Nuclear Energy Research Initiative (NERI) Program

DE-FG03-99SF21923/A00

NERI Project No. 990010: "Effects of Water Radiolysis in Water Cooled Nuclear Reactors"

Topical Report: End of Project Year 1

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Summary:

The aim of this project is to develop an experiment-and-theory based model for the radiolysis of non-standard aqueous systems like those that will be encountered in the Advance Light Water reactor. Three aspects of the radiation chemistry of aqueous systems at elevated temperatures are considered in the project:

- the radiation-induced reaction within the primary track and with additives,
- the homogeneous production of H_2O_2 at high radiation doses, and
- the heterogeneous reaction of the radiation-induced species escaping the track.

The goals outlined for Phase 1 of the program were:

- the compilation of information on the radiation chemistry of water at elevated temperatures,
- the simulation of existing experimental data on the escape yields of e_{aq}^-, OH, H_2 and H_2O_2 in γ radiolysis at elevated temperatures,
- the measurement of low LET and high LET production of H_2O_2 at room temperature,
- the compilation of information on the radiation chemistry of water – (metal) oxide interfaces, and
- the synthesis and characterization the heterogeneous water – oxide systems of interest.

These topics have all been addressed and the results of the investigations are summarized in the following Task reports. The knowledge obtained will provide a sound basis for Phase 2 of the program.

Task Reports:

Task 1. (Investigator: Simon M. Pimblott, NDRL)

Compilation of Experimental Radiation Chemistry of Water at Elevated Temperatures

An extensive review of the scientific literature on γ radiolysis of water and aqueous solutions at room and at elevated temperatures has been performed. There is a large amount of data on the nonhomogeneous track chemistry at room temperature, and the track structure and diffusion-limited kinetics are well parameterized. This wealth of knowledge contrasts with the limited information about the effects of radiation

on aqueous solutions (and on aqueous solution – metal oxide interfaces) at elevated temperatures. The majority of the studies at elevated temperatures were performed at AECL, Canada or at the Cookridge Radiation Laboratory, UK. The two groups focused on measuring the rate coefficients of the reactions of the radiation-induced radicals and ions of water. Their data is the foundation of our compilation of kinetic data, although other measurements from other researchers were reviewed and included. The majority of the temperature dependences can be fitted with an Arrhenius type expression, $k = A \exp(-E_a/k_B T)$. This type of parameterization provides a satisfactory empirical estimate of the rate coefficient, but it should not be taken to have any mechanistic implications.

Radiation-induced radicals are very reactive, and so most of their reactions are close to diffusion-controlled at room temperature. At elevated temperature, however, deviations from diffusion-control are apparent. Consequently, the temperature dependence has to be described using two components, $k_{obs}^{-1} = k_{diff}^{-1} + k_{react}^{-1}$, one for the encounter process, k_{diff}, and one for the reaction process, k_{react}. The temperature dependence of the bi-radical reaction $OH + OH \rightarrow H_2O_2$ is shown in Figure 1. The partitioning of the rate coefficient into the two components clearly demonstrates that the reaction is less than diffusion controlled. The best fit to an Arrhenius type expression, with $A = 1.04 \times 10^{10}$ M^{-1}s^{-1} and $E_a = 7.7$ kJ, is also included in the figure. There are noticeable deviations at low and high temperatures.

Figure 1.1 Temperature dependence of OH+OH reaction. (o) Empirical fit to experimental data. (Dash line) Fit to Arrhenius Equation with A = 1.04 x 10^{10} M^{-1}s^{-1} and E$_a$ = 7.7 kJ. Solid lines: 1, k$_{diff}$; 2, k$_{react}$; 3, k$_{obs}$.

The temperature dependences of the diffusion coefficients of the radiation-induced ions and of the water molecule are partially known, however, the diffusion-coefficients of the neutral radicals are poorly characterized even at room temperature. In the diffusion-kinetic calculations performed, it was necessary to assume that these species have diffusion coefficients with the same temperature dependence as the self-diffusion of water.

