EFFECT OF IONIZING RADIATION ON MOIST AIR SYSTEMS

DONALD T. REED* AND RICHARD A. VAN KONYNENBURG**
*Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL 60439
**Lawrence Livermore National Laboratory, P. O. Box 808, Livermore, CA 94550

ABSTRACT

The radiation chemistry of nitrogen/oxygen/water systems is reviewed. General radiolytic effects in dry nitrogen/oxygen systems are relatively well characterized. Irradiation results in the formation of steady state concentrations of ozone, nitrous oxide and nitrogen dioxide. In closed systems, the concentration observed depends on the total dose, temperature and initial gas composition. Only three studies have been published that focus on the radiation chemistry of nitrogen/oxygen/water homogeneous gas systems. Mixed phase work that is relevant to the gaseous system is also summarized. The presence of water vapor results in the formation of nitric acid and significantly changes the chemistry observed in dry air systems. Mechanistic evidence from the studies reviewed are summarized and discussed in relation to characterizing the gas phase during the containment period of a repository in tuff.

INTRODUCTION

The radiation chemistry of moist and dry air systems has been studied sporadically over the past sixty years. The ability of ionizing radiation to induce the oxidation of nitrogen was first recognized by Soddy [1] in 1911. Since then, interest in the field has developed in relation to nitrogen fixation [2-6], metal corrosion problems in a radiation field [7-10] and the removal of NO_x from flue gases [11,12]. Although general effects have been characterized, particularly in dry air systems, there still remain a considerable number of unresolved issues in the fundamental radiation chemistry of the moist air system.

More recent interest in the radiation chemistry of moist air systems has been expressed in connection with the disposal of high-level nuclear waste in deep geologic repositories. For the proposed repository beneath Yucca Mountain in southern Nevada, which is being investigated by the Nevada Nuclear Waste Storage Investigations (NNWSI) project, the expected environment for most of the waste packages during the first part of the containment period consists of an atmosphere composed of air, water vapor, and some carbon dioxide. This environment will initially be subjected to ≤0.1 Mrad/hr gamma radiation levels following the emplacement of nuclear waste containers. Determining the effect of radiation on this environment is an important aspect of characterizing the post-emplacement environment of the waste package.

The primary objectives of this paper are to summarize past work in the general area of the gas phase radiolysis of moist air systems and relate it to the conditions expected in a tuff repository. In addition to characterizing the effects of radiation on the environment of the waste package, it is also a necessary step in relating the environments in which materials test data are obtained to the conditions expected throughout repository history.

Although the radiolytic "fixation" of nitrogen can occur via both the oxidation and reduction of nitrogen, the emphasis of this review is on the oxidation mechanism. Ammonia has been reported in one instance [2] as the major radiolytic product in aerated systems subjected to ionizing radiation. This result, however, has not been reproduced elsewhere and is in conflict with the other work summarized in this review. Nevertheless, the

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formation of ammonia cannot be ruled out entirely in that it may be generated in systems containing high hydrogen to oxygen ratios. Ammonia formation has been reported as a minor product in high absorbed-dose experiments under these conditions [13]. Due to the anticipated absence of an aqueous phase in a tuff environment during the first part of the containment period and the expected presence of air throughout repository history, fixation of nitrogen is expected to occur via oxidation rather than reduction.

ANTICIPATED RANGE OF CONDITIONS IN THE GAS PHASE PRESENT IN A TUFF REPOSITORY

The proposed location of the repository horizon in the Yucca mountain site is a welded devitrified tuff rock formation. This site is unsaturated and is located about 350 m below the surface and about 200 m above the water table. The composition of the pre-emplacement gas phase is water, air, and some carbon dioxide. The total pressure at repository elevation is 660 torr (0.88 bar) corresponding to a boiling point of 96°C for water.

The emplacement of high-level nuclear waste containers in a tuff repository will have a complex effect on the pre-emplacement environment. This effect has not yet been fully characterized. Three major changes induced by emplacement, however, will have a significant effect on the composition of the gas phase. These are: (1) heating of the repository to temperatures in excess of 250°C [14], (2) potential alteration of the in-situ hydrologic properties throughout the site system as the result of repository heating and construction, and (3) the presence of significant levels of gamma radiation in the vicinity of each emplaced waste package.

