Radiation Effects in Nuclear Waste Materials
(Project Number: 73750)

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Research Objective

The objective of this project is to develop a fundamental understanding of radiation effects in glasses and ceramics, as well as the influence of solid-state radiation effects on aqueous dissolution kinetics, which may impact the performance of nuclear waste forms and stabilized nuclear materials. This work provides the underpinning science to develop improved glass and ceramic waste forms for the immobilization and disposition of high-level tank waste, excess plutonium, plutonium residues and scrap, other actinides, and other nuclear waste streams. Furthermore, this work is developing predictive models for the performance of nuclear waste forms and stabilized nuclear materials. Thus, the research performed under this project has significant implications for the immobilization of High-Level Waste (HLW) and Nuclear Materials, two mission areas within the Office of Environmental Management (EM). With regard to the HLW mission, this research will lead to improved understanding of radiation-induced degradation mechanisms and their effects on dissolution kinetics, as well as development of predictive models for waste form performance. In the Nuclear Materials mission, 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. The research uses plutonium incorporation, ion-beam irradiation, and electron-beam irradiation to simulate the effects of alpha decay and beta decay on relevant glasses and ceramics. The research under this project has the potential to result in improved glass and ceramic materials for the stabilization and immobilization of high-level tank waste, plutonium residues and scraps, surplus weapons plutonium, highly-enriched uranium, other actinides, and other radioactive materials.

Research Progress and Implications

This report summarizes work after 3 years of a 3-year project. This project has been terminated, and no funding was received for work in Fiscal Year 2004. Only progress achieved since the last annual report is reported here.

Alpha-Decay Effects in Ceramics

Preliminary nuclear magnetic resonance (NMR) studies were carried out on Pu-containing zircon samples by Dr. Ian Farnan (Cambridge University, UK) under his UK funding support. As part of this work, a triple containment magic-angle spinning rotor insert system has been developed by Dr. Farnan, and a sample handling procedure has been formulated for safely analyzing highly radioactive solids by high resolution solid state NMR. The protocol and containment system have been demonstrated for magic angle spinning (MAS) experiments on ceramic samples containing 5-10 wt% ^{239}Pu and ^{238}Pu at rotation speeds of 3500 Hz. The technique has been used to demonstrate that MASNMR experiments can be successfully applied to highly-active actinide-containing solids. More specifically, in the case of zircon, the work demonstrated MASNMR can be used to measure the amorphous atomic number fractions produced during accelerated internal radioactive decay. This allows detailed characterization of local atomic structure to be determined in potential ceramic (and glass) waste forms in which short-lived alpha-emitters are incorporated to study the long-term effects of radiation damage from alpha decay. This is the

first example of MASNMR spectroscopy on samples containing short-lived actinide isotopes. These preliminary results have been prepared and submitted for publication by Dr. Farnan under his UK support. While further work is needed to confirm preliminary observations and to investigate what appears to be significant new finding, no further work is planned due to project termination and lack of other funding sources.

New capabilities for Raman spectroscopy of actinide-containing compounds have become operational. Original plans were to perform Raman spectroscopy analysis of the Pu-containing zircons. Due to lack of programmatic funding, further work was terminated. Alternative funding for this critical work is being sought elsewhere.

Alpha-Decay Effects in Glasses

The leaching studies on Pu-containing glasses have been completed. In this work, single-pass flow-through tests were conducted to study the effects of self-radiation damage from alpha decay on dissolution kinetics of three radiation-aged Pu-bearing (1 mass% PuO₂) borosilicate glasses over a pH range of 9 to 12 at about 88°C. The chemical compositions of the glasses were identical except the ²³⁹Pu/²³⁸Pu isotopic ratio, which was adjusted at the time of preparation to yield dose rates that varied by a factor of 200. The accumulated doses in these glasses at the time of testing were 1.3×10^{16} , 2.9×10^{17} , and 2.6×10^{18} alpha-decays/g. Release of Al, B, Cs, Na, Si and U to solution increased with increasing pH, whereas, Ca, Pu, and Sr were invariant over the pH interval. Average dissolution rates, based on B release, were identical within experimental uncertainty for all three glass compositions and increased with pH. Release rates of Pu were 10²- to 10⁵-fold slower compared to all other elements, and were not affected by isotopic composition, self-radiation damage sustained by the glass, or pH. These data demonstrate that self-radiation damage does not significantly affect glass dissolution rates, despite exposure to internal radiation doses for >20 years. The results of this work have been prepared and submitted for publication.

NMRMAS and Raman spectroscopy of these Pu-containing glasses had been planned, but project termination will not allow such work to go forward. Such studies could provide valuable information on local environment, defects and bonding.

Simulation of Radiation Effects Using Ion Beams

There has been no new work using ion beams.

Simulation of Radiation Effects using Electron Beams

This work has been carried out at the University of Michigan and is focused on understanding radiation-damage processes in complex glasses and developing the necessary protocols to perform accelerated radiation effects testing. Much of this work is enabled by the advanced analytical electron microscope (AEM) capabilities and expertise available at the University of Michigan. Under this project, electron irradiation damage has been studied in three sodium borosilicate glasses, three iron phosphate glasses, and an aluminophosphate glass using a modern analytical electron microscope has been studied. The results indicate that all these glasses

decompose under irradiation with 200 kV electrons). Migration of alkali elements from the center of the irradiated regions to the peripheries under irradiation occurred in the alkali-element containing glasses and results in the formation of alkali-depleted and alkali-enriched phases. The formation of bubbles was only observed in the alkali-element containing iron phosphate and aluminophosphate glasses, not in the sodium borosilicate glasses when irradiated over a broad of dose rates. In the borosilicate glasses, phase separation into distinctly separate boron-rich and silicon-rich phases occurred under electron irradiation at doses higher than 4.0×10^{11} Gy. The separated phases remain as amorphous states even at a much high doses (2.1×10^{12} Gy). These results indicate that most silicon atoms remain tetrahedrally coordinated in the glass under irradiation, except some possible reduction to amorphous silicon. The particulate boron-rich phase that formed at high doses was identified as amorphous boron that may contain some oxygen. In the Fe-containing borosilicate glasses, the Fe is associated with the boron-rich phases after phase separation. Phase separation into iron-rich and aluminum rich phases was also observed in the iron phosphate and aluminophosphate glasses.

Planned Activities

This project has been terminated and no additional work is planned. Some critical experiments have not been completed. Some results have not yet been prepared for publication and, consequently, may never be published.

Information Access

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