RADIOLYTIC AND THERMAL PROCESSES RELEVANT TO DRY STORAGE OF SPENT NUCLEAR FUEL

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PROGRAM OVERVIEW:

Thousands of tons of metallic uranium spent-nuclear-fuel (SNF) remain in water storage across the DOE complex.

DOE plans to remove this fuel and seal it in overpack canisters for "dry" interim storage for up to 75 yrs. while awaiting permanent disposition.

In a collaborative effort among PNNL, Rutgers Univ. BNL, and the Univ. of California, we are performing basic research on the radiolytic reactions, drying processes, and corrosion behavior of SNF materials and related oxides.

SOME PROGRAM ISSUES - PROGRESS:

Issue: What is the realistic potential of producing explosive mixtures of H_2 and O_2 during dry storage?

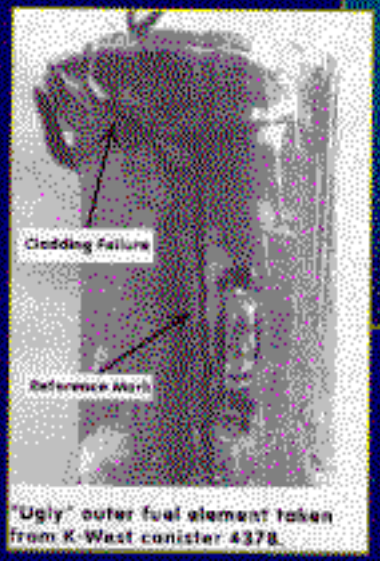
Progress: We have examined the electronic mechanisms involved in radiation damage of ZrO_2, a common cladding material. Evidence indicates that the electronic properties of ZrO_2 may enhance radiolysis of interfacial water. Similar work on UO_2 single crystals and U_xO_y thin-films has begun.

Issue: What are the dominant phases present in SNF and will proposed pre-treament steps be effective?

Progress: Though the stochiometry and partitioning between phases is not fully known, uranium-oxide hydrates and uranium hydrides are present in damaged SNF. Thermal gravimetric analysis and modeling indicates that dehydration is slow due to kinetics and transport issues.

Zr-based alloys are used in nuclear reactors as cladding for fuel rods and pressure tubes

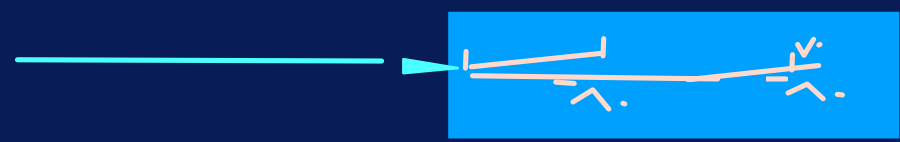
- low neutron capture cross section
- good mechanical properties
- corrosion resistant (stable native oxide)



"Ugly" outer fuel element taken from K-West canister 4378.

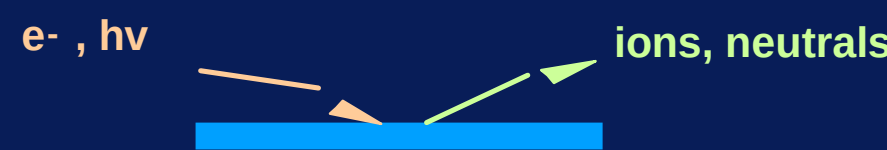
however, prolonged exposure to radiation leads to corrosion, embrittlement, and cladding failure

Our Approach

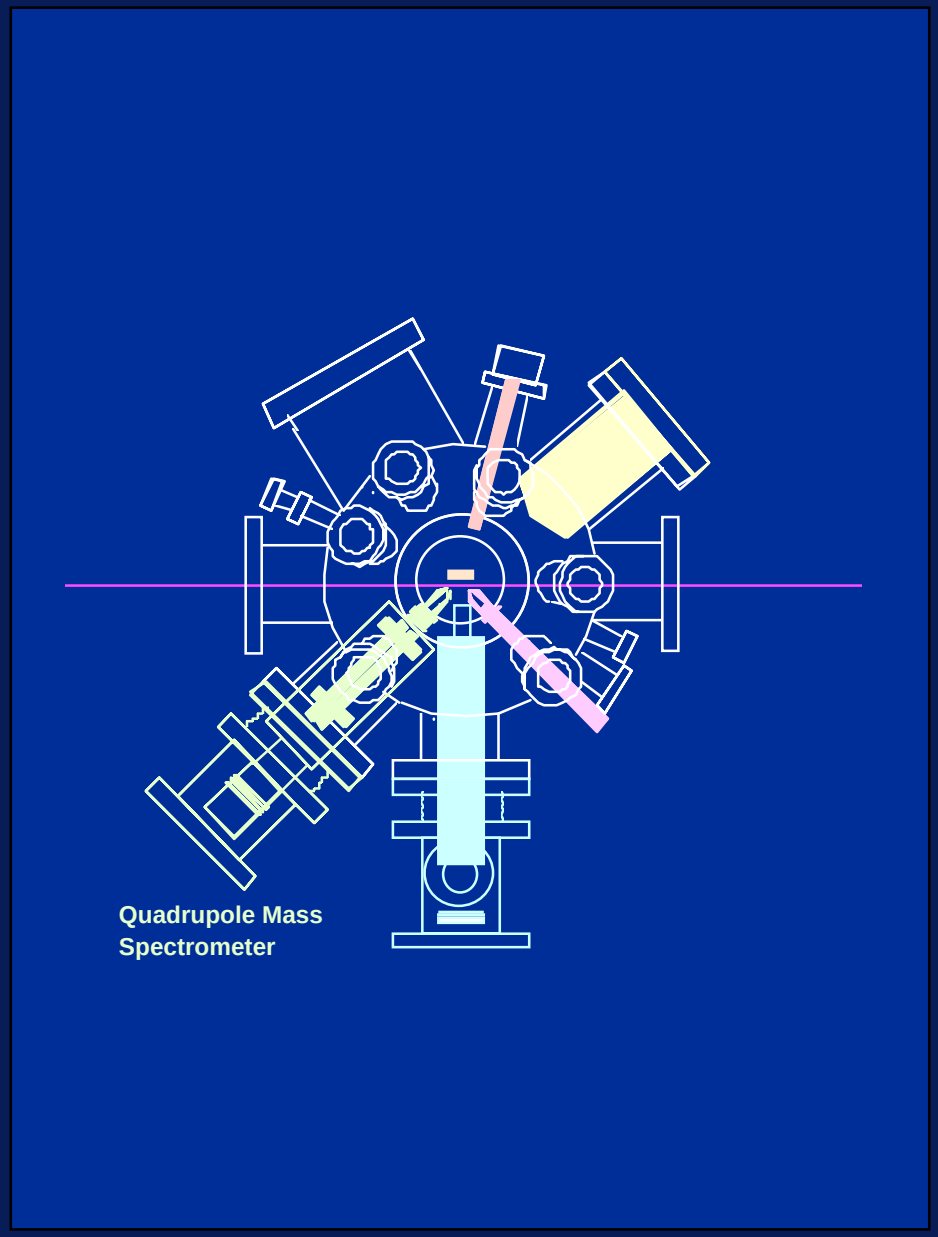


- In a material under radiation bombardment, a beta or Compton electron (E ~ 10^5-10^7 eV) can easily generate 10^4 or more low-energy (5 - 100 eV) secondary electrons, which have energies sufficient to induce a range of non-thermal reactions.

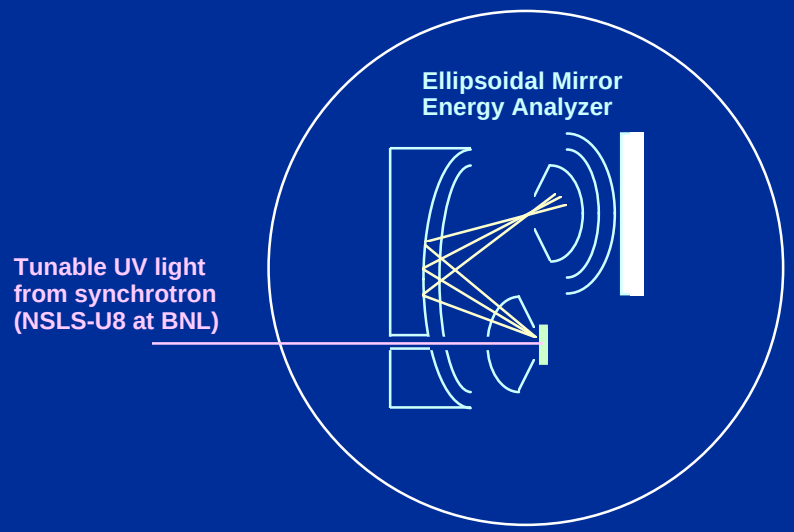
- We simulate the effects of an ionizing radiation environment by bombarding a material with a beam of monoenergetic, low-energy electrons or photons.



- By monitoring the desorption products as a function of incident energy, we find the thresholds for desorption of various species from a material. Pairing this information with knowledge of the electronic structure, we can identify the electronic excitations that lead to radiation damage and material modification.

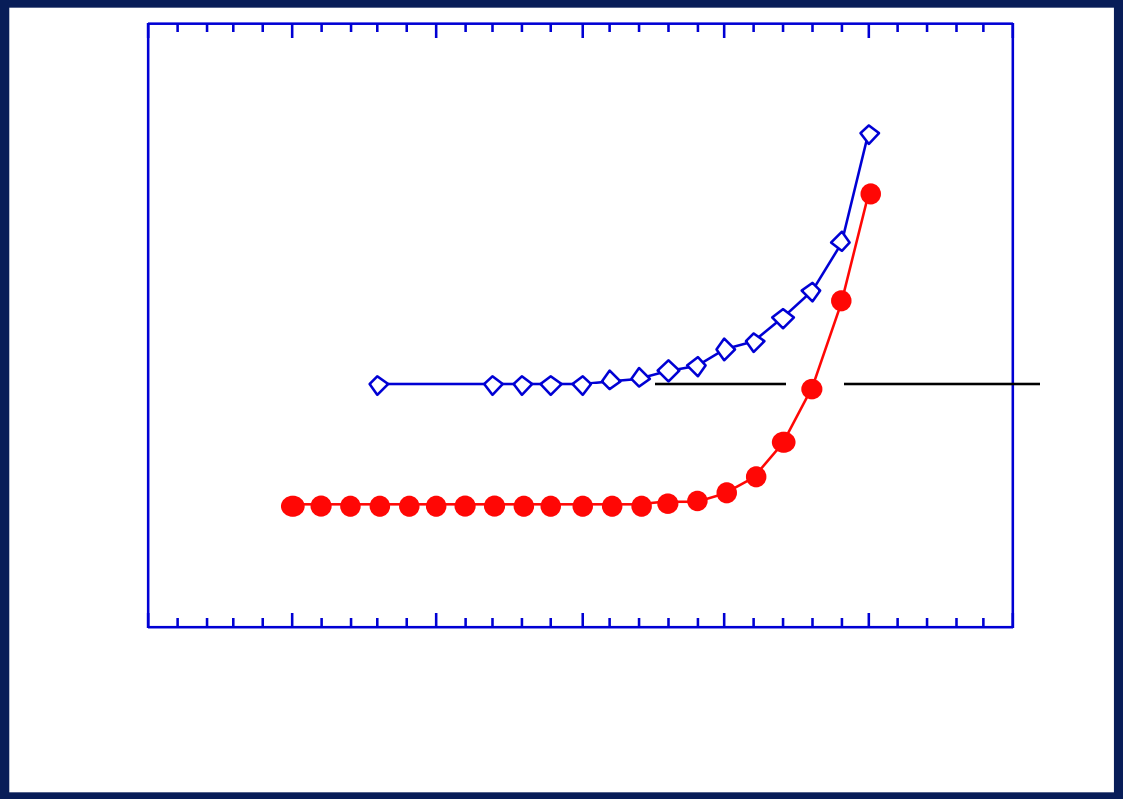

Quadrupole Mass
Spectrometer

Ultrahigh Vacuum System for Photon-Stimulated Desorption and Photoelectron Spectroscopy



