Conf-910435--66

APR 2 4 1991

ANL/CP--71207

DE91 010792

EFFECT OF IONIZING RADIATION ON THE WASTE PACKAGE ENVIRONMENT

D. T. REED
Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439-4837
(70) 972-7964

R. A. VAN KONYNENBURG
Lawrence Livermore National Laboratory
P. O. Box 808
Livermore, CA 94550
(415) 422-0456

ABSTRACT

The radiolytic production of nitrogen oxides, nitrogen acids and ammonia are discussed in relation to the expected environment in a high-level waste repository that may be constructed at the Yucca Mountain site if it is found to be suitable. Both literature data and repository-relevant data are summarized for air-water vapor systems. The limiting cases of a dry air and a pure water vapor gas phase are also discussed. Design guidelines and recommendations, based solely on the potential consequence of radiation enhancement of corrosion, are given.

I. INTRODUCTION

The Yucca Mountain Site Characterization Project (YMP) is evaluating the suitability of Yucca Mountain in southwestern Nevada as a site for a high-level nuclear waste repository. The emplacement of a nuclear waste container in such a repository would subject the immediate environment of the container to significant levels of gamma radiation based on the current design. The interaction of gamma radiation with the near-environment of the waste package is an important factor in assessing its overall performance[1] because the radiolytic species generated can be detrimental to waste package performance.

Ionizing radiation would potentially affect processes during both the containment and controlled release periods of repository history. For the containment period, the following data are needed: (1) the yield of nitrogen oxides and acids in moist air systems, (2) the yield of ammonia in moist air systems, (3) the yield of organic acids in CO_2-containing systems, and (4) the interaction of these products with the various components of the waste package. We have already shown that the radiolytic products generated will have important implications for the selection of the container material.[2,3]

In the controlled release period the potential effect of ionizing radiation on radionuclide migration is the most important concern. The yields and nature of the products generated during the unsaturated period might also impact radionuclide release by altering the composition of the ground-water, if the unanticipated condition of site inundation occurred. This is, however, beyond the scope of this paper.

Herein we have focused on literature data and experimental data that relate to the first two radiolytic concerns identified for the containment period. With respect to the formation of NO_x, literature values for initial processes were evaluated and compared to the results of the long-term gamma experiments that we performed in the 25 to 200°C temperature range. More detailed work on the potential formation of ammonia in oxygen-containing systems was performed. Design factors that affect the overall yield of these products are considered.

II. WASTE PACKAGE ENVIRONMENT

The expected environment at the proposed Yucca Mountain site during the initial phase of repository history would be a gas phase that consists primarily of air, carbon dioxide, and water vapor. This gas phase would be in contact with the atmosphere with a total pressure of approximately 660 torr, corresponding to atmospheric pressure at the elevation of the proposed repository. Emplacement of high-level nuclear waste containers would perturb the preemplacement environment by heating it to temperatures in excess of 200°C (ambient is 27°C) and subjecting the gas phase present to significant levels of ionizing radiation.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

The expected temperatures in the waste package will depend on several design considerations that have not yet been completely resolved. Initial results on the waste package scale were reported by O'Neal et al.[4] and showed that waste package temperatures would exceed 100°C for the duration of the 300-1000 y containment period. More recently, the variability of borehole temperatures was calculated by Johnson and Montan[5] to be higher than previously thought. When waste emplacement scenarios and variability in the thermal loading of the waste was taken into account, maximum temperatures in the waste packages ranged between 60 and 220°C. The temperature range we have adopted for experimental purposes, when all factors are considered, is 27 to 250°C.

The composition of the preemplacement gas phase has been well characterized[6] as water vapor-saturated air with up to 0.13 mole% carbon dioxide. Within the total pressure constraint, the emplacement of high-level nuclear waste would affect the gas phase primarily by evaporating water. The range of conditions that are deemed anticipated in the waste package environment are: pure water vapor, dry air and humid air (between the two extremes). The relative humidity, defined as the ratio of water vapor pressure to the equilibrium vapor pressure of water at that temperature, would be set by the availability of water and the temperature of the waste package. Based on the temperature calculations just discussed, this would range between 3.9 and 35% (see Figure 1) for central panels. At the edge of the repository, some package temperatures may never exceed 96°C meaning that near-100% relative humidity could exist throughout repository history.
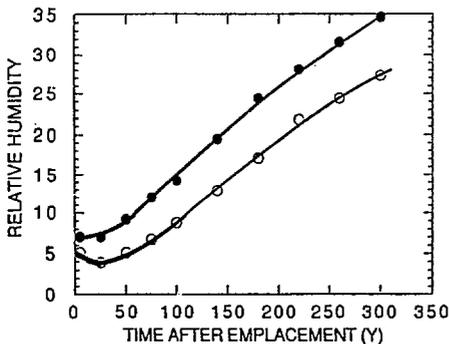

Figure 1. Maximum Relative Humidity Predicted for the Central Boreholes in Panel 14 (o) and Panel 6 (●).

