# Co-Precipitation of Trace Metals in Groundwater and Vadose Zone Calcite: *In Situ* Containment and Stabilization of Strontium-90 and Other Divalent Metals and Radionuclides at Arid Western DOE Sites

**EMSP Project Number: 87016**

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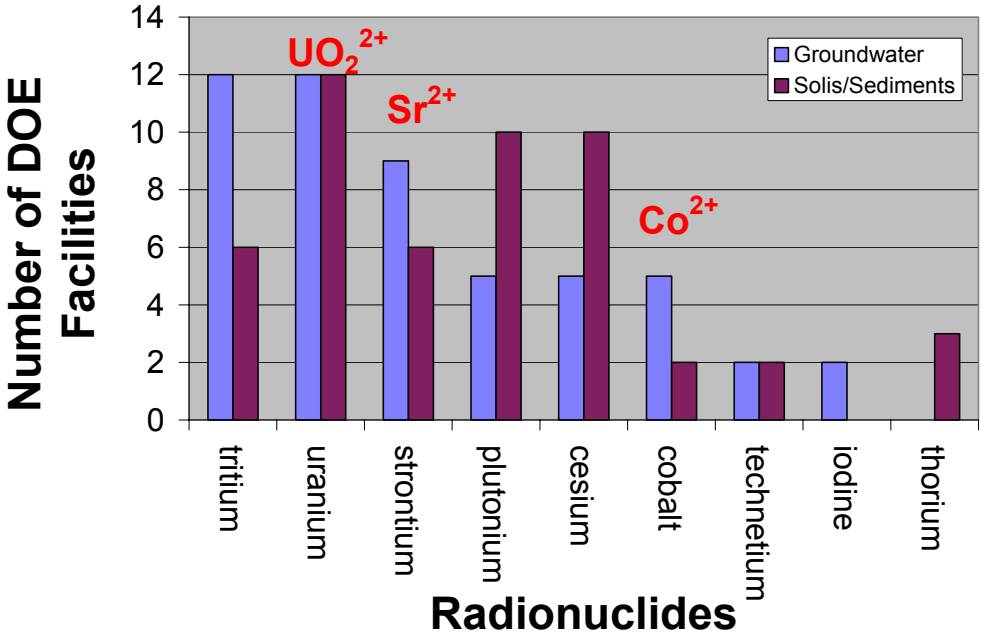
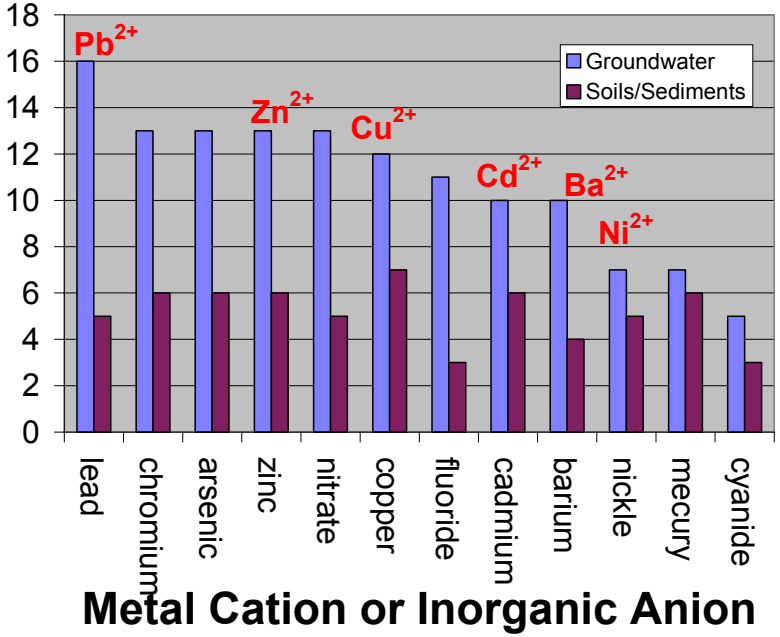
# Objectives

- Elucidate release mechanisms for sorbed trace metals and their subsequent sequestration by co-precipitation in calcite as induced by urea hydrolysis
- Evaluate the influence of microbial calcite precipitation on the partitioning/retention of strontium and other divalent metals in groundwater at the field-scale
- Identify specific microbial community characteristics that signify subsurface geochemical conditions that are conducive to calcite precipitation

# Divalent Metals and Radionuclides are Common at DOE sites




Riley and Zachara 1992

# $^{90}$Strontium Contamination

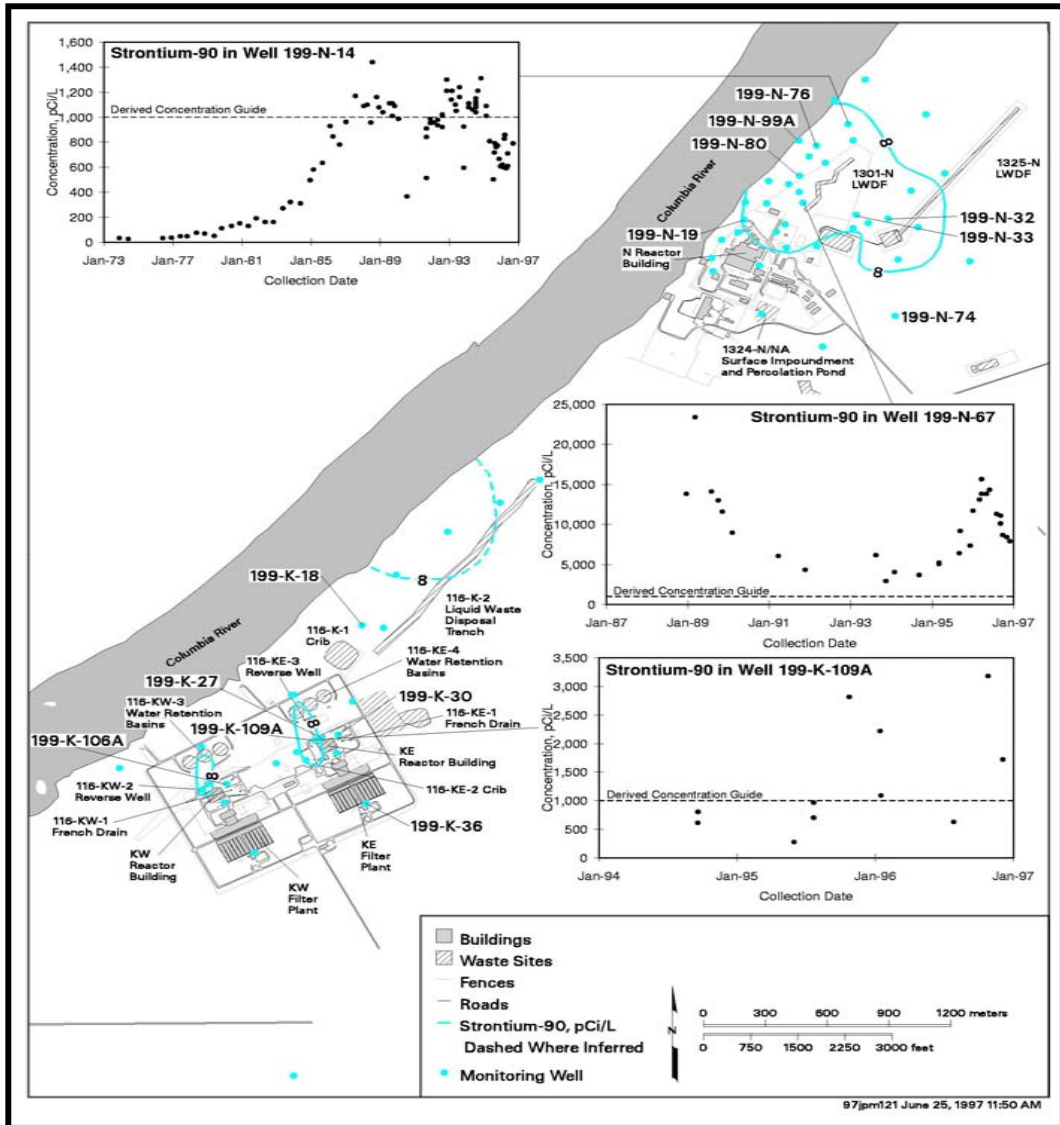
INEEL groundwater, perched water (INTEC)

