Dosimetry Modeling for Predicting Radiolytic Production at the Spent Fuel - Water Interface

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Abstract - *The radiolysis of water in contact with spent nuclear fuel (SNF) will produce oxidants and reductants that can affect the dissolution of the fuel in a geologic disposal site. These products are created by initial radiolytic species which are a function of the type of radiation being emitted by the SNF, i.e. alpha, beta and/or gamma, as well as the energy of this radiation, the fuel grain size (and resulting surface-to-volume ratio) and the fuel-to-water ratio. These products interact with the surface of the fuel, creating new species and ultimately affecting the dissolution rate. The objective of the work reported here is to develop a systematic dosimetry model to determine the dose to water from the SNF as a function of these variables. This dose is calculated for different radiation types as a function of decay for the average fuel composition expected at Yucca Mountain. From these dose calculations the production rate of initial radiolytic products can be estimated. This data provides the basis for subsequent determination of the resulting chemical interactions at the fuel/water interface predicted by published theoretical and experimental data.*

I. INTRODUCTION

The radiolysis of water in contact with spent nuclear fuel (SNF) will produce oxidants and reductants that can affect the dissolution of the fuel in a geologic disposal site. These products are a function of 1) the species, spatial distribution and magnitude of the radiolytic products produced by the radiation emanating from the surface of the fuel and 2) the resulting chemistry among these products in combination with the chemistry of the water, surrounding materials (e.g., cladding, degraded waste package materials), and the surface of the fuel. The species that are initially produced are a function of the types of radiation being emitted by the SNF, i.e. alpha, beta and/or gamma. The radiation is a function of source term strength. The initial spatial distribution of the radiolytic species formed is a function of the radiation type and energy, fuel grain size (and resulting surface-to-volume ratio) and the fuel-to-water ratio. These resulting products interact with the surface of the fuel, creating new species and ultimately affecting the dissolution rate.

Various authors have studied this complex problem with both theoretical modeling and experimental studies. These have included modeling and measurements on various fuel forms including spent fuel pellets, fuel fragments and fuel powders [1,2,3,4], fresh fuel of UO_2 doped with various radioisotopes simulating spent fuel [5,6,7], thin plate anodes of UO_2 [8,9], and nanoparticles of UO_2 suspended in water [10]. These systems have been irradiated by sources including external beams of gamma-rays [11,12], internally doped radioisotopes creating gamma, beta and alpha radiation fields [5,6,7], and accelerator-based or external alpha sources [8,9]. Other experiments have directly introduced both radicals and radiolytically produced molecules (primarily hydrogen peroxide) [13,14,15,16,17]. Dosimetry studies of the radiolysis of water have also been reported for alpha, beta and gamma radiation as a function of burnup for CANDU fuel [18]. Two review articles give an overview of the status of this work as of 2000 [19,20].

With respect to dosimetry, Sunder [18] has calculated radiation dose in a water layer in contact with used pellets of CANDU UO_2 fuel. He notes that:

> "It is well known that low linear energy transfer (LET) radiation, e.g. beta and gamma, produces more radicals than high LET radiation, e.g. alpha. Alpha radiolysis of water results predominately in the formation of molecular radiolysis products. Radical oxidants are more effective in causing the oxidation of UO_2 fuel than the molecular oxidants. Therefore, it is necessary to know the dose rate in water for each of the different types of ionizing radiation associated with the used fuel in order to evaluate the effects of water radiolysis on the corrosion rate of the fuel."

Sunder assumed naturally enriched reactor fuel with a burnup of 685 GJ/kg U (~190 MWh/kg U) and calculated the radiation fields at the fuel pellet/water interface for alpha, beta and gamma irradiation as a function of time. For alpha and beta radiation he used the simplifying assumption that the dose at the interface is proportional to the stopping power ratio across this interface. Gamma dose rates were determined using known gamma heating decay rates in the fuel.

The objective of the work reported here is to develop a more detailed dosimetry model to determine the dose to water from the SNF as a function of different types of radiation, fuel surface-to-volume ratio (from intact pellets to grain sized fragments), and fuel-to-water ratio. The dose to water is calculated for different radiation types (alpha, beta and gamma) as a function of decay for the average fuel composition expected at Yucca Mountain. From this the production rate of initial radiolytic products can then be estimated. This data will subsequently be used with published theoretical and experimental data to predict the resulting chemical interactions at the fuel/water interface.

II. DESCRIPTION OF ACTUAL WORK

This work involves accurate modeling of the radiation dose for a variety of fuel/water configurations ranging from intact fuel pellets to the worst case scenario where individual fuel grains are saturated with water. This latter geometric model takes into account the possible ultimate state of the fuel/water interface in a repository as the fuel disintegrates into small grains or as water is able to penetrate into fissures or grain boundaries in the fuel, maximizing the fuel surface area. More importantly, it approximates the configuration used most often by Gray and Wilson [21] in single-pass flowthrough tests to determine the dissolution rate of spent fuel under oxidizing conditions The dosimetry model also includes the effect of different types of radiation, fuel surface-to-volume ratios, grain-to-water ratios and different radiation types (alpha, beta and gamma).

