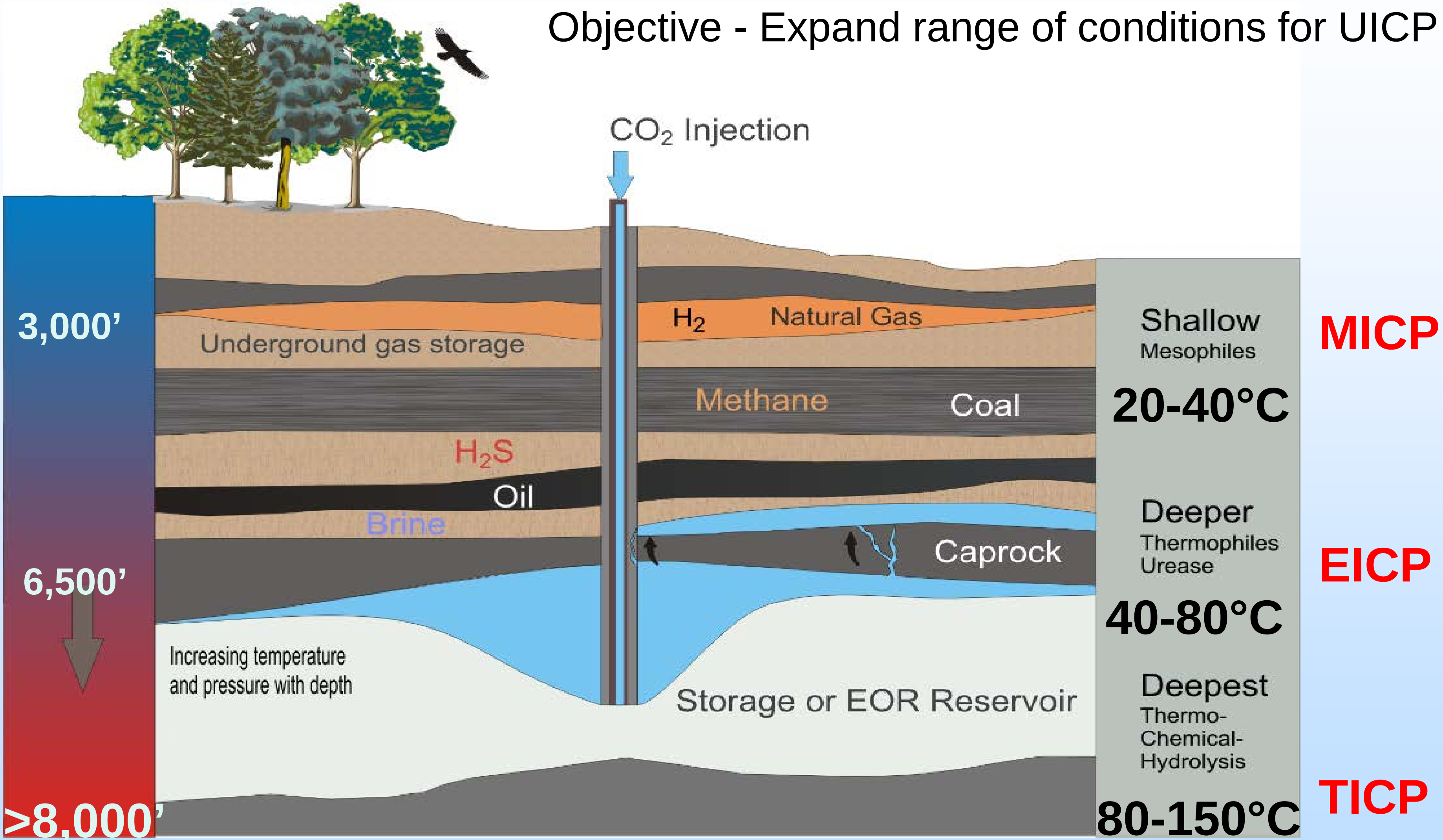
Objective - Expand range of conditions for UICP

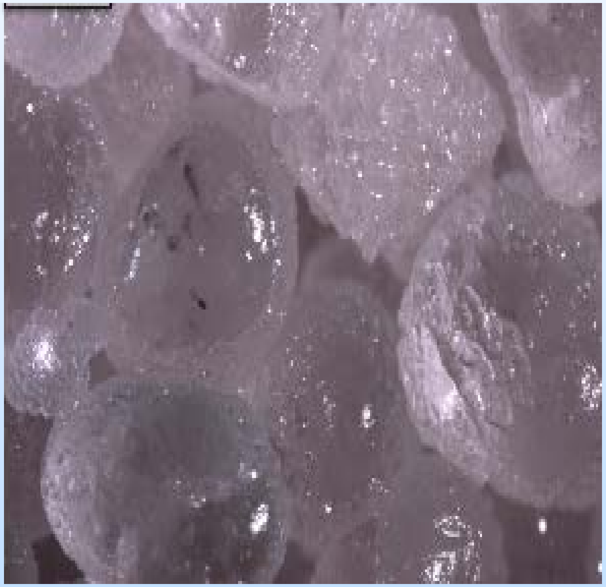



Advancing technologies for mitigating subsurface gas leakage

# Mineralization

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

- The 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



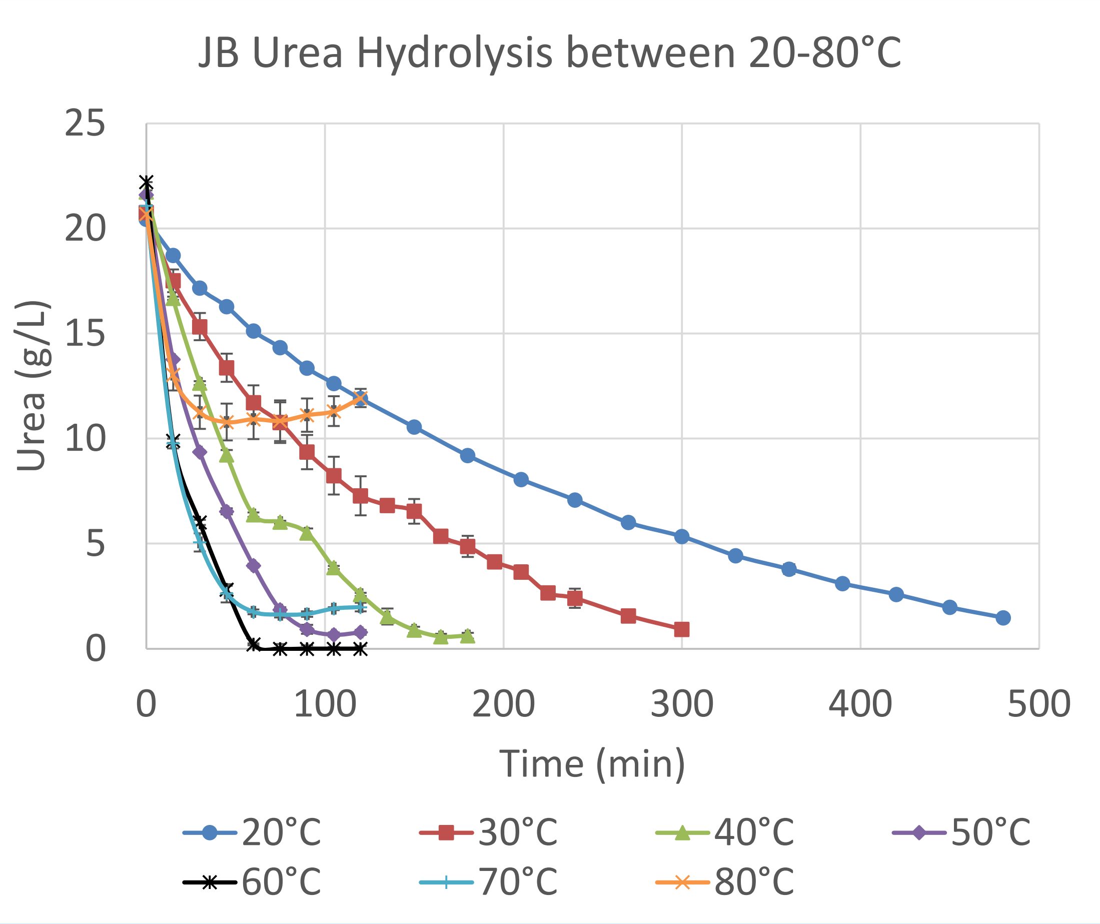
# Accomplishments: Objective 1

*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
- Enzyme inactivation rates
- Develop injection strategies to control mineral precipitation
    - Seal core
- Immobilization of enzyme to protect from denaturation

# JACK BEAN UREASE KINETICS




- Fast 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*

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

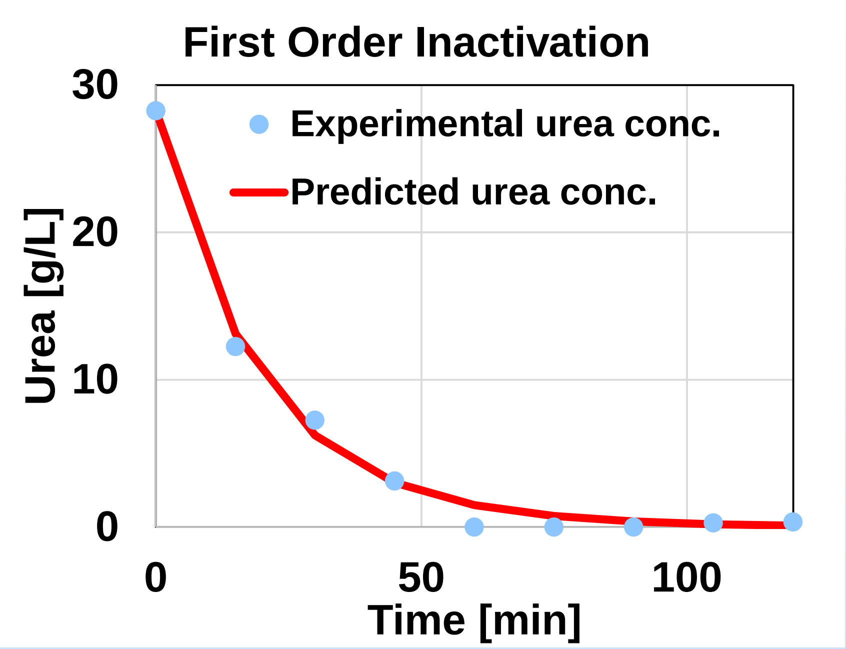
## *Series Inactivation*

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

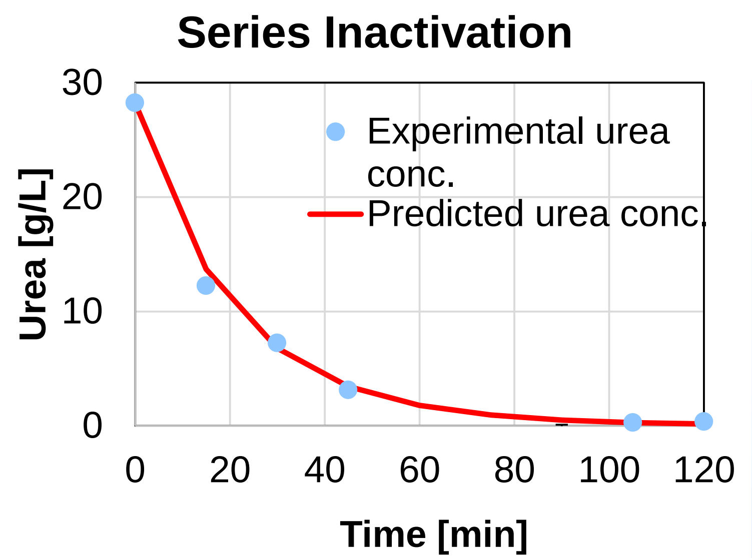
## *Series Parallel Inactivation*

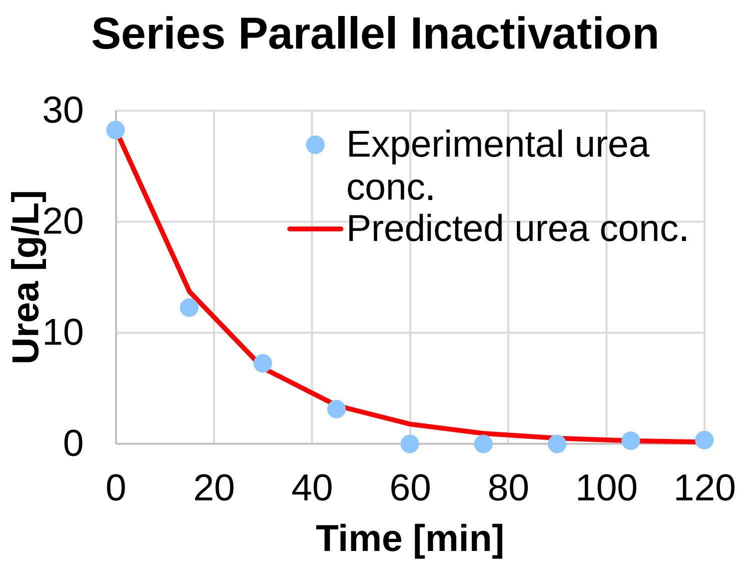
$$\begin{tikzcd} E_N \arrow[rr, "k_1"'] \arrow[dr, "k_3"'] & & E_I \arrow[dl, "k_2"] \\ & E_D & \end{tikzcd}$$

# JACK BEAN UREASE KINETICS & RATES




Computationally, least expensive



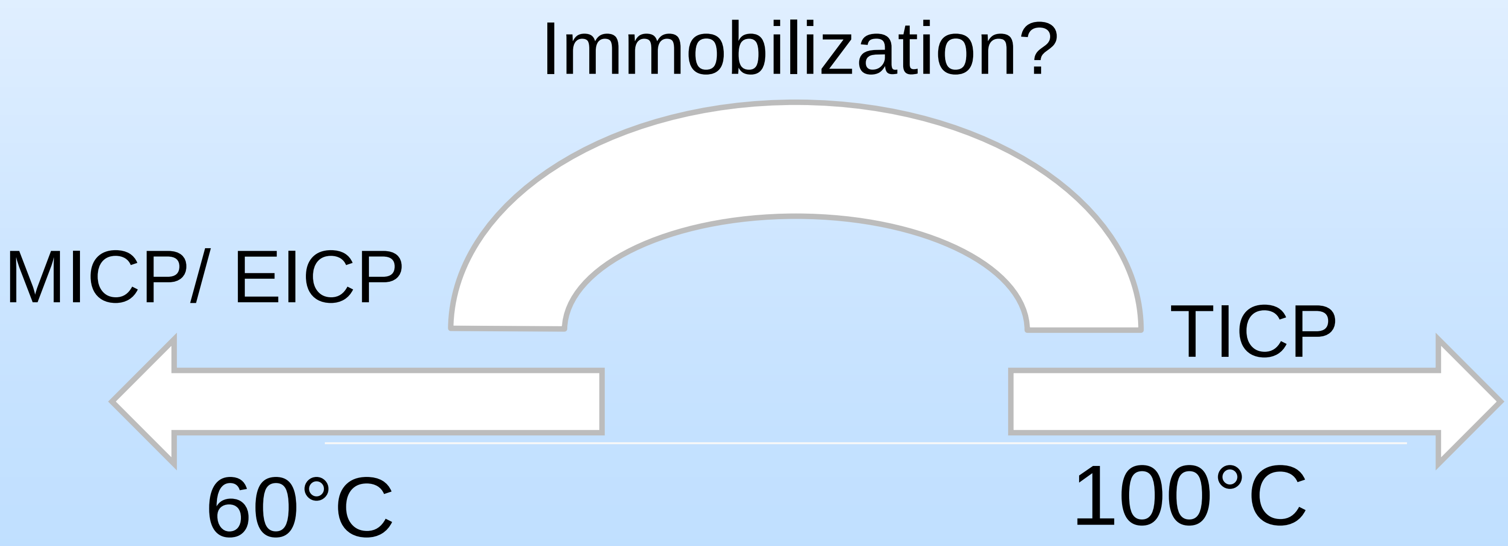



# IMMOBILIZATION

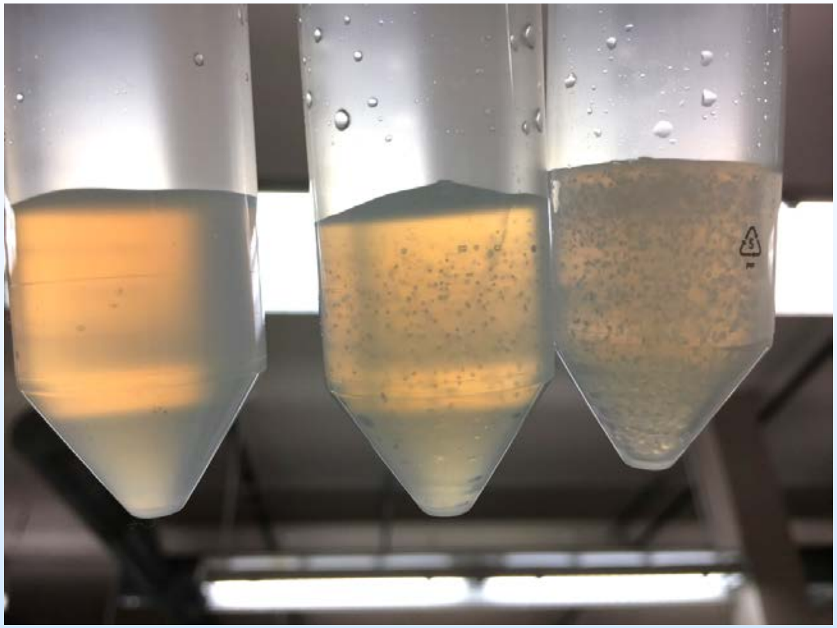
Enzyme activity down after 60°C due to thermal inactivation

Thermal ureolysis beyond 100-110°C

Fill the gap



# IMMOBILIZATION

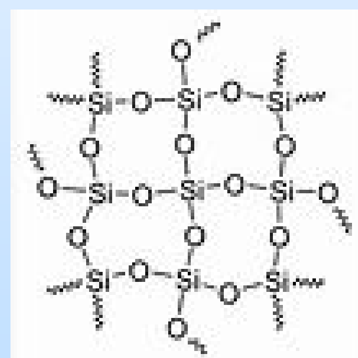


Ludox® gel with mineral.

Ludox® colloidal silica gel used.

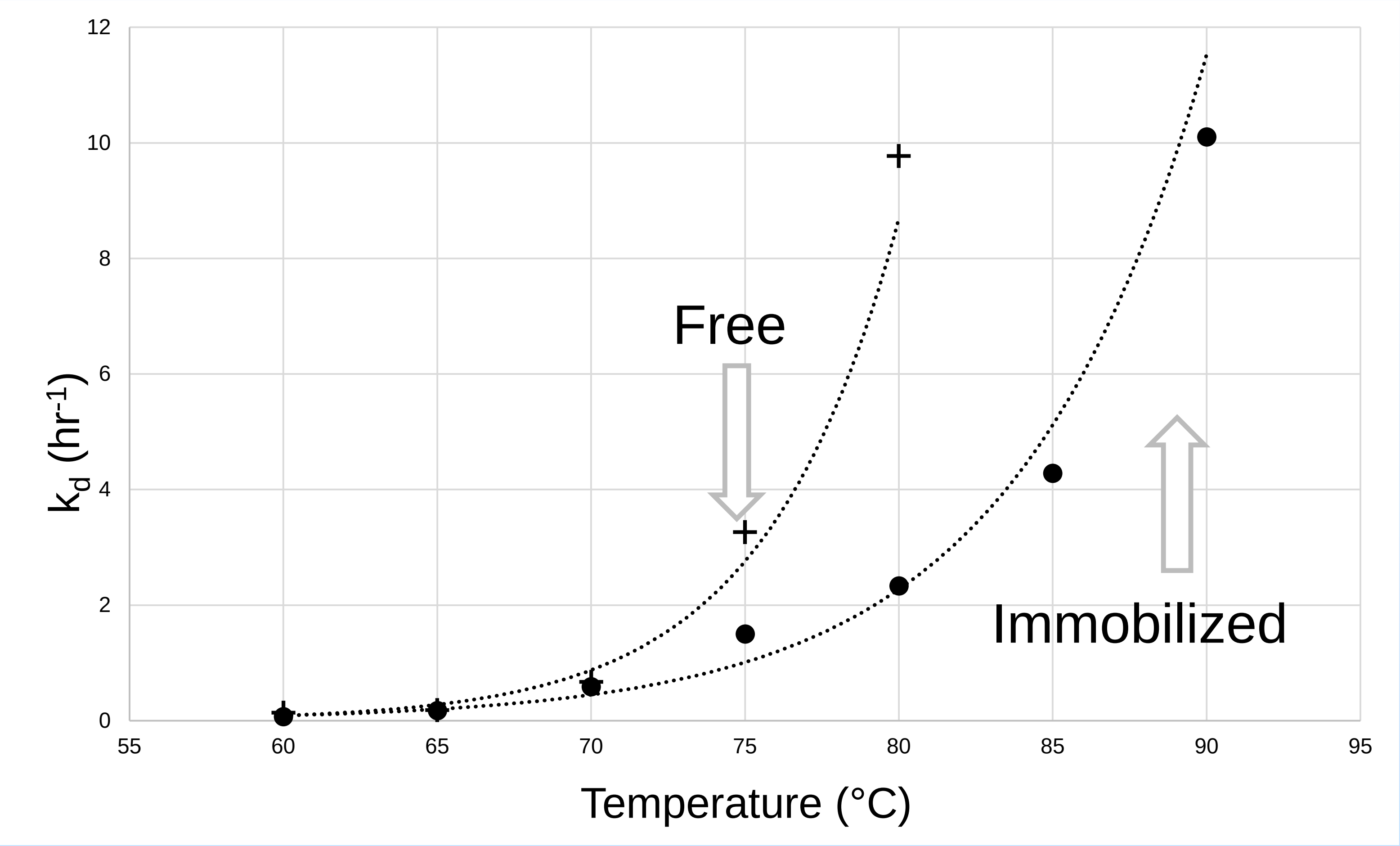
JB become trapped in polymer matrix.

Gel becomes enzymatically active.



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

# IMMOBILIZATION



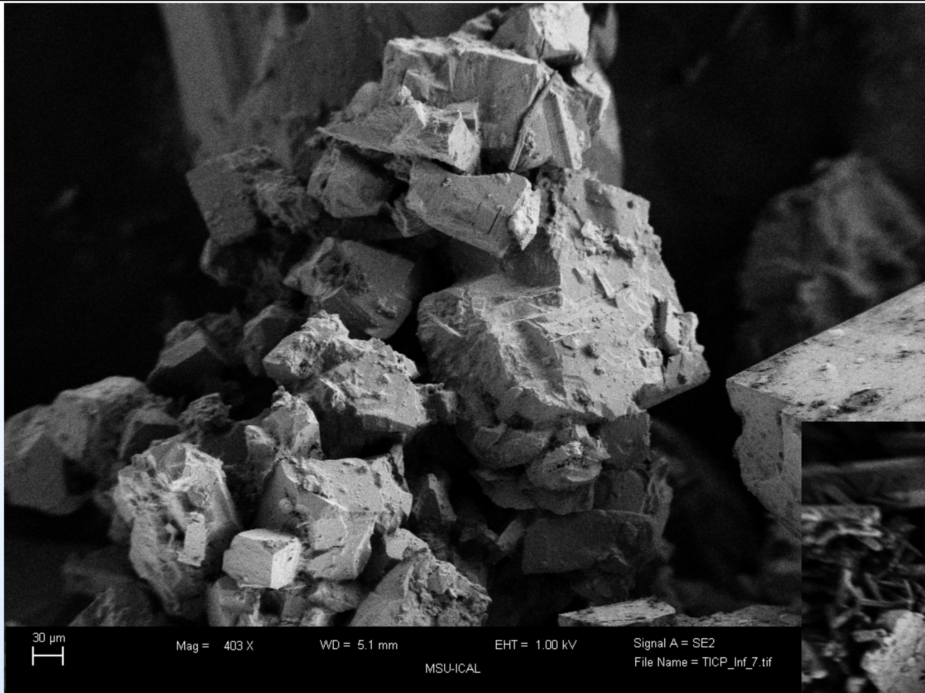

The first order thermal inactivation rate constant ($k_d$) for immobilized enzyme is lower than free enzyme- protection from degradation.

