

Radiation Chemical Effects in Experiments to Study the Reaction of Glass in an Environment of Gamma-Irradiated Air, Groundwater, and Tuff

R. A. Van Konynenburg

May 2, 1986



Main/legacy - 70

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial products, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

Prepared by Nevada Nuclear Waste Storage Investigations (NNWSI) Project participants as part of the Civilian Radioactive Waste Management Program. The NNWSI Project is managed by the Waste Management Project Office of the U.S. Department of Energy, Nevada Operations Office. NNWSI Project work is sponsored by the Office of Geologic Repositories of the DOE Office of Civilian Radioactive Waste Management.

Radiation Chemical Effects in Experiments to Study the Reaction of Glass in an Environment of Gamma-Irradiated Air, Groundwater, and Tuff

R. A. Van Konynenburg

Manuscript date: May 2, 1986

LAWRENCE LIVERMORE NATIONAL LABORATORY
University of California • Livermore, California • 94550



TABLE OF CONTENTS

Abstract.....	1
1. Introduction.....	3
2. Description of Experiments and Results.....	5
3. Discussion.....	15
3.1 Overview.....	15
3.2 Changes in Composition due to Heating.....	16
3.3 Overview of Major Features and Expected Observable Results.....	17
3.4 Gas Phase.....	19
3.5 Liquid Phase.....	20
3.6 Gas and Liquid Phases Considered Together.....	29
3.7 Interactions with the Solid Phase.....	30
3.8 Decomposition of Water.....	32
3.9 Fixation of Nitrogen.....	33
3.10 Hydrogen Ion Production.....	36
3.11 Nitrite-Nitrate Ratio.....	36
3.12 Likely Effects on Glass Reaction.....	40
3.13 High Gas-to-Liquid Volume Ratio Experiments.....	40
3.14 Anomalous Tests.....	42
4. Conclusions.....	45
5. Application to the Repository.....	47
References.....	51

RADIATION CHEMICAL EFFECTS IN EXPERIMENTS TO STUDY
THE REACTION OF GLASS IN AN ENVIRONMENT OF
GAMMA-IRRADIATED AIR, GROUNDWATER, AND TUFF

ABSTRACT

The results of experiments performed by John K. Bates et al. on the reaction of nuclear waste glass with a gamma-irradiated 90°C aqueous solution were analyzed using theory developed from past research in radiation chemistry. The aqueous solution they used is similar to what would be expected in a water-saturated environment in a nuclear waste repository in tuff. The purpose of our study was to develop an understanding of the radiation-chemical processes that occurred in the Bates et al. experiments so the results could be applied to the design and performance analysis of a proposed repository in unsaturated tuff in Nevada. For the Bates et al. experiments at the highest dose (269 Mrad), which originally contained about 16 ml of "equilibrated" water taken from Nevada Test Site Well J-13 and 5.4 ml of air, we predicted that water decomposition to H₂ and O₂ would produce a pressure increase of at least 1.0 MPa at 20°C. We also predicted that nitrogen fixation from the air would occur, producing an increase of 1.6 x 10⁻⁴ M in total fixed nitrogen concentration in solution. In addition, an equimolar production of H⁺ would occur, which would be buffered by the HCO₃⁻ in the water. The fixed nitrogen in solution was predicted to be present as NO₂⁻ and NO₃⁻ with the ratio influenced by the presence of materials catalytic to the decomposition of H₂O₂. We found reasonable agreement between our predictions and the observations of Bates et al., where comparisons were possible. We apply the results to the proposed Nevada repository to the degree possible, given the different expected conditions.

1. INTRODUCTION

The Nevada Nuclear Waste Storage Investigations (NNWSI) Project is evaluating the tuff deposits at Yucca Mountain in Nye County, Nevada, as a possible location for a high-level nuclear waste repository. Lawrence Livermore National Laboratory (LLNL) is responsible for waste package development for this site. An important aspect of this development is to predict the extent of release into the environment of radionuclides from the nuclear waste expected at the site. The waste form planned for the first defense high-level nuclear waste to be emplaced (as well as for the waste from the West Valley, New York, facility) is borosilicate glass. Accordingly, we are studying the behavior of borosilicate glass under conditions similar to those in the expected tuff repository environment.

We anticipate that the repository will be located in the unsaturated zone above the water table. We also expect that during the first 300 to 1000 years the waste form will be protected by sealed outer containers, and that the thermal power density from nuclear decay will be sufficient to prevent liquid water from coming into contact with most of the packages during this period. The maximum gamma dose rate near waste packages containing the glass waste form is expected to be about 5.5×10^3 rem/hour at the time of emplacement.¹ The dominant gamma emitter during the containment period will be ¹³⁷Cs, with a half-life of 30.17 years. The gamma dose rate would thus decay by about 10 half-lives during a 300-year period, which is equivalent to about three orders of magnitude. The resulting dose rate would be a few rem/hour maximum after 300 years. Nevertheless, there is a small probability that some liquid water could contact some of the glass during the time when a significant gamma radiation dose rate was still present.

Past studies have shown that gamma irradiation can increase the rate and extent of reactions of nuclear waste glasses with deionized water and aqueous solutions compared to what is observed in the absence of radiation; Pederson and McVay provide a recent review of these studies.² The largest increases have been seen when air was in contact with the solution, because of the production of nitric acid during irradiation and the resulting lowering of the pH.³⁻⁶ Smaller increases have been attributed to the transient radical species produced by irradiation of the water, particularly the hydroxyl radical OH.⁷

We expect that a repository located in tuff at Yucca Mountain would be open to gaseous exchange with the atmosphere because of the fractures and connected porosity of the rock. Therefore the potential for nitric acid production would exist. The presence of dissolved CO₂ also raises the possibility of production of carboxylic acids, which can act as chelating agents increasing corrosion and dissolution rates.⁸⁻¹² However, the expected water composition includes bicarbonate as the major anion, which would tend to buffer any tendency toward a more acid pH. In addition, where water is in contact with tuff, considerable buffering would be supplied by the feldspar minerals, which readily exchange Na⁺, