PROGRESS IN ASSESSING THE EFFECT OF IONIZING RADIATION ON THE ANTICIPATED WASTE PACKAGE ENVIRONMENT AT THE YUCCA MOUNTAIN POTENTIAL REPOSITORY SITE

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ABSTRACT

Progress in establishing the effect of ionizing radiation on the anticipated air/water vapor waste package environment is summarized. This work was performed at Argonne National Laboratory (ANL) in support of the Yucca Mountain Site Characterization Project. The radiolytic issues that have been identified are presented. Long-term gamma experiments with gas compositions ranging from dry air to high-humidity air were completed. The predominant nitrogen fixation products in all air-like systems studied were nitrogen dioxide and nitric acid. Yields between 0.8 and 2.3 mole/100 eV have been measured. Ammonia formation, although not predominant, was also observed at temperatures below 100°C. The ammonia yields were low, and the concentration did not build up with increased absorbed dose. The status of the issues identified is 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 potential high-level nuclear waste repository. The emplacement of a nuclear waste container in such a repository would subject the near-field environment to significant levels of gamma radiation in the current waste package design. The presence of gamma radiation will lead to the formation of gaseous species that may affect container durability. The effect of gamma radiation is, therefore, an important factor in assessing the overall performance of the waste package [1].

The near-field environment of the waste package in the potential Yucca Mountain repository [2] is expected to consist of an air-water vapor gaseous environment throughout most of repository history. The composition of the gas phase, as long as the repository remains unsaturated, will be a function of (1) the initial gas phase present, (2) waste package temperature, (3) the gamma radiation level, (4) material-specific surface interactions, and (5) gas exchange/transport throughout the repository horizon.

During the containment period, gamma dose rates of up to 0.1 Mrad/h may be present. The high gamma radiation levels will be short-lived, on a geologic repository timescale, with a half-life of approximately 30 y and an effective lifetime of approximately 300 y. Should container and cladding failure occur, alpha and beta particles escaping from the surface of the waste form will interact with the gaseous environment present. In the unexpected event of inundation of the waste package with groundwater, the alpha and beta particles escaping the waste form will interact directly with the aqueous medium present. Factors relating to all these scenarios should be addressed to assess the overall effect of ionizing radiation.

The main objectives of this paper are to (1) state the issues we have identified that are associated with the presence of ionizing radiation in the expected near-field environment, (2) provide a summary of progress we have made toward the resolution of these issues, and (3) discuss the overall status of these issues. We have previously reviewed the general literature with respect to gas phase radiolysis of air-water vapor systems [3], published initial results we have obtained [4,5], and reported the results of preliminary material interaction studies we have completed [6-8].

II. TECHNICAL ISSUES ASSOCIATED WITH THE PRESENCE OF IONIZING RADIATION IN THE NEAR-FIELD ENVIRONMENT OF THE WASTE PACKAGE

The work performed at ANL in support of the YMP was driven by the technical issues related to the presence of ionizing radiation that we identified for the expected environment. Our work focused on issues related to container material performance. Ionizing
radiation, however, will potentially affect both container material performance and radionuclide release from the waste package. The most important issues we have identified in the expected environment of the repository are:

**Containment Period: Unsaturated Environment**

- Nature and yield of radiolytic products in air/water vapor systems. This includes the following species:
  - Nitrogen oxides and acids
  - Ammonia
  - Ozone, hydrogen peroxide
  - Organic acids
  - Hydrogen
- Interaction between the radiolytic products generated and the materials in the engineered barrier system. This relates primarily to the corrosion of the container.
- Structural damage due to the interaction of gamma radiation with the host rock and material in the engineered barrier system.

**Isolation Period: Unsaturated Environment**

- Nature and yield of radiolytic products in air-water vapor systems.
- Interaction of these radiolytic products with the waste form (glass and spent fuel).
- Radiolytic oxidation/reaction of C-14 and other volatile radionuclides that may be present.

