A Review of Radiolysis Concerns for Water Shielding in Fission Surface Power Applications

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Abstract. This paper presents an overview of radiolysis concerns with regard to water shields for fission surface power. A review of the radiolysis process is presented and key parameters and trends are identified. From this understanding of the radiolytic decomposition of water, shield pressurization and corrosion are identified as the primary concerns. Existing experimental and modeling data addressing concerns are summarized. It was found that radiolysis of pure water in a closed volume results in minimal, if any net decomposition, and therefore reduces the potential for shield pressurization and corrosion.

Keywords: radiolysis, water shield, water decomposition,

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INTRODUCTION

With the space program focus to emphasize more on permanent return to the Moon and eventually manned exploration of Mars, there has been a renewed look at fission power to meet the difficult technical & design challenges associated with this effort. This is due to the ability of fission power to provide a power rich environment that is insensitive to solar intensity and related aspects such as duration of night, dusty environments, and distance from the sun, etc. One critical aspect in the utilization of fission power for these applications of manned exploration is shielding. Although not typically considered for space applications, water shields have been identified as one potential option due to benefits in mass savings and reduced development cost and technical risk (Poston, 2006). However, the water shield option requires demonstration of its ability to meet key technical challenges including such things as adequate natural circulation for thermal management and capability for operational periods up to 8 years. Thermal management concerns have begun to be addressed and are not expected to be a problem (Pearson, 2007). One significant concern remaining is the ability to maintain the shield integrity through its operational lifetime. Shield integrity could be compromised through shield pressurization and corrosion resulting from the radiolytic decomposition of water.

RADIOLYSIS

Process

The radiolysis process can be separated by function into three distinct stages. First incident radiation deposits its energy into the water through various interaction mechanisms resulting in ionized or excited water. Then, the water begins to rapidly adjust to the almost instantaneous presence of the ionized and excited water even before the molecules can adjust through their normal agitation. Atomic adjustments ensue and result in the formation of chemically active free radicals. With the presence of chemically active species, diffusion driven chemical processes then occur. During this stage both water decomposition and reformation can result through competing reactions. In a closed volume, the decomposition products accumulate which in return lead to water reformation. The reactions compete until decomposition-reformation equilibrium is reached (Monson, 1955).
Energy Deposition

Although the water in a water shield would be exposed to a mixed field of charged and uncharged radiation, the resulting effect of ionizing radiation would be charged particles. X-rays and γ-rays will create a varying spectrum of electrons primarily from photoelectric effect and Compton scattering. Fast neutrons will scatter losing their energy and creating ionized nuclei such as recoil protons. Thermal neutrons can be absorbed in the nucleus and release high energy γ-rays (2.2 MeV for H) or release an α particle such as from the neutron absorption by boron in borated water. The energy deposited results in ionized water (H$_2$O$^-$) and excited water (H$_2$O$^+$). This occurs within 10$^{-15}$ seconds within local regions of the charged particle track.

Atomic Adjustment

Rapidly after the formation of H$_2$O$^-$ and H$_2$O$^+$, atomic process adjust for the added energy resulting in the formation of the following chemically active radicals through the corresponding mechanisms. These radical yields result within 10$^{-12}$ to 10$^{-12}$ seconds, at which point they begin to randomly migrate driven by diffusion (Turner, 1995).

$$H_2O^+ + H_2O \rightarrow H_2O^+ + OH$$
$$H_2O^+ \rightarrow \left[ \begin{array}{c} H + OH \\ H_2O^+ + e^- \end{array} \right]$$
$$e^- \rightarrow e_{aq}$$

Chemical Reactions

With the chemically active radicals diffusing, the spatial distribution or location of the radicals becomes the determining aspect of what chemical reactions occur. If the radicals are close enough to react with each other and undergo radical-radical reactions, water decomposition results through the following reactions.

$$H + H \rightarrow H_2$$
$$OH + OH \rightarrow H_2O_2$$

Water decomposition results in the formation of the molecular decomposition products hydrogen (H$_2$) and hydrogen peroxide (H$_2$O$_2$). Hydrogen peroxide can also decompose into oxygen (O$_2$) (Monson, 1955) which would be more significant in a water shield application with temperatures above 200°F. As such, the expected molecular decomposition products are H$_2$(g) and O$_2$(g). Depending on the extent of decomposition and specifics of the shield design, this could result in corrosion, formation of explosive mixtures in a gas space above the water, or shield pressurization.