- **Up to 84 pCi $L^{-1}$ in a 1.6 $km^2$ groundwater plume**
- **Up to 320,000 pCi $L^{-1}$ in perched water**

Hanford soils, groundwater (100N)

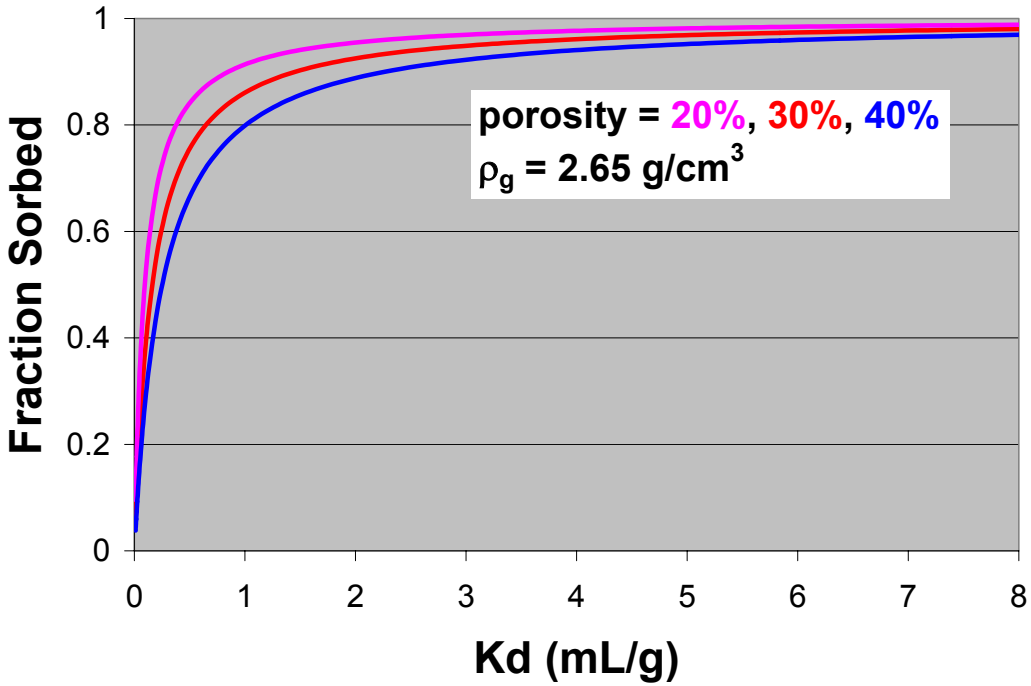
- **Est in-ground inventory of 75 to 89 Ci**
- **Groundwater levels up to 6000 pCi $L^{-1}$**

**EPA Regulatory Limits for $^{90}$Sr in drinking water: 8 pCi $L^{-1}$**



# Groundwater Remediation: Treating the Solid Subsurface Media

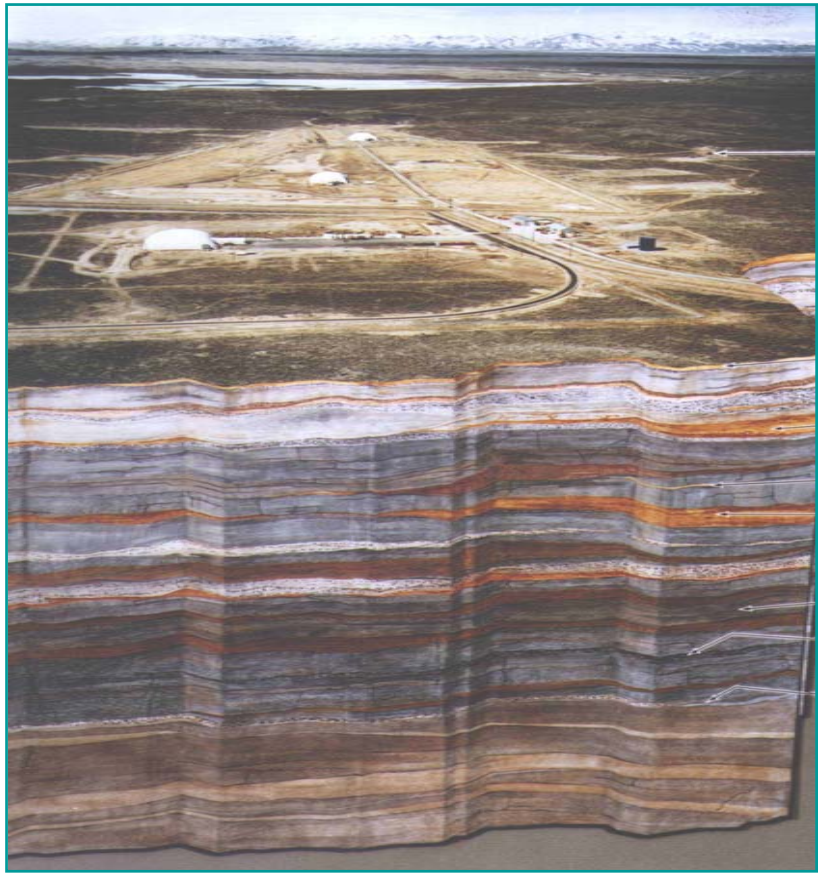
- Even for contaminants that are mobile in water, most of the contaminant mass is sorbed to the aquifer matrix (Palmer and Fish 1997)




$$R_f = 1 + K_d \rho_g \frac{1-\theta}{\phi} = \frac{1}{1 - \textbf{fraction sorbed}}$$