The temperature dependences of the yields of e_{aq}^-, H, H$_2$, OH and H$_2$O$_2$ following γ irradiation have been investigated using radical scavengers. The yields of the principal reducing, e_{aq}^-, and oxidizing, OH,

radicals are quite well known and increase with increasing temperature. There are some discrepancies between different experimental studies for H_2; however, the yield is either independent of temperature or increases slightly with increasing temperature (< 30% at 300 °C). The yield of H atom is not accessible directly and can only be obtained in conjunction with H_2. The sum of the yields of H and H_2 is more-or-less independent of temperature. The yield of H_2O_2 appears to decreases with increasing temperature in contrast to H_2, however, there is no reliable information above 100 °C.

Simulation of Radiation Chemistry at Elevated Temperatures

The NDRL suite of computer codes, TRACKKIN, for the simulation of low-LET track chemistry in water was extended to include the effects of temperature. These codes address two aspect of the radiolysis; the structure of the radiation track and the chemistry of the resulting spatially nonhomogeneous distribution of radiation induced reactants. The track structure is simulated using a collision-to-collision methodology, employing experimentally based cross-sections for liquid water. The Independent Reaction Times methodology is employed for modeling the radiation chemical kinetics. This diffusion-kinetic treatment of low-LET radiation chemistry relies upon the generation of random reaction times from initial coordinate positions from reaction time distribution functions. The track structure simulation and diffusion-kinetic simulation techniques have been described in detail previously.

The principal effect of elevated temperature on the track structure of energetic electrons in water is due to changes in the inter-event mean-free path. This property depends inversely upon the density of water so increasing temperature increases the separation between intra-track energy loss events. Consequently, i) the dose distribution of the track is more diffuse at elevated temperatures than that at room temperature, and ii) the spurs (clusters of radiation-induced reactants) comprising the nonhomogeneous spatial distribution of reactants are more isolated. Figure 1.2 compares the dose distribution of a 1 keV electron at 25 °C and at 300 °C. This spreading of the track structure is significant as chemistry in clusters emphasizes stochastic
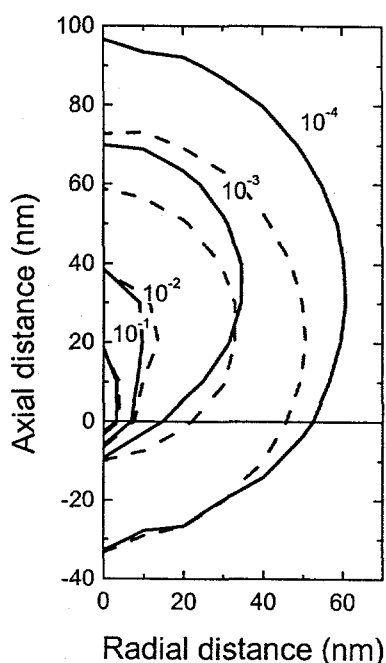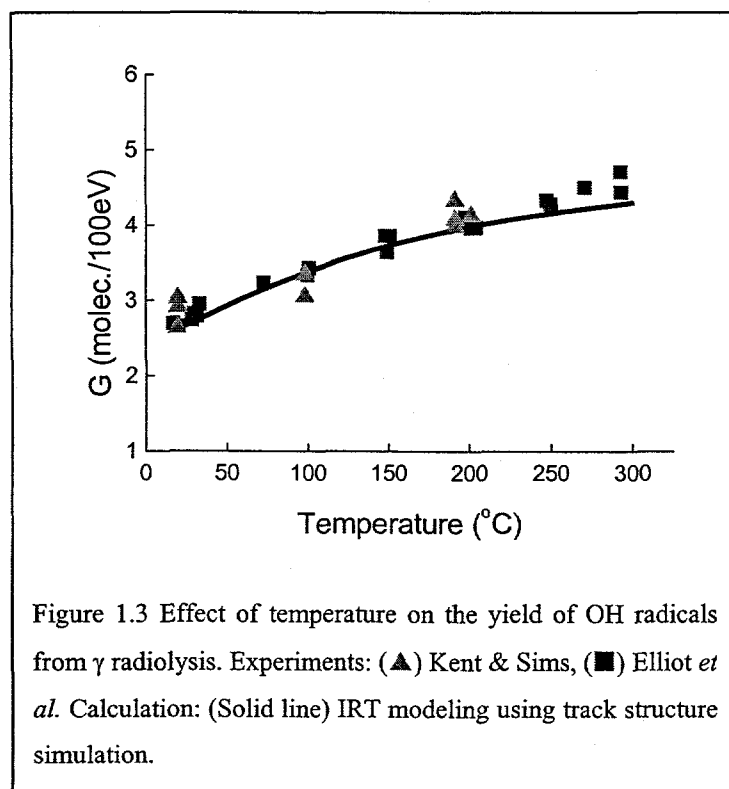