If the radicals are spaced apart, it will be more probable that they will diffuse into the bulk of the water without reacting. In this case, the radical decomposition products will be available for reacting with the molecular decomposition products in (2) resulting in radical-molecular reactions that promote water reformation through the following mechanisms.

$$\left[ \begin{array}{c} H + H_2O_2 \rightarrow H_2O + OH \\ OH + H_2 \rightarrow H + H_2O \end{array} \right] \xrightarrow{\text{diffusion}} H_2 + H_2O \rightarrow 2H_2O$$
$$\left[ \begin{array}{c} OH + H_2O_2 \rightarrow H_2O + HO_2 \\ H + HO_2 \rightarrow H_2O_2 \end{array} \right] \xrightarrow{\text{diffusion}} H + OH \rightarrow H_2O$$
$$\left[ \begin{array}{c} H + O_2 \rightarrow HO_2 \\ OH + HO_2 \rightarrow H_2O + O_2 \end{array} \right] \xrightarrow{\text{diffusion}} H + OH \rightarrow H_2O$$

$$2H_2 + O_2 \rightarrow 2H_2O$$
Reaction (3) is beneficial since it converts decomposition products into water which promotes the water reformation process. Although reactions (4) and (5) also reform water, it is done without replenishing the radicals (the products do not consist of additional radicals). As such, reactions (4) and (5) reform water but reduce the rate of the water reformation process. In addition, however, the recombination of hydrogen and oxygen in reaction 6 reforms water and promotes the water reformation process. This reaction can be thermally catalyzed or radiation induced.

**Trends and Behavior**

From this understanding of the radiolytic decomposition of water, the affects of key processes parameters can be predicted and compared with some of the extensive experimental and simulated work already conducted.

**Linear Energy Transfer (LET)**

As mentioned earlier, the effect of ionizing radiation on water is to generate charged particles that deposit their energy in the water inducing the first stage of radiolysis. Linear Energy Transfer (LET) quantifies the energy deposited to the water from the charged particles. With increasing LET, more localized energy deposition would occur resulting in more radical production along the track of the charged particle. As such, there would be a high probability of radical-radical interactions corresponding to the large density of radicals in the track. This is illustrated in figure 1 (Allen, 1961). Therefore, increasing LET will favor more water decomposition. Figure 2 (Allen, 1961) indicates this by how H and OH radicals decrease while H2O2 and H2 molecules increase with increasing LET.

**FIGURE 1.** "Schematic of water decomposition by charged particles. Each dot represents deposition of 20 ev, or approximately, one water molecule decomposed. Upper line, 40 kev electron, LET 0.08 ev/A. Middle, 18 Mev deuteron, 0.5 ev/A. Bottom, 5,5 Mev a-ray, 9 ev/A. A 1 Mev-electron would on the average show no events in the length here depicted" (Allen, 1961).

**FIGURE 2.** "The affect of LET on the yield of radical and molecular decomposition products. Yield is indicated by a G value that represents the number of species per 100 eV absorbed energy." (Allen, 1961).
Experimental data in Figure 3 (Monson, 1955) confirms this trend through the effect of epithermal neutrons and gamma fluxes on water decomposition indicated by the pressure of the decomposition products. Water in a quartz ampoule at 77°F was irradiated in the ORNL X-10 reactor. When an equilibrium condition was reached, as indicated by a flat slope, various shields were placed around the ampoule. On one run, a paraffin shield removed the epithermal flux allowing the gamma flux to dominate and thereby showing the effect of the low LET radiation. On the other run, a lead shield removed the gamma flux allowing the epithermal flux to dominate and show the effect of increased localized energy deposition. As expected, the gamma flux (low LET radiation) results in reformation where the epithermal neutron flux results in water decomposition. The difference in equilibrium levels between the two runs is due to differences in water purity which will be discussed later but has no bearing on this discussion.