# THERMAL UREOLYSIS- TICP

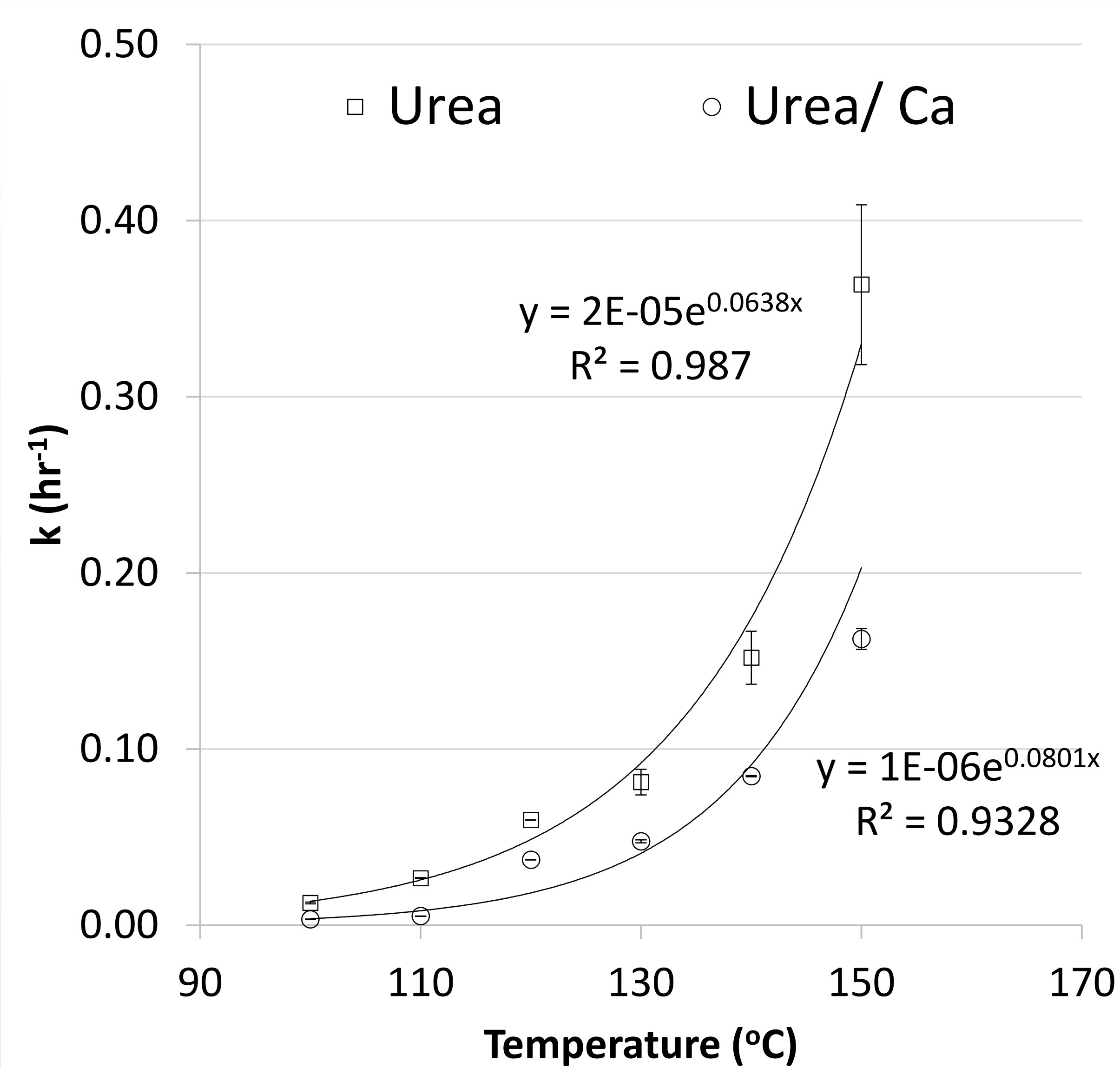
Aragonite vs Calcite

Mineral material properties

Use of organics




# THERMAL UREOLYSIS- TICP



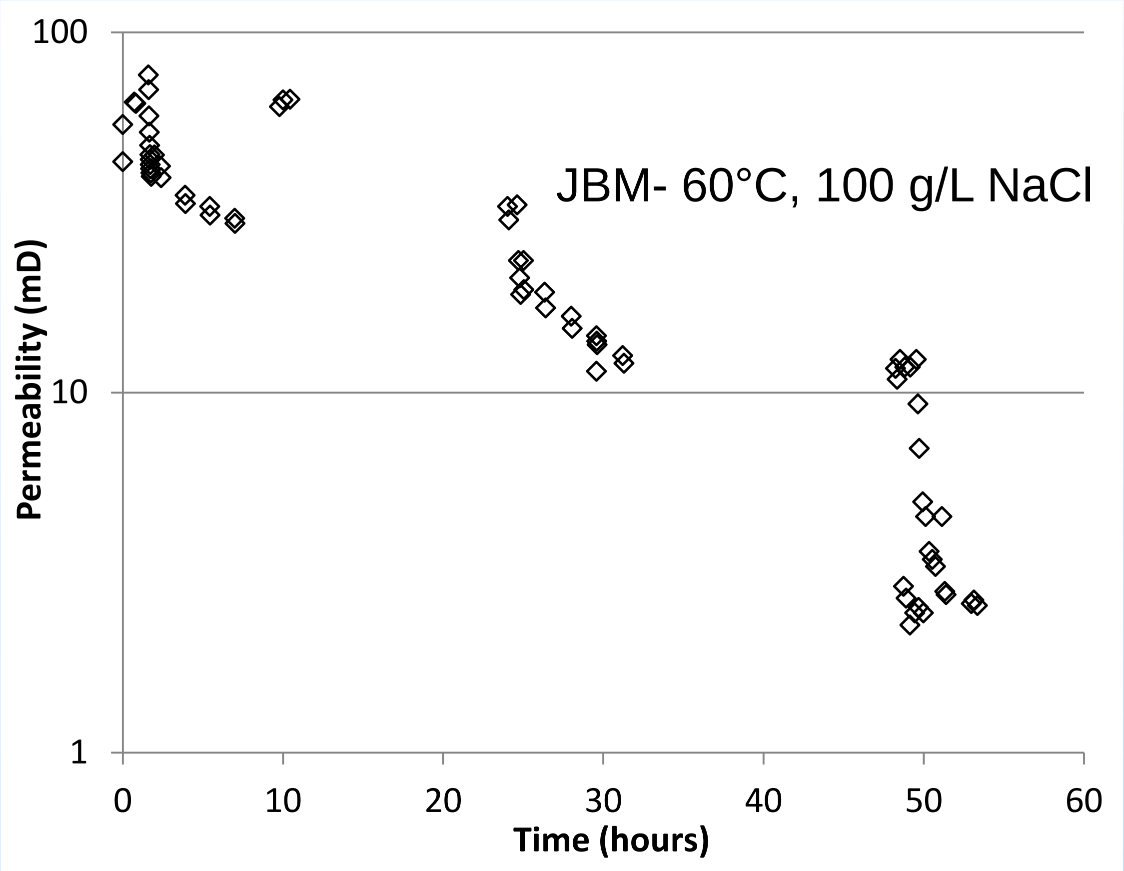

Enzyme limited to temps < 80°C

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

Increase U/Ca concentrations for increased precipitation

# Summary: Objective 1

*Made significant progress- laboratory studies in batch and in core.*

# Accomplishments: Objective 2

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

# $CO_2$ EXPERIMENT

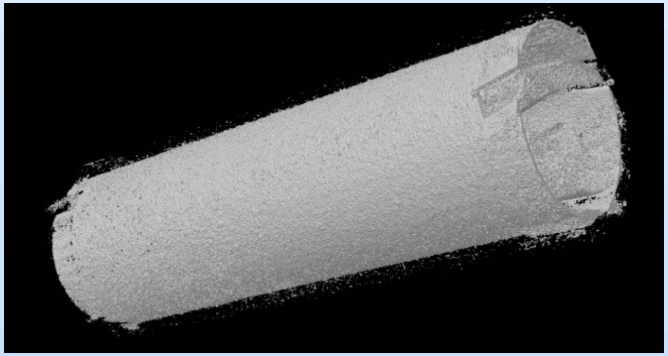
- 1in. X 2in. sandstone and cement core
- Soaked core with $CO_2$ saturated brine
- Mineralization pulses
- Challenged core with $CO_2$ saturated brine
- Scanned the core with X-ray-CT and NMR rock core analyzer
  - pre-mineralization
  - post-mineralization
  - post- mineralization $CO_2$ challenge

# $CO_2$ EXPERIMENT

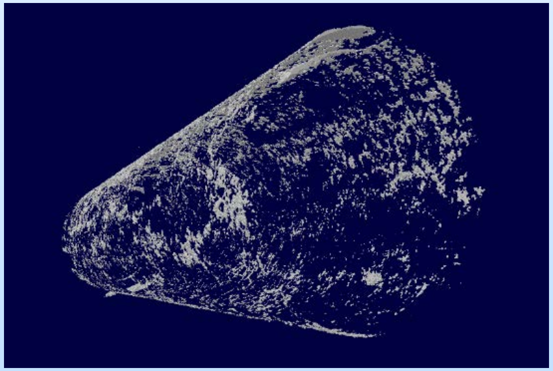
NMR and CT

| 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 |

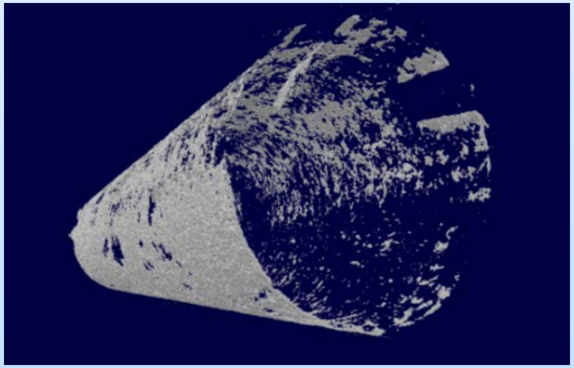
Pre-Mineralization



Post-Mineralization



Post $CO_2$

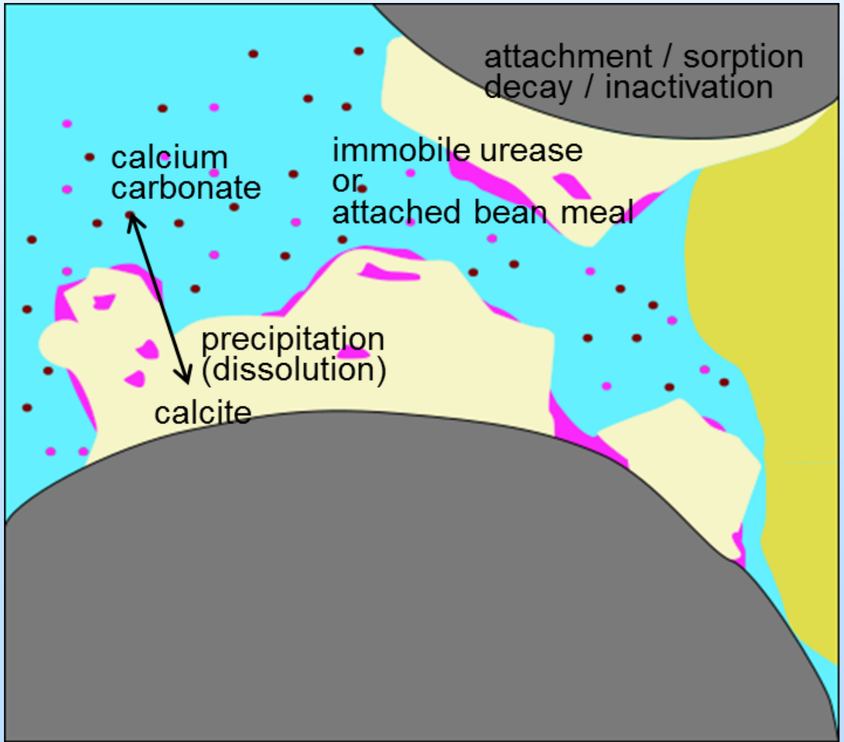


Ryanne Daily, Linn Thrane, Sarah Codd, Olivia Firth

# Accomplishments: Objective 3

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

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





- 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 (EICP) in a well.*

Gorgas, Alabama Dec. 2018

EICP

(heat treated cells-only enzyme)

Added $CO_2$

(sodium bicarbonate + HCl)

Sampled

(geochemistry and microbiology)

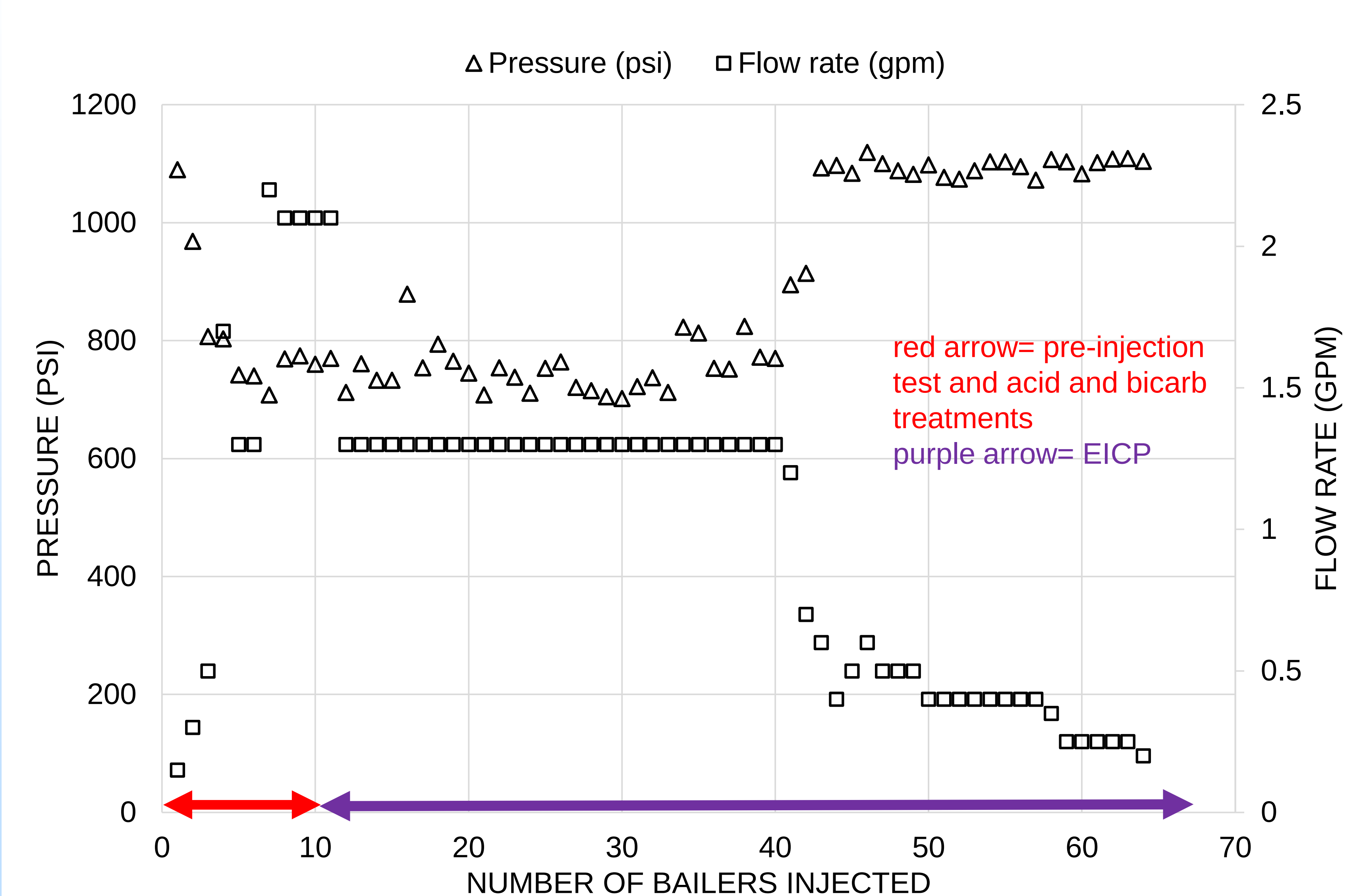
# Accomplishments: Objective 4

Sampling downhole fluids- before, after addition of HCl and sodium bicarbonate to generate acidic conditions and $CO_2$, mid EICP, and at the end of the EICP treatment – geochemistry and microbial ecology


Dr. Catherine Kirkland, Montana Emergent Technologies, Loudon Technical Services, Arda Akyel

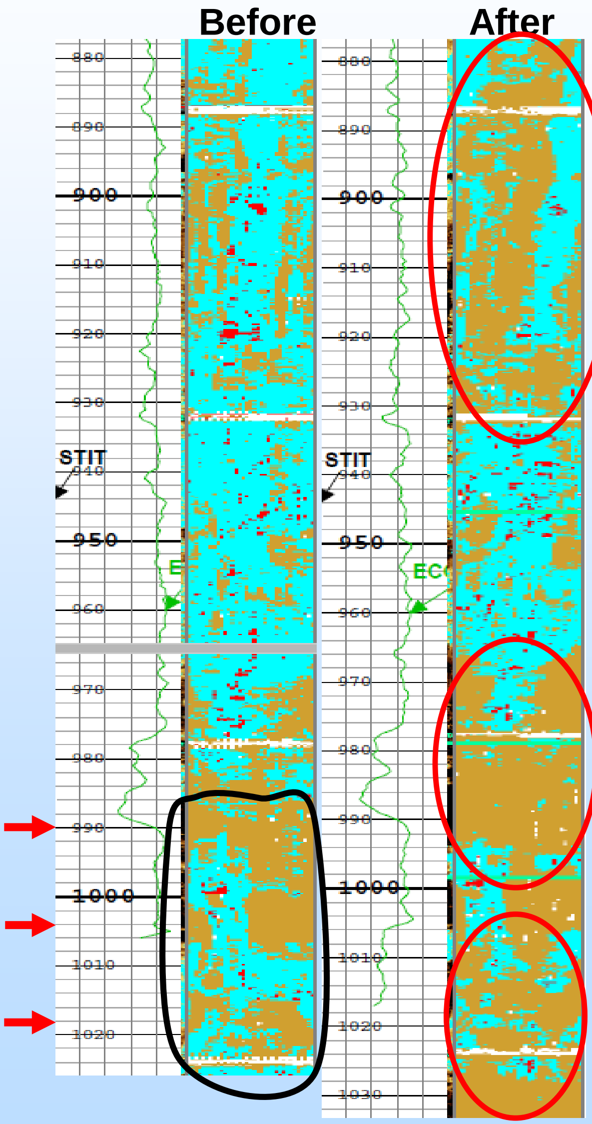
Dr. Djuna Gulliver, NETL

# Accomplishments: Objective 4



# Accomplishments: Objective 4

Logged the well before and after EICP treatment to assess efficacy of sealing




Dr. Catherine Kirkland, Montana Emergent Technologies, Loudon Technical Services, MSU

# Lessons Learned

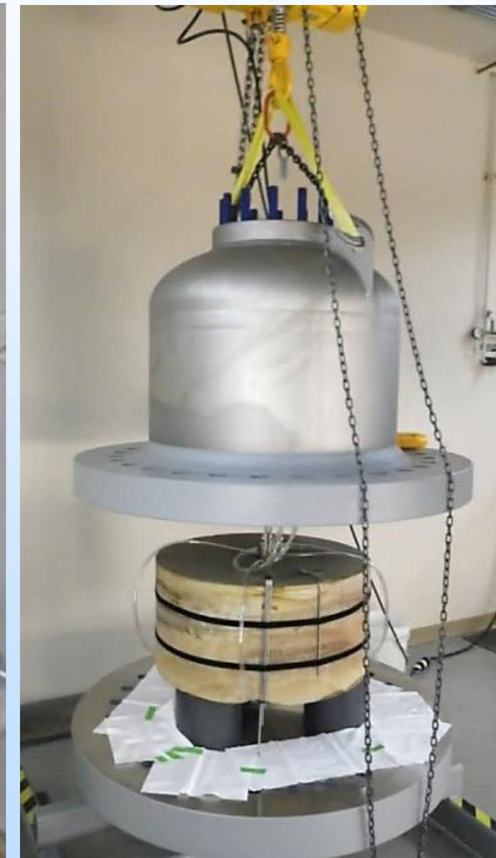
- Mineralization can be expanded to higher temperature applications
- Understand kinetics of reactions and how mineral forms
- Scaling up the processes for field application
- Addition of $CO_2$ to the well by chemical means (formation in situ)
- Heat treating cells but enzyme remains active
- Sealing was accomplished in the presence of $CO_2$

# 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)
  - 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](10.1016/j.petrol.2014.12.008)

# SUMMARY & FUTURE

## Summary

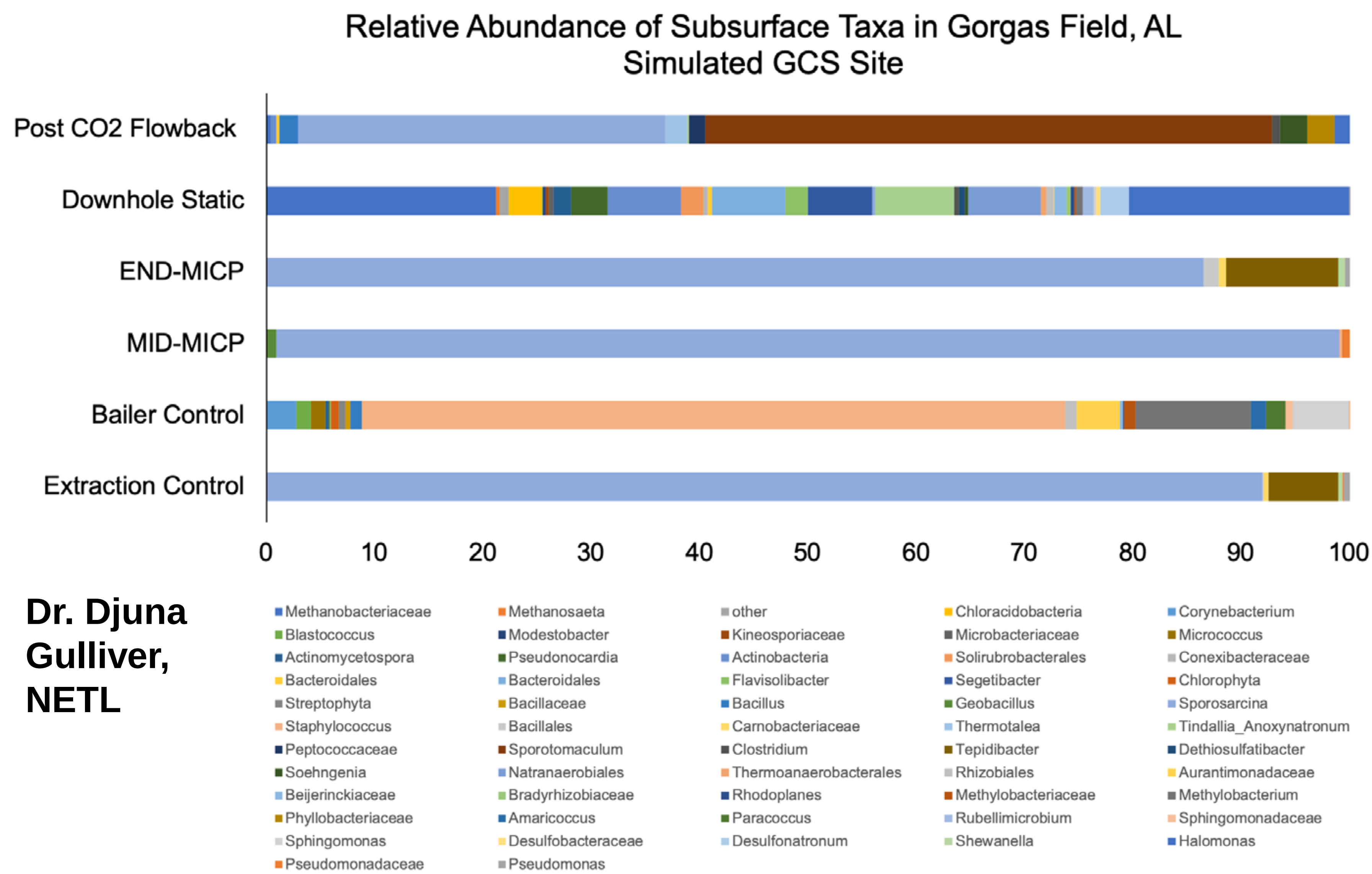
- JB urease kinetics and inactivation
- Thermal hydrolysis of urea > 80°C (100°C)
- Model updates
- Field experiment

## Future EICP and TICP

- Mineralization strength (TICP or EICP)
- Extraction of enzyme from cell
- Field: mineral seal characterization and well plugging