The factors important to the radiation chemistry of a tuff repository have been discussed elsewhere [15]. Those important in defining the gas phase composition in an irradiated environment are:
1. The total pressure of the gaseous system will remain at or near ambient throughout repository history.
2. The composition of the unperturbed gas phase consists of water vapor, air (primarily nitrogen and oxygen), and some carbon dioxide.
3. Following emplacement of the waste packages, the range in partial pressure for each of these gases is:
    Water Vapor = 0-660 torr
    Nitrogen = 0-530 torr
    Oxygen = 0-130 torr
    Carbon Dioxide = 0-130 torr
4. The only significant type of ionizing radiation present outside the waste container will be gamma radiation. The absorbed gamma dose rate will be less than 0.1 Mrad/hr.
5. Greater than 99% of the gamma radiation will be absorbed within one meter of the surface of the waste container. The absorbed dose per waste package during the containment period will be on the order of 20,000 Mrad at the surface of the container for spent fuel. Absorbed doses near defense high-level waste containers will be lower. Less than 0.1% of the gamma energy deposited in the vicinity of the waste packages will be absorbed by the gas phase present and contribute to changes in the composition of the gas phase.

The radiolytically induced fixation of nitrogen was first reported by Soddy [1] in 1910 when he observed that the exposure of air to radon resulted in the formation of nitrous oxide. This observation was later confirmed by Lind and Bardwell [16] who made the additional observation that ozone and acid-forming nitrogen oxides were being generated in much greater quantities. Since these early observations, the radiation chemistry of nitrogen/oxygen/water systems and associated radiolytic products has received a moderate amount of attention in connection with corrosion [8-10], nitrogen fixation [2-6], and nitrogen oxide removal from flue gases [11,12]. Additional related work has been done because nitrous oxide has been recommended and used as a gas phase dosimeter [17,18].

General Reviews

General reviews of the radiation chemistry of nitrogen/oxygen systems have been written previously. A general overview of gas phase radiolysis of nitrogen, oxygen, water and nitrous oxide is given in Spinks and Woods [19]. Early work in the synthesis and decomposition of nitrogen oxides was summarized by Lind [20]. A more recent review on the radiation chemistry of nitrogen and nitrogen compounds was written by Johnson [21]. Yield data, rate constants for the reactions of primary and secondary intermediate products, and details concerning the initial processes in the radiation chemistry of nitrogen oxide systems were summarized by Willis and Boyd [22,23].

The radiolysis of air/water systems is poorly understood and expected to be complex. This complexity is in large part due to the fact that the composition of the gas phase system being irradiated is evolving as a function of time (absorbed dose). The products generated are not inert. They actively participate in radiolytic processes and will, at some point, begin to interact directly with the ionizing radiation and contribute to the primary product yields. In a closed system, the gas phase composition will approach a steady state condition with a balance between the formation and decomposition of nitrogen oxides. This steady state composition is a function of the dose rate, initial gas phase composition, vessel material, temperature and, to a lesser extent, the total pressure of the system.

Initial Radiolytic Processes in the Oxidation of Nitrogen

The initial absorption of gamma radiation in gaseous systems that are at high pressure (the three-body limit for air is approximately 10 torr at 25°C) occurs predominantly via the Compton effect for incident gamma energies between 0.1 and 5 MeV (mean gamma energy for spent fuel is about 0.6 MeV). The net result of this interaction is the formation of a secondary gamma and a high energy electron. It is these electrons that are primarily responsible for energy deposition in the gaseous system. The total absorption of energy by the gaseous system will be governed by the gamma mass energy absorption coefficient whereas the partitioning of the energy absorbed between the components of the gas phase will be proportional to the electron density of the gas molecule.

The absorption of energy by the three gas phase components initially present results in the following primary products:

$$N_2 \xrightarrow{\quad\quad} N_2^+, N^+, e^-, N, N_2^* \tag{1}$$
$$H_2O \xrightarrow{\quad\quad} H_2O^+, H^+, OH^+, e^-, H, OH, H_2O^* \tag{2}$$
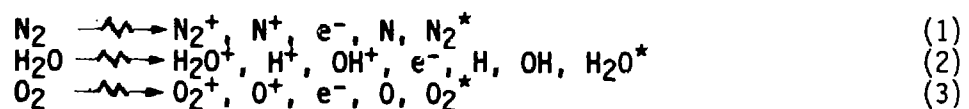$$O_2 \xrightarrow{\quad\quad} O_2^+, O^+, e^-, O, O_2^* \tag{3}$$

