

# In Situ Calcite Precipitation for Contaminant Immobilization

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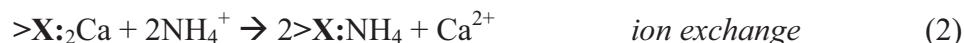
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**ABSTRACT:** The precipitation of calcite induced by urea hydrolyzing microorganisms represents a novel new approach for remediation of trace metal and radionuclide contaminants. Calcite, a common mineral in the arid western U.S., can form solid solutions with trace metals. We have previously shown that the hydrolysis of urea by subsurface microorganisms can lead to the precipitation of calcite, and to the coprecipitation of strontium. Because the ability to hydrolyze urea is widespread within the microbial world, this remediation approach would not require bioaugmentation with foreign microbes. In this paper we present results of laboratory estimations of in situ urea hydrolysis rates in an environment contaminated with the radionuclide strontium-90, and provide an example of how those rate determinations can support predictions of the rate and extent of calcite precipitation in the subsurface. Immobilization of contaminants in calcite is particularly attractive in environments that are already saturated with respect to calcite, because of the long-term sustainability of the sequestration mechanism. The bulk of any newly precipitated calcite will remain stable once engineered manipulations cease.

### **INTRODUCTION**

Subsurface radionuclide and trace metal contaminants throughout the U.S. Department of Energy (DOE) complex pose one of DOE's greatest challenges for long-term stewardship. DOE is committed to cleaning up the environmental legacy of nuclear weapon and civilian nuclear research and development programs at 132 sites throughout the United States (DOE, 2000). In total, these sites represent millions of cubic meters of contaminated media (ERRRD, 1997) with recurring contaminants. To meet this challenge, better remediation technologies, longterm stewardship options, and alternate cleanup approaches are required. One approach growing in acceptance by DOE and regulators is in situ containment and stabilization (NRC, 2000). This approach is less costly than excavation and disposal, and minimizes worker exposure because contaminated materials are not brought to the surface. Containment and stabilization also minimizes the generation of secondary wastestreams, and the small on-site footprint limits the risk of collateral environmental damage and avoids offsite risks such as transportation.

One promising stabilization mechanism for divalent trace metal ions (e.g.,  $^{90}\text{Sr}$ ,  $^{60}\text{Co}$ , Pb, Zn, Cd) is co-precipitation in calcite. Calcite, a common mineral in the arid western U.S., can form solid solutions with trace metals. The rate of calcite precipitation is susceptible to manipulation using either abiotic or biotic means. Changes in calcite precipitation rates can also change trace metal partitioning. We have been evaluating the potential for using microbial urea hydrolysis to accelerate subsurface calcite precipitation and trace metal co-precipitation. Urea hydrolysis causes the acceleration of calcium carbonate precipitation by increasing pH and alkalinity, and also by liberating reactive cations (e.g., Ca, or divalent trace metals) from the aquifer matrix via exchange reactions involving the ammonium ion derived from urea:



where  $>\text{X}$ : is a cation exchange site on the aquifer matrix.

This contaminant immobilization approach has several attractive features. Urea hydrolysis is catalyzed by the urease enzyme, which is produced by many indigenous and diverse subsurface microorganisms. Addition of foreign microbes, or bioaugmentation, is typically unnecessary. The fact that the microbes are already present in the subsurface, and dispersed, means that the reactive components (e.g., carbonate and Ca or Sr) are generated in situ. Thus the reaction can be disseminated over a larger volume and/or farther away from an amendment injection point, as compared to direct addition of the active reactants at a well (which could lead to clogging). A final particularly attractive characteristic of this approach is its potential for long-term sustainability; the remediation scheme is geared toward environments that are already saturated with respect to calcite, and in such systems the bulk of any newly precipitated calcite will remain stable once engineered manipulations cease. This means that the co-precipitated contaminants will be effectively sequestered over the long term.

We have previously reported on laboratory experiments demonstrating calcite precipitation induced by microbial cultures isolated from the environment and by reference urea hydrolyzing cultures (Fujita, Ferris et al., 2000). In the laboratory we have also investigated the effects of temperature on calcite precipitation rates (Ferris, Phoenix et al., 2004) and the partitioning of strontium into calcite generated under ureolytic conditions (Fujita, Redden et al., 2004). More recently our focus has been on testing our abilities to manipulate and monitor these processes in an actual field setting. We recently reported on a field trial that we conducted in the Snake River Plain Aquifer (SRPA) in southeast Idaho (Fujita, Taylor et al., 2008). In that experiment we demonstrated that additions of dilute molasses and urea to a deep basaltic aquifer could stimulate increases in populations and activity of ureolytic microorganisms, and also obtained evidence of increased subsurface calcite precipitation. One of the ways that we evaluated ureolysis activity was using a ureolysis rate estimation method in which recovered water samples are spiked with  $^{14}\text{C}$ -labeled urea and the evolution of  $^{14}\text{CO}_2$  is measured over time.

In this paper we provide data for samples from another site to which the ureolysis rate estimation method was applied, and provide an example of how these data can be used to predict the amount of calcite that could be precipitated by treatment with urea. The site is the Idaho Nuclear Technology and Engineering Center (INTEC), located at the Idaho National Laboratory (INL) in Idaho, USA. The INL is a U.S. Department of Energy facility where research on nuclear energy generation has been conducted for six decades. At INTEC, reprocessing of spent nuclear fuel occurred from 1952 to 1991. As a result of leaks during waste transfer operations, radionuclide and other contaminants have entered the vadose zone under INTEC (DOE, 2006). The vadose zone under the INL is characterized by layers of volcanic basalt interspersed with thin (less than a few meters) alluvial sediment deposits; the latter are known as interbeds. Above the aquifer (generally

> 140 meters below land surface in the vicinity of INTEC), water infiltrated from atmospheric precipitation or surface or near-surface discharges accumulates in perched water bodies that develop in and on top of low permeability interbeds. Contaminants detected in perched water zones under INTEC include nitrate, tritium,  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ , and  $^{129}\text{I}$ . The  $^{90}\text{Sr}$  in particular would be amenable to the calcite precipitation remediation approach.

## MATERIALS AND METHODS

Water samples were collected in 2005 from 6 different wells accessing contaminated perched water zones under INTEC, at screened depths ranging from 28 to 46 mbls. In 2005, measured Sr-90 concentrations in the wells ranged from 13,000 to over 190,000 pCi/L (DOE/ID, 2006). For comparison of ureolytic activity between contaminated and uncontaminated subsurface water, uncontaminated water samples were also collected for testing from two wells accessing the SRPA in the vicinity of INTEC.

The protocol for estimating in situ rates of ureolysis has been described previously (Fujita, Taylor et al., 2008). Briefly, nine milliliters of sample is added to a 25 ml flask along with 59 nmol [ $^{14}\text{C}$ ] urea (8.5 mCi/mmol; Sigma, St. Louis, MO) for a total volume of 10 ml. Triplicate flasks are incubated at 21°C for 0, 24 or 48 hours. The reaction is stopped with the addition of 2N  $\text{H}_2\text{SO}_4$ , and evolved  $^{14}\text{CO}_2$  is captured in filter paper saturated with 2N NaOH, suspended above the solution. The  $^{14}\text{CO}_2$  is measured using scintillation cocktail (Scintisafe Plus 50%, Fisher) and an ultra low-level liquid scintillation counter (1220 Quantulus Wallac, Turku, Finland). Ideally such  $^{14}\text{C}$  tracer techniques for estimating in situ activity are carried out immediately after sample recovery, in order to minimize changes to the native microbial community (Wright and Burnison, 1979), but this was not possible for all of the samples. Because of delays imposed by logistical and regulatory issues related to the contamination of the samples, for the perched water samples the rate estimations could not be made until one month after sample collection. The rate determinations for the uncontaminated aquifer samples were made immediately after sample collection.

Rate data from the samples was incorporated into a mixed equilibrium-kinetic model developed using the 1-dimensional reactive transport module of The Geochemist's Workbench® (GWB; RockWare, Golden, CO). In the model, aqueous speciation and cation exchange processes are treated as equilibrium reactions, while urea hydrolysis and calcite precipitation/dissolution are treated as kinetic processes. The default thermodynamic database provided with GWB and an INTEC site-specific Vanselow cation exchange model (Vanselow 1932) were used in the simulation. The model was set up to simulate the addition of urea to the top of a perched water body in a sedimentary interbed, in which the primary advective transport is downward. The vertical flow domain consisted of a saturated 1-meter thick zone with a porosity of 20%. Based on analyses of core collected at an uncontaminated analog site at the INL, the interbed sediments were assumed to contain <1% calcite and 20% clay (dominated by smectite), with a cation exchange capacity of 21 cmol/kg (unpublished data).