In order to accurately model the dose for this variety of geometric configurations, these new results utilize Monte Carlo methods. The Monte Carlo code MCNP5 [22] is used for beta and gamma transport. Gamma-ray transport modeling is straightforward in MCNP5 and requires only the specification of a gamma-ray energy in the source (fuel) region with the subsequent tallying of the energy deposited in the water. To model beta spectra, MCNP5 calculations are run at discrete electron energies in the source region and the resulting dose to the water for each initial energy is integrated over the beta spectrum of interest. Both of these calculations will be done for representative gamma-ray and beta E_{max} energies and the dose to water tabulated as a function of energy.

For alpha transport, a Monte Carlo based, random walk routine written in Mathematica [23] has been developed. This model randomly selects the point of origin in a fuel volume and a direction vector for each alpha decay and then calculates the energy deposited in both fuel and water using stopping power data for UO_2 and water.

These modeling tools provide a mechanism for accurately determining the dose to water and can also be used to determine the spatial distribution of this dose as function of distance from the fuel/water interface.

Since the dose contributed by the three principal radiation types changes with the decay of the spent fuel, the absolute dose to water changes and the radiolytic products formed change as the mix of alpha, beta and gamma radiation changes with time. To model this effect, the Yucca Mountain Environmental Impact Statement [24] was used to define the contents of the SNF. This report assumes that the average PWR

fuel to be placed in Yucca Mountain will be represented by 3.75% enriched fuel burned to 41,200 MWD/MT and allowed to decay for 23 years. Using the isotopic concentrations present at 23 years of decay, the principle fission product decay chains were modeled by simple decay equations and the four primary transuranic decay chains are modeled using coupled, first-order rate equations solved with the Polymath 6.0 code package [25]. These isotopic concentrations are then combined with decay yields to determine the dose to water for each type of radiation. G-values [18,26] could then be used to determine the production rate of radiolysis products in the water.

III. RESULTS

III.A Alpha Dosimetry

The dose to water from alpha particles has been simulated using Mathematica for a range of spent nuclear fuel material sizes from 15 microns spheres (representing the typical grain size likely in the repository) up to the size of typical PWR fuel pellets. Figure 1 shows the fraction of energy deposited in water for a variety of fuel grain sizes in a cubic array of spherical grains. The surface-to-volume (S/V) ratio for these grains ranges from 4000/cm at a radius of 7.5 micron to 125/cm at a 240 micron radius. The fuel-to-water ratio in this geometry is approximately 1:1. Statistical variation in the random walk solution causes some scatter in the data.

The results indicate that the fraction of initial alpha energy absorbed in water is approximately linear with energy for all except the smallest grain size. For the smallest grain size, where the range of the alpha particle (~30 microns) is

larger than the grain (15 microns), the fraction of energy deposited in the water is approximately equal to the ratio of stopping powers between uranium dioxide and water (~0.3). For all other grain sizes, this assumption fails as the system becomes heterogeneous relative to alpha range. It is also found that the fraction of energy absorbed in water for larger particle grain sizes can be approximated by using the results for a 240 micron radius particle and multiplying by the ratio of the volume of the outer 30 microns (approximately the range of alpha particles in fuel) of the particle divided by the total volume of the particle. The 240 micron radius particle is sufficiently large relative to the alpha particle's range to represent an infinitely large, flat surface. In this manner the fraction of energy absorbed in water from alpha decay in a typical fuel pellet (S/V ratio ~ 4.7/cm) varies linearly from 0.0007 to 0.0019 from 4 to 8.5 MeV.

Figure 2 shows the fraction of energy deposited in water for fuel grains surrounded by an infinitely large volume of water as a function of initial alpha energy. These values are higher than for the array of closely packed grains given by Figure 1 since there is no grain-to-grain energy transfer.

The spatial distribution of the deposited alpha energy at the surface of the fuel material will have an important effect on the near-surface chemical reactions. A single fuel grain was simulated in an infinite bath of water and the fraction of initial energy deposited in water was tallied in 10 micron increments.