The radiation levels at the container surface may be as high as 0.1 Mrad/h but will decrease rapidly, with respect to repository-relevant times, with an effective half-life of approximately 30 y. The total absorbed dose at the surface of the container will depend on the initial gamma flux present, which is a function of the design of the waste package, the radionuclide content of the waste form (glass loading or burnup of the spent fuel) and the age of the waste form. To a first approximation, this is proportional to the initial dose rate and is 5×10^{10} rad in the first 300 y for an initial dose rate of 0.1 Mrad/h.
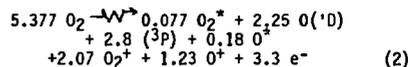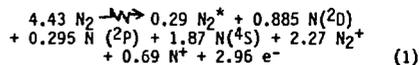
III. RADIOLYTIC YIELDS IN AIR-WATER VAPOR SYSTEMS

The expected environment for most of the containment period is an air-water vapor mixture that would exist at temperatures that range between 27 and 250°C at a total pressure of 660 torr. The key radiolytic products in this environment are: (1) nitrogen fixation products: nitrogen acids, nitrogen oxides and ammonia; (2) hydrogenous species: atomic and molecular hydrogen; and (3) oxygen-containing oxidizing species: oxy-radicals, ozone, and hydrogen peroxide. The expected yield of these species and results of the long-term yield studies conducted in support of the YMP are summarized in this section.
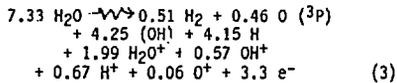
A. Primary Yields of Bulk Components

The bulk components of the ambient environment are nitrogen, oxygen, argon, carbon dioxide, and water vapor. Argon, although it can affect homogeneous gas phase reactions by energy transfer, is stable to radiolytic decomposition. Carbon dioxide is slowly decomposed to oxygen and carbon monoxide and would undergo condensation reactions to generate higher molecular weight organic compounds. We have not directly investigated its contribution to the overall radiation chemistry and its consideration is beyond the scope of this paper.

The following self-consistent listing of the primary yields in the remaining gases (units of molec/100 eV) was proposed:[7]

$$4.43 \ N_2 \xrightarrow{\ \wedge\wedge \ } 0.29 \ N_2^* + 0.885 \ N(^2D)$$
$$+ 0.295 \ N \ (^2P) + 1.87 \ N(^4S) + 2.27 \ N_2^+$$
$$+ 0.69 \ N^+ + 2.96 \ e^- \tag{1}$$

$$5.377 \ O_2 \xrightarrow{\ \wedge\wedge \ } 0.077 \ O_2^* + 2.25 \ O(^1D)$$
$$+ 2.8 \ (^3P) + 0.18 \ O^*$$
$$+ 2.07 \ O_2^+ + 1.23 \ O^+ + 3.3 \ e^- \tag{2}$$

DISCLAIMER

$$7.33 \; H_2O \xrightarrow{\sim\!\!\sim\!\!\sim} 0.51 \; H_2 + 0.46 \; O \; (^3P)$$
$$+ \; 4.25 \; (OH) + 4.15 \; H$$
$$+ \; 1.99 \; H_2O^+ + 0.57 \; OH^+$$
$$+ \; 0.67 \; H^+ + 0.06 \; O^+ + 3.3 \; e^- \qquad (3)$$

These are relatively insensitive to changes in the temperature. Actual yields of molecular products observed when air-water vapor systems are subjected to gamma radiation will, however, depend on the secondary reactions of these products with each other and subsequent molecular products that are formed in the irradiated system. This, as is discussed in the next few sections, will depend on dose rate, the surfaces present, and temperature.

