

H₂ Production in the Radiolysis of Water on UO₂ and Other Oxides

Jay A. LaVerne^{*,†} and Lav Tandon[‡]

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556,
and Chemistry Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

Received: May 19, 2003; In Final Form: September 28, 2003

The production of H₂ in the γ -ray and 5 MeV helium ion radiolyses of water adsorbed on 0.4 and 1 μ m particles of UO₂ has been examined. The yields of H₂ determined with respect to the total energy deposited in the oxide–water system is 0.016 molecule/100 eV, which is about the same as similarly sized CeO₂ particles. Radiation chemical yields of H₂ increase substantially with decreasing number of adsorbed water layers when the yield is determined with respect to the energy deposited directly by γ -rays in the water. A yield of about 40 molecules of H₂ per 100 eV energy directly absorbed by four layers of water on UO₂ compared to 0.45 molecule/100 eV in bulk liquid water strongly suggests that energy is being transported from the oxide through the water interface. The results with UO₂ have been combined with data on ZrO₂ and CeO₂ to give H₂ yields for a wide range of water loading. H₂ is mainly produced from chemisorbed water in the γ -radiolysis of ZrO₂, and its yield decreases in the presence of O₂ to values comparable to those for UO₂ and CeO₂. The yields of H₂ in the 5 MeV helium ion radiolysis of water on UO₂, CeO₂, and ZrO₂ are similar, indicating that these materials may be suitable for estimating H₂ production in transuranic waste.

Introduction

The radiolytic decomposition of water adsorbed on oxide surfaces has many significant applications,¹ but knowledge on the fundamental effects is difficult to obtain because of several factors associated with the presence of the heterogeneous boundary. In addition to the standard radiolytic processes, energy, charge, or matter can be transferred through the interface while catalytic or steric effects can also alter the decomposition or reactivity of adsorbed molecules. The challenge is to determine if the radiolytic decomposition of water at or near the surface of an oxide is different from that in the bulk, and to understand the mechanisms responsible. While the basic radiation chemistry is very interesting, the practical aspects of the radiolysis of water on or near solid interfaces are equally important. Water chemistry at surfaces in the radiation fields of nuclear reactors can be different from that in the bulk liquid, and the self-radiolysis of water adsorbed on nuclear waste materials in sealed storage containers can lead to the formation of potentially explosive gases. The production of H₂ is especially important because enhancement of its yield can cause serious engineering and management problems.

Some of the earliest radiation chemistry literature report an enhancement in the radiolytic decomposition of adsorbed molecules compared to the liquid or gas state.^{2–5} Several recent and more detailed studies have focused on the production of H₂ in the radiolysis of water adsorbed on different surfaces.^{6–26} The mechanism for the production of H₂ in bulk liquid water has recently been proposed to include a mixture of intra-track radical and ionic processes.^{27,28} Intra-track processes are important up to about 1 μ s following the passage of a γ -ray in liquid water, and the yield of H₂ at this time is 0.45 molecule/100 eV of total energy absorbed.^{27,29} The high local density in the α -particle radiolysis of water increases intra-track processes

to give a yield of H₂ of about 1.2 molecules/100 eV.^{28,29} For comparison, the yield of H₂ from the γ -radiolysis of water adsorbed on BeO is as high as 4.4 molecules/100 eV energy adsorbed by the entire system.⁸ More recently, the yield of H₂ has been determined to be as high as 150 molecules/100 eV energy absorbed directly by the water layers adsorbed on ZrO₂.²⁵ Clearly, one or more processes can lead to an enhanced formation of H₂ from water irradiated on or near oxide surfaces.

The exact mechanism for the enhanced yield of H₂ in the radiolysis of adsorbed water is still unknown. Excess electrons in the water phase are observed in the pulsed radiolysis of aqueous dispersions of SiO₂.^{30,31} Combination reactions of these excess electrons are suggested as a source of excess H₂.³² Dissociative electron attachment of low-energy electrons, recombination of electron–hole pairs, and exciton reactions are all possible mechanisms for excess H₂ production in the radiolysis of adsorbed water.^{23,24,33–36} All of these processes and others can be contributing in various magnitudes to the radiolytic formation of H₂ from adsorbed water. The results reported in this work will give a little more information toward solving the mechanism of H₂ production in the radiolysis of water adsorbed on ceramic oxide surfaces.

In this work, the formation of H₂ in the radiolysis of water adsorbed on UO₂, CeO₂, and ZrO₂ particles is examined. The amount of water loading and the atmospheric gas were varied to determine their effects on H₂ formation. The results in an inert argon atmosphere are compared with recently published data on CeO₂ and ZrO₂ particles in similar environments.²⁵ The present work extends the data to a new oxide, UO₂, and increases the range of water loading by examining a sample CeO₂ with a large surface area. Experiments were performed with water adsorbed on UO₂, CeO₂, and ZrO₂ in an oxygen atmosphere to help elucidate reaction mechanisms. Oxygen is a very good radical and charge scavenger. From a practical point of view, the presence of H₂ and O₂ at certain ratios can lead to deflagration of sealed waste storage containers.³⁷ The irradiations

[†] University of Notre Dame.

[‡] Los Alamos National Laboratory.

were performed with both γ -rays and 5 MeV helium ions (α -particles) in order to examine the effect due to the linear energy transfer (LET = stopping power, $-dE/dx$) of the radiation. LET has a significant influence on the production of H_2 in bulk water by varying the concentration of precursors and thereby any second-order reactions involving them.²⁹ The results reported here give fundamental knowledge related to the mechanism for the formation of H_2 from the radiolysis of water adsorbed on oxide surfaces and provide useful information for the management of nuclear waste materials.

