

# Final Report

## U.S. Department of Energy

### Radiolytic and Thermal Processes Relevant to Dry Storage of Spent Nuclear Fuels

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## Executive Summary

The purpose of this project was to deliver pertinent information which can be used to make decisions concerning the safety and treatment issues associated with dry storage of spent nuclear fuel materials. In particular, we have an improved understanding of: i) water interactions with failed-fuel rods and metal-oxide materials; ii) the role of thermal processes and radiolysis (solid-state and interfacial) in the generation of potentially explosive mixtures of gaseous  $H_2$  and  $O_2$ , and iii) the potential role of radiation assisted corrosion during fuel rod storage. The project meets several major DOE/EMSP science needs for the Spent Nuclear Fuel Focus Area: i)"Stabilization of spent nuclear fuel, including mechanism of pyrophoricity and combustion parameters for various fuel types"; ii)"Characterization of spent nuclear fuel"; iii)"Development of methods to remove moisture without damage to fuel elements" iv)"Characterization of corrosion, degradation, and radionuclide release mechanisms, kinetics, and rates for fuel matrices.

Radiation-induced gas generation in nuclear materials and matrices is an extremely important problem of the applied nuclear technology. One of the key problems is an incomplete understanding of many fundamental processes causing the gas evolution and material damage under irradiation. The new scientific knowledge, gained in this project, will improve trustworthiness and reliability of the gas generation and fuel degradation prognoses for the spent fuel dry storage. This will decrease the risks associated with SNF storage and significantly reduce related costs.

Several research groups worked in a tight collaboration on the two major portions of the project scope: S.C. Marschman (*RPL/PNNL*), T.M. Orlando, N.G. Petrik, J.P. Cowin and W.C. Simpson (*CS&D/EMSL/PNNL*), studied electronic excitations and radiation induced damage of the fuel cladding material surface, and a radiation-induced gas generation from the water/cladding and water/fuel interfaces; T. E. Madey, M. N. Hedhili, B. V. Yakshinskiy (*Rutgers University*), J. Yarmoff (*University of California*), and R. Dobrozemsky (*Technical University of Vienna, Austria*) studied water – uranium oxide interactions, radiation induced damage of the  $UO_2$  surface and radiolysis of water on the  $UO_2$  surface.

The most scientifically important and relevant results from the EMSP project are summarized briefly below:

- The breakdown of  $UO_2$  and  $ZrO_2$  films under extreme radiation conditions has been systematically studied using low-energy electron and photon bombardment of well-characterized  $ZrO_2$  surfaces. Protective properties of these oxides are important to the integrity of uranium fuel and Zr-alloy fuel-rod cladding. We are the first clarifying the mechanism of oxygen removal

from such surfaces. This involves ionization of cation core levels, followed by interatomic Auger decay resulting in rapid ejection of “hot”  $O^+$  ions. This mechanism of the oxide film radiation damage should lead to the oxide metallization and possible loss of the protection properties of the oxide layer. Corrosion prognoses for fuel and fuel cladding should have a term of radiation-induced corrosion based on the  $O^+$  ions radiation-stimulated desorption.

- Low energy electron diffraction, X-ray photoelectron spectroscopy, low energy ion scattering and electron stimulated desorption results indicate that adsorbed water is completely dissociated on  $UO_2$  at 300K and that O atoms are incorporated into the surface. The results also suggest diffusion of oxygen into the bulk. This explains many unclear phenomena of the corroded fuel drying behavior and radiation/thermal-induced gas generation.
- $ZrO_2$ , and some other oxides increase the  $H_2$  yield from the adsorbed water as compared with the radiolysis of pure gas-phase water. A proposed mechanism is based on the migration of excitons to the surface and their resonant coupling with the  $H_2O$  adsorption complex. Gas generation calculations for radiolysis of water films adsorbed on the Zircaloy fuel cladding should include an absorbed energy term related to the surface oxide.
- Strong dependence is observed for the yields of water radiolysis products on the thickness of  $H_2O$  films. Molecular products have extremely low yields in the thin water layers (0 to 2 monolayers). Radical emission is dominating in the thin water layers. In other words, from the point of view of radiolysis, thin adsorption layers behave almost *like vapor water*, but thicker layers should be considered more *like condensed water*. G-values for the adsorbed water radiolysis appear to not be constant, but *depend on the water film thickness*. This dependence should be taken into account during gas generation calculations for radiolysis of water films adsorbed on the fuel and fuel cladding surfaces.
- A high vacuum chamber has been designed, assembled and tested for the experiments with K-West Basin fuel samples, conducted in the Radiation Processing Laboratory of PNNL. The new facility is equipped with a low energy (5-500 eV) electron gun; a high resolution focused ion gun and a secondary electron detector and mass-spectrometer, and allows radiolysis experiments with actual spent fuel samples. This is a unique experimental facility with such capabilities for the spent nuclear fuel studies.
- From the results of the K-East canister samples test runs and analyses, thermal decomposition of the hydrates appear to drive the release of water, resulting in sample weight loss at temperatures between 75 °C and 425 °C. At temperatures above 425 °C, the weight losses observed were due

to reduction of higher oxides of uranium. These test results and analyses indicate that most of the hydrated species present in the K-East Basin canister sludge will thermally decompose at temperatures below 400 °C.

Several important new fundamental discoveries were made in this work. They are widely presented and published, and they are accessible to engineers and researchers working in field of nuclear materials. This program stimulated re-focusing of two basic science laboratories (EMSL at PNNL and Dept. of Physics at Rutgers University) on the problems, related to the spent fuel storage technology. New *state-of-art* research facilities were created and will be used in follow-up projects. New unique materials were synthesized to model nuclear materials in the Radiation Surface Science studies. An important result of the project is the development of an integrated team of scientists who are available to the DOE to help review spent-fuel safety concepts and safety response actions by DOE contractors.

We have proposed a continuation of this project to do experiments with actual radioactive materials. It should bridge our basic results with particular engineering projects of the spent nuclear fuel storage facilities. Another important application of the project results could be in the NERI or other reactor-based programs to develop an advanced corrosion and hydriding resistant fuel cladding for the higher burn-up operation with new types of proliferation-resistant fuels.

Several laboratories have expressed an interest to the project: LANL, Radiation Laboratory, Univ. of Notre Dame, ANL, Savannah River Technology Center, SRI International, and BNL.