# Immobilization of $^{90}Sr$ in Calcite

- $T_{1/2}$ for $^{90}Sr$ is ~30 yr; 300 yr immobilization results in loss of >99.9% original activity
- Co-precipitation of Sr in calcite at arid western sites is compatible with the long term subsurface biogeochemistry
  (Log SI for calcite in SRPA ~ 0.2 -0.5)
- Where practical, *in situ* immobilization is cost effective, minimizes exposure, and eliminates secondary waste streams



# *In Situ* Containment and Stabilization Approach

- Alter *in situ* calcite precipitation kinetics to increase the rate of metal co-precipitation

$$(1-\chi)Ca^{2+} + \chi Sr^{2+} + 2HCO_3^- \rightarrow Ca_{(1-\chi)}Sr_{\chi}CO_3 + CO_2 + H_2O$$

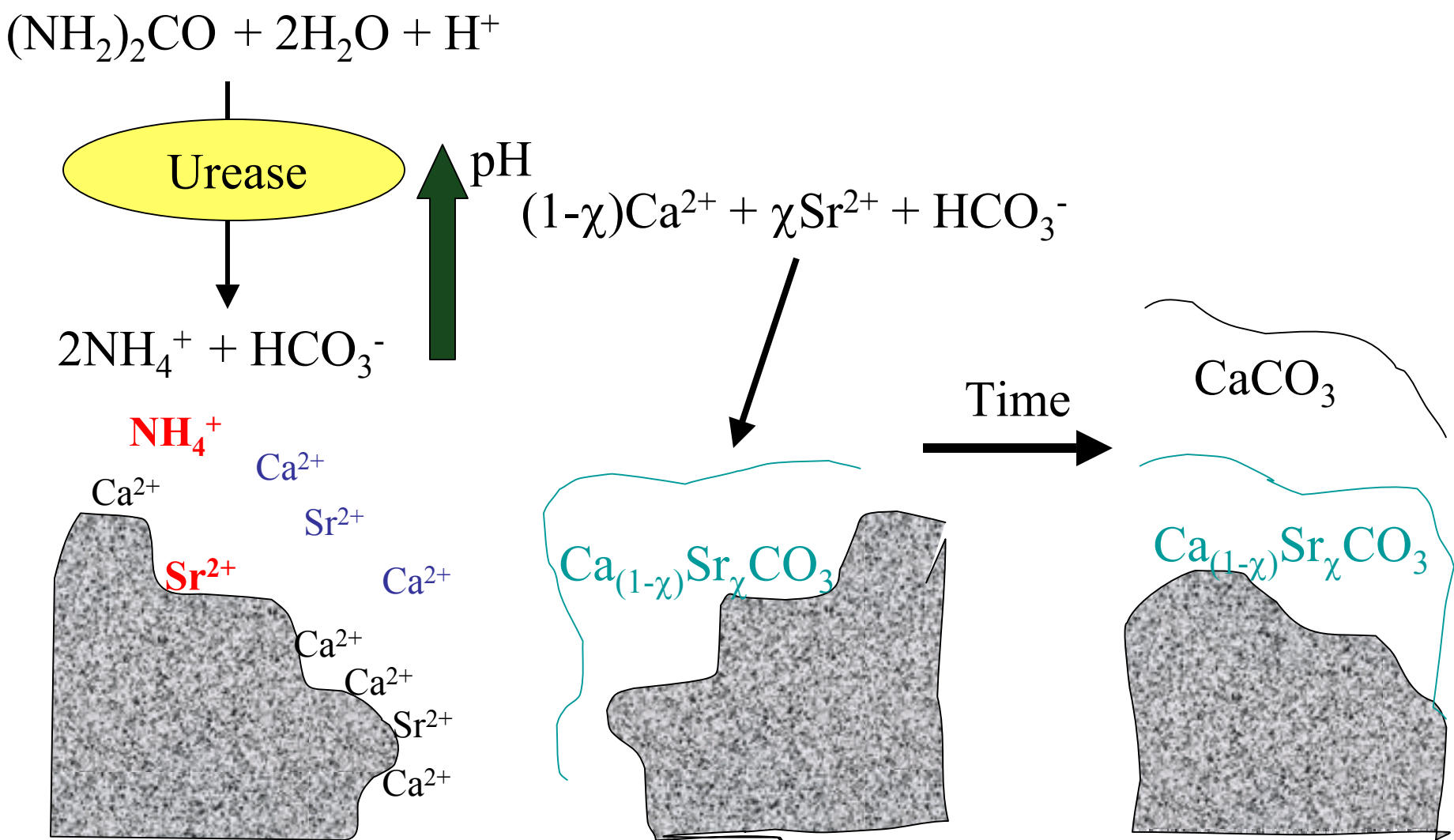
- Microbially hydrolyze urea to increase pH and carbonate alkalinity

$$H_2NCONH_2 + 2H_2O + H^+ \rightarrow 2NH_4^+ + HCO_3^-$$

- Desorb cations for co-precipitation in calcite ($M^{2+} = Ca^{2+}, Sr^{2+}$)

$$>X_2{:}M^{2+} + 2NH_4^+ \rightarrow 2{>}X{:}NH_4^+ + M^{2+}$$

# Application Concept



# Results to Date

- Demonstrated in laboratory and field the linkage between urea hydrolysis and calcite precipitation.
- Observed that Sr is incorporated into calcite precipitated by urea hydrolyzers, with higher distribution coefficient than in abiotic systems.
- Determined that urea hydrolyzers are ubiquitous in the SRPA.
- Developed PCR primers specific to bacterial urease subunit C.