B. Radiolytic Yield of Nitrogen Oxides and Acids in Air-Water Vapor Systems

The general radiation chemistry of moist air systems, with respect to the formation of nitrogen oxides, was previously reviewed.[8] The key step in the formation of nitrogen oxides is the radiation-induced breakdown of molecular nitrogen to atomic nitrogen. In dry air and low humidity systems, this then leads primarily to the direct formation of nitrogen dioxide and nitrous oxide along with trace concentrations of other oxides. Of the nitrogen oxides generated, nitrogen dioxide is the most important with respect to evaluating waste package performance. In dry air it directly oxidizes the metal and in humid air it is converted to nitric acid. This, depending on the relative humidity of the irradiated system, can be adsorbed onto the surface of the components of the waste package leading to detrimental effects.

1. Nitrogen Acids

Nitrogen acids are generated in moist air systems by oxidation of nitrogen dioxide and nitric oxide according to the following reactions:

$$OH + NO \longrightarrow HONO \qquad (4)$$

$$OH + NO_2 \longrightarrow HONO_2 \qquad (5)$$
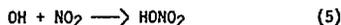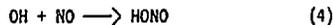
These reactions have been investigated in the temperature range of interest to the YMP. The rate constants and kinetics of these reactions have been extensively investigated in relation to atmospheric chemistry (acid rain production).[9,10] The rate constants for both these

reactions are high with a negative temperature dependence and also increase with increasing system pressure. These dependencies are consistent with the exothermicity of the reaction.

The reaction of the hydroxy radical with nitrogen oxides to form nitrogen acids is thermodynamically favorable over the temperature range of interest to the YMP. Once formed, however, the acids are not thermodynamically stable with respect to the bulk components of the air-water vapor mixture at elevated temperatures (above 120°C) and will undergo thermal decomposition. The kinetics of this process and the competitive process of nitrogen acid solvation in water films present have not been well characterized. The overall fate of the nitrogen acids at elevated temperatures is therefore not well understood.

In the irradiated air-water vapor system, the nitrogen oxides generated are rapidly converted to nitrogen acids by the OH radical generated from water vapor $[G(OH) = 4.25 \text{ to as high as } 8.2 \text{ molec/100 eV}].$[11] Nitric acid is the predominant product since nitrogen dioxide is more stable in the irradiated system and persists at a higher concentration in the gas phase than nitric oxide. In low-humidity systems, the yield of nitric acid is equal to the yield of nitrogen dioxide in the analogous dry air system (same nitrogen/oxygen ratio). The yield of nitrogen dioxide in the gas phase, based on our work, is shown as a function of absorbed dose in Figure 2 for dry and and low-humidity air at 120°C.
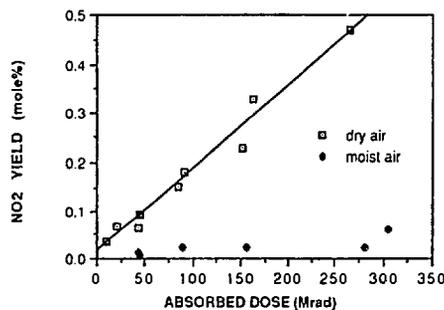

Figure 2. Yield of NO_2 in Dry and Low-Humidity Air at 120°C.

In high humidity systems, e.g., water vapor to air ratios greater than 0.1, the yield of nitrogen dioxide has not been well characterized. A nitrate yield of 1.9 was reported by Linacre and Marsh[12] for high LET radiation (mixed gamma-neutron), and a yield of 2.5 was reported by Jones[13] for high dose rate beta radiation. We have typically seen lower yields (0.5 to 1.5 molec/100 eV) in the longer-term and lower dose rate gamma studies. These appear to depend on the water vapor to air ratio of the system. The initial results we have obtained at 28 and 90°C are shown in Figure 3. For the purpose of modeling, yields in the range of 0.5 to 2.5 molec/100 eV need to be considered.

2. Nitrogen Oxides

Nitrous oxide, nitric oxide, nitrogen dioxide (and its dimer nitrogen tetroxide), and nitrogen pentoxide have been identified in the gas phase radiation and photochemistry of nitrogen-oxygen mixtures. For the temperatures and pressures relevant to the YMP, only nitrous oxide, nitric oxide, and nitrogen dioxide are important to consider. Under these conditions, nitric oxide is rapidly converted to nitrogen dioxide and does not increase in concentration with absorbed dose. The presence of water will also keep its concentration low due to reaction (4) in high-humidity systems. Nitrogen dioxide, when formed, is rapidly converted to nitric acid as discussed in the previous section.