Average water chemistry parameters for the contaminated perched water at INTEC based on sampling of 4 monitoring wells in June of 2004 are given in Table 1; these data were used as input to the model. Calcite precipitation was described using a second-order chemical affinity based rate law with the rate constant estimated from the result of an aquifer-scale hydrochemistry evaluation of the Snake River Plain Aquifer (Colwell,

Smith et al., 2005). The simulated treatment consisted of the perched water amended with 10 mM, 50 mM, or 100mM urea followed by almost urea-free (1 uM urea) groundwater; GWB requires a finite concentration for all aqueous species considered in a simulation. Several simulations of a 0.5 month urea treatment followed by a recovery period of 11.5 months were conducted in order to illustrate key spatial and temporal aspects of the calcite precipitation process. During the 1-year total simulation 18 pore-volumes of fluid passed through the flow domain.

**TABLE 1. Average water chemistry parameters used in model.**

Constituent/Parameter	Units	Measured or calculated value
Ca <sup>2+</sup>	mg L <sup>-1</sup>	67.1
Mg <sup>2+</sup>	mg L <sup>-1</sup>	19.6
Na <sup>+</sup>	mg L <sup>-1</sup>	34.0
K <sup>+</sup>	mg L <sup>-1</sup>	4.72
SO <sub>4</sub> <sup>2-</sup>	mg L <sup>-1</sup>	33.4
Cl <sup>-</sup>	mg L <sup>-1</sup>	43.5
NO <sub>3</sub> <sup>-</sup>	mg L <sup>-1</sup>	45.6
Alkalinity (as CaCO <sub>3</sub> )	mg L <sup>-1</sup>	194.
<sup>90</sup> Sr	pCi L <sup>-1</sup>	51,000
pH		7.49
Temperature	°C	14.1
Log (Q/K) <sub>calcite</sub> *		0.19
Log fugacity of CO <sub>2</sub> (f <sub>CO2</sub> )		-2.20

\*Where Q is the ion activity product {Ca<sup>2+</sup>}{CO<sub>3</sub><sup>2-</sup>}, and K is the solubility product for calcite.

## RESULTS AND DISCUSSION

The ureolysis rates determined in the laboratory using the <sup>14</sup>C-labeled urea method are presented in Table 2.

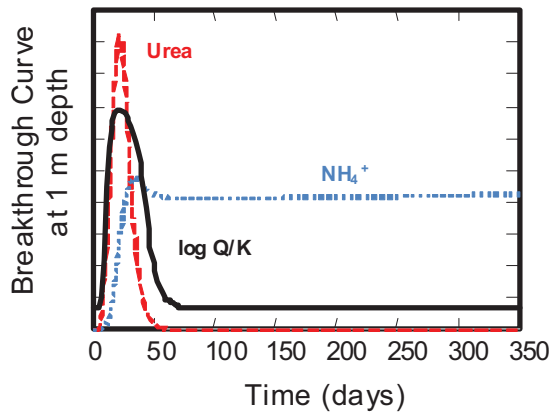
**TABLE 2. Estimated ureolytic activity measured in water samples from INTEC.**

Well name	Sample description	urea hydrolysis rate (nmol L <sup>-1</sup> d <sup>-1</sup> )
55-06	INTEC perched water	10.53 ± 1.07
MW-2	INTEC perched water	28.66 ± 2.51
MW-5-2	INTEC perched water	6.06 ± 2.61
MW-10-2	INTEC perched water	16.77 ± 0.90
ICPP-2018	INTEC perched water	5.35 ± 0.62
ICPP-2019	INTEC perched water	14.79 ± 5.60
CPP-01	INTEC deep groundwater	Below quantifiable level
CPP-02	INTEC deep groundwater	1.79 ± 0.44

The results of the in situ rate estimation experiments indicated that the contaminated INTEC perched water samples had significant ureolytic activity, and the observed rates were higher than in the uncontaminated deep aquifer samples. The INTEC aquifer

samples (CPP-01 and CPP-02) showed rates that were similar to the “background” rates we have measured in UP-1, another uncontaminated deep well accessing the SRPA within the city of Idaho Falls (Fujita, Taylor et al., 2008). Speciation calculations indicated slight supersaturation with respect to calcite ( $\log Q/K = 0.20$ ) and a  $\text{CO}_2$  fugacity of  $10^{-2.2}$  (compared to the atmospheric level of  $10^{-3.5}$ ).

The range of urea hydrolysis rates observed for the INTEC perched water ranged from  $5.4$  to  $29 \text{ nmol L}^{-1} \text{ d}^{-1}$  (see Table 1); a representative value of  $20 \text{ nmol L}^{-1} \text{ d}^{-1}$  per day was selected and used to estimate a first order rate constant for the simulations. Because our measured hydrolysis rates do not include the contribution from attached microorganisms, for the simulations the first-order rate constant was increased by a factor of ten, based on previous experience comparing laboratory and integrated field rates at another location in the SRPA (Fujita, Taylor et al., 2008). The resulting value that was used for the first order rate constant in the simulations was  $0.03 \text{ d}^{-1}$ .