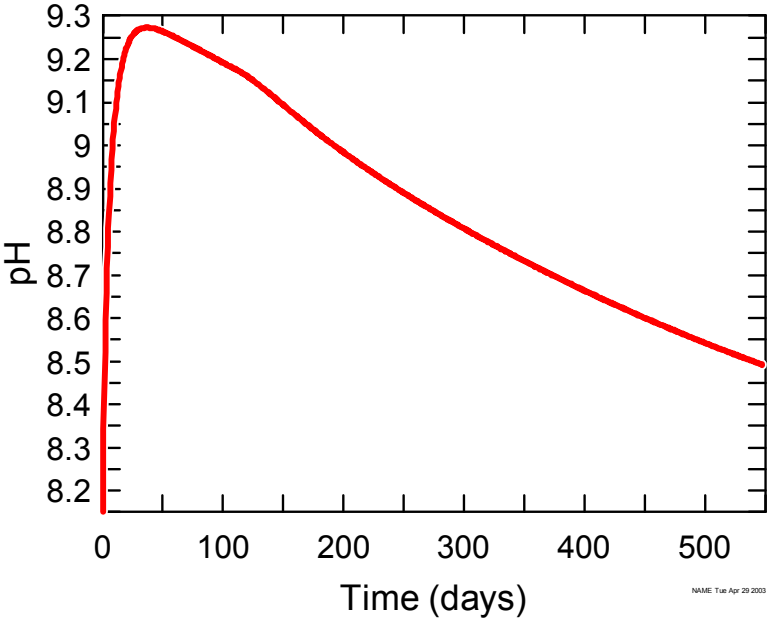
# Model Aquifer System

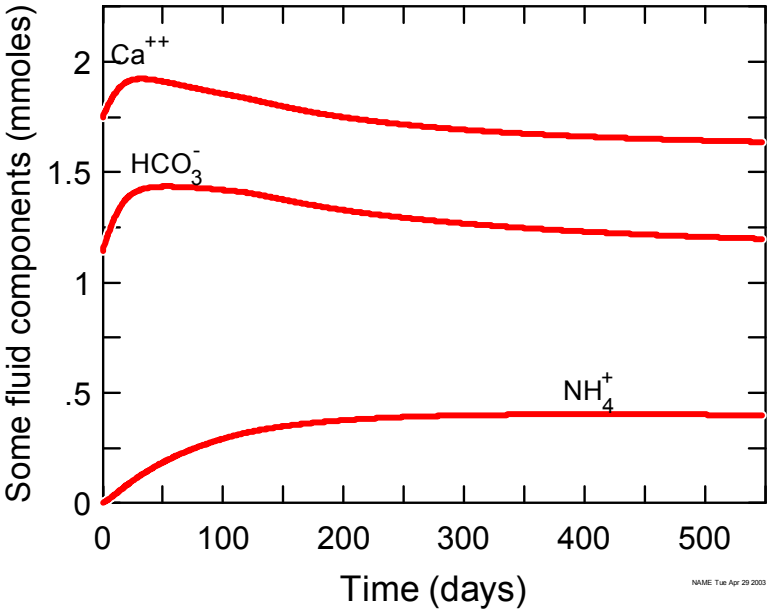
| | mg $L^{-1}$ | | mg $L^{-1}$ |
|---|---|---|---|
| $Ca^{2+}$ | 70.1 | $Na^{+}$ | 25.8 |
| $Mg^{2+}$ | 10.9 | $K^{+}$ | 4.0 |
| $HCO_3^{-}$ | 69.8 | $Cl^{-}$ | 124 |
| $NO_3^{-}$ | 5.2 | $SO_4^{2-}$ | 43.0 |
| pH | 8.15 | [1]CEC | 1.5 |
| T ($^{o}$C) | 14 | [2]$Kd_{Sr}$ | 5.0 |

[1](meq 100 $g^{-1}$) [2](mL $g^{-1}$)

- 6.67 liter total volume (15% porosity)
- 1 liter (1 kg) of water
- 5.67 liter (15.3 kg) of geomedia (CEC only reactivity)
- 2.70 kg $liter^{-1}$ (grain density)
  2.29 kg $liter^{-1}$ (bulk density)
- React 2 mmoles aqueous urea
- Kinetics
  - 1st order for urea hydrolysis
  - 2nd order chemical affinity for calcite precipitation
- Geochemist's Workbench simulations

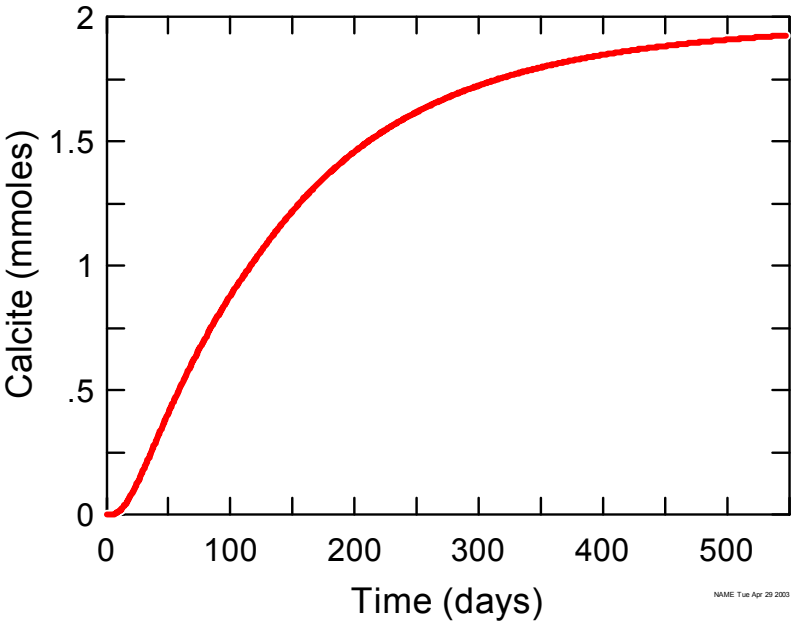
# Batch System Calculations (No Transport)

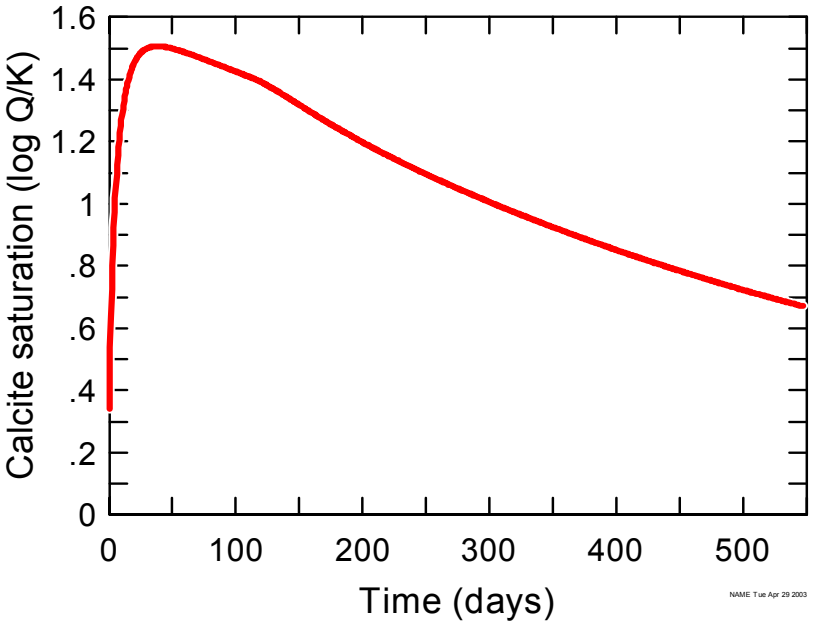



- pH and $HCO_3^-$ initially rises due to urea hydrolysis, then decrease as calcite precipitates.
- $Ca^{2+}$ initially rises due to exchange with $NH_4^+$, then decrease as calcite precipitates.