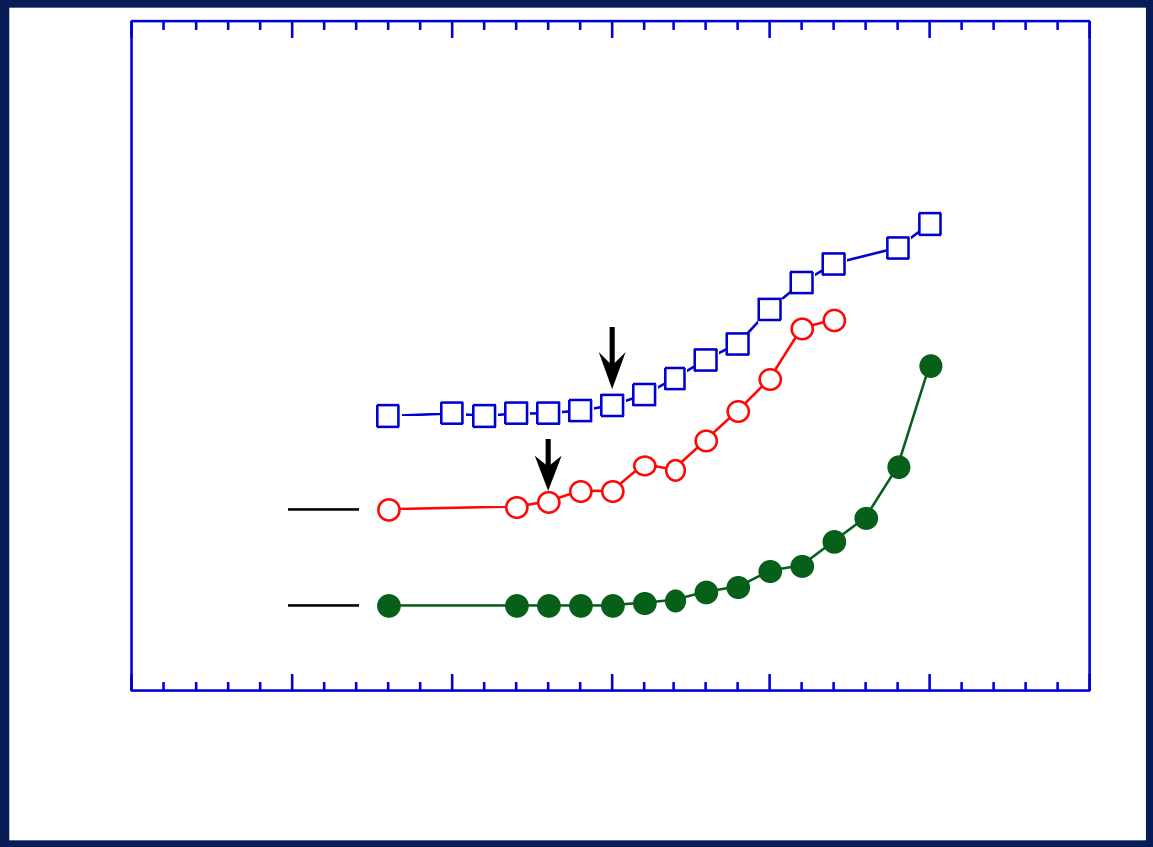
- Fix pass energy, ramp photon energy
  (set for positive particles) – cation PSD spectrum
- Fix photon energy, ramp pass energy
  (set for positive particles) – cation PSD KE distribution
- Fix photon energy, ramp pass energy
  (set for negative particles) – SPXS spectrum

THRESHOLDS FOR THE ELECTRON STIMULATED DESORPTION (ESD) OF O^+ IONS FROM THE SURFACE OF AMORPHOUS AND CUBIC ZrO_2



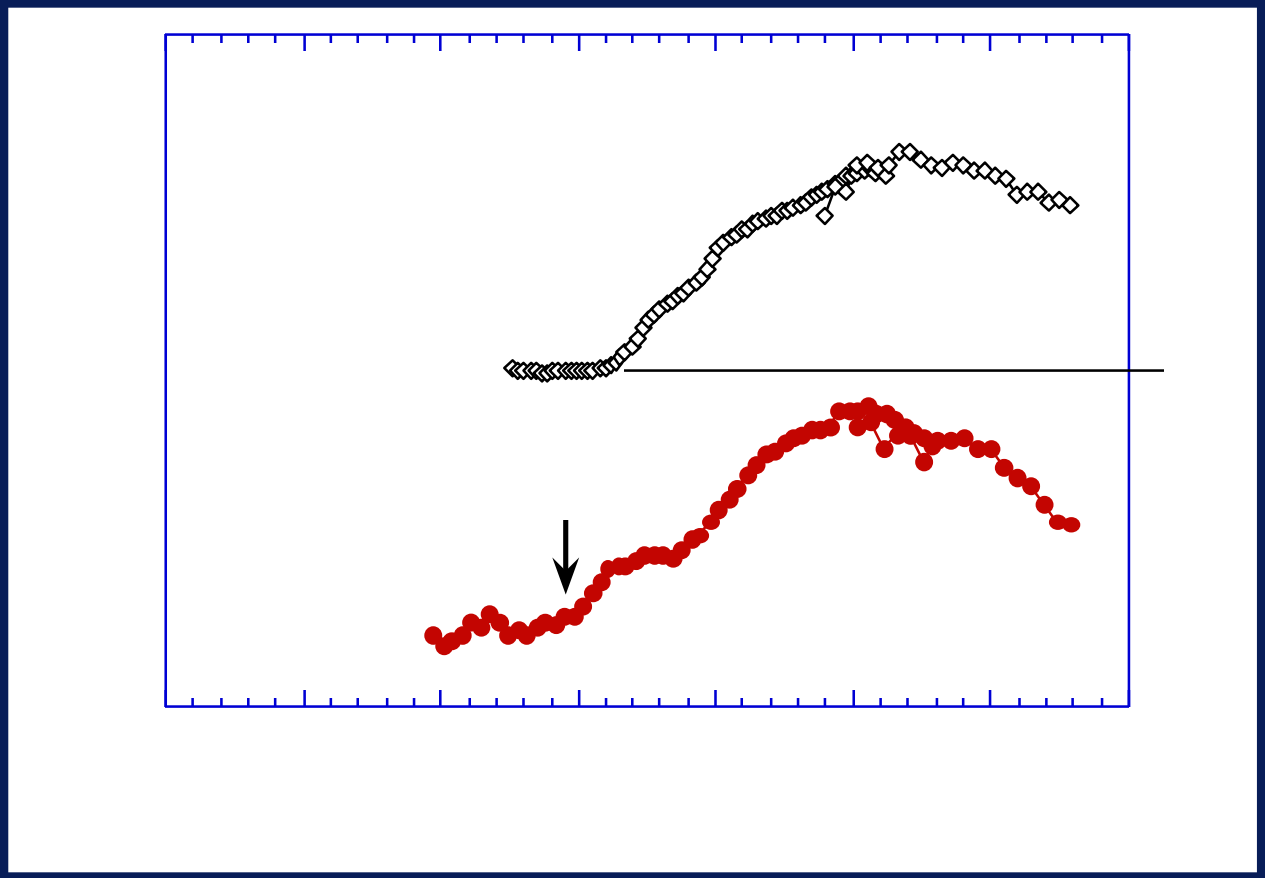
The data, representing the O^+ yield as a function of incident electron energy, are offset vertically for display. The size of the symbols represents the estimated uncertainty in the measurements

THRESHOLDS FOR THE ELECTRON STIMULATED DESORPTION (ESD) OF O^+, H^+ AND OH^+ IONS FROM THE SURFACE OF CUBIC ZrO_2 FOLLOWING EXPOSURE TO WATER VAPOR



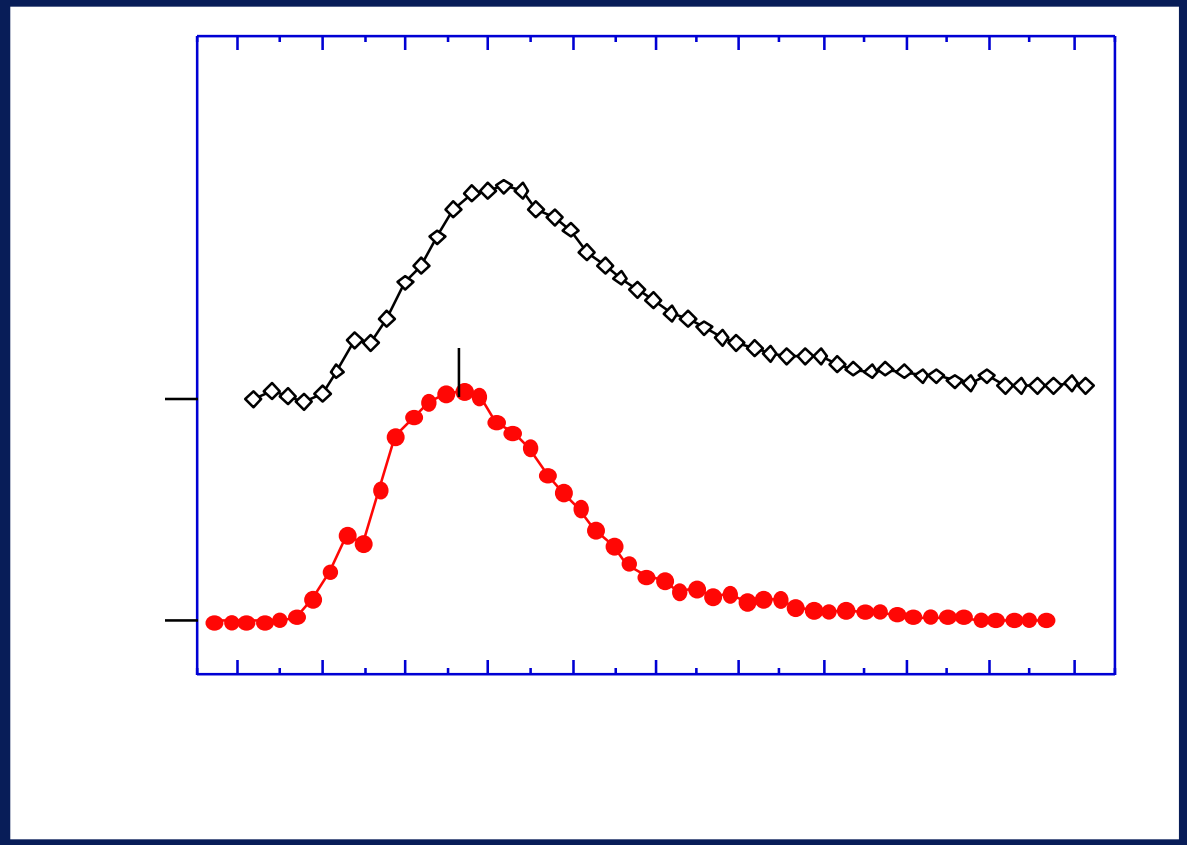
The data are offset vertically for display and the size of the symbols represents the estimated uncertainty in the measurements