Figure1.2 Comparison of the dose distribution of a 1 keV electron at 25 °C (dashed contours) and at 300°C (solid contours). Dose in eV/nm^3.

effects and should lead to increased recombination relative to molecular product formation.

The reaction times distribution for a pair of radiation-induced reactants depends upon their separation, their transport properties, and the rate of reaction upon diffusive encounter. In addition, physical parameters, such as the relative dielectric coefficient and the density of water have to be considered in the simulations as they affect the diffusion-reaction kinetics by modifying the inter-ionic forces and the rates of processes involving the solvent - water. The input parameters used to describe the diffusion and reaction of the radiation-induced radicals and molecular products were derived from the compilation described above. The effects of temperature on the physical properties of water are well known.

Stochastic radiation chemical kinetic simulations have been made for water over the temperature range 25 °C to 300 °C. The predictions of these calculations were compared with available experimental data for γ radiolysis. Good agreement is found for all of the radiation-induced species and for the combined yield of H and H_2. For the radicals e_{aq}^- and OH the calculations quantitatively - reproduce the measured yields and their temperature dependence. The predictions of the calculations for the yield of OH radicals are compared with the available experimental data in Figure 1.3. The simulations also accurately reproduce the measured yield of H_2 at room temperature. They predict almost no temperature dependence, an increase of only about 20% over the room temperature value at 300 °C. This is somewhat less than the increase measured by Elliot and co-workers, but greater than that measured by Lebedeva and co-workers. The limited temperature dependence is not unexpected: the

Figure 1.3 Effect of temperature on the yield of OH radicals from γ radiolysis. Experiments: (▲) Kent & Sims, (■) Elliot *et al.* Calculation: (Solid line) IRT modeling using track structure simulation.

majority (~ 67%) of the radiation-induced H_2 produced at room temperature arises from ultra-fast processes that will not be affected by temperature. The sum of the predicted yields of H and H_2 is practically independent of temperature, and in good agreement with the experimental estimates. The calculations accurately predict the correct yield of H_2O_2 at room temperature and show a negative temperature dependence; however, the rate of decrease predicted is faster than observed in the experiments. The discrepancy found is under investigation.

The good agreement found between the stochastic simulations and the experimental data for the yields from γ radiolysis of water at elevated temperatures demonstrates the potential of this modeling approach. This promise will be tested in Phase 2 of the project, which extends the present work to the nonhomogeneous radiation chemistry following high LET irradiation of water at elevated temperatures. There is almost no experimental data on the high-LET radiolysis of water at elevated temperatures.

A poster presentation of the studies described was made at the Radiation Chemistry Gordon Conference Plymouth State College, and the work is currently being prepared for submission for scientific publication. This will be the first publication of stochastic calculations of the effects of temperature on water radiolysis.
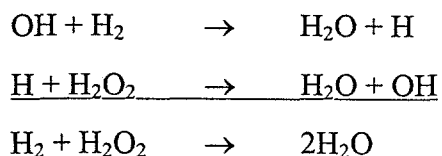
Manuscripts in Preparation

"Simulation of the Gamma Radiolysis of Water at Elevated Temperatures",

Marie Begusova & Simon M. Pimblott, for submission to Journal of Physical Chemistry A.

