Integrating geochemical, reactive transport, and facies-based modeling approaches at the contaminated Savannah River F-Area

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Objective

This study aims at understanding key hydrogeochemical processes dictating pH behavior and U transport at the Savannah River F-Area in South Carolina, USA. A nearly 1 km long acidic plume has developed under this site from the disposal of low-level acidic radioactive waste solutions into seepage basins overlying relatively permeable, mostly sandy sediments. The impact of chemical and physical heterogeneities on contaminant mobility is of particular interest.

Approach and Results

Various geochemical, horizontal 1D, and vertical 2D reactive transport simulations are conducted, that include the effects of mineral dissolution and precipitation, as well as H+ and U(VI) sorption using surface complexation models. Simulations consider the historical 35-year discharge of U-bearing nitric acid solutions, followed by a post-discharge period of 65 years. The concept of “reactive facies”, integrating sediment chemical and hydrophysical properties with geophysical signatures, is explored to spatially distribute linked physical and chemical heterogeneities at local and field scales. Results of isotopic studies are also used to constrain the modeling effort. Simulations are conducted in a step-wise manner, first considering only the saturated zone then increasing complexity by including the vadose zone and a free water table.

Simulations indicate that H^+ sorption reactions on goethite and kaolinite (the main minerals at the site besides quartz), and the precipitation of Al minerals could delay the pH rebound for decades. Such slow rebound is likely to be exacerbated by residual saturation of the plume below the discharge basins. U concentrations potentially could decrease faster than pH from dilution with clean recharge water.

Two reactive facies are identified in the main formation at the site, each with distinct effects on predicted plume migration. Heterogeneous reactive properties (i.e., surface areas) within each facies, however, do not appear to affect the simulated historical pattern of the plume, because sorption sites become quickly saturated by the massive H^+ and U influx during the discharge period. Consequently, intra-facies heterogeneities mostly affect the predicted pH and U transport at early times and at the plume edges, and are expected to become relevant over the long term only once contaminant concentrations have decreased below sorption saturation levels. Rigorous uncertainty quantification studies are underway to further evaluate the effect of key model input parameters on model predictions.

Calcite Growth from the Molecular Scale.

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Calcite ($CaCO_3$) growth and dissolution play important roles in determining ocean and subsurface geochemistry, such as buffering pH and serving as a biomineral for a large number of organisms. An understanding of the molecular-level mechanisms by which calcite grows and dissolves may enhance our ability to understand and predict the response of calcite to changes in these environments.

While abundant measures of calcite growth and dissolution rates exist, these are often made by measuring the solution composition over time, a method which convolutes the multiple reactions that occur on the mineral surface itself and these studies therefore have limited value in understanding reaction mechanisms. Historically, most surface sensitive techniques applied to this problem have probed calcite reactivity under stoichiometric solution compositions, which also cannot distinguish between the independent reactivities of calcium and carbonate. Using *in situ* atomic force microscopy, Stack and Grantham[1] and others[2] have recently shown that the ratio of calcium-to-carbonate plays an important role in determining overall reaction rate.

Here, we will evaluate the efficacy of analytical crystal growth models applied to the advance of monomolecular steps on the calcite surface. In particular we will focus on how well they capture the response of step velocity under varying saturation index as well as aqueous calcium-to-carbonate ratio. We will use strontium and its inhibitio of growth as an indicator of how well these models are capturing the salient aspects of reactions such as the nucleation and propagation of kinks on steps. At the time of writing, no single model yet derived captures the entirety of the richness of reactivity observed.

As an alternative to pre-defined analytical models fit to experimental data, we also will show the results of rare event theory molecular dynamics simulations applied to the same kink site reactions on the calcite surface. This method was recently successfully applied to the barite ($BaSO_4$) {120} steps[3]. These have the potential to give accurate reaction rates and mechanisms independent of a crystal growth model.

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