## 1.0 Research Objectives

The scientific and engineering demands of the Department of Energy (DOE) Environmental Restoration and Waste Management tasks are enormous. For example, several thousand metric tons of metallic uranium spent nuclear fuel (SNF) remain in water storage awaiting disposition. Of this inventory, 2300 metric tons are N-Reactor fuel that have been stored for up to 24 years in the Hanford, Washington K-Basins. No significant precautions were taken to prevent the fuel from corroding since the fuel rods were intended to be reprocessed. Termination of reprocessing has left these fuels stranded in prolonged water storage and an appreciable quantity of the fuel has corroded. In addition, other defense fuels including the aluminum-clad fuels at the Savannah River Site and Idaho National Engineering Laboratory have corroded during interim storage in water. In 1994, the DOE began to implement a strategy for moving water-stored Hanford fuels into dry interim storage and a Record of Decision<sup>1</sup> (ROD) documenting this action was put forth by the Department of Energy on March 4, 1996. Several documents<sup>1-4</sup> including this ROD and the final environmental impact statement (FEIS)<sup>1</sup>, evaluated and documented concerns regarding the potential for releases of radionuclides to the environment. The DOE plans to remove metallic uranium SNF from water storage and seal it in overpack canisters for "dry" interim storage, for up to 75 years. Much of the SNF that will be stored will have been severely corroded during water storage. Chemically bound water not removed during proposed drying operations may lead to long-term corrosion and generation of combustible H<sub>2</sub> and O<sub>2</sub> gas-mixture via radiolysis. No thoroughly tested model is currently available to predict fuel behavior during "dry" storage. The PNNL collaborating with the Rutgers University studied the thermo-chemical and radiolytic reactions of actual and prototype SNF materials. The purpose of this project is to deliver pertinent information which can be used to make decisions concerning the safety and treatment issues associated with dry storage of spent nuclear fuel materials. In particular, we set out to establish an understanding of: i) water interactions with failed-fuel rods and metal-oxide materials; ii) the role of thermal processes and radiolysis (solid-state and interfacial) in the generation of potentially explosive mixtures of gaseous H<sub>2</sub> and O<sub>2</sub>, and iii) the potential role of radiation assisted corrosion during fuel rod storage. The project meets several major DOE/EMSP science needs for the Spent Nuclear Fuel Focus Area: 1) Stabilization of spent nuclear fuel, including mechanism of pyrophoricity and combustion parameters for various fuel types; 2) Characterization of spent nuclear fuel; 3) Development of methods to remove moisture without damage to fuel elements; and 4) Characterization of corrosion, degradation, and radionuclide release mechanisms, kinetics, and rates for fuel matrices.

## 2.0 Methods and Results

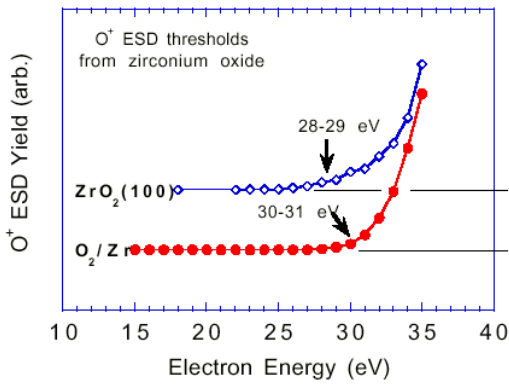
### 2.1 Radiation-induced degradation of the oxide surface

Photon- and electron-stimulated desorption (PSD and ESD) of positive ions from yttrium-stabilized cubic ZrO<sub>2</sub>(100) and undoped amorphous ZrO<sub>2</sub> surfaces were studied<sup>5,6</sup>. Undoped 15 - 30 Å ZrO<sub>2</sub> films were grown on Zr foils (99.94%) oxidized *in situ* via room- temperature exposure to O<sub>2</sub> (99.999%). The ESD measurements were carried out at PNNL in an ultra-high vacuum chamber (base pressure  $2 \times 10^{-10}$  Torr) equipped with a low-energy electron gun, a quadrupole mass spectrometer (QMS), an ion sputter gun, and an Auger electron spectroscopy (AES) system. The PSD and SXPS measurements were carried out at beam-line U8-a at the National Synchrotron Light Source at Brookhaven National Laboratory. For both types of zirconia, O<sup>+</sup> is the primary ionic desorption product. Figure 1 shows a threshold for ESD of O<sup>+</sup> from yttria-stabilized cubic zirconia (YSZ) at ~ 26-27 eV. For the amorphous zirconia the O<sup>+</sup> ion yield increasing measurably at ~ 29-30 eV. The PSD threshold from YSZ is  $\sim 31 \pm 1$  eV (Figure 2). This is essentially the same as the O<sup>+</sup> ESD and PSD thresholds ( $\sim 30 \pm 1$  eV) from undoped amorphous ZrO<sub>2</sub> surfaces. The PSD O<sup>+</sup> kinetic energy distributions extend from zero to ~ 7 eV with a peak at ~ 2 eV and

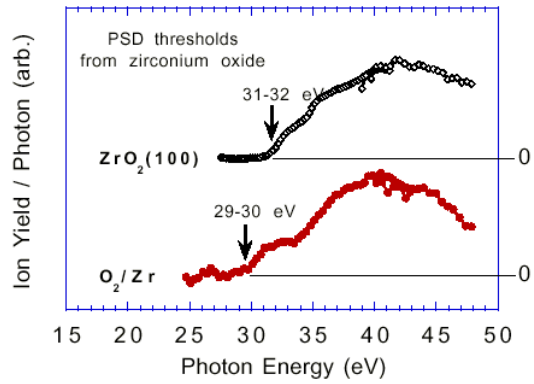
are similar from both surfaces (Figure 3). A comparison of the ion threshold data with photoelectron spectra (Figure 4) indicates that desorption of  $O^+$  is primarily initiated by ionization of the Zr(4p) core level. All of the evidence is consistent with the Knotek-Feibelman desorption mechanism, in which the  $O^+$  ions are produced and ejected from the surface via a multi-electron Auger decay process.

Rutgers University studied  $H^+$  and  $O^+$  ESD of clean  $UO_2(001)$  surface<sup>7</sup> and found the  $O^+$  desorption threshold at 25eV, and the kinetic energy distribution peaked at 3.5eV (Figure 5b). The  $O^+$  desorption threshold is correlated to the ionization of the oxygen 2s level, rather than the U 6p levels (Figure 5a).

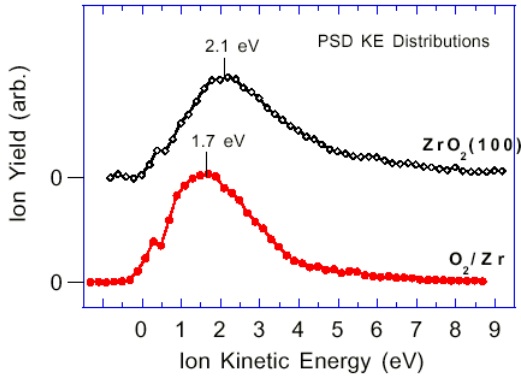
These are the first observations of the Auger – mediated  $O^+$  emission from such important nuclear materials as  $ZrO_2$  and  $UO_2$ . This mechanism of the oxide film radiation damage should lead to the oxide metallization and possible loosening of the protection properties.