Task 2. (Investigator: Jay A. LaVerne, NDRL)

Radiation-induced Production of Hydrogen Peroxide

The yield of hydrogen peroxide in the radiolysis of water has been examined with the goal of understanding the mechanism of its production and how various scavengers can influence its yield. Hydrogen peroxide is a source of corrosion for many structural materials in nuclear reactors and its yield is usually kept to minimum levels with the use of different additives. One common technique is to add various amounts of molecular hydrogen. Molecular hydrogen is a good scavenger of the OH radical, which is the main precursor to hydrogen peroxide. The appropriate reactions are as follows.

$$OH + H_2 \quad \rightarrow \quad H_2O + H$$
$$H + H_2O_2 \quad \rightarrow \quad H_2O + OH$$
$$H_2 + H_2O_2 \quad \rightarrow \quad 2H_2O$$

With an infinite supply of molecular hydrogen, the net sum of these two reactions is to drive the hydrogen peroxide yield to zero with the reformation of water. The above reactions are relatively slow and do not occur to much extent within the non-homogeneous region of the particle track. Radicals must escape the particle track into the bulk water in order to drive these reactions. Furthermore, the overall process is a chain reaction and almost impossible to predict with present models, especially for incident heavy particles like the protons and oxygen ions produced by neutron recoils.

In the radiolysis of neat water, H_2O_2 is constantly being formed and depleted and its concentration is never more than a few μM so it is difficult to evaluate the effects of added scavengers. It can be more informative to examine the depletion of H_2O_2 by molecular hydrogen in the radiolysis of 50 μM solutions of hydrogen peroxide. In the γ radiolysis (LET = 0.2 eV/nm) of these solutions, H_2 was indeed found to decrease H_2O_2 concentrations with increasing dose. The H_2O_2 concentration decreases to zero in H_2 saturated solutions at a dose an order of magnitude less than in deaerated solutions alone. Irradiation with protons of 10 MeV (LET = 13.4 eV/nm) gives results somewhat similar to that with γ rays except that the decrease in H_2O_2 concentration with increasing dose is slower. However, in the tracks of 2 MeV protons (LET = 34.8 eV/nm) the LET is sufficiently high that the yield of H_2O_2 increases with increasing dose in deaerated solutions and decreases in H_2 saturated solutions. The concentration of radicals in the tracks of the 2 MeV protons are sufficiently high that they preferably react with each other and few escape the particle track to react with the added solutes. The H_2 is able to scavenge OH radicals before the track has completely relaxed and the extra source of radicals is sufficient to drive the H_2O_2 concentration down with increasing dose, although at a much slower rate than in γ radiolysis. Even added H_2 is not sufficient to scavenge enough OH radicals in the tracks of 5 MeV helium ions (LET 156 eV/nm) to decrease the H_2O_2 concentration. There is some average LET between the 2 and 10 MeV protons for which there is a depletion of H_2O_2 when using added H_2. Reactors obviously have a wide range of particles irradiating the water and specific local effects must be considered. Current models cannot predict these results because the amount of radicals escaping the particle tracks and the extent that added H_2 can compete for radicals within the particle track are not known. Future efforts will try to develop simplistic predictive models.

Experiments and models of the γ radiolysis of water show that with increasing temperature there is an increased yield of radicals that escape the non-homogeneous regime of the track. Concurrent with this result is a decrease in H_2O_2 yields because of the fewer intra-track reactions. The increase in radical concentration in the bulk water should result in a greater effect of H_2 on decreasing H_2O_2 concentrations. A system for measuring the effect of H_2 on H_2O_2 yields in the γ radiolysis of water at high temperatures has been designed and is currently under construction. The main problem with the determination of H_2O_2 yields at high temperatures is its thermal instability to decompose back to OH radicals. The proposed technique allows for rapid cooling of the sample following the radiolysis. In order to better accommodate these demands and allow for the addition of H_2, a compact furnace with a sealed quartz cell will be used. The whole furnace will be irradiated, and the sample quickly extracted and quenched with ice water following the irradiation. Published work using a similar technique suggests that the proposed technique will work satisfactorily. The

irradiation cell and furnace is expected to be complete within a few months and experiments will commence following the appropriate dosimetric studies.

