WSRC-MS-2002-00728

Evaluation of Hydrogen Generation from Radiolysis from Breached Spent Fuel

by
D. W. Vinson
Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808
R. W. Deible

R. L. Sindelar

A document prepared for DOE SNF AND FISSILE MATERIALS MANAGEMENT at Charleston, SC, USA from 9/17/2002 - 9/20/2002.

DOE Contract No. **DE-AC09-96SR18500**

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U. S. Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161,
phone: (800) 553-6847,
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/help/index.asp

Available electronically at http://www.osti.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831-0062,
phone: (865)576-8401,
fax: (865)576-5728
email: reports@adonis.osti.gov

WSRC-MS-2002-00728

EVALUATION OF HYDROGEN GENERATION FROM RADIOLYSIS FROM BREACHED SPENT FUEL

Dennis W. Vinson, Richard W. Deible, and Robert L. Sindelar
Westinghouse Savannah River Company
Aiken, SC 29808

ABSTRACT

Ionizing radiation from spent nuclear fuel (SNF) can cause radiolytic decomposition of water and generation of hydrogen. Factors affecting hydrogen production include the type of radiation (alpha, gamma, and neutron), the linear energy transfer (LET) rates from the radiation, the water chemistry and dissolved gases, and physical conditions such as temperature and pressure. A review of the mechanisms for the radiolytic generation of hydrogen applicable to breached SNF has been performed. A qualitative evaluation of the potential for generation of hydrogen in the pure water used in water-filled shipping casks at the Savannah River Site (SRS) is made.

INTRODUCTION

On-site shipments of spent nuclear fuel at the Savannah River Site are made in water-filled, vented casks. The SNF generates a mixed field of ionizing radiation to the water. This radiation field is generally dominated by gamma-rays and a limited flux of fast neutrons. The fuel cladding effectively attenuates beta and alpha particle radiation. However, a small fraction of the SNF exhibits some degree of fuel cladding penetration due to pitting corrosion and mechanical failure. Breaches in the fuel cladding allow the exposure of small volumes of water in the cask to alpha and beta ionizing radiation. The current analysis addresses the impact of ionizing radiation from breached SNF with an emphasis on the production of flammable gas in the air volume of the water-filled cask.

Ionizing radiation can cause radiolytic decomposition of water. Generally, the amount of decomposition of pure water is extremely small and often may be assumed negligible [1-3]. The extent of water decomposition is a strong function of the absorbed energy density of the incident radiation, i.e. radiation that exhibits high linear energy transfer (LET) tends to favor water decomposition, while low LET radiation leads to little or no net water decomposition [2-4].

When water is first irradiated, no back reaction exists initially since there are no decomposition products present to be converted to water. The initial rate of decomposition is therefore equal to the rate of the forward reaction. If the decomposition is allowed to proceed within a closed system, accumulation of decomposition products leads to a back reaction by which some of the products are converted to water; the rate of decomposition, accordingly, is reduced. As the concentration of decomposition products increase, the rate of the back reaction also increases in accordance with the mass-action law, and the rate of decomposition is eventually reduced to zero; that is, an equilibrium condition is achieved in which the rate of the back reaction exactly equals the rate of the forward reaction.

OVERVIEW OF MECHANISMS OF WATER DECOMPOSITION AND RECOMBINATION

Hydrogen gas production is a complex process involving decomposition of water molecules, recombination of decomposition products back to water (back reactions), chemical reaction of the decomposition products to from hydrogen peroxide and molecular hydrogen (H_2), and the formation of various radicals such as OH, HO_2, etc. The initial chemical reactions for radiolysis of water can be represented by the expression:

$$H_2O \xrightarrow{\text{incident radiation}} H_3O^+_{aq},\ OH,\ e^-_{aq},\ H,\ H_2O_2,\ H_2 \qquad \text{(Rx. 1)}$$

These reactions are the processes that constitute the forward reaction converting water to decomposition products. The free radicals of Rx. (1) may also react, however, according to:

$$H + H_2O_2 \rightarrow OH + H_2O \quad \text{(Rx. 2)}$$
$$OH + H_2 \rightarrow H + H_2O \quad \text{(Rx. 3)}$$

with the net result:

$$H_2 + H_2O_2 \rightarrow 2H_2O \quad \text{(Rx. 4)}$$

and these are the processes which constitute the back reaction converting decomposition products back to water.

