

Effect of groundwater solutes on uraninite stability: laboratory and field studies

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In-situ bioremediation strategies target the immobilization of uranium in contaminated sites by stimulating microbial reduction of U(VI) to less soluble U(IV). Biogenic uraninite and U(IV) bound to biomass are among the resulting products of U(VI) bioreduction. Uraninite is the preferred form of U(IV) for *in-situ* bioremediation as it is less soluble than other U(VI) and U(IV) species. Understanding the effect of groundwater solutes on uraninite stability in reduced sediments is crucial for the success of bioremediation strategies.

We performed laboratory and field studies to investigate the effect of groundwater solutes on uraninite dissolution by integrating aqueous chemistry and solid characterization methods. Uraninite dissolution under anoxic and oxic conditions with an influent solution containing dissolved inorganic carbon was lower in the presence of Ca than in de-ionized water. X-ray absorption spectroscopy (XAS) and solution chemistry analyses suggest that adsorbed or precipitated Ca²⁺ phases may inhibit oxidative uraninite dissolution.

We performed field experiments in oxic and anoxic wells at the Old Rifle, CO site to better understand the oxidative dissolution of uraninite over 650 days. By placing biogenic uraninite in tubes covered with a membrane that allowed diffusive exchange and placing the tubes in the aquifer (~ 10 mM inorganic carbon), uranium loss could be quantified. After 102 days, around 50% uranium loss was observed from the tubes deployed under oxic conditions. However, only less than 3% loss was observed from the anoxic well. After 650 days, 65% and 85% loss was observed under oxic conditions whereas the corresponding U loss in the anoxic control remained negligible. Ca K-edge EXAFS linear combination and shell by shell fits suggest that: a) Ca²⁺ adsorbed to the surface of uraninite; and b) it is possible that a U-Ca-O phase formed a thin layer on the surface of reacted biogenic uraninite. Our results suggest that Ca and other groundwater solutes increase the long-term stability of uraninite in subsurface environments.