

***In situ* Metal Sequestration by Microbially Mediated Precipitation of Calcium Carbonate**

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Coupled Processes and *In Situ* Stabilization

- *In situ* stabilization results from a transient perturbation of the biogeochemical environment
 - Application of treatment
 - Remobilization of contaminants from less stable form
 - Sequestration in more stable form
- Stabilization ***must*** persist for decades to centuries after active treatment ends
 - Biogeochemical environment will revert to pre-treatment background conditions
 - Coupling between the rates of local biogeochemical processes and the global fluxes

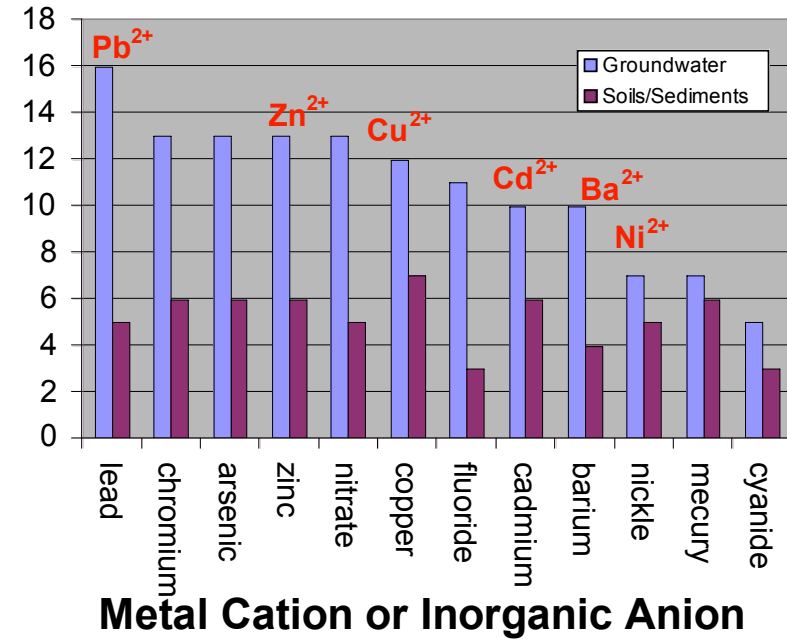
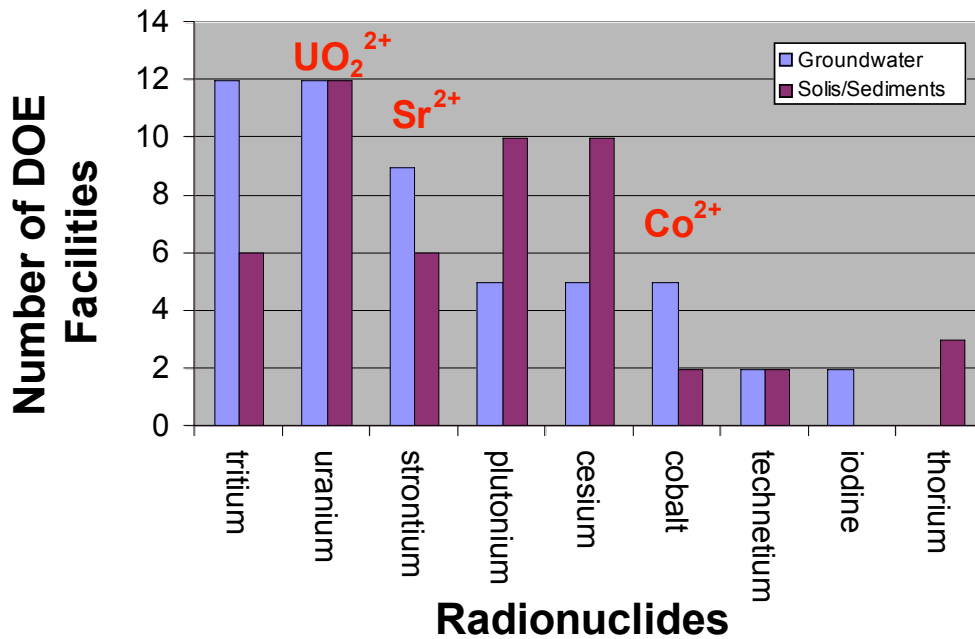
Proposed Stabilization Strategy

- Manipulate the kinetics of calcite precipitation in an aquifer in order to increase the rate of coprecipitation of divalent metals (eg. $^{90}\text{Sr}^{2+}$, $^{60}\text{Co}^{2+}$, Pb^{2+} , Cd^{2+}) from the aqueous phase.



- Co-precipitation of metals in calcite at arid western sites is compatible with the long term subsurface biogeochemistry

Divalent Metals and Radionuclides are Common at DOE sites



Riley and Zachara 1992

⁹⁰Strontium Contamination

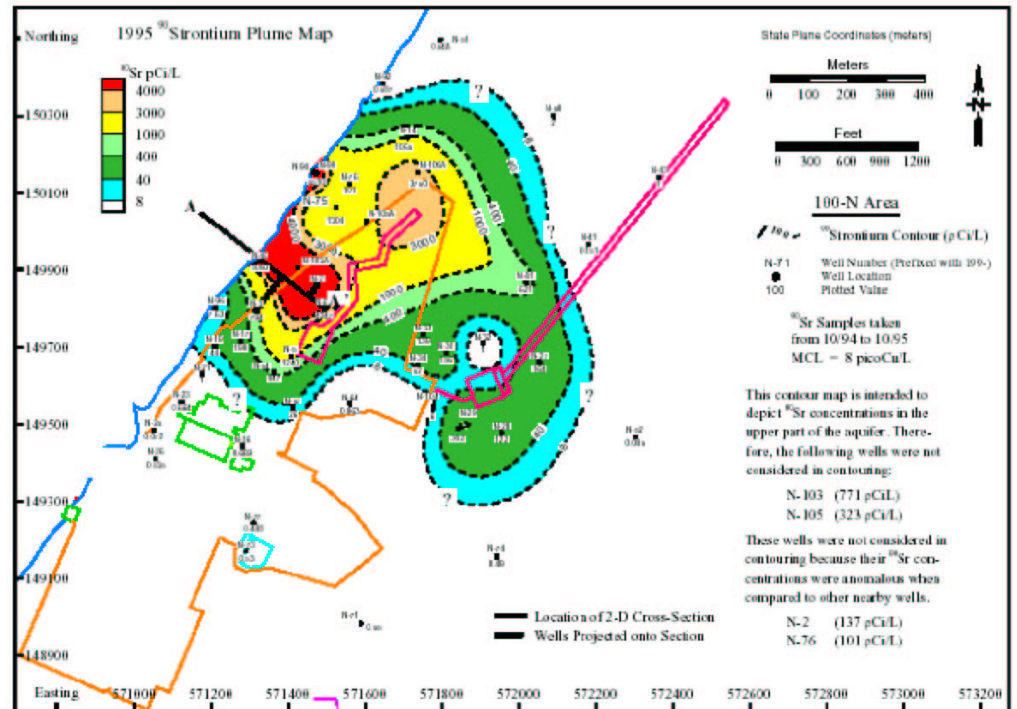
INL groundwater, perched water (INTEC)

- Up to 84 pCi L⁻¹ in a 1.6 km² groundwater plume
- Up to 320,000 pCi L⁻¹ in perched water
- 18,000 Ci released

Hanford soils, groundwater (100N)

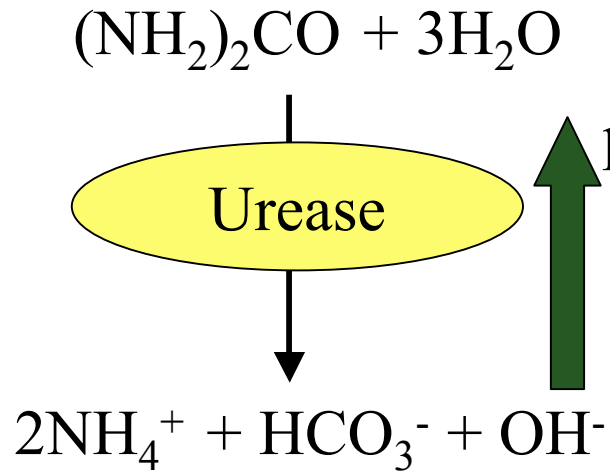
- Est in-ground inventory of 75 to 89 Ci
- Groundwater levels up to 6000 pCi L⁻¹

EPA Regulatory Limits for ⁹⁰Sr in drinking water: 8 pCi L⁻¹

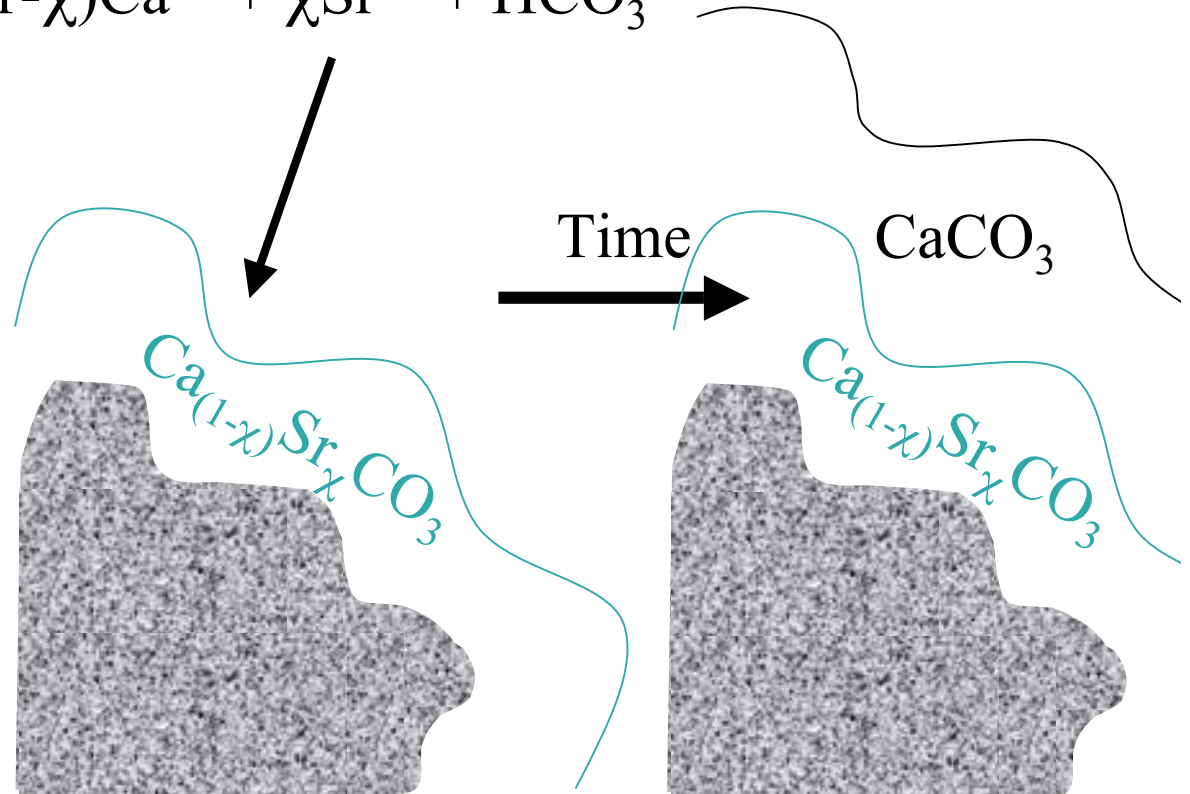
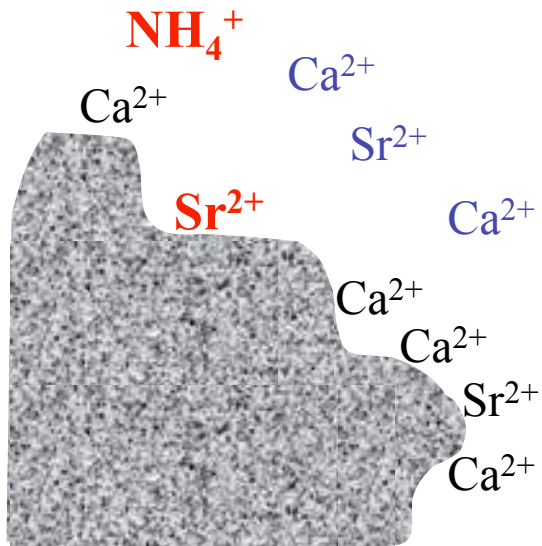


