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

Publication Date: **June 25, 2004**

Principal Investigator: **Sheng Dai**
Chemical Sciences Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831
Tel: (423) 576-7307
E-mail: i9d@ornl.gov

***Co-Principal Investigators*: Lynn Boatner, Ray F. Schumacher**

***Postdocs*: Zuojiang Li, Shannon M. Mahurin,**

***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 second half of a three-year project.

Significant progress has been made in this current EMSP project, including investigation of the redox chemistry of actinides in glass matrixes, fluorescence and UV-VIS properties of actinides in immobilized glasses, correlation between the bonding states of uranium and the basicity of the glass matrix, in-situ probing of the actinide concentration using a non-destructive, deconvoluted fluorescence technique, and observation of phase separation phenomena in glass matrixes. Methods were developed to conveniently measure the concentration of uranium oxide immobilized in glass melts. Our primary experiments focused on the spectroscopic characterization of uranium, the bonding states of uranium and their relationship to the chemical properties of glass compositions and the processing conditions. Only those significant results are briefly summarized here.

1). The fluorescence spectroscopic study of uranium in borosilicate glasses

1.1. Structural heterogeneity probed by fluorescence spectroscopy

Uranium glass exhibits strong fluorescence with good quantum yield and long emission lifetimes that are sensitive to both the local environment and mobility of the uranyl ion. Fluorescence techniques are well suited for examining the site distribution and structural stability of actinides in glass matrices due to the sensitivity of the fluorescent species to local environments. Our results showed that the deconvoluted fluorescence profiles are highly depended on the glass matrix and the processing conditions. The fluorescence distribution can be used as a facile method to monitor the structural homogeneity, and therefore, as an indicator for the immobilization efficiency.

1.2. Uranium as an in-situ probe for concentration determination in borosilicate glass

The uranium fluorescence, which was strong and had a long decay profile at low uranium concentrations, showed a significant decrease in intensity and a reduced decay profile as the uranium concentration increased primarily due to self-quenching and the increased interactions among uranium species. In particular, increasing the concentration of the uranium in the glass matrix induces uranium aggregation and clustering that results in energy transfer between neighboring atoms. This energy transfer leads to self-quenching which reduces the overall fluorescence intensity and a shorter fluorescence lifetime that is consistent with the measured lifetime distributions.

Our experiment results showed that the deconvoluted fluorescence distributions can not only be used to monitor the homogeneity of the immobilized glass, it can also be used as an in-situ probe for the uranium concentration in homogeneous glass system. The linear relationship between the lifetime distribution and uranium concentration can provide rapid, non-destructive determination of uranium quantities in the immobilized glass, which is a discovery that has great application potential in remote sensoring of uranium in immobilized glass during the processing period.

1.3. The fluorescence fingerprints of uranium in borosilicate glass

The fluorescence fingerprint spectra of uranium in borosilicate glass have also been investigated in this research work. It was found that the fluorescence spectra are not only determined by the structural heterogeneity in different glass matrixes, they are also highly depended on the concentration of uranium in the glass matrix. The increase of uranium concentration in a specific glass system causes self-quenching of uranium fluorescence and therefore the loss of fluorescent emissions of high energy. All these spectroscopic studies are consistent with each other.

2). The Raman spectra of uranium in molten borosilicate glass

The measurement of the Raman spectra of uranyl species in glasses at high temperature is difficult because of the strong black body radiation, which masks the weak Raman bands. To overcome this problem, we developed a confocal Raman system to measure the Raman spectra of uranyl species in molten conditions. The distinctive feature of uranyl ions in borosilicate glass is the appearance of the peak at ~770 cm^{-1}, which is related to the O=U=O symmetric stretching vibration. This peak is located at 870 cm^{-1} in aqueous solutions, 710 cm^{-1} in sol-gel glass and ~800 cm^{-1} on oxide supports. The lower frequency of the symmetric stretch indicates that there is a very strong equatorial interaction of uranyl ions with the borosilicate matrix. The Raman spectra also show some fingerprint bands associated with matrix lattice vibrations at lower wavenumbers.

3). The redox chemistry of uranium in borosilicate glasses

The redox states and bonding conditions of uranium in borosilicate glasses significantly affect

the stability and the leaching rate of radionuclides from the immobilized glass. We developed a reflective diffusive UV-VIS-NIR spectroscopy technique and applied it to the exploration of redox chemistry of uranium in borosilicate glass.

3.1. Effect of oxygen fugacity on the redox state of uranium in the immobilization process

In order to investigate the influence of oxygen fugacity on redox chemistry of uranium and the spectroscopic properties of uranium in glasses, air, high-purity nitrogen, and nitrogen-plus-carbon were used to control the oxygen concentration above the uranium sample during the immobilization process. It was found that a highly reducing atmosphere was obtained by simply placing carbon near the glass samples during the vitrification process. The samples prepared at these conditions exhibited characteristics of U(VI), U(V) and U(IV). Controlling the oxygen fugacity provided a simple and efficient method to control the redox states of uranium in molten glasses.

3.2. Effect of the basicity of glass matrix on the redox states of uranium

Additionally, the basicity of glass matrix remarkably affects the balance of redox states for uranium in borosilicate glass. The spectroscopic properties and characteristics of uranium were measured for a series of samples with gradually increasing basicity. It was found that higher redox state is more favorable in glass matrix with higher basicity. However, the coordination chemistry of uranium may change in a highly basic glass system. Therefore, the overall control of the uranium in borosilicate glass involves both the processing atmosphere and the total basicity of the glass media.

4). Phase separation in borosilicate glass and its effect on the immobilization stability

The phase separation phenomena for borosilicate system were also investigated in our study, primary using the Transmission Electron Microscopy. When borosilicate glass phase separates into two interconnected, silica-rich and boron-rich phases, the chemical durability of uranium is also significantly altered. The boron-rich phase is chemically leachable which leads to remarkable microscopic stresses that accelerate the leaching rate. Our results proved that phase separation also occurs in certain borosilicate frits used for radionuclides immobilization. Nevertheless, little attention has been given to the phase segregation phenomenon and the leaching properties of uranium immobilized in glass. Our preliminary results show that phase immiscibility as well as the nanoscale crystallization should be taken into consideration in the high level waste processing and further investigations are underway in our lab.