THRESHOLDS FOR THE PHOTON STIMULATED DESORPTION (PSD) OF POSITIVE IONS FROM THE SURFACE OF AMORPHOUS AND CUBIC ZrO_2



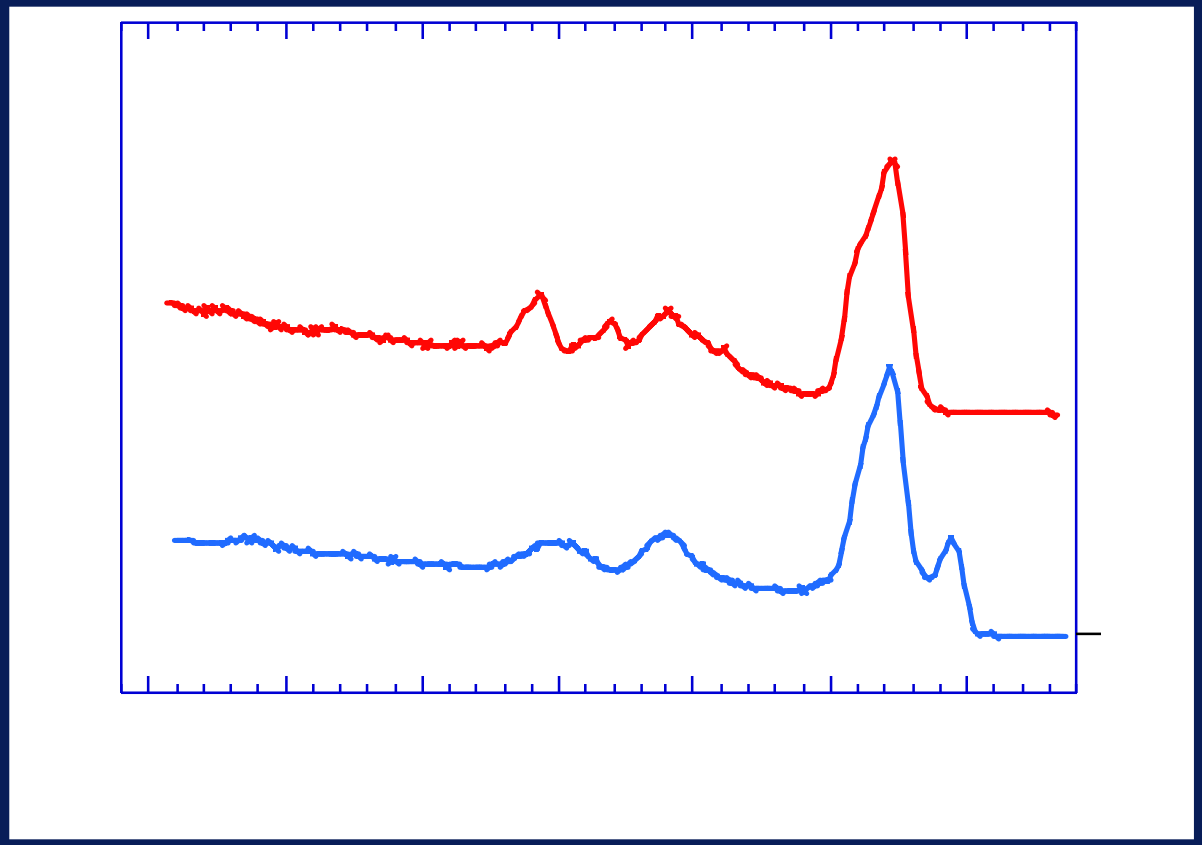
The data, representing the ion yield as a function of incident photon energy, are offset vertically for display. The size of the symbols represents the estimated uncertainty in the measurements

THE PHOTON STIMULATED DESORPTION (PSD) KINETIC ENERGY DISTRIBUTIONS OF POSITIVE IONS FROM THE SURFACE OF AMORPHOUS AND CUBIC ZrO_2



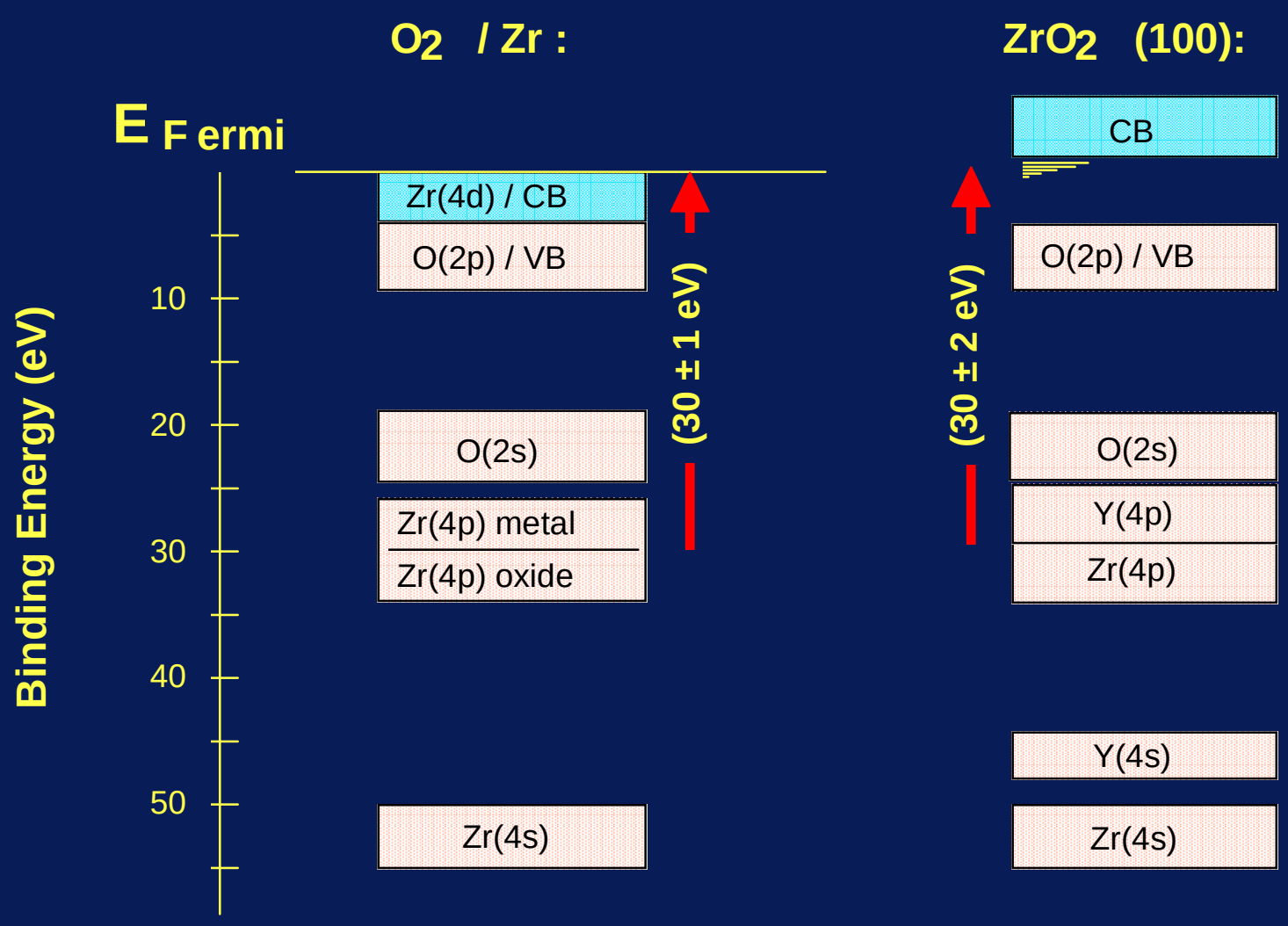
The data, representing the ion yield as a function of ion kinetic energy for a photon energy 70 eV, are offset vertically for display.

SOFT X-RAY PHOTOELECTRON SPECTRA OF THE SURFACE OF AMORPHOUS AND CUBIC ZrO_2, FOR A PHOTON ENERGY OF 100 eV

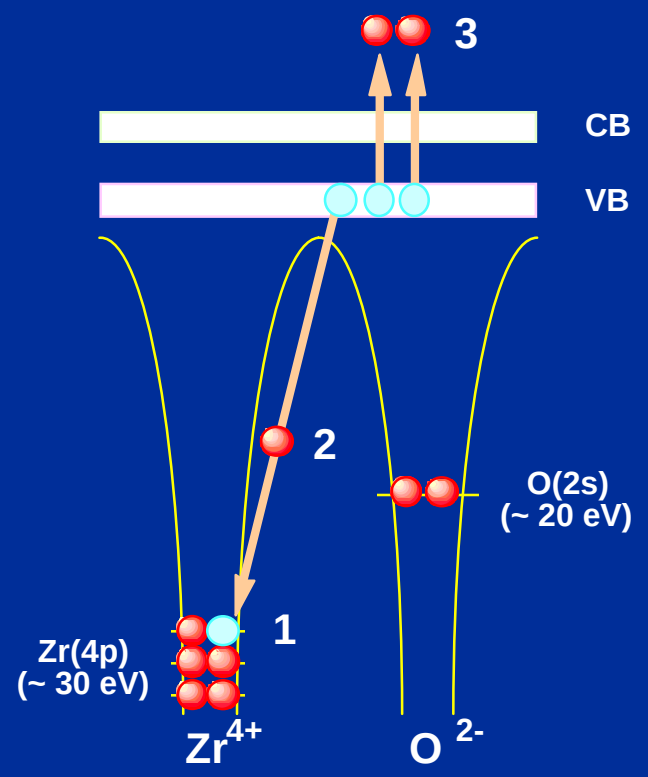


The data, representing the photoelectron yield per incident photon , are offset vertically for display.