Experimental Section

Two lots of isotopically depleted (99.8 wt % ^{238}U) uranium oxide powder were obtained from Los Alamos National Laboratory and assayed to be 99.9% pure. Oxide composition was determined to be 87.9 wt % U; that is, the oxide is predominately UO_2 . The CeO_2 (99.9%) powder was obtained from Alfa Aesar. Particle area measurements were determined on a Quantachrome Autosorb 1 surface area analyzer using the BET (Brunauer–Emmett–Teller) method of surface area calculation. Specific areas of the powders were determined to be 0.51 and 1.24 m^2/g for UO_2 and 8.07 m^2/g for CeO_2 . The densities of the oxides are 10.96 g/cm^3 for UO_2 and 7.13 g/cm^3 for CeO_2 . Perfect spheres have a specific area equal to $6/\rho d$, where ρ is the oxide density and d is the diameter. The estimated particle diameters are 1073 and 442 nm for UO_2 and 104 nm for CeO_2 , respectively. The other CeO_2 (2.92 and 4.18 m^2/g) and ZrO_2 (1.99 m^2/g) powders examined here are from the same manufacturing lots as used and characterized previously.²⁵

The CeO_2 and ZrO_2 powders were normally baked at 500 °C for 48 h to remove adsorbed water and any hydrocarbon contaminants. In a few specific cases discussed below, the ZrO_2 was baked for longer periods of time. The UO_2 powders were dried at 100 °C for 48 h under vacuum. A relatively milder condition for drying the UO_2 was chosen in order to minimize oxidation of the oxide to UO_3 or U_3O_8 . The oxides were cooled under vacuum, weighed, and placed in a constant humidity chamber. Several different relative humidity chambers were used, and each was maintained at a constant humidity using a salt slush.³⁸ The salts used in this work and their relative humidity at 25 °C are the following: LiCl , 11.30%; $\text{Mg}(\text{NO}_3)_2$, 52.89%; NaCl , 75.29%; and KCl , 84.34%.³⁹ Water was from a Millipore Milli-Q UV system, and water alone was used to obtain a relative humidity of about 95%. The oxides were periodically removed from the constant relative humidity chambers and weighed to determine total water adsorbed. The average area of a water molecule was assumed to be 0.22 mg/m^2 based on studies with PuO_2 .⁴⁰ This value is not expected to be significantly different for the oxides examined here. The number of water layers on the particle surface was determined from the fraction of water loading as determined by weight and the average area covered per water molecule. For example, a 0.27 wt % water loading on a 0.51 m^2/g UO_2 particle corresponds to 24 water layers (0.27 g of $\text{H}_2\text{O}/(100 \text{ g of } \text{UO}_2 \times 0.51 \text{ m}^2/\text{g of } \text{UO}_2 \times 0.00022 \text{ g of } \text{H}_2\text{O}/\text{m}^2)$. Water probably does not adsorb monolayer by monolayer in an orderly manner, but the calculations give useful mean values that can be used as guides.

The heavy ion radiolysis experiments were performed using the facilities of the Nuclear Structure Laboratory of the University of Notre Dame Physics Department. The 10 MeV FN Tandem Van de Graaff in this facility was used to accelerate ^4He ions to an energy of 5 MeV incident to the sample. Absolute dosimetric techniques were used as in the previous study on

oxides and detailed elsewhere.^{41,42} Energy loss of the helium ions in passing through all windows was determined from a standard stopping power compilation.⁴³ The samples were irradiated with completely stripped ions at a charge beam current of about 2 nA. Sample cells similar to those in a previous study²⁵ were used and the range of the helium ions ($\sim 0.013 \text{ mm}$) is smaller than the sample thickness, so the ions are completely stopped in the sample. The radiation chemical yields represent all processes from the initial particle energy to zero and are therefore track-averaged yields. However, only a small portion of the total sample is actually irradiated ($\phi = 6.4 \text{ mm}$, $L \sim 0.013 \text{ mm}$), so the local dose rate is about 2 kGy/s . The use of absolute dosimetry directly gives the total energy deposited in the entire sample. The particles are small relative to the beam diameter and randomly distributed, so the partition of energy between the oxide and the adsorbed water is assumed to be equal to the relative electron densities as determined by the weight fraction of each compound and its total number of electrons. Irradiations were performed at room temperature (23 °C) and the dose rate was sufficiently small so that no significant macroscopic heating was observed.

Radiolysis with γ -rays was performed using a Shepherd 109 ^{60}Co source at the Radiation Laboratory of the University of Notre Dame. The sample cell and dosimetric technique are the same as in the previous study.²⁵ The dose rate was about 150 Gy/min as determined using the Fricke dosimeter.⁴⁴ The Fricke dosimeter gives the amount of energy deposited per gram of each target material relative to that for water. Energy absorbed by the water is directly obtained from the dosimetry and weight of the water in the sample. Energy absorption by the total sample was estimated from the weight of both the oxide and water using a 10% higher dose rate than given by the Fricke dosimeter to allow for effects due to high Z materials.²⁵ Total sample weights were typically 1–2 g. The production of H_2 was below the lower detection limit in the self-radiolysis of the UO_2 samples on the time scale of a typical experiment.