Nitrous oxide, however, increases in concentration with absorbed dose and appears to be relatively stable towards reaction with metals and secondary products that build up in the gas 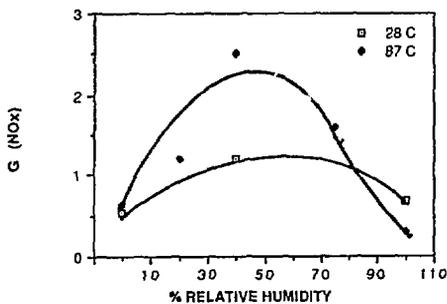phase. The yield, contrary to previous reports in the literature, is significantly affected by the presence of water vapor in the system. Typical yields we have obtained in low humidity systems, at 28, 90, and 150°C, are shown in Figure 4. Here a low-yield "induction" period is initially present that depends on the temperature. At the point where water was depleted in the system and at temperatures of 120°C or above, the yield was the same as observed in dry air systems. This is made evident by the up-turn in the 28 and 90°C data shown.

To further establish the low-humidity results, we investigated the yield of nitrous oxide in high-humidity systems at 90°C. Here, the build-up of nitrous oxide was linear with absorbed dose at a fixed relative humidity. A change from dry air to 100% water vapor saturation (0 to 525 torr of water vapor) decreased the nitrous oxide yield, in glass vessels, from 0.6 molec/100 eV to 0.03 molec/100 eV. Further work is planned at several temperatures to establish the yield over the entire range of temperatures relevant to the YMP.

C. Radiolytic Yield of Ammonia in Air-Water Vapor Systems

The potential formation of ammonia in O_2-N_2-H_2O vapor systems has also been investigated. This is an important considera-tion in evaluating material performance of some materials, such as some copper-based alloys, that are susceptible to ammonia cracking. Data pertaining to this system reported in the literature appear to be conflicting.
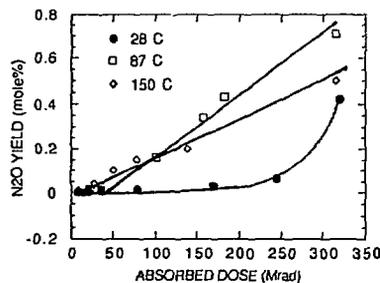

Figure 3. Yield of Nitrate, in molec/100 eV, as a Function of Relative Humidity.

Figure 4. Yield of Nitrous Oxide in Low-Humidity Air as a Function of Temperature and Absorbed Dose.

Irradiation of an N_2-H_2O vapor system containing a small amount of oxygen (0.1 mole%) resulted in the formation of ammonia and nitrous oxide as the predominant fixation products. The relationship between ammonia formation, nitrous oxide formation, and the depletion of oxygen is shown in Figure 5. The disappearance of oxygen is first order with respect to its concentration and cannot be accounted for solely by the buildup of nitrous oxide. Nitrous oxide formation is not well correlated with the concentration of oxygen in the system, indicating that the water vapor present (which accounts for most of the oxygen present in the system) was involved in the oxidation process. In this system, ammonia formation at $G(NH_3) = 0.03$ molecule/100 eV occurred, even though oxygen was present.
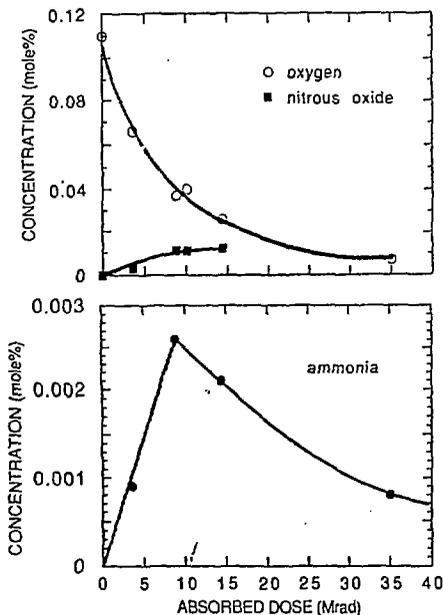

Figure 5. Concentration of Oxygen, Nitrous Oxide and Ammonia Following Irradiation of Water Vapor Saturated 0.1% O_2 in N_2 Mixture at 28 ± 2°C.