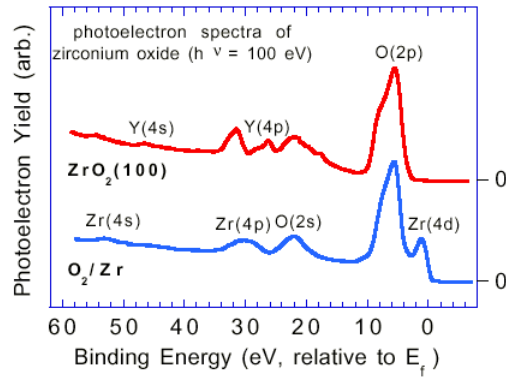
**Figure 1.** Thresholds for the ESD of  $O^+$  ions from the surface of amorphous and cubic  $ZrO_2$



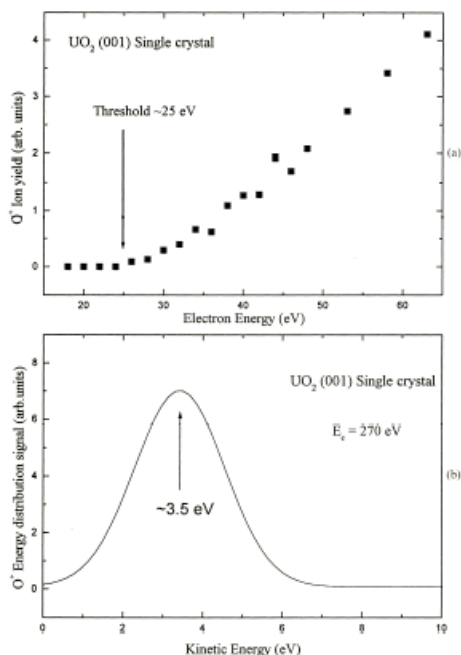
**Figure 2.** Thresholds for the PSD of positive ions from the surface of amorphous and cubic  $ZrO_2$ .



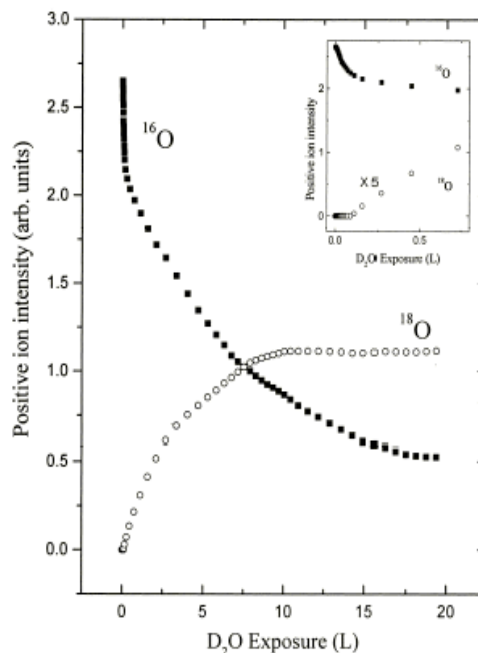
**Figure 3.** 70 eV x-ray PSD kinetic energy distributions of positive ions from the surface of amorphous and cubic  $ZrO_2$ .



**Figure 4.** Soft x-ray photoelectron spectra of the surface of amorphous and cubic  $ZrO_2$ , for photon energy of 100 eV.



**Figure 5.** (a) The threshold for  $O^+$  ESD from clean  $UO_2$  and (b)  $O^+$  kinetic energy distribution ( $E_c=270$  eV).



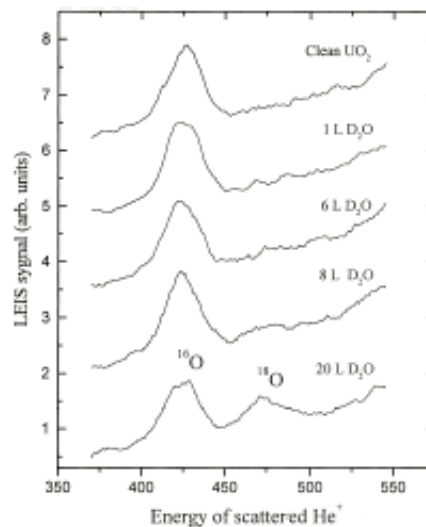
**Figure 6.** Variation of  $^{16}O^+$  and  $^{18}O^+$  signals as a function of  $D_2^{18}O$  exposure.

## 2.2 Radiolysis of water on the surface of nuclear materials

### 2.2.1 Radiolysis of water chemisorbed on the $UO_2$ surface at ambient temperature

Rutgers University studied interactions of water vapor with  $UO_2(001)$  by using low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), low energy ion scattering (LEIS) and electron stimulated desorption (ESD)<sup>7</sup>. The ESD cross-section was estimated for both lattice oxygen ( $^{16}O$ ) and adsorbed oxygen from dissociation of water ( $^{18}O$ ) by measuring the ESD ion yield decrement versus time; the total cross-section for desorption of  $^{16}O$  from clean  $UO_2$  is  $3 \times 10^{-19} \text{ cm}^2$ , which is different from the value  $1.5 \times 10^{-18} \text{ cm}^2$  corresponding to the total cross-section for desorption of  $^{18}O$  from  $UO_2$  exposed to  $D_2^{18}O$ .

Upon exposure to  $D_2^{18}O$  at 300K, the XPS and ESD results show no evidence of OD formation after water exposure. However, an ESD  $^{18}O^+$  signal appears; both  $^{16}O^+$  and  $^{18}O^+$  signals reach a saturation value after 20L exposure (Figure 6). Further, LEIS spectra show an  $^{18}O$  peak after water dosage (Figure 7). These results indicate that the water is completely dissociated on  $UO_2(001)$  and that  $^{18}O$  atoms are incorporated in the surface. The results also suggest a *diffusion of oxygen into the bulk*.

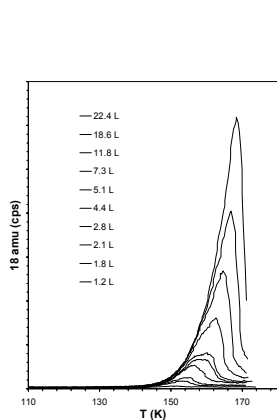


**Figure 7.** LEIS spectra obtained using 1 keV  $He^+$  for different  $D_2^{18}O$  exposures at room temperature.

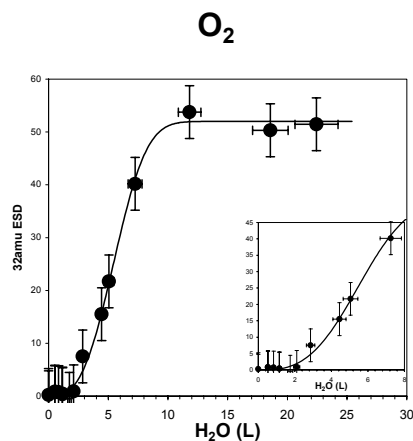


### 2.2.2 Radiolysis of water multilayers on the surface of UO<sub>2</sub> and other materials

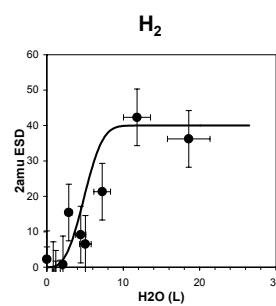
UO<sub>2</sub> thin films (< 10 nm) on the Molybdenum (100) single crystal surface were prepared using a magnetron sputtering method (Thomas Gouder, Institute for Transuranium Elements, Karlsruhe, Germany). Thermal stability and stoichiometry of UO<sub>2</sub> films were characterized by means of x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), as well as high resolution electron microscopy. Nano-films of water (0 - 60 monolayers (ML)) were deposited onto UO<sub>2</sub> surfaces at 100K (see TPD in the Fig. 8), and irradiated with 100 eV electrons. Monitoring O<sub>2</sub> and H<sub>2</sub> production versus water film thickness (Fig. 9 and 10), we have observed *extremely low yields of the molecular products in the 0 – 2 ML thin water layers*.