There are also other reactions in which the free radicals, H and OH, may take part:

$$OH + H_2O_2 \rightarrow H_2O + HO_2 \quad \text{(Rx. 5)}$$
$$H + HO_2 \rightarrow H_2O_2 \quad \text{(Rx. 6)}$$

with the result:

$$H + OH \rightarrow H_2O \quad \text{(Rx. 7)}$$

or:

$$H + O_2 \rightarrow HO_2 \quad \text{(Rx. 8)}$$
$$OH + HO_2 \rightarrow H_2O + O_2 \quad \text{(Rx. 9)}$$

with the same net result. The effect of these processes is to reduce the back reaction rate, thereby promoting decomposition by removing H and OH radicals that are necessary to the back-reaction processes of Rx. (2-4).

A reaction that complements the back reaction of Rx. (2-4) is:

$$2H_2 + O_2 \rightarrow 2H_2O \quad \text{(Rx. 10)}$$

this reaction may be considered both as radiation-induced and as a catalyzed thermal reaction (catalysis being effected by certain impurities in the water).

To illustrate the complexity of the dynamic decomposition/recombination reactions caused by irradiation of water, the following additional reactions have been observed in the irradiated water at low dose rates: [5]

$$OH + O_2^- \rightarrow O_2 + OH^- \quad \text{(Rx. 11)}$$
$$H + O_2^- \rightarrow HO_2^- \quad \text{(Rx. 12)}$$
$$e^- + O_2 \rightarrow O_2^- \quad \text{(Rx. 13)}$$
$$e^- + H_2O_2 \rightarrow OH + OH^- \quad \text{(Rx. 14)}$$
$$e^- + O_2^- + H_2O \rightarrow HO_2^- + OH^- \quad \text{(Rx. 15)}$$
$$e^- + H^+ \rightarrow H \quad \text{(Rx. 16)}$$
$$e^- + H_2O \rightarrow H + OH^- \quad \text{(Rx. 17)}$$
$$OH + HO_2 \rightarrow H_2O + O_2 \quad \text{(Rx. 18)}$$
$$HO_2 + O_2^- \rightarrow O_2 + HO_2^- \quad \text{(Rx. 19)}$$

The list is not exhaustive; reactions that would be considered negligible or impertinent have been excluded [5].

Gamma radiation results in the formation of free radicals only at widely separated intervals along the radiation tracks. The diagram drawn in Fig. (1a) depicts the formation of H and OH radicals in the track of a 1 MeV electron. Radicals are formed in small clusters or spurs of the order of 10 Å in diameter, which are themselves separated by distances of the order of 1000 Å. The probability that a radical will escape from the spur before combining with another radical is, under these circumstances relatively high, and radical yields are larger than molecular yields. The free radicals, therefore, get little chance to react with each other to form decomposition products in accordance with reactions represented in Rx. (1). Instead, many drift away from the tracks into the bulk of the water and become available for reacting with decomposition products in accordance with Rx. (2-4). The ratio of the number of pairs of free radicals that form decomposition products to the number of pairs that become available for recombining the decomposition products is about one to four [3,6]. This results in a weak forward reaction and a very strong back reaction, and in pure water, gamma radiation alone produces no net water decomposition and H_2 production. In fact, gamma radiation provides a reserve of species that promote recombination, and radiation of another nature that may tend to produce decomposition must first overcome this excess capacity for recombination before any decomposition can result.

The diagram drawn in Fig. (1b) depicts the formation of H and OH radicals in the track of a 1 MeV alpha particle. The high LET coefficient of alpha particle radiation ensures that spurs overlap to form what is effectively a cylinder, and the inter-radical distances within the spurs are reduced. Diffusion of radicals away from the track can occur in only two dimensions. The probability that a radical will escape from the spur before combining with another radical is, under these circumstances relatively low, and molecular yields are larger than radical yields. This results in a very strong forward reaction and a weak back reaction. However, the system is further complicated by the increased likelihood of reactions between the radicals produced by the primary reactions and the decomposition products produced by secondary reactions. An example of a this type of reaction, referred to as a "third order" reaction for the purposes of this report, is when the H_2O_2, formed by the recombination of two OH's in the track, with a third OH radical as described by Rx. (5).