# Accomplishments: Objective 4

Geochemistry and microbiology




**Dr. Djuna Gulliver, NETL**

# 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.**

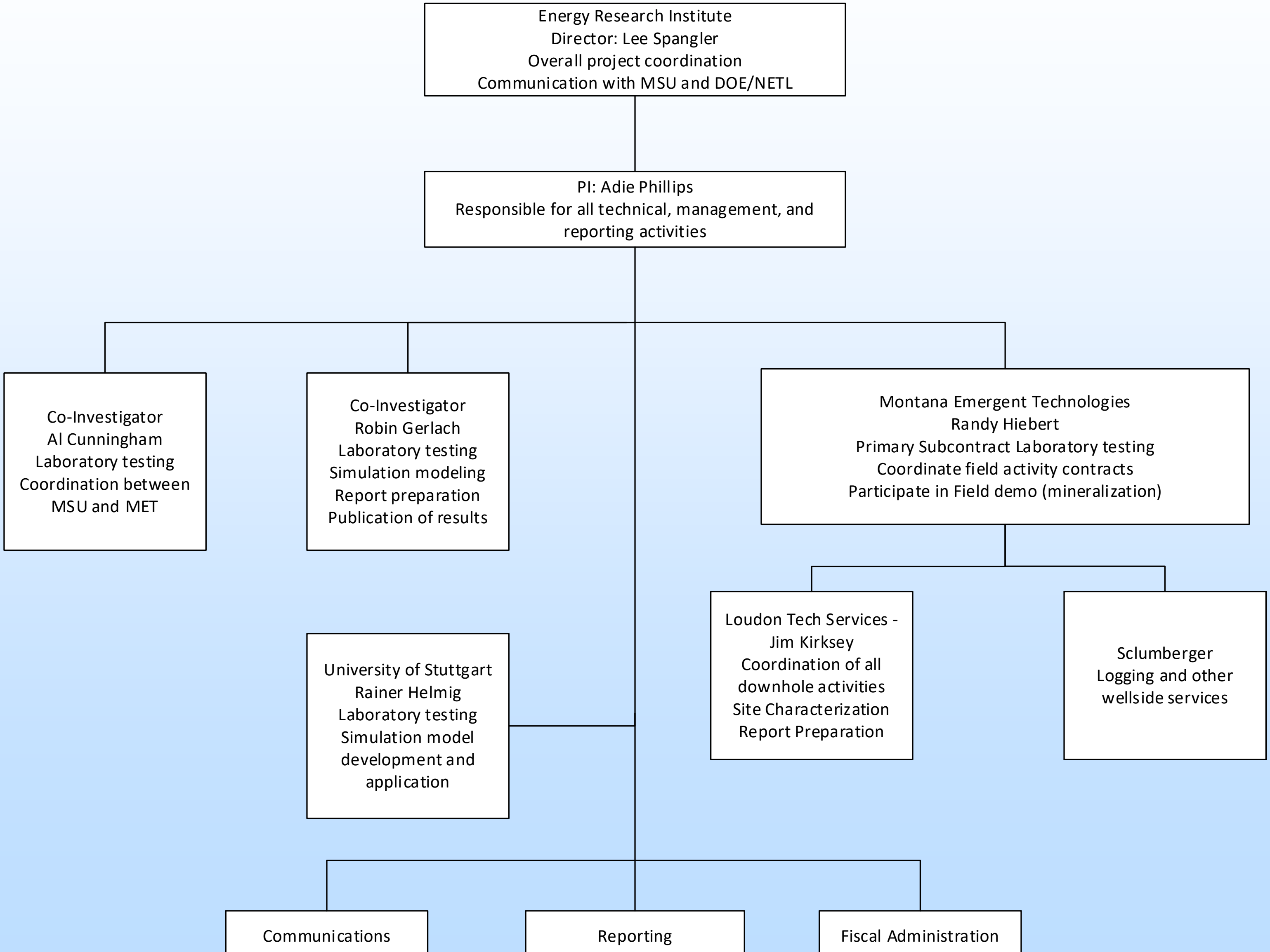
- Active enzyme as the catalyst as well as direct thermal hydrolysis of urea drive mineralization precipitation developing **engineered mineralization sealing at greater depths and higher temperatures** to address the FOA requirement to *“prevent or remediate detected leaks in complicated environments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

# **Project Overview**: Goals and Objectives

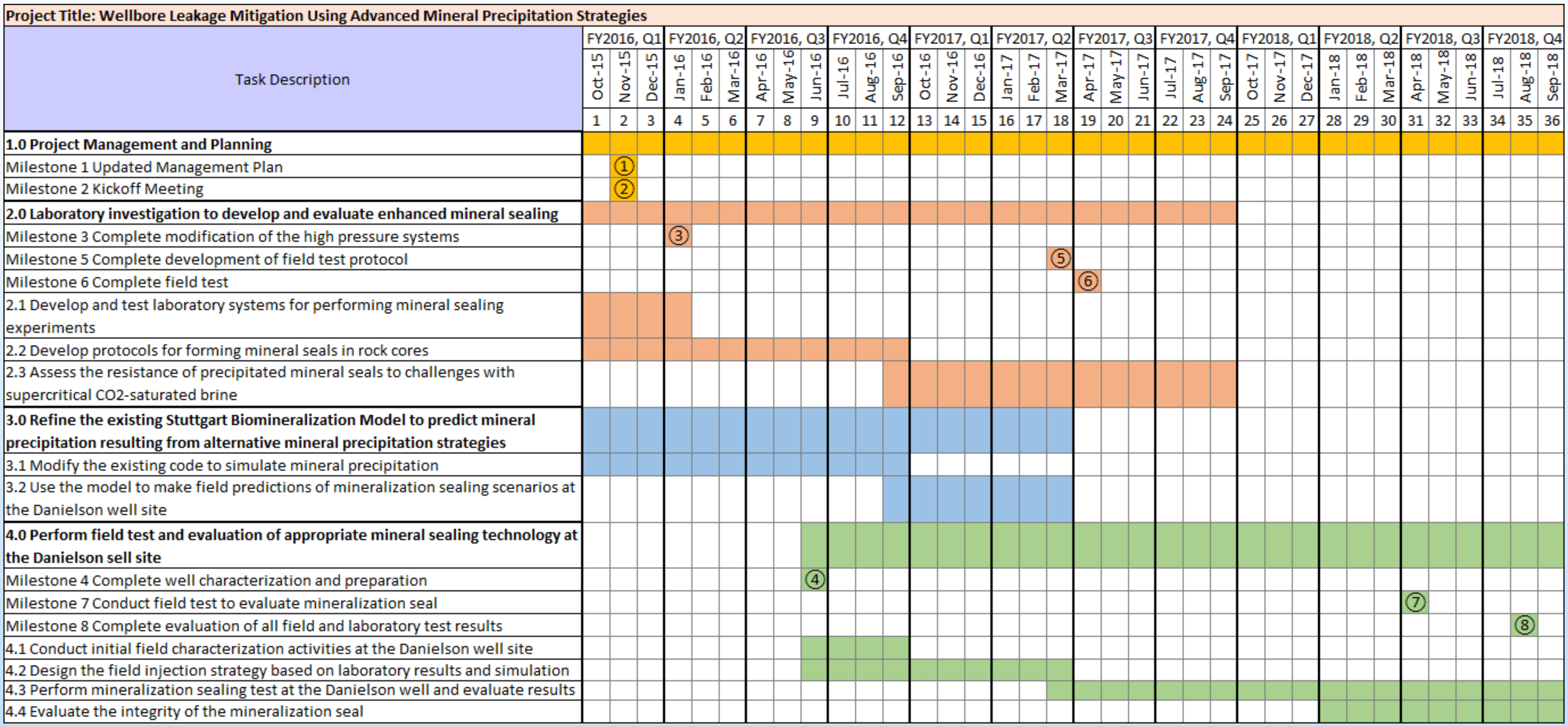
Objectives

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

# Organization Chart



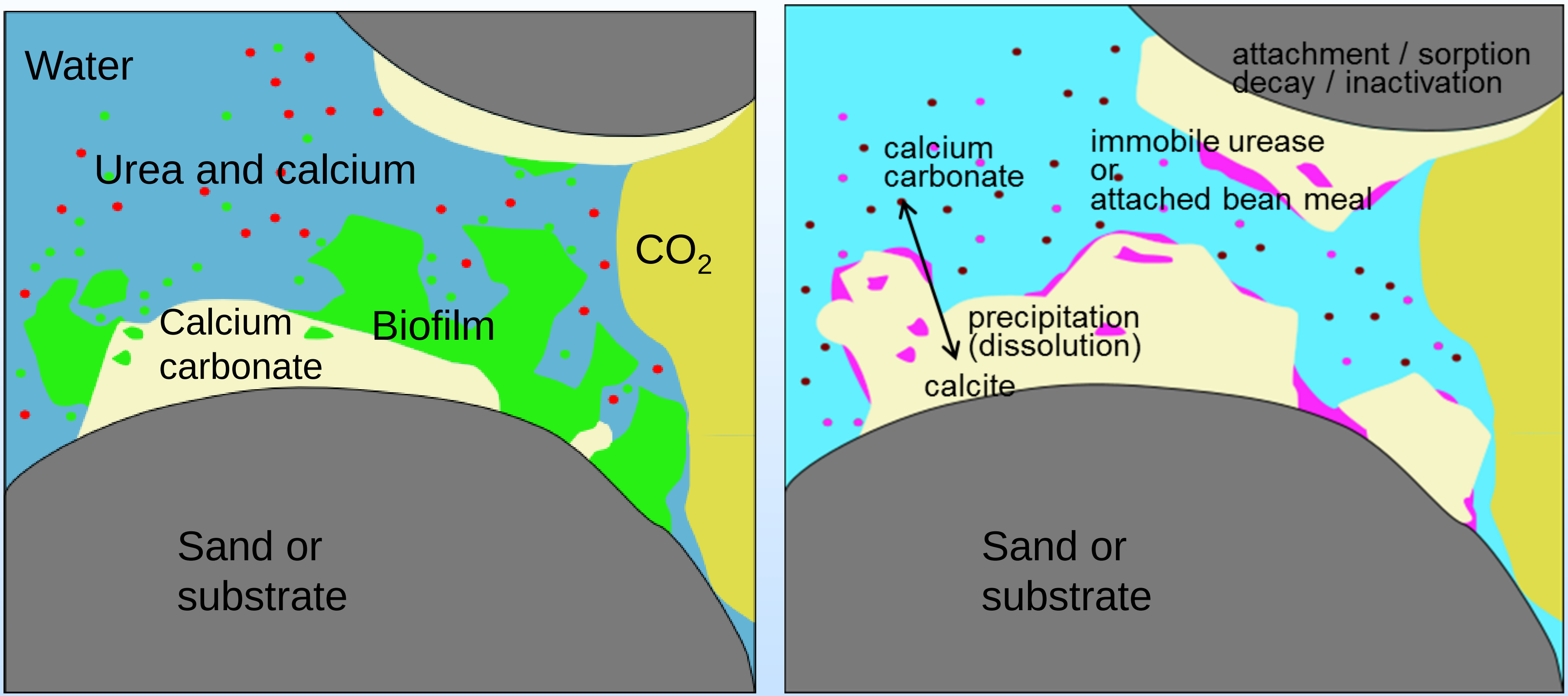
# Gantt Chart


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)

