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MEMORANDUM TO: Fritz Sturz, Chief Technical Review Section
Spent Fuel Project Office

FROM: Allen Howe, Nuclear Engineer, Technical Review Section
Spent Fuel Project Office /S/

SUBJECT: Estimate of Hydrogen Production From Radiolysis in Spent Fuel Casks

Following the unanticipated gas burn during VSC-24 cask loading at Point Beach on May 27, 1996, the Spent Fuel Project Office (SFPO) initiated a review to estimate the production of hydrogen by radiolysis in a spent fuel storage cask. The NMSS staff conducted a limited literature search on radiolysis and made some simplified calculations to estimate a hydrogen production rate. The details are attached.

From this review, the following points are clear:

- Radiolytic decomposition of water (and production of hydrogen gas) in a spent fuel storage cask is a complex process influenced by the types and intensities of radiation present, the boron concentration, and the presence of chemical impurities and dissolved gases.

- Experimental results show that in a mixed radiation field with a constant gamma source, a minimum threshold of neutron interaction with boron is required to produce a net yield of hydrogen gas. Other experiments have shown that gamma radiation is effective in the recombination of free hydrogen gas in a mixed radiation field.

- Gamma radiation dominates the radiation dose rates in the spent fuel storage cask.

- On the basis of this review, the net production of hydrogen gas from radiolysis in a spent fuel storage system is expected to be small (well below the quantities needed for combustion) but an absolute net hydrogen production rate cannot be quantified.

Based on the above, the staff believes that radiolysis was not a significant contributor to the hydrogen gas production at Point Beach and is not expected to be a source for other spent fuel storage systems. A more definitive quantification of the net hydrogen production rate could be obtained by significant additional research, data collection from systems in place, and possible experimentation. This further research is not recommended because hydrogen production is expected to be low and the anticipated response to NRC Bulletin 96-04 that requests licensees to demonstrate the safety of the cask loading and unloading operations.

Attachment: As stated

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Background

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. Hydrogen gas production is a complex process involving decomposition of water molecules, recombination of decomposition products back to water (back reactions), chemical reactions of the decomposition products to form hydrogen peroxide and molecular hydrogen (H_2), and the formation of various radicals such as OH, HO_2, etc.

The literature states that mixed radiation fields will produce a competitive effect between water decomposition and recombination. In experiments, 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]. These results suggest that gamma radiation plays a role in recombination.

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 key variable in this experiment was the α energy density from the $B^{10}(n,\alpha)Li^7$ reaction. The experiments found that a minimum boric acid concentration (proportional to the α energy density) was required before any appreciable H_2 production was observed. This is further evidence of a H_2 removal factor. Once H_2 production began, it was linear with increasing boric acid concentration and thus α energy density.

Calkins[3] reported that hydrogen gas evolution from experiments with borated water was a linear function of the rad dosage calculated as En - Eγ. Where En is the combined energy absorption from neutron moderation and the neutron-alpha reaction with boron and Eγ was the γ energy absorption.

The production of H_2 from decomposition in an air free boric acid solution can be generally expressed as follows:

dH_2/dt = gross production - removal

Much work has gone into quantifying H_2 production from various types of radiation. The production factor is referred to as a "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 used in this discussion are provided below:

Beta, gamma $G(H_2)_\gamma = 0.45$
neutrons $G(H_2)_n$ 1.12 (fast scattering)
For thermal neutrons, $G(H_2)_\gamma$ is used due to the production of gammas (2.2MeV) from neutron capture in hydrogen
$B^{10}(n,\alpha)Li^7$ $G(H_2)_\alpha = 1.70$

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

gross production $= G(H_2)_\alpha(E_\alpha) + G(H_2)_\gamma(E_\gamma) + G(H_2)_\gamma(E_{th})$

where: E_α = α energy absorption density (eV/cm^3-min) (assume all α energy deposited in water)
E_γ = γ energy absorption density (eV/cm^3-min)
E_{th} = thermal neutron capture energy absorption density (eV/cm^3-min)

The experiments by Hart, et al, measured a γ energy absorption density of 11.9E20 eV/liter-min and a thermal neutron flux of 8.34E13 n/cm^2-min in the experiment. A fast neutron flux was not discussed and is assumed to be negligible. The H(n, γ)D and the $B^{10}(n,\alpha)Li^7$ reaction rates can be calculated to provide energy absorption densities from those reactions.