# Batch System Calculations (No Transport)

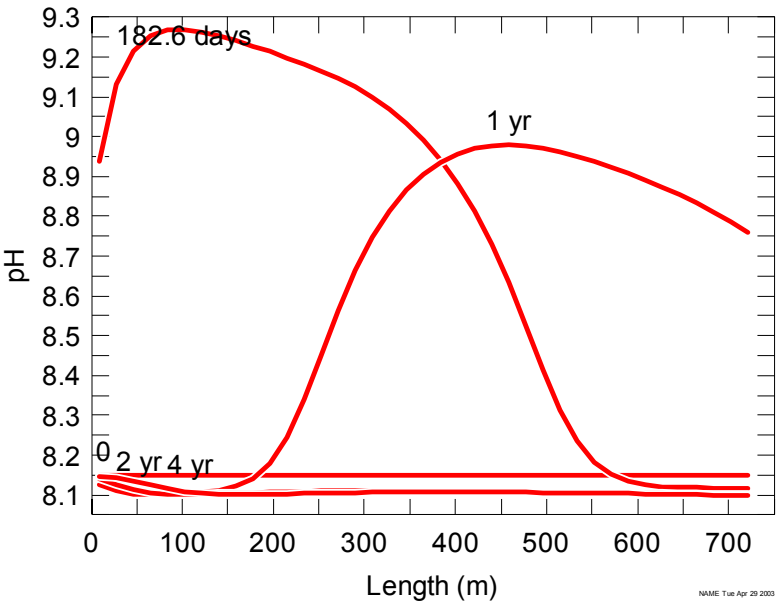


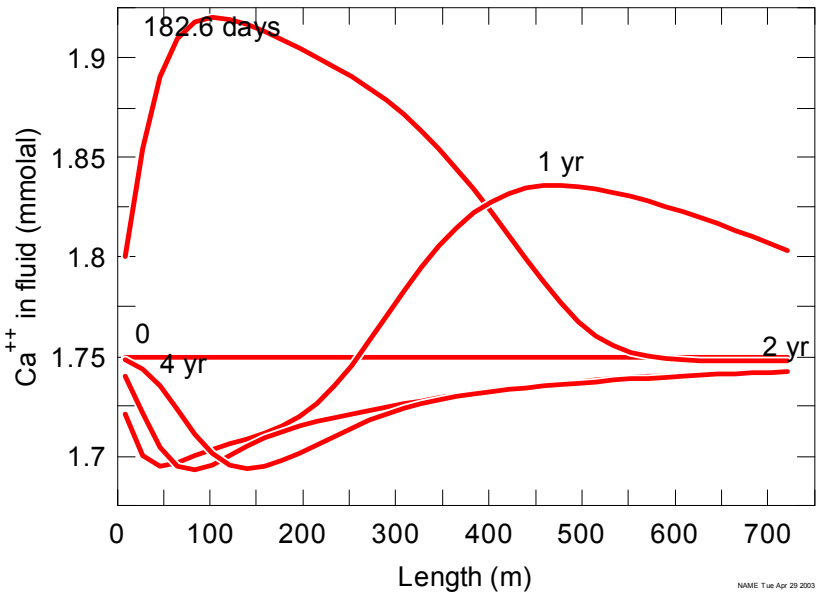




- Hydrolysis of 2 mmol urea results in precipitation of almost 2 mmole of calcite.
- Q/K rises rapidly as urea hydrolyzes faster than calcite precipitates, Q/K falls as the two rates become equivalent.

# Reactive Transport

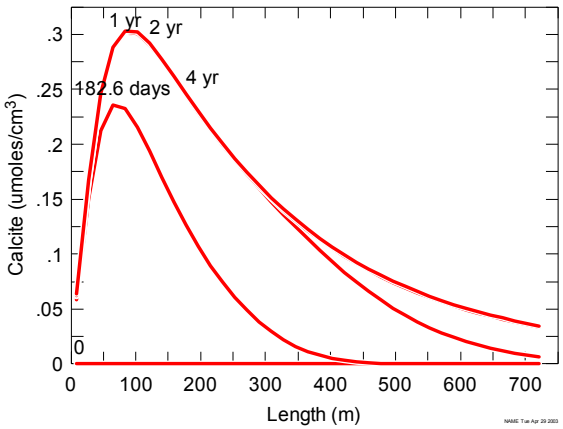
## (6 month injection, 1-D, 730 m, 1 pore volume year$^{-1}$)

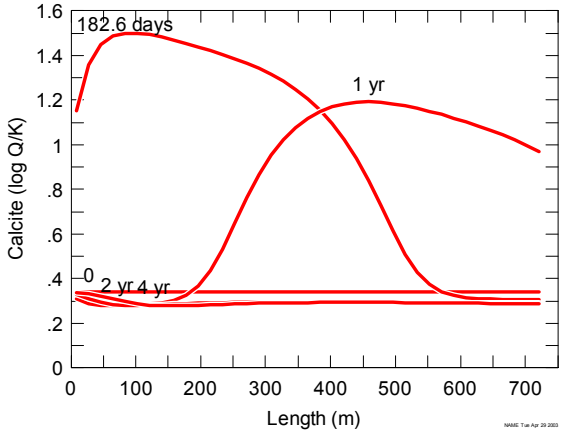



- High pH moves through system. Near ambient pH values return in less than 18 months
- High [$Ca^{2+}$] moves through system in early times as $NH_4^+$ exchanges for $Ca^{2+}$. During later times low [$Ca^{2+}$] moves through system as $Ca^{2+}$ exchanges for $NH_4^+$

# Reactive Transport
## (6 month injection, 1-D, 730 m, 1 pore volume year$^{-1}$)




- Calcite precipitates through the entire regions and is essentially complete within 2 years.
- Q/K is elevated (> 30) during early times and slightly depressed (but > 1) during later times. This condition persists until $NH_4^+$ is swept from the system (decades).

# Future Project Activities

- **Task 1: Evaluate ureolytic activity of subsurface microbial communities (INEEL).**
- **Task 2: Conduct biotic and abiotic experiments to develop coupled chemical/transport models (UI, UT).**
- **Task 3: Conduct single well push-pull field experiments (INEEL, UI).**
- **Apply research at a contaminated DOE site (INTEC, Hanford's 100 Area)**