Should the waste package become saturated with groundwater and the container becomes breached, the following radiolytic issues are important:

**Isolation Period: Saturated Environment**

- Yield of radiolytic products during the unsaturated phase of repository history. These will redissolve into the groundwater and, in part, define the groundwater composition.
- Radiolytic alteration of the aqueous environment in contact with the waste form.
- Interaction of radiolytic products with dissolved radionuclides. This will potentially affect radionuclide speciation and migration.

- Radiolytic effects on waste form dissolution.

An underlying issue that applies to all those just listed is the modeling of radiolytic effects to support design analysis and performance assessment.

**III. NITROGEN OXIDE AND ACID FORMATION IN AIR-WATER VAPOR SYSTEMS**

We initially performed a literature review on the general radiation chemistry of air and air-water vapor systems [3]. Four important limitations in the existing data were (1) the lack of long-term data on the yields at dose rates relevant to the YMP, (2) the effect of high humidity on these yields, (3) the effect of surfaces expected to be present in the waste package on the overall yields obtained, and (4) the lack of data, for all these, at elevated temperatures. Progress we have made in these areas is reported in this section.

**A. General Radiation Chemistry of Air and Air-Water Vapor Systems**

The radiation chemistry of N₂/O₂/H₂O systems has been investigated in previous studies [9-16]. Within the last year, experimental and modeling results relevant to the radiation chemistry of flue gas systems have also been published [17-19]. These, although not directly relevant to the YMP site, help provide additional insight to the mechanistic details of irradiated air-water vapor systems.

The primary radiolytic products, which are those species formed as a result of the direct interaction of ionizing radiation, have been fairly well characterized for the major components of air [15,18]. The primary yields of these products are given in Table I for oxygen, nitrogen, carbon dioxide, and water. It is important to note that these yields are relatively insensitive to changes in pressure, temperature and the environment. They, in effect, serve as an upper limit to the net decomposition/alteration possible in the irradiated system. This is especially important for nitrogen, since it is only decomposed via direct interaction of radiation, meaning that the nitrogen fixation yield will not exceed the net decomposition of nitrogen. Typical decomposition yields observed experimentally are significantly less than that theoretically possible because of recombination and quench effects.

Considering air and air-water vapor systems together, the most important radiolytic products are the oxidation products of nitrogen (NO, NO₂, NO₃, N₂O₅, HNO₂, and HNO₃), the reduction products of nitrogen (ammonia) and ozone. In the irradiated air-water vapor
Table 1. Primary Decomposition Yields of Major Components of Air

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>100 eV</td>
<td>0.29 N₂⁺ + 0.885 N(2p)⁺ + 0.295 N(2p)⁺ + 1.87 N(3s)⁺ + 2.27 N₂ + 0.69 N⁺ + 2.96 e⁻</td>
</tr>
<tr>
<td>O₂</td>
<td>100 eV</td>
<td>0.077 O₂⁺ + 2.25 O(1p)⁺ + 2.8 O(3p)⁺ + 0.180 O⁺ + 2.07 O₂⁺ + 1.23 O⁺ + 3.3 e⁻</td>
</tr>
<tr>
<td>H₂O</td>
<td>100 eV</td>
<td>0.51 H₂ + 0.46 O(3p)⁺ + 4.25 OH⁺ + 4.15 H⁺ + 1.99 H₂O⁺ + 0.01 H₂⁺ + 0.57 OH⁻ + 0.67 H⁺ + 0.06 O⁺ + 3.3 e⁻</td>
</tr>
<tr>
<td>CO₂</td>
<td>100 eV</td>
<td>4.72 CO + 5.16 O(3p)⁺ + 2.24 CO₂⁺ + 0.51 CO⁺ + 0.07 C⁺ + 0.21 O⁺ + 3.03 e⁻</td>
</tr>
</tbody>
</table>

system, the most important processes that lead to the formation of radiolytic products along with the fate of these species, are given in Table 2. The extent to which these species are formed is system-specific. In past investigations, wall effects have been well documented and actual yields measured are significantly less than predicted by the primary yields listed in Table 1. This simply indicates that reaction steps that lead to the reformation of initial reactants as well as decomposition reaction steps can effectively compete with the formation processes.

