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*Combined effects of hydrology, geochemistry, and biology on the remediation of U(VI) in microfluidic experimental systems (micro models)*

**Abstract**

The objective of this work has been to characterize the combined effects of hydrology, geochemistry, and biology on the bioremediation of U(VI). Our underlying hypothesis was *bioremediation of U(VI) in groundwater is controlled by transverse mixing with an electron donor along plume margins, and that* ***iron*** *bioavailability in these zones critically affects U(VI) reduction kinetics and U(IV) re-oxidation*. Our specific objectives are to a) quantify reaction kinetics mediated by biological versus geochemical reactions leading to U(VI) reduction and U(IV) re-oxidation, b) understand the influence of bioavailable iron on U(VI) reduction and U(IV) re-oxidation along the transverse mixing zones, c) determine how transverse mixing limitations and the presence of biomass in pores affects these reactions, and d) identify microbial populations that develop along transverse mixing zones and how the community development is influenced by the presence of iron and the concentration of electron donor.

The experimental tasks have utilized etched silicon microfluidic pore networks (micromodels) to simulate micro-scale hydraulic mixing zones within aquifer material. These micromodels have been used previously to understand the influence of transverse mixing (of electron donor and electron acceptor), biomass architecture, and biogeochemical reactions on contaminant fate and transport. We have used micromodels in the presence and absence of ferric iron, to assess the critical role that total iron plays in uranium bioremediation. Electron donors including acetate and lactate, U(VI), and Fe(III)-reducing cells have been introduced to the micromodels in a controlled manner to characterize the mechanisms and kinetics of both U(VI) reduction and U(IV) reoxidation, and to correlate this with biofilm structure along the transverse mixing zone(s). We have also used strictly abiotic experimental systems to determine the influence of abiotic reductants such as sulfides and hydroquinones on U(VI) reduction in the presence and absence of Fe(III).

Experiments with batch cultures (to support the micromodel development) were run with Geobacter metallireducens and uranyl adsorbed to the surfaces of either ferrihydrite or aluminum oxide. U(VI) was reduced by hydroquinones (as a model reductant) irrespective of whether the system contained aluminum or iron, suggesting that adsorbed U(VI) is available even when iron is not present. However, the buffer selection and concentration of bicarbonate was critical to reduction in the presence or absence of iron. Increasing bicarbonate decreases reduction of U(VI) in both iron and aluminum suspensions. In addition, aqueous uranyl is not reduced in bicarbonate buffer, where it is immediately reduced in HEPES buffer. This has implications for past experiments in which HEPES buffered suspensions were used to establish rates and mechanisms of adsorbed uranyl reduction, as HEPES seems to increase the capacity for reduction, while bicarbonate (which is the environmentally relevant buffer) decreases uranyl reduction in the presence of solids.

In addition, the abiotic precipitation of uranium (U(VI)) was evaluated in a microfluidic pore network (i.e. micromodel) to assess the efficacy of using a phosphate amendment to immobilize uranium in groundwater and mitigate the risk of this contaminant to potential down-gradient receptor sites. U(VI) was mixed transverse to the direction of flow with hydrogen phosphate ($HPO_4^{2-}$), in the presence or absence of calcium ($Ca^{2+}$) or sulfate ($SO_4^{2-}$), in order to identify precipitation rates, the morphology and types of minerals formed, and the effects of mineral precipitates on pore blockage. Each reactant was initially at 100 μM. Precipitation occurred over the time scale of hours to days, and rates varied with influent conditions. Relative to when only U(VI) and $HPO_4^{2-}$ were present, precipitation rates were 2.3 times slower when $SO_4^{2-}$ was present, and 1.4 times faster when $Ca^{2+}$ was present; larger crystals formed in the presence of $SO_4^{2-}$. Raman backscattering spectroscopy and micro X-ray diffraction (μ-XRD) results both showed that the only mineral precipitated was chernikovite, also known as hydrogen uranyl phosphate; $UO_2HPO_4$.