Temperature effects can be separated in terms of the two competing reactions. Effects on water decomposition are minimal if any (Draganic, 1971), (Allen, 1961). However, increasing temperatures supports water reformation and decreases decomposition (Calkins, 1958). This is due reaction (6). Experimental evidence indicates that at low temperatures, when concentrations of hydrogen and oxygen are high, this reaction substantially bolsters water reformation but not in the vapor phase. However, other experimental results in Figure 4A (Monson, 1955) indicate that the recombination at high temperatures is also appreciable and occurs in both the liquid and vapor phase of water. Oxygen and hydrogen were added, in near stoichiometric proportions, to the vapor phase of an ampoule containing water at 202°F. The total pressure of the ampoule increased with the partial pressure contribution of the added gases. As irradiation begins and catalyzes reaction (6), water reformation occurs indicated by the drop in total pressure. Figure 4B (Monson, 1955) shows that the rate of recombination also increases with temperature up to about 300°F where above this it seems to become independent of temperature although remaining fairly high. In addition to reducing decomposition, higher temperature correspondingly lowers the equilibrium concentration of decomposition products. Experimental evidence in Figure 4C (Monson, 1955) shows increasing the temperature from 97°F to 230°F reduced the equilibrium partial pressure from 14 to 1.2 psi attributing this to reaction (3).
Dose

If an equilibrium decomposition-reformation is reached, dose does not affect the net decomposition beyond a point. If equilibrium is not established, possible in some borated waters, decomposition will continue with increasing dose. When water is first irradiated, only the decomposition process occurs since there are no molecular decomposition products to reform into water. In a closed system, the molecular decomposition products begin to accumulate, some of which are reformed into water effectively slowing down the rate of decomposition. As the concentrations of decomposition products increase, water reformation also increases, in accordance with the mass-action law, until the rate of decomposition is eventually reduced to zero and an equilibrium condition is reached. Equilibrium states have been observed in both the experimental data in Figure 3 and modeling predictions in Figure 5 (Bjergbakke, 1989).

Dose Rate

Higher dose rates increase interaction density and lead to a higher radical density. This will increase the probability of radical-radical interactions resulting in more decomposition. In a closed volume, as discussed previously, it will also cause more water reformation. The net effect will be to not only speed up the evolution to the equilibrium state but result in a higher equilibrium concentration of molecular decomposition products as shown in Figure 6 (Bjergbakke, 1989). The equilibrium shift may result from the initial decomposition in the close volume occurring much more rapidly.

FIGURE 5. Radiolytic products in air-free pure water at 1 Gy/sec adapted from Bjergbakke, 1989.

FIGURE 6. Formation of Radiolytic Products in Air-free Pure Water Following a 100 Gy electron pulse delivered in 1 x 10^-6 seconds Adapted from Bjergbakke, 1989.
Draganic provides an overview of the extensive work conducted regarding this trend. In short, multiple facets of research concluded that there is not strong dependence on pH. Only in extreme cases of multimolar solutions represent an area that requires special study. The dependence on the radical and molecular yields on pH in water undergoing $\gamma$ radiolysis was derived from measurements on formic acid-oxygen solutions shown in Figure 7 (Draganic, 1971).

**FIGURE 7.** The affect of pH on Radical and Molecular Yields of Water $\gamma$-radiolysis adapted from Draganic.

### Pressure

Draganic documents multiple experiments regarding pressure. The overall conclusions were that pressure does not affect the overall yields of the primary reducing species and that there is no effect on the primary yields of free radical and molecular products in an acid medium. Although the rate constants of some of the reactions studied were appreciably affected by changes in pressure, no effect of pressure on the primary yields of water radiolysis could be proved.

### Impurities

Reactions involving ionic impurities and decomposition products depend on the availability of the H and OH radicals which is primarily a function of the $\gamma$ flux. As such, the effects of impurities are expected to be of considerable importance when the $\gamma$ flux is high and relatively ineffective when the $\gamma$ flux is low (Monson, 1955).

Ionic impurities reduce water reformation by removing the H and OH radicals through reactions with them. Br, I$^-$, and Cu$^{2+}$ ions are among the most reactive and as such, solutions with even the most dilute concentrations will result in extremely high equilibrium concentrations and a net increase in the decomposition rates. In conditions that would result in equilibrium partial pressures of less than 10 psi in pure water, solutions of KBr, KI, and CuSO$_4$ may produce pressures more than 1,500 psi. Similarly, a 0.0088N solution of HCl produced a pressure of 350 psi; 1.03N of H$_2$SO$_4$ resulted in the same pressure as pure water (Calkins, 1958) (Monson, 1955). Additional supporting experimental evidence is provided by Hart, E.J. Water purity associated with a specific resistance of 10$^6$ ohm-cm was identified in the CP-3 & CP-3$'$ reactors, by Monson, to provide negligible decomposition.

Suspended impurities do not affect water decomposition or reformation since they do not react with the H and OH radicals. However, impurities such as copper, rhodium, palladium, platinum, silver, iodine, tin, iron and titanium have shown potential to catalyze water reformation at temperatures above 400°F (Calkins, 1958) (Monson, 1955).