Manuscripts in Preparation

"Molecular hydrogen effect on hydrogen peroxide formation in the radiolysis of water",

Barbara Pastina & Jay A. LaVerne, for submission to Journal of Physical Chemistry A.

Task 3. (Investigator: Dani Meisel, NDRL)

Compilation on the Radiation Chemistry of Water -- (Metal) Oxide Interfaces

A literature search of the radiation chemistry of iron-oxide and zirconium-oxide water interfaces was conducted. It showed that charge transfer from aqueous species to solid iron-oxide particles has been studied extensively and that a kinetic model has been developed for that system. There is little data for zirconium-oxide particles.

Pulse Radiolysis of Zirconia Suspensions

Zirconia suspensions of average particle diameter 5 - 10 nm are available at 10 %w zirconia. These mono-disperse suspensions are acidic (pH 3-4) and thus the particles are positively charged. Synthetic procedures to change the pH to alkaline were developed and the suspensions were concentrated using the ultra-filtration technique. Particle sizes increased significantly following this procedure.

Pulse radiolysis experiments were conducted on zirconia suspensions at high particle concentrations. The yield of the hydrated electron was measured following a pulse of high-energy electrons in the presence of acceptor molecules. The yield of reduction equivalents increases with the zirconia loading. Under heavy loading of zirconia, a significant percentage of the energy is absorbed by the zirconia, but that fraction contributes to the radiolysis of water (e.g., gas generation unless prevented). The probability that an electron escapes from a particle into the bulk water is higher than the probability that it will escape recombination if it were originally produced in the water. The apparent consequence of these observations is that energy originally deposited in zirconia seems to cross the solid/liquid interface and to give higher radiation chemical yields in the aqueous phase than if the energy was absorbed in the water alone.

Experiments measuring the escape yield of electrons from zirconia into water employing several different scavengers (zwitterion-viologen and methyl-viologen) were used to determine the effect of the scavenger charge and its interaction with the surface potential on the yield. It was found that adsorption of the electron acceptor onto the surface, due to electrostatic interaction with surface, enhances the yield of electron capture at the surface. This, therefore, leads to the conclusion that a) escape of electrons from the solid particles can be intercepted by the addition of acceptors, and b) the same acceptors also compete with charge recombination within the particles.

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Initial experiments to measure the yield of holes that escape from the solid zirconia particles indicate that escape of holes does occur. Similar to electrons in zirconia (and silica), but contrary to holes in silica, the escape of holes minimizes charge separation across the solid/liquid interface. Quantitative measurements are now underway to determine if the same number of equivalents of holes escape as those of the electrons. In parallel, direct measurements of H_2 generation from zirconia suspensions have started.

Manuscripts in Preparation

"Ionizing Radiation Effects in Suspensions of ZrO_2 Nanoparticles",

　　　Mona Tréguer and Dan Meisel, for submission to Journal of Physical Chemistry B.

Task 4: (Investigator: Thom Orlando, PNNL)