Small amounts of ammonia have also been observed in long-term irradiation of air-water vapor mixtures. This confirms that, although overall yields are low, the presence of oxygen does not entirely preclude the formation of some ammonia. Actual yields obtained will depend on the water vapor to oxygen ratio and the relative humidity of the irradiated system. This is currently being evaluated in more detail.

D. Radiolytic Formation of Atomic and Molecular Hydrogen in Air-Water Vapor Mixtures

The buildup of hydrogen in the gas phase is an important consideration because of the susceptibility of some materials to hydrogen embrittlement. Radiolytically, hydrogen is generated as a result of the decomposition of water (see Eq. 1). The rate of buildup will, therefore, depend on the mole fraction of water vapor in the gas phase.

The primary yields of molecular and atomic hydrogen from water vapor are 0.45 to 0.51 and 4.2 to 7.2 molec/100 eV, respectively. In air-containing systems, atomic hydrogen is rapidly converted to the hydroperoxy radical ($HO_2\cdot$). This will substantially lower the effective concentration of atomic hydrogen at the container material surface and lower the overall yield of hydrogen in the system. The best approximation for the overall yield of hydrogen from water vapor is its primary yield of 0.51 molec/100 eV. Experimentally, we have always observed small amounts of hydrogen in irradiated air-water vapor systems but there has not been a systematic buildup of hydrogen concentration with absorbed dose. This indicates that the behavior of hydrogen, if it does not migrate away from the irradiation zone, is to build up to a small concentration (generally <1 mole%) that is fixed by the radiation chemistry of the gas phase.

E. Radiolytic Formation of Ozone, Hydrogen Peroxide, and Oxy-Radicals in Air-Water Vapor Mixtures

Oxy and hydroxy radiolytic products contribute to the overall corrosion rates observed. Ozone is generated by reaction of atomic oxygen with molecular oxygen and builds up to a small steady-state concentration when pure oxygen is irradiated. Its contribution, based on the low overall yields and low reactivity with metals in irradiated systems, relative to other radiolytic products, is expected to be minor.

Hydrogen peroxide is generated as a molecular product in irradiated systems containing water vapor as a the result of secondary reactions of the oxy-radicals OH and HO_2. Yields here are also low and the concentration does not build up with absorbed dose. The yield of OH from water vapor was 4.25 to 8.2 molec/100 eV, which is relatively high. There is direct evidence that this along with other transients, will contribute to the overall corrosion observed by direct interaction with the container material surface. The predominant effect, however, is its contribution to the nitrogen fixation process and production of nitrogen acids, which was previously discussed.

IV. RADIOLYTIC YIELDS IN THE PURE WATER VAPOR AND DRY AIR LIMITING CASES

Two anticipated but less likely environments under consideration by the YMP are the pure water vapor and the dry air gas phases. These are special cases of the moist air environment just discussed. Radiolytic yields in these two limiting cases are discussed in this section.

A. Radiolytic Yields in Water Vapor

The gas phase chemistry of water vapor has been investigated extensively, and the primary yields are well established (see Eq. 1). This gas phase may exist for several years in the initial stages of repository history as the water content of the host rock is heated and boiled, creating a water-vapor "bubble". Although no oxygen is present, corrosion will occur in irradiated systems due to the radiolytic production of oxidants.

The most important difference relative to the air-water vapor system just discussed is that, since no nitrogen is present, nitrogen fixation will not occur. Uniform corrosion, due to the oxidizing species generated, will be the predominant form of corrosion in this environment. An oxide tarnish was observed in our experiments when 70/30 copper-nickel was placed in an irradiated pure water vapor system.

The most important molecular product in the gas phase irradiation of water vapor is hydrogen. The non-scavengeable yield of hydrogen (primary yield) is $G(H_2) = 0.51$ molec/100 eV with long term yields given as $G(H_2) = 8.0 \pm 1$ molec/100 eV.[11] This, combined with the high primary yield of atomic hydrogen [$G(H) = 4.1$ to 7.2 molec/100 eV], suggests that hydrogen embrittlement may be the most important radiation-induced technical concern in this environment.

Three oxidants are generated in this environment. These are the hydroxy radical [$G(OH) = 8.2$ molec/100 eV], and low concentrations of hydrogen peroxide and oxygen. At container temperatures below the boiling point of water, the oxidants are concentrated in the water film on the surface of the metal which has led to greatly accelerated uniform corrosion rates with product formation typical of what is observed in aqueous systems. As the temperature is raised with a fixed amount of water vapor, the relative humidity is rapidly decreased leading to more direct interaction between the oxidants and the metal. Corrosion rates are also expected to decrease as the relative humidity is decreased.