Effects from decomposition products essentially depend on the proportions of H$_2$ to O$_2$ or H$_2$O$_2$. Excess H$_2$ can reduce decomposition by removing H$_2$O$_2$ and O$_2$ through reactions (3) and (6). At high temperatures subjected to an average neutron and gamma irradiation levels in a reactor, initial introduction and maintenance of H$_2$ concentrations equivalent to 5 to 10 psi partial pressure reduced decomposition of pure water to practically zero and maintained the O$_2$ concentration closely equal (Monson, 1955). Experimental results were shown in Figure 4A and simulation
results are shown in Figure 8 (Bjergbakke, 1989). Additional confirmations are provided by Hart, E.J. (1956) and Allen, A.O. (1961).

The presence of excess O₂ promotes H₂O₂ formation and increases the decomposition equilibrium concentrations. In simulation shown in Figure 8B (Bjergbakke, 1989), air saturated water resulted in 10,000 times higher concentration of H₂O₂ than air free water shown earlier in figure 6. Additional confirmations are provided by Hart, E.J. (1956).

Borated water does not affect decomposition in a γ field but can lead to continuous decomposition in a neutron field due to the generation of high LET α particles from the ¹⁰B(n,α)⁷Li interaction. Experimental research by Hart, E.J. has shown that no net decomposition is noticed until boron concentration reaches a critical level to overcome the surplus radicals available for recombination from the γ flux shown in figures 8A and 8B (Hart, 1956). Above this level, water decomposition, indicated by H₂ production, is linearly proportional to alpha energy deposition and therefore the boron concentration (Hart, 1956) (Allen, 1961) (Calkins, 1958). However, figure 8C (Hart, 1956) shows H₂ addition increases the critical boron concentration for net decomposition allowing for higher concentrations of borated water before decomposition occurs.

WATER SHIELD APPLICATION

A water shield for a 40kWe 8 year design was selected as a baseline. The shield contains 800 kg of water at an average temperature of 392 K (246 °F) and a boron concentration of 500 ppm. Average dose in water is 29 Grad with an average dose rate of 0.42 MRad/hr.
Decomposition of pure, air-free water in a mixed gamma and neutron flux is unlikely. Similar behavior is expected in borated water if boron concentrations are below a critical level. At temperatures at or above 202°F (367 K), radiation-induced recombination of H₂ and O₂ occurs in both the water and vapor stage bolstering water reformation and lowering the equilibrium decomposition product concentrations. The experimental results number 1 and 2 in Figure 10 (Calkins, 1958) support this indicating a maximum H₂ partial pressure of 6 psi and 2 psi for O₂.

Data from test numbers 1 and 2 in Figure 10 are compared to the water shield application in Table 1. The data is at comparable temperatures and dose for the eight-year shield lifetime. The data reflects higher thermal neutron flux where the shield would be exposed to a higher fast flux tending towards more decomposition. However, the shield would also be exposed to more gamma fluence that would support recombination. Overall, Table 1 indicates that the relevant radiolysis parameters for the selected baselines are similar to the experiments in Figure 10 which thereby should be fairly representative of the expected results in the water shield.

In test numbers 5 and 6 (Figure 10), significant decomposition is indicated by gas evolution and test termination with pressure rise up to 60 psi attributed to the boron in the water. Footnote 1 in Figure 10 explains that gas evolution, and hence decomposition, was found to be a linear function of rad dosage. Recalling work by Hart, E.J., this linear behavior of decomposition indicates that boron levels were beyond critical concentrations in those tests. Hart’s work identified a critical boron concentration of 0.02 M in their experiments. The baseline design has been shown to benefit from boric acid concentrations around 0.046 M. Although this concentration is higher than the work identified a critical boric acid concentration of 0.02 M in their experiments. The baseline design has been shown to benefit from boric acid concentrations around 0.046 M. Although this concentration is higher than the critical level identified in Hart’s experimental work, it is unclear if it surpasses the critical concentration for the water shield since Hart’s critical concentration may not necessarily be directly applied due to differences in other relevant radiolysis factors. For example, the water shield’s critical concentration may be higher than 0.02 M since it is exposed to a lower dose rate than in Hart’s work. Regardless, Hart demonstrated that the addition of 1-12 can effectively increase the critical concentration which can be employed as part of the shield design if necessary.

