

Coupled Abiotic Fe, S, and U Redox Reactions in Rifle IFRC sediments

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Uranium (U) is a priority contaminant at DOE UMTRA sites, and the mobility of U is governed by a complex array of biogeochemical processes. Our work is a summary of several related laboratory studies of abiotic reactions and processes affecting U, in particular processes that are coupled with Fe and S abiotic redox reactions. In addition, a tracer test was conducted at the Rifle IFRC site in which Fe(II) was injected into the alluvial aquifer without an added electron donor.

When ⁵⁷Fe(II) is added to Rifle sediments in a batch reactor in an artificial groundwater solution, a large fraction (60–100%) is quickly oxidized to ⁵⁷Fe(III) on sediment surfaces. Mossbauer results indicate that the oxidation is coupled to transformation of a ferrihydrite-like mineral to a nanoparticulate, Fe(II)/⁵⁷Fe(III)-like mineral phase. The fraction oxidized decreases as Fe(II) loading increases, indicating a finite limit for oxidation per unit sediment. Increasing pH from 7.2 to 8.3 or including HCO₃⁻ had no effect on percent oxidation or mineral transformation.

The effect of Fe(II) addition on U reactions with sterilized Rifle sediment was studied in pH 7.2 and 8.3 solutions equilibrated with 400 ppm CO₂. XANES results indicate U(VI) reduction to U(IV) at both pH values, with the extent of U reduction increasing with increasing Fe(II) concentration. Greater levels of U reduction were observed at pH 8.3 compared to pH 7.2, and this effect may be due to the greater uptake of Fe(II) onto sediments at higher pH. For example, 18% of solid phase U was U(IV) at both pH 7.2 and 8.3 for similar Fe(II) loadings. Greater U reduction was observed in the absence of CO₂ compared to 400 ppm CO₂. At pH 8.3, 54% of U was reduced in the absence of CO₂ while 36% was reduced under 400 ppm CO₂ at an Fe(II) loading of 55 μmol/g.

Aqueous Fe(II) concentrations reach 50–100 μM in biostimulation experiments at the IFRC site. A field experiment was performed in which pulses of groundwater with added Fe(II) were injected into multi-level sampling wells. Groundwater had low dissolved O₂(g) (0.6–2.5 μM), pH (7.1–7.4), aqueous U(VI) (0.18 μM), and low Fe(II) (0–4 μM). Aqueous Fe(II) in the injection wells increased with each pulse of added Fe(II), reaching injection concentrations (45 μM) after the 6th injection. In shallower ports (18, 21 ft bgs) the Fe(II) concentrations remained elevated during the 3 week experiment, while Fe(II) concentrations decreased more quickly in deeper ports (24 ft bgs). Despite the appearance of a conservative tracer (Br) in wells 0.8–1.4 m downgradient of the injections, no Fe(II) was detected in downgradient wells. A single pulse of high pH (pH 8.4) groundwater was injected following the Fe(II) injections in one of the wells. Little change in U(VI) concentration was observed in any of the wells at ambient pH, suggesting negligible or no U reduction occurred. Complex changes with time were observed following the high pH injection, which may have been caused by both U(VI) desorption and a small amount of U reduction.

Kinetics of abiotic U(VI) reduction by aqueous sulfide were also studied using a batch reactor. The effects of pH, dissolved carbonate, Ca(II), U(VI), and S(-II) concentration were evaluated in separate experiments. The U reduction rate increased with increasing S(-II) concentration, while it was slowed by increased dissolved carbonate or Ca concentration. The U reduction product was identified as nanoscale uraninite. Thermodynamic modeling showed that the concentrations of non-carbonato U(VI) species, which changed as a function of the experimental variables, correlated with observed changes in U reduction rate. At Rifle groundwater conditions, the U reduction was slow but measurable. Reactive transport modeling is needed to evaluate whether this reaction is of significance under sulfate-reducing conditions in Rifle biostimulation experiments.