# Supplemental Information (Contact Information)

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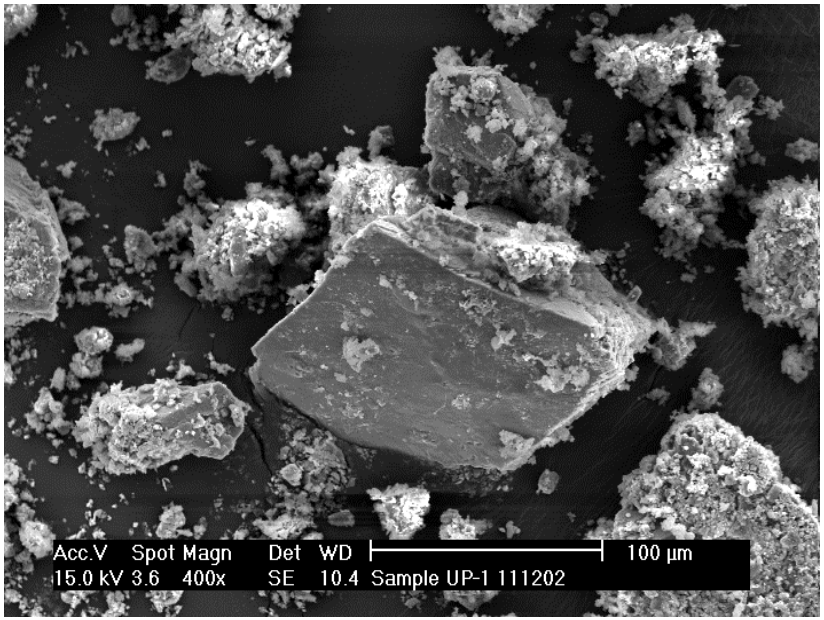
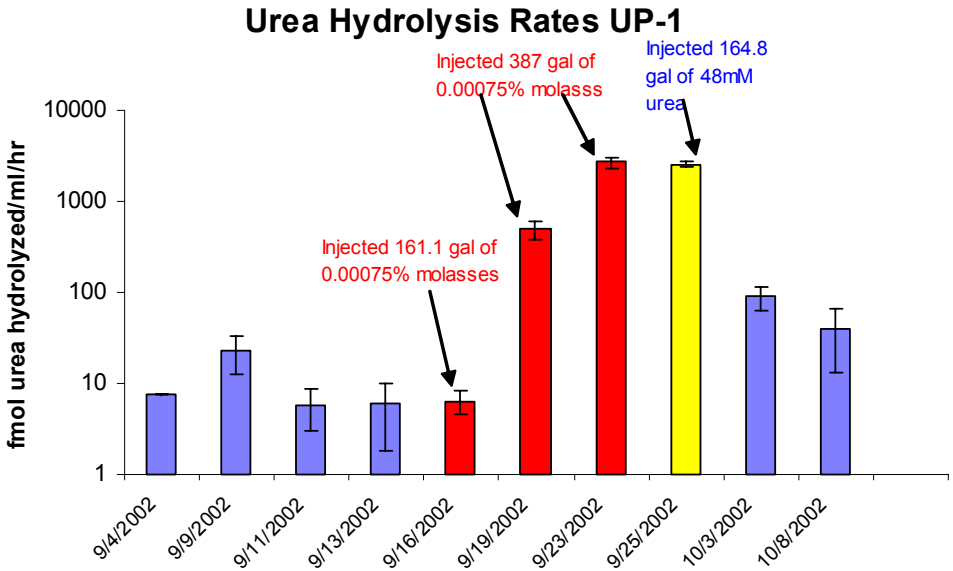
# Supplemental Information
# Results to Date (1)




- Demonstrated in laboratory and field the linkage between urea hydrolysis and calcite precipitation.

# Supplemental Information
# Results to Date (2)

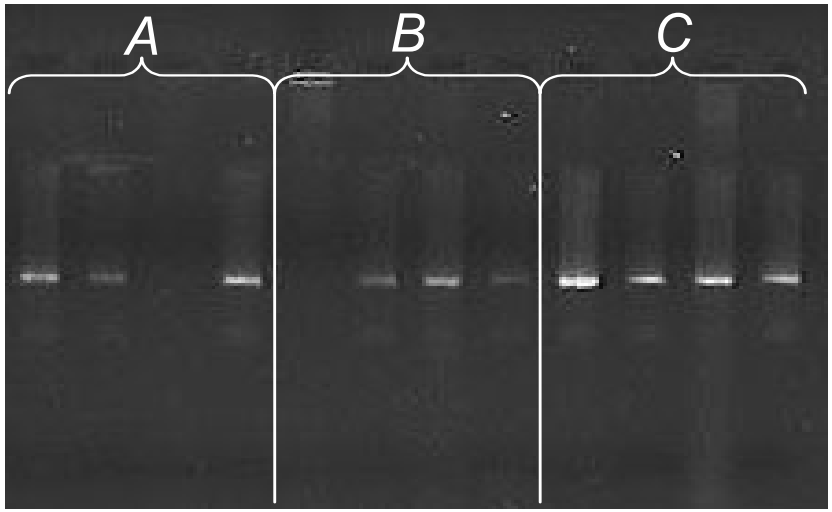
**Sr:Ca ratios in precipitates, estimated from solution data**

| Sample generated by: | Estimated Sr:Ca |
|---|---|
| *B. pasteurii* + urea | 0.047 |
| Ammonium carbonate | 0.034 |
| Ammonium carbonate + *B. pasteurii* | 0.027 |

- Observed that Sr is incorporated into calcite precipitated by urea hydrolyzers, with higher distribution coefficient than in abiotic systems

# Supplemental Information
# Results to Date (3)

- Determined that urea hydrolyzers are ubiquitous in the SRPA.
- Developed PCR primers specific to bacterial urease subunit C.
- Developed $^{14}C$ tracer technique to estimate *in situ* ureolysis rate.




Data from single well push-pull experiment (4 reps from each time point). A – pre urea and molasses addition; B – during addition; C – post addition. The PCR data suggests that following urea and molasses addition the urease gene target was detected more consistently and in greater abundance.

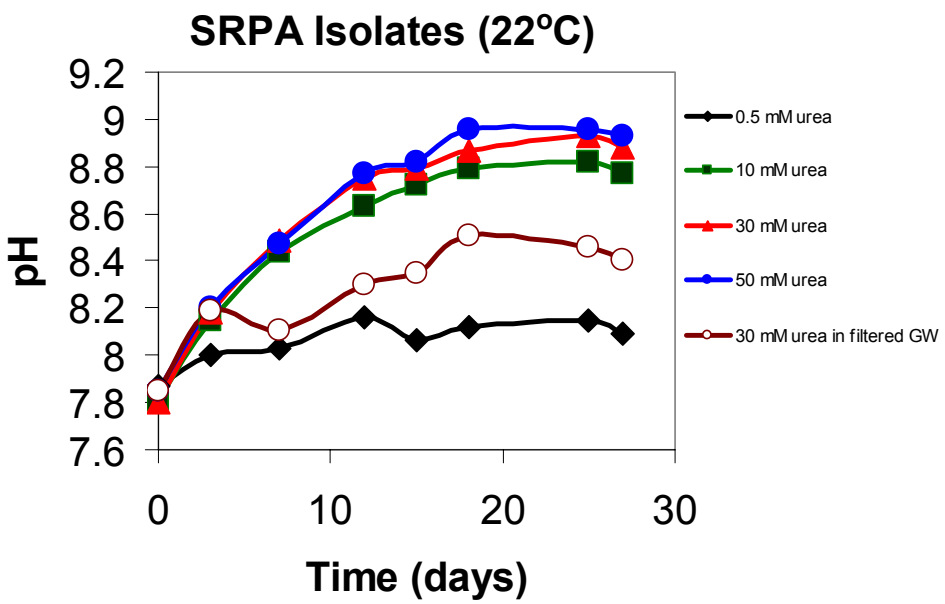
# Supplemental Information
# Kinetic Model (1)
## Urea Hydrolysis