Table I summarizes the physical parameters of the gas phase components expected in an irradiated moist air system. As indicated in Table I, the ionization potential of nitrogen lies considerably above that of oxygen, water and the nitrogen oxides. The interaction of intermediates generated from these molecules with nitrogen is relatively small, although some energetically favorable mechanisms have been identified. This is especially true at high pressures (>10 torr) where vibrationally hot molecules are collisionally quenched very rapidly. There is, for this reason, no significant contribution to the net yield of atomic nitrogen from the energy absorbed in other gases that may be present.

The partitioning of absorbed energy, subsequent to irradiation, has been investigated by Willis and Boyd [23] for several gases. Energy partitioning was weakly dependent on the nature of the gas and was approximately distributed as follows: 60% was used in the formation of ions, 30% was used in the formation of electronically excited molecules, and 10% of the energy was deposited in subexcitation processes (vibrational and rotational energy). For nitrogen, these values are 56.6% (formation of N_2^+, N^+, and e^-), 34.7% (formation of N_2^*), and 8.7% respectively. The combined contributions of the ions and excited states formed lead to the following primary yields:

$$G(N_2^+) = 2.2 \text{ ions/100 eV}$$
$$G(N^+) = 0.7 \text{ ions/100 eV}$$
$$G(N_2^*) = 2.9 \text{ molec/100 eV}$$
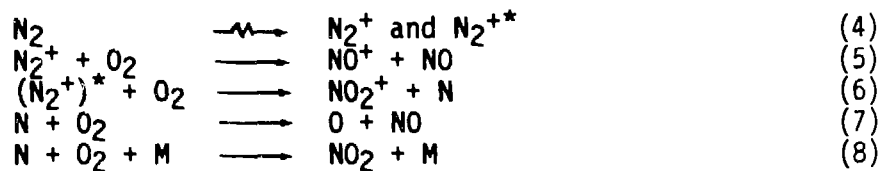$$G(N) = 2.6\text{-}5.6 \text{ atoms/100 eV}$$

The range in the yield of atomic nitrogen reflects its dependence on two initial processes: $G(N) = 2G(N_2^* \rightarrow 2N) + 2G(N_2 \rightarrow N^+ + N + e)$. The contribution from both of these processes is a function of the experimental conditions since N_2^* is in part generated via recombination of N_2^+

Table I. Physical Properties of Gas Molecules Important to the Radiation Chemistry of Moist Air Systems

Gas Molecule	Molecular Weight	Boiling Point, (°C) @ 1 atm	# Electrons Z	First Ionization Potential (eV)
N_2	28.0134	-195.8	14	15.6
O_2	31.9988	-182.962	16	12.06
O_3	47.9982	-111.9	24	12.3
H_2O	18.0153	100	10	12.6
N_2O	44.01	-88.5	22	13.0
NO	30.01	-151.8	15	9.25
NO_2	46.01	21.2	23	9.8
N_2O_5	108.01	47 (decomp)	54	-
HNO_3	63.01	83	32	-

and N^+ must react with molecular nitrogen to generate additional atomic nitrogen. Yield values up to 7.3 ± 1.5 have been reported for atomic nitrogen. Although the yields reported are based on data obtained at 20-25°C, no large temperature dependence of the primary yields is expected.

The mechanistic aspects of the oxidation of nitrogen have been the subject of several studies. Two general mechanisms, ionic and free radical, have been proposed. The ionic mechanism, as proposed by Pshezhetsky and Dimitriev [24-26], is:

$$N_2 \xrightarrow{\quad\quad} N_2^+ \text{ and } N_2^{+*} \tag{4}$$
$$N_2^+ + O_2 \longrightarrow NO^+ + NO \tag{5}$$
$$(N_2^+)^* + O_2 \longrightarrow NO_2^+ + N \tag{6}$$
$$N + O_2 \longrightarrow O + NO \tag{7}$$
$$N + O_2 + M \longrightarrow NO_2 + M \tag{8}$$