Growth and Characterization of Crystalline ZrO_2 Films

　　　Cubic and monoclinic single crystal zirconia films were grown on yttrium stabilized zirconia (YSZ) 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 1.5×10^{-5} Torr during the growth. It was observed that cubic single crystal zirconia (100) films could be grown on YSZ(100) substrate up to a 70 Å thickness at a substrate temperature of 650°C with the growth rate of 0.2-0.3 Å/s. No half-order streaks were observed in the reflection high-energy electron diffraction (RHEED) pattern during this growth. On the other hand, very weak half order streaks appeared in the RHEED pattern for the growth on YSZ(111) from the beginning of the growth. The cubic single crystal structure along with minor phase of non-cubic nature remained during the growth of ZrO_2(111) until the thickness of about 400 Å. Beyond 400 Å thicknesses, RHEED pattern changed from streaks to transmission spots all over the RHEED screen. Well-aligned
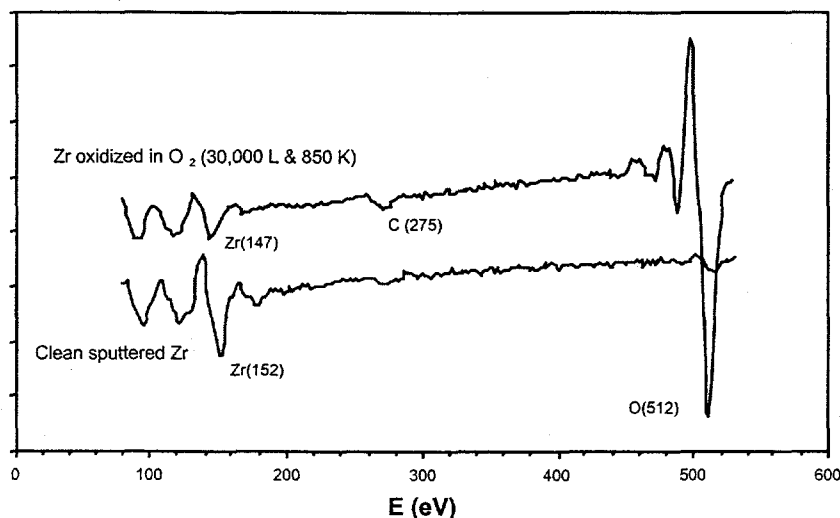
Figure 4.1 AES spectra of the Ar^+ ion sputtered and UHV cleaned pure zirconium foil (99.94%) surface before (lower trace) and after (upper trace) exposure to 30,000L of ultra-pure oxygen (99.999%) at 850 K.

single crystal monoclinic phase of $ZrO_2(100)$ was obtained during the growth from 70 Å thick films up to 2000 Å thick film. Although some transmission spots were seen in the RHEED pattern during the growth of thick $ZrO_2(100)$ films, streaks were still visible in the RHEED pattern during the growth. XRD measurements were carried out to identify the crystal structure of these films. Rutherford backscattering and channeling (RBS/C) measurements were performed to investigate the crystalline quality of the films. Currently, we are in the process of analyzing the XRD and RBS/C data and a paper will be published at the end of the analysis.

Characterization of Oxidized Zirconium Metal

Nominal pure ZrO_2 films were grown by isothermal oxidation of pure (99.94%) zirconium metal foils. The samples were initially cleaned via Ar^+ ion sputtering in UHV and then dosed with 30,000 Langmuirs of ultra-pure oxygen (99.999%). Auger Electron Spectroscopy (AES) was used to characterize the films grown. The AES spectra, which are shown in Figure 4.1, indicate a stoichiometry of approximately ZrO_2. The films appear to be stable and the lack of significant carbon and other contaminants features near 200-400 eV illustrates general cleanliness.
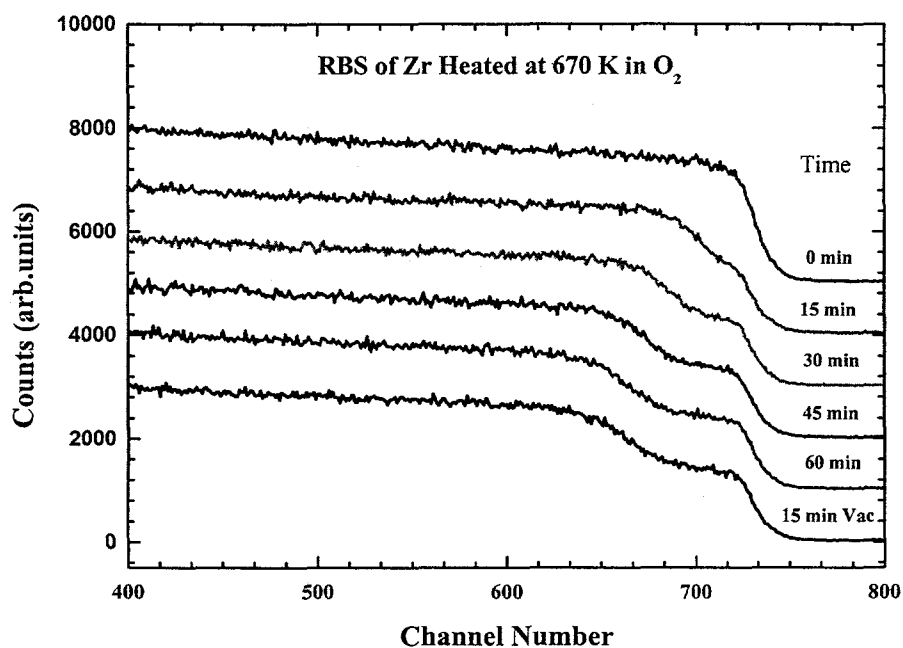