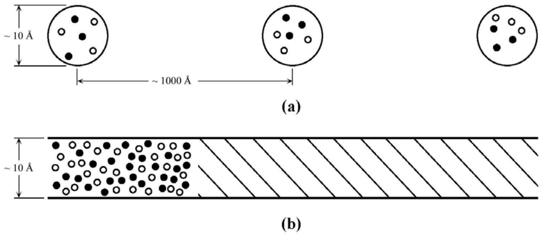

Figure 1 Schematic depicting the formation of H and OH radicals in the track of a 1-MeV electron (a) and alpha particle (b). [7]

Reaction (5) requires some activation energy and does not occur on every encounter of the reactants. However, in the α-ray track the concentration of radicals is so large that most H_2O_2 molecules may undergo many encounters with OH radicals before they can escape the track. The presence of third order reactions provides a mechanism by which the presence of radicals leads to the recombination of molecular decomposition products to reform water molecules, thus reducing the net yield of water decomposition.

When water is irradiated by gamma rays and alpha particles simultaneously, the rate of decomposition is greatly reduced from that which would exist if alpha particle radiation alone were present. This important effect occurs, as indicated above, because the free radicals formed by the gamma rays and dispersed into the bulk of the water by diffusion help to convert the decomposition products produced by the alpha particles to water through Rx. (2-3). As the intensity of alpha particle radiation is increased from zero for a given gamma radiation intensity, the rate of decomposition remains zero until the alpha particle radiation intensity is sufficient to overcome the reserve recombination capacity of the gamma radiation. Further increase of the alpha particle radiation intensity then results in a progressively higher initial rate of decomposition.

The back reaction is augmented by radiation induced recombination of hydrogen and oxygen to form water in accordance with Rx. (10). Experimental evidence indicates that, at low temperature, the back reaction is substantially bolstered by this process (when the concentrations of hydrogen and oxygen are high) in liquid water [3]. The effect of such recombination is to reduce the decomposition rate and the equilibrium decomposition product concentrations.

EXPERIMENTAL RESULTS IN CALCULATIONS OF RADIOLYTIC HYDROGEN GENERATION

Mixed radiation fields will produce a competitive effect between water decomposition and recombination. Experiments have shown that reducing the neutron flux in a mixed gamma-neutron field resulted in reduced rates of decomposition. Likewise, reducing the gamma flux increased rates of decomposition [1].

Experimental data indicate that the reaction of water with pile radiation is reversible, and relatively low equilibrium pressures are obtained. In fact, exposure of pure, air-free liquid water to ionizing radiation such as X-rays, γ-rays, and nuclear pile radiation failed to cause any decomposition of the water [2,4]. However, the researchers report that heavy particle radiation, such as α-rays, cause the continuous decomposition of water even at low intensities.

The addition of boron to water in the form of boric acid is common in nuclear reactors for criticality control. The exposure of boron to thermal neutrons results in the nuclear reaction $^{10}B(n, \alpha)^{7}Li$. Experimental data indicate that when borated water is irradiated, an irreversible reaction for hydrogen production occurs [1-2].

A series of experiments by Hart, McDonnell, and Gordon [2] used varying concentrations of boric acid solutions in a constant gamma-neutron field to measure hydrogen production. The boric acid solutions ranged from 0.01 M up to 0.1 M boric acid. The key variable in this experiment was the alpha energy density from the $^{10}B(n, \alpha)^{7}Li$ reaction. The experiments found that a minimum boric acid concentration (proportional to the alpha energy density) was required before any appreciable H_2 production was observed. This is further evidence of a H_2 removal factor for the gamma field. Once H_2 production began, it was linear with increasing boric acid concentration and thus alpha energy density.

Christensen and Bjergbakke [8] calculated the effects of radiolysis of water exposed to mixed alpha and beta radiation originating from spent fuel. In this analysis, it is assumed that water has penetrated the fuel cladding and produced a 30-µm thin surface film on the surface of the fuel pellets. Consistent with other literature data [1-2], it was found that beta radiation lowers the yield of hydrogen in the system. The source of irradiation considered in the analysis included alpha and beta radiation from PWR and BWR spent fuel after storage times ranging from 40 to 10^6 years. The alpha radiation is assumed to have a range of 30-µm, while the range of the beta radiation was not noted.

An evaluation of the hydrogen production in pure water that has penetrated the fuel cladding was conducted [8]. It was determined that the combined beta plus alpha radiation field produced a concentration of 167 µM H_2 in the water after a storage time of 40 years. The volume of water that would be effected by alpha radiation due to alpha decay of actinides in spent fuel would be extremely small considering the alpha particle range of 30-µm.