The free radical mechanism was initially proposed by Harteck and Dondes [27-30] and includes the following steps:

$$N_2 \xrightarrow{\quad\quad} 2N \tag{9}$$
$$O_2 \xrightarrow{\quad\quad} 2O \tag{10}$$
$$N + O_2 \longrightarrow O + NO \tag{11}$$
$$2NO + O_2 \longrightarrow 2NO_2 \tag{12}$$
$$N + NO_2 \longrightarrow 2NO \tag{13}$$
$$\longrightarrow O + N_2O \tag{14}$$
$$\longrightarrow 2O + N_2 \tag{15}$$
$$N + NO \longrightarrow O + N_2 \tag{16}$$
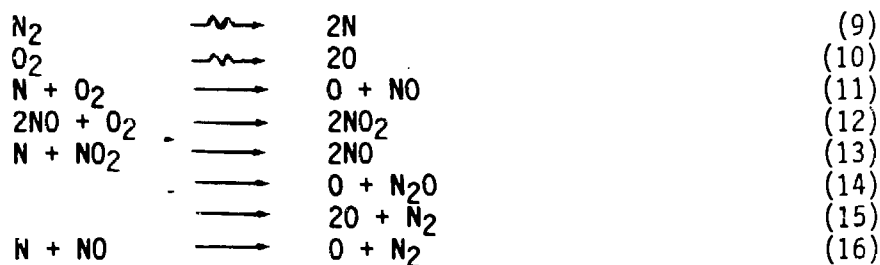
It is difficult to separate ionic, free radical and excited state processes on a primary reaction level. Attempts, however, have been made to look at the formation of nitrogen oxides under conditions where only one of these mechanism should be operable. Varney [31] showed that nitrogen activated in a discharge reacts with oxygen to form nitrogen oxides even when all ionic species were removed by an applied potential. Pshezhetsky and Dimitriev [25] correlated the formation of nitrogen oxides with the appearance potential of N_2^+ suggesting that ionic processes, in particular the ionization of nitrogen, were the predominant processes leading to the oxidation of nitrogen. It is apparent from these results that the oxidation of nitrogen occurs via both general processes. The extent that each process contributes to the net yield of atomic nitrogen depends on the particular system being considered.
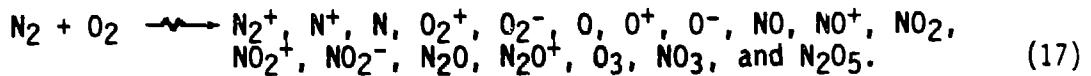
The controversy over the dominant mechanism has not yet been completely resolved although it has become more evident that, under the conditions of most of the experiments reported, the free radical process was the dominant process. The arguments for this have been strengthened by more recent work showing that ionic clustering occurs very rapidly at higher pressures [32]. This, combined with the rapid reaction of thermal electrons with oxygen and nitrogen oxides, quickly lowers the probability of ion recombination reactions that are needed to account for observed atomic nitrogen yields. Low dose rates, typical of those expected under repository-relevant conditions, will also decrease the potential for ion recombination to form a dissociative nitrogen excited state that subsequently forms atomic nitrogen. The most important point, with respect to long-term projection of radiation induced change in air and moist air systems, is that both mechanisms identify atomic nitrogen as the key primary/secondary product in the oxidation of nitrogen molecules.

The dry air systems (mixtures of oxygen and nitrogen) have been more extensively studied than moist air systems. Since no water is present, the radiation chemistry is relatively simple. This section presents a brief summary of the work completed since it is the basis for much of the interpretation of the moist air systems.

The most important work on the radiation chemistry of oxygen/nitrogen mixtures was done by Harteck and Dondes and published in a series of papers on the subject [3,4,27-30]. Others have looked at nitrogen/oxygen systems [11,12,33-35] but full discussion of this is beyond the scope of this paper.

The following intermediate products have been identified:

$$N_2 + O_2 \longrightarrow N_2^+, N^+, N, O_2^+, O_2^-, O, O^+, O^-, NO, NO^+, NO_2,$$
$$NO_2^+, NO_2^-, N_2O, N_2O^+, O_3, NO_3, \text{ and } N_2O_5. \qquad (17)$$

Immediately following irradiation the major products are nitrous oxide, ozone and nitrogen pentoxide. In time ozone begins to decompose, initiating the decomposition and final conversion of nitrogen pentoxide to nitrogen dioxide. The long term products are nitrous oxide and nitrogen dioxide. The steady state concentrations reached in a closed nitrogen/oxygen system have been well characterized as a function of temperature and initial gas phase composition.

