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Title: Phase Chemistry of Tank Sludge Residual Components

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Problem: In the late 1940s, the Hanford nuclear facility in eastern Washington began reprocessing spent nuclear fuel. This treatment reclaimed usable U and Pu, but left behind large volumes of high level radioactive waste (HLW). A change in U.S. nuclear policy terminated reprocessing in the 1980s, but the HLW produced in the intervening decades remains stored in underground, steel-lined, concrete tanks. It is estimated that tank leaks have released about 1 million curies of radiation to the ambient Hanford soils. SX tank farm remediation is scheduled to begin in 2004, though the prohibitive cost of sampling and handling HLW has precluded direct detailed analysis of the chemical state of waste in the tanks. Technetium-99 (^{99}Tc) is a long-lived fission product of U present in significant concentrations in Hanford waste. ^{99}Tc is a particular concern in tank remediation because of its high solubility at the Eh-pH conditions present in both the tank waste and the ambient Hanford soils. An understanding of the solid phase chemistry of the HLW stored in the Hanford tanks and the fate of ^{99}Tc within these wastes is needed to initiate remediation. The Hanford HLW is compositionally complex and variable; therefore, we are examining experimentally the aging dynamics of simplified systems whose bulk chemistry approximates that of the tank sludges. Results will provide a baseline for the evolution of the dominant solid phases and their role in separating ^{99}Tc from the solution phase.

Research Objective:

About four or five distinct reprocessing technologies were used at various times in Hanford's history. After removing U and Pu (or later ^{137}Cs and ^{90}Sr), the strongly acidic HLW was "neutralized" to high pH (>13) and stored in steel-lined tanks. High pH was necessary to prevent tank corrosion. While each technology produced chemically distinct waste, all wastes were similar in that they were high pH, concentrated, aqueous solutions. Dominant dissolved metals were Fe and/or Al, usually followed by Ni, Mn, or Cr. In an effort to reduce waste volume, many of the wastes were placed in evaporators or allowed to "self-boil" from the heat produced by their own radioactive decay. Consequently, today's HLW has been aging at temperatures ranging from 20° to 160°C.

Previous studies of synthetic HLW sludge analogues have varied in their exact synthesis procedures and recipes, although each involved "neutralization" of acidic nitrate salt solutions by concentrated NaOH. Some recipes included small amounts of Si, SO_4^{2-} , CO_3^{2-} , and other minor chemical components in the Hanford sludges. The work being conducted at the University of Colorado differs from previous studies and from parallel current investigations at Sandia National Laboratories in the simplicity of the synthetic sludge we are investigating. We are emphasizing the dominant role of Fe and Al, and secondarily, the effects of Ni and Si on the aging kinetics of the solid phases in the sludge.

We are also investigating the uptake of rhenium (in the form of ReO_4^-) as an analogue for the soluble form of ^{99}Tc , in the solids vs. the solutions.

Research Progress and Implications: At the University of Colorado, we are in the second year of investigating the aging of simplified sludge compositions (Wakoff and Nagy, 1999). Iron and aluminum comprise the bulk of most HLW sludges at Hanford; therefore, low Al/Fe sludges are synthesized to approximate Bismuth Phosphate and PUREX wastes, whereas high Al/Fe sludges simulate REDOX waste. The behavior of rhenium as an analogue for technetium (^{99}Tc) in the aging sludges is also being monitored. Experimental samples are prepared as acidic Fe(III)-Al nitrate solutions and then “neutralized” at room temperature to pHs of 13.1-13.7. These samples are aged in a water bath at 90°C for three months. Solids and solutions are fully characterized at the ends of the experiments by X-ray diffraction, atomic force microscopy (for crystallite morphology), and specific surface area; and, by UV-Vis spectroscopy (Fe and Al), ICP-MS (Re), and pH measurement, respectively. Transformation of solids from amorphous precipitates to crystalline materials (hematite, goethite, bayerite, and gibbsite depending on initial solution composition) is complete after only 120 hours. Aging has been investigated in the presence and absence of 40 ppm Re (as perrhenate: ReO_4^-). While Re oxides are expected to be fully soluble at the pH/Eh conditions of the experimental solutions, the similarities (size, charge, stereochemistry) among the monovalent aqueous anions of Re, Al, and Fe suggest that perrhenate may interact strongly with precipitating metal-oxyhydroxides. Differences in transformation rates of the solids have been observed in both the low and high Al/Fe systems when Re is present. Also, the low Al system solids retain more Re with aging time than the high Al solids, although the concentrations are relatively small at ~ 10-100 ppb Re. Partition coefficients of Re between solid and solution are being determined as a function of aging time.

In a related investigation we have used atomic force microscopy coupled with solution sorption experiments and EXAFS spectroscopy to determine the role of Fe-oxyhydroxide mineral (goethite and lepidocrocite) surfaces in controlling sorption of a divalent cation, Cd^{2+} (Manceau et al., 2000). Such work is significant for understanding sorption of Cs^+ or Sr^{2+} onto Fe-oxyhydroxides in tank sludges and in groundwater/sediment systems such as at Hanford in the vadose zone or the Savannah River site.

Planned Activities: Experiments in progress include those in which Ni and Si have been added as solution components. Ni may aid the formation of a layered-double hydroxide phase, which could incorporate perrhenate along with NO_3^- and CO_3^{2-} in the anionic interlayer of this phase’s structure. Silicon is known to inhibit the transformation rates of Fe oxyhydroxides, which may also contribute to higher Re partition coefficients into the solids with aging, primarily due to the higher surface area and amorphous nature of the initial Fe-phase that forms, ferrihydrite.

References:

1. Wakoff, B. and Nagy, K. L., 1999, Aging behavior and rhenium partitioning in simplified Hanford water-tank sludges (abstract), American Chemical Society Annual Fall Meeting, 218: 59-NUCL, Symposium on First Accomplishments of U.S. DOE Environmental Management Science Program.
2. Manceau, A., Nagy, K. L., Spadini, L., and Ragnarsdottir, K. V., 2000, Mechanism of cadmium adsorption on lepidocrocite, *Journal of Colloid and Interface Science* (in review).