Project 86898

This project, renewal of a previous EMSP project of the same title, is in its first year of funding at the University of Illinois at Chicago. The purpose is to continue investigating rates and mechanisms of reactions between primary sediment minerals found in the Hanford subsurface and leaked waste tank solutions. The goals are to understand processes that result in (1) changes in porosity and permeability of the sediment and resultant changes in flow paths of the contaminant plumes, (2) formation of secondary precipitates that can take up contaminants in their structures, and (3) release of mineral components that can drive redox reactions affecting dissolved contaminant mobility. A post-doctoral scientist, Dr. Sherry Samson, has been hired and two masters of science students are beginning to conduct experimental research. One research project that is underway is focused on measurement of the dissolution rates of plagioclase feldspar in high pH, high nitrate, high Al-bearing solutions characteristic of the BX tank farms. The first set of experiments is being conduced at room temperature. Subsequent experiments will examine the role of temperature because tank solutions in many cases were near boiling when leakage is thought to have occurred and temperature gradients have been observed beneath the SX and BX tank farms. The dissolution experiments are being conducted in stirred-flow kinetic reactors using powdered labradorite feldspar from Pueblo Park, New Mexico. Solution compositions are analyzed for pH changes using solid-state electrodes calibrated in solutions of known hydroxyl concentrations and for the concentrations of elements derived from the dissolving feldspars. Simple tank simulants (NaOH-NaNO3-Al(NO3)3) and a few simulants more closely approximating the complex compositions of the tanks are being investigated. After obtaining rates as a function of pH and solution composition, conditions that are likely to be conducive to formation of secondary uranium-silicates will be selected for controlled precipitation experiments. The specific goal is to understand the chemical conditions needed to form the types of U-silicates observed by J. Zachara and co-workers at PNNL in the wellbore sediments from beneath the BX-tank. The optimum experimental dissolution conditions will be supplemented by reaction-path thermodynamic calculations of the stability of various U-silicates that form during the dissolution of the feldspar. These thermodynamic calculations have already been completed. A second project that is in progress is to examine the effect of temperature on biotite dissolution kinetics. Biotite dissolution is thought to provide the primary source of a reductant, Fe(II), to the leaked solutions that results in the immobilization of chromate anion (Cr(VI)O42-) as a chromium(III)-hydroxide phase, and may play a role in pertechnetate (Tc(VII)O4-) mobility. Stirred-flow reactor experiments are being conducted to measure biotite dissolution rates under oxidative conditions as a function of temperature from 25 to 70 degrees C.