**Figure 8.** Water TPD from UO<sub>2</sub> film surface.



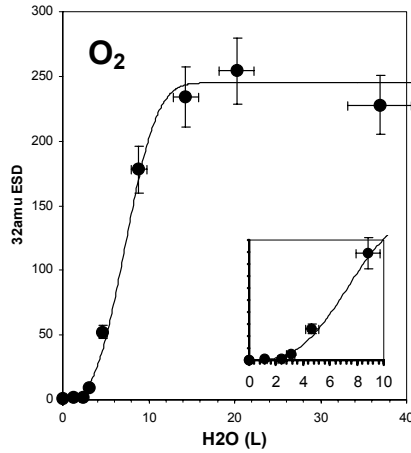
**Figure 9.** O<sub>2</sub> yield vs. water coverage of the UO<sub>2</sub> film surface during 100 eV electron irradiation @ 100K



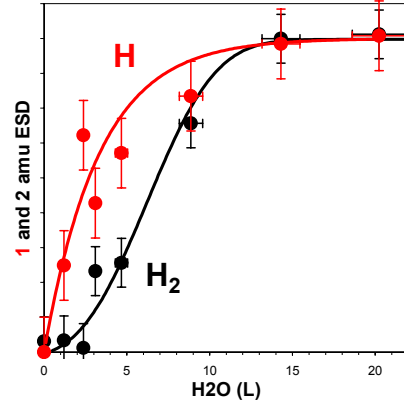
**Figure 10.** H<sub>2</sub> yield vs. water coverage of the UO<sub>2</sub> film surface during 100 eV electron irradiation @ 100K

Possible inhibiting effect of the UO<sub>2</sub> substrate was checked in the experiments with clean Mo(100) single crystal. Obtained results were similar and substrate-independent (Fig. 11 and 12). On the other hand, emission of the H-atoms is most efficient from the thin (0 – 2 ML) water overlayers (Fig. 12). Discovered anti-correlation in behavior of radical and molecular products of water radiolysis may be interpreted in terms of competition between H-atom emission and their recombination, producing H<sub>2</sub> molecules. Radical emission dominates in thin water layers while recombination dominates in the thicker layers (> 2 ML) where the radicals spend more time being gaseous.

In other words, the data show that from the point of view of radiolysis, thin adsorption layers (0 to 2 ML) behave almost *like vapor water* producing mostly radicals, but thicker layers should be considered more *like condensed water*, producing molecular products. It is also important to note, that *G-values* for the adsorbed water radiolysis are not constant, but *depend on the water film thickness* (!). Note: we are dealing with about the same concentrations of the adsorbed water, as should be expected in the SNF dry storage.



**Figure 11.** O<sub>2</sub> yield vs. water coverage of the Mo(100) surface during 100 eV electron irradiation @ 100K



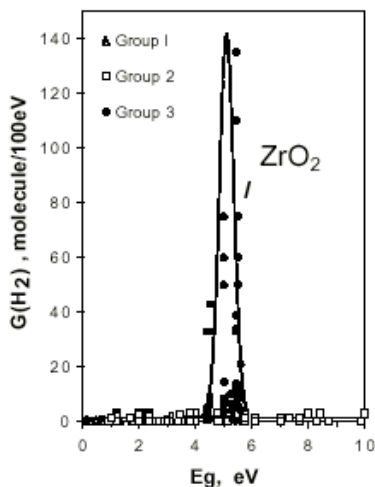
**Figure 12.** Normalized H and H<sub>2</sub> yields vs. water coverage of the Mo(100) surface during 100 eV electron irradiation @ 100K

### 2.2.3 Gamma-radiolysis of water deposited on the surface of various oxides at ambient temperature.

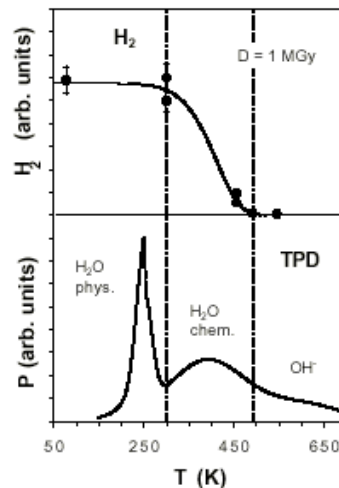
Thirty powdered ultra-pure (>99.99%) grade crystal oxides were studied in gamma-radiolysis experiments. Specific areas of the oxides were determined utilizing the standard Brunauer-Emmett-Teller method. The oxide samples were heated up to 773 K under vacuum, and water vapor was then deposited into the ampoule. The amount of water vapor was approximately a monolayer:  $(0.6 - 1.0) \times 10^{19} \text{ m}^{-2}$ . The samples were then irradiated with <sup>60</sup>Co gamma quanta at  $315 \pm 5 \text{ K}$  with an absorbed dose rate  $1.8 \pm 0.15 \text{ Gy/s}$ . Molecular hydrogen was analyzed by gas chromatography. The experiments were done in collaboration with the Project and Research Institute of Complex Power Technology “VNIPIET” and the Institute of Technology (both St. Petersburg, Russia).

According to the radiation-chemical yield the oxides can be generally classified into three groups: i) *MnO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub>, CuO and Fe<sub>2</sub>O<sub>3</sub>* oxides which lower the H<sub>2</sub> yield as compared with the radiolysis of pure gas-phase water; ii) *MgO, CaO, SrO, BaO, ZnO, CdO, Cu<sub>2</sub>O, NiO, Cr<sub>2</sub>O<sub>3</sub>, Cr(OH)<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, Nb<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub>* oxides with H<sub>2</sub> yields which are similar to or slightly greater than radiolysis of pure gas-phase water; and, iii) *ZrO<sub>2</sub>, Ga<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, Sm<sub>2</sub>O<sub>3</sub>, Eu<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, Er<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>* oxides which increase the H<sub>2</sub> yield as compared with the radiolysis of pure gas-phase water. The hydrogen yields were calculated on an electron fraction basis relative to the energy of  $\gamma$  rays directly absorbed by the H<sub>2</sub>O molecules<sup>8</sup>. There are several parameters such as *the oxide band-gap, water adsorption form and energy (exciton) migration distance* which can collectively contribute to “enhanced” radiolysis yields at interfaces. Figure 13 presents data of “effective”  $G(\text{H}_2)$  vs. band-gap ( $E_g$ ) energy which shows a narrow resonant maximum at  $E_g = 5.0 \pm 0.5 \text{ eV}$ . This corresponds to the energy of *H-OH* bond in the water molecule (5.1 eV). We show that the energy transfer occurs only to the first adsorption layer of water. As shown for *ZrO<sub>2</sub>* more than 80% of all the released hydrogen arises from the chemisorbed water, which has a TPD peak at 300-450K (Figure 14). Water radiolysis enhancement for *ZrO<sub>2</sub>* and other promoters is the result of effective energy transfer at the oxide/water interface, presumably due to migration of excitons to the surface and their resonant coupling with the H<sub>2</sub>O adsorption complex. *Thus, the standard G-value definition may have to be modified when discussing radiolysis at interfaces.*

These results imply that the radiation-induced yield of hydrogen and oxygen gas will be higher from the fuel cladding surfaces than from the fuel material itself. This is a very important issue to investigate with respect to verifying of the long-term “dry” storage strategy.



