# 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

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Radionuclide and metal contaminants such as $^{90}Sr$ are present beneath U.S. Department of Energy (DOE) lands in both the groundwater (e.g., 100N area at Hanford, WA) and vadose zone (e.g., Idaho Nuclear Technology and Engineering Center at the Idaho National Laboratory [INL]). In situ containment and stabilization of these contaminants is a cost-effective treatment strategy. However, implementing in situ containment and stabilization approaches requires definition of the mechanisms that control contaminant sequestration. We are investigating the in situ immobilization of radionuclides or contaminant metals (e.g., $^{90}Sr$) by their facilitated coprecipitation with calcium carbonate in groundwater and vadose zone systems. Our facilitated approach relies upon the hydrolysis of introduced urea to cause the acceleration of calcium carbonate precipitation (and trace metal coprecipitation) by increasing pH and alkalinity and liberating cations from the aquifer matrix by exchange reactions:

$$H_2NCONH_2 + 3H_2O \rightarrow 2NH_4^+ + HCO_3^- + OH^-$$
$$>\mathbf{X:}_2Ca + 2NH_4^+ \rightarrow 2>\mathbf{X:}NH_4 + Ca^{2+}$$
$$Ca^{2+} + HCO_3^- + OH^- \rightarrow CaCO_3(s) + H_2O$$

where **>X:** is a cation exchange site on the aquifer matrix. Subsurface urea hydrolysis is catalyzed by the urease enzyme, which is produced in situ by native urea-hydrolyzing microorganisms. Because the precipitation process tends to be irreversible and many western aquifers are saturated with respect to calcite, the co-precipitated metals and radionuclides will be effectively removed from the aqueous phase over the long term.

Our research has shown that (1) urea-hydrolyzing microorganisms are ubiquitous in the Snake River Plain Aquifer underlying the INL and also occur beneath the Hanford 100N area; (2) urea hydrolysis and calcite precipitation are linked in laboratory and field settings; and (3) $Sr^{2+}$ is incorporated into calcite precipitated by urea-hydrolyzing bacteria with higher distribution coefficients than in abiotic systems. These experimental results and observations have been embodied in a geochemical and reactive transport computer code that allows field-scale simulations of the urea hydrolysis-calcite precipitation process. The mixed equilibrium-kinetic model accounts for urea hydrolysis by ureolytic bacteria and calcite precipitation/dissolution using kinetic expressions. Cation exchange reactions and metal partitioning into the precipitated calcite are treated as equilibrium processes. Simulations of hypothetical remediation strategies using mM levels of urea show that almost 1 mmol of calcite is precipitated per mmol of hydrolyzed urea, with most of the precipitated cations being derived from exchange of $NH_4^+$ with the aquifer matrix. Because of the cation exchange reactions and the near absence of $NH_4^+$ in the groundwater, the long-term persistence of the precipitated calcite is a function of the applied urea concentration and the total cation exchange capacity of the aquifer matrix. Our simulation results suggest that with appropriate urea introduction strategies calcite precipitation can provide for the long-term in situ sequestration of radionuclides and metals.