B. General Experimental Approach

Experiments to determine the long-term yield of nitrogen oxides and acids were performed in both stainless steel and glass vessels ranging in size from 150 cc to 2 liters. Prior to use, each vessel was disassembled, cleaned according to established procedure, reassembled, evacuated, and leak checked. Both vessel types were fitted with a Nupro H-series stainless steel bellows valve.

The desired atmosphere, in the dry air and low-humidity air experiments, was introduced into the vessel by expanding either dry air, or air that had been pre-equilibrated with water vapor at room temperature into the irradiation vessel. High humidity experiments were prepared by first adding pure water vapor up to a desired pressure at elevated temperature (usually 80-90°C), cooling the vessel to room temperature, and adding the desired amount of air. The total pressure, at the temperature of each experiment, was 660 torr which is the ambient pressure at the elevation of the potential repository site.

The bulk composition of the gas phase was analyzed before irradiation by gas chromatography. The irradiations were performed in ovens in the ANL M-wing gamma irradiation facility at fixed locations with dose rates between 0.4 Mrad/h and 0.01 Mrad/h. At the end of the experiment, the vessels were removed and the contents analyzed for gaseous components (O₂, N₂O, CO, CO₂, N₂O by gas chromatography) and condensable fixations products (nitrate, nitrite, and ammonia by ion specific electrode analysis or ion chromatography), by rinsing the walls of the vessel and analyzing the rinse solution.

C. Nitrogen Oxide Formation in Dry Air

In dry air, only nitrogen oxides are important since there is no source of hydrogen or OH. The most important of these are nitrous oxide and nitrogen dioxide. The net fixation of nitrogen, at a total dose of up to 300 Mrad, was less than 1%. Experiments were performed at temperatures between 30 and 210°C. Temperature effects were noted but were, in general, small.

The formation of nitrous oxide was linear with absorbed dose and exhibited, at most, a small induction period. A typical plot showing this linearity is given in Figure 1. Yield data as a function of temperature are summarized in Table 3. G(N₂O) was between 0.5 and 0.8 molec/100 e, based on energy absorbed by air, depending on temperature.

NOₓ, in dry air systems, exists primarily as NO₂ (nitrogen pentoxide has been reported in the literature as a minor constituent but was not analyzed for in our experiments). Nitric oxide levels did not build up appreciably in the gas phase. The nitrogen dioxide production was comparable to, or slightly higher than that of, nitrous oxide and was linear with absorbed dose. A typical plot is shown in Figure 2.

D. Formation of Nitrogen Oxide and Acids in Low and High Humidity Air

The presence of water vapor in the gas phase during irradiation provides a source of atomic hydrogen and hydroxy radicals as well as associated secondary products generated by their interaction with the bulk components of the gas phase. The most important effect, with respect to the oxidation of nitrogen, is the conversion of nitrogen oxides to nitrogen acids. This process depends on the water vapor content of the gas phase and its relative humidity.
Table 2. Formation and Fate of Key Molecular and Transient (Ionic and Free Radical) Species in Irradiated Moist Air Systems

<table>
<thead>
<tr>
<th>Molecular Species Initially Present</th>
<th>Formation</th>
<th>Fate</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N_2)</td>
<td>NA</td>
<td>Fixation Products: (NO_x, N_2O, NH_3).</td>
</tr>
<tr>
<td>(O_2)</td>
<td>NA</td>
<td>Oxidation Products: (NO_x, N_2O, CO, CO_2, Ozone).</td>
</tr>
<tr>
<td>(CO_2)</td>
<td>NA</td>
<td>(CO = CO_2) equilibration.</td>
</tr>
<tr>
<td>(H_2O)</td>
<td>NA</td>
<td>Generates (H, OH); Thermal reactions.</td>
</tr>
</tbody>
</table>