**Figure 13.** Hydrogen yields vs. oxide band gap for radiolysis of  $\text{H}_2\text{O}$  molecules adsorbed on the surface of various oxides. Oxides from groups I, II and III are marked differently.

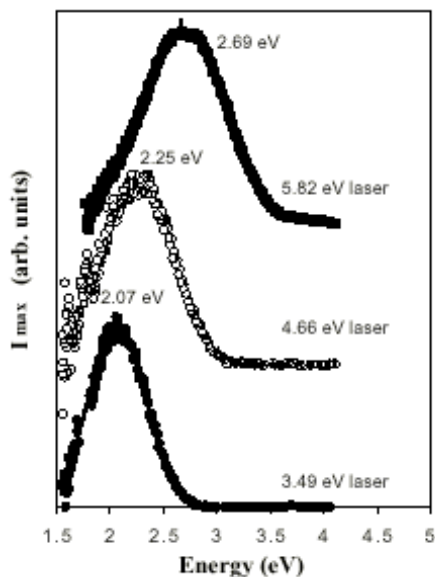


**Figure 14.** Hydrogen yield (upper panel) vs. temperature of the oxide heat pre-treatment for radiolysis of  $\text{H}_2\text{O}$  molecules adsorbed on the  $\text{ZrO}_2$  surface and TPD of water on zirconia (lower panel).  $D = 1 \text{ MGy}$

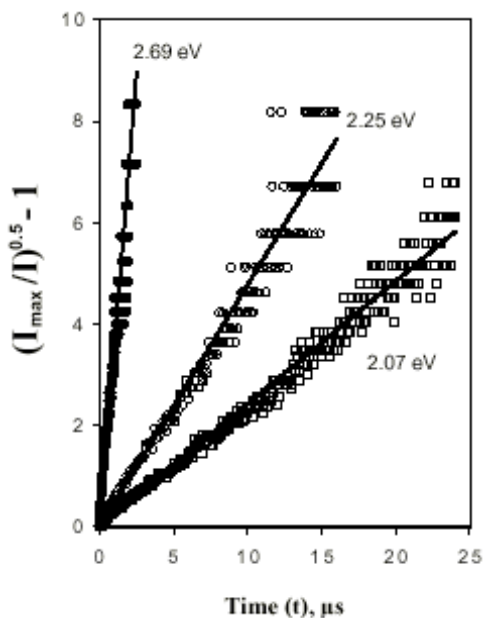
#### 2.2.4 Time-resolved measurements of $\text{ZrO}_2$ recombination luminescence

Typically, mobile electrons, holes and excitons from the substrate contribute to the “enhancement” of radiolytical decomposition of the adsorbed water. Their effective range is directly related to carrier mean free paths and excited state lifetimes. These parameters can be studied with a technique known as laser-stimulated luminescence (LSL)<sup>9-13</sup>. Time- and energy-resolved LSL measurements were utilized to investigate the dynamics of electronic excitations in  $\text{ZrO}_2$ . The LSL studies were carried out with  $\text{ZrO}_2 \times 9.5 \text{ mol \% Y}_2\text{O}_3$  single crystals. We observed luminescence from the decay of three unique excited states, at 2.70, 2.27 and 2.10 eV following 213-, 266- and 355-nm (5.82, 4.66, and 3.49 eV) laser excitation, respectively (Figure 15). Each LSL band exhibits a different excited state lifetime varying from 0.1 to 100  $\mu\text{s}$  depending on the excitation energy and temperature. The emission kinetics is hyperbolic for all of the luminescence bands (Figure 16). This indicates a recombination nature of the luminescence.

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 those centers to intrinsic F-centers and extrinsic F-type centers, which are located in the band gap. We suggest that recombination primarily involves electrons, trapped at intrinsic and extrinsic defect sites, and mobilized holes. Finally, from the luminescence experiments, we have obtained fundamental migration parameters - excitation efficiency, lifetime and migration activation energy for the electron-hole pairs in the zirconia.



**Figure 15.** Spectra of the  $\text{ZrO}_2\text{-}9.5\%\text{Y}_2\text{O}_3$  crystal luminescence induced by 5.82 eV, 4.66 eV and 3.49 eV laser excitations.



**Figure 16.** Linear approximation for decay kinetics of 2.69, 2.25 and 2.07 eV bands of laser stimulated luminescence at 150 K in hyperbolic coordinates.

### 2.2.5 Synthesis and characterization of crystalline zirconia films with controlled elemental composition.

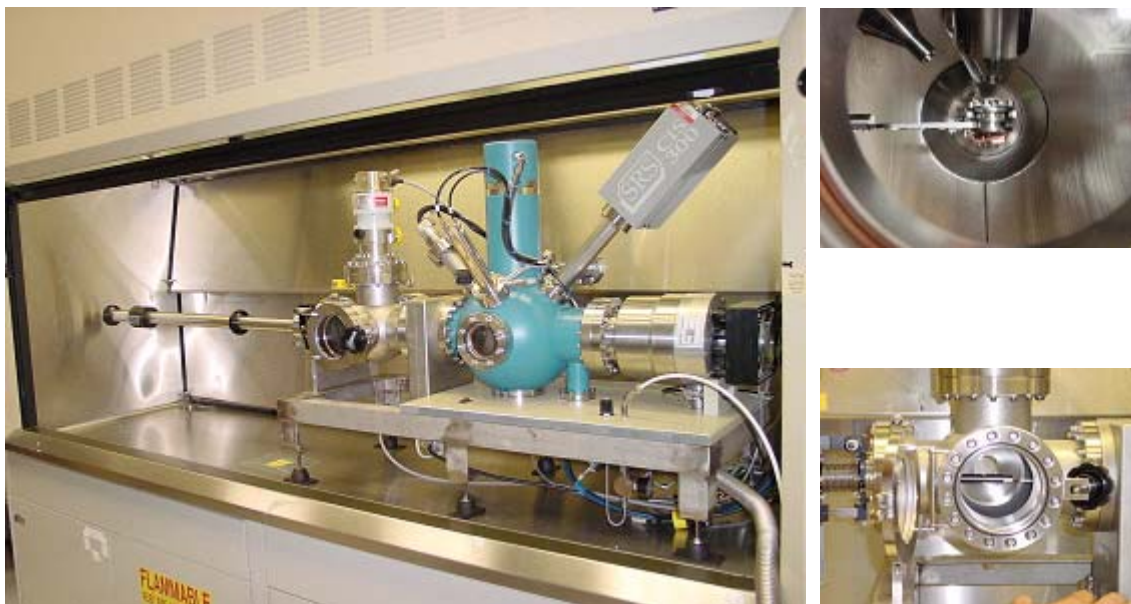
***A pure zirconia film growth by molecular beam epitaxy method.*** A serious difficulty in study of  $\text{ZrO}_2$  surface processes is associated with the problem of synthesis of pure stabilizer-free zirconia films and/or single-crystals, as well as have a doped material with composition, modeling composition of oxide films on the real Zircaloy fuel cladding. Cubic and monoclinic single crystal zirconia films were grown on yttrium stabilized zirconia substrates by oxygen plasma assisted molecular beam epitaxy method. Growth rate, thickness and the substrate temperature were optimized to achieve the cubic and monoclinic single crystal films. The oxygen partial pressure in the system was  $1.5 \times 10^{-5}$  Torr during the growth. It was observed that cubic single crystal zirconia (100) films could be grown on an YSZ(100) substrate<sup>14</sup> up to a 70 Å thickness at a substrate temperature of 650°C with the growth rate of 0.2-0.3 Å/s. A well-aligned single crystal monoclinic phase of  $\text{ZrO}_2(100)$  was obtained during the growth from 70 Å thick films up to 2000 Å thick film.