CALCULATION OF NET H_2 PRODUCTION

The net production of H_2 from radiolysis in an aqueous solution can be generally expressed as follows:

$$dH_2/dt = gross\ production - removal \qquad \text{(Eq. 1)}$$

Much work has gone into quantifying H_2 production from various types of radiation. The production factor is referred to as the "G" value and is usually expressed in terms of molecules produced (in this case, H_2) per 100 eV of absorbed energy. The G_{H_2} values are equal to 0.45 for betas and gammas [9], 1.12 for fast neutrons [10], and 1.70 for alpha particles [10].

The gross hydrogen production can be calculated from the following expression:

$$\left(dH_2/dt\right)_{\mathrm{Prod}} = G_{H_2,n}E_{a,n} + G_{H_2,\gamma}\left(E_{a,\gamma} + E_{n,\gamma}\right) + G_{H_2,\alpha}\left(E_{a,\alpha} + E_{n,\alpha}\right) \qquad \text{(Eq. 2)}$$

where:
$E_{a,n}$ = energy absorption density (eV/cm^3-min) due to fast neutrons,
$E_{a,\gamma}$ = energy absorption density (eV/cm^3-min) due to gammas,
$E_{a,\alpha}$ = energy absorption density (eV/cm^3-min) due to alpha particles (assume all alpha energy deposited in water),
$E_{n,\alpha}$ = energy absorption density (eV/cm^3-min) due to alpha particles produced by the $^{10}B(n,\alpha)^{7}Li$ reaction,
$E_{n,\gamma}$ = energy absorption density (eV/cm^3-min) due to gammas produced by the $H(n,\gamma)D$ reaction, and
G_{H_2} = G-values for molecular hydrogen production by gamma, neutron, or alpha particle radiation (molecules H_2/100 eV).

The experiments by Hart, et al., [2] measured a gamma energy absorption density of 11.9 × 10^{20} eV/liter-min and a thermal neutron flux of 8.34 × 10^{13} n/cm^2-min in the experiment. A fast neutron flux was not discussed and is assumed to be negligible. The $H(n,\gamma)D$ and the $^{10}B(n,\alpha)^{7}Li$ reaction rates can be calculated to provide energy absorption densities from those reactions.

H_2 removal is assumed to be due only from the gamma interaction and can be expressed as:

$$\left(dH_2/dt\right)_{\mathrm{Rem}} = G_{H_2,r}(E_{a,\gamma} + E_{n,\gamma}) \qquad \text{(Eq. 3)}$$

Given the net H_2 experimental production rates and calculated gross production rates, values for the removal rates, $G_{H_2,r}$, can be derived. The following $G_{H_2,r}$ values were calculated for each boric acid concentration considered in the experiment.

Table 1 Calculation of H_2 Removal Rates using Experimental Data from Hart, et al. [2]

Boric Acid Conc. (mol/l) [2]	Net H_2 Prod. (μmol/l•min) [2]	$G_{H_2,r}$ (H /100eV)	$E_{n,\alpha}$ (eV/cc•min)	$E_{n,\alpha}$ / $E_{a,\gamma}$
0.02	0	1.02	1.77×10^{18}	1.48
0.0313	21±2	1.10	2.77×10^{18}	2.32
0.05	53±2	1.27	4.42×10^{18}	3.71
0.0732	93±5	1.48	6.47×10^{18}	5.43
0.10	147±2	1.62	8.84×10^{18}	7.42

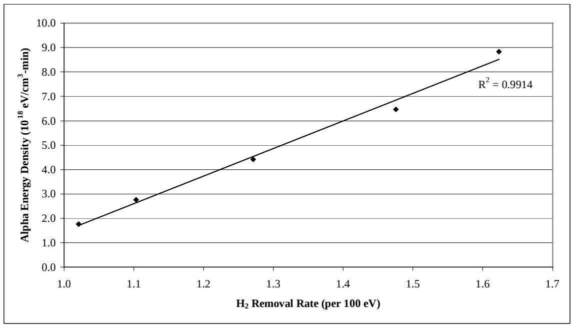

Figure 2 **Alpha Energy Density as a function of H_2 Removal Rate, G_r**

From Fig. 2, the hydrogen removal factor ($G_{H_2,r}$) varies nearly linearly with the alpha energy absorption density. The gamma/neutron fluxes are constant in these experiments [2]. It has been found that, on an equivalent energy basis, irradiation of borated water by a pile flux of fast neutrons, slow neutrons, and gamma rays produced considerably more hydrogen than irradiation of nonborated water by the same pile as demonstrated by the experiments of Hart, et al. [2]. The experimental data from these experiments are consistent with the generally accepted rule that net H_2 production rates are linear functions of the absorbed energy, calculated as $E_n - E_\gamma$ where $E_n = E_{a,\alpha} + E_{n,\alpha} + E_{a,n}$. Data from Ref. [2] has been manipulated to demonstrate the linear behavior of the absorbed energy as shown in Fig. 3.