Radiolytically Generated Molecular Products

| \(N_2O\)                          | Reduction of \(NO_2\) | Relatively stable, will reform \(N_2, O_2\), and \(NO_2\) at high concentrations. |
| \(NO\)                            | \(N_2 + O = NO + O\)   | Low steady state concentration present, oxidizes to \(NO_2\) and \(HNO_2\). |
| \(NO_2\)                          | \(NO + O_2 = NO_2 + O\) | Reduction to \(N_2O\), oxidation to \(HNO_3\) in presence of water vapor, build up in gas phase in a dry system. |
| \(HNO_3\)                         | \(OH + NO_2 = HNO_3\)  | Precipitation/sorption. |
| \(HNO_2\)                         | \(OH + NO = HNO_2\)     | Precipitation/sorption. |

Transient Species

| OH                               | C-T* reaction with \(H_2O\) | Oxidizing agent. |
| O                                | \(O_2\) irradiation          | Oxidizing agent. |
| N                                | \(N_2\) irradiation          | Nitrogen fixation products. |
| H                                | C-T* reaction with \(H_2O\)  | Reducing agent. |

*Charge transfer reaction.

Figure 1. Yield of \(N_2O\) in Dry Air at 28 and 90°C

Figure 2. Formation of \(NO_2\) in Dry Air and Low-Humidity Air
Table 3. Yield of Nitrous Oxide as a Function of Irradiation Conditions

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Dry Air Yield (molecules/100 eV)</th>
<th>High-Humidity Air* Yield (molecules/100 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>28</td>
<td>0.83 ± 0.08</td>
<td>0.06 ± 0.02**</td>
</tr>
<tr>
<td>90</td>
<td>0.81 ± 0.08</td>
<td>0.87 ± 0.05**</td>
</tr>
<tr>
<td>120</td>
<td>0.57 ± 0.05</td>
<td>0.62 ± 0.06</td>
</tr>
<tr>
<td>150</td>
<td>0.69 ± 0.07</td>
<td>0.54 ± 0.05</td>
</tr>
<tr>
<td>200</td>
<td>0.74 ± 0.07</td>
<td>0.50 ± 0.05</td>
</tr>
</tbody>
</table>

*Air saturated with water vapor at room temperature.

**These plots were nonlinear. 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.

The only radiolytically generated nitrogen fixation product that could be observed by gas chromatography was nitrous oxide. Several low humidity experiments were performed where the water vapor content was 70-80% RH at room temperature. In these systems, the nitrous oxide yield was significantly reduced by the presence of water vapor and appeared to be more directly affected by the relative humidity rather than the mole% of water vapor. When water vapor was depleted from the gas phase, the yields approached that observed in the dry air system. Example results are shown in Figure 3 and were included in the data presented in Table 3.

A series of experiments was performed in high humidity systems to establish the long-term yield trends as a function of water vapor content and relative humidity. The long-term formation of nitrous oxide was linear with absorbed dose but decreased with increasing relative humidity (see Figure 4). The initial yield of nitrous oxide, however, was not linear. Here, an induction period was evident.

The most important effect of the presence of water vapor in the gas phase is the oxidation of nitrogen dioxide to nitric acid:

\[ \text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 \]  

(1)

In the low-humidity experiments performed, we analyzed for nitrate on the vessel wall as a vessel rinse, and nitrate as nitric acid in the gas phase by condensing the gas phase into a secondary vessel. This established qualitatively, the partitioning of the nitrogen fixation products. When detectable amounts of water vapor were in the gas phase, nitrogen acids, which appeared mostly in the vessel rinse, were the only fixation products of importance. There was only a small buildup of nitrogen dioxide in the gas phase. Nitric acid yields were linear with absorbed dose with a net yield between 0.8 and 1.2 molec/100 eV in the 30-210°C temperature range investigated.

To establish the initial yield of nitric acid in high-humidity systems, we performed low-absorbed dose experiments as a function of water vapor content. Nitric acid was the predominant nitrogen fixation product generated. The moles of nitrate measured as a function of absorbed dose are shown in Figure 5. The NO₃ formation, based on a
Initial yields obtained were consistent with what is reported in the literature. A second effect we noted was that, contrary to reports in the literature, the presence of water vapor in the gas phase had a significant effect on both the extent of nitrogen fixation and the nature of the radiolytic products formed. In high moisture systems (room temperature and 90°C) nitrous oxide yield was suppressed, NOx yields increased, and detectable levels of ammonia were generated. This is in contrast to the results of others [20] who reported no effect of water content on N2O and NOx yield and the absence of ammonia formation even when only trace amounts of oxygen were present in the system [21].