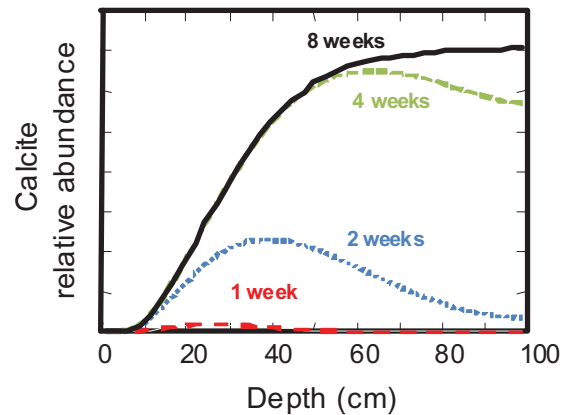
**FIGURE 1. Simulated breakthrough curves for urea, ammonium and log of calcite saturation index, for 10 mM urea addition.**

The results of simulations using the 3 different urea concentrations (10, 50, and 100 mM) were qualitatively the same (similar shapes for breakthrough curves and distributions of calcite). Consequently only results from a single simulation (10 mM urea) are presented here; the conclusions are analogous for the higher urea concentrations. Figure 1 shows the aqueous breakthrough curves for ammonium, urea, and  $\log (Q/K)_{\text{calcite}}$  at the base (100 cm depth) of the vertical flow domain. The vertical scale of each breakthrough curve has been arbitrarily adjusted so that all three curves can be displayed on single figure. Because urea is not expected to adsorb to the

site sediments (Fujita, Taylor et al., 2008) it moves through the system attenuated only by hydrolysis. The ammonium produced by urea hydrolysis interacts with the sediments via cation exchange of sorbed calcium for aqueous ammonium and the arrival of the peak ammonium concentration is delayed relative the peak urea concentration. Additionally, as urea is flushed from the system by “clean” infiltrating water containing minimal aqueous ammonium, the dissolved calcium exchanges for sorbed ammonium resulting in a near steady state long-term ammonium concentration. The arrival of the maximum in the calcite saturation state ( $\log Q/K$ ) tracks the urea, showing the relationship between urea hydrolysis and calcite precipitation. Following passage of the urea concentration maximum, the calcite saturation state curve more closely tracks the ammonium breakthrough curve, reflecting the continued desorption of calcium (and thus maintenance of a higher  $\log Q/K$ ) after urea has been largely flushed from the system.



The distribution of calcite as a function of time and position is shown in Figure 2. Early calcite precipitation is confined to the upper part (but not the top) of the flow domain, but with time precipitation moves deeper into the system. After 8 weeks calcite is distributed uniformly in the lower half of the section; these results are indistinguishable from those at 1 year. The simulation results indicate that calcite precipitation is not localized but spread across a large area and that urea will migrate from its point of introduction before significant calcite precipitation occurs. The relative position of the precipitation front will be a function of both the urea hydrolysis rate and the rate of advective transport.



**FIGURE 2. Simulated distribution of calcite with depth, for 10 mM urea addition, at different times.**

## CONCLUSIONS

These results suggest that the contamination history in the perched water has not significantly impaired the intrinsic ureolytic activity of the native microbial community. Testing of the contaminated INTEC perched water yielded ureolysis rates even higher than in the deep uncontaminated aquifer water; this could be a reflection of higher overall microbial numbers in the shallower water. In general the SRPA is considered an oligotrophic aquifer (Colwell and Lehman, 1997; Lehman, O'Connell et al., 2004), and the shallower perched water may contain higher nutrient concentrations due to the more dynamic fluxes that occur from surface infiltration. Unfortunately we were not able to determine cell counts for the samples used in this study, due to logistical issues associated with the radioactive contamination. In our previous field experiment in an SRPA well, we were successful in increasing ureolytic activity by two orders of magnitude by the addition of dilute molasses and urea; similar stimulation by adding nutrients may be possible as well in the perched water at INTEC. Additionally, the simulation results presented in this study suggest that calcite precipitation can be induced well beyond the point at which urea is introduced into the system; the extent of the treatment zone is a function of the urea hydrolysis rate and the advective transport of the urea. Both of these parameters are subject to manipulation by engineering design; the hydrolysis rate could be modified with the targeted introduction of nutrients, and the advective transport could be modified through design of injection and extraction schemes.

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