ELECTRONIC STRUCTURE OF ZIRCONIUM OXIDE



Knotek-Feibelman Mechanism



1) ionization of cation core level
2) inter-atomic Auger decay
3) ejection of Auger electron(s)
4) reversal of the Madelung potential
5) ejection of O^{+} ion

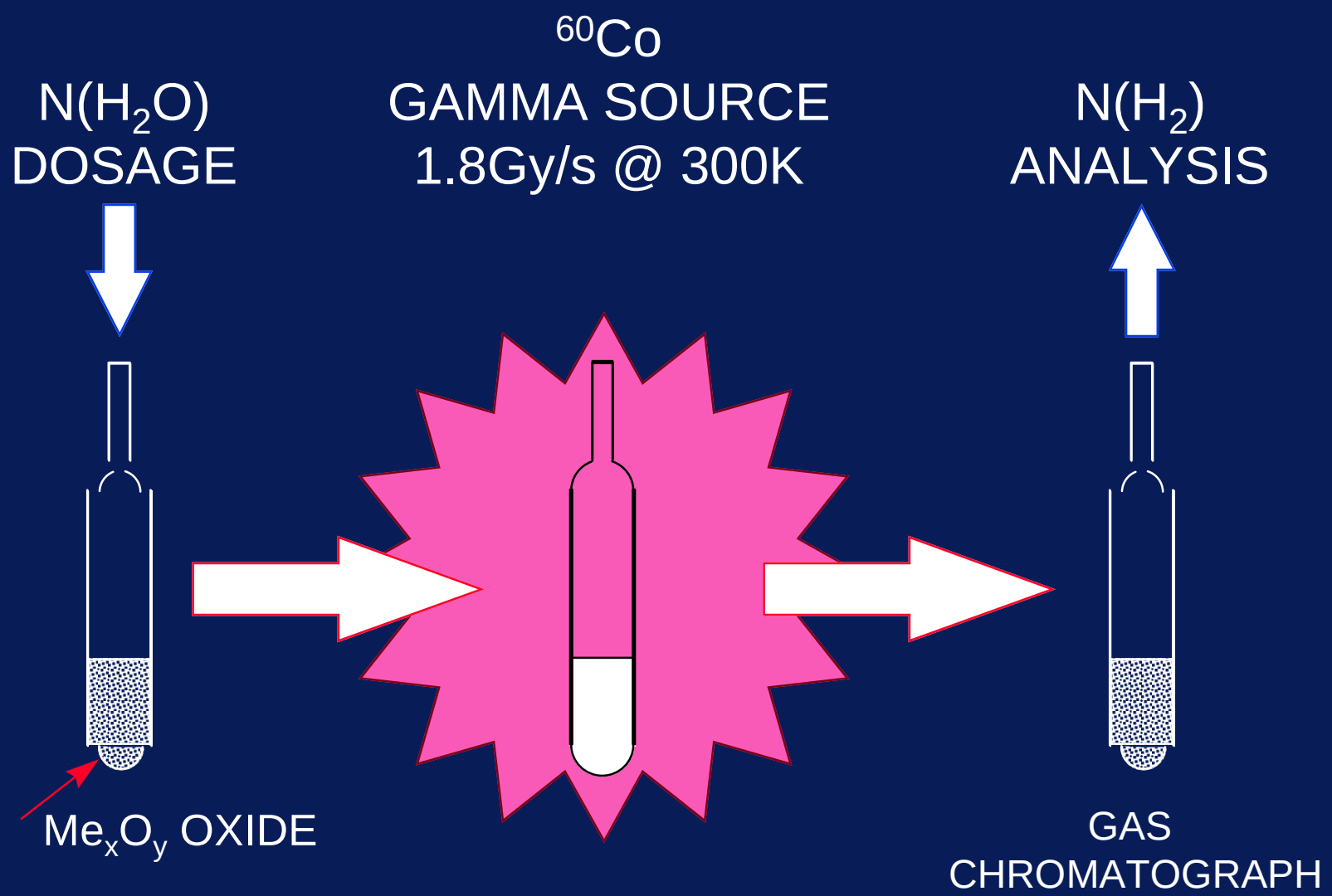
ZrO_2 DAMAGE MECHANISM:

Stimulated desorption of O^+ from ZrO_2 involves a multi-electron Auger decay process. (See *M. Knotek and P. Feibelman, Phys. Rev. Lett. 40, (1978) 964).*

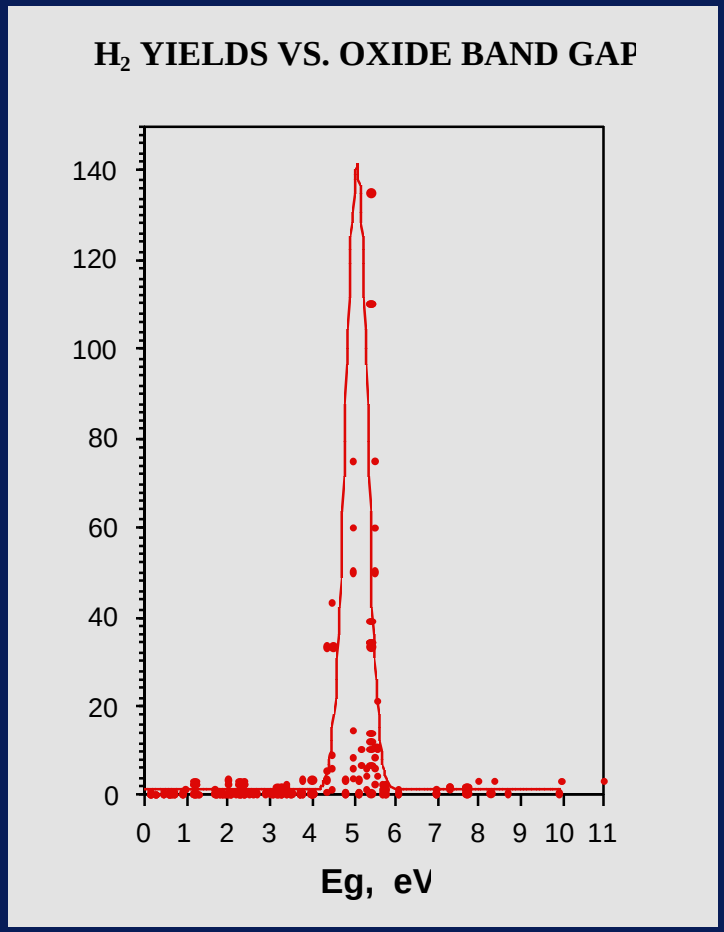
In this model, a Zr(4p) core hole, formed by the impact of an incident electron or photon, is filled by a valence electron residing on a neighboring oxygen atom. To conserve energy, one or two additional electrons are ejected from the same atom. Once formed, the O+ desorbs due to the reversed Madelung potential.

We are presently examining the neutral oxygen yields.

EXPERIMENTAL



- **HYDROGEN YIELDS FROM WATER ADSORBED ON DIFFERENT OXIDE SURFACE PLOTTED VS. OXIDE BAND GAP SHOW MAXIMUM NEAR 5 eV**
- **5.1 eV IS AN ENERGY OF H-OH BOND BREAKING IN WATER MOLECULE**



ACCORDING TO EFFECT ON THE H_2 YIELD OXIDES CAN BE CLASSIFIED INTO THREE GROUPS:

INHIBITORS : $G(H_2)=10^{-3}-10^{-1}$ $(100eV)^{-1}$

Oxides which lower the H_2 yield as compared with the radiolysis of pure gas-phase water:

MnO_2 , Co_3O_4 ,CuO and Fe_2O_3

INDIFFERENT : $G(H_2)=0.1-3$ $(100eV)^{-1}$

Oxides with H_2 yields which are similar to or slightly greater than radiolysis of pure gas-phase water:

MgO, CaO, SrO, BaO, ZnO, CdO, Cu_2O, NiO, Cr_2O_3 , $Cr(OH)_3$, Al_2O_3 , CeO_2 , SiO_2 , TiO_2 , Nb_2O_5 and WO_3

PROMOTERS : $G(H_2) > 3$ $(100eV)^{-1}$ (up to 100-130)

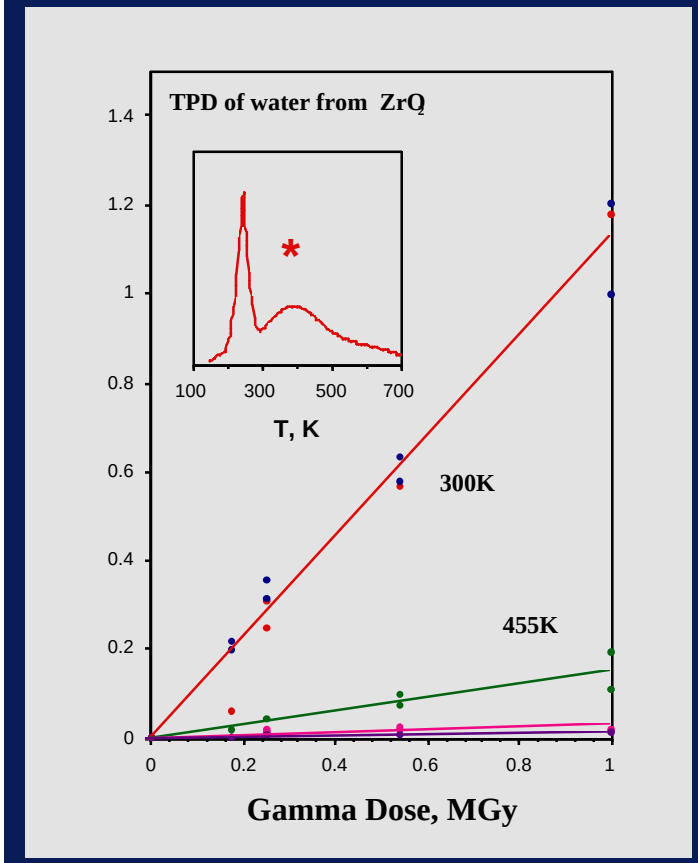
Oxides which increase the H_2 yield as compared with the radiolysis of pure gas-phase water:

Ga_2O_3 , Y_2O_3 , La_2O_3 , Nd_2O_3 , Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Yb_2O_3 , Er_2O_3 , HfO_2 and ZrO_2

NOTE: the G-values quoted above are defined in terms of the radiant energy adsorbed directly by the water molecules.