The last important point to make concerning the yield data is that steady state concentrations of the major molecular products were not established in either dry air or high-humidity air systems at the highest absorbed doses we investigated. Nitrous oxide and NOx buildup continued at a linear rate beyond absorbed doses of 300 Mrad. Under repository-relevant conditions, in an open system, the establishment of steady state conditions may occur due to a balance between the radiolytic formation of products, their diffusion or advective transport away from the waste package and their interaction with the components of the waste package and the host rock. This, however, is determined by site-specific characteristics and waste package design rather than radiolytic considerations alone.

IV. POTENTIAL FORMATION OF AMMONIA IN AIR/WATER VAPOR SYSTEMS

The issue of ammonia formation is important to the YMP because ammonia is a known cracking agent for some copper-based materials. Its formation in the expected waste package environment is a key issue because, in its absence, copper-based materials are predicted to have high resistance to environmentally assisted cracking (EAC). We have pointed out [6-8], however, that there are some concerns with respect to overall material performance of copper-based materials in irradiated air/water vapor systems that go beyond the issue of ammonia formation.

In work supported by the YMP, we have addressed the issue of ammonia formation in two ways: (1) we have tracked the formation of ammonia in air-water vapor mixtures, along with nitrogen oxides and nitrogen acids, as a function of temperature and absorbed dose, and (2) we have begun to address the issue of the role of oxygen and hydrogen in the formation of ammonia. This latter work addresses the more
mechanistic aspects of the problem so that parametric effects can be established through modeling efforts.

A. Yield of Ammonia in Air/Water Vapor Mixtures

Ammonia, according to reports in the existing literature [21], is readily formed when nitrogen-hydrogen mixtures are irradiated. The formation mechanism is similar to that observed for the oxidation of nitrogen in that it is preceded and limited by the direct radiolytic formation of atomic nitrogen which subsequently reacts with molecular hydrogen, and associated radiolytic products, to form ammonia. $G(\text{NH}_3)$ is approximately 1 mole/100 eV for 80/20 mixtures of nitrogen and hydrogen.

In the presence of oxygen, however, ammonia formation is suppressed in favor of the formation of nitrogen oxides and acids. There is one exception to this noted in the literature. Sato and Steinberg [22] reported that when air that is bubbled through water is irradiated, very high ammonia yields are sometimes observed. This occurred even though substantial amounts of oxygen were clearly present.

To address the issue of ammonia formation in the presence of air, we performed two sets of experiments. The first and more extensive set of experiments addressed the issue of long-term formation of ammonia in air/water vapor mixtures as a function of temperature and absorbed dose. This provided the most realistic estimates of likely concentrations of ammonia in the expected waste package environment. Second, we reinvestigated the phenomenon reported by Sato and Steinberg to check their results.

The long-term experiments have been performed in both stainless steel vessels and glass vessels for absorbed doses up to 80 Mrad. At low temperature (<100°C) trace amounts of ammonia (typically 1 to 10 ppmv) were observed. Ammonia did not build up in concentration with increased absorbed dose indicating that a steady state concentration, set by the composition of the gas phase, was being established. In these systems, hydrogen formation was observed (from radiolytic decomposition of water) and may have been a necessary precursor to the ammonia formation observed.

At elevated temperatures (>150°C), even with a high water vapor content, only nitric acid was observed as a condensable fixation product. These experiments were performed to absorbed doses of up to 16 Mrad which minimized the presence of hydrogen in the gas phase. We cannot resolve, based on our experiments, whether ammonia is being generated and subsequently oxidized or there are changes in the formation mechanism with increased temperature.

The results obtained from the gamma irradiation of 0.1N sulfuric and formic acid solutions in the presence of bubbled air supported, to an extent, the results reported in the literature [22]. In the sulfuric acid system, the concentration of ammonia increased linearly with dose up to ~11.5 Mrad and then remained constant. This trend was also observed by Sato and Steinberg [22] under almost similar experimental conditions. The maximum ammonia concentration obtained in our experiments was, however, much lower (0.12 ppm N instead of 1.0 ppm N). In the higher dose experiments, nitrate production was also noted. No nitrite was evident in any of the solutions analyzed.

