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Phase Chemistry of Tank Sludge Residual Components

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Research Objective

The proposed research will provide a scientific basis for predicting the long-term fate of radionuclides remaining with the sludge in decommissioned waste tanks. Nuclear activities in the United States and elsewhere produce substantial volumes of highly radioactive semi-liquid slurries that traditionally are stored in large underground tanks while final waste disposal strategies are established. Although most of this waste will eventually be reprocessed a contaminated structure will remain which must either be removed or decommissioned in place. To accrue the substantial savings associated with in-place disposal will require a performance assessment which, in turn, means predicting the leach behavior of the radionuclides associated with the residual sludges. The phase chemistry of these materials is poorly known so a credible source term cannot presently be formulated. Further, handling of actual radioactive sludges is exceedingly cumbersome and expensive. This proposal is directed at: (1) developing synthetic nonradioactive sludges that match wastes produced by the various fuel processing steps, (2) monitoring the changes in phase chemistry of these sludges as they age, and (3) relating the mobility of trace amounts of radionuclides (or surrogates) in the sludge to the phase changes in the aging wastes.

Research Progress and Implications

This report summarizes work carried out during the first year of a three year project. A prerequisite to performing a meaningful study was to learn in considerable detail about the chemistry of waste streams produced by fuel reprocessing. At Hanford this is not a simple task since over the last five decades four different reprocessing schemes were used: the early $BiPO_4$ separation for just Pu, the U recovery activity to further treat wastes left by the $BiPO_4$ activities, the REDOX process and most recently, the PUREX processes. Savannah River fuel reprocessing started later and only PUREX wastes were generated. It is the working premise of this proposal that most of the phase chemistry in the wastes was defined when the acidic process fluids were first neutralized prior to storage. The only notable exception being that some silicates obviously formed later under highly caustic conditions. Waste stream chemistries for each process have been established and surrogate sludges prepared. Aging of these different recipes have begun at 25º, 60º, and 90º C and the phase chemistry of the different mixes is being monitored.

One rather surprising development was the rapid formation of a cancrinite-group zeolite phase. This class of zeolites is unusual in that the structure contains a discrete anion, typically nitrate or carbonate in mineralogic studies, but the material may also sequester pertechnetate. Smaller amounts of a phosphate-containing zeolite also formed. A second unanticipated result was that goethite did not form as the dominant iron-containing phase in spite of the long heating some samples have experienced. Rather, X-ray diffraction suggests early formation of a mixture of ferrihydrite and layered material similar to reevesite ($Ni_6Fe_2CO_3(OH)_{16}.4H_2O$), with no subsequent tendency to form better crystallized phases. This disparity is ascribed to the high ionic strength and complex chemistry of the solutions from which the phases precipitated. We also detected a number of phases that would be expected based on bulk sludge chemistry such as boehmite and apatite, as well as a number of soluble salts (sodium sulfate phosphate, fluoro-phosphate, and, of course, sodium nitrate) that should disappear when the waste is leached.

As a reality check, the proposal also calls for comparisons with actual tank wastes. First, a substantial body of unpublished TEM data on Hanford tank sludges is to be synthesized (J. Liu). This report is in preparation and should be in draft form this Summer. TEM studies of the synthetic sludges are also underway and verify that: (1) the iron containing phase in the synthetic material is quite similar to that in actual sludges, and (2) that the zeolites noted previously may also occur in real sludges. Early attempts to duplicate $BiPO_4$ process wastes failed due to an incomplete understanding of the different waste streams. In particular, the sucrose appropriate to a PUREX waste was included in the $BiPO_4$ waste recipe. TEM studies revealed that this reduced the Bi to the metallic state. These experiments are being started again with the hope of forming the iron bismuth silicate hydroxide sometimes noted in early sludges.

Several mid-course corrections were needed once preliminary research results were available. In particular, a planned detailed study of aluminum phosphates was not initiated since it did not form in the sludge synthesis experiments, and present tank sluicing plans should dissolve any that already exists. Instead a detailed study of the evolution of apatite was initiated. Secondly, a recently completed tank closure demonstration at Savannah River, and conceptual designs for tank closure at Hanford, both imply that a reducing portland cement grout will probably be in intimate contact with the sludge. This could significantly impact the behavior of readily reduced radionuclides like Tc and U. Hot tests have been performed on a simple reducing grout composed of a dilute slurry of portland cement powder, ferrous ammonium sulfate and manganous chloride. As expected, in the first day the concentration of both Tc and U dropped by more than a factor of 50. But, exposure to air for an additional day caused the Tc to rebound. The behavior of Tc correlates well with the re-oxidation to pertechnetate. Indeed, repeating the same procedure with difficult to reduce perrhenate showed no dip in concentration, thus confirming that there is nothing in the system hydrous iron oxide - portland cement that serves as a sink for XO_4^- type anions. The behavior of U is more complex. After an initial precipitous drop additional U was slowly removed from solution to the point where it was no longer detectable (about 0.1 ppm U). Geochemical modeling using the code REACT suggests that portland cement alone should reduce U solubilities below the level noted after the first precipitous drop. Thus, it is likely that there is a kinetic barrier to the formation of solubility limiting U-phases. Other REACT models dealing with radionuclide sorption on hydrous iron oxides in various environments are also underway.

Planned Activities

The primary focus of this proposal is on how the aging of sludge will impact radionuclide mobility. First, it was necessary to verify that representative materials could be produced outside of tanks. That has been completed. In the next six months bulk sludge syntheses experiments will be carried out in the presence of radioisotopes (or their surrogates). In the same time frame ageing studies will be initiated on simplified subsystems. The simplified systems to be addressed are: (1) hydrous iron oxides (and their hydrotalcite-like equivalents) in the presence of major amounts of Al and minor amounts of Ni and Cr (K.L. Nagy), (2) apatite - in particular the transition from hydroxyapatite to fluorapatite and its impact on coprecipitated radionuclides -or surrogates (P.v. Brady), and (3) the Fe-Bi-O,OH system (J.L. Krumhansl). The last year of the grant will focus on the desorption of radionuclides (or surrogates) from both the bulk sludges and the simplified subsystem materials.

Other Access To Information

Web page construction in progress: **http://www.sandia.gov/eesector/gs/gc/sludge.html**