Identifying Key Controls on the Behavior of an Acidic-U(VI) Plume at the Savannah River Site using Reactive Transport Modeling

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Acidic waste solutions containing low level radioactivity from numerous isotopes were discharged to a series of unlined seepage basins at the F-Area of the Savannah River Site, South Carolina, from 1955 through 1989. Although the site has gone through many years of active remediation, the groundwater remains acidic, and the concentrations of U(VI) and other radionuclides are still significant. Monitored Natural Attenuation (MNA) is a desired closure strategy for the site, based on the premise that clean background groundwater will eventually neutralize the groundwater acidity, causing an increase in pH and driving natural immobilization of U(VI) through sorption. The development of the understanding of the long-term pH and U(VI) sorption behavior at the site is critical to assess MNA and in-situ treatment over the long term.

We use reactive transport (RT) models and uncertainty quantification (UQ) to explore key controls on the U(VI)-plume evolution and long-term mobility at this site through considering U(VI) adsorption by sediments and key hydrodynamic processes. Two-dimensional RT simulations through the saturated and vadose zones were conducted by considering the dissolution and precipitation of Al and Fe minerals, as well as H^+ and U(VI) surface complexation. Simulations indicate that mineral dissolution and precipitation together with sorption reactions on goethite and kaolinite (primary minerals present with quartz) could buffer pH at the site for long periods of time.

UQ techniques were applied with RT modeling in order to: (1) identify the complex physical and geochemical processes that control the migration of the acidic-U(VI) plume in the pH range where it is highly mobile, (2) evaluate those physical and geochemical parameters that are most controlling, and 3) attempt to predict the future plume evolution constrained by historical chemical and hydrological data. UQ-RT results show that model results are most sensitive to the reactive surface area available for sorption, discharge rates, the relative rates of H^+ influx and kaolinite dissolution. The plume behaviour also appears to be sensitive to parameters controlling the amount of residual U(VI) in the vadose zone, which acts as a buffering zone in the modeled system.

Iron isotope fractionation during femtosecond laser ablation of magnetite determined by aerosol size sorting experiments

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Aerosol particles generated from femtosecond laser ablation (fs-LA; 198nm laser manufactured by Photon Machines) of natural magnetite were size sorted using a Micro-Orifice Uniform-Deposit Impactor (MOUDI). The MOUDI separates particles by size based on aerodynamic properites using 10 stages. Aerosols were collected using fluences of 1, 2, and 4 J/cm^{2} and there is a positive correlation between total Fe collected per laser shot; 25, 50, and 100 picograms of Fe per laser shot were harvested from the impactor, respectively. The aerosol size distribution of the fs-LA generated particles were determined by analyzing Fe concentration for each stage of the impactor using ^{57}Fe isotope dilition mass spectrometry (~10^5 laser shots) or spectroscopically via the ferrozine technique (~10^6 laser shots). The size distribution of aerosol particles done at different fluences are the same; all are unimodal with a peak at an aerodynamic size between 180 to 320 nm.

Sized aerosol particles have been analyzed for their Fe isotope composition. The smallest sized particles have $\delta^{56}Fe$ values that are less than the magnetite substrate by 0.5‰, whereas larger sized particles ($\geq$180–320 nm stage) have $\delta^{56}Fe$ values that were up to +0.7‰ greater than the magnetite substrate. There are no differences in isotope compositions as a function of fluence. In all experiments, the integrated Fe isotope composition of all the stages matches that of the magnetite substrate. This isotopic mass balance highlights that although the process of fs-LA produces Fe isotope fractionation, if the generated aerosol is quantitatively delivered and ionized, one can obtain accurate Fe isotope measurements. Indeed, for sample-standard comparisons, accuracy of Fe isotope compositions will hinge on having similar transport efficiencies spatially in the ablation cell. For example, if 12% of the particles $\geq$ 180–320 nm in aerodynamic size are not transported to the ICP source, and these particles consist of 70% of the total Fe mass with $\delta^{56}Fe$ values that are 0.7‰ greater than the bulk substrate, the measured Fe isotope composition would be inaccurate by -0.1‰. This can easily be monitored, however, by comparing Fe yields derived by total ion signal. Using the above example, there would be a ~9% decrease in the total Fe ion signal.

The correlation between Fe isotope composition and particle size may result from condensation wherein the first condensed particles from fs-LA generated vapor have low $\delta^{56}Fe$ values. As condensation continued and some particles coarsened, they inherited higher $\delta^{56}Fe$ values from the isotopically heavy vapor.