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Project Title: **Radiolytic and Thermal Process Relevant to Dry Storage of Spent Nuclear Fuels**

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Radiolytic and Thermal Processes Relevant to Dry Storage of Spent Nuclear Fuel

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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. 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 after the 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 now available to predict fuel behavior during preprocessing, processing, or storage. In a collaborative effort among 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 ensure validity and applicability to the problems associated with developing dry storage strategies for DOE-owned SNF.

Research Progress

Several oxide surfaces, which are present on SNF (i.e., UO_2, ZrO_2, and Al_2O_3), have been prepared and studied using a variety of surface science methods. Specific emphasis is on understanding the interaction of water with these surfaces as it relates to the kinetics of drying. Studies on the electronic structure and mechanisms of non-thermal dissociation/damage of the materials and interfacial water have also been carried out in an effort to assess the non-thermal mechanisms and cross-sections for producing molecular hydrogen and oxygen from interfacial water. Though these tasks are correlated, they are described separately for the sake of clarity.

Photon- and Electron-Stimulated Desorption of O^+ From Zirconia

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. This results in the formation and rapid ejection of O^+ ions (Simpson et al. 1999). Simpler one- and two-electron processes can lead to the desorption of neutral and molecular oxygen.

Controlled radiolysis of water-covered ZrO_2 surfaces has begun to clarify the interaction of adsorbates with secondary electrons, electronhole pairs, and excitons near the surface. 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. This depends on the specific oxide involved and can be correlated with the band-gap of the oxide particles as well as the adsorbate-substrate interaction. A mechanism has been proposed that accounts for these differences, based on the migration of excitons to the surface and their resonant coupling with the water adsorption complex (Petrik et al. 1999a).

Laser-Stimulated Luminescence of Yttria-Stabilized Cubic Zirconia Crystals

The kinetics of laser-stimulated luminescence (LSL) of yttria-stabilized cubic zirconia (YSZ) single crystals was investigated (Petrik et al. 1999b). These experiments probed the valence band structure and defect states of zirconia; specifically, excitation of $ZrO_2 \cdot 9.5\%Y_2O_3$ (100) and (110) using nsec pulses of 213 nm (5.82 eV), 266 nm (4.66 eV), and 355 nm (3.49 eV) photons produce LSL bands with Gaussian profiles and peak maxima at 460 nm (2.69 eV), 550 nm (2.25 eV) and 600 nm (2.07 eV), respectively. LSL involves a single-photon process for energy densities below ~1.0 MW/cm^2. Decay times vary from 0.1 to 100 µs depending on the excitation energy and temperature. Decay kinetics are hyperbolic indicating that all LSL bands result from recombination. The LSL quenches with increasing temperature and activation energies obtained using the Mott approximation are 0.10 ± 0.01, 0.20 ± 0.02, and 0.45 ± 0.04 eV for the 2.69, 2.25, and 2.07 eV LSL bands, respectively.

The various activation energies, decay kinetics, and excitation/emission energies correspond to the presence of several emission centers which can be associated with anion vacancies. We tentatively assign these centers to intrinsic F-centers and extrinsic F-type centers. The latter are associated with one and two Y^{3+} ions in the nearest neighborhood positions. Since the normalized temperature dependencies of the decay coefficients are similar for all the LSL bands, we suggest that recombination primarily involves electrons, trapped at intrinsic and extrinsic defect sites, and mobilized holes.

Nuclear-Stimulated Desorption at the Surfaces of Model SNF Materials

Radiolytic degradation of the integrity of spent nuclear fuel (SNF) is an important concern for these highly radioactive materials, which have been in storage for a number of years awaiting reprocessing and interim isolation. Nuclear stimulated desorption (NSD) methods have been applied to models of SNF materials to assess the importance of various degradation mechanisms. These include the microscopic damage from the initially energetic nuclear recoil event, as well as secondary damage from the usually nonradioactive atoms, which are dislodged in the initial event. Interfacial nuclear decay and radiolysis processes that evolve flammable gases have also been studied on Al_2O_3 and ZrO_2 surfaces using intense radioactive sources with radiochemical tracer techniques.

Interaction of Water with UO_2 (001)

Uranium oxide exists in a range of stochiometries, from UO_2 to UO_3. In the present work, the interaction of water with UO_2 (001) using low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS), low-energy electron ion scattering (LEIS) and electron-stimulated desorption (ESD) has been studied. The clean UO_2(001) exhibits ordered c(2x2) LEED patterns in excellent agreement with previous published data. The x-ray photoelectron spectrum of the U 4f peaks exhibits a clear single satellite at 6.8 eV on the high binding energy side of U 4f5/2 , which has been assigned to a shake-up excitation of an electron from the O 2p-U bonding band to partially occupied or unoccupied localized metal 5f levels. Electron stimulated desorption (ESD) measurements of clean UO_2 indicate the desorption of H^+ and O^+; the O^+ desorption threshold is at ~22 eV, and the kinetic energy distribution is peaked at 3.5 eV. The O^+ desorption threshold is correlated to the ionization threshold of the oxygen 2s level, rather than the U 6p levels. Upon exposure to D_2O^{18} at 300K, the XPS and ESD results show no evidence of OD formation after water exposure. However an ESD O^{18+} signal appears. Both O^{16+} and O^{18+} signals reach a saturation value after 20 Langmuir exposure. Further, LEIS spectra show an O^{18} peak after water dosage. These results indicate that the water is completely dissociated on UO_2 (001) and that O^{18} atoms are incorporated in the surface. The results also suggest a diffusion of oxygen in the bulk.

