Environmental Management Science Program

Project ID Number 60392

Radiolytic and Thermal Process Relevant to Dry Storage of Spent Nuclear Fuels

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June 1, 1998

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Research Objective

This project involves basic research in chemistry and physics aimed at providing information pertinent to the safe long-term dry storage of spent nuclear fuel (SNF), thousands of tons of which remain in water storage across the DOE complex. The Hanford Site K-Basins alone hold 2300 tons of spent fuel, much of it severely corroded, and similar situations exist at Savannah River and Idaho National Engineering and Environmental Laboratory. The DOE plans to remove this fuel and seal it in overpack canisters for “dry” interim storage for up to 75 years while awaiting permanent disposition. Chemically-bound water will remain in this fuel even following proposed drying steps, leading to possible long-term corrosion of the containers and/or fuel rods themselves, generation of H_2 and O_2 gas via radiolysis (which could lead to deflagration or detonation), and reactions of pyrophoric uranium hydrides. No thoroughly tested model is currently available to predict fuel behavior during pre-processing, processing, or storage. In a collaboration between Rutgers University, Pacific Northwest National Laboratory, and Brookhaven National Laboratory, we are studying the radiolytic reaction, drying processes, and corrosion behavior of actual SNF materials, and of pure and mixed-phase samples. We propose to determine what is omitted from current models: radiolysis of water adsorbed on or in hydrates or hydroxides, thermodynamics of interfacial phases, and kinetics of drying. A model will be developed and tested against actual fuel rod behavior to insure validity and applicability to the problems associated with developing dry storage strategies for DOE-owned SNF.

Research Progress and Implications

This report summarizes work after eight months of a three-year project.

Relevant oxide surfaces of UO_2 , ZrO_2 , and Al_2O_3 have been prepared and characterized by x-ray photoelectron spectroscopy. Measurements are being made of the desorption of water from these surfaces, using accurate thermal desorption methods to elucidate the effects of temperature on the surface-water interaction. Interfacial nuclear decay and radiolysis processes that either affect the structural integrity of relevant materials or evolve flammable gases have been studied on Al_2O_3 and ZrO_2 surfaces using intense radioactive sources with radiochemical tracer techniques. Processes for generating thin (0.1-mm) uranium oxide films have been developed using three different processes: metal sputtering; electrodeless plating; and thermal treatment of uranyl nitrate deposited from solution on tungsten. Such films have been characterized by electron microscopy, revealing in partially-nitrated specimens “shrink cracks” that may have profound implications for their chemical reactivity. A promising computational model of the effects of particle size and sample thickness has been developed and substantiated with experiments on MgO and TiO_2 powders. This will be applied to the analogous problems for SNF materials.

The breakdown of zirconia films (important to the integrity of Zr-alloy fuel-rod cladding) under extreme radiation conditions has been systematically studied using low-energy electron and photon bombardment of well-characterized ZrO_2 surfaces. These studies have clarified the mechanism of oxygen removal from such surfaces, which involves the ionization of shallow metal cation core

levels, followed by interatomic Auger decay resulting in the formation and rapid ejection of O^+ ions. Simpler one- and two-electron processes can lead to the desorption of neutral and molecular oxygen. These complex processes are being studied using sensitive laser detection schemes to determine the exact quantum-state distributions of the species produced. Controlled radiolysis of water-covered ZrO_2 surfaces has begun, to clarify the interaction of adsorbates with secondary electrons, electron-hole pairs, and excitons near the surface. Preliminary experiments do not suggest enhancement of hydrogen production from adsorbed water, but this needs confirmation. A related study of the radiolysis of water adsorbed on a series of powdered oxides using ^{60}Co gamma-irradiation reveals that the hydrogen yield from radiolysis can be significantly greater, approximately equal to, or significantly less than the yield from pure gas-phase water, depending on the specific oxide involved. Particularly interesting is that strong enhancement of the radiolysis (up to X 200) is seen only for a narrow range of oxide bandgaps. A mechanism has been proposed that accounts for these effects, based on the migration of excitons to the surface and their resonant coupling with the water adsorption complex.

Planned Activities

The thermal and electron-stimulated desorption kinetics of water from well-characterized UO_2 surfaces will be measured using a radiotracer techniques with tritiated water. The surface radiolysis studies with radioactive sources will be extended to uranium oxide systems. High-intensity 10-MeV femtosecond electron pulses will be used to simulate the effects of beta-ray and resulting cascades of lower-energy electrons. A final agreement on radiological protocols for the EMSL laboratory will allow UO_2 samples to be studied with the full array of instrumentation available there. The powder drying model will be tested against other oxides, including those of uranium. The radiation chemistry of zirconia will soon be extended to alumina and oxides of uranium. The influence of radiolysis on adsorbate materials will be clarified and these experiments will be extended to uranium oxides.