***Characterization of pure zirconia films grown on the zirconium metal surface.*** Nominal pure  $\text{ZrO}_2$  films were grown by isothermal oxidation of the  $\text{Ar}^+$  ion sputtered and UHV cleaned pure zirconium foil (99.94%) with the controlled dosing of ultra-pure oxygen (99.999%). AES spectra show good stoichiometry, cleanliness, and stability of such films. Exposure of the film to hydrogen results in increased surface hydrogen as well as a small increase of hydrogen in the metal substrate. Exposure of the film to water vapors results in additional surface hydrogen as well as increased hydrogen in the oxide and at the oxide-metal interface. These unique and well characterized  $\text{ZrO}_2$  materials will be utilized in our future experiments on mechanistic understanding and modeling of radiation-induced processes on the surface of the spent fuel cladding (gas generation and corrosion). Conducting parallel experiments with real materials and their well-characterized prototypes is the only approach giving reliable quantitative data for the predictive models of the SNF behavior.

## 2.3 Studies of radiolytic and thermal processes on actual spent nuclear fuel samples

### 2.3.1 Spent fuel surface science chamber

One of the most important features of the project was the ability to carry out fundamental investigations on radioactive fuel elements and materials. For this purpose, a high vacuum chamber has been designed, constructed and tested for surface science experiments with actual SNF samples, within the Radiation Processing Laboratory at the PNNL (Figure 17). The new facility is equipped with a high-resolution focused ion gun and secondary electron detector. These allow selective irradiation of different portions of the sample with  $\text{He}^+$ ,  $\text{Ar}^+$  and other ions. The combination of the ion gun with the secondary electron



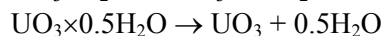
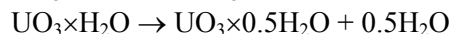
**Figure 17.** High vacuum chamber for ESD, SEM and SIMS study of spent nuclear fuel.

detector and mass-spectrometer provide a method to carry out secondary electron microscopy (SEM) imaging of the sample and detection of the sputtered ions for secondary ion mass spectrometry (SIMS) applications. A VG Microtech LEG41 electron flood gun is utilized as an irradiator for the ESD experiments. The gun has two operation modes : 0 - 80 eV variable and 500 eV fixed for the electron energy with a maximum electron beam current 20  $\mu\text{A}$ . The electron gun has been modified for pulsed operation. The chamber is pumped out with a turbo-molecular pump down to a residual pressure of  $\sim 10^{-8}$  Torr. A precision leak-valve provides controlled dosage of He, Ar,  $\text{H}_2\text{O}$ ,  $\text{O}_2$  and other gases into the chamber for ion irradiation and surface reactions. A gate valve and convenient load-lock system are significant parts of the design, ensuring easy and radiologically safe change of radioactive fuel samples.

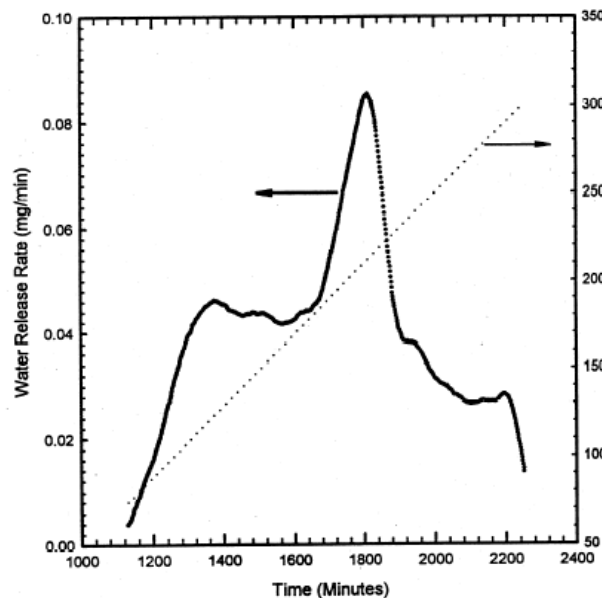
### 2.3.2 Measure and model kinetics of water desorption from corroded SNF

A series of tests were conducted by Pacific Northwest National Laboratory to evaluate the drying behavior of sludge taken from the Hanford K-East Basin storage canisters <sup>15</sup>. Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and mass spectrometry (MS) techniques were utilized to investigate a drying behavior of the K-East sludge. A Netzsch STA 409 TGA/DSC/MS system was used to monitor the weight change, heat release/consumption and volatilized species during heating of the samples. The test temperatures ranged from ambient to about 625°C. Water is the main released species. The complete release of the large fraction of free water remaining in the sample did not occur until the sample was heated to 75 °C. The thermal decomposition of the hydrates effectively started when the sample temperature was about 75 °C. The largest fraction of hydrated species thermally decomposed

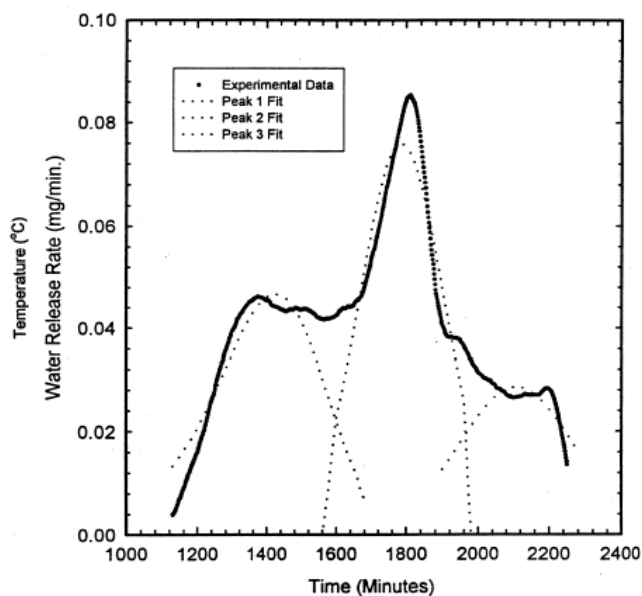
within the temperature range of 75 °C to 300 °C. The release rate curves (i. e., first derivative of the weight loss data) for this temperature range exhibit characteristics similar to a multistep thermal decomposition reaction for the hydrate (Figure 18). The structure of the decomposition rate curves show three distinct peaks, which suggests a probable decomposition of three different hydrated species, each characterized by a thermal decomposition rate constant. Of the three hydrated species, the other two were considered as products of the previous hydrate. Three following reaction steps were identified from the release rate curves:



The experimental data for each deconvoluted peak was therefore fitted with a first-order kinetics equation using nonlinear regression (Figure 19). These test results and analyses indicate that most of the hydrated species present in the K-East Basin canister sludge will thermally decompose at temperatures below 400 °C.