- **FOR ZrO_2 MORE THAN 80% OF ALL THE RELEASED HYDROGEN ARISES FROM THE CHEMISORBED WATER (TPD AT 300-450K)**
- **HYDROXYL GROUPS MAKE A NEGLIGIBLE CONTRIBUTION TO THE OBSERVED HYDROGEN YIELD.**
- **THE ENERGY TRANSFER OCCURS ONLY TO THE FIRST ADSORPTION LAYER OF WATER**
- **THIS IS A LOW ENERGY MECHANISM OF THE ENERGY TRANSFER**

Effect of ZrO_2 pre-heating on H_2 production kinetics



- **Er_2O_3 :** 1→2→4 monolayers of H_2O .Hydrogen yield decreases

Effect of the surface water concentration on the hydrogen yields from the Er_2O_3.

H_2O, molecule/nm^2	10	20	40
$G(H_2)$, molecule/100 eV absorbed by H_2O	135	33	12
$G(H_2)$, molecule/100 eV absorbed by Er_2O_3	0.05	0.03	0.02

- **ZrO_2 :** 0.1 →1 monolayer of H_2O .Hydrogen yield increases.

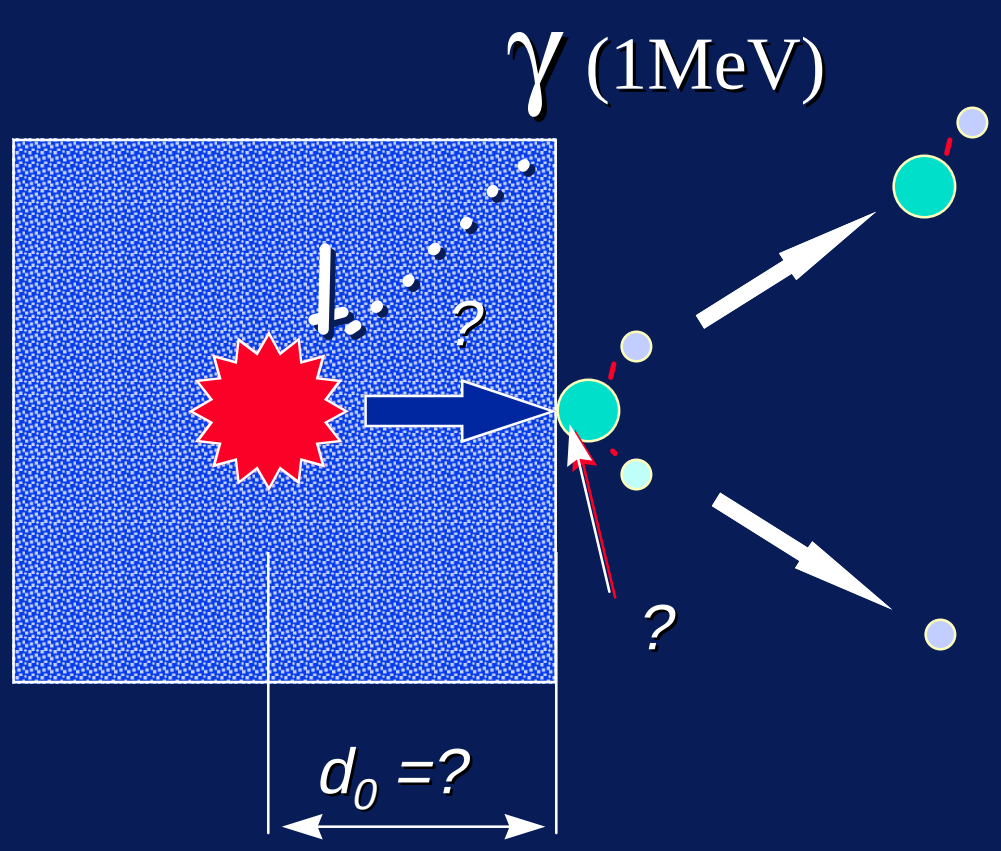
The first portions of the adsorbing water react with dehydroxylated surface producing "indifferent" hydroxyls

Dosing of water on the dehydroxylated surface of ZrO_2 powder.

H_2O dosed, molecule/nm^2	1.0 ± 0.1	5.0 ± 0.5
H_2 released, nmole after gamma irradiation:	1.0 MGy : < 0.2 1.5 Mgy : < 0.2	0.5 MGy : 156 0.75 Mgy : 540
$G(H_2)$, (100 eV)$^{-1}$	< 0.1	50 ± 10

ZrO_2 : Amounts of water desorbing at different temperatures after vacuum treatment at 473K : 4 molecule/nm^2 ; at 773K : 8 molecule/nm^2

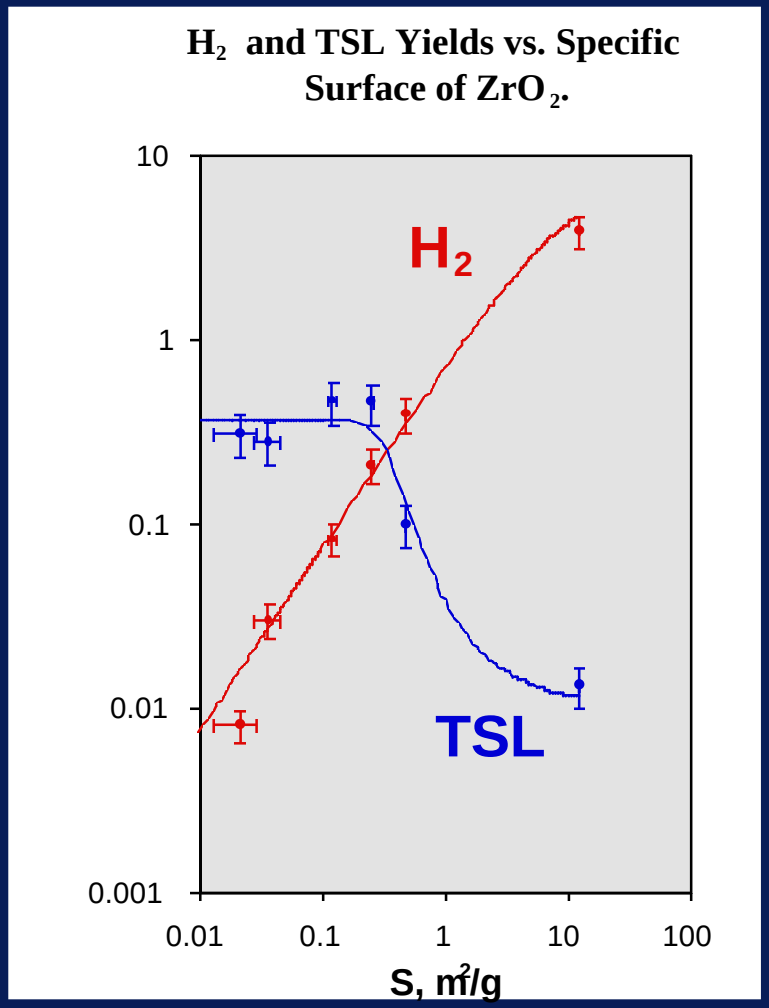
- **THE HIGHER G-VALUES (>3) ARE DUE TO EFFECTIVE ENERGY TRANSFER AT THE OXIDE-WATER INTERFACE**
- **THE STANDARD G-VALUE DEFINITION HAS TO BE MODIFIED WHEN DISCUSSING RADIOLYSIS AT INTERFACES**

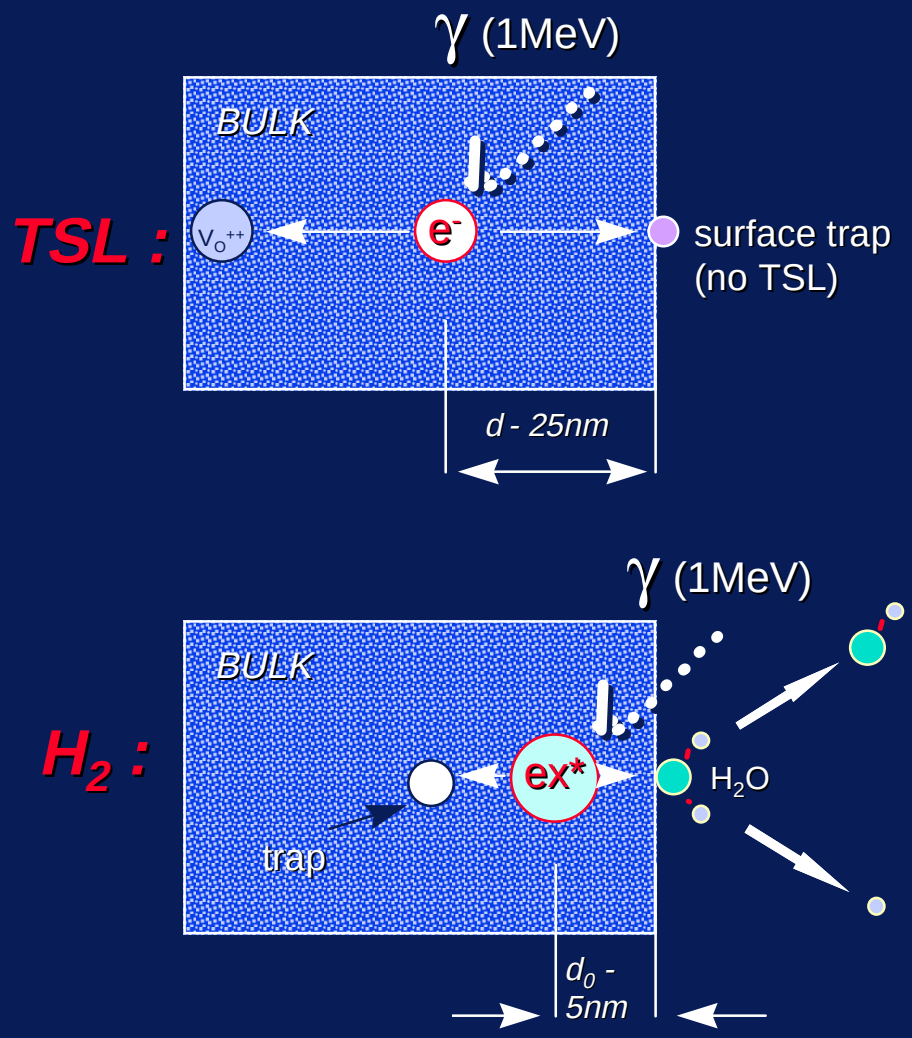


QUESTIONS:

- WHAT KIND OF PARTICLES OR EXCITATIONS TRANSFER THE ENERGY TO THE SURFACE?
- DISTANCE OF THE ENERGY MIGRATION?
- REACTION OF THE ADSORBED MOLECULE WITH MIGRATING PARTICLES OR EXCITATIONS?