Contaminant inventories are largely associated with the solid media, not the water

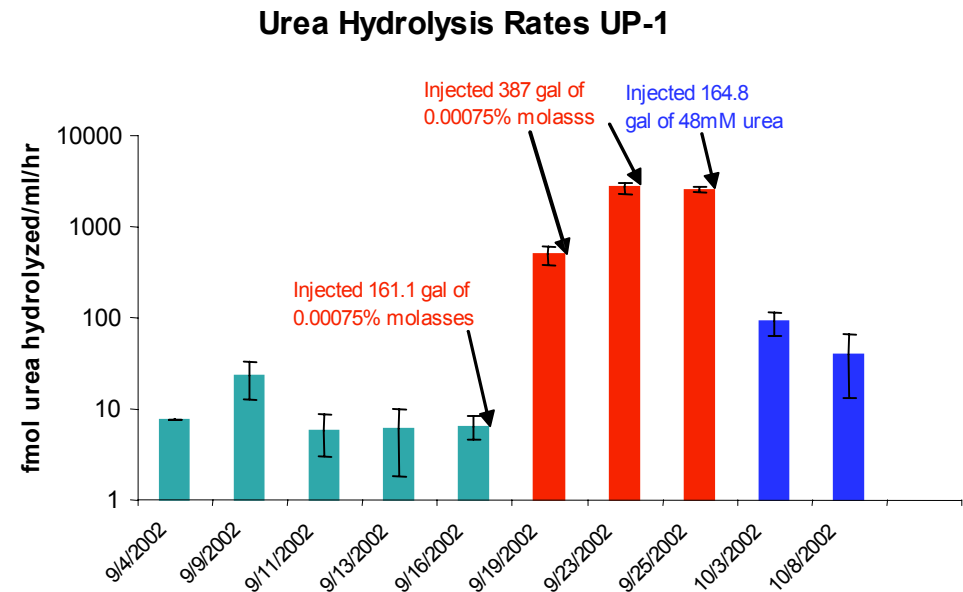
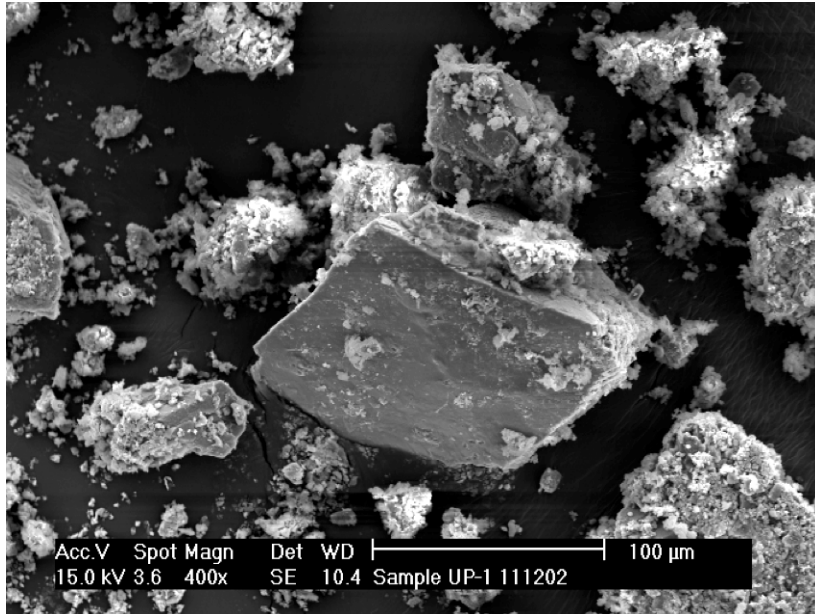
In Situ Stabilization Concept