$$H_2NCONH_2 + 2H_2O \rightarrow 2NH_4^+ + CO_3^{2-}$$

$$\frac{d[urea]_{total}}{dt} = -k_{urea}[urea]$$

$$\frac{d[NH_4^+]_{total}}{dt} = 2k_{urea}[urea]$$

$$\frac{d[CO_3^{2-}]_{total}}{dt} = k_{urea}[urea]$$



# Supplemental Information
# Kinetic Model (2)
## Calcite Precipitation

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$

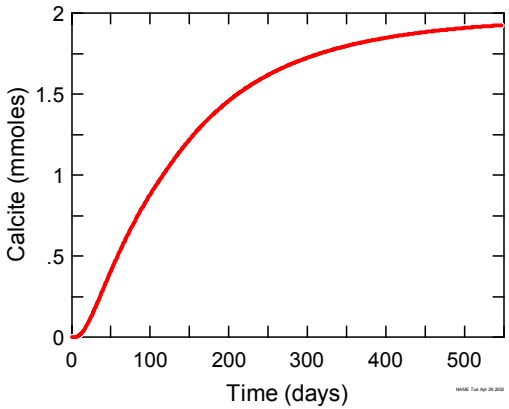
$$\frac{d[calcite]}{dt} = k_{calcite}(S-1)^2$$

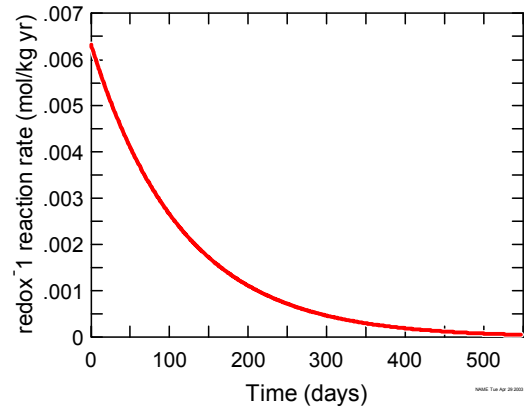
$$S = \frac{Q}{K} = \frac{a_{Ca^{2+}} a_{CO_3^{2-}}}{K_{eq}}$$

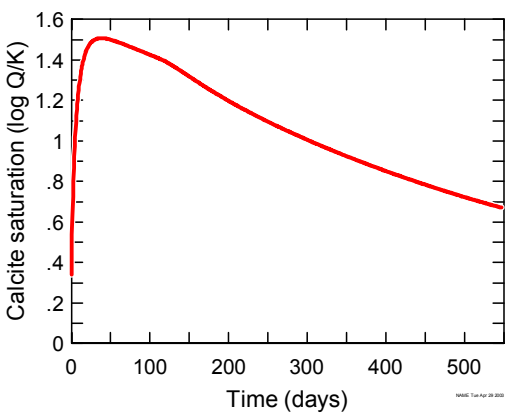
NETPATH model of McLing (1994) suggests that ~0.3 mmole (net) of calcite precipitate per liter of groundwater as it travels across the INEEL site (~50 years)

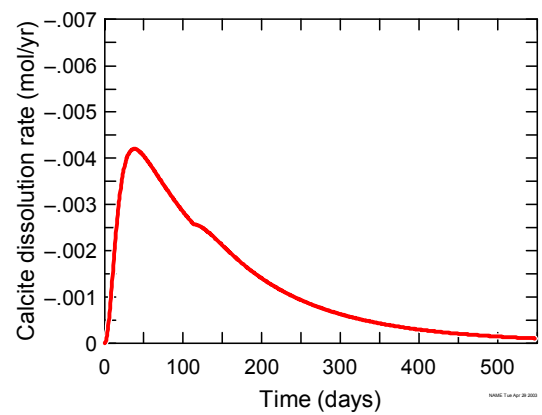
S → 2.2

# Supplemental Information
# Batch System Calculations (1)
## (No Transport)

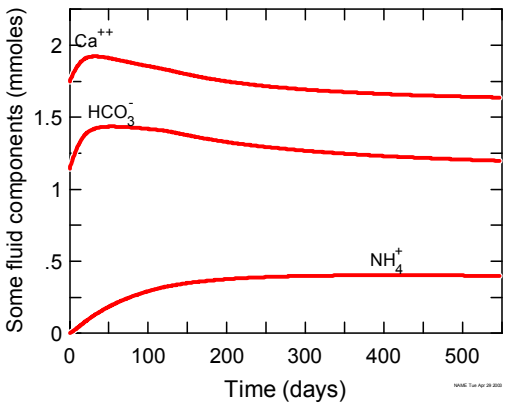


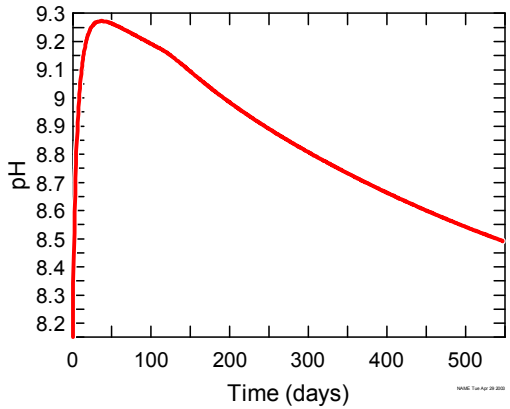



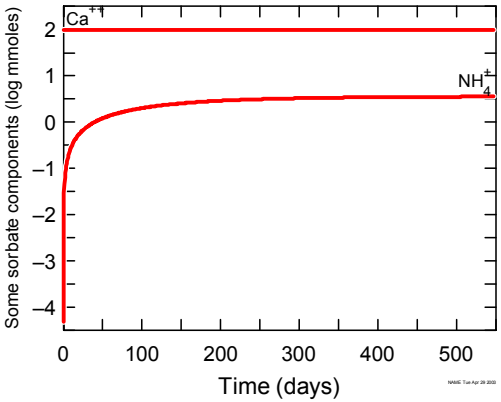



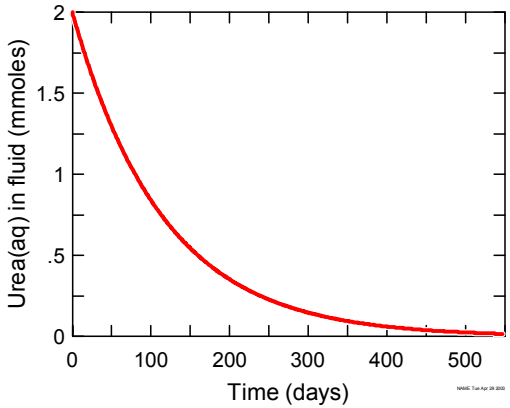



# Supplemental Information
# Batch System Calculations (2)
## (No Transport)



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# Reactive Transport (1)
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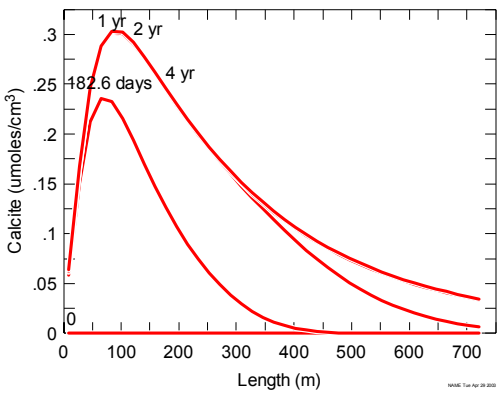