# 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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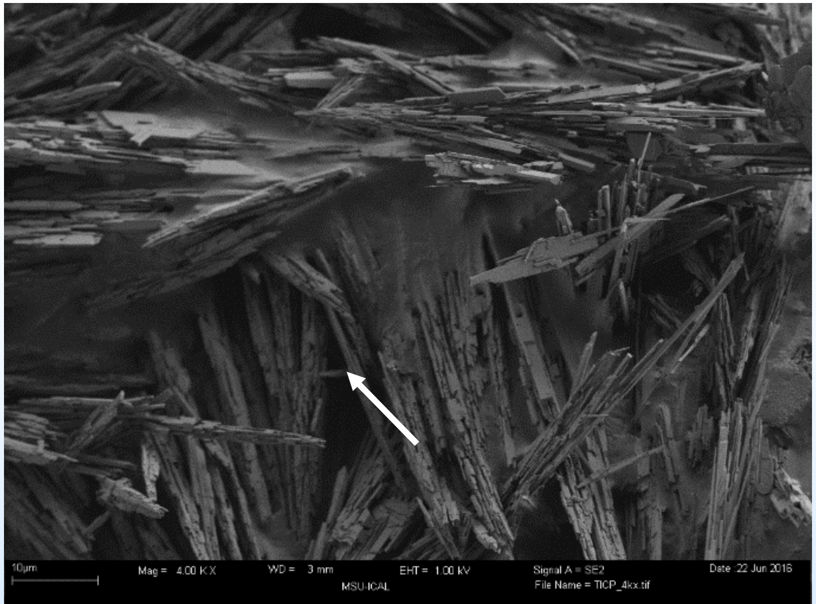
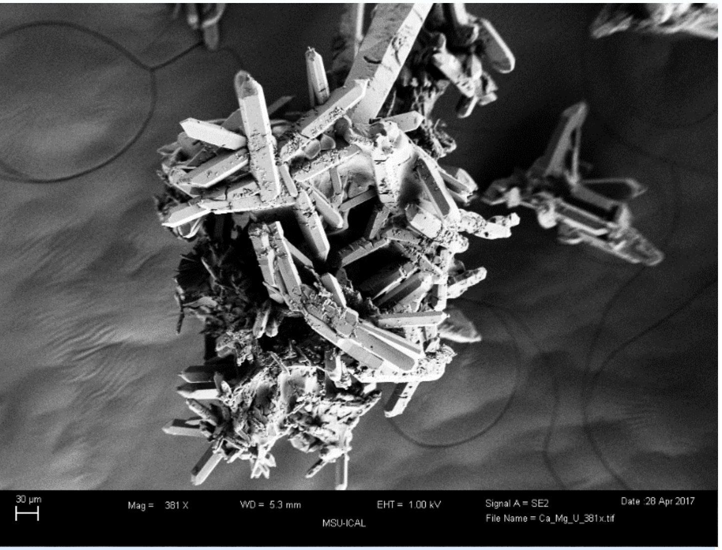
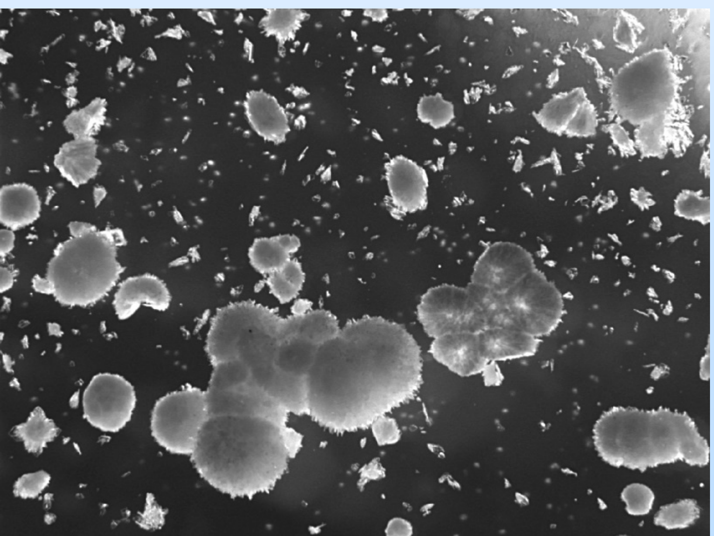
# THERMAL HYDROLYSIS- TICP

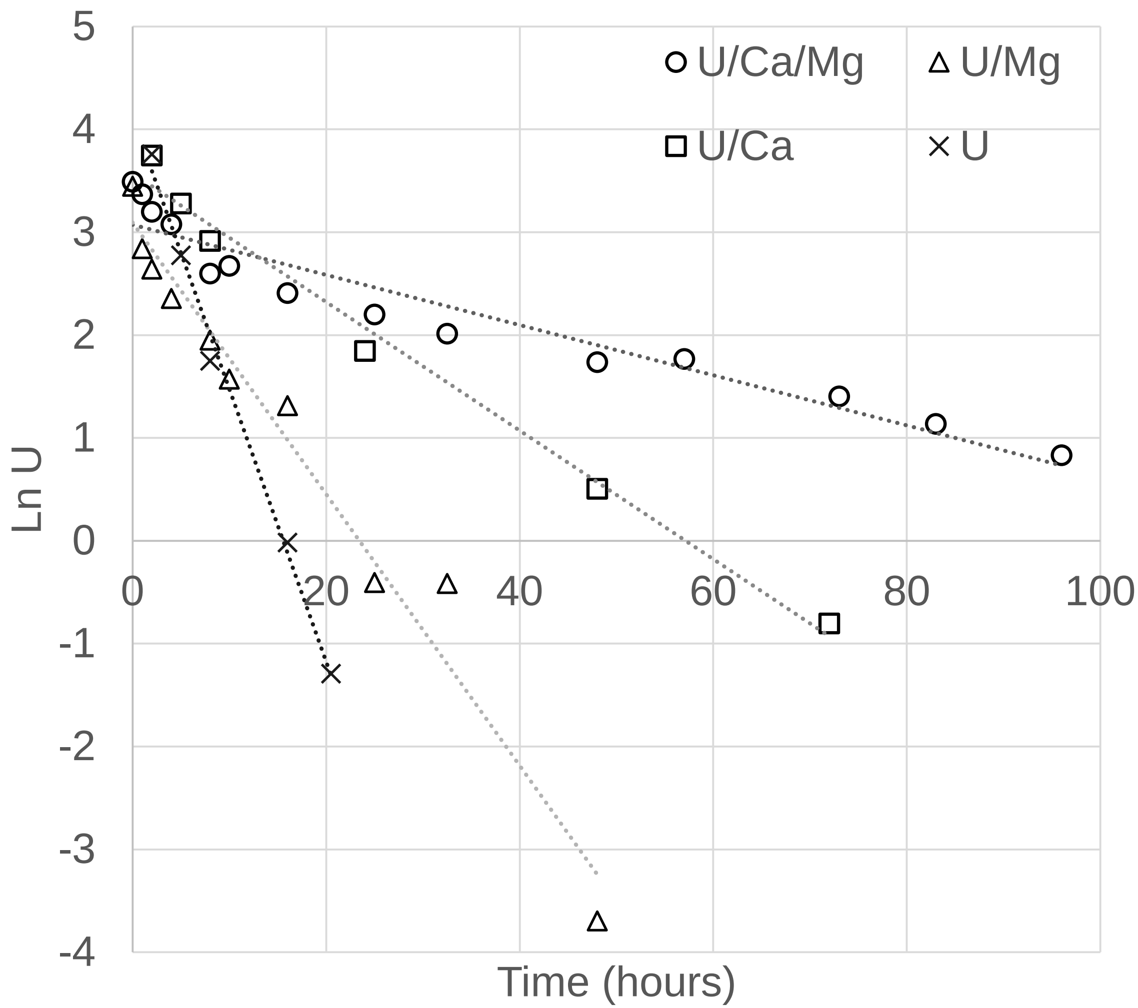




# ALTERNATIVE MINERALS-TICP





# 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

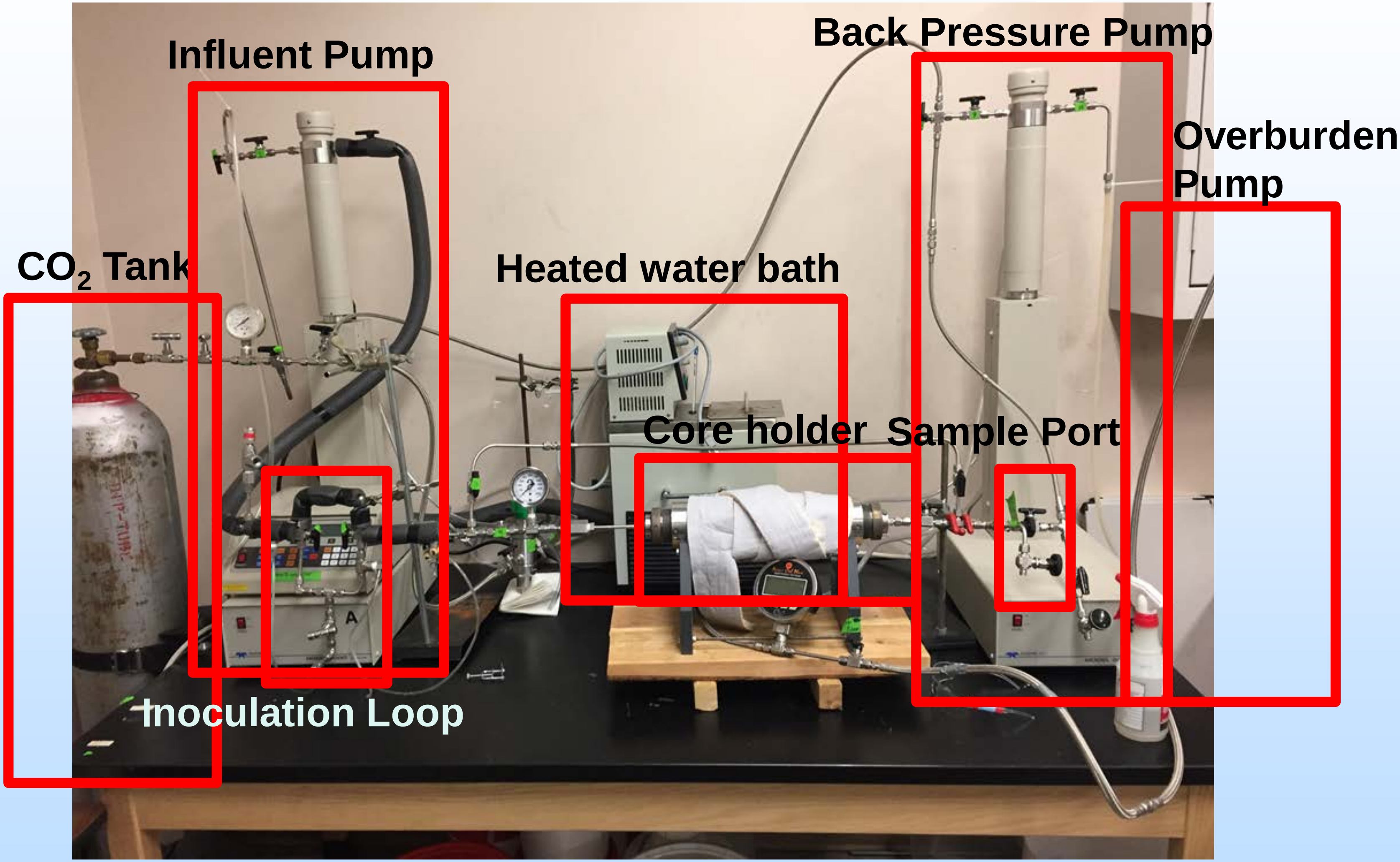
Rate equation: $\frac{dU}{dt} = k_a(T) * [U] * [A(T)]$