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

removal $= G_r(E_\gamma + E_{th})$.

Given the net H_2 experimental production rates and calculated gross production rates, experimental G_r values can be derived. The following experimental G_r values were calculated for each boric acid concentration.

Boric Acid Concentration (moles/liter)	Net H_2 production (μmole/min)	G_r (H_2/100eV)	E_α (10^{18}eV/cm^3-min)	E_α/E_γ
0.02	0	0.99	1.77	1.49
0.0313	21 ± 2	1.07	2.76	2.32
0.05	53 ± 2	1.24	4.415	3.71
0.0732	93 ± 5	1.44	6.46	5.43
0.10	147 ± 2	1.59	8.83	7.42

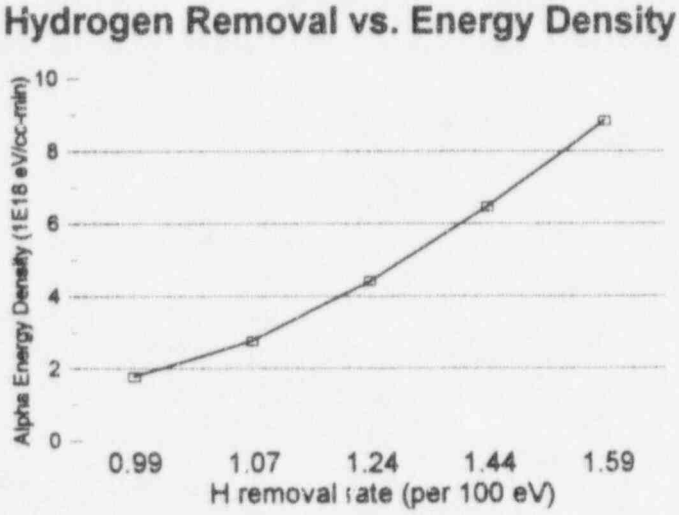

Figure 1

From the graph, the hydrogen removal factor (G_i) varies nearly linearly with the α energy absorption density in the higher energy ranges and appears to be approaching a minimum value for lower energy ranges. G_i would be expected to approach $G(H_2)_\gamma$ for a pure gamma field where no net H_2 production is observed. The gamma/neutron fluxes are constant in this case.

VSC-24 Conditions

The conditions in the VSC-24 cask before draindown include the presence of spent fuel pool water with a minimum concentration of boron at 2850 ppm. Boron is usually in the form of dissolved boric acid assumed to be H_3BO_3. The pool water contains some concentration of dissolved gases from exposure to air (primarily nitrogen and oxygen) and the products of radiolytic decomposition from the fuel in the pool. The cask is at roughly atmospheric pressure depending on the tightness of the fit of the shield lid and the water temperatures range from 80 to 120°F.

Data on the fuel assemblies loaded in the cask at Point Beach:

Westinghouse 14X14 bundles	
peak decay heat 0.403 kw/assembly	(design basis ≤ 1kw/assembly)
peak gamma source 2.47E15 γ/sec - assembly	(design basis 6.8E15 γ/sec - assembly)
peak neutron source 9.28E7 n/sec - assembly	(design basis 1.2E8 n/sec - assembly)

The design basis values except boron concentration were used for this evaluation since the decomposition rate is dependant upon the radiation dose rates and will provide a bounding condition. Boron concentration used was 3000 ppm.

Qualitative Radiolysis Estimate

The staff ran a SAS1 calculation for a cylindrical homogenous model with a fuel water mix representative of the fuel basket to estimate neutron and gamma fluxes and dose rates. The staff also ran a dry model to see the difference in dose rates and therefore estimate the fraction of radiation absorbed in the water. The results follow:

Wet	radial wall neutron dose rate at axial centerline	0.556 rem/hr
	radial wall neutron flux at axial centerline	7.69E3 n/cm² sec
	radial wall gamma dose rate at axial centerline	2.64E4 rem/hr
	radial wall gamma flux at axial centerline	1.92E10 γ/cm² sec
Dry	radial wall neutron dose rate at axial centerline	1.67 rem/h
	radial wall neutron flux at centerline	2.17E4 n/cm² sec
	radial wall gamma dose rate at axial centerline	2.98E4 rem/h
	radial wall gamma flux at axial centerline	2.13E10 γ/cm² sec

An estimate of the absorbed energy deposition (related to dose) is based on the method given in reference 3 using the following input data.

