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

Colorado
University of Colorado at Boulder

Pacific Northwest National Laboratory

EMSP
Environmental Management Science Program

Barry R. Bickmore, Kathryn L. Nagy — *University of Colorado at Boulder*
R. Jeff Serne, Steven B. Yabusaki — *Pacific Northwest National Laboratory*

INTRODUCTION

Leaks from 67 single-shell radioactive waste tanks at the Hanford Site have released about 1 million curies to the underlying sediments since the late 1950s. Future remediation activities may add to and/or mobilize the existing inventory of contaminants in the vadose zone.

Prevailing questions are

- *Where are the contaminants beneath the tanks?*
- *What processes led to their current disposition?*
- *What processes will control their future mobility?*

Leaking tank fluids have extreme bulk compositions with high pH, high Al, and high ionic strength. These fluids will cause primary minerals in the vadose zone to dissolve and secondary minerals to precipitate changing porosity and permeability. Secondary minerals may also precipitate as colloids, and adsorb to other minerals or be transported in solution. Sorption and desorption of radionuclides will vary with the amount of surface area of the new minerals and may fluctuate as the amounts of these new minerals continue to react in the ambient environment.

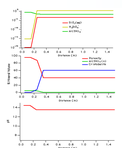
The purposes of our project are

- *To quantify the dissolution kinetics of primary minerals under the extreme conditions expected when leaking tank fluids interact with the Hanford vadose zone*
- *To determine the nature and kinetics of precipitation reactions that will occur as leaked fluids drop in temperature and interact with components from dissolved primary minerals*
- *To model how these reactions will affect flow conditions in the vadose zone sediments*

Our approach includes

- *Kinetic dissolution and precipitation experiments using batch and flow-through reactors*
- *Identification and characterization of precipitated phases*
- *Saturated and unsaturated flow column experiments to simulate temperature gradients and realistic reactive surface areas*
- *X-Ray Microtomography to assess changes in flow conditions in column experiments*
- *Reactive-transport modeling that integrates feedback between dissolution, precipitation, and changes in porosity and permeability*

MODELING



Modeling of Reaction of Simulated Tank Solution with Silicate Sediments

- Simple one-dimensional, saturated flow of simulated tank fluid through quartz sediments.
- Aluminate in the tank fluid does not begin to precipitate until quartz begins dissolving, and the pH is reduced.
- The pore volume in the column also sharply increases due to the dissolution of quartz.

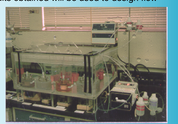
KINETIC EXPERIMENTS

Batch kinetic experiments are underway using quartz as the primary mineral, and the results obtained will be used to design flow-through experiments.

Conditions varied during the experiments include:

- pH (9-14)
- Temperature (25-90 ˚C)
- Ionic Strength (up to 2 m $NaNO_3$)
- Al concentration (0-0.6 m $Al(NO_3)_3$)
- Saturation State

Flow-Through Reactor Set-Up



Pre-Modeling to determine saturation state is carried out using the Pitzer model in conjunction with the *Geochemist's Workbench*. Pitzer interaction parameters have been taken from the literature or estimated for the aqueous species likely to be present.

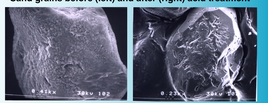
The **quartz sand** was carefully **prepared** by treatment with concentrated sulfuric acid, followed by soaking in 75 ˚C deionized water.

- The acid removes mineral impurities including oxyhydroxide grain coatings, and soaking in deionized water removes any amorphous material on the grain surfaces that was generated during the acid attack.
- This careful preparation of the quartz surfaces yields linear dissolution behavior from the beginning of the experiment.

Surface area was estimated using the NIH Image analysis program:

- Digital photos of reflected light microscopy images of the sand grains were taken.
- The horizontal area of each grain was measured.
- Particle radii were calculated assuming circular areas; particle volumes were calculated using these radii and assuming spherical shapes. The surface area was assumed to be twice that of a sphere.

Sand grains before (left) and after (right) acid treatment

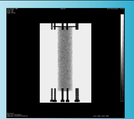


COLUMN EXPERIMENTS

Column experiments will test the applicability of the rate laws obtained from kinetic experiments. Columns will be packed with mixtures of pure quartz anorthite, and/or orthoclase. Both **Saturated and Unsaturated Flow** setups will be used.