Figures 3-5 show the distribution of energy for the 7.5 micron radius grain (the smallest considered), the 30 micron radius grain (approximately the range of
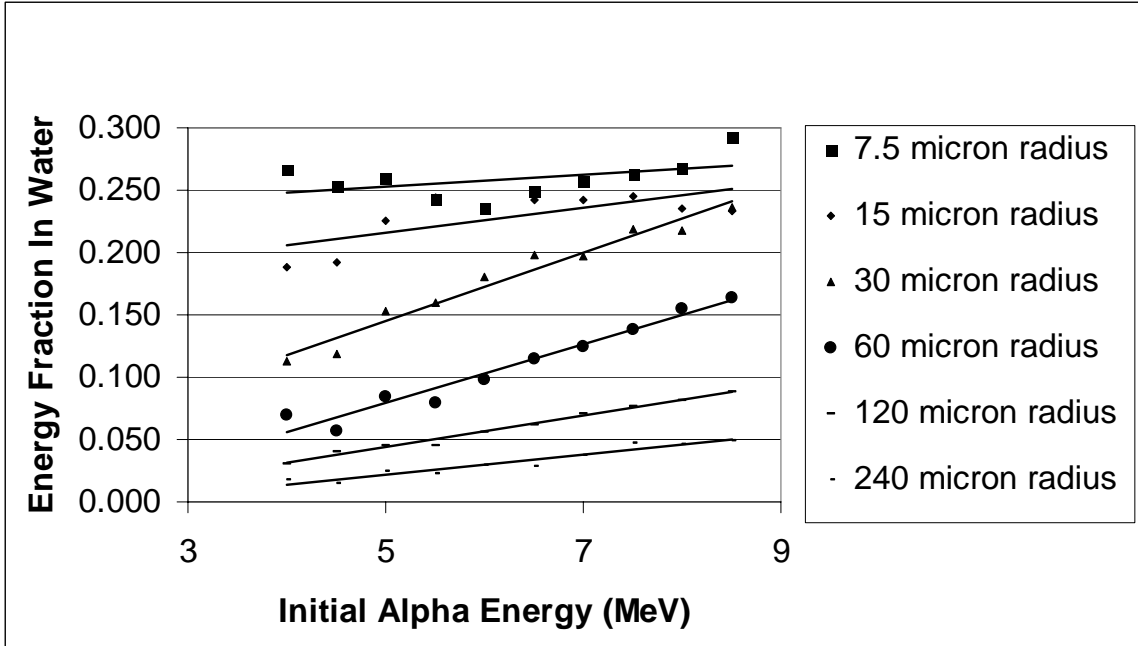
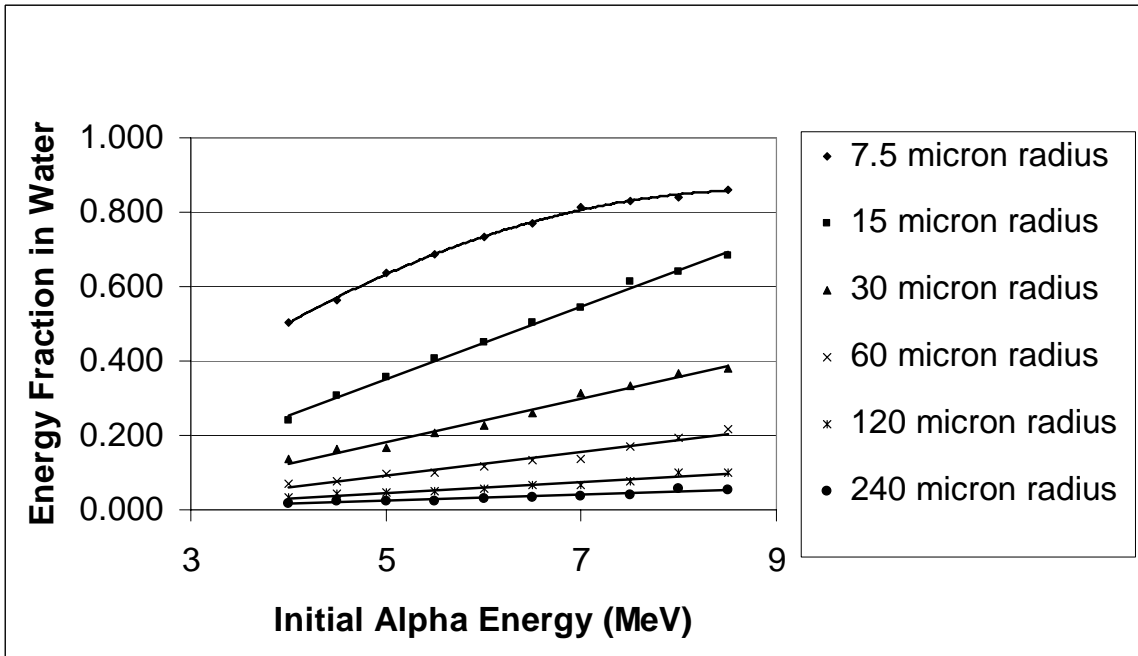Fig 1. Alpha energy fraction absorbed in water for an infinite matrix of fuel grains