The irradiation of 0.1N formic acid solution in the presence of bubbled air also resulted in the formation of ammonia. This was only observable at absorbed doses exceeding 14 Mrad. The maximum amount of ammonia observed was much less than that reported elsewhere [22] and less than that observed in the sulfuric acid system. In past radiolytic investigations of formic acid systems, substantial production of $\text{H}_2\text{O}_2$ and $\text{CO}_2$ occurred in oxygen-containing solutions with $\text{H}_2$ as the predominant product in oxygen-free solutions. This may, in part, account for the higher nitrate yields we observed relative to the sulfuric acid system.

The direct fixation of dissolved nitrogen gas in aqueous systems was recently reviewed and shown [23] to have a yield that is very low ($<3.4 \times 10^{-4}$ mole/100 eV). The observed formation of both nitrate/nitrite and ammonia in the bubbled systems appears to be due to fixation of gaseous nitrogen in the irradiated gas phase (bubbles) rather than fixation of dissolved nitrogen. The enhanced yields, relative to the homogeneous moist air system is due to "energy transfer" in the form of atomic hydrogen to the gas phase enhancing the efficiency of the ammonia formation process in the air system.

B. Yield of Ammonia in Oxygen-Depleted Systems: Role of Oxygen

Since it is clear from the results just summarized that conditions leading to ammonia formation can exist we have begun to investigate ammonia formation on a more mechanistic level. The emphasis of the work completed was the role of oxygen in the suppression of ammonia. We have only partially addressed this important issue.
The radiolytic formation of ammonia in systems containing oxygen was investigated in two systems: 0.1% oxygen in a 20/80 hydrogen-nitrogen mixture and 0.1% oxygen in nitrogen saturated with water vapor at room temperature.

Gamma irradiation of O2-H2-N2 gas mixtures resulted in a rapid depletion of oxygen to form small amounts of nitrous oxide. Ammonia formation was significantly lowered but was not completely quenched by the presence of oxygen. Long-term ammonia yields were comparable to that reported in the literature for N2-H2 systems and were not strongly dependent on temperature (G(NH3) = 0.7-1.0 molec/100 eV). In the O2-H2O-N2 system, measurable levels of ammonia (G ≈ 0.03-0.04 molec/100 eV) and nitrous oxide were observed. Oxygen depletion was much slower than in the O2-H2-N2 system.

The initial yield trends and temperature dependence of the long-term yields were also investigated in a 0.1% oxygen, 3-5% water vapor and 94-96% nitrogen gas mixture. Net change in the nitrogen concentration, even in the higher absorbed-dose experiments, was small with <1% of the nitrogen converted to nitrous oxide and NO2/NH3. Some depletion of water vapor content may have occurred in the variable-temperature experiments. The depletion of oxygen was first order with respect to the concentration of oxygen.

In contrast to the O2-H2-N2 system, where no nitrate/nitrite production was noted and little nitrous oxide production occurred, nitrous oxide and nitrite were observed as fixation products in the O2-H2O-N2 system. Nitrous oxide formation was not linear with absorbed dose but did not go through a maximum due to a lowering of the oxygen concentration as was noted in the oxygen-hydrogen-nitrogen system. In the O2-H2O-N2 system, water vapor is potentially the greater source of oxygen for nitrogen fixation. Oxygen from the water vapor molecule was clearly contributing to the formation of NOx in the high-temperature experiments.

Ammonia was also observed as a fixation product at temperatures below 100°C. The yield of ammonia was not linear with absorbed dose and, in fact, decreased as oxygen was depleted in the irradiated system. Initial yields were 0.1 molec/100 eV, decreasing to 0.03 at higher absorbed doses.

The total amount of ammonia detected (rinse + condensate) decreased somewhat with increasing temperature, with the yield at room temperature being 0.045 ± 0.01 molec/100 eV with an apparent decrease to 0.03 ± 0.01 at 90 and 150°C. The decrease noted was, however, within the stated uncertainty of the analyses made. A comparison of these initial ammonia yields with the long-term yields observed at room temperature, indicated that the net yield continued to decrease with increased absorbed dose.