Desorption of Tritiated Water from Uranium Oxide Films Under Atmospheric Conditions

In preliminary experiments in the laboratory of R. Dobrozemsky and T.U. Vienna, we have measured the desorption rate of tritiated water, HTO, from UOx films using radiotracer techniques. Our preliminary results indicate that the HTO desorption rate is considerably faster in atmospheric air than in vacuum. This interesting observation suggests that HTO desorption is accelerated by coadsorption of atmospheric molecules. More measurements are planned on new films to confirm and quantify this effect.

Electron-Bombardment of Spent Nuclear Fuel Elements

An ultrahigh vacuum system has been designed and modified to permit electron-bombardment studies of actual SNF material in a hot-cell facility. This will allow us to look at the role electronic excitation and hydride damage play in the production of hydrogen gas from actual fuel samples. We have obtained a Gatan Precision Ion Milling System (originally designed for milling TEM samples) to perform these electron bombardment studies. Electron-stimulated desorption (ESD) tests on metallic uranium spent nuclear fuel specimens are underway and the gases generated and released will be monitored in real time using a mass spectrometer.

Planned Activities

Measurements of the thermal and electron-stimulated desorption kinetics of water from well-characterized UO_2 and U-metal surfaces will continue. Studies using thin-films and radiotracer techniques with tritiated water will also be continued. The surface radiolysis studies with radioactive sources will be extended to uranium oxide systems and actual fuel materials using a hot-cell facility at PNNL. Finally, the mechanism of nonthermal production of hydrogen from water covered zirconia surfaces will be examined using state-resolved laser detection schemes.

Information Access

This project involves three organizations: Pacific Northwest National Laboratory, Rutgers University, and Brookhaven National Laboratory. The information is shared with DESH and Numatec. In addition, we participate in national and international meetings of scientific societies, such as the American Chemical Society, the Electrochemical Society, the American Physical Society, the American Nuclear Society, and the IEEE. We also publish essentially all of our work in the open literature. The following is a list of publications and conference presentations for the project.

References

Petrik NG, AB Alexandrov, AI Vall, and TM Orlando. 1999a. *Gamma radiolysis of water on oxide surfaces: Parameters controlling the energy transfer* (in press).

Petrik NG, DP Taylor, and TM Orlando. 1999b. "Laser-stimulated luminescence of yttria-stabilized cubic-zirconia crystals." *J. Appl. Phys.* 85:6770.

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desorption of O^+ from zirconia." *Surf. Sci*. 423:225.

Publications

Hedhili MN, BV Yakshinskiy, and TE Madey**.** "Interaction of water with UO_2 (001)." *Surf. Sci* (in preparation).

Haustein P. "Nuclear stimulated desorption studies of oxides relevant to spent fuel material." *J. Nucl. Materials* (in preparation).

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Presentations

Haustein P. August 22-26, 1999. "Nuclear stimulated desorption at the surfaces of model SNF materials: Experiment and computer simulation." Annual Symposium on "First Accomplishments of the Environmental Management Science Program," Annual Meeting, Am. Chem. Soc., New Orleans (invited talk).

Hedhili MN, BV Yakshinskiy, and TE Madey. March 21-25, 1999. "Interaction of water with UO_2 (001)." National American Physical Society Meeting, Atlanta.

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Orlando TM. March 21-25, 1999. "Quantum-resolved studies of condensed phase reactions." Symposium on "Free radicals in the Condensed Phase," Annual Meeting, Am. Chem. Soc., Anaheim, California (invited talk).

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Orlando TM, NG Petrik, AB Alexandrov, and WC Simpson. February 24, 1999. "Nonthermal processes on oxide surfaces and interfaces." Los Alamos National Laboratory, Los Alamos, New Mexico (invited talk).

Orlando TM, NG Petrik, AB Alexandrov, and WC Simpson. February 24-25, 1999. "Nonthermal processes on oxide surfaces and interfaces." DOE Laboratory Catalysis Research Symposium, Albuquerque, New Mexico.

Orlando TM, NG Petrik, AB Alexandrov, and WC Simpson. February 26, 1999. "Nonthermal processes on oxide surfaces and interfaces." Department of Chemistry, University of Utah, Salt Lake City (invited talk).

Petrik N, S Marshman, DM Camaioni, and TM Orlando. August 22-26, 1999. "Nonthermal surface and interface processes in the storage of spent nuclear fuel and mixed wastes." Annual Symposium on "First Accomplishments of the Environmental Management Science Program." Annual Meeting, Am. Chem. Soc., New Orleans.