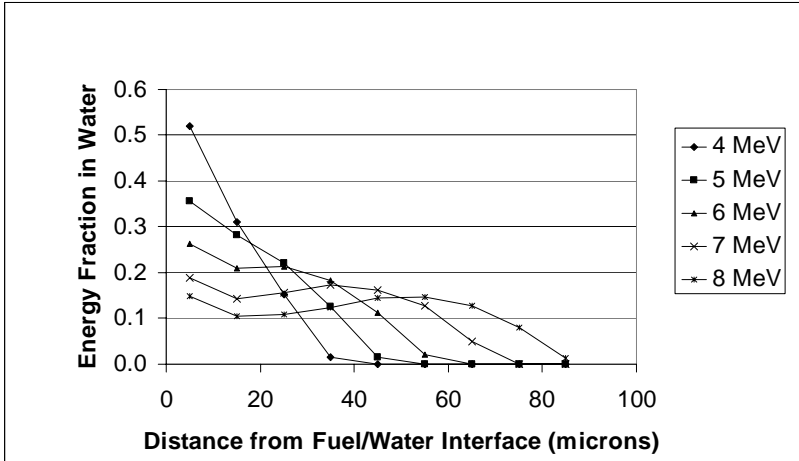Fig 2. Alpha energy fraction absorbed in an infinite water volume around a single fuel grain

Fig 3. Alpha energy deposition distribution as a function of distance from a 7.5 micron radius fuel grain
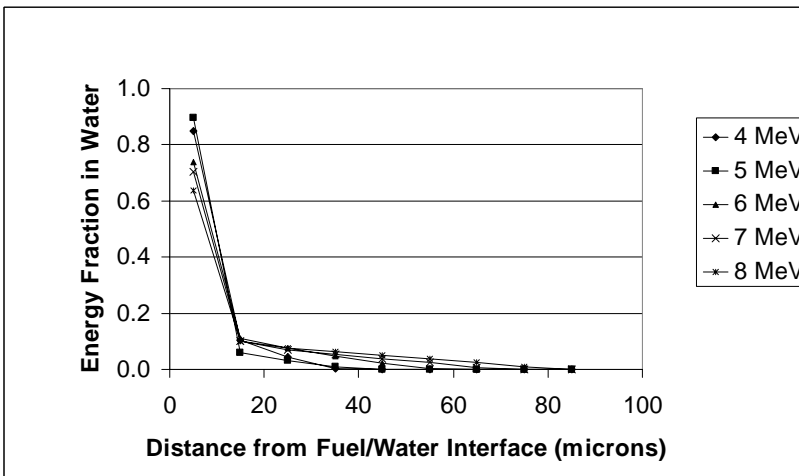

Fig 4. Alpha energy deposition distribution as a function of distance from a 30 micron radius fuel grain
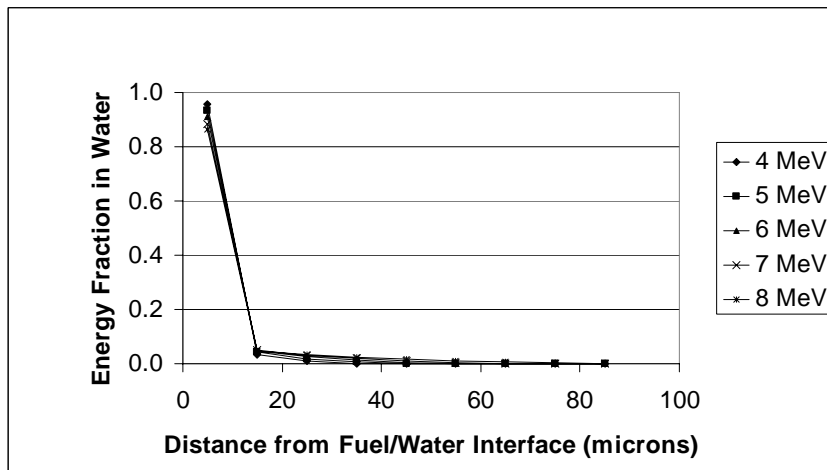

Fig 5. Alpha energy deposition distribution as a function of distance from a 240 micron radius fuel grain

alpha particles) and the 240 micron radius grain (approximating the effect of emissions from an infinitely large surface), respectively. For the small grain, sufficient alpha energy leaves the fuel at high enough energies to produce a Bragg curve of energy deposition. For fuel particles with radii at or above the alpha particle range, most of the energy is left in the first 10 microns of thickness.