pH ↑

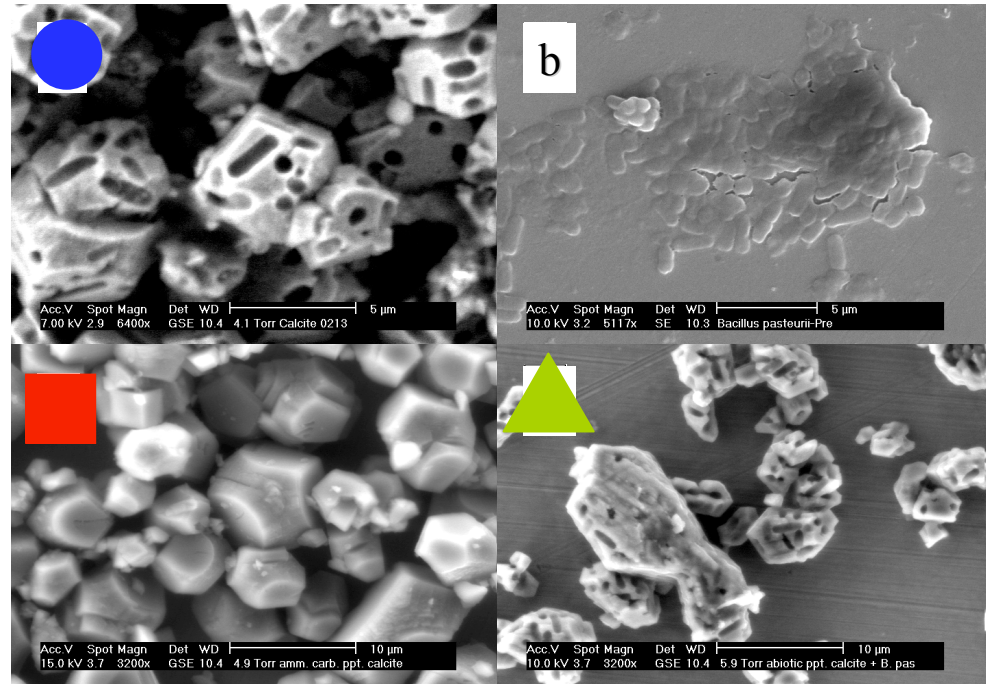
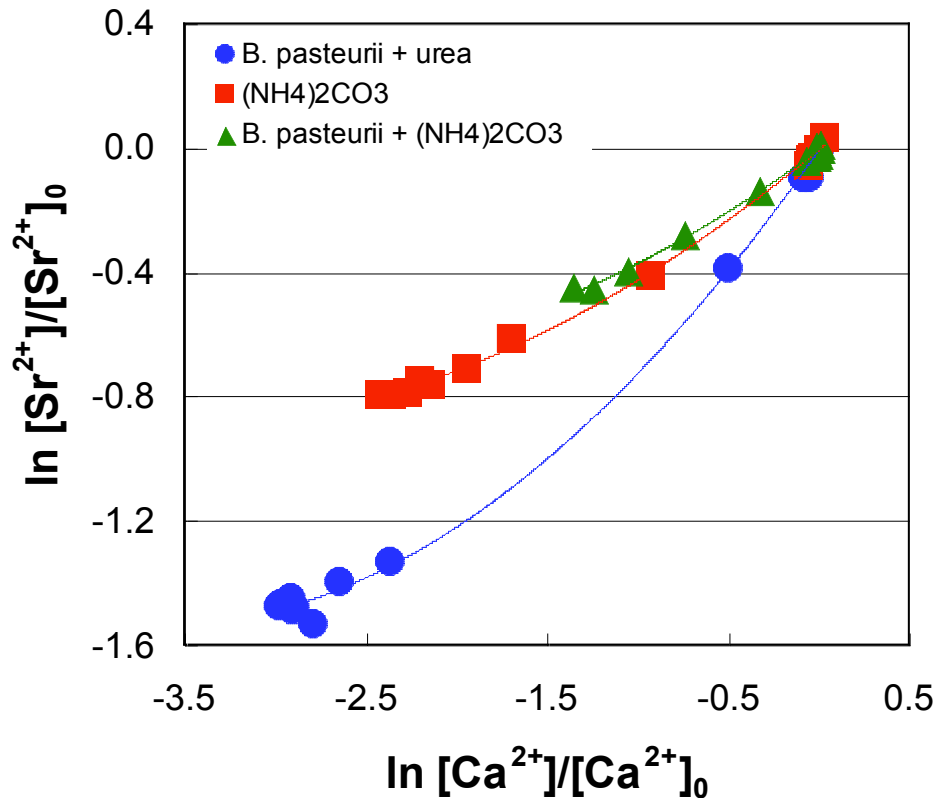


Results to Date (1)



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

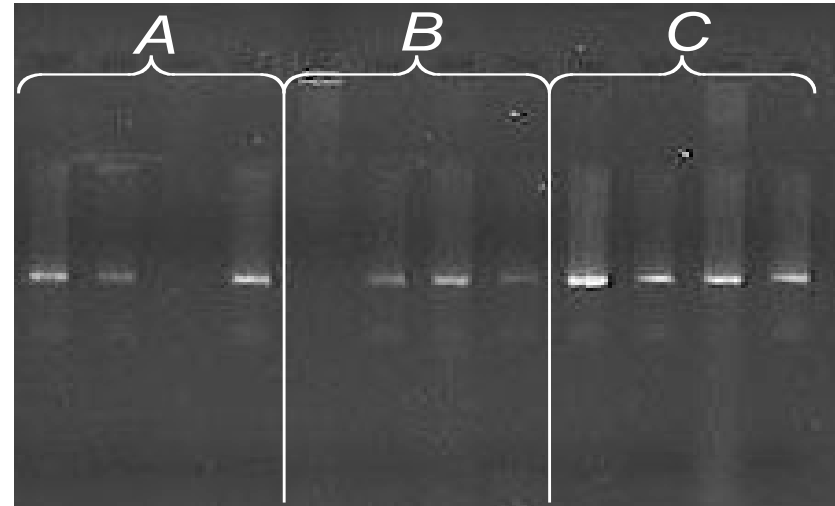
Results to Date (2)



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

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.

