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Title: 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. 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. Data obtained will be directly useful to other EMSP projects addressing contaminant mobility in the vadose zone.

We are addressing 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  $\text{NaNO}_3$  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 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**

This report summarizes work after ~ 1.75 years of a 3 year project. The goal of the first phase is to obtain kinetic rate laws to describe the dissolution of primary minerals, as well as the precipitation of secondary phases, as they contact high pH, high ionic strength, high aluminum fluids. Column experiments using quartz and 0.3 and 3 M NaOH have been conducted at PNNL. At Colorado, batch experiments have been performed to measure the dissolution kinetics of quartz, and the kinetics and thermodynamics of the precipitation of secondary nitrate-cancrinite.

In the batch experiments, quartz sand ~0.3 mm in diameter was used. In order to purify the quartz, we used magnetic separation and sustained treatment with sulfuric acid. Quartz surfaces were further conditioned by soaking for 3 days in 75 °C deionized water. X-ray Fluorescence Spectroscopy determined the purity of the treated quartz sample at 99.9%  $\text{SiO}_2$ , and Auger Electron Spectroscopy could detect no impurities on the surfaces of the quartz grains. Sand was placed in plastic bottles, which were filled with solution. The bottles were placed in a

constant temperature bath (59.2, 75.0, and 88.7 °C), and one bottle at a time was removed for measurement of pH and Si and Al concentrations. Most solutions investigated were 2 m NaNO<sub>3</sub>, with 0.0001, 0.001, 0.005, or 0.01 m Al(NO<sub>3</sub>)<sub>3</sub>. A free OH<sup>-</sup> concentration of 1, 0.1, 0.01, or 0.004 m was obtained by adding enough NaOH, taking into account the formation of Al(OH)<sub>4</sub><sup>-</sup> complexes in solution. Also, solutions with 0.005 m Al(NO<sub>3</sub>)<sub>3</sub> and 0.1 m free OH<sup>-</sup> were made with 0.5, 1.0, 2.0, and 4.0 m NaNO<sub>3</sub>.

The *Geochemist's Workbench* 3.0 (GWB) was used to model the speciation of the reacting solutions. Equilibrium constants for reactions among the solution components and interaction parameters for Pitzer's model were taken from the literature and incorporated into a GWB database. We modified one of the thermodynamic databases to account for Pitzer ion interaction parameters relating to all aqueous species known to be present in these solutions, including an approximation for polysilicate species.

Initial quartz dissolution rates were measured because of the solution saturation effect and because of the precipitation of nitrate-cancrinite at elevated dissolved Si concentrations.

Measurements of quartz dissolution under these conditions have demonstrated that while Na<sup>+</sup> does not appreciably affect the dissolution rate, Al(OH)<sub>4</sub><sup>-</sup> can depress the rate significantly. The data are consistent with the hypothesis that Al(OH)<sub>4</sub><sup>-</sup> adsorbs to the quartz surface as an Al(OH)<sub>4</sub><sup>-</sup>-Na<sup>+</sup> ion pair, blocking the surface from nucleophilic attack by water and OH<sup>-</sup>. The degree of rate depression appears to depend solely on the Al(OH)<sub>4</sub><sup>-</sup> concentration and the *in situ* pH. Therefore, we surmise that the amount of Al(OH)<sub>4</sub><sup>-</sup> adsorption is temperature invariant.

This observation agrees well with the assumption of Dove (1994, *Am. J. Sci.*, 294, 665-712.), who created a mechanistic model of quartz dissolution in Na<sup>+</sup> solutions based on surface speciation, assuming the distribution of surface species was temperature invariant. However, attempts to extend Dove's model to include Al(OH)<sub>4</sub><sup>-</sup> adsorption were unsuccessful because of problems with her triple layer model. Therefore, a Langmuir-type model was adopted to describe the Al(OH)<sub>4</sub><sup>-</sup> adsorption reaction and predict the degree of rate depression.