The kinetic radiation equilibrium partial pressure of each primary gas phase component (nitrogen, oxygen, nitrous oxide and nitrogen dioxide) was characterized at two temperatures [3]. The results for a 20% oxygen/80% nitrogen mixture are shown in Table II. These data correspond to a total pressure of 1 atmosphere, high LET, and high (>100 Mrad/h) dose rate conditions. Under these conditions, increasing temperature increased the extent of nitrogen fixation.

Further work [3] has identified the conditions under which nitrogen fixation is maximized. The effects of temperature, pressure and dose rate were interpreted with respect to lowering the steady state of nitric oxide which reduces nitrogen fixation by scavenging atomic nitrogen. The temperature range of 20°C to 100°C does not favor nitrogen fixation because nitric oxide removal is relatively slow. Temperatures in excess of 250°C are not favorable because of thermal equilibrium between nitrogen dioxide and nitric oxide. An increase in pressure facilitates nitric oxide removal and therefore increases nitrogen fixation. High dose rates also facilitate nitric oxide removal from the gaseous system.

Table II. Steady-State Partial Pressures Following Irradiation of an 80/20 Nitrogen/Oxygen Mixture

Gas	Initial Pressure (torr)	Pressure Following Irradiation	
		@ 40°C	@ 150°C
Nitrogen	608	587	519
Oxygen	152	125	100
Nitrogen Dioxide	0	25	83
Nitrous Oxide	0	23	58

The optimum conditions for nitrogen fixation identified were: dose rates in excess of 600 Mrad/hr, pressures in excess of 5 atmospheres, temperatures in the range of 175°C to 225°C, and an initial nitrogen/oxygen ratio of 4 (approximately air). The highest yields obtained for the formation of nitrogen dioxide were 4-5 molecules/100 eV absorbed. Under these conditions, irradiation depletes all oxygen from the system and the two major radiolytic products are nitrogen dioxide and nitrous oxide. Nitrogen dioxide yields were greater than nitrous oxide under all experimental conditions investigated. The yield ratio of nitrogen dioxide to nitrous oxide varied from two to ten depending on the total pressure of the system and initial nitrogen/oxygen ratio.

IRRADIATION OF MOIST AIR SYSTEMS

The moist air system is most analogous to the expected environment in a tuff repository. Water vapor, because the expected temperature in the vicinity of the waste package will exceed the boiling point of water for the duration of the containment period, is expected to be a significant component of the gas phase present. Information on the radiolytic fixation of nitrogen in this type of system has been obtained in homogeneous gas phase studies and indirectly in heterogeneous (mixed gas/liquid phase) studies.

There have been only three published studies that focused on the radiation chemistry of air containing appreciable amounts of water. Primak and Fuchs [7] were the first to relate the formation of metal nitrates as a corrosion product to the production of nitric acid in irradiated moist air. Jones [36] measured the nitric acid yield in air containing up to 1.4% water vapor. More recently, Tokunaga and Suzuki [11] have studied the radiation chemistry of moist air systems containing nitric oxide at 120°C. The general conditions of the experiments performed are summarized in Table III.

A less reliable, but important, source of information on the radiation chemistry of moist air systems are mixed liquid-water/air studies [2,13,37,38]. In these systems an excess of water was present, fixing the partial pressure of water at the water vapor pressure throughout the duration of the experiment. The reported yields for nitrogen fixation in some of the mixed phase systems studied are considerably higher than those reported for homogeneous systems. The results reported in both the gas phase and mixed phase experiments are discussed in more detail in the following sections.

Primak and Fuchs

Primak and Fuchs [7], as a result of the observation of metal corrosion in the Argonne CP-3 heavy-water reactor, investigated the reaction products formed on nickel wire exposed to air systems in the presence of a high mixed gamma/neutron flux. Sealed glass ampules containing nickel wire were irradiated for varying lengths of time for four different gas compositions. The sealed ampules were placed in a small tube in the central thimble of the CP-3 reactor. Absorbed doses and dose rates were poorly characterized because of the proximity of the samples to the reactor core.