III.B Beta Dosimetry

Beta dosimetry was simulated with MCNP5 assuming the same geometries described above. Figure 6 shows water absorbed fractions as a function of E_{max} for a 7.5 micron radius grain and a 240 micron radius grain. The effect of grain size is much less evident for betas than for alphas in this size range as would be expected, since the range of the betas is much larger. The 7.5 micron grain size in a 1:1 fuel-to-water ratio approximates a homogeneous mixture and the ratio of energy deposited in each component is similar to the ratio of the stopping powers in these two materials. At 1 MeV this ratio is 0.16, in good agreement with the MCNP5 calculation. For larger grain sizes this approximation fails as the fuel grain beta self-absorption begins to dominate.

Figure 7 gives the energy absorbed in water for beta emissions from an intact fuel pellet, which is significantly less than for fuel grains due to self-absorption of beta energy in the pellet. For this calculation the pellets were assumed to be in a fuel assembly lattice structure for a typical PWR. No cladding was modeled.

The spatial distribution of the deposited beta energy was calculated by MCNP5 in the water gap between an infinite array of fuel pellets. This spatial distribution is shown in Figure 8 as a function of beta E_{max} energy. At lower energies, the energy of the beta particles emerging from the surface of the fuel are at reduced energies and most of the remaining energy is deposited in a fraction of a millimeter. For higher energy betas the dose distribution between adjacent pellets begins to become more constant.

III.C Gamma Dosimetry

Figure 9 gives the absorbed fraction of energy in water for grains of fuel in an infinite matrix for grain sizes from 7.5 microns in radius to 240 microns in radius. The discontinuity evident at approximately 0.1 MeV is due to the K-edge in uranium. The large photoelectric effect in uranium at lower energies also absorbs more of the gamma energy, reducing the absorbed fraction in this energy range. Figure 10 gives the same data for an intact fuel pellet assumed to be in a fuel assembly lattice. The spatial distribution of dose has not been considered for gamma rays as it is assumed to be essentially uniform in the water surrounding the fuel for all reasonable geometries. As can be seen, a comparison of the water dose for the 240 micron grains vs. the fuel pellets is not as dissimilar as for alphas or betas due to the long effective range of gammas.

III.D. Use of Simplifying Assumptions for Estimating Dose

The calculations in the previous sections can be used to test the assumption by Sunder [18] that the dose at the fuel/water interface can be approximated by the ratio of the
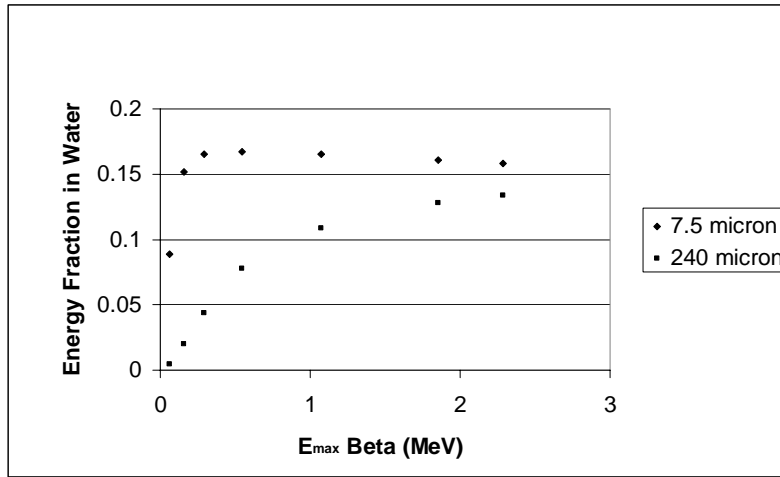
Fig 6. Beta energy fraction absorbed in water for an infinite matrix of fuel grains
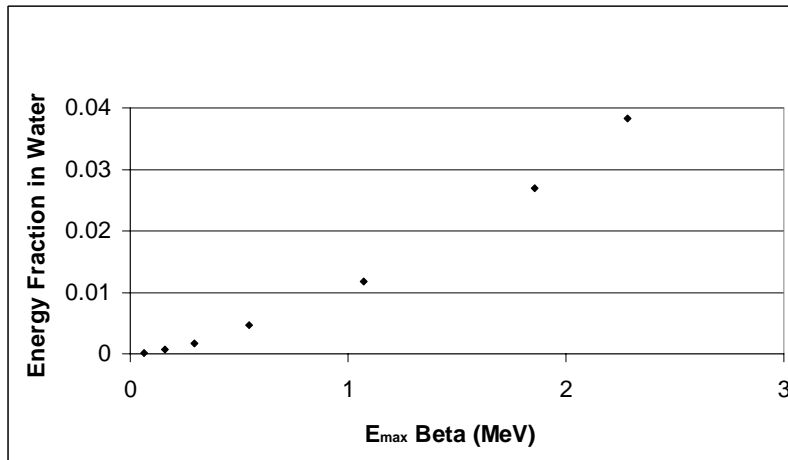