Hydrogen was determined using an inline technique with an SRI 8610C gas chromatograph with a thermal conductivity detector. Certain experiments monitored the formation of O_2 by sampling some of the effluent from the thermal conductivity detector with a quadrupole mass spectrometer (Balzers, QMA140 analyzer with axially mounted secondary electron multiplier) through a capillary tube ($\phi = 25 \text{ }\mu\text{m}$, $L = 20 \text{ cm}$). Ultrahigh purity argon or oxygen was used as the carrier gas with flow rates of about 50 mL/min . The sample and chromatographic configuration were as previously described, including using a four-way valve for sample purging and isolation.²⁵ Calibration of the detector was performed by injecting pure gases with a gastight microliter syringe. The estimated error in gas measurement is about 5%.

Results and Discussion

Water Adsorption on the Oxides. Moisture and any residual hydrocarbons were removed from the oxides by baking. The CeO_2 and ZrO_2 are stable and could be baked to 500 °C for days. Milder conditions, 100 °C for 48 h in a vacuum, were used for UO_2 in order to prevent oxidation of the oxide to UO_3 or U_3O_8 . The lack of a color change and no variation in the surface area suggested that the UO_2 was not oxidized under these conditions, but a small amount of chemisorbed water could remain on the oxide surface. The oxides were cooled in a vacuum, weighed, and transferred to constant humidity chambers to allow water to adsorb on the surfaces. Periodically, the oxides were removed from the chambers and reweighed to determine water adsorption from the weight gain.

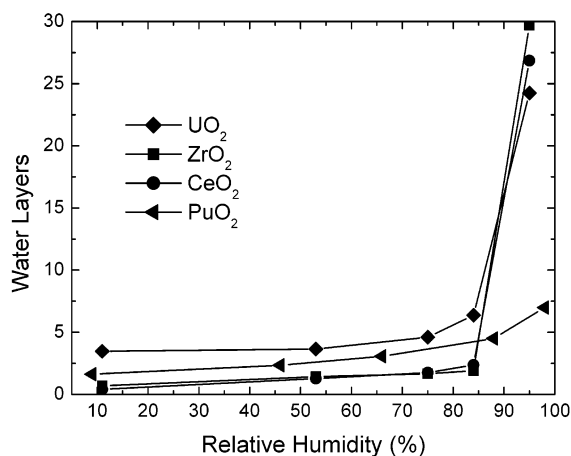


Figure 1. Number of water layers as a function of relative humidity: (◆) UO₂ at 0.51 m²/g, this work; (■) ZrO₂ at 1.99 m²/g, ref 25; (●) CeO₂ at 4.18 m²/g, ref 25; (▲) PuO₂ at 9.5 m²/g, ref 45.

Previous experiments have shown that the rates of adsorption and desorption of water on CeO₂ and ZrO₂ are relatively slow,²⁵ and similar results are found with the UO₂ in this work. Several days are required for adsorbed water to reach equilibrium and several hours for that water to be desorbed. Equilibrium between adsorption and desorption is assumed to occur when the weight of the oxide and adsorbed water remains constant. Figure 1 shows the equilibrium number of water layers adsorbed on the different oxides as the relative humidity varies from 11 to 95%. All the values for UO₂ and the data at the lowest relative humidity for CeO₂ and ZrO₂ are from this work, while the PuO₂ and other data are from the literature.^{25,45} For conversion to other units, 100% relative humidity at 25 °C corresponds to a vapor pressure of 23.75 mmHg or about 3.1% of the atmosphere. The lowest water loading could be in error by 30% because of the small sample size (~2 g) and the accuracy of the analytical balance.

The equilibrium number of water layers at low relative humidity is nearly independent of the relative humidity for each oxide and varies from about 1 water layer for CeO₂ to 4 water layers for UO₂. Very high humidity (>85%) is required for multiple water layers to accumulate on CeO₂, ZrO₂, and UO₂. One study on the adsorption of water on PuO₂ also shows the accumulation of multiple water layers at relative humidity above 85%.⁴⁶ This high humidity region probably represents the adsorption of water in macropores on the surface. The results suggest that for practical applications associated with the management of waste materials a working environment of a few percent to 85% relative humidity will result in a relatively constant number of water layers being formed. In opposite terms, the weight percent of water gain can be used to give a rough estimate of surface area. A few water layers correspond to less than 0.1% of the total weight for particles of the size examined in this work so that the initial deposition of energy by ionizing radiation is predominately in the solid oxide in these systems.

γ-Radiolysis. The formation of H₂ induced by the passage of ionizing radiation in bulk water is still not completely understood, but scavenging experiments show that the hydrated electron and its precursors have a dominant role.^{27,28} Dissociative recombination of the water molecular cation and the precursor to the hydrated electron occurs on the order of a few hundred femtoseconds and is responsible for a large fraction of H₂ production.²⁸ Reactions of hydrated electrons and H atoms occurring from a few hundred picoseconds to about 1 μs are responsible for most of the rest of H₂ production in γ-radiolysis,

although other processes such as dissociative electron attachment may also be important.^{29,33,34} The time scales of these reactions are very dependent on the nonhomogeneous distribution of reactive species, i.e., their concentration, produced by the ionizing radiation. Time scales of reaction can be shifted considerably with different types of radiation, but by about 1 μs following the passage of a γ-ray, the track or string of spurs induced by the radiation has dissipated and the radiolytic products are homogeneously distributed in the medium.⁴⁷ In the γ-radiolysis of water, the microsecond radiation chemical yield of H₂ is about 0.45 molecule/100 eV of energy absorbed.²⁷ Radiation chemical yields, *G*-values, are expressed as the number of molecules of H₂ (or other product) formed per 100 eV of energy adsorbed in the region of interest.