- TSL AND HYDROGEN YIELDS HAVE DIFFERENT "CRYSTAL SIZE EFFECTS" AS RESULT OF COMPETITION BETWEEN THE INTERACTIONS OF ELECTRONIC EXCITATIONS WITH BULK AND SURFACE DEFECTS.
- DIFFERENT ELECTRONIC EXCITATIONS ARE INVOLVED IN BOTH PROCESSES





LOW ENERGETIC MECHANISMS PROPOSED IN LITERATURE TO EXPLAIN RADIOLYSIS IN HETEROGENEOUS SYSTEMS

LOW ENERGETIC MECHANISMS OF INTERFACIAL RADIOLYSIS

ENERGY MIGRATION TO THE SURFACE

- e^- and h^+
- e^- or h^+
- ex^*

REACTION WITH ADSORBATE ON THE SURFACE

Recombination

- $e^- + AB \rightarrow AB^- + h^+ \rightarrow AB^* \rightarrow A+B$
- $h^+ + AB \rightarrow AB^+ + e^- \rightarrow AB^* \rightarrow A+B$

Exciton Coupling

- $e^- + h^+ + S \rightarrow ex^*_S + AB \rightarrow AB^* \rightarrow A+B$
- $ex^* + AB \rightarrow AB^* \rightarrow A+B$

Coupling with Surface Defects

- $ex^* + S \rightarrow [F + V]_S + AB \rightarrow$ .....
- $e^- + S \rightarrow F_S + AB \rightarrow AB^- \rightarrow A+B^-$
- $h^+ + S \rightarrow V_S + AB \rightarrow AB^+ \rightarrow A^+ + B$

Dissociative Attachment

- $e^- + AB \rightarrow AB^- \rightarrow A + B^-$
- $h^+ + AB \rightarrow AB^+ \rightarrow A^+ + B$

MECHANISM OF THE ENERGY TRANSFER TO WATER MOLECULES:

$$\gamma(1MeV) + ZrO_2 \rightarrow ex^* (\sim 5eV)$$

$$ex^* (\sim 5eV) + H_2O_{ADS} \rightarrow H_2O^*(A^{3,1}B_1)_{ADS}$$

$$H_2O^*(A^{3,1}B_1)_{ADS} \rightarrow H + OH \text{ or } H_2 + O$$

PARAMETERS CONTROLLING THE ENERGY TRANSFER:

- THE OXIDE BAND GAP AND WATER ADSORPTION FORM

THE DISSOCIATION THRESHOLD OF THE H_2O_{ADS} COMPLEX SHOULD OVERLAP THE EXCITON ENERGY SPECTRUM

- ENERGY MIGRATION DISTANCE

THE ENERGY (EXCITON) MIGRATION DISTANCE SHOULD BE MUCH LONGER THAN CRYSTAL LATTICE PARAMETER TO PROVIDE HIGH EFFICIENCY OF THE WATER RADIOLYSIS IN COMPARISON TO HOMOGENEOUS PROCESS

MECHANISM FOR ENHANCEMENT OF INTERFACIAL WATER RADIOLYSIS

- Enhancement of H_2 production during irradiation of water in contact with oxides occurs due to the production of electronic excitations (excitons). Most of these excitations originate in the bulk but migrate to the surface.
-
- ZrO_2 is one of the most effective catalysts for radiolytic production of H_2. This is because the ZrO_2 exciton spectrum overlaps the dissociative excited states of adsorbed water molecules (~ 5 eV).

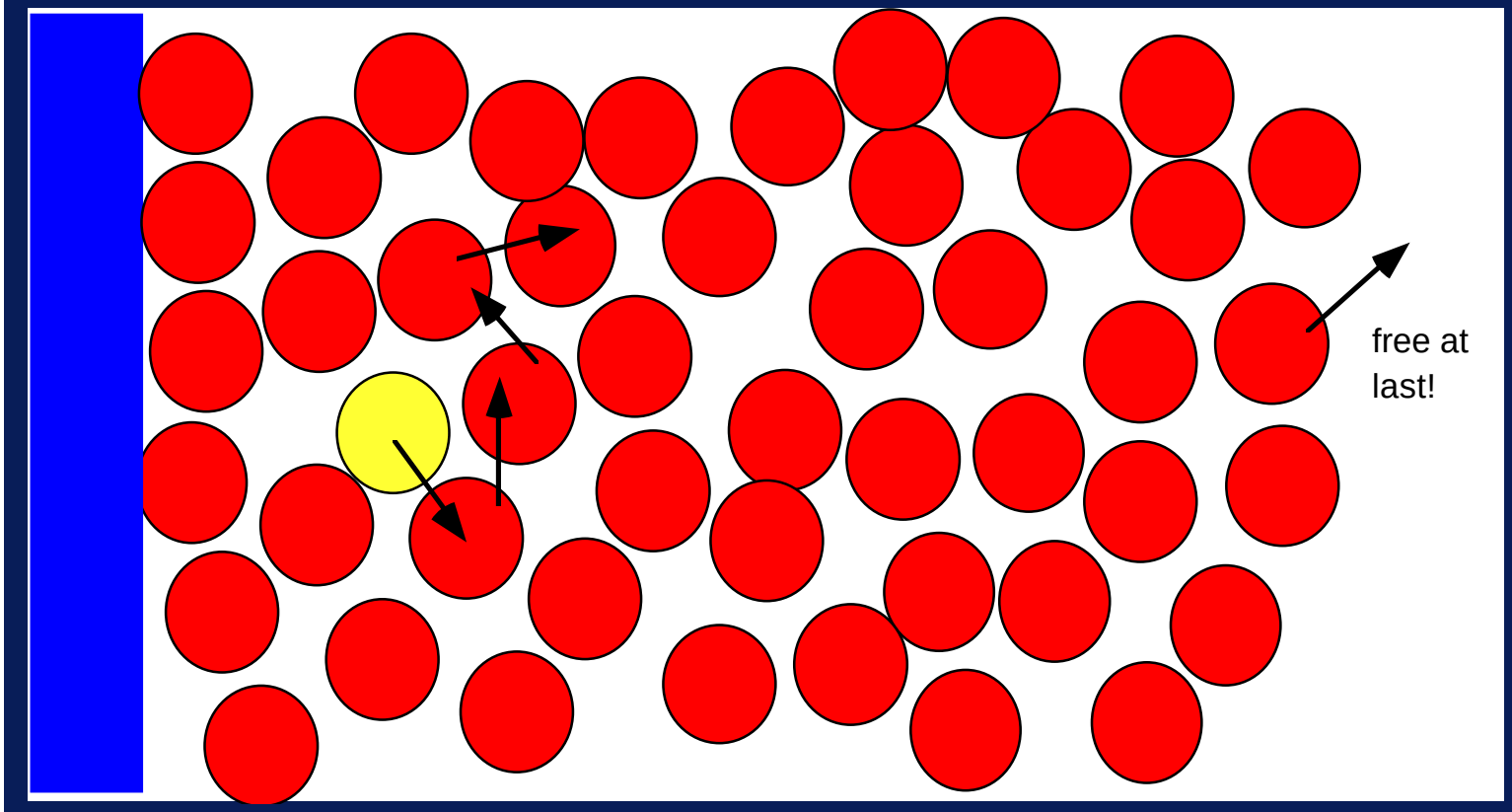
- Uranium oxides have low exciton energies (~ 1-2 eV) and may not promote water radiolysis.

DRYING of SPENT FUELS

ISSUES:

- PHASE DECOMPOSITION BEHAVIOR
- POWDER - PROBLEMS OF TRANSPORT
- SURFACE PHASES IMPORTANT
- THERMODYNAMIC CONSIDERATIONS NOT ENOUGH (must include kinetics and transport).

RE-ADSORPTION REQUIRES "REDRYING" PHASE



- the number of evaporations over d^2, is approximately

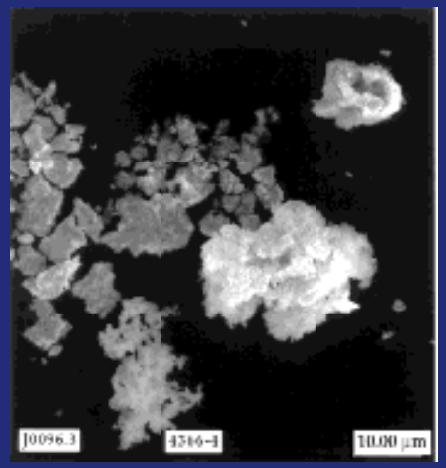
$\sim (L/d)^2$

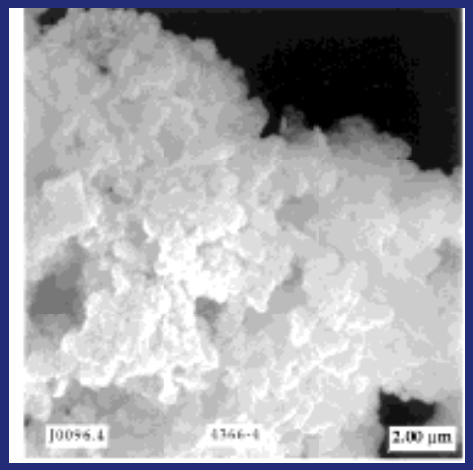
$\sim 10^8 - 10^{15}$

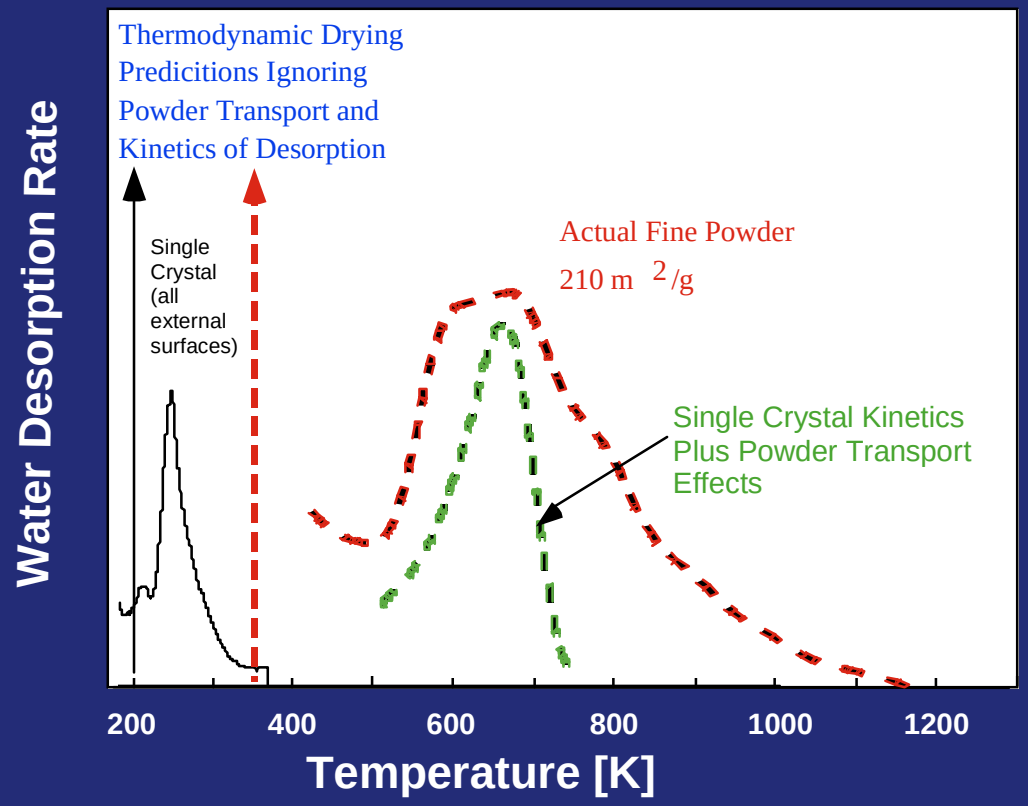
Fine Powders: Micrographs of Spent Fuel Sludge