The average neutron energy is 2.29MeV
The neutron flux inside the "fueled zone" was assumed to be 10X the "dry"wall flux equal to 2.17E5 n/cm^2 sec

The average gamma energy was assumed at 0.362 MeV
The gamma flux inside the "fueled zone" was assumed to be the "wet"wall flux equal to 1.92E10 γ/cm^2 sec

Boron concentration used was 3000 ppm. The calculated macroscopic cross-section was $\Sigma_{aB} = 0.0987$/cm. The thermal neutron flux was assumed to be 10X the "wet" flux at energies of 10eV and below equal to 1.00E4 n/cm^2 sec.

Alpha energy absorption density $E_\alpha = 2.3E9$ eV/cm^3-sec (assumes all energy deposited in water)

Gamma energy absorption density $E_\gamma = 1.92E14$ eV/cm^3-sec

Fast neutron energy absorption density $E_f = 2.20E11$ eV/cm^3-sec

Thermal neutron energy absorption density $E_{th} = 3.08E8$ eV/cm^3-sec

The gross H_2 production is $G(H_2)_\alpha(E_\alpha) + G(H_2)_\gamma(E_\gamma) + G(H_2)_\gamma(E_{th}) + G(H_2)_f(E_f)$
$= 8.665E11$ molecules H_2/cm^3-sec

Considering the case for design basis fuel where there is no removal of hydrogen, the gross production rate for the entire VSC-24 water volume (5.21E6 cm^3, p.11-47, SAR) is calculated at 7.5E-6 moles per second. This equates to about 0.65 moles of hydrogen produced in 24 hours. This calculated value is far less than the approximately 4 moles found in the cask about 12 hours after the burn (16cc/kg dissolved and 5.44% in the free space). These values alone confirm that another mechanism for hydrogen production existed in the VSC-24.

Considering only the gross H_2 production rate is conservative since removal is ignored. If little hydrogen is assumed to remain in solution, this rate yields a sufficient quantity of H_2 for a flammable mix in the 30-gallon free space of the VSC-24. Absent additional research and/or experimental data, there is no direct way to calculate a net H_2 production rate for a spent fuel storage cask. However, a gross production without removal is not expected because gamma radiation dominates the radiation dose rates in the spent fuel storage cask. The E_α/E_γ for the cask is 1.20E-5 as compared to the experimental threshold E_α/E_γ value of 1.49. This comparison suggests very little H_2 production from the alpha interaction and significant removal potential by the gamma flux. Thus, little net H_2 production is expected.

If the net H_2 production is assumed to be zero, a G_r can be calculated and compared with experimental values.

H_2 removal $= G_r(E_\gamma + E_{th})$

Therefore G_r = (8.665E11 molecules H_2/cm^3-sec)/ $(E_\gamma + E_{th})$ = 0.00451 molecules H_2/eV
= 0.451 molecules H_2/100 eV

This value is comparable to $G(H_2)_\gamma$ and well below the values shown in figure 1. Smaller removal factors would yield net H_2 production but do not correlate to the experimental observations. Additionally, reference 3 states that the net H_2 production rates are a linear function of the absorbed

energy calculated as E_n-E_γ where $E_n = E_\alpha + E_{th} + E_f = 2.23E11$ eV/cm^3-sec. In this case, E_γ is greater and thus there is no net H_2 production rate.

Conclusion

The staff believes that radiolysis was not a significant contributor to the H_2 generation at Point Beach. The above calculations are based on experimental results that qualitatively show that net H_2 generation rates should be small. Significant research and/or experimentation would be necessary to quantify the net H_2 production in a spent fuel cask. This research is not recommended because other causes of H_2 generation were identified at Point Beach and all cask users have been requested to demonstrate safety in response to NRC Bulletin 96-04.

REFERENCES

1. R. G. Sowden, "Radiolytic problems in Water Reactors", J. Nucl. Material., 8 (1963) p. 81

2. E.J. Hart, W. R. McDonnell, and S. Gordon, "The Decomposition of Light and Heavy water Boric Acid Solutions by Nuclear Reactor Radiations," Proceedings of the First U.N. International Conference on Peaceful Uses of Atomic Energy, Geneva, 1955, Vol. 7, p. 593

3. H. Etherington, editor, Nuclear Engineering Handbook, 1958, p. 10-126, McGraw Hill Co., Contribution from V.P. Calkins, "Radiation Damage to Liquids and Organic Materials"