**Figure 18.** Water release rate curve showing three peaks between 75 and 300 °C for TGA of water thermal evolution from Hanford spent fuel rod "sludge" from K-Basin.



**Figure 19.** The three theoretical release peaks (solid lines) and the three experimental release data (dashed lines).

### 3.0 Relevance, Impact and Technology Transfer

#### a. How does this new scientific knowledge focus on critical DOE environmental management problems?

The project meets several major DOE/EMSP science needs for the Spent Nuclear Fuel Focus Area:

- i)"Stabilization of spent nuclear fuel, including mechanism of pyrophoricity and combustion parameters for various fuel types";
- ii)"Characterization of spent nuclear fuel";
- iii)"Development of methods to remove moisture without damage to fuel elements"
- iv)"Characterization of corrosion,

degradation, and radionuclide release mechanisms, kinetics, and rates for fuel matrices.

- b. **How will the new scientific knowledge that is generated by this project improve technologies and cleanup approaches to significantly reduce future costs, schedules, and risks and meet DOE compliance requirements?**

The new scientific knowledge, gained in this project, will improve trustworthiness and reliability of the gas generation and fuel degradation prognoses for the spent fuel dry storages. In particular, the following important revisions are proposed: i) gas generation calculations for radiolysis of water films adsorbed on the Zircaloy fuel cladding should include an absorbed energy term related to the surface oxide; ii) gas generation calculations for radiolysis of water film adsorbed on the fuel and fuel cladding surfaces should use corrected primary radiation-chemical yields, which are dependent on the H<sub>2</sub>O film thickness; iii) corrosion prognoses for fuel and fuel cladding should have a term of radiation-induced corrosion based on the O<sup>+</sup> ions radiation-stimulated desorption. These revisions will decrease a risk of the SNF storage and significantly reduce all the related costs.

- c. **To what extent does the new scientific knowledge bridge the gap between broad fundamental research that has wide-ranging applications and the timeliness to meet needs-driven applied technology development?**

Radiation-induced gas generation in nuclear materials and matrixes is an extremely important problem of the applied nuclear technology. Thousands of tons of radioactive materials and wastes generate toxic and flammable gases throughout the Country right now. This process is sometimes not satisfactorily predicted and controlled. One of the key problems is in bad understanding of many fundamental processes causing the gas evolution and material damage under irradiation. New basic findings, made in this work, make this gap smaller.

- d. **What is the project's impact on individuals, laboratories, departments, and institutions? Will results be used? If so, how will they be used, by whom, and when?**

This was a basic research project focused on delivering pertinent information which can be used to make decisions concerning the safety and treatment issues associated with dry storage of spent nuclear fuel materials. Several important new fundamental discoveries were made in this work. They are widely presented and published, and they are accessible to engineers and researchers working in field of nuclear materials. This program stimulated re-focusing of two basic science laboratories (EMSL at PNNL and Dept. of Physics at Rutgers University) on the problems, related to the spent fuel storage technology. New *state-of-art* research facilities are created and will be used in the follow-up projects. New unique materials were synthesized to model nuclear materials in the Radiation Surface Science studies.

- e. **Are larger scale trials warranted? What difference has the project made? Now that the project is complete, what new capacity, equipment or expertise has been developed?**

A high vacuum chamber has been assembled for the experiments with K-West Basin fuel samples, conducting in the Radiation Processing Laboratory of PNNL. This new facility allows secondary electron microscopy imaging, secondary ions mass-spectroscopy and ESD of spent fuel samples from the K-West Basin. We are generating proposals for the follow-up researches with radioactive materials.

- f. **How have the scientific capabilities of collaborating scientists been improved?**

An important result of the project is the development of an integrated team of scientists who are available to the DOE to help review spent-fuel safety concepts and safety response actions by DOE contractors.

g. **3.3.1 How has this research advanced our understanding in the area?**

Several important basic phenomena were observed first or proposed first in this work: i) radiation-induced emission of  $O^+$  ions from  $UO_2$  and  $ZrO_2$  surface as result of core level ionization; ii) resonant energy transfer from  $ZrO_2$  excitons to adsorbed water molecules; iii) recombination luminescence of  $ZrO_2$  crystals, involving trapped electrons and mobile holes; iv) dependence of the radical and molecular products of water radiolysis on the thickness of the  $H_2O$  films in the nanometer region.

h. **What additional scientific or other hurdles must be overcome before the results of this project can be successfully applied to DOE Environmental Management problems?**

We have proposed a continuation of this project to do experiments with actual radioactive materials. It should bridge our basic results and particular engineering projects of the spent nuclear fuel storage facilities. Another important application of the project results could be in the NERI or other reactor-based programs to develop advanced corrosion- and hydriding resistant fuel cladding for the higher burn-up operation with new types of proliferation-resistant fuel.

i. **Have any other government agencies or private enterprises expressed interest in the project? Please provide contact information.**

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## **4.0 Project Productivity**

The project has accomplished all of the proposed goals. The work plan was not revised, the project remained on schedule. The extension was strictly for the writing of the final report.

## **5.0 Personnel Supported**

In addition to the principle investigator and collaborators, two post doctoral fellows Matt Sieger and Bill Simpson, and two visiting scientists Nick Petrik and Alex Alexandrov were involved in the project.

## **6.0 Publications**

### **Peer-reviewed journals:**

W. C. Simpson, W. K. Wang, J. A. Yarmoff and T. M. Orlando, "Photon- and Electron-Stimulated Desorption of  $O^+$  from Zirconia", Surf. Sci. 423, 225 (1999).

Petrik N.G., Alexandrov A.B., Vall A.I. " Interfacial Energy Transfer during Gamma Radiolysis of Water on the Surface of  $ZrO_2$  and Some Other Oxides". J. Phys. Chem. B, 105(25), 5935-5944 (2001)

V. Shutthanandan, S. Thevuthasan, J.S. Young, T.M. Orlando, W.J. Weber "Hydrogen-Damage Interactions in Yttrium Stabilized Zirconia", J. Nucl. Mater. 289, 128 (2001).