The main oxidizing product in the γ-radiolysis of liquid water is not O₂, but H₂O₂.^{29,47} Only H₂ was observed in the γ-radiolysis of UO₂ in agreement with earlier studies on CeO₂ and ZrO₂.²⁵ Any O₂ produced in the radiolysis of these oxides has a yield at least an order of magnitude less than that of H₂. A high ratio of H₂ to O₂ was similarly observed with CeO₂ and ZrO₂.²⁵ PuO₂,²⁶ and wet UO₂.⁴⁸ The stable oxidizing product in the radiolysis of bulk water is H₂O₂; however, it is difficult to imagine H₂O₂ being solvated in the few water layers available. Separate experiments have found that the addition of ZrO₂ to H₂O₂ solutions results in rapid peroxide decomposition to give O₂.⁴⁹ The rate of H₂O₂ decay is dependent on the relative amount of solid oxide surface present, but the decay should be within the irradiation time period in the experiments performed here. Therefore, H₂O₂ is highly unlikely to be formed in conjunction with H₂ from the radiolysis of water adsorbed on UO₂ as well as CeO₂ and ZrO₂. Studies on the low-energy electron radiolysis of ice find O atoms and this species could be produced in the present situation.⁵⁰ The self-radiolysis of water adsorbed on PuO₂ is proposed to incorporate oxygen into the bulk oxide leading to the oxidation of Pu(IV) to Pu(VI); oxygen could also be bound to the particle surface in these studies.⁵¹ There have been several studies suggesting the oxidation of UO₂ to either UO₃ or U₃O₈ following α- or γ-radiolysis of water in contact with nuclear fuel.^{48,52–57} Peroxides are found in natural UO₂ deposits and are thought to be formed by self-irradiation in the presence of water.⁵⁸ Any of these oxidation processes or others could be responsible for the lack of observable O₂ production in the radiolysis of water adsorbed on UO₂, but further analysis is beyond the scope of the present study.

An understanding of the processes occurring with the different oxides can be obtained by examining the H₂ yields relative to the total energy loss in the oxide and water system. For particles of the sizes examined here, almost all of the energy is deposited in the oxide. The observed H₂ yields with respect to the energy absorbed by both the oxide and water are shown in Figure 2 as a function of the weight percent of water on UO₂. Previous data²⁵ for ZrO₂ and CeO₂ are included in Figure 2 along with new data for CeO₂ with a large surface area and water loading. It should be stressed that the *G*-values of Figure 2 are determined relative to the total energy deposited in the system (oxide and water). Above about 0.5% water loading, the H₂ yields steadily increases with the addition of water, giving a near universal response for several sized particles of UO₂ and CeO₂. The results for H₂ production from UO₂ at very low water loading seem to be slightly higher than suggested by the results for CeO₂. However, the UO₂ was dried under relatively mild conditions to avoid oxidation of the uranium. Residual water, especially chemisorbed water, probably remains on the oxide surface and

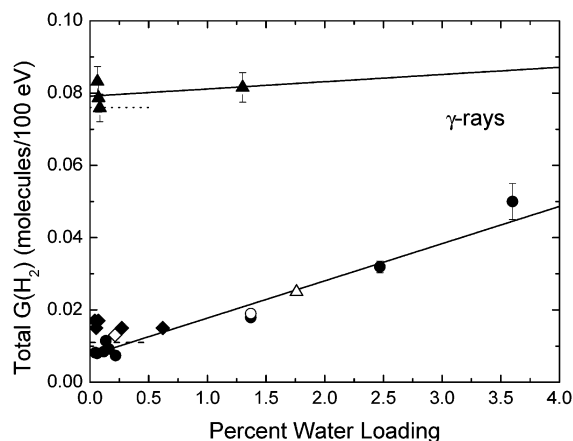


Figure 2. Production of H₂ relative to amount of total energy deposited by γ -rays as a function of the weight percent of water on the oxides: (◆) UO₂, this work; (●) CeO₂, this work and ref 25; and (▲) ZrO₂, ref 25. Closed symbols are for an argon atmosphere, and open symbols are for an oxygen atmosphere. The dotted line is the limiting yield for chemisorbed water on ZrO₂, and the dashed line is the limiting yield for less than a monolayer of water on CeO₂.

the measured G -values correspond to slightly higher water loading than plotted in Figure 2.

The H₂ yields from the γ -radiolysis of water on ZrO₂ are about 8 times larger than those for UO₂ and CeO₂ at low water loading. A strong argument has been made that some, but not all, oxides with a band gap at about 5 eV exhibit an excess in H₂ production over that observed with oxides having different band gap energy.²⁴ The proposed mechanism is the formation and migration of an exciton in the bulk oxide, which couples in a resonant process with the adsorbed water to give "excess" H₂. This "excess" H₂ is observed in the γ -radiolysis of water on ZrO₂ and gives yields above that due to the transfer of energy from the oxide to water at the interfaces of UO₂ and CeO₂; see Figure 2. Reports in the literature suggest that the band gap for UO₂ and oxides of other actinides are more similar to CeO₂ than to ZrO₂, which is supported by the H₂ yields given here.^{59–64} The radiation yields of H₂ observed here support the conclusion that CeO₂ and UO₂ are good surrogates for oxides of transuranic elements with respect to the radiolysis of adsorbed water.