The presence of oxygen in N2-H2 and N2-H2O systems suppressed but did not prevent the radiolytic formation of ammonia. In N2-H2 systems, 0.1 molec% oxygen resulted in a lowering of ammonia formation by a factor of ten relative to the pure N2-H2 system. The initial yield, with oxygen present was 0.1 molec/100 eV compared with 1.0 molec/100 eV in the high absorbed dose studies. In the N2-H2O system, overall ammonia yields were in the range of 0.03 to 0.1 depending on absorbed doses and were comparable to those initially obtained in the O2-N2-H2 system. Increasing the temperature to 150°C had a small effect on net ammonia yields observed.

The role of oxygen, with respect to ammonia formation, was not the same in the N2-H2 and N2-H2O systems. In the N2-H2 system, oxygen was rapidly depleted and lowered ammonia yields by reaction primarily with the hydro- genous precursor to ammonia (presumably atomic hydrogen) to form water vapor. Only a small percentage of the oxygen present reacted with atomic nitrogen to generate NOx or N2O. In the N2-H2O system, the presence of oxygen enhanced ammonia formation. This was proposed to be the result of competition between the OH and H free radicals in the water vapor-containing system. As oxygen concentrations decrease, ammonia is increasingly oxidized by OH resulting in a net decrease in ammonia yields. The overall effect of oxygen on ammonia formation will, therefore, be the sum of (1) reaction with atomic nitrogen, which prevents ammonia production and increases in importance with increasing oxygen concentrations; (2) relative rate of reaction with atomic hydrogen and OH; and (3) the relative rate of reaction between OH + O2 and OH + NH3.

V. SUMMARY OF PROGRESS AND STATUS OF RADIOLYTIC ISSUES

Significant progress has been made toward characterizing the general effect of ionizing radiation on the expected waste package environment during the containment period. We have established the long-term yield of nitrogen oxides and nitrogen acids as a function of temperature, absorbed dose, and water vapor content of the air-water vapor mixture. Nitrite formation does not appear to be significant in air-like systems. We have also addressed, in general terms, the issue of radiolytic formation of ammonia in air-containing systems. Realistic yields of ammonia are low and approach zero at temperatures above 150°C. Hydrogen, which is generated radiolytically from water vapor, is
detected as a gaseous component. Its concentration does not increase with absorbed dose as would be predicted from the pure water vapor yields listed in Table 1.

A number of issues, related to radiolytic product formation, have not been addressed. The most important of these is a parametric study of the effect of changes in the relative concentration of the gas phase components on the net yields observed. Significant changes in the gas composition can occur within the realm of anticipated scenarios. The fate and stability of nitric acid at high temperatures is also not fully understood. This is key to assessing its role in container corrosion. In more general terms, the relationship between corrosion of any material and the gas phase radiation chemistry has not been clearly established. This needs to be addressed as part of the material selection process.

Two additional issues related to the environment that have not been extensively addressed are (1) the potential formation of organic acids when carbon dioxide is present in the gas phase and (2) the effect of material-specific interaction on the long-term yields. The formation of organics is of concern because of potential effects on both container corrosion and radionuclide solubility/migration in the environment. The interactions of the gas phase components with materials in the waste package are important because they may compete with the container material and reduce net corrosion.

The last issue related to the radiolytic alteration of the gas phase is the development of a model description of the effects of ionizing radiation that will support waste package performance assessment. This requires a systematic analysis of the YMP-relevant data, its support by detailed modeling using fast reaction kinetic codes, and a simplified yield vs. environment model that will be usable in performance assessment. No significant progress has been made in this area that is specific to the YMP environment.

Lastly, we have not, in our work, emphasized issues related to the isolation period and radionuclide migration. There is clear evidence in the literature that these are, however, very important issues. These remain as issues that need to be experimentally addressed by the YMP.

VI. ACKNOWLEDGMENTS

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VII. REFERENCES