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

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

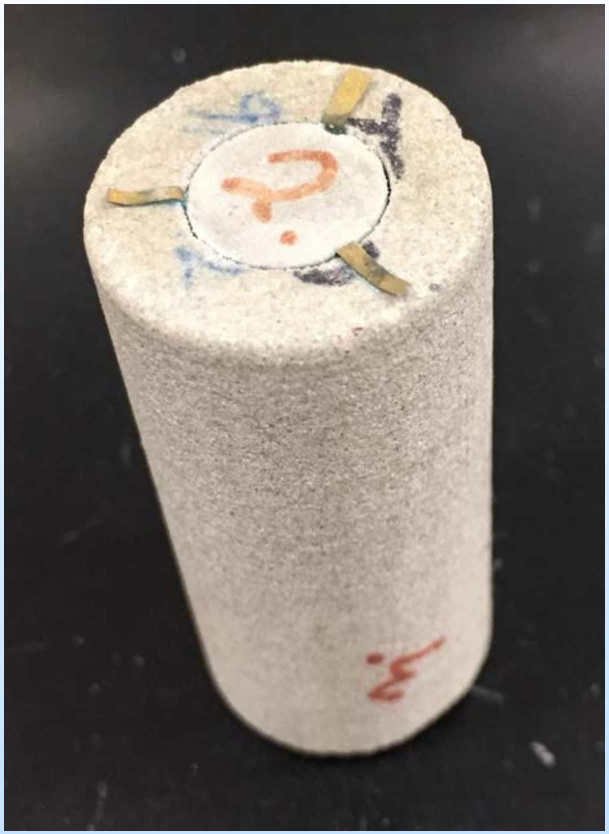
Series-parallel: $A(T) = \left(1 + \frac{\boldsymbol{\beta_1 k_1}}{\boldsymbol{k_2 - k_1} - k_3}\right)\boldsymbol{e^{-(k_1 + k_3)t}} - \frac{\boldsymbol{k_1 \beta_1}}{\boldsymbol{k_2 - k_1} - k_3}\boldsymbol{e^{-k_2 t}}$

# $CO_2$ EXPERIMENT



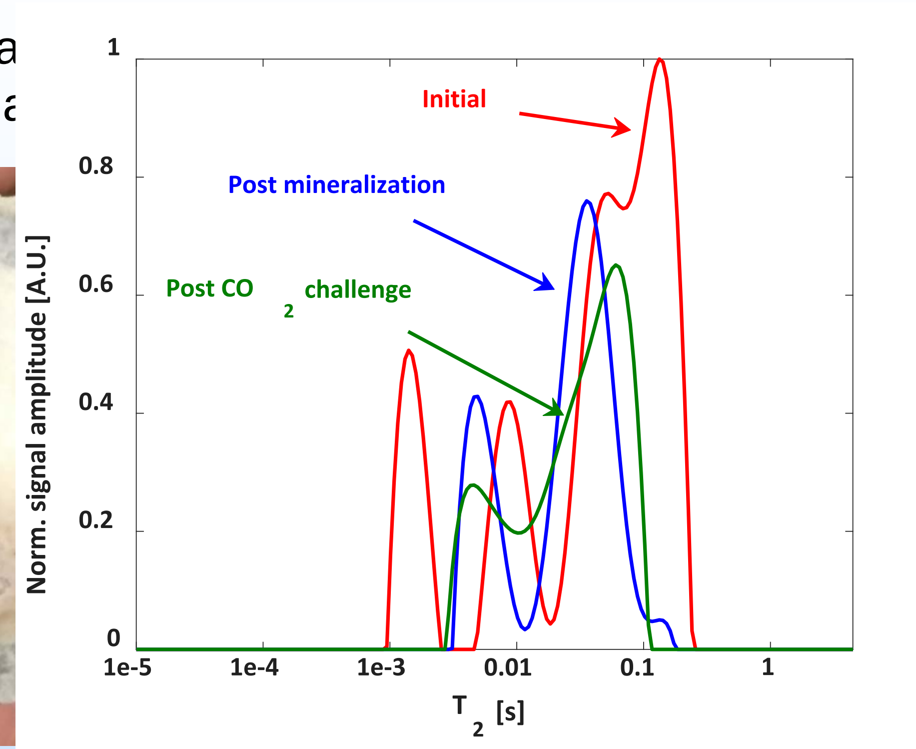
# $CO_2$ EXPERIMENT

Pre-Mineralization

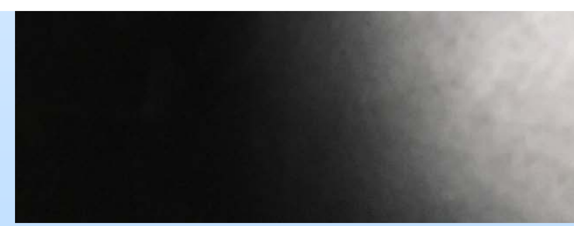


Post-Minera

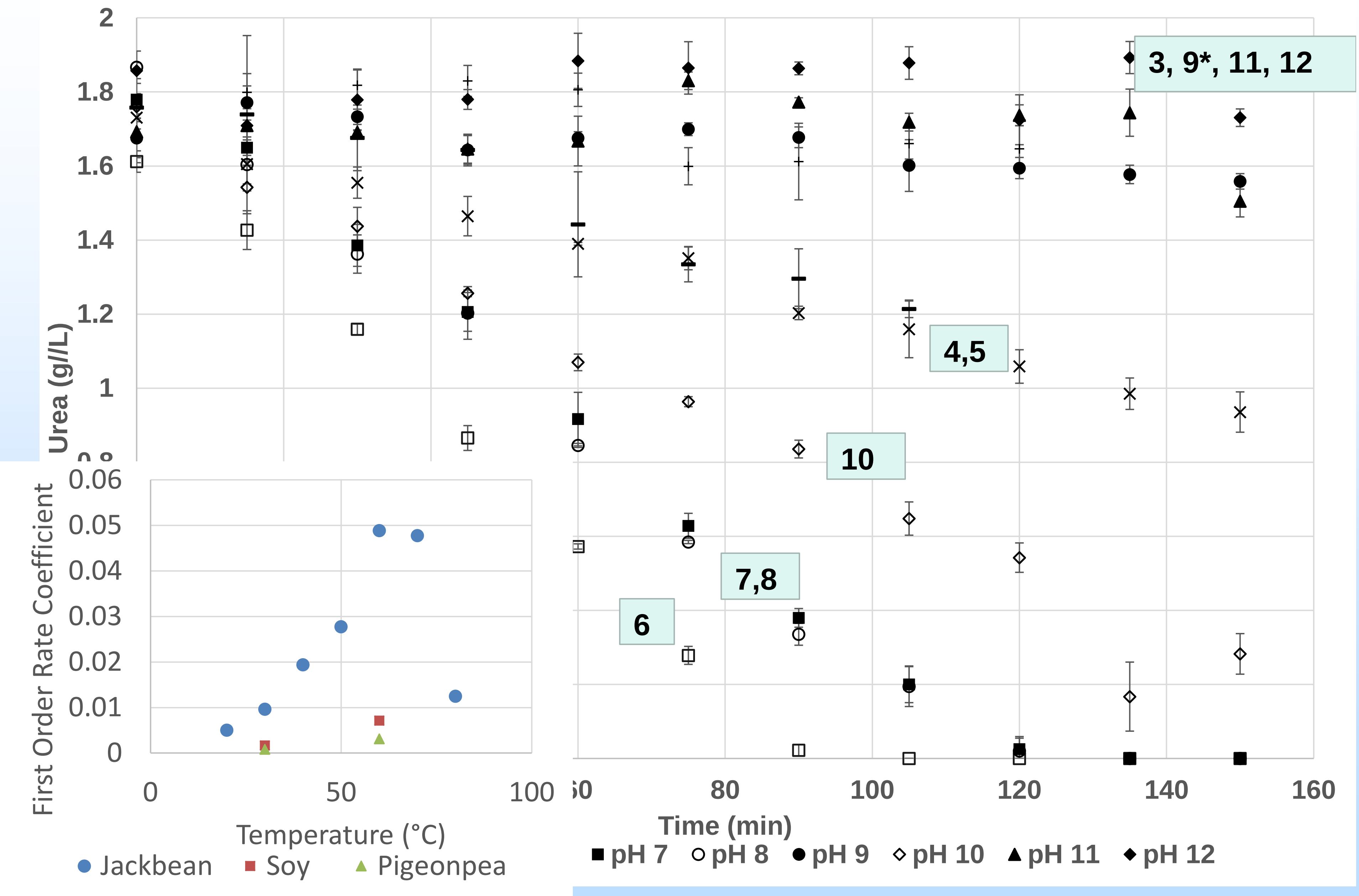
Pre-$CO_2$ cha







# Kinetics of ureolysis- JBM



# Accomplishments: Objective 4

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CENTER FOR BIOFILM ENGINEERING

2) Heat kill system using stainless steel coils and heated water
3) Used those heat killed cells and nutrients (urea calcium solutions) to promote mineralization in the wellbore channel


# 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

# ENZYME MINERALIZATION- EICP