Reactivity of Primary Soil Minerals and Secondary Precipitates beneath Leaking Hanford Waste Tanks

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Research Objective

Since the late 1950s, leaks from 67 single-shell tanks at the Hanford Site have released about 1 million curies to the underlying sediments. There is a risk that future remediation activities may add to and/or mobilize the existing inventory of contaminants in the vadose zone. At issue is the distribution of contaminants beneath the tanks, and the processes that led to their current disposition and will control their future mobility. The high ionic strength, high pH, and high aluminum concentrations in the tank liquids can significantly alter the vadose zone sediments through dissolution of primary minerals and precipitation of secondary minerals. Dissolution and precipitation directly influence (1) the flow paths that control contaminant transport and (2) the reactivity of the solid matrix that controls contaminant mobility. The impact of these processes, however, depends on mineral reaction kinetics and the dynamic interaction of the reactions with the flow field and contaminant sorption, neither of which are well-known for this extreme chemical system. Precipitation of Al-hydrous oxides is expected as tank solutions mix with ambient Hanford soils and solutions. Depending on the mixing conditions, stable or metastable phases might precipitate, while reaction rates will depend on the kinetic factors of temperature, solution composition, and reactive surface area. Polymeric Al-species may precipitate as colloids, and adsorb to other minerals or be transported in solution. Dissolution of primary minerals will provide components that can reprecipitate with Al as clays, zeolites, or layered double hydroxides. Sorption and desorption of radionuclides will be a function of the amount of surface area of the neoformed phases and may fluctuate as the amounts of these reactive phases vary with changes in the ambient environment. Data obtained will be directly useful to other EMSP projects addressing contaminant mobility in the vadose zone.

We intend to address three specific issues:

1. Recognized factors that control the kinetics of dissolution and precipitation must be quantified for the unnatural system of tank solutions mixing with soils, including effects of high pH, high ionic strength (especially NaNO₃ solutions), temperature, and saturation state.
2. A clear understanding of the roles of nucleation mechanism, nucleation sites on soils minerals, and the role of reactive surface area in simultaneous dissolution and precipitation reactions are the key unknown components in comprehending this contaminated soil system.
3. Results obtained in (1) and (2) will help build a mechanistic understanding of how tank fluids migrate through the vadose zone. Local changes in porosity and permeability will dictate preferential flow paths which directly regulate the transport of later arriving chemical species. Changes in mineral surface area affect sorption site distribution. A comprehensive model is needed that integrates these feedback mechanisms with all the critically available data.

Research Progress and Implications

The goal of the first phase of the project is to obtain kinetic rate laws to describe the dissolution of quartz and feldspar, as well as the precipitation of secondary phases, as high pH, high ionic strength,
high aluminum fluids come into contact with the primary phases. This work involves fundamental kinetic measurements conducted at the University of Colorado, and saturated column experiments at PNNL. Preliminary column experiments using quartz and Hanford sediment, and 0.3 and 3 m NaOH have been conducted at PNNL. At Colorado, work has commenced as of January 2000 on three fronts: sample collection and characterization, thermodynamic calculations, and experimental design.

High purity, natural quartz sand and synthetic gibbsite have been obtained. Quartz will be examined as a primary dissolving mineral, whereas gibbsite will be used to obtain solutions in equilibrium with respect to that phase under the conditions of interest as well as examined for its own dissolution and precipitation kinetics. In order to purify the quartz, we have used magnetic separation and sustained treatment with sulfuric acid. Quartz surfaces will be further conditioned by treatment with boiling deionized water. The purity of the bulk quartz sample and the quartz surfaces before and after the various treatments are being assessed by X-ray Fluorescence Spectroscopy and Auger Electron Spectroscopy, respectively. Gibbsite was X-rayed to determine its purity, and particles < 10 µm in diameter were removed via size-settling in low pH, low ionic strength solutions. Size separation was verified using Scanning Electron Microscopy.

We modified one of the thermodynamic databases in the Geochemist’s Workbench geochemical modeling software to account for Pitzer ion interaction parameters relating to the aqueous Al species of interest in our experimental systems and their interactions with Na. Calculations fairly accurately reproduce published gibbsite solubility data. Pitzer coefficients for H₃SiO₄⁻ and H₂SiO₄²⁻ have also been included at 25°C, and we are working on approximating temperature-dependent coefficients for these Si species. If polynuclear Si species need to be considered at higher pHs, we will approximate activity coefficients within the Pitzer formalism starting by refitting activity coefficients calculated using SIT (specific-interaction-theory).

Most of the equipment needed to run the initial kinetic experiments has been obtained. We have designed protocols to minimize interference from carbonate species, and to obtain unambiguous kinetic data. We expect to start the kinetics experiments within one month.

**Planned Activities**

At Colorado, the kinetic experiments will be conducted in two stages. Batch experiments will be used to make a first assessment of kinetic rates and reaction products. Given the approximate rates obtained from the batch experiments, single-pass stirred-flow reactor experiments will be performed to more tightly constrain rates as functions of saturation state, solution composition, and temperature. Experiments will be performed from 25 to 90°C, and from pH 9-14 in 0 and 2 m NaNO₃, with pH adjusted by titrating with NaOH. Batch experiments will be started within one month and stirred-flow reactor experiments within three months. Analysis of the column experiments conducted at PNNL will be completed within four months. Such analysis will include rate calculations based on measured effluent Si and pH; characterization of the solids with X-ray diffraction and selective extraction of amorphous precipitates; and determination of changes in saturated hydraulic conductivity, moisture retention, and particle size. Subsequent kinetic work will be determined based on the initial results from all sets of experiments.