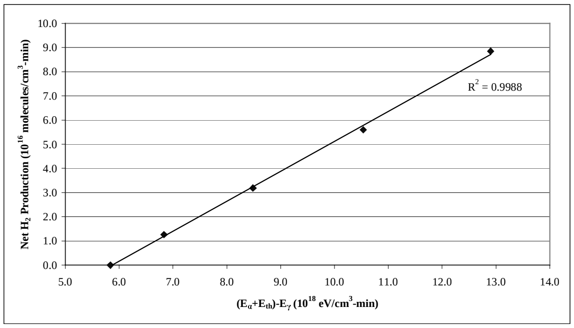

Figure 3 **Net H_2 Production as a function of Absorbed Energy**

EVALUATION OF HYDROGEN GENERATION DUE TO RADIOLYSIS IN BREACHED SNF

It has been demonstrated that the extent to which incident radiation effects the decomposition and/or recombination of water is dependent upon water chemistry, the LET of the radiation, and the amount of energy transferred to the water. Accurate calculations of the energy transferred to a medium from radiative particles through the mechanisms of electron excitation and ionization, which account for up to 98 percent of the total energy transfer, can be made only with considerable difficulty. However, approximations can be readily made. Approximations of the energy transferred from neutralized heavy particles to a medium through the mechanisms of momentum loss, which account for only a couple percent of the total energy transfer, are nearly impossible, even with involved mathematical equations. The following describes the methodology for predicting hydrogen generation due to radiolysis through the utilization of approximate calculations of the energy absorbed by a material from each of the principal components of the expected radiation.

DETERMINATION OF ABSORBED ENERGY

Absorption of Fast Neutron Energy

The rate of energy absorption, $E_{a,n}$, from a fast neutron (> 0.01 MeV) flux ϕ_n with an average neutron energy E_n can be approximated by the following equation:

$$E_{a,n} = \frac{\phi_n \Sigma_s E_n}{2\rho} \times M_{H_2O} \qquad \text{(Eq. 4)}$$

where ρ is the density of the material, ½ is the fraction of the initial energy of the neutron transferred to the hydrogen atom per collision, and Σ_s is the macroscopic scattering cross section of hydrogen in the material being considered. Σ_s is equal to $\sigma_s N_H$ where σ_s is the microscopic scattering cross section for hydrogen, and N_H is equal to the number of hydrogen atoms per cubic centimeter of material. M_{H_2O} is the total mass of water subject to the radiation flux. More accurate predictions may be made by calculating the absorbed energy over small incremental energy ranges and using the flux and scattering cross section corresponding to each energy range. These energies are then summed to obtain the total absorbed energy for a given assembly according to the following equation.

$$E_{a,n} = \left(\sum_{g=1}^{27} \frac{1}{2\rho} \left[\phi_n^g \sigma_s^g N_H E_n^g \right] \right) \times M_{H_2O} \qquad \text{(Eq. 5)}$$

where σ_s is the energy dependant fast neutron scattering cross section of the cask water that may be approximated by the energy-dependant scattering cross section for hydrogen where that of water is unavailable.

Absorption of Gamma Radiation Energy

The rate of energy absorption, $E_{a,\gamma}$, from a gamma flux ϕ_γ with average gamma energy E_γ can be approximated by the following equation:

$$E_{a,\gamma} = \phi_\gamma \mu_\gamma E_\gamma \times M_{H_2O} \qquad \text{(Eq. 6)}$$

where μ_γ is the energy absorption coefficient (cm^2/gram) of the material for gamma radiation of energy E_γ. μ_γ represents the fraction of energy dissipated by a narrow beam of gamma rays in traversing an absorber. It is the product of the probability of an interaction and the probable fraction of photon energy lost in the absorber as a result of the interaction. M_{H_2O} is the total mass of water subject to the radiation flux. More accurate predictions may be made by calculating the absorbed energy over small incremental energy ranges and using the flux and energy absorption coefficient corresponding to each energy range. These energies are then summed to obtain the total absorbed energy according to the following equation.

$$E_{a,\gamma} = \left(\sum_{g=1}^{18} \left[\phi_\gamma^g \mu_\gamma^g E_\gamma^g \right] \right) \times M_{H_2O} \qquad \text{(Eq. 7)}$$

where μ_γ is the energy-dependant energy absorption coefficient of the cask water.