Figure 4.2 RBS spectra of surface oxidized Zr samples after various heating cycles in oxygen. The thickness of the oxide layer increases as a function of heating time.

A thin Zr foil was also oxidized at 400 °C in oxygen at 1×10^{-6} Torr. Figure 4.2 shows RBS spectra collected after various sample heating times (0 to 60 minutes) at 400 °C and in and oxygen pressure of 1×10^{-6} Torr. The step, which develops at the leading edge of the spectra, is the result of oxide film growth, the width of the step being a measure of the oxide film thickness (approximately 1400 Å after 60 minutes), and the relative step height giving the film stoichiometry (ZrO_2). The bottom curve was obtained by heating in vacuum with the oxygen removed and demonstrates that the films are thermally stable at 400 °C. Subsequent x-ray diffraction measurements confirmed that the film structure is mostly the monoclinic phase.

These unique and well-characterized ZrO_2 materials will be utilized in our future experiments on mechanistic understanding and modeling of radiolysis and radiation-induced corrosion of nuclear reactor fuel surfaces. Current work is focusing on understanding the adsorption and thermal desorption behavior of water at these interfaces and the development of techniques for growing Fe_3O_4 are underway.
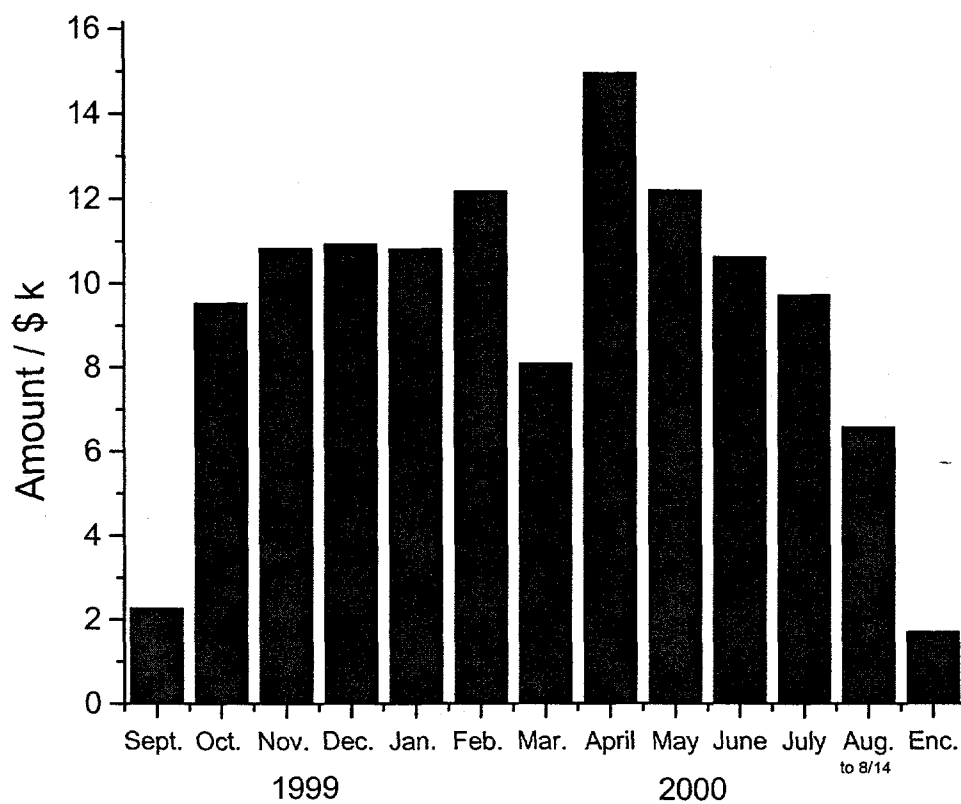
Note: Dr. Thom Orlando has accepted a position as a Full Professor in the Department of Chemistry at Georgia Tech. and will be relocation from PNNL from August 2000. Having been given appropriate authorization from DOE, this component of the program will be moved to Georgia Tech at that time.