Transport/Kinetics Effects

(using MgO data, U oxide data not available yet)







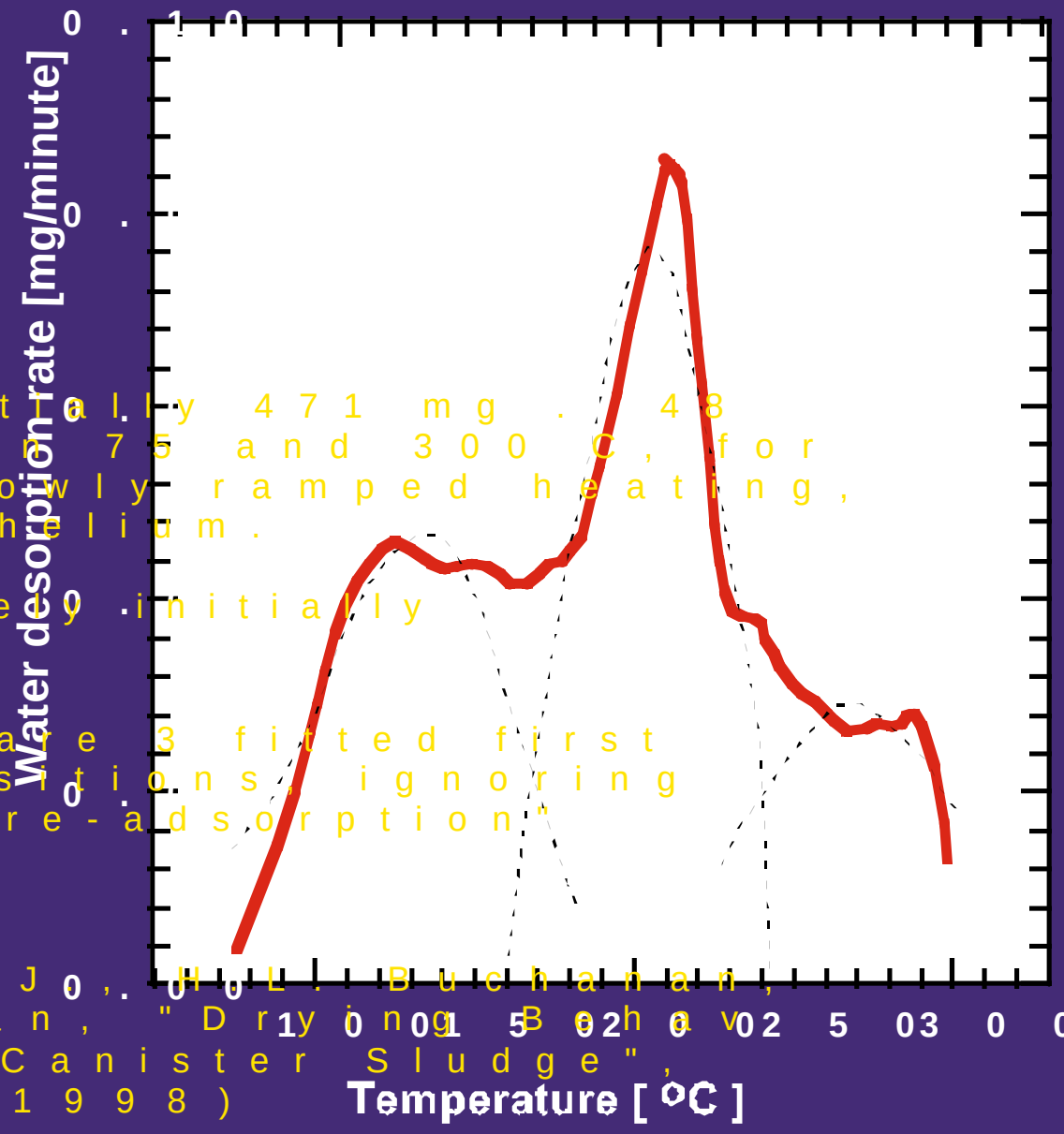
Thermal evolution of water from Hanford spent fuel rod "sludge" from K-Basin.

"Run 45" of initially 471 mg. 48 mg lost between 75 and 300 C, for 10 hours of slowly ramped heating, under .14 torr helium.

Material is largely initially $U_3O_2(OH)_2$

Dashed curves are 3 fitted first order decompositions, ignoring transport and "re-adsorption"

From Abrefah, J., H.L. Buchanan, S.C. Marsch-man, "Drying Behavior of K-East Canister Sludge", PNNL-11628 (1998)



ADVANTAGES FOR THE CHARACTERIZATION OF U OXIDES AS THIN FILMS

Can be safely handled as non-radioactive material.

Releasable from Radiological Control and usable in any apparatus.

Cheap and easily renewable.

Easily chemical tailored (UO_2 -> UO_3, etc.)

Simulates corrosion conditions.

Opportunity to do surface science experiments and to study nonburied interfaces between the thin oxide layer and its substrate.

THIN FILM GROWTH VIA VACUUM DEPOSITION

MAGNETRON SPUTTER DEPOSITION

[Gouder & Colmenares, 1993, 1995; Gouder et al., 1995; Gouder, 1997]

URANIUM THIN-FILMS HAVE BEEN GROWN ON Pt, Pd, AND GRAPHITE FOILS USING PURE U TARGETS AND PURE Ar AS THE BACKGROUND GAS.

DEPOSITION TIME: 1 - 60S.

Growth of U oxide thin films using a similar technique is in progress.

EVAPORATIVE DEPOSITION

[Miyake et al., 1990]

U ELECTRON-BEAM EVAPORATED ON NICKEL.

XPS → UO_2.

XRD ‡ UO_2 (VERY LOW CRYSTALLINITY)

UO_2 CHANGES TO U_3O_8 AT HIGHER T > 400 ^{o}C

THIN FILM GROWTH VIA WET CHEMICAL DEPOSITION

ELECTRODEPOSITION

[Katz & Rabinowitch, 1958; Levine & Lamanna, 1965]

1. ELECTRODEPOSITION OF UO_2 AND U_3O_8 FROM AQUEOUS SOLUTION OF URANYL (ANODE: ROTATING Pt, CATHODE: FIXED Cu).

U_3O_8 AFTER IGNITION.

2. ELECTRODEPOSITION OF U_3O_8 ON A Ni-PLATED Cu DISC FROM ALKALINE SOLUTION (DILUTE AMMONIUMOXALATE).

EFFICIENCY ABOUT 85-95 %.

IGNITION of $UO_2(NO_3)_2 6H_2O$

[website:http://www.uic.com.au/uicchem.htm; Smith et al., 1982; Benedict et al.,1981; Bordere et al., 1993]

URANYL NITRATE CONCENTRATED BY EVAPORATION AND HEATED STRONGLY TO PRODUCE UO_3.

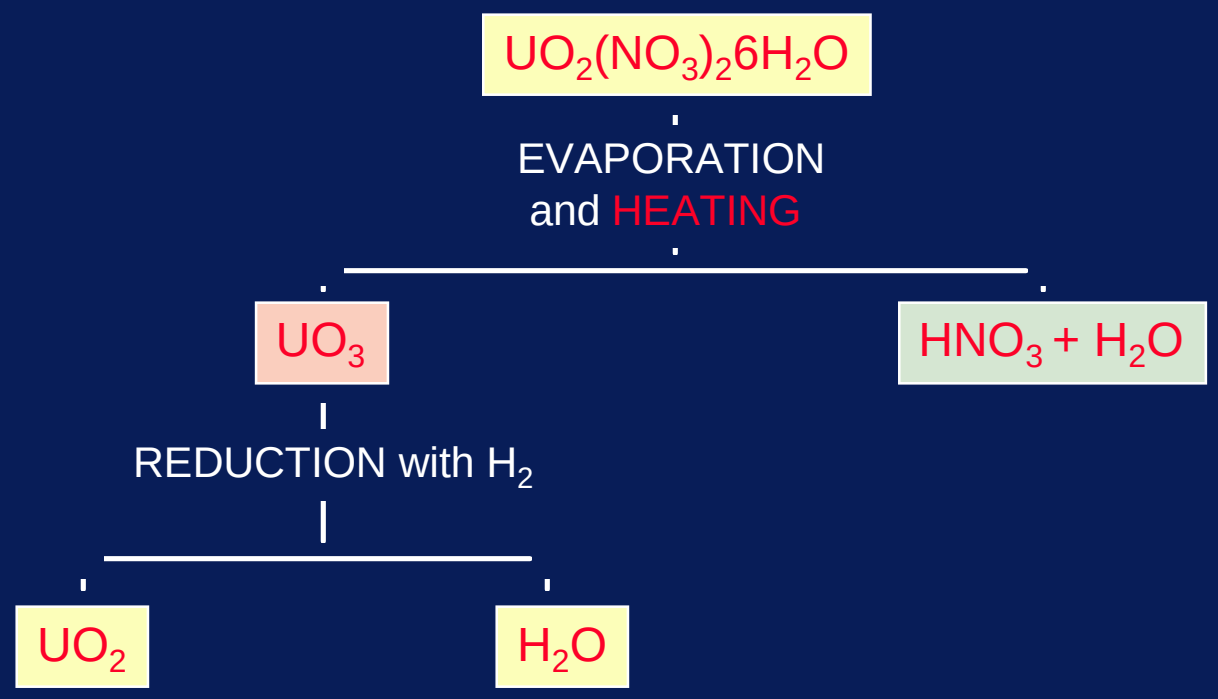
$UO_3 \rightarrow UO_2$ REDUCTION WITH H_2.