Absorption of Alpha Particle Energy

Typically, shipping containers are used to transport spent fuel that has intact cladding. As such, there is no significant source of alpha particle radiation. However, there are two sources of alpha particle radiation that may be encountered. The first of these sources is the presence of ^{10}B in the container. ^{10}B is commonly used as a thermal neutron absorber in nuclear reactors and in many spent fuel pools, due to its large cross section. Generally, ^{10}B is employed as natural boron in boric acid additions to the water. The side effect of the use of ^{10}B as a neutron absorber is the release and subsequent absorption of a total of 2.33 MeV energy per neutron capture in the ejected alpha particle and recoil ^{7}Li nucleus through the ^{10}B(n,α)^{7}Li reaction. Quantification of the energy associated with this reaction will be deferred to the section on the absorption of thermal neutrons.

The second source of alpha particle radiation in shipping containers is a product of actinide decay in the fuel meat material. Radioactive isotopes with a molecular weight of more than approximately 200 g/mole have a tendency of decaying by alpha particle emission. These alpha particles range in energy from about 4 MeV to about 9 MeV. However, the range of alpha particles is extremely small. Alpha particle range in materials other than air can be calculated from the range in air by using the Bragg-Kleeman rule:

$$R = R_a \left(\frac{\rho_a}{\rho} \right) \sqrt{\frac{M}{M_a}} = 3.2 \times 10^{-4} \frac{\sqrt{M}}{\rho} R_a \qquad \text{(Eq. 8)}$$

where R is the range in a substance of physical density ρ and atomic weight M, and R_a, ρ_a, and M_a are the range, density, and average atomic weight of air. Using this equation for several common SNF assembly materials and 8.75 MeV alpha particles, alpha particle ranges of 20 µm, 40 µm, and 60 µm are calculated for uranium-metal, zirconium, and aluminum, respectively.

The alpha particle ranges are not sufficient to penetrate SNF cladding that is typically more than 300 µm thick. Therefore, only the outer few tens of microns thickness of the fuel meat region can contribute the radiolytic decomposition of water and only in regions of breached cladding.

The short range of alpha particles leads to the assumption that the total energy from all alpha particles incident upon or generated within an aqueous solution is transmitted to the solution to generate dense volumes of hydrogen and hydroxyl radicals. The number and energy of alpha-decay particles can be approximated by using the actinide activity in the fuel meat material. Table 2 provides a list of alpha particle energies and the likelihood of an alpha particle emission per disintegration for various radioactive isotopes. The product of the activity, in disintegrations per second, the α-energy, in MeV, and the probability is the alpha particle energy source (MeV/second) in the fuel meat region of the assembly. This source is assumed uniformly distributed in the fuel meat region.

Table 2 Probability of Alpha Decay and Maximum Alpha Particle Energy for Select Actinides [11]

Isotope	α-Energy (MeV)	Probability (%/decay)
^{211}Bi	6.7513	99.72
^{212}Bi	6.20736	36
^{212}Po	8.785	100
^{215}Po	7.5265	99
^{216}Po	6.9066	100
^{219}Rn	6.94632	100
^{220}Rn	6.40488	100
^{223}Ra	5.9791	100
^{224}Ra	5.78905	100
^{227}Ac	5.0427	1.38
^{227}Th	6.14664	100
^{228}Th	5.52026	100
^{231}Pa	5.1482	100
^{232}U	5.41373	100
^{234}U	4.8564	100
^{235}U	4.6793	100
^{236}U	4.5698	100
^{238}U	4.2703	100
^{237}Np	4.9573	100
^{238}Pu	5.59327	100
^{239}Pu	5.2437	100
^{240}Pu	5.25596	100
^{241}Pu	5.1393	0.0024
^{242}Pu	4.9831	100
^{241}Am	5.63794	100
^{242m}Am	5.5851	0.48
^{243}Am	5.4387	100
^{242}Cm	6.21576	100
^{243}Cm	6.1674	99.74
^{244}Cm	5.9018	100
^{245}Cm	5.6233	100