After 2-10 days, nitrate-cancrinite, a feldspathoid mineral with a zeolite-like crystal structure, precipitated onto the quartz surfaces in many of the 88.7 °C experiments, cementing the grains together. Estimates of the K<sub>eq</sub> for the precipitation reaction differ for solutions with 0.1 or 1.0 m OH<sup>-</sup> (log K<sub>eq</sub> = 30.4 ± 0.8 and 36.2 ± 0.6, respectively). It is inferred that the difference in solubility is attributable to more perfect crystallinity (i.e., fewer stacking faults) in the higher-pH cancrinite structure. This hypothesis is supported by electron micrographs of crystal morphology and measured rates of Na volatilization under an electron beam. Precipitate crystallinity may be important for radionuclide mobility, because stacking faults in the cancrinite structure can negate its zeolitic cation exchange properties. The log of the precipitation rate depends linearly on the activity of Al(OH)<sub>4</sub><sup>-</sup> in solution. The evolution of Si concentration in experimental solutions was successfully modeled by considering the dependence of quartz dissolution rate on Al(OH)<sub>4</sub><sup>-</sup> activity, cancrinite precipitation, and the reduction of reactive surface area of quartz due to coverage by cancrinite.

At PNNL, flow-through column experiments were conducted in 0.3 M and 3.0 M NaOH with quartz sand (98% pure). Experiments ran for ~200 days and effluent compositions, changes in hydraulic conductivity, moisture retention, particle size, and mineralogy before and after treatment were monitored. X-ray microtomography of the columns before and after the experiments showed visually evidence of particle aggregation and moisture retention.

After passing 0.3-M and 3.0-M NaOH through the quartz sand columns for 194 days, some of the particles had become brittle and there was an enrichment of darker particles. SEM

and EDX analyses showed that the particles that had become brittle were primarily feldspars and the darker particles were likely ilmenite ( $\text{FeTiO}_3$ ). After NaOH treatment, sieve analysis revealed that there was increased particle aggregation. The 0.3-M NaOH treated sand had a reduction of hydraulic conductivity and greater moisture retention than the control (a 0.03-M  $\text{NaClO}_4$  treatment). The 3-M NaOH treated quartz columns also had a small reduction in hydraulic conductivity but the moisture retention decreased versus applied pressure (opposite trend from the 0.3-M treatment). The cause for these different hydrologic responses between the 0.3 and 3.0 M NaOH treatments may be due to the greater amount of aggregation measured in the 3.0-M NaOH treated sand and to the existence of possibly more precipitated gel coatings in the 0.3-M NaOH treated sand. These Al and Si gel coatings may have permitted water to be trapped in their amorphous structure thus causing the observed change in moisture retention properties. Thus we do not suggest that the caustic-attack change in moisture retention properties was the result of dissolution-caused lowering of the particle-size distribution.

In summary, these studies showed that under caustic chemical conditions, approximated by 0.3-M NaOH, significant changes in the mineralogy were observed. Under flowing conditions, some aggregation of solids was observed likely from cementation via an Al/Si gel or carbonate. The gels/amorphous precipitates increased the moisture retention characteristics but had only minor effects on the saturated hydraulic conductivity of the soil.

These findings will be of significant value for workers who attempt to model the evolution and transport of leaked waste fluids in the Hanford subsurface. Not only are the kinetics and thermodynamics of primary mineral dissolution and secondary phase formation now known under some of the relevant conditions, but it has been shown that the standard model for predicting quartz dissolution rates (Dove, 1994) is inadequate under these conditions.

### **Planned Activities**

Batch kinetics experiments using nearly pure K-feldspar have been initiated. These are similar in design to the quartz experiments. Effect of pH,  $\text{NaNO}_3$  concentration, and Al concentration on dissolution rates and secondary phase formation are being evaluated as a function of temperature. Similar experiments on biotite dissolution are also underway. Biotite dissolution is considered to be a source of ferrous iron that may act as a reductant for  $\text{CrO}_4^{2-}$  (Cr(VI)) to the immobile Cr(III) species.

The Hanford sediment was too fine grained to resolve the much finer pore structure using XMT in the column experiments. In the coming year, we will use a coarser sediment to obtain quantitative information from XMT regarding porosity changes, void creation, and other characteristics related to fluid flow properties.

### **Information Access**

Bickmore B. R., Nagy K. L., Young J. S., and Drexler J. W. (2001a) Nitrate-cancrinite precipitation on quartz sand in simulated Hanford tank solutions. *Environ. Sci. Tech.*, submitted.

Bickmore B. R., Nagy K. L., Gray A. K., and Moschetti M. (2001b) The effect of adsorbed  $\text{Al}(\text{OH})_4^-$  on the dissolution rate of quartz. In *Eleventh Annual V. M. Goldschmidt Conference*, Abstract #3296. LPI Contribution No. 1088, Lunar and Planetary Institute, Houston (CD-ROM).