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Project Title: **Microstructural Properties of High Level Waste Concentrates and Gels with Raman And Infrared Spectroscopies**

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Microstructural Properties of High Level Waste Concentrates and Gels with Raman and Infrared Spectroscopies

Mid-Year Progress Report

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Goals of Project:

year 1: Initial efforts will focus on developing an understanding of the aluminate chemistry in concentrates. FTIR, Raman, and ^{27}Al NMR experiments will be undertaken with heats of gelation measured by DSC and related to aluminate composition and speciation. The necessary optics for a Raman mircroprobe to the JY U1000 Raman spectrometer will be purchased and interfaced. Measurements of viscosity, density, and surface tension for each gel prepared will be conducted and related to the vibrational measurements with these macroscopic characteristics. Measurements of water activity will be initiated and correlated with spectroscopic observables.

year 2: Raman spectroscopic measurements on bulk slurries/gels will be completed, and Raman microscopy experiments initiated. The Raman microscopy will require development and adaptation of an existing microscope to the JY U1000 spectrometer. Infrared spectral features will be correlated to water activity to evaluate the presence of liquid voids in gels and slurries, and evaluate the effect of organic salts on water activity. Heats of gelation will be measured for the concentrates and correlated to the micro-Raman measurements and liquid void fraction.

year 3: Final vibrational spectroscopic studies will be completed. Data will be collated and used to refine the microscopic understanding of the behavior of waste concentrates. This information will be utilized to formulate an understanding in order to make predictions of aluminate waste behavior as a function of temperature and water content. The third year's efforts will be refined to further the understanding of these materials. Specific objectives include: (1) a spectroscopically based determination of aluminate monomer/dimer equilibrium constant , (2) completion of aluminate phase diagram, (3) precise determination of the role of water activity and free vs. bound water in aluminate speciation, (4) identification and characterization of key aluminate dimeric/oligomeric species via their vibrational spectroscopic signatures, and (5) characterization of alumino-carbonate species in solution derived from incorporation of atmospheric CO_2 into aluminate slurries.

Technical Description of Work:

Nearly half of the high level radioactive waste stored at Hanford is composed of highly alkaline concentrates referred to as either salt cakes or Double-Shell Slurry (DSS), depending on their compositions and processing histories. The major components of these concentrates are water, sodium hydroxide, and sodium salts of nitrate, nitrite, aluminate, carbonate, phosphate, and sulfate. In addition, there are varying amounts of assorted organic salts such as EDTA, glycolate, and citrate. Although measurements of the bulk properties of these wastes (e.g. viscosity, gel point, density) have been reported, little is known about how the macroscopic characteristics are related to the microscopic physico-chemical properties. Viscosity, solids volume percent, and gas retention can dramatically change with relatively small changes in composition and temperature. Furthermore, these same properties are important in determining safe storage conditions as well as in planning retrieval, pretreatment, and disposal of the wastes. The focus of this effort will be on aluminate chemistry since large inventories of waste with aluminum are located at Hanford and Savannah River and little is known about the microstructure of these complex mixtures.

The goal of the proposed work is to relate molecular scale information to macroscopic behavior. The approach will utilize FTIR, Raman, and ^{27}Al NMR spectroscopies along with thermo-physical heats of gelation to relate the physico-chemical properties of these concentrates to macroscopic behavior. The primary experimental approach will include the following:

- Water vapor pressure measurements for concentrates to determine water activity as a function of composition and temperature.
- FTIR, Raman, and ^{27}Al-NMR spectroscopies to determine the form and solubility of aluminate in caustic slurries.
- Micro-Raman spectroscopy to identify and quantify phases of each species for a variety of concentrates.
- Measurements of the heat of gelation and its dependence on water activity, presence of organics, and other properties.
- Spectroscopic tools to assess the influence of organic salts on microstructural properties of slurries.

Accomplishments to Date:

The major focus of this research effort has been to explore the chemical mechanisms associated with gels and slurries and relate these to the observed general behavior. Experimentally, samples of known composition have been prepared that simulate the dominant components of Hanford caustic aluminates. The chemical components are known and the activity of water is controlled.

Raman spectroscopic studies have been utilized to probe the speciation of the aluminate (monomer vs. dimer) and the identification of the solid phases present. Raman bands for aluminate indicate formation of dimers and oligomers in solution. These Raman data provide new insight into the structure of caustic aluminate solutions.

Infrared spectroscopy has also been used to monitor water activity. Water in these systems can be free, coordinated to Na^+ and $Al(OH)_4^-$ monomer ions, or structurally associated with monosodium or

trisodium aluminate solids. The data indicate that the activity of water defines the stability of solid phases and provides information about precursors to precipitation.

^{27}Al-NMR studies have been pursued to study the coordination of Al in these solutions. The NMR studies reveal a tetrahedral coordination of aluminum. The ^{27}Al-NMR experiments do not effectively show the formation of dimeric or oligomeric coordinated aluminum environments. Vibrational spectroscopic methods do, however, as noted above, discriminate between aluminate monomers and dimers/oligomers. Moreover, Raman depolarization ratio studies reveal subtle differences in dimer and oligomer properties in response to changing mixture compositions.

Connecting these data to actual tank waste is best accomplished using a phase diagram. Evaporation lines can be used to predict which solids will precipitate. Depending upon the location within the phase diagram, dilution of supernatant will result in precipitation. The current data are being mapped into a phase diagram and experiments are being pursued to complete key regions of the diagram that heretofore have not been explored.

Projections:

We are on schedule to complete the scope of work noted above for the third year with the current funding level. Data will be collected to complete publication of the results in a refereed journal (project PI and the university collaborators already have created a rough draft of a paper to be submitted to 'Environmental Science and Technology') and final report.

Additional Information:

Considering the long-term significance of this research, the future direction of this research effort will be explored within the last half-year of this work and a proposal formulated.