Coordination meetings:

Project coordination meeting of the NDRL and PNNL co-PIs took place three times during the first year of the program (Phase 1). Two of these meetings took place at the NDRL, while the third was at the Radiation Chemistry Gordon Conference (RCGC) held at Plymouth State College. The discussions at the RCGC also included Dr. Craig Stuart - a representative of the project consultants, AECL - and Drs. D. Bartels and C. Jonah - members of the Argonne National Laboratory NERI program group.

Preliminary Cost Performance:

NDRL:

Bar chart titled "Amount / $ k" (y-axis, 0 to 16) versus months. X-axis labels: Sept., Oct., Nov., Dec., Jan., Feb., Mar., April, May, June, July, Aug. to 8/14, Enc. The year labels "1999" and "2000" span the lower axis.

PNNL: Funding provided directly as separate grant to PNNL

Nuclear Energy Research Initiative (NERI) Program
DE-FG03-99SF21923/A00
Topical Progress Report

Status Summary - Phase 1:

Milestone/Task Description	Planned Completion Data	Actual Completion
Task 1. 1. Compilation of information on radiation chemistry of water and aqueous solutions at elevated temperatures.	8/14/2000	Compilation completed. Web publication in progress.
2. Algorithms for TRACKKIN code that include the effects of temperature on energy loss and the results of calculations on hydrogen yields at elevated temperatures.	8/14/2000	Coding completed. Calculation of chemical kinetics following g irradiation at room and at elevated temperatures (0 – 300oC) completed. Submission for scientific publication in progress
Task 2. 1. Results of hydrogen peroxide yields from gamma and high LET irradiation in the presence of H_2 scavengers at high dose.	8/14/2000	Experiments completed. Submission for scientific publication in progress
2. Schematics for the high temperature cell for gamma irradiation.	8/14/2000	Completed
Task 3. 1. Compilation of information on radiation chemistry of water at interfaces of interest.	8/14/2000	Literature survey completed
2. Tested procedures to synthesize (or concentrate dilute suspensions of) iron and zirconium oxide.	8/14/2000	Completed
3. Results from the irradiation of these oxides.	8/14/2000	Experiments completed for zirconium oxide. Submission for scientific publication in progress
Task 4. 1. Growth and Characterization of Crystalline ZrO_2 Films	8/14/2000	Completed
2. Characterization of Oxidized Zirconium Metal	8/14/2000	Completed

NERI Progress Chart

ID	Task Name	Duration	Start date	Finish date	1999		2000				2001				2001		
					Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3
1	Radiation chemistry model development	3 years	8/15/99	8/14/02	■	■	■	■	Γ ■	■	■	■	Φ ■	■	■	■	Φ ■
2	High temperature and high LET effects	3 years	8/15/99	8/14/02	■	■	■	■	Γ ■	■	■	■	Φ ■	■	■	■	Φ ■
3	Interfacial effects of radiation	3 years	8/15/99	8/14/02	■	■	■	■	Γ ■	■	■	■	Φ ■	■	■	■	Φ ■
4	Low energy electrons at surfaces and interfaces	3 years	8/15/99	8/14/02	■	■	■	■	Γ ■	■	■	■	Φ ■	■	■	■	Φ ■
	Progress	3 years															

Key		Task		Summary	■	Rolled up progress	
		Progress		Rolled up task			
		Milestone	Φ	Rolled up milestone	Γ		