An attempt was made to probe the identity of the reactants passing through the oxide–water interface that lead to the formation of H₂. Excitons, electrons, and other energy carriers can be scavenged by the presence of suitable solutes in the liquid. However, the addition of solutes to water adsorbed on the surface would be difficult and they would certainly alter characteristics of the system. One of the simplest methods for modifying the system is to change the inert argon atmosphere to O₂. Molecular oxygen is a good scavenger of electrons and excitons. No effect was observed on the H₂ yields in the radiolysis of UO₂ and CeO₂ systems in an O₂ atmosphere compared to an argon one. However, the G -value for H₂ in the γ -radiolysis of water on ZrO₂ in an O₂ atmosphere decreased to about the value expected for UO₂ and CeO₂; see Figure 2. The species responsible for the "excess" H₂ production in ZrO₂ reacts with O₂, giving a little more knowledge on its identity.

Another method to characterize the nature of the transients leading to H₂ formation is to determine if reaction is occurring predominately in relatively free physisorbed water, or at the water–oxide interface with chemisorbed water. Water chemisorbed on oxide surfaces will decompose to form surface hydroxides because of the more favorable energy configura-

tion.⁶⁵ Chemisorbed water could have different radiolytic properties than bulk water, and it should be able to react with transients from the solid oxide that migrate to the interface, but not through it into the outer water layers. An attempt was made to measure H₂ yields with only chemisorbed water by controlled drying of the oxides. Experiments found that ZrO₂ could be dried at 500 °C for up to 48 h to give a H₂ yield of 0.076 molecules/100 eV, shown by the dotted line in Figure 2. This result agrees well with the extrapolated results from higher water loading. These drying conditions are likely to leave only chemisorbed water and indicate that these molecules are responsible for most of the H₂ in the radiolysis of ZrO₂. On the other hand, all water was driven from CeO₂ with relatively mild drying conditions. No H₂ was observed in the radiolysis of CeO₂ heated to 500 °C for 24 h, or ZrO₂ heated to 500 °C for 72 h corresponding to the complete loss of all water. Low relative humidity gives a fraction of a water monolayer on CeO₂, and H₂ yields were determined to be 0.011 molecule/100 eV from the oxide in equilibrium with water at 11% relative humidity. This G -value probably represents the limiting H₂ yield at the lowest water levels on most oxides. The relatively poor precision in the data is due to the uncertainties in water levels, and the extremely small G -values.

Water is strongly chemisorbed on ZrO₂, and the radiolytic decay of that water produces significantly more H₂ than the other two oxides examined here. Previous work suggested that excitons are responsible for H₂ production in ZrO₂.²⁴ There is the possibility that the higher H₂ yields with ZrO₂ are due to exciton formation and migration to the oxide–water interface, where strongly chemisorbed water is more likely to decompose to H₂ than loosely bound or physisorbed water. This work does not preclude that other species besides excitons can lead to H₂ formation. The decomposition of water bound at the interface would probably result in oxygen species attached to the oxide surface. This binding would explain the negligible production of O₂ in these systems. The identification of radiolytically produced species on the oxide surface and the use of selective surface probe molecules will be required to further resolve the radiation chemistry occurring at these surfaces.

The production of H₂ from the radiolysis of water adsorbed on the surface of UO₂ was also examined as a function of the energy directly absorbed in the water layer. Energy deposited directly in the water layer should give a G -value for H₂ of 0.45, and any significant deviation in this value would be due to the heterogeneous effect of the oxide boundary. The G -value for the formation of H₂ from water in equilibrium with UO₂ at 95% relative humidity is about 5.5 when determined with respect to the amount of energy directly deposited in the adsorbed water. More than 20 water layers are present at this relative humidity, and the radiolytic H₂ yield is an order of magnitude greater than in bulk water. The large increase in yield over that expected from bulk water agrees well with many of the other studies on H₂ formation from adsorbed water.^{24–26,32} Clearly, the increase in H₂ formation can be significant at the heterogeneous interface of water and some solid ceramic oxides. The enhanced yield of H₂ observed here is solely due to a radiolytic effect. Successive irradiations of the same dose produced identical amounts of H₂, suggesting the yield is linear up to doses of about 50 kGy. Adsorbed water left in contact with UO₂ without external irradiation did not produce any detectable gaseous product, suggesting that self-radiolysis can be ignored with these oxide samples because they are isotopically depleted.

The dependence of H₂ on the fraction of water loading was determined in the γ -radiolysis of UO₂. H₂ yields determined

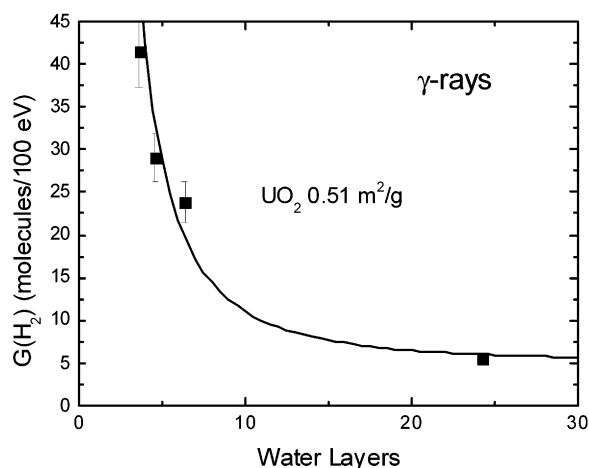


Figure 3. Production of H₂ relative to amount of energy directly deposited by γ -rays in the water adsorbed on UO₂ as a function of the number of water layers. The yield of H₂ in bulk water is 0.45 molecules/100 eV, ref 27.