B. Radiolytic Yields in Dry Air

In dry air, the most important radiolytic products are nitrous oxide, nitrogen dioxide and ozone. Ammonia and nitrogen acids are not generated, because no hydrogen source exists. Nitrous oxide (see Table 1) and nitrogen dioxide production is linear with absorbed dose and varies slightly with temperature. Radiolytic enhancement of corrosion, in this environment, is relatively small and has been characterized both in the literature and in our work. In dry air systems at temperatures below 100°C, the oxide film generated is the result of interaction between the metal surface and the nitrogen oxides generated rather than radiolytic products of oxygen (ozone). At higher temperature, thermal oxidation overwhelms the radiolytic contribution to corrosion.

Table 1. Yield of Nitrous Oxide as a Function of Irradiation Conditions

Temperature, °C	Nitrous Oxide Yield (Molecules/100 eV)	
	Dry Air	Moist Air[a]
28	0.83 ± 0.08	0.06 ± 0.02[b]
90	0.81 ± 0.08	0.87 ± 0.05[b]
120	0.57 ± 0.05	0.62 ± 0.06
150	0.69 ± 0.07	0.54 ± 0.05
200	0.74 ± 0.07	0.50 ± 0.05

[a]Air saturated with water vapor at room temperature.
[b]The buildup of nitrous oxide was non-linear. The 28°C yield value was the initial yield (low dose), the yield at 90°C corresponded to the linear formation of nitrous oxide observed after a 50 Mrad "induction" period.

V. RADIOLYTIC WASTE PACKAGE DESIGN ISSUES

The last aspect we have considered is the relationship between the radiation chemistry of the moist air system and waste package design. Unlike many technical concerns being considered by the YMP, those related to radiolysis can be substantially controlled through modifications in the design of both the repository and waste package. The most important aspects of the design are: (1) self shielding to reduce the gamma flux, (2) the free volume present in the near-waste package environment, and (3) the overall repository temperature, which depends on the spacing and heat-loading of the high-level waste packages.

B. Self Shielding

Self shielding is primarily accomplished by increasing the thickness of the container wall but could also include other design modifications such as placing filler material in the container. The idea of lowering the gamma dose rate by increasing the container thickness is not a new one. In the waste package designed by the Swedish HLW program that was approved for licensing, a 20 cm thick container was proposed to attenuate the gamma flux and remove radiolysis as an issue. In the Basalt Waste Isolation Project, which was concerned with the HLW site formerly considered at Hanford, a thickness of 8.5 cm was proposed that was also defined by the need to attenuate the gamma radiation flux outside the container.

The container thickness proposed by the YMP in the past is 1 to 3 cm with 1 cm as the thickness that is most referenced. This corresponds to an initial dose rate that is as high as 0.1 Mrad/h corresponding to absorbed doses of 50,000 Mrad during the first 300 y of repository history. These radiation levels have been shown to have a significantly detrimental effect on the corrosion of copper based materials and may also lead to enhanced corrosion of stainless steels. Attenuation of this dose should be a design consideration in the development of future design concepts even if radiation-tolerant materials are selected.

Although cost is not considered an important factor in preliminary design considerations, it becomes increasingly important in the latter stages of design. An excessively thick container, therefore, will have a substantial impact on overall costs and may introduce complications related to weldability of the material. In this context, a design guideline that recognizes the relationship between the radiation chemistry of the expected environment and the most likely degradation mode for the container material

needs to be developed. This does not exist for the YMP and past efforts in this area in other U.S. HLW projects have been inadequate.

B. Free Volume Outside the Waste Container

In the unsaturated system, the radiolytic products are generated in the free volume or air gap between the container and the host rock in the reference borehole waste package design. Minimization of the volume of this air gap would proportionally decrease the yield of radiolytic products and reduce the potential for radiolysis to affect container material degradation.

Although the waste package design is not yet firm, in our estimation the gap between the borehole wall and the emplaced container would probably not exceed 10 cm. This corresponds to a free volume of approximately 1200 Liters for each spent fuel waste package. Minimization of this volume, to a substantial extent, could greatly reduce the detrimental effects of radiolysis.