Fig 7. Beta energy fraction absorbed in water for an infinite matrix of fuel pellets
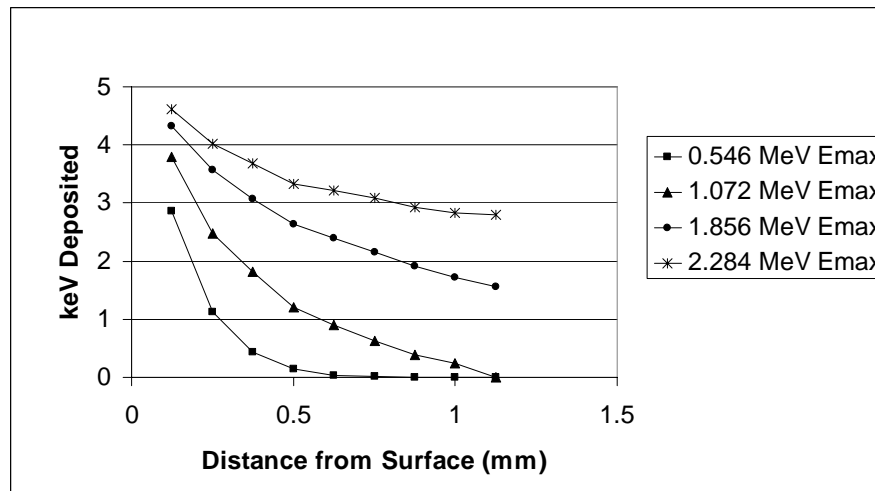
Fig 8. Beta energy deposition distribution as a function of distance from a typical PWR fuel pellet
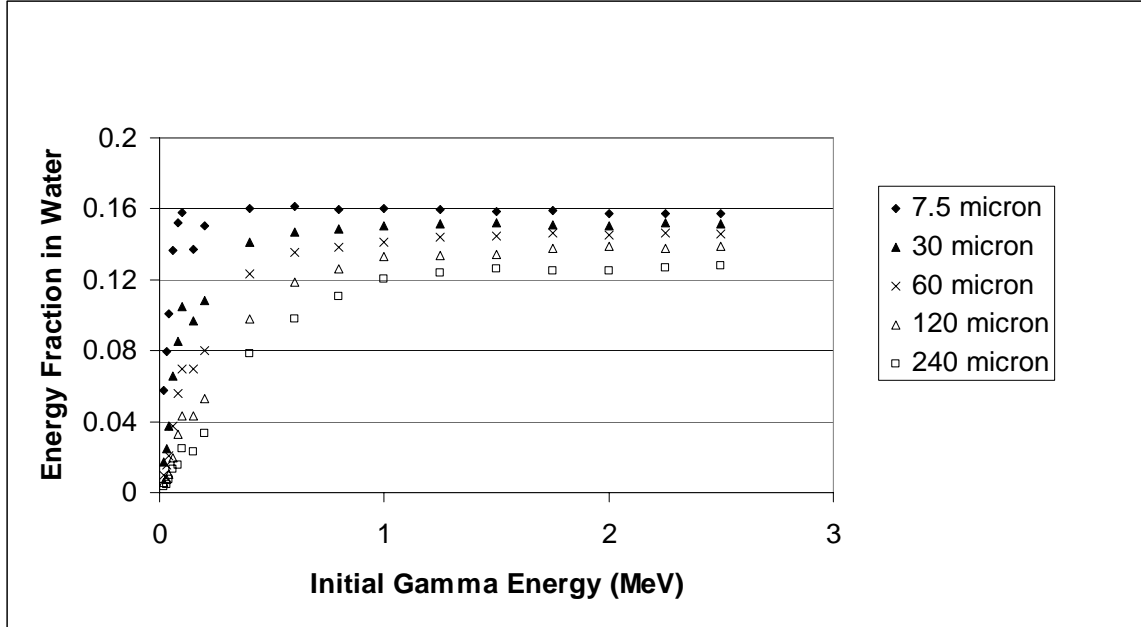