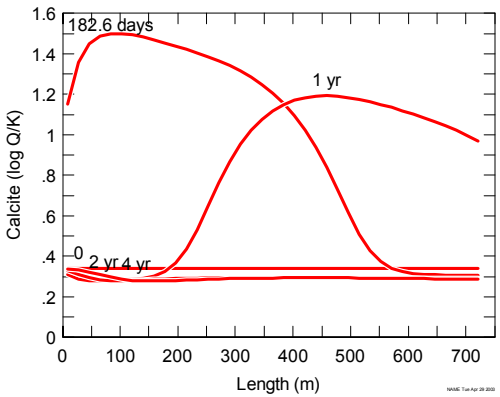


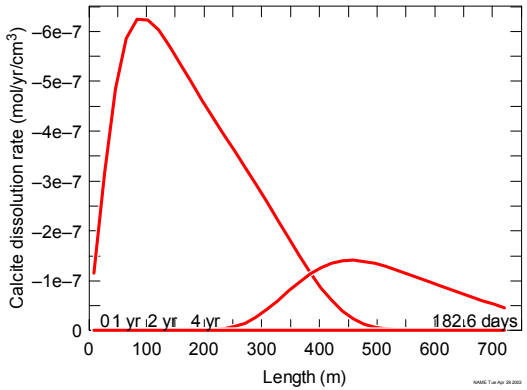


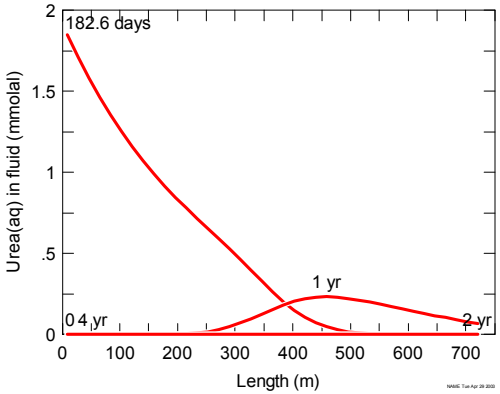

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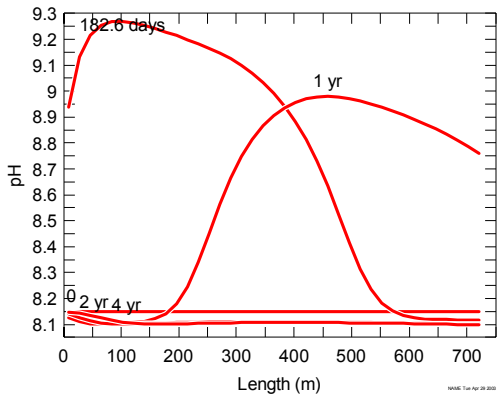


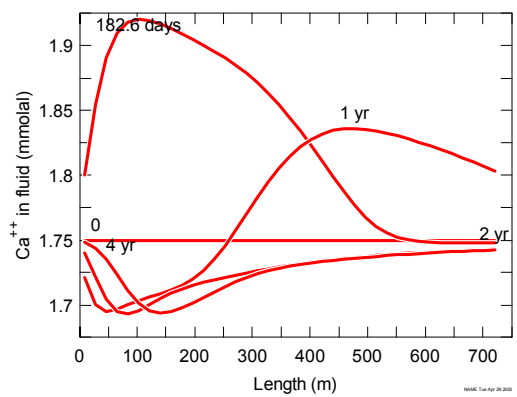


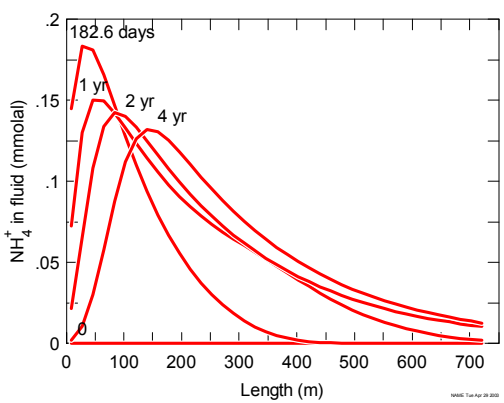


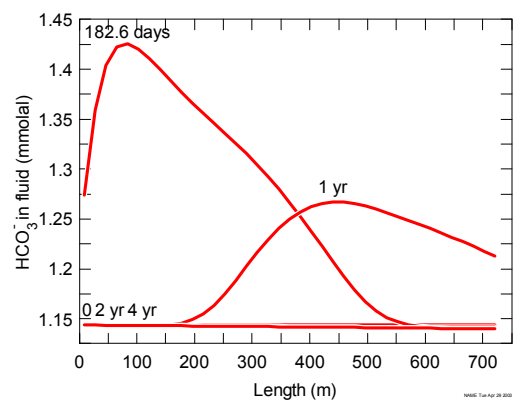

# Supplemental Information
# Research Task 1

**Evaluate ureolytic activity of subsurface microbial communities (INEEL).**

- Develop $^{14}C$ tracer technique to estimate *in situ* ureolysis rate.
- Estimate numbers of urease positive organisms, e.g. MPN-PCR, real time PCR.
- Correlate biomass to urease activity, using pure cultures and mixed SRPA cultures (non-enriched) and comparing to cell-free urease.
- Test urea and nutrient amendments in greater detail.
- Develop method to verify urea hydrolysis in field--e.g., RT-PCR for urease mRNA.

# Supplemental Information
# Research Tasks 2

**Conduct biotic and abiotic experiments to develop coupled chemical/transport models (UI, UT).**

- Continuously fed batch experiments containing solid surfaces, urease (either intracellular or extracellular), and urea to determine distribution coefficients (Sr in calcite) as a function of precipitation rate.
  - Precipitation rates will be controlled by controlling the rate of urea introduction.
- Column experiments to examine links between flow, urea hydrolysis and calcite precipitation rates.
- Development of mixed kinetic/equilibrium reaction model based on Geochemist's Workbench and HYDROBIOGEOCHEM.

# Supplemental Information
# Research Task 3

**Conduct single well push-pull field experiments (INEEL, UI).**

- Injections of urea, carbon source and possibly other nutrients. Also some experiments where urease is also injected (potential option at sites where natural ureolytic activity is low).
- Install MLS with solid substrates in dialysis cells, for post experiment recovery of precipitates.
- Apply microbiological and molecular techniques developed in Task 1 (e.g., $^{14}C$, MPN-PCR, RT-PCR) and other methods for assaying microbial community (e.g., DGGE, FISH for specific organisms).
- Use data to refine model started under Task 1.