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 (°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 geomeia (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

Single Well Field Experiment

- First order urea hydrolysis rate constant
 - $1.3\text{E-}07 \text{ sec}^{-1}$
- Field base retardation factor for NH_4^+
 - 20



Kinetic Model

Calcite Precipitation



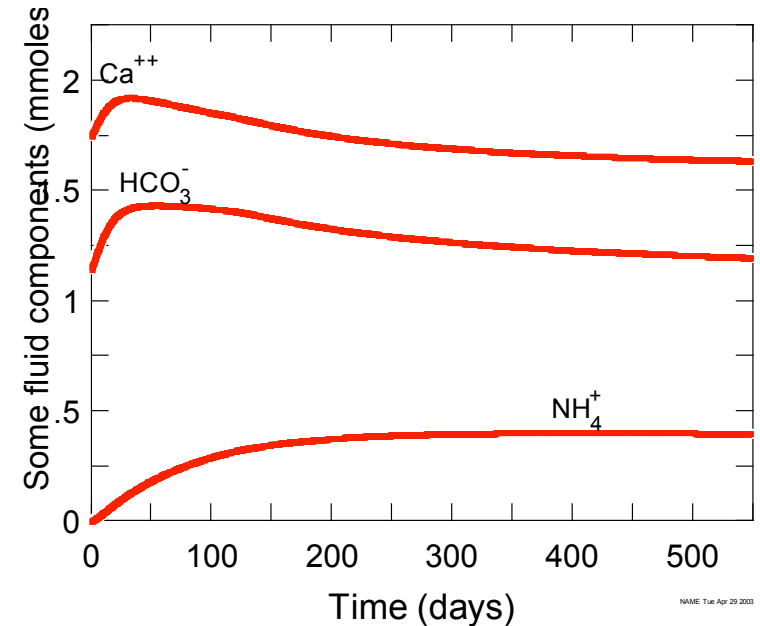
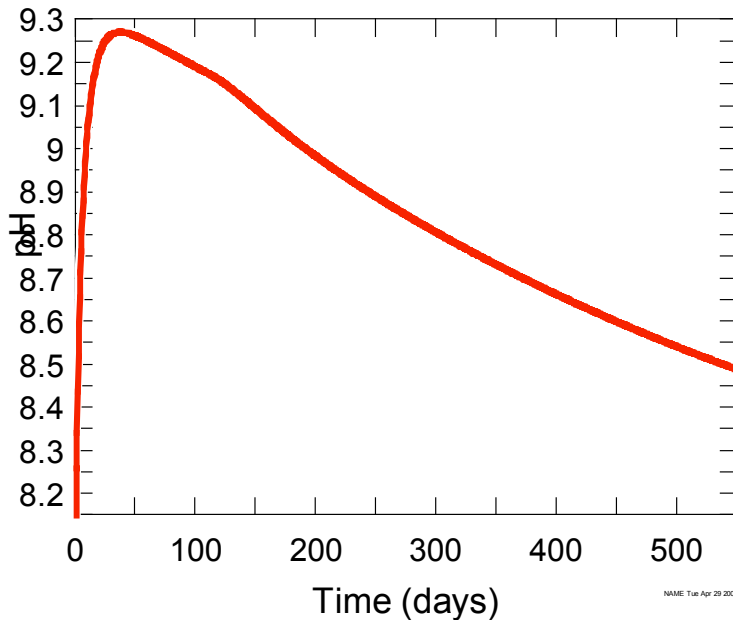
$$\frac{d[\textit{calcite}]}{dt} = k_{\textit{calcite}} (S - 1)^2$$

$$S = \frac{Q}{K} = \frac{a_{\text{Ca}^{2+}} a_{\text{CO}_3^{2-}}}{K_{eq}}$$

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)

