

Project Title: Chemistry of Actinides in Molten Glasses and Its Correlation to Structural Performance of Solid Glasses: Filling the Knowledge Gap (Project 81926)

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Progress Report:

RESEARCH OBJECTIVE

This proposal focuses on the following basic objectives to generate critical information for the following research *Needs*: (a) to conduct spectroscopic speciation of uranium compounds in glass-forming melts as a function of the acid-base composition of the glasses and melt temperatures, and to use these data to develop a general thermodynamic model for the dissolution of actinide species in oxidic glass matrices, (b) to build a scientific basis for a new methodology to measure the basicity of glasses via optical spectra of *in-situ* immobilized actinides and to use this optical basicity as a primary actinide structure indicator for solid glass matrices, (c) to define the local environment of actinides in solid glasses via fluorescence lifetime distribution methods, (d) to correlate the above spectral “fingerprints” of actinides in solid and molten glasses with glass stability and the leaching rates of individual actinide species from a glass matrix.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes the work accomplished during the first half of a three-year project. Since our previous report, we have completed the installation of the equipment necessary to meet the objectives of the proposal, specifically the spectroscopic investigation of actinides in glasses of various compositions through a wide range of temperatures. The solubility, fluorescence spectroscopy, and Raman spectroscopy of uranyl in synthetic frits obtained from the Savannah River Site were studied. Our initial experiments involved the use of spectroscopic methods to obtain information concerning homogeneity of the local environment experienced by uranyl ions in different types of glass. Using a pulsed nitrogen laser to excite the uranyl-glass samples and a photodiode and multichannel scaler to detect and store the fluorescence signal, lifetime distributions were obtained for uranyl dissolved in three different solid glasses: a silica sol-gel glass, Frit 202 glass (a simulant glass for vitrification of radionuclides), and a commercial pyrex glass. In addition to the lifetime distributions, we also measured the steady-state fluorescence curves for the three samples. The uranyl ion contained in the commercial

pyrex glass showed a single lifetime at approximately 370 μs indicative of excellent homogeneity throughout the glass, while the other glasses showed multiple peaks at various lifetimes. In addition, a red shift in the emission spectrum of the uranyl ion in the frit and commercial pyrex glass indicates stronger bonding of the ion in these glasses as compared to the sol-gel glass. These results are consistent since the sol-gel glass is a low temperature glass that was expected to exhibit weaker bonding of the uranyl to the glass matrix as well as display multiple local environments. Furthermore, Frit 202 is designed to immobilize uranium in a waste stream combined with a number of other contaminants. In the absence of these secondary contaminants, the frit glass is known to phase separate. The multiple lifetime distribution of the uranyl ion in the Frit 202 sample can be attributed to this phase separation since our experiments were performed on the frit without the secondary contaminants.

Frit 165, composed of SiO_2 , Na_2O , Li_2O , B_2O_3 , MgO , and ZrO_2 , shows very good solubility to UO_3 when heated at 1150° C for 6 hours. Glasses that appeared quite homogeneous with coloring that ranged from light yellow to dark green when the UO_3 composition was increased from 0.2 to 20.0 wt% were formed. Despite the uniform appearance of the glasses, structural heterogeneities were observed using fluorescence spectroscopy. The fluorescence lifetime of uranyl in the Frit 165 decayed rapidly with increasing UO_3 concentration due to self-quenching and the formation of structural heterogeneities. The steady-state fluorescence spectra of these uranium-doped glasses also changed notably with increasing UO_3 composition. For samples doped with a lower concentration of uranium (<10 wt%), fluorescence spectra with wider distributions were observed in addition to the red shift of peak position. Using a continuous model analysis, the fluorescence lifetime distributions were computed for these samples. The results indicate that there are two bonding sites for uranium in samples doped with less than 1 wt% UO_3 . The bonding sites in which long lifetime fluorescence is emitted gradually disappear as the doping concentration is increased. When the doping amount is higher than 10 wt%, dramatic structural changes occur and the uranium experiences a more heterogeneous environment. These results are in good agreement with the observations of fluorescence spectra and the lifetime decay profiles. In addition, this immobilization limit is also consistent with the previous report. Thus, we have successfully demonstrated the effectiveness of fluorescence techniques in determining structural information and the homogeneity of the local environments experienced by uranyl in a solid glass matrix with a view towards ultimately establishing the stability of the uranyl in the matrix.

We also observed that the bonding state of uranium in molten glasses is highly dependent on the compositions of the frits. Optical basicity can be used to correlate $\log[\text{U(V)}/\text{U(VI)}]$ to the compositions of frits provided these samples are prepared under the same conditions. We are currently preparing a series of samples and prove this theory. The research will lead to a theoretical basis for predicting the structure and equilibrium of uranyl in different frits.

In addition to the fluorescence techniques, we have also installed a Renishaw Raman system capable of measuring Raman emission from 10 cm^{-1} to 4000 cm^{-1} with approximately 1 cm^{-1} resolution. The system is currently configured for three excitation lines: 488.0nm, 514.5nm, and 632.8 nm. A high-temperature stage (Linkam) with an upper limit of 1600°C coupled with a long working distance microscope objective enables us to acquire Raman spectra across a wide temperature range. We have successfully completed some preliminary Raman experiments on the dissolution of uranyl (UO_2^{2+}) in a

glass matrix. Raman spectra of uranium mixed with borosilicate glass (made by grinding a microscope slide into a powder) were obtained at incremental temperature values up to approximately 1100°C. The solubility of the uranium in this particular type of molten glass was quite poor producing large heterogeneities in the uranium concentration throughout the glass melt. However, we have demonstrated the application of the high-temperature Raman technique to the analysis of uranyl in molten glass.

PUBLICATION

S. M. Mahurin, S. Dai, and R. F. Schumacher, "Fluorescent lifetime investigation of phase separation in uranyl-doped glasses," *J. Non-Crys. Solid.*, submitted.