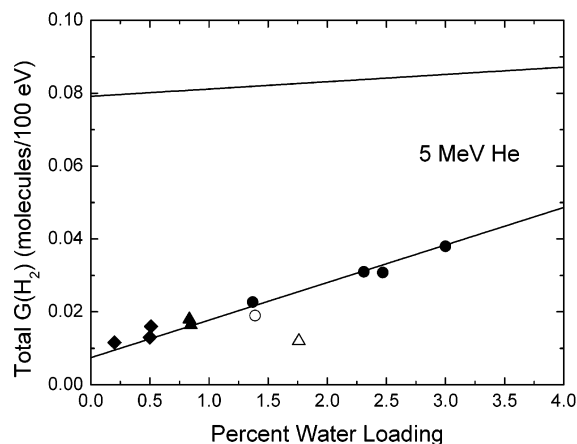


Figure 4. Production of H₂ relative to amount of total energy deposited by 5 MeV ⁴He ions as a function of the weight percent of water on the oxides: (◆) UO₂, this work; (●) CeO₂, this work and ref 25; and (▲) ZrO₂, ref 25. Closed symbols are for an argon atmosphere, and open symbols are for an oxygen atmosphere. The solid lines are the γ -radiolysis results from Figure 2.

relative to the energy absorbed directly in the water are found to increase with decreasing number of water layers. Figure 3 shows the results for H₂ yields as a function of the number of water layers in the γ -radiolysis of UO₂. The H₂ yield of about 40 molecules/100 eV for four water layers is 2 orders of magnitude greater than that found in bulk water. Experiments with two sizes of particles show no apparent difference due to the oxide surface area, only on the amount of water loading. A *G*-value of 50 corresponds to 2 eV per molecule of H₂ formation, which is energetically impossible. Clearly, a mechanism exists for the transport of energy from the bulk oxide to the water layer leading to an apparent increase in H₂ yields when *G*-values are calculated according to the energy directly absorbed by the water.

5 MeV He Ion Radiolysis. The results for the 5 MeV helium ion radiolysis of water on UO₂, CeO₂, and ZrO₂ are shown in Figure 4 as a function of the percent water loading. The solid lines in the figure are the same lines as in Figure 2. These H₂ yields are determined with respect to the total energy deposited in the system (oxide and water). In all cases, the water is in equilibrium at 95% relative humidity. It can be seen that there is virtually no difference between the H₂ yields in the γ -radiolysis or the helium ion radiolysis of water adsorbed on UO₂

and CeO₂. On the other hand, the H₂ yields for ZrO₂ show a marked decrease in helium ion radiolysis compared to the γ -radiolysis. The results for the three different oxides of various sizes suggest that H₂ yields in the 5 MeV helium ion radiolysis of adsorbed water are independent of the type of particle. Such a result justifies the use of CeO₂ and UO₂ as surrogate materials for the prediction of H₂ yields from radioactive waste.

Experiments were performed in an oxygen atmosphere instead of the inert argon one. The presence of O₂ had very little effect on H₂ yields from CeO₂, but did decrease the H₂ yields from ZrO₂. These results are similar to that observed with γ -radiolysis and indicate that the precursor to "excess" H₂ from water on ZrO₂ is slightly different than the other oxides. Frenkel defects due to the displacement of an atom to form an interstitial/vacancy pair are especially common with heavy ions because of the large relative momentum transfer possible in nuclear collisions.^{66,67} The local density of Frenkel defects in a heavy ion track is much greater than found in γ -radiolysis and leads to considerable self-trapping of excitations, the potential precursor to H₂.^{68,24} A further characterization of the surface of these oxides will be required to resolve the mechanism of H₂ formation. Information on the binding of O₂ and other oxygen species at the oxide surface will be especially useful.

Conclusions

These experiments have examined the production of H₂ in the radiolysis of water adsorbed on up to micron-sized particles of UO₂. Radiation chemical yields of H₂ increase substantially with decreasing number of adsorbed water layers when the yield is determined with respect to the energy deposited directly by γ -rays in the water. These H₂ yields reach values of 40 molecules/100 eV for four water layers on UO₂. The corresponding yield for H₂ in liquid and gaseous water is only about 0.45 molecule/100 eV, indicating that energy is being transferred through the oxide–water interface. This transfer of energy through phases implies that simple dosimetry based on direct energy deposition in the different phases is not appropriate. For instance, an estimation of H₂ production in sealed waste containers will be grossly underestimated based on calculations of energy deposition directly in the water phase alone.

The yields of H₂ determined with respect to the total energy deposited in both the oxide and water were found to increase with increased water loading, and they are virtually the same for UO₂ and CeO₂. At very low water loading, the radiolysis of ZrO₂ with γ -rays produces about 8 times more H₂ than UO₂ or CeO₂ does. In all of the experiments, the O₂ yield was at least an order of magnitude less than that of H₂. Most of the H₂ produced in radiolysis of water on ZrO₂ appears to come from chemisorbed molecules, and the transients are sensitive to the presence of excess O₂. The yield of H₂ in the 5 MeV helium ion radiolysis of water on UO₂ and CeO₂ is the same as with γ -rays, but the results with ZrO₂ are substantially lower and similar to that of the other oxides. A change in LET affects second-order reactions, so these results suggest that such processes in the bulk oxide can quench the precursor responsible for the large H₂ yields from water on ZrO₂.