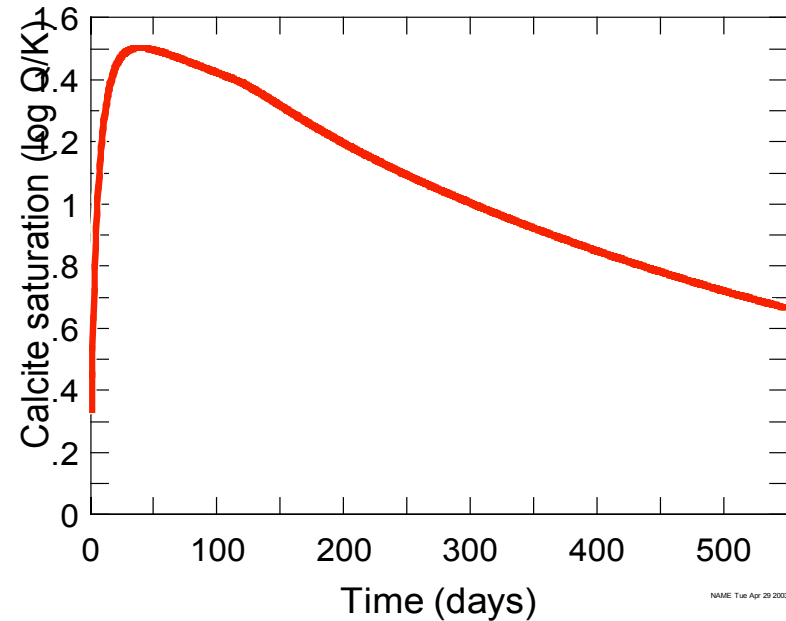
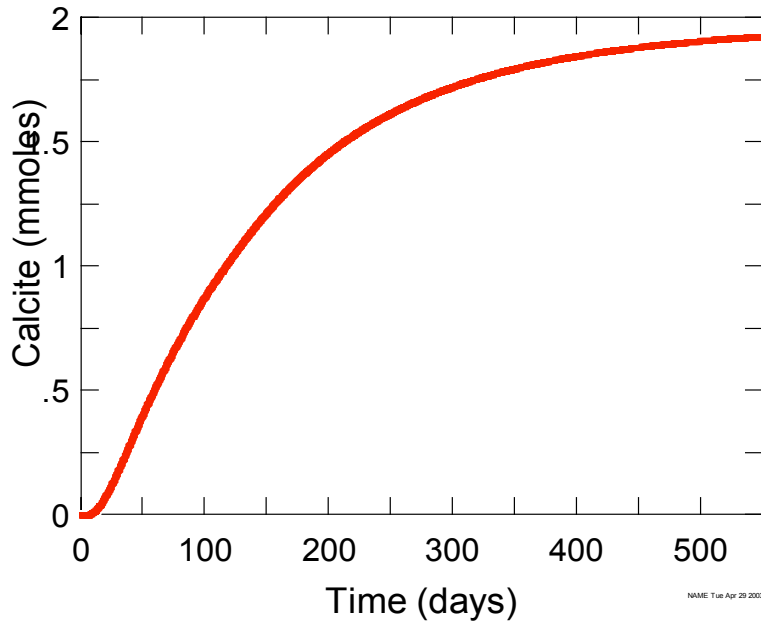
$S \rightarrow 2.2$

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.

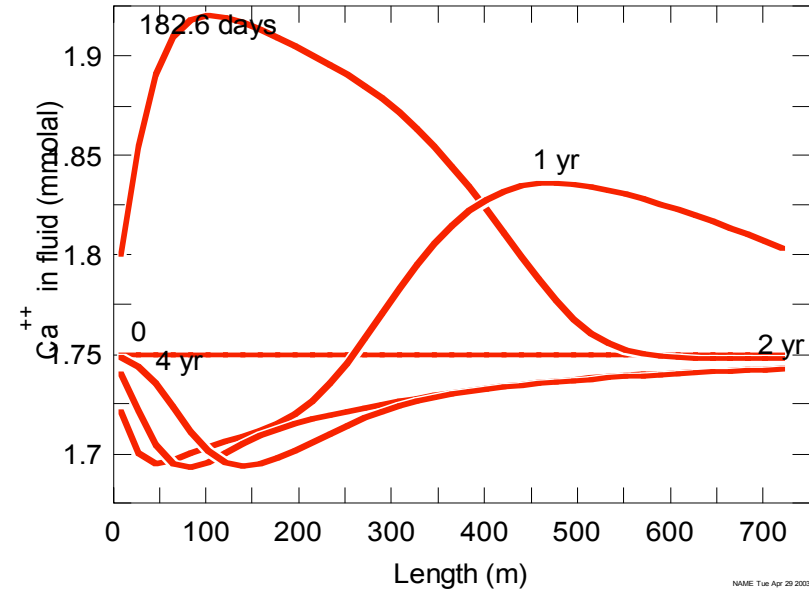
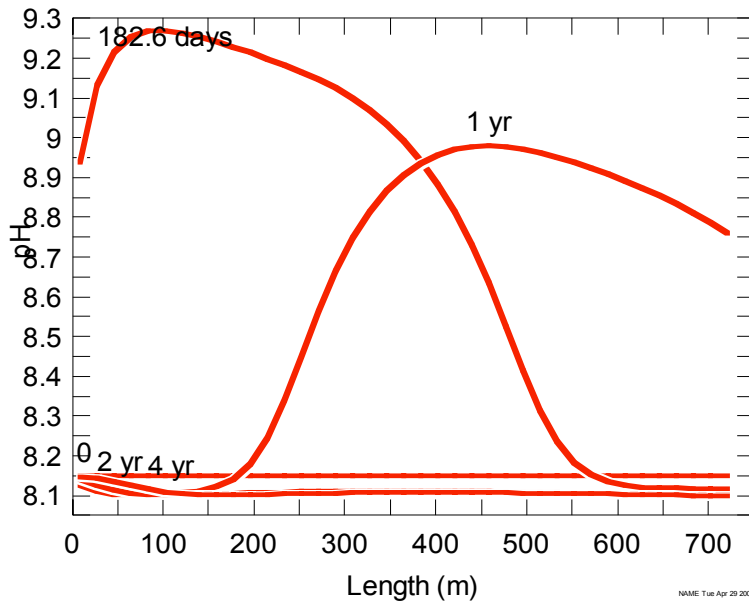
Batch System Calculations (No Transport)