No metal nitrates were observed on the nickel in experiments that initially contained dry air. No corrosion products were observed in experiments containing only 20-30 torr of water and no air. Air containing 4.0 torr of water vapor resulted in an increase in corrosion product formation that was initially linear with exposure time reaching a

Table III. Experimental Conditions under which the Radiation Chemistry of
Moist Air Systems has been Investigated

Investigators	Radiation Source and Type	Dose Rate (Mrad/hr)	Absorbed Dose (Mrad)	Temperature °C	N_2/O_2	Mole % of Water Vapor
Primak and Fuchs [7]	CP-3 reactor, mixed gamma and neutron	Unspecified	Unspecified	40	Air	0.53-3.7
Jones [36]	100 μA beam of 1 MeV electrons	370	430	Ambient	0-1	0.033-1.4
Tokunaga and Suzuki [11]	2 mA, 1.5 MeV electron accelerating tube	405-1044	8	120	7.3	0-13
Linacre and Marsh [13]	Harwell pile, mixed gamma and neutron	4×10^{18} n/cm^2	16-1600	80	Air	Vapor pressure
Sato and Steinberg [2]	^{60}Co Gamma facility	2.5	37.5-75	Ambient	Air	Vapor pressure

plateau after 20 Mwh of exposure. Air initially containing 28 torr of water vapor resulted in corrosion product formation that was approximately linear with exposure time up to a total exposure of 50 Mwh.

From these results it was clear that both water and air were necessary to facilitate the formation of nitric acid and consequently corrode the metal present. In samples containing moist air, nitric acid formation continued until the water vapor was depleted from the gas phase. Once nitric acid ceased to form, as in their experiment with an initial partial pressure of water of 4 torr, corrosion stopped.

Jones

The results of Primak and Fuchs qualitatively characterized the connection between gas phase composition and the radiolytic formation of nitric acid. It was not, however, possible to quantitatively determine the yield of nitric acid from their data since the absorbed dose, dose rate and type of radiation present were poorly characterized. Jones [36], using spectroscopic methods for the detection of nitrogen oxides and nitric acid, was the first to quantify the yield of nitric acid in moist air systems.

The general experimental conditions of this work were summarized in Table III. As indicated, nitric acid yields were determined for moist air systems containing up to 1.4 mole % water vapor at room temperature over a wide range of initial mole % of oxygen. The irradiation vessel used was a 380 mL gold-plated brass vessel with sodium chloride windows. Infrared spectroscopy was used to monitor the concentration of nitric acid, nitrous oxide and nitrogen dioxide as a function of time.

Jones made several interesting observations concerning the radiation chemistry of the moist air systems studied. Nitric acid and ozone were the major radiolytic products formed initially. The formation of nitric acid was linear with absorbed dose and proceeded to a total concentration that was stoichiometrically equivalent to the amount of hydrogen initially present in the water. The depletion of water in the system initiated the decomposition of nitric acid, which was also linear with absorbed dose, to reform water and form a stoichiometrically equivalent amount of nitrogen dioxide. Subsequent to the conversion of nitric acid to nitrogen dioxide, the formation of nitrogen dioxide continued at a lower rate. The ozone initially generated disappeared immediately prior to the depletion of water vapor. No nitric acid formation was observed in systems that initially contained nitrogen dioxide even when water was present.

Yield values for the formation and decomposition of nitric acid, nitrous oxide and nitrogen dioxide were determined as a function of the initial mole % composition of oxygen. All formation yields reported had the same general dependence on the oxygen content. Initially there was a rapid increase with % oxygen to a maximum at 15%, followed by a rapid decrease to a plateau value in the 25-50% oxygen content region. The maximum nitric acid yield was 2.25 molecules/100 ev. No detailed mechanistic explanation was provided for the results observed.

Tokunaga and Suzuki

No further work on the radiation chemistry of moist air systems was reported until recent interest in the radiolytic removal of NO_2 and SO_2 from flue gases [11]. The experimental conditions in the work reported by Tokunaga and Suzuki were summarized in Table III. Of particular interest to the high-level waste management problem is the higher temperatures at which the work was performed and the more detailed information on the mechanism for the formation of nitric acid.

Premixed gases composed of nitric oxide, water and air were irradiated in a flowing system. The experiments reported were conducted in a one liter stainless steel box-type reaction vessel. The temperature of all experiments was 120°C. The ionizing radiation source was an electron accelerating tube which produced 2 mA of 1.5 Mev electrons. NO and NO_2 analysis was carried out with a chemiluminescence type analyzer.