The rate at which energy (MeV/s) is transmitted to the water due to alpha decay of the actinides in the fuel is then given by the following equation:

$$E_{a,\alpha} = \sum_{i=1}^{N_{assy}} \left(\frac{R_{\alpha}^{i} \times ESA^{i}}{V_{m}^{i}} \times \sum_{j} \left(E_{\alpha}^{j} \times A^{i,j} \times P^{j} \Big/ 100 \right) \right) \text{(Eq. 9)}$$

where R_{α}^{i} is the range (cm) in the fuel meat material of the most energetic alpha-decay particle in assembly *i*, *ESA^{i}* is the total surface area (cm^2) of exposed fuel meat for assembly *i*, V_{m}^{i} is the total meat material volume (cm^3) of assembly *i*, E_{α}^{j} is the alpha-decay particle energy (MeV) from the decay of isotope *j*, *A^{i,j}* is the activity (disintegrations/sec) of isotope *j* in assembly *i*, and *P^{j}* is the probability of a disintegration of isotope *j* being an alpha emission. The value of ESA can be obtained through visual inspection at the time of cask loading.

Absorption of Thermal Neutrons Energy

Thermal neutrons do not transfer energy to hydrogenous media through ionization processes. The energy of a thermal neutron is 0.0253 eV. Therefore, insignificant energy would be lost by the thermal neutron flux due to scattering events. The source of energy transferred to water from thermal neutrons is secondary radiation following neutron capture. The primary reactions associated with this source of absorbed energy are the ^{10}B(n,α)^{7}Li and H(n,γ)D reactions that have thermal neutron cross sections of 790 b and 0.332 b, respectively. The rate of energy absorption (eV/s) due to the ^{10}B(n,α)^{7}Li and H(n,γ)D reactions in an aqueous solution, assumed water, can be calculated from Eqs. (10) and (11), respectively.

$$E_{n,\alpha} = \phi_n \frac{N_B \sigma_a}{\rho} E_r \times M_{H_2O} \qquad \text{(Eq. 10)}$$

where E_r = 2.33 × 10^6 eV, effective total energy of the α and ^{7}Li recoil nuclei; ϕ_n is the thermal neutron flux in n/cm^2-sec; σ_n = 7.59 × 10^{-22} cm^2, cross section of natural boron; N_B is the atom density in atoms of boron per cubic centimeter in the solution (water) of density ρ (g/cm^3); and M_{H_2O} is the total mass of the solution (water) subject to the radiation flux.

$$E_{n,\gamma} = \phi_n \frac{N_H \sigma_a}{\rho} E_\gamma \times M_{H_2O} \qquad \text{(Eq. 11)}$$

where E_γ = 2.2 × 10^6 eV, energy of the emitted photon; ϕ_n is the thermal neutron flux in n/cm^2-sec; σ_n = 3.32 × 10^{-25} cm^2, cross section of natural hydrogen; N_H is the atom density in atoms of hydrogen per cubic centimeter in the solution (water)of density ρ (g/cm^3); and M_{H_2O} is the total mass of the solution (water) subject to the radiation flux.

Predicting the thermal flux created from the SNF assemblies is difficult. However, because there is no boron in the water of the 70-ton cask, there will be no contribution to the total absorbed energy from the ^{10}B(n,α)^{7}Li reaction. The H(n,γ)D reaction results in the production gamma rays that have been shown to promote recombination reactions. Therefore, assuming a thermal neutron flux equal to zero would be conservative.

GROSS H_2 PRODUCTION

The resulting rates of energy absorption by the water from the incident radiation and appropriate G-values are substituted into Eq. (2) to determine the gross H_2 production rate.

The calculated gross H_2 production rate in moles per day is a conservative estimate of the generation of H_2. This estimate does not take credit for the removal of H_2 from the cask by recombination. Adding additional conservatism to the calculation by assuming minimal hydrogen retention in solution leads to the determination of a conservative estimate of the minimum time to required to exceed the flammability limit for hydrogen in the free space of the water filled cask. Absent additional research and/or experimental data, there is no direct way to calculate the net H_2 production rate for a spent fuel storage cask. However, it is unreasonable to assume that H_2 production proceeds without recombination because the absorbed dose to the water is dominated by gamma radiation and gamma radiation has been shown to promote recombination. The ratio of absorbed alpha energy to that of gamma rays, $E_{a,\alpha}/(E_{a,\gamma}+ E_{n,\gamma})$ may be compared to the experimental threshold value of 1.48 (see Table 1) found for the buildup of H_2. The data indicate that the reduction in the alpha to gamma energy absorption reduces the net hydrogen production. A value lower than the threshold suggests very little H_2 production potential from the alpha interaction and significant removal (recombination) potential by the gamma flux. Thus, little net H_2 production would be expected.