Acknowledgment. The authors thank Professor Ani Aprahamian for making the facilities of the Notre Dame Nuclear Structure Laboratory available. The latter is funded by the National Science Foundation. The 94-1 Program from Los Alamos National Laboratory of the U.S. Department of Energy supported the work described herein. The DOE Nuclear Materials Stewardship Program, through the Nuclear Materials Project

Office in the Albuquerque Operations Center, supports the 94-1 Program. The authors also thank John Fitzpatrick and Julie Bremser of Los Alamos National Laboratory for providing the depleted uranium oxides and performing particle size and surface area characterization, respectively. This contribution is NDR-4453 from the Notre Dame Radiation Laboratory, which is supported by the Office of Basic Energy Sciences of the U.S. Department of Energy.

References and Notes

- (1) Understanding the Role of Water on Electron-Initiated Processes and Radical Chemistry; U.S. Department of Energy Workshop, Sept 26–28, 2002, Richland, WA.
- (2) Caffrey, J. M., Jr.; Allen, A. O. *J. Phys. Chem.* **1958**, *62*, 33.
- (3) Sutherland, J. W.; Allen, A. O. *J. Am. Chem. Soc.* **1961**, *83*, 1040.
- (4) Rabe, J. G.; Rabe, B.; Allen, A. O. *J. Am. Chem. Soc.* **1964**, *86*, 3887.
- (5) Rabe, J. G.; Rabe, B.; Allen, A. O. *J. Phys. Chem.* **1966**, *70*, 1098.
- (6) Garibov, A. A.; Melikzade, M. M.; Bakirov, M. Ya.; Ramazanov, M. Kh. *High Energy Chem.* **1982**, *16*, 101.
- (7) Rustamov, V. R.; Bugaenko, L. T.; Kurbanov, M. A.; Kerimov, V. K. *High Energy Chem.* **1982**, *16*, 148.
- (8) Garibov, A. A.; Melikzade, M. M.; Bakirov, M. Ya.; Ramazanov, M. Kh. *High Energy Chem.* **1982**, *16*, 177.
- (9) Garibov, A. A. *Proceedings of the Fifth Symposium on Radiation Chemistry*; Dobo, J., Hedvig, P., Schiller, R., Eds.; Akademiai Kiado: Budapest, 1983; p 377.
- (10) Garibov, A. A.; Bakirov, M. Ya.; Velibekova, G. Z.; Elchiev, Ya. M. *High Energy Chem.* **1984**, *18*, 398.
- (11) Nechaev, A. *Radiat. Phys. Chem.* **1986**, *28*, 433.
- (12) Aleksandrov, A. B.; Gusev, A. L.; Petrik, N. G. *Russ. J. Phys. Chem.* **1987**, *61*, 102.
- (13) Garibov, A. A.; Gezalov, Kh. B.; Velibekova, G. Z.; Khudiev, A. T.; Ramazanov, M. Kh.; Kasumov, R. D.; Agaev, T. N.; Gasanov, A. M. *High Energy Chem.* **1987**, *21*, 416.
- (14) Nakashima, M.; Tachikawa, E. *J. Nucl. Sci. Technol.* **1987**, *24*, 41.
- (15) Gezalov, K. B.; Gasanov, A. M.; Garibov, A. A.; Abdullayeva, K. I. *Radiat. Phys. Chem.* **1988**, *32*, 615.
- (16) Garibov, A. A.; Velibekova, G. Z.; Kasumov, R. D.; Gezalov, Kh. B.; Agaev, T. N. *High Energy Chem.* **1990**, *24*, 174.
- (17) Garibov, A. A.; Parmon, V. N.; Agaev, T. N.; Kasumov, R. D. *High Energy Chem.* **1991**, *25*, 86.
- (18) Garibov, A. A.; Agaev, T. N.; Kasumov, R. D. *High Energy Chem.* **1991**, *25*, 337.
- (19) Aleksandrov, A. B.; Bychkov, A. Yu.; Vall, A. I.; Petrik, N. G.; Sedov, V. M. *Russ. J. Phys. Chem.* **1991**, *65*, 847.
- (20) Garibov, A. A.; Velibekova, G. Z.; Agaev, T. N.; Dzhaferov, Ya. D.; Gadzhieva, N. N. *High Energy Chem.* **1992**, *26*, 184.
- (21) Nakashima, M.; Aratono, Y. *Radiat. Phys. Chem.* **1993**, *41*, 461.
- (22) Nakashima, M.; Masaki, N. M. *Radiat. Phys. Chem.* **1996**, *47*, 241.
- (23) Petrik, N. G.; Alexandrov, A. B.; Orlando, T. M.; Vall, A. I. *Trans. Am. Nucl. Soc.* **1999**, *81*, 101.
- (24) Petrik, N. G.; Alexandrov, A. B.; Vall, A. I. *J. Phys. Chem. B* **2001**, *105*, 5935.
- (25) LaVerne, J. A.; Tandon, L. *J. Phys. Chem. B* **2002**, *106*, 380.
- (26) Vladimirova, M. V.; Kulikov, I. A. *Radiokhimiya* **2002**, *44*, 83.
- (27) Pastina, B.; LaVerne, J. A.; Pimblott, S. M. *J. Phys. Chem. A* **1999**, *103*, 5841.
- (28) LaVerne, J. A.; Pimblott, S. M. *J. Phys. Chem. A* **2000**, *104*, 9820.