Results obtained in nitric oxide or nitrogen dioxide in either nitrogen, dry air, or moist air systems were reported and discussed. Initially irradiation decreased the NO concentration and rapidly formed nitrogen dioxide. The concentration of nitrogen dioxide went through a maximum at a total absorbed dose of 3 Mrad. The decrease in its rate of formation was accompanied by the initiation of nitric acid formation. In contrast to the results reported by Jones, nitric acid formation was a function of the moisture content. No nitric acid formation was observed in dry air and air/nitrogen oxide systems. No yields were reported for the various systems studied.

The dependence of nitric acid formation on the water content of the gas phase was explained by proposing the following reaction step for nitric acid formation:

$$NO_2 + OH \rightarrow HNO_3 \tag{18}$$

The presence of water vapor affects the radiation chemistry of the nitrogen/oxygen system in two ways. First, increased moisture content will reduce the amount of energy absorbed by the nitrogen to form atomic nitrogen, which remains the key step in the oxidation of nitrogen. Second, based on the mechanism just presented, a necessary step in the oxidation of nitrogen dioxide to form nitric acid is reaction with OH free radicals which are generated from the radiolytically induced decomposition of water.

Mixed-Phase Experiments

Results from mixed-phase experiments, in which air saturated with water vapor has been irradiated, have also been reported [2,13,37,38]. These provide data on nitrogen fixation under a fixed partial pressure of water. The aqueous phase present, however, makes interpretation of the radiation chemistry more difficult because decomposition products from the water (hydrogen for low LET and hydrogen and oxygen for high LET radiation) now need to be taken into consideration. The general conditions under which the experiments were performed were listed in Table III.

Wright, Linacre, Marsh, and Bates [37] examined nitrogen fixation in nitrogen/water and air/water systems. This work was expanded with the results published in a more extensive report [13]. Sealed silica tubes, approximately 50 cc in volume, were filled with varying ratios of air or nitrogen to water. These were irradiated with primarily thermal and fast neutrons (4×10^{18} n/cm^2) from the Harwell pile. The important conclusions made, relative to this review were: (1) The fixation of nitrogen occurred exclusively in the gas phase. (2) Irradiation of air/water mixtures initially produced only nitrogen oxides (no ammonia). (3) Irradiation of nitrogen/water mixtures generated both nitrogen oxides and ammonia in what appeared to be competing processes. Ammonia was generated subsequent to nitrate formation and was only detectable at higher doses. (4) It was initially reported that the fixation of nitrogen to form nitrate was due to reaction between water and nitrogen rather than oxygen and nitrogen since initial oxygen content in the gas phase had no effect on observed yields. A dependency of the yield on the initial mole % of oxygen was noted, however, in the second report issued [13].

(5) The nitric acid yield for air was 1.5 molecules/100 ev absorbed by the nitrogen component of the gas phase. This increased to 1.9-3.2 at higher initial partial pressures of oxygen.

Sato and Steinberg [2] measured the nitrogen fixation yield in a gamma-irradiated aqueous phase through which air was bubbled at various flow rates. The reaction vessel was a glass reactor fitted with a quartz frit through which air entered the aqueous phase. The conclusions and results reported in this work contrast sharply with all other work reported. In their system only nitrite and ammonium ions were observed. Ammonium was the initial primary product which, because of the presence of oxygen, was oxidized to some extent to nitrite. No nitrate formation was reported. Yields for the fixation of nitrogen (formation of aqueous ammonia and nitrite) were as high as 400 molecules/100 ev absorbed in the gas phase present. Significant contribution from the energy absorbed in the aqueous phase was suggested to explain the very high yields obtained.

Burns et al. [38] recommended a yield value of 1.9 molecules/100 eV for the formation of nitric acid in heterogeneous water/air systems. No mechanistic work was done, however, the following equation was given for the yield of nitrate, as a function of gas/liquid ratio:

$$N = 2C_0R[1 - \exp(-1.45 \times 10^{-5} \text{ GDt})] \tag{19}$$

Here N is the concentration in moles/L at time t, C_0 is the concentration of nitrogen in the air in moles/L, R is the air/liquid volume ratio, G is the yield value of nitric acid and D is the dose rate in Mrad/hr.