If the net H_2 production is assumed to be zero, a $G_{H_2,r}$ can be calculated and compared with experimental values. The calculated value may be compared to $G_{H_2,\gamma}$ and the experimentally derived values of $G_{H_2,r}$ shown in Table 1 and Figure 2. A value of $G_{H_2,r}$ that is comparable to $G_{H_2,\gamma}$ and that is considerable below the values of $G_{H_2,r}$ shown in Table 1 and Fig. 2 provides confidence of the existence of significantly higher recombination potential than is required to result in zero net H_2 production. Additionally, Fig. 3 illustrates the linear behavior of net H_2 production as a function of E_n - E_γ, where $E_n = E_{a,\alpha} + E_{n,\alpha} + E_{a,n}$ and $E_\gamma = E_{a,\gamma} + E_{n,\gamma}$. If the value of the function is less than about 5.8 then no net production rate is predicted.

CONCLUSIONS

An evaluation of the potential for hydrogen production due to the exposure of the relatively pure water, similar to that of the cask water from the SRS basins, to mixed alpha and gamma radiation has been performed. It has been demonstrated that this mixed radiation field will lead to competitive H_2 production/removal reactions. A small value of the ratio of absorbed alpha energy to absorbed gamma energy, combined with the small calculated “G” value for hydrogen radical recombination, provide qualitative evidence that the net H_2 generation rates should be small. Literature data further support the complete suppression of pure water decomposition by radiation fields that are dominated by gamma radiation, as is the condition of most SRS fuel/cask configurations.

Acknowledgments

This work was supported by the U. S. Department of Energy under contract no. DE-AC09-96SR18500.

REFERENCES

1. Etherington H., editor, **Nuclear Engineering Handbook,** Contribution from V. P. Calkins, ***"Radiation Damage to Liquids and Organic Materials,"*** McGraw Hill Co., pp. 10-126 (1958).
2. Hart, E. J., McDonell, W. R., and Gordon, S., ***"The Decomposition of Light and Heavy Water Boric Acid Solutions by Nuclear Reactor Radiations,"*** Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva 1955, P/839, Vol. 7, p. 593, United Nations, New York (1956).
3. U. S. Atomic Energy Commission, **The Reactor Handbook,** vol. 2, Engineering, H. O. Monson, ***"Water Decomposition,"*** McGraw-Hill Book Company, Inc., New York, pp. 175-191 (1955).
4. ***"Three Mile Island: A Report to the Commissioners and to the Public,"*** Volume II, Part 2, Nuclear Regulatory Commission, Special Inquiry Group.
5. Boyd, A. W., Carver, M. B., and Dixon, R. S., ***"Computed and Experimental Product Concentrations in the Radiolysis of Water,"*** Radiation Physics and Chemistry, Volume 15, No. 2/3, Pergamon Press Ltd., pp. 177-185 (1980).
6. Hochanadel, C. J., ***"Effects of Cobalt •-Radiation on Water and Aqueous Solutions,"*** Journal of Physical Chemistry, Volume 56, pp. 587-594 (May 1952).
7. Sowden, R. G., ***"Review Article: Radiolytic Problems in Water Reactors,"*** Journal of Nuclear Materials 8, No. 1, North-Holland Publishing Co., Amsterdam, p 87 (1963).
8. H. Christensen and E. Bjergbakke, ***"Alpha-Radiolysis of Aqueous Solutions,"*** Scientific Basis for Nuclear Waste Management IX, Materials Research Society Symposia Proceedings, Volume 50, ed. L. O. Werme, Stockholm, Sweden, pp. 401-408 (September 1985).
9. **Fundamental Processes in Radiation Chemistry**, P. Ausloos, ed., Interscience Publishers (1968).
10. Choppin, G. R. and Rydberg, J., **Nuclear Chemistry: Theory and Application**, Pergamon Press (1989).
11. Browne, E. Dairiki, J. M., and Doebler, R. E., ***"Table of Isotopes,"*** Seventh Edition, eds. C. M. Lederer and V. S. Shirley, John Wiley & Sons, Inc. (1978).