X-Ray Microtomography(XMT) will be used to characterize the density distribution (solids vs. porosity) of the column sediments.

Unsaturated Flow Column with XMT Apparatus



XMT Creates 2D and 3D images of Packed Columns with 20-50 µm Resolution.

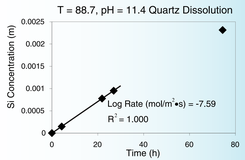
PRELIMINARY RESULTS

Two **batch kinetic experiments** have been performed at **T = 88.7 ˚C, pH ~11.4**, using quartz sand as the primary mineral. In one experiment, 0.01 m $Al(NO_3)_3$ was also added.

Hydrous Al phases were undersaturated by at least an order of magnitude in the experiment where Al was present.

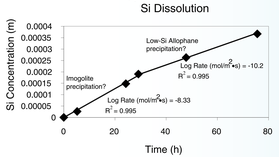
With no Al present, quartz dissolution proceeds at a log rate of -7.59 mol Si/m^2•s, which is in good agreement with published rates for similar conditions.

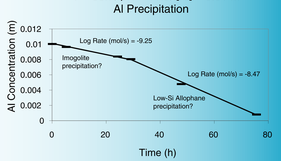
- Schwartzentruber *et al.* (1987) reported a log dissolution rate of -7.05 at 90 ˚C and Dove (1994) derived an equation that predicted a log rate of -7.95 under the same conditions.



With 0.01 m Al present, [Si] rises almost an order of magnitude more slowly than when Al is not present. [Al] simultaneously decreases. At 29 h Si dissolution rate decreases and Al precipitation rate increases.

- If we assume that Al adsorbed to the quartz surface does not retard the dissolution reaction under these conditions, we can calculate the Si/Al ratio of the precipitated phase.
  (Si dissolved without Al – Si dissolved with Al)/Al precipitated) equals ~ 0.5, from 0 to 29 h.
  This suggests that imogolite ($Al_2SiO_3(OH)_4$) initially precipitates. (The solids have yet to be analyzed.)
- From 29 to 76 h the ratio is lower (~ 0.2), indicating that a low-Si allophane ($[Al(OH)_3]_{0.8}[SiO_2]_{0.2}$) may have precipitated.





WORKING HYPOTHESES

Unpublished data by Wakoff and Nagy suggest that many of the leaking tank fluids should be saturated with respect to boehmite. Therefore, as pH and temperature drop, gibbsite or another oxyhydroxide of Al might precipitate.

Aluminosilicate species may form in solution as primary minerals dissolve.

Aluminosilicate minerals may precipitate.

- Allophane and Imogolite
- Smectite Clays
- Zeolites
- Layered Double Hydroxides

PRELIMINARY RESULTS

Why would the precipitation reaction change to a lower Si phase mid-experiment if the [Si] is still rising?

- Calculations show that by the time of the inflection point in the Si dissolution and Al precipitation curves, enough imogolite could have precipitated to cover all the surface area of the sand grains with a layer 172 nm thick.
- Perhaps the quartz grain surfaces became covered to such an extent that the dissolution reaction was retarded.
- Assuming the precipitation reactions are controlled by the Si release rate, a lower Si release rate might have led to the precipitation of a lower Si/Al phase.

SUMMARY

At ~ 90 ˚C Al from simulated tank solutions just undersaturated with respect to hydrous Al oxides reacts rapidly with quartz grains to precipitate solids with apparent compositions of imogolite and allophane.

It is not known yet whether these precipitated phases nucleate and grow on the quartz surface or as colloids in solution.

Work in progress includes characterizing the precipitated solids, investigating higher Al concentrations in solution to represent the range of tank fluid compositions, and determining the effects of pH and temperature.

REFERENCES CITED

Dove, P.M. (1994) The dissolution kinetics of quartz in sodium chloride solutions at 25˚ to 300˚C, *American Journal of Science* 294:665-712.

Schwartzentruber, J., Furst, W., and Renon, H. (1987) Dissolution of quartz into dilute alkaline solutions at 90 ˚C: A kinetic study, *Geochimica et Cosmochimica Acta* 51:1867-1874.