- 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

Reactive Transport

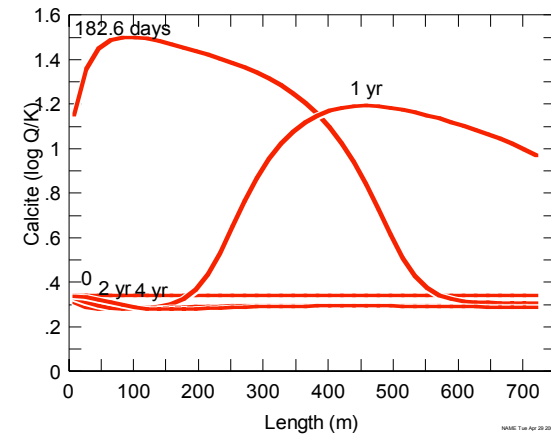
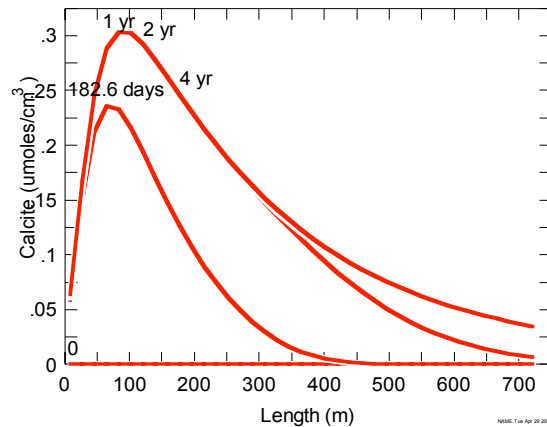
(6 month injection, 1-D, 730 m, 1 pore volume year⁻¹)



- High pH moves through system. Near ambient pH values return in less than 18 months
- High [Ca²⁺] moves through system in early times as NH₄⁺ exchanges for Ca²⁺. During later times low [Ca²⁺] moves through system as Ca²⁺ exchanges for NH₄⁺