N.G. Petrik, A.B. Alexandrov, T.M. Orlando, A.I. Vall "Radiation-Induced Processes at oxide Surfaces and Interfaces Relevant to Spent Nuclear Fuel Storage", Trans. ANS 81,101 (1999)



- N. G. Petrik, D. P. Taylor, and T. M. Orlando, "Laser-Stimulated Luminescence of Yttria-Stabilized Cubic-Zirconia Crystals", J. Appl. Phys. 85, 6770 (1999).
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- D.P. Taylor, W.C. Simpson, K. Knutsen, M.A. Henderson, T.M. Orlando "Photon-Stimulated Desorption of Cations from Yttria-Stabilized Cubic  $\text{ZrO}_2$ ", Appl. Surf. Sci. 127 - 129, 101 (1998)

#### Unreviewed publications:

- 1997-1998 Progress Report: <http://apollo.osti.gov/em52/1998projsum/60392.pdf>  
 1998-1999 Progress Report: <http://apollo.osti.gov/em52/1999projsum/60392.pdf>  
 EMSP Workshop, July 1998: <http://apollo.osti.gov/em52/1998posters/id60392.pdf>

#### Prepared for publication:

- S. Thevuthasan, S.I. Yi, Y.J. Kim, T.T. Tran, G.S. Herman, V. Shutthanandan, S.A. Chambers, C.H.F. Peden, and T.M. Orlando "Surface Structure Determination of Y- $\text{ZrO}_2$ (001) Using Mass Separated Recoil Spectroscopy and X-Ray Photoelectron Diffraction", Surf. Sci. in preparation.
- P. Haustein, "Nuclear Stimulated Desorption Studies of Oxides Relevant to Spent Fuel Material", J. Nucl. Mater. in prep.

## 7.0 Interactions

- "Interfacial Radiolysis Effects Relevant to Spent Nuclear Fuel and Mixed Radioactive Wastes Storage"  
 N. G. Petrik, K. Knutsen, S.C. Marschman, T. M. Orlando. . Proc.11-th Ann. Pacific Northwest Symposium of the American Vacuum Society, Forest Grove, OR, Sept. 14-15 (2000)
- "Hydrogen-Damage Interactions in Yttrium Stabilized Zirconia", V. Shutthanandan, S. Thevuthasan and T.M. Orlando, 102nd American Ceramic Society Annual Meeting, St. Louis, Missouri, April 30 - May 3, 2000.
- "Radiation-Induced Processes at Oxide Surfaces and Interfaces Relevant to Spent Nuclear Fuel Storage". Petrik N.G., Alexandrov A.B., Orlando T.M., Vall A.I. **Invited presentation** at the 1999 American Nuclear Society Winter Meeting, Long Beach, CA, November 14 - 18, 1999.
- "Interfacial Radiolysis Effects Relevant to Spent Nuclear Fuel and Mixed Radioactive Waste Storage". Petrik N.G., Orlando T.M., Camaioni D.M., Marschman S.C. 218-th American Chemical Society National Meeting, New Orleans, LA, August 22 - 26, 1999.
- "Interaction of Water with Uranium Oxide Surfaces", M. N. Hedhili, B. V. Yakshinskiy, T. E. Madey, R. Dobrozemsky, J. Yarmoff, Annual Symposium on "First Accomplishments of the Environmental Management Science Program", Annual Meeting, Am. Chem. Soc., New Orleans, LA, August 22-26, 1999.
- "Surface Structure Determination of Yttrium Stabilized  $\text{ZrO}_2$ (001) using X-Ray Photoelectron Diffraction", S. Thevuthasan, S.I. Yi, Y.J. Kim, T.T. Tran, S.A. Chambers, C.H.F. Peden, and T.M. Orlando, 46th National Symposium, Am. Vac. Soc. (1999).
- "Nuclear Stimulated Desorption at the Surfaces of Model SNF Materials: Experiment and Computer Simulation", Peter Haustein, **Invited Talk**, Annual Symposium on "First Accomplishments of the Environmental Management Science Program", Annual Meeting, Am. Chem. Soc., New Orleans, LA, August 22-26, 1999.
- "Interaction of water with  $\text{UO}_2$  (001)", M. N. Hedhili, B. V. Yakshinskiy, and T. E. Madey, National American Physical Society Meeting, Atlanta, GA, March 21-25, 1999.
- "Quantum-Resolved Studies of Condensed Phase Reactions", T. M. Orlando, **Invited Talk**,

Symposium on “Free radicals in the Condensed Phase”, Annual Meeting, Am. Chem. Soc., Anaheim, CA, March 21-25, 1999.

“Nonthermal Processes on Oxide Surfaces and Interfaces”, T. M. Orlando, N. G. Petrik, A. B. Alexandrov, and W. C. Simpson, **Invited Talk**, Dept. of Chemistry, University of Utah, Salt Lake City, UT Feb. 26, 1999.

“Nonthermal Processes on Oxide Surfaces and Interfaces”, T. M. Orlando, N. G. Petrik, A. B. Alexandrov, and W. C. Simpson, DOE Laboratory Catalysis Research Symposium, Albuquerque, NM, Feb. 24-25, 1999.

“Nonthermal Processes on Oxide Surfaces and Interfaces”, T. M. Orlando, N. G. Petrik, A. B. Alexandrov, and W. C. Simpson, **Invited Talk**, Los Alamos National Laboratory, Los Alamos, NM Feb. 24, 1999.

Gamma Radiolysis of Water on Oxide Surfaces. Petrik, N.G., Alexandrov, A.B., Vall, A.I., Orlando, T.M.. Gordon Research Conference on Radiation Chemistry, Newport, RI, July 5-10 (1998)

Gamma Radiolysis of Water on Oxide Surfaces. Petrik, N.G., Alexandrov, A.B., Vall, A.I., Orlando, T.M. Surface Analysis '98, Richland, WA, June 16 - 19 (1998)

Laser-Stimulated Luminescence of Yttria-Stabilized Cubic Zirconia Crystals. Petrik, N., Taylor, D., Simpson, W, Orlando, T.. Proc.9-th Ann. Pacific Northwest Symposium of the American Vacuum Society, Troutdale, OR, Sept. 18-19 (1997)

## 8.0 Transitions

This was a basic research, which purpose was to deliver pertinent information which can be used to make decisions concerning the safety and treatment issues associated with dry storage of spent nuclear fuel materials. Possible use and application of the results are discussed in the “Relevance, Impact and Technology Transfer” section.

## 9.0 Patents

None.

## 10.0 Future Work

Results obtained in this program lead to the submission of a renewal proposal “Radiolytic and thermal processes relevant to dry storage of spent nuclear fuel”. The goal of this program is to deliver a basic, mechanistic and quantitative information concerning radiolytic / thermal gas generation from and radiation-chemical degradation of the major components of the SNF storage: spent fuel, fuel cladding and rubble. This program will:

- Utilize a unique experimental capability that was constructed and supported by our previous EMSP project to investigate actual spent nuclear fuel materials. The capability to examine the radiolytic reactions on the surfaces of highly radioactive spent nuclear fuel materials does not exist elsewhere in the DOE Complex or in the western hemisphere.
- Provide quantitative data and mechanistic understanding of the adsorption/desorption parameters, temperature stability, and dissociation products for the different forms of water molecules bound to the major components of the SNF storage: spent fuel, fuel cladding and rubble;

- Provide quantitative data and a mechanistic understanding on radiation-induced gas-generation from the surface of real SNF samples, fuel cladding and rubble components with different forms of adsorbed and structural water;
- Complete the development of a predictive model for the radiation/thermal induced gas generation in the dry SNF storage facility.

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