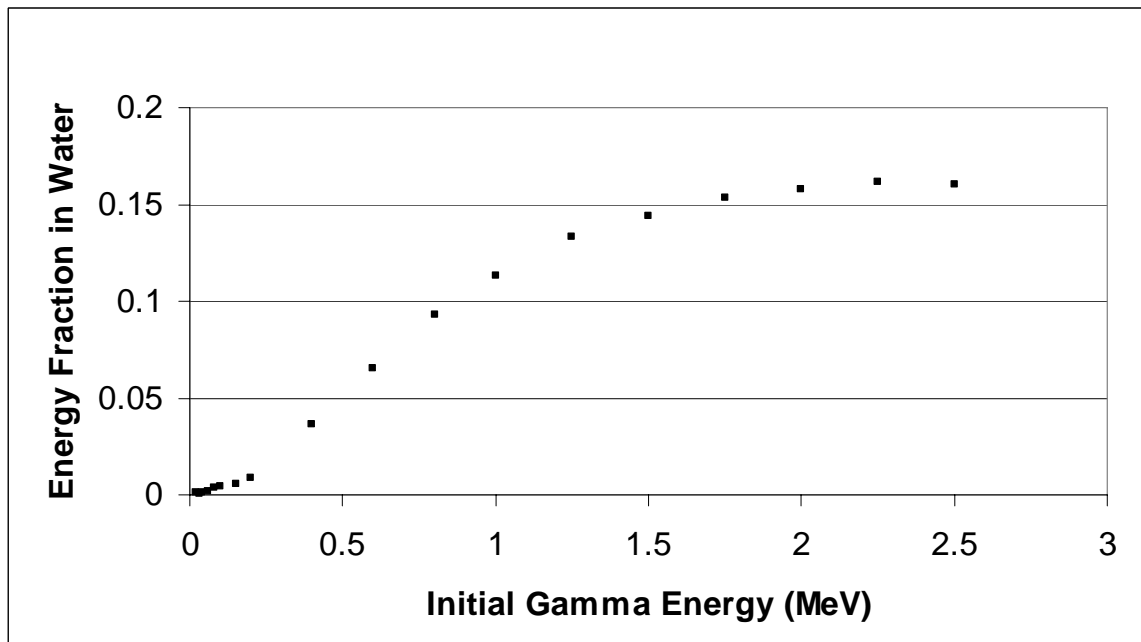Fig 9. Gamma energy fraction absorbed in water for an infinite matrix of fuel grains

Fig 10. Gamma energy fraction absorbed in water for an infinite array of fuel pellets

stopping powers at the interface for alpha and beta particles. This assumption is approximately valid when considering the volume of material within the particle's range from the fuel-water interface or for small grain sizes which approximates a homogeneous mixture. As more heterogeneous systems are considered and/or as the average dose is calculated over a volume of material on the order of or greater than the range of the particles, this assumption fails.

For example the dose ratio for betas for 7.5 micron radius grains in an infinite matrix (see Figure 6) is in good agreement with the stopping power ratio of approximately 0.16. When the grain is 240 microns in radius, this estimate is in error by approximately a factor of 2. Similarly, the alpha dose ratio for 7.5 micron radius grains (see Figure 1) is also in good agreement, but begins changing significantly for grains as small as 15 micron radius. These effects may become significant in determining reactions between radiolytic products and the fuel surface depending upon whether the reactions are strictly due to near surface phenomenon or are more a property of bulk concentration of radiolytic products.

III.E. Dose to Water from SNF

Using data from the Yucca Mountain Environmental Impact Statement [24] the isotopic concentrations as a function of time were calculated using first-order rate equations for the principle fission product decay chains and the four primary transuranic decay chains. A typical result for the Cm-245 decay chain is given in Figure 11.

The emission rates of all three types of radiation can then be calculated based upon these isotopic activities and data on alpha, beta and/or gamma yields and energies. Finally, for each of these emissions, the fraction of energy deposited in the water is known for different fuel geometries from Figures 1, 6, 7, 9 and 10. The result is the dose rate to water from each type of radiation.

Assuming that the fuel has been fractured into 7.5 micron radius grains in an infinite matrix with a 1:1 ratio of water to fuel, the resulting dose from alpha, beta and gamma irradiation is given in Figure 12. The dose rates early in the life of a repository are unrealistic since they assume a completely fractured fuel form at this time, but the results have been included to show the relative magnitude of dose contributed by the three types of radiation and for use in evaluating experimental data using simulated, fractured fuel. As expected, the alpha dose dominates starting around 500 years.

Figure 13 shows similar data for intact fuel pellets. The disparity between alpha dose and beta/gamma dose is greatly reduced in this case due to the self-absorption of alpha energy by the fuel pellets.