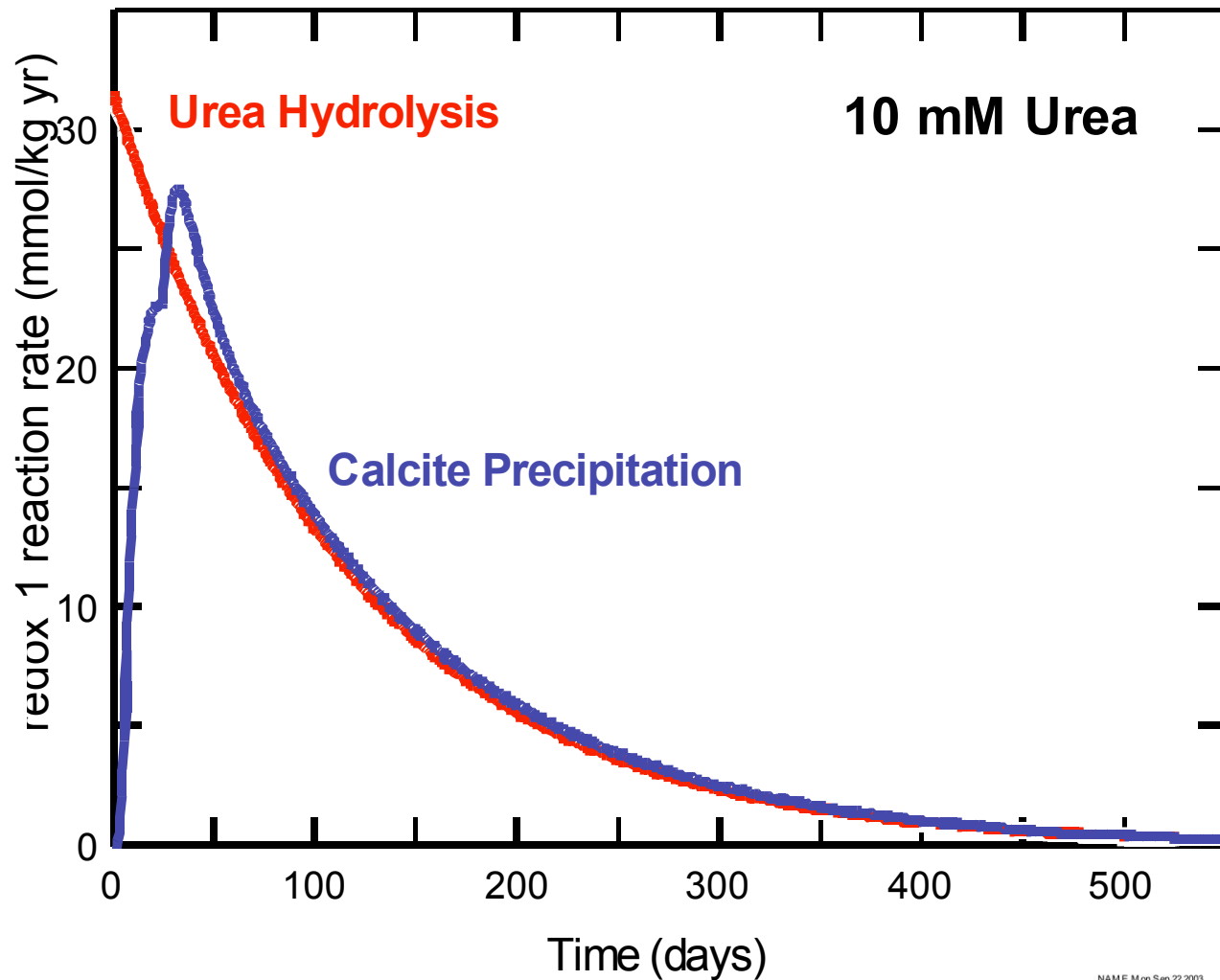
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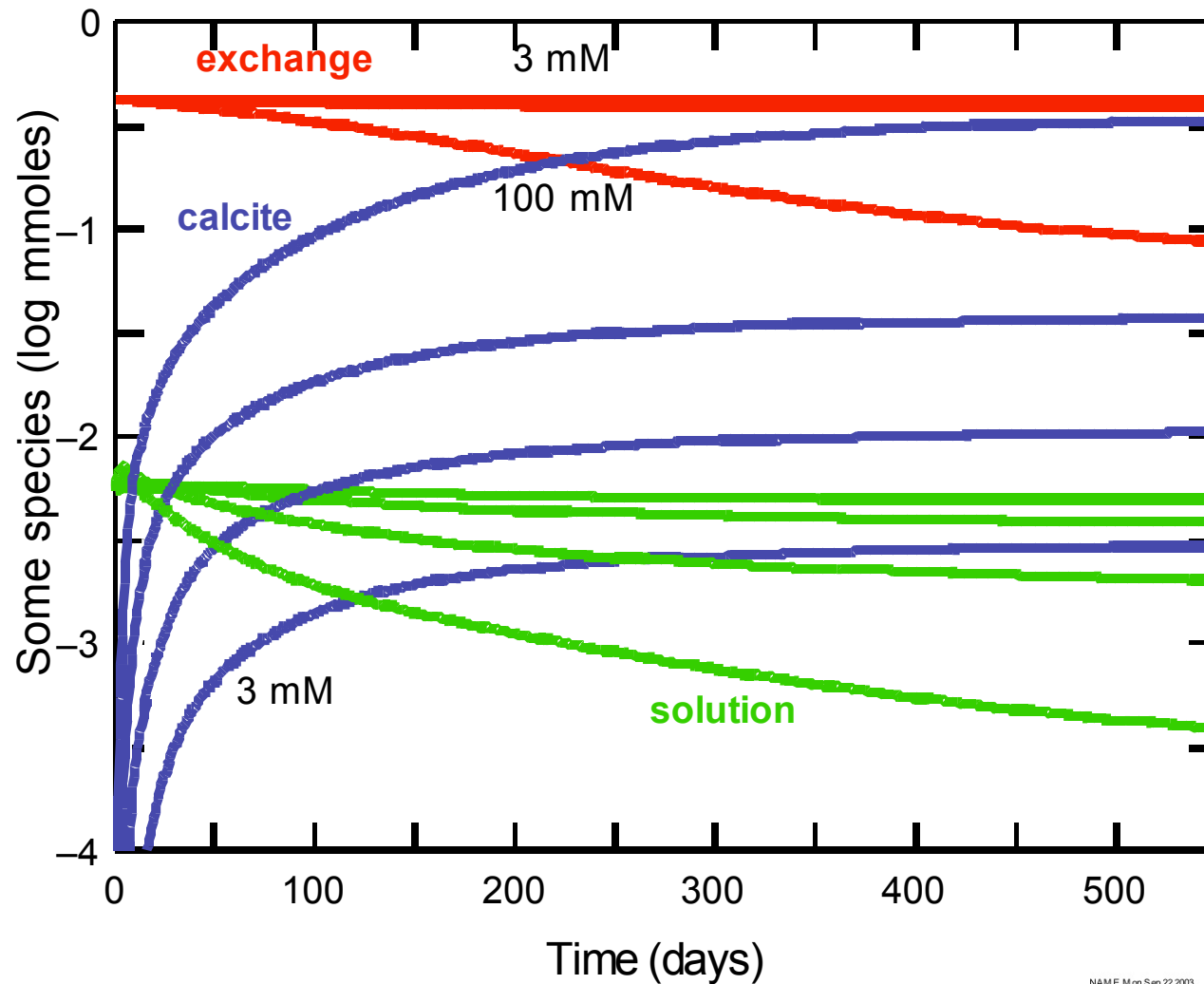


- Calcite precipitates through the entire regions and is essentially complete within 2 years.
- Q/K is elevated (> 30) during early times and slightly depressed (but > 1) during later times. This condition persists until NH_4^+ is swept from the system (decades).

Simulation – Calcite and Urea Kinetics



Simulation – Strontium Distribution



Summary of Simulations

- Urea hydrolysis can be used to manipulate *in situ* biogeochemistry and facilitate calcite precipitation
- The system is rock dominated – the solutions changes are small in comparison to the changes in the aquifer host rock
- pH and HCO_3^- initially rise due to urea hydrolysis, then decrease as calcite precipitates
- Ca^{2+} initially rises due to exchange with NH_4^+ , then decreases as calcite precipitates

Summary of Simulations

- Hydrolysis of urea results in precipitation of almost equivalent molar amounts of calcite
- Initially the urea hydrolysis rate (R_U) is faster than the calcite precipitation rate (R_C), followed by a brief period over which $R_C > R_U$, and finally a long period over which $R_C \sim R_U$
- Small, but significant amounts of strontium are incorporated into the precipitated calcite
- Multiple treatments will be required to fully sequester strontium-90

Future Work

- Drilling 5-spot well field at INL Vadose Zone Research Park
- Multi-well experiments to assess field rates