- (29) Allen, A. O. *The Radiation Chemistry of Water and Aqueous Solutions*; Van Nostrand: New York, 1961.
- (30) Schatz, T.; Cook, A. R.; Meisel, D. *J. Phys. Chem. B* **1998**, *102*, 7225.
- (31) Dimitrijevic, N. M.; Henglein, A.; Meisel, D. *J. Phys. Chem. B* **1999**, *103*, 7073.
- (32) LaVerne, J. A.; Tonnies, S. E. *J. Phys. Chem. B* **2003**, *107*, 7277.
- (33) Rowntree, P.; Parenteau, L.; Sanche, L. *J. Chem. Phys.* **1991**, *94*, 8570.
- (34) Kimmel, G. A.; Orlando, T. M.; Vezina, C.; Sanche, L. *J. Chem. Phys.* **1994**, *101*, 3282.
- (35) Cobut, V.; Jay-Gerin, J.-P.; Frongillo, Y.; Pataua, J. P. *Radiat. Phys. Chem.* **1996**, *47*, 247.
- (36) Klyachko, D. V.; Rowntree, P.; Sanche, L. *Surf. Sci.* **1997**, *389*, 29.
- (37) Eller, P. G.; Mason, R. E.; Horrell, D. R.; McKee, S. D.; Rink, N. A.; Leasure, C. S. *Gas Pressurization from Calcined Plutonium Oxides*; Report LA-UR-99-3804; Los Alamos National Laboratory: Los Alamos, NM, 1999.
- (38) American Society for Testing Materials E104-85; 1996. Standard Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions.
- (39) *CRC Handbook of Chemistry and Physics*, 77th ed.; Chemical Rubber Company: Boca Raton, FL, 1996–1997; p 15-24.
- (40) Haschke, J. M.; Ricketts, T. E. *J. Alloys Compd.* **1997**, *252*, 148.
- (41) LaVerne, J. A.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91*, 5770.
- (42) LaVerne, J. A.; Schuler, R. H. *J. Phys. Chem.* **1987**, *91*, 6560.
- (43) Ziegler, J. F.; Biersack, J. P.; Littmark, U. *The Stopping Power and Range of Ions in Solids*; Pergamon: New York, 1985.
- (44) Pastina, B.; LaVerne, J. A. *J. Phys. Chem. A* **1999**, *103*, 1592.
- (45) Benhamou, A.; Beraud, J. P. *Analysis* **1980**, *8*, 376.
- (46) Stakebake, J. L.; Dringman, M. R. Report RFP-1056, the Dow Chemical Company, Rocky Flats Division, Golden, CO, 1968.
- (47) LaVerne, J. A. *Radiat. Res.* **2000**, *153*, 487.
- (48) Eriksen, T. E.; Eklund, U.-B.; Wermel, L.; Bruno, J. J. *Nucl. Mater.* **1995**, *227*, 76.
- (49) Hiroki, A.; LaVerne, J. A. Unpublished results.
- (50) Kimmel, G. A.; Orlando, T. M. *Phys. Rev. Lett.* **1995**, *75*, 2606.
- (51) Haschke, J. M.; Allen, T. H.; Morales, L. A. *Science* **2000**, *287*, 285.
- (52) Christensen, H.; Sunder, S.; Shoesmith, D. W. *J. Alloys Compd.* **1996**, *213/214*, 93.
- (53) Sunder, S.; Miller, N. H. *J. Nucl. Mater.* **1996**, *231*, 121.
- (54) Taylor, P.; Hocking, W. H.; Johnson, L. H.; McEachern, R. J.; Sunder, S. *Nucl. Technol.* **1996**, *116*, 222.
- (55) Wronkiewicz, D. J.; Bates, J. K.; Wolf, S. F.; Buck, E. C. *J. Nucl. Mater.* **1996**, *238*, 78.
- (56) Sunder, S.; Shoesmith, D. W.; Miller, N. H. *J. Nucl. Mater.* **1997**, *244*, 66.
- (57) Sattouy, G.; Ardois, C.; Corbel, C.; Lucchini, J. F.; Barthe, M.-F.; Garrido, F.; Gosset, D. *J. Nucl. Mater.* **2001**, *288*, 11.
- (58) Burns, P. C.; Hughes, K.-A. *Am. Miner.* **2003**, *88*, 1165.
- (59) Strehlow, W. H.; Cook, E. L. *J. Phys. Chem. Ref. Data* **1973**, *2*, 163.
- (60) Young, R. A. *J. Nucl. Mater.* **1979**, *87*, 283.
- (61) Gubanov, V. B.; Rosen, A.; Ellis, D. E. *J. Phys. Chem. Solids* **1979**, *40*, 17.
- (62) Naito, K.; Tsuji, T.; Ouchi, K.; Yahata, T.; Yamashita, T.; Tagawa, H. *J. Nucl. Mater.* **1980**, *95*, 181.
- (63) Winter, P. W. *J. Nucl. Mater.* **1989**, *161*, 38.
- (64) Dudarev, S. L.; Castell, M. R.; Botton, G. A.; Savrasov, S. Y.; Muggelberg, C.; Briggs, G. A. D.; Sutton, A. P.; Goddard, D. T. *Micron* **2000**, *31*, 363.
- (65) Boehm, H. P. *Discuss. Faraday Soc.* **1971**, *52*, 264.
- (66) Kotomin, E. A.; Popov, A. I. *Nucl. Inst. Methods Phys. Res. B* **1998**, *141*, 1.
- (67) Chadderton, L. T. *Radiation Damage in Crystals*; John Wiley & Sons: New York, 1965.
- (68) Itoh, N. *Nucl. Inst. Methods Phys. Res. B* **1996**, *116*, 33.