IGNITION of $UO_2(NO_3)_2\ 6H_2O$

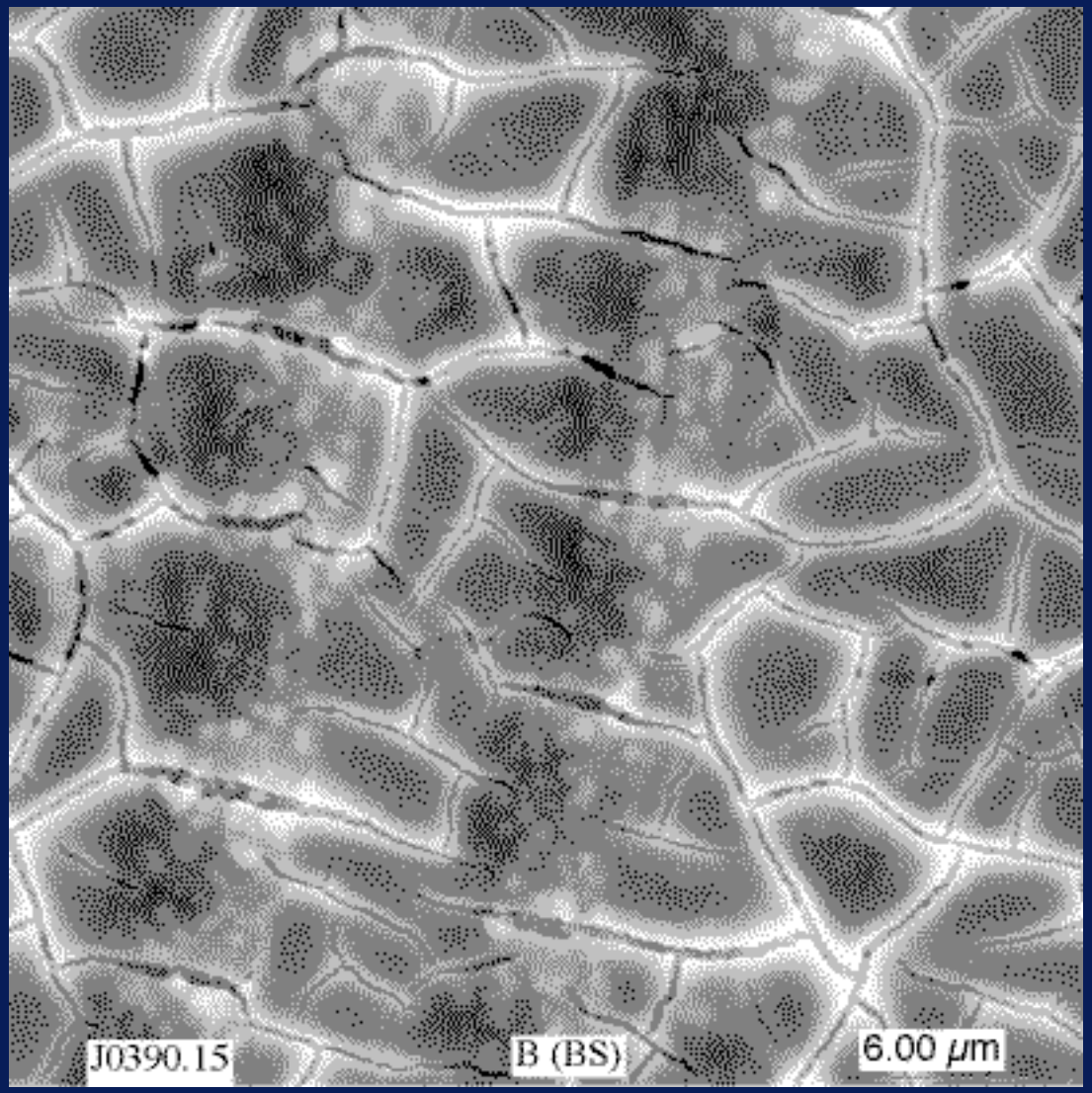
NET PROCESS:

$$UO_2(NO_3)_2 6H_2O \rightarrow UO_3 + 2HNO_3 + 5H_2O$$

$$UO_3 + H_2 \rightarrow UO_2 + H_2O$$



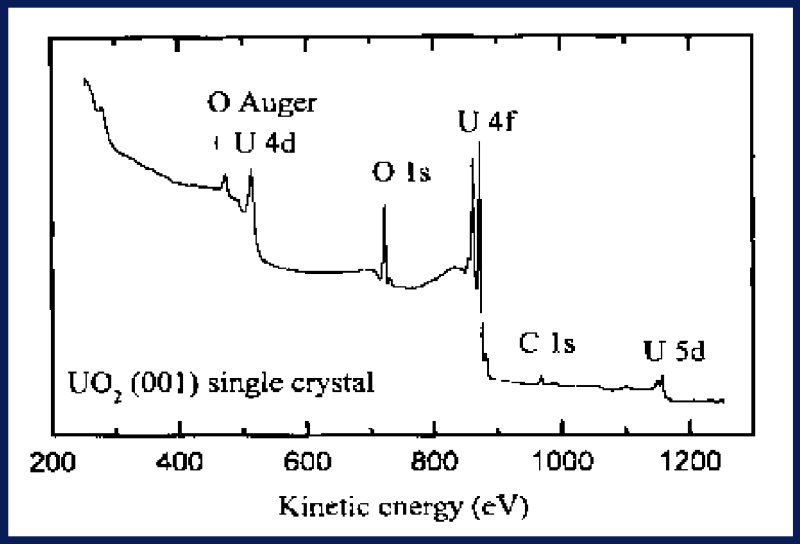
THIN FILM OF $UO_2(NO_3)_2 \bullet 6H_2O$ on W

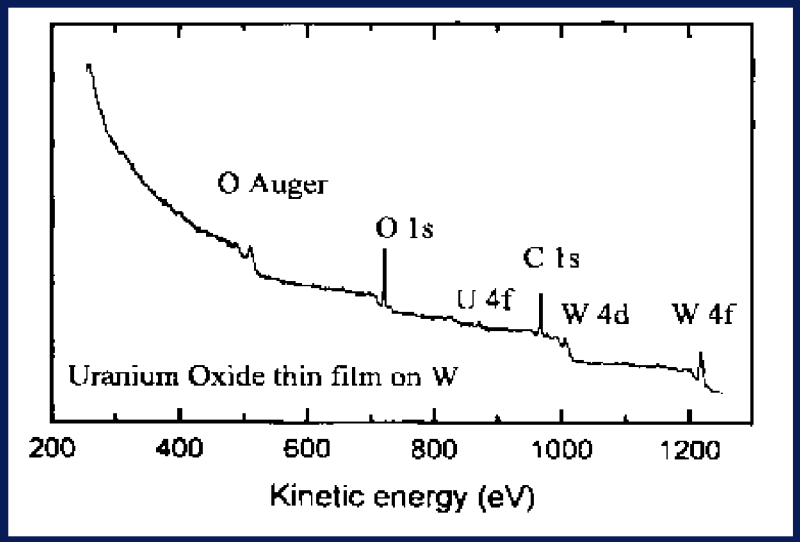


Notice shrinkage cracks in electron micrograph, probably from the loss of water in vacuum.

Also notice film is translucent to electrons.

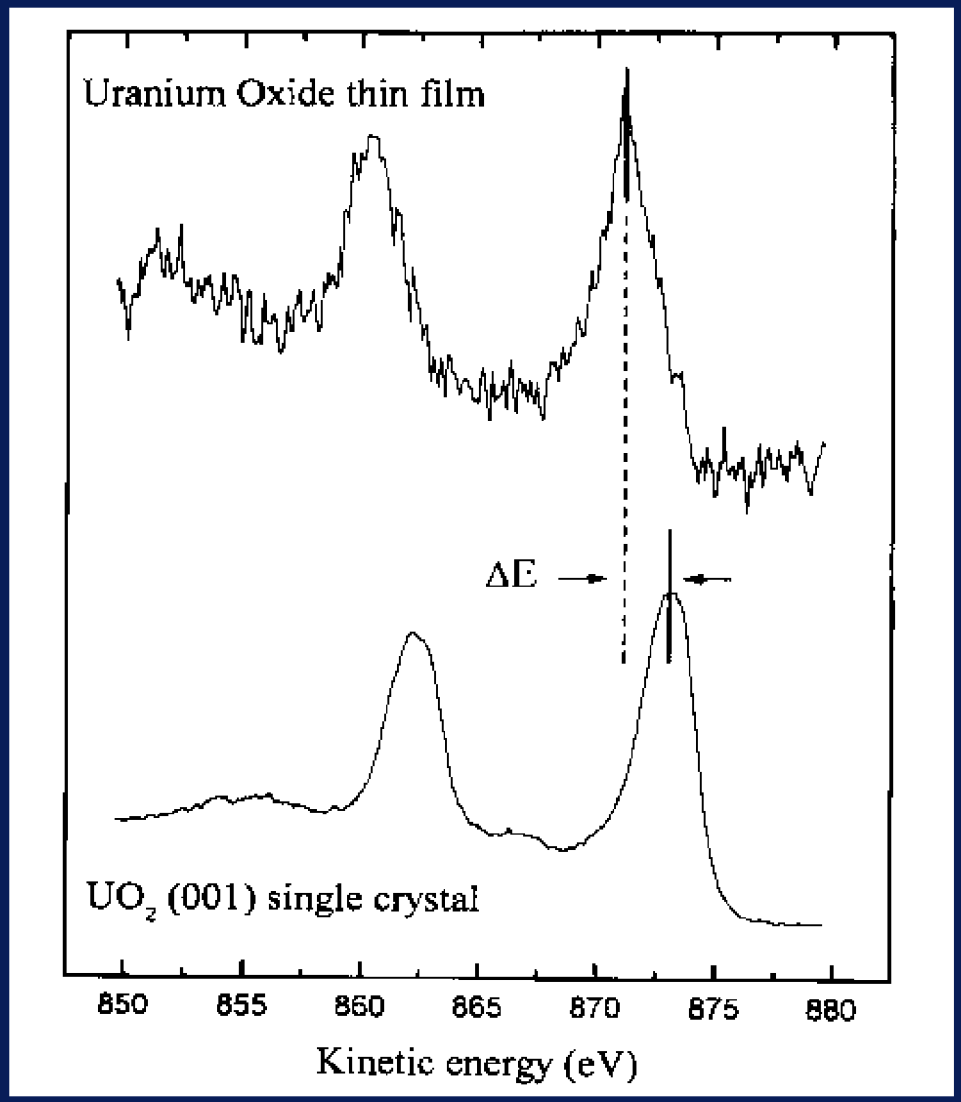
XPS SPECTRA FOR UO_2 (001) SINGLE CRYSTAL AND FOR URANIUM OXIDE THIN FILM DEPOSITED FROM SOLUTION ONTO OXIDIZED W.





The single crystal has been gently Ar-sputtered, and only a small carbon contaminant is seen.
The UO_x thin film features are obscured by a large background from the W substrate.

COMPARISON OF THE U $4f_{5/2,7/2}$ FEATURES FROM THE UO_2 (001) SINGLE CRYSTAL AND THE UO_X THIN FILM.



The chemical shift E ~ 2.5 eV indicates that the U in the film is more highly oxidized than the U in UO_2.

Future Activities

Electron- and photon-stimulated radiolysis of water covered ZrO_2, UO_2 and UO_3 interfaces.

Nuclear stimulated desorption studies of water/oxide interfaces.

Perfect uranium-oxide thin-film growth techniques.

Characterize water adsorption and desorption kinetics from UO_2 or UO_3 crystals, powders and thin films.

Develop a phenomenological model for interface radiolysis which can be used to help validate storage strategies.