SUMMARY AND COMPARISON OF RESULTS IN IRRADIATED MOIST AIR SYSTEMS

There remain a significant number of apparent discrepancies and gaps in the experimental results just reviewed. Some of these discrepancies can be resolved by considering the differences in the experimental conditions of the studies performed. Many of these discrepancies, particularly in the heterogeneous experiments that have been performed, can only be resolved by further experimentation.

Homogeneous and Heterogeneous Water/Air Systems

The most important event in the fixation of nitrogen is the direct interaction of ionizing radiation with nitrogen. It is the subsequent dissociation of the nitrogen excited states formed initially and following ion recombination that results in the formation of atomic nitrogen. The yield of atomic nitrogen, which is the key intermediate in the fixation of nitrogen, ranges between 3.9 and 5.6 depending on experimental conditions. Yields as high as 7.3 ± 1.5 have however been reported [39]. This yield does not significantly depend on temperature and represents the limiting yield for nitrogen fixation. Primary products of oxygen, water, and nitrogen oxides do not react significantly with nitrogen molecules to generate atomic nitrogen.

In dry air systems, the primary radiolytic products formed upon irradiation are nitrogen dioxide and nitrous oxide (minor amounts of ozone, nitric oxide and nitrogen pentoxide are also formed). Irradiation in a closed system resulted in the formation of steady-state concentrations of the nitrogen oxides that depended on the dose rate, temperature, total pressure, and initial nitrogen/oxygen ratio. The maximum yield of nitrogen oxide under the experimental conditions investigated was 6 molecules/100 eV.

The addition of water to the dry air system resulted in the formation of nitric acid in place of nitrogen dioxide with nitrous oxide being generated to a lesser extent. Initial rate data indicated that nitrogen

dioxide was formed first and subsequently oxidized to nitric acid by reaction with the OH free radical. In high dose experiments, nitric acid was preferentially formed until the water in the gas phase was depleted. At this point, the nitric acid was decomposed to reform nitrogen dioxide. No ammonia formation was observed in any of the systems studied.

The yield of nitric acid depends on the water content of the gas phase, initial nitrogen/oxygen ratio and irradiation vessel material [20,36,40]. The maximum yield reported, under the conditions investigated, was 2.25 molecules/100 eV. The yields, however, have not been characterized under a wide range of conditions. Yields approaching that of nitrogen dioxide in the dry air systems should be attainable under optimum conditions.

In heterogeneous air/water systems the yields obtained are more variable due to uncertainties in the gas phase compositions. They are generally less than 2 molecules/100 eV. Only oxidation of nitrogen was observed in systems that initially contain air, which is consistent with observations in dry air systems and moist air systems. In nitrogen/water systems, ammonia production was observed at high absorbed doses, raising the possibility that its formation may be possible in systems with a high hydrogen/oxygen ratio.

Application to Repository-Relevant Conditions

The radiation chemistry of moist air systems has not been investigated over the full range of conditions expected in a tuff repository. An accurate description of the gas phase present in the vicinity of the waste package cannot be made even if unknowns concerning gaseous transport and mixing at the site are ignored. The importance of the inability to accurately model the environment depends on the predicted modes of interaction between the radiolytic products generated and the material components in the waste package.

Although many gaps in the data exist, the clear dependence of nitrogen fixation on the direct interaction of ionizing radiation with nitrogen places an upper limit for the yield of nitric acid and nitrogen dioxide: $G(NO_2$ or $HNO_3) < G(N)$. Conditions present in the near-field environment of the waste package (proximity of tuff rock, container material, and perhaps a restricted air supply) will tend to lower yields considerably. From the perspective of mass-action processes, such as uniform corrosion, the moles of nitrogen oxides that can be generated are limited by this yield and are insignificant relative to the expected mass of container material and host rock present.

A more complex problem is the possibility that nitrogen fixation products, i.e., nitrogen oxides and ammonia, may contribute to non-uniform degradation of the container material; e.g., environmentally assisted cracking and pitting. The phenomena of concentrating radiolytic products in droplets formed by condensation on container material has been noted already [15]. The potential for the formation of ammonia, which is the major radiolytic "fixation" product in reducing environments, needs to be addressed further because of the susceptibility of copper-based materials to ammonia-induced cracking. In a tuff repository, this may occur if a high hydrogen/oxygen ratio develops in the gas phase present. This is not considered likely; however, full evaluation of this concern can only be made after the repository site has been better characterized.

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