ABSTRACT: Subsurface radionuclide and metal contaminants throughout the U.S. Department of Energy (DOE) complex pose one of DOE’s greatest challenges for long-term stewardship. One promising stabilization mechanism for divalent ions, such as the short-lived radionuclide $^{90}$Sr, is co-precipitation in calcite. We have previously found that nutrient addition can stimulate microbial ureolytic activity, that this activity accelerates calcite precipitation and co-precipitation of Sr, and that higher calcite precipitation rates can result in increased Sr partitioning. We have conducted integrated field, laboratory, and computational research to evaluate the relationships between ureolysis and calcite precipitation rates and trace metal partitioning under environmentally relevant conditions, and investigated the coupling between flow/flux manipulations and precipitate distribution.

A field experimental campaign conducted at the Integrated Field Research Challenge (IFRC) site located at Rifle, CO was based on a continuous recirculation design; water extracted from a down-gradient well was amended with urea and molasses (a carbon and electron donor) and re-injected into an up-gradient well. The goal of the recirculation design and simultaneous injection of urea and molasses was to uniformly accelerate the hydrolysis of urea and calcite precipitation over the entire inter-wellbore zone. The urea-molasses recirculation phase lasted, with brief interruptions for geophysical surveys, for 12 days followed by long-term monitoring which continued for 13 months. Following the recirculation phase we found persistent increases in urease activity (as determined from $^{14}$C labeled laboratory urea hydrolysis rates) in the upper portion of the inter-wellbore zone. We also observed an initial (first 2 weeks) increase in urea concentration associated with injection activities. After injection ceased, we observed a decreased urea concentration and increased in ammonium and dissolved inorganic carbon (DIC). Based on the loss of urea and the appearance of ammonium, a first order rate constant for urea hydrolysis of 0.18 day$^{-1}$ and an associated $Rf$ value for ammonium of 11 were estimated. The rate constant is approximately 6 times higher than estimated for previous field experiments conducted in eastern Idaho. Additionally, DIC carbon isotope ratios were measured for the groundwater. Injected urea had a $\delta^{13}$C of -40.7±0.4 ‰ compared to the background groundwater DIC $\delta^{13}$C of -16.6±0.2‰. Observed decreases in groundwater DIC $\delta^{13}$C of up to -19.8‰ followed temporal trends similar to those observed for ammonium and suggest that both the increase in ammonium and the shift in $\delta^{13}$C are the result of urea hydrolysis.

Analysis of a conservative tracer test conducted one year after the end of recirculation and comparison with a pre-injection tracer test indicated that the urea and molasses amendment resulted in preferential blocking of flow access to lower permeability zones and consequent flow focusing within the most conductive portion of the aquifer. Additionally, exchangeable ammonium was observed in the lower portion of the post-injection core. Although direct observation of calcite precipitation was not possible because of the high pre-existing calcite content in the site sediments, an observed $\delta^{13}$C decrease for solid carbonates from sediment samples collected following urea injection (compared to pre-injection values) is likely the result of the incorporation of inorganic carbon derived from urea hydrolysis into newly formed solid carbonates.