C. Overall Repository Temperature

The temperature in the waste package depends in part on the thermal loading of each container and the arrangement of the containers in the repository. The Nuclear Waste Technical Review Board (NWTRB), in its first report to Congress, has proposed that consideration be given to lowering the overall temperatures in the proposed repository. This was based on repository performance considerations.

From the perspective of corrosion in an irradiated air-water vapor system, higher rather than lower temperatures are preferred. This will lower the relative humidity at the surface of the container and therefore reduce the likelihood of localized effects since the radiolytic products generated will not condense on the container surface. In this context, keeping the relative humidity below 15-40% will keep the corrosion in the low relative-humidity regime which will benefit the overall durability of the container.

VI. CONCLUSIONS AND RECOMMENDATIONS

The key radiolytic yields in the range of conditions expected in the proposed YMP site were identified. The potential effects of nitrogen acid and ammonia formation need to be considered for the expected environment. Hydrogen and atomic hydrogen are the most important radiolytic products in the water vapor system.

The final waste package and repository design will be determined based on a weighted consideration of many factors. From the sole perspective of corrosion in irradiated air-water vapor systems, the important design factors are:

1. The material selected should be compatible with the irradiated air-water vapor mixture, which is the expected environment at the waste package.

2. Consideration should be given to minimizing the effective absorbed dose in the gas phase by considering thicker containers and reduced free volume surrounding the container. This should be done systematically by the development of a technically based design guideline.

3. Maximizing the temperatures in the waste package will lower the likelihood of significant radiolytic effects on container corrosion.

VII. ACKNOWLEDGMENTS

VII. REFERENCES

1. R. A. Van Konynenburg, "Radiation Chemical Effects in Experiments to Study the Reaction of Glass in an Environment of Gamma-Irradiated Air, Groundwater, and Tuff," Lawrence Livermore National Laboratory report UCRL-53719 (1986).

2. D. T. Reed, V. Swayambunathan, B. S. Tani, and R. A. Van Konynenburg, "Corrosion Product Identification and Relative Rates of Corrosion of Candidate Metals in an Irradiated Air-Steam Environment," Materials Research Society Symp. Proc., Scientific Basis for Nuclear Waste Management XIII, p. 517 (1990).

3. D. T. Reed and R. A. Van Konynenburg, "Corrosion of Copper-Based Materials in Irradiated Moist Air Systems," presented at Materials Research Society Symp. Proc., Scientific Basis for Nuclear Waste Management XIV (1990).

4. W. C. O'Neal, D. W. Gregg, J. N. Hockman, E. W. Russell, and W. Stein, "Preclosure Analysis of Conceptual Waste Package Designs for a Nuclear Waste Repository in Tuff," Lawrence Livermore National Laboratory report UCRL-53595 (1984).

5. G. L. Johnson and D. N. Montan, "Thermal Calculations Pertaining to a Proposed Yucca Mountain Nuclear Waste Repository," Lawrence Livermore National Laboratory report UCRL-ID-103534 (1990).

6. D. C. Thornstenson, E. P. Weeks, H. Haas and J. C. Woodward, "Physical and Chemical Characteristics of Topographi-cally Affected Airflow in an Open Borehole at Yucca Mountain, Nevada," in Proc. of the Top. Mtg. on Nuclear Waste Isolation in the Unsaturated Zone Focus 89, p. 256 (1989).

7. H. Matzing, "Chemical Kinetics of Flue Gas Cleaning by Electron Beam," Kenforschung Szentrum Karlsruhe Laboratorium fur Aerosolphysik und Filter Technik, West Germany, KFK 4494 (1989).

8. D. T. Reed and R. A. Van Konynenburg, "Effect of Ionizing Radiation on Moist Air Systems," Proc. Materials Research Society Symposium on the Scientific Basis for Nuclear Waste Management, XI (1988).

9. D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry," J. Phys. Chem. Ref. Data 9, 295 (1980).

10. D. L. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, "Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry," J. Phys. Chem. Ref. Data 11, 327 (1982).

11. R. S. Dixon, "Dissociation of Water Vapor by Photolytic, Radiolytic and Electron Impact Methods," Rad. Res. Rev. 2, 237 (1970).

12. J. K. Linacre and W. R. Marsh, "The Radiation Chemistry of Heterogeneous and Homogeneous Nitrogen and Water Systems," Chemistry Division AERE Harwell, AERE-R-10027, England (1981).

13. A. R. Jones, "Radiation-Induced Reactions in the N_2-O_2-H_2O System," Rad. Res. 10, 655 (1959).