Both Figure 12 and 13 present the average dose to water around either fuel grains or fuel pellets. This average dose to the water would be constant throughout the water volume for the 7.5 micron radius grains in Figure 12 since the range of all emissions is on the order of or greater than the size of the particles and/or inter-granular water. This system approximates a homogeneous fuel/water mixture. This is not the case for fuel pellets as indicated by the spatial distribution of deposited alpha energy (see Figure 5) and beta energy (see Figure 8). For the alpha case, essentially all of the energy is left in the first 10
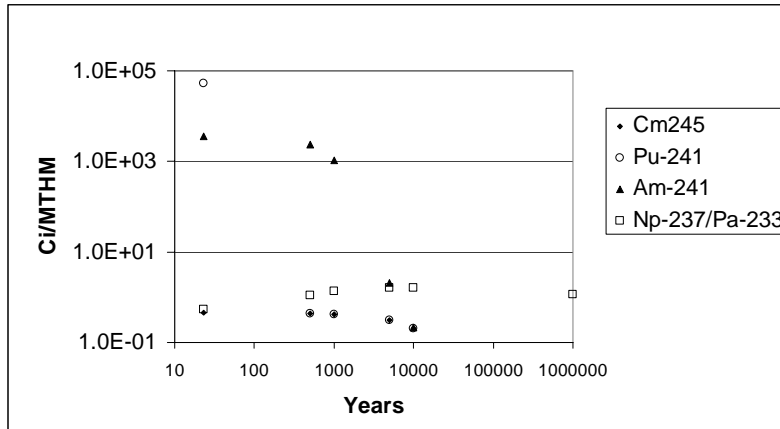
Fig 11. Activity (Ci/MTHM) verses time for isotopes in the Cm-245 decay chain
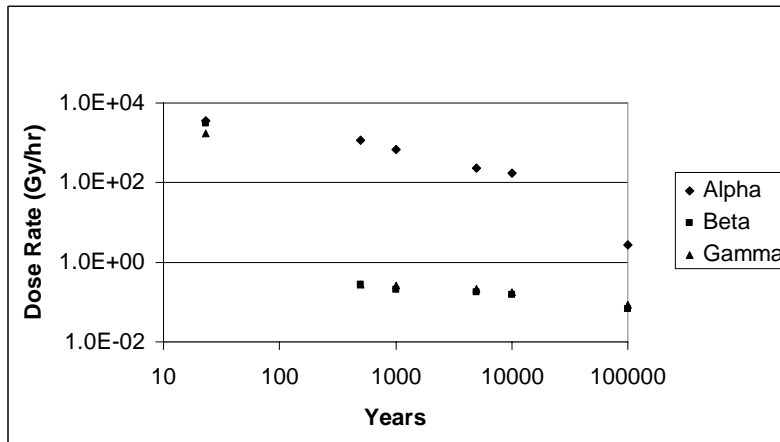

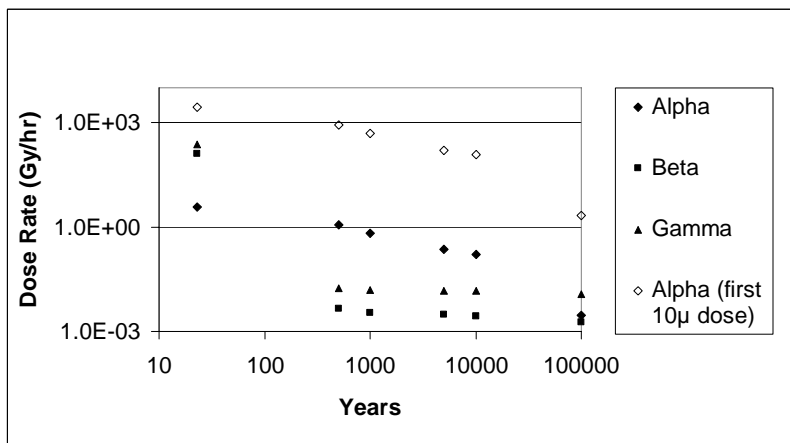Fig 12. Dose rate to water (Gy/hr) verses time for a matrix of 7.5 micron radius fuel grains

Fig 13. Dose rate to water (Gy/hr) verses time for a matrix of fuel pellets

microns. Thus the dose to water within the first 10 microns from the surface would be approximately three orders of magnitude higher (based upon a simple volume ratio of total water per pellet to water in the first 10 microns around the pellet) and the rest of the water would receive no dose. This would displace the alpha data in Figure 13 up by a factor of 1000 (as designated "Alpha 10μ dose"). The spatial distribution for beta energy is more difficult to estimate since it changes significantly depending upon the energy of the emitted beta particles. The dose at the surface is at most a factor of 2 – 5 above the average dose.

The gamma dose can be assumed to be relatively constant between adjacent fuel pellets.

IV. CONCLUSIONS

These representative data form the basis for a methodology to accurately calculate the dose to water so that the initial radiolytic production rate can be determined as a function of fuel geometry for all types of radioactive emissions. These basic data, in conjunction with the calculated isotopic concentrations in fuel as a function of time for typical Yucca Mountain spent nuclear fuel, allow the calculation of initial radiolysis products for a variety of possible fuel conditions. The results can then be used in conjunction with experimental data and/or theoretical calculations to better understand the mechanisms affecting the dissolution of UO_2 in contact with water in a geologic environment. It is clear that existing data on dissolution rates of fresh fuel using grain-sized specimens may have a significant contribution from the radiolytic production of radicals and molecules resulting from the relatively large dose to which the water was subjected.

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