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Title: **Radiation Effects in Nuclear Waste Materials**

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Specific DOE Problems Being Addressed

Radiation effects from the decay of radionuclides may impact the long-term performance and stability of nuclear waste forms and stabilized nuclear materials. Thus, the research performed under this project has significant implications for the High-Level Waste and Nuclear Materials focus areas within the current DOE/EM mission. In the High-Level Waste (HLW) focus area, the results of this research will lead to improvements in the understanding of radiation-induced degradation mechanisms and effects on dissolution kinetics, as well as predictable models for waste form performance. In the Nuclear Materials focus area, the results of this research will lead to improvements in the understanding of radiation effects on the chemical and structural properties of materials for the stabilization and long-term storage of plutonium, highly-enriched uranium, and other actinides. Consequently, this research will result in improved glass and ceramic waste forms for the immobilization of high-level tank waste, plutonium residues and scraps, surplus weapons plutonium, and other actinides.

Research Objective

This research project is investigating radiation effects in glasses and ceramics at the atomic, microscopic, and macroscopic levels. By using experimental and computer simulation approaches, this research endeavors to develop the underpinning science and models necessary to assess radiation effects on the performance of glasses and ceramics designed for the immobilization of high-level tank waste and nuclear materials. The ultimate objective of this project is to provide the scientific understanding and rationale for developing improved glass and ceramic waste forms and to develop scientifically based predictive models for the performance of nuclear waste forms and stabilized nuclear materials.

Research Progress and Implications

This report summarizes work after 3 years of a 3-year project. Work to date has resulted in 35 publications and papers in preparation. Highlights of the research are presented below.

Radiation effects in three compositionally identical Pu-doped (1 wt %) simulated waste glasses, with varying (239/238) isotopic ratios, have been studied. The radiation dose in these glasses is equivalent to 20, ten thousand, and one million years, respectively. Changes in density, stored energy, local structure, and valence states have been determined. The results indicate that the accumulation of defects giving rise to the stored energy precede the rearrangement of the glass network that manifests as volume changes. The stored energy could enhance dissolution kinetics. Electron spin resonance measurements indicate no evidence for radiolytic decomposition into oxidizers or reduced elements.

Detailed experimental and computer simulation studies of radiation effects and annealing in Pu-containing zircon (10 wt % Pu-238) have been performed. Alpha decay induces a crystalline to amorphous transformation, in which both long-range order and edge-sharing relationships between SiO_4 and ZrO_8 polyhedra are lost, leading to 18.4% swelling. Computer simulation of the amorphization process is in excellent agreement with experimental results. A tentative model of amorphization over geologic time periods has been developed. Annealing studies indicate that decomposition into constituent oxides should not occur under repository conditions.

There is a critical lack of understanding regarding ionization effects from beta decay on nuclear waste glasses. Borosilicate glasses are known to be sensitive to ionization damage above a threshold dose. To study ionization effects under more realistic conditions, seven different glasses have been irradiated at relevant temperatures (50, 100, 150, and 200°C) over 2.5 years with gamma radiation to doses of 25, 75, and 150 MGy. The highest dose is only equivalent to about 25 years of storage for DOE HLW glasses, which indicates the difficulty in performing realistic testing. To date, changes in volume are negligible. Minor changes in the Raman, polarized-Raman, and FTIR spectra are observed. Significant changes, which are believed to be due to electronic defects, are observed in UV-Vis-NIR optical absorption spectra of the sodium-borosilicate glass compositions. Some changes in Fe oxidation states have been observed.

Single crystals of synthetic $ZrSiO_4$ and polycrystals of $A_2Ti_2O_7$ pyrochlores (A=Y, Sm, Gd, Lu) have been irradiated with different ions over a wide range of temperatures to develop kinetic models of radiation effects. The results of these studies show that amorphization in these materials is a complex process controlled by a variety of parameters that impact long-term performance models. For both systems, the data suggest that irradiation with light ions (helium through xenon) may not provide accurate simulation of the dose dependence of amorphization due to α-decay events. In the case of the pyrochlores, there is no significant effect of the A-site cation on the kinetics of amorphization, and there is excellent correlation with data from studies of actinide-doped pyrochlores. However, a significant effect of A-site cation on the dissolution kinetics of as-prepared samples was observed, and the results suggest incongruent leach of the Gd, Lu, and Y relative to Ti. Irradiation-induced amorphization increased the dissolution kinetics of $Gd_2Ti_2O_7$ and $Lu_2Ti_2O_7$ by at least an order of magnitude, which is consistent with the observed increase in Cm and Pu release kinetics in an actinide-doped pyrochlore.

Ionization from beta decay during interim and early storage (<500 years) can significantly impact the structure and properties of nuclear waste glasses. Much of this impact comes from the longer-lived electronic excitations, known as self-trapped excitons. The decay of self-trapped excitons can lead to permanent defects, and the presence of self-trapped excitons can lead to significant changes in the migration energetics for defects or the diffusion of incorporated radionuclides. A computational framework to study these processes did not exist prior to this project but has been developed using DFT, *ab initio*, and semi-empirical methods.

Molecular dynamics (MD) simulations have been used to determine threshold displacement energies in MgO (a test case) and $ZrSiO_4$. The MD simulations have revealed the dynamic nature of atomic displacement processes in these oxides. The migration energies for native vacancies in $ZrSiO_4$ have been determined by energy minimization methods. Results show that both zirconium and oxygen vacancies readily migrate, which may assist damage recovery processes. Energy minimization methods have also been used to determine the energetics of Pu^{3+} and Pu^{4+} incorporation in zircon to identify the most stable defect configuration for each oxidation state and to assist in the interpretation of XAS data. These computational capabilities are available to other EMSP, EM, and DOE projects to determine the energetics of radionuclide incorporation and self-diffusion in different nuclear waste forms and phases.

Planned Activities

The above research efforts have been phased out. The only ongoing activity is the preparation of publications related to work accomplished over the initial 3-year term of this project. A renewal proposal has been submitted to continue this effort, an important aspect of which is dissolution measurements of samples that have been characterized during the initial 3-year term.