### TABLE 1. Experimental Data Test Factors Comparison to Water Shield Application

<table>
<thead>
<tr>
<th>Application</th>
<th>Water Type</th>
<th>Water Temperature (°F)</th>
<th>Dose (59 rad)</th>
<th>Thermal Neutron Flux (n/cm²)</th>
<th>Fast Neutron Flux (n/cm²)</th>
<th>Avg Photon Energy (MeV)</th>
<th>2 Fluence (n/cm²)</th>
<th>Roentgens</th>
</tr>
</thead>
<tbody>
<tr>
<td>water reactor</td>
<td>demineralized</td>
<td>220-250</td>
<td>3.37 x 10¹⁴</td>
<td>2.78 x 10¹⁷</td>
<td>1.00</td>
<td>2.01 x 10¹⁰</td>
<td>1.06 x 10¹⁰</td>
<td>1.06 x 10¹⁰</td>
</tr>
<tr>
<td>water reactor</td>
<td>distilled</td>
<td>220-250</td>
<td>3.37 x 10¹⁴</td>
<td>2.78 x 10¹⁷</td>
<td>1.00</td>
<td>2.01 x 10¹⁰</td>
<td>1.06 x 10¹⁰</td>
<td>1.06 x 10¹⁰</td>
</tr>
<tr>
<td>water shield</td>
<td></td>
<td>246</td>
<td>7.30 x 10¹⁴</td>
<td>5.71 x 10¹⁹</td>
<td>1.52</td>
<td>2.78 x 10¹⁰</td>
<td>19 x 10¹⁰</td>
<td>19 x 10¹⁰</td>
</tr>
</tbody>
</table>
Hydrogen Considerations

Due to the effect of the net H₂ concentration on equilibrium, and hence decomposition and shield pressurization, it is important to understand the balance between all sources of H₂ production and loss. Additional H₂ production could result from corrosion of some materials with water where H₂ is formed without additional formation of O₂. This could have the effect of increasing H₂ concentration and pressure in a non-equilibrium state if there were no other removal mechanisms. Alternatively, in addition to water reformation, H₂ can be lost in the water through any degasification mechanisms (mechanical or diffusion into gas space) or completely out of the shield through diffusion. This could result in low H₂ to O₂ or H₂O₂ ratios leading to increased decomposition. However, equilibrium is expected as experiments have shown with the key factor being H₂ concentration proportions to that of O₂ or H₂O₂. In another regard, the net H₂ concentration and partial pressure could affect corrosion or hydrogen damage in some materials. As such, hydrogen damage or corrosion, other sources of H₂, and H₂ loss by diffusion through the shield should be kept in mind while determining material selection for the water shield tank.

Pressurization

High equilibrium partial pressure of decomposition products are not expected for air free pure water irradiated by neutrons and gamma radiation. This is equally expected for borated water that is below the critical concentration where the decomposition effects from alpha particles do not overwhelm the recombination effects from the gamma radiation. This critical concentration is both a factor of boron and hydrogen concentrations. As such, shield pressurization should not be a concern as long as decomposition is minimized by maintaining a high purity of water and a relatively higher concentration of H₂ as compared to O₂ or H₂O₂.

Corrosion

The potential for corrosion of the shield can arise from exposure to decomposition products, hydrogen and possible varying pH of the water. The likelihood for corrosion can be significantly reduced by minimizing water decomposition through bolstering water reformation (operating temperatures higher than 200 °F, maintaining excess H₂, minimizing O₂ concentrations in the water, etc.). As well, proper material selection can provide additional margin of resistance.

CONCLUSION

Water shields have been identified as an option for fission surface power applications. Corresponding to this application, shield pressurization and corrosion resulting from the radiolytic decomposition of water has been identified as concerns with regards to feasibility and practicality; specifically to weight and shield integrity. A review of the radiolytic decomposition process has indicated key parameters to be the radiation type and intensity, water temperature, dose rate, and water purity. A review of both experimental and modeling data has revealed that the decomposition of water can be minimized. In general, (1) oxygen should be removed as much as economically feasible, (2) small amounts of hydrogen should be dissolved in the water before irradiation, (3) a slight over pressure of a few psi hydrogen should be maintained during irradiation, and (4) the water should remain relatively pure on the order of 10⁶ ohm-cm. Through minimizing decomposition, low equilibrium partial pressures on the order of a few psi can be expected and if coupled with careful material selection, should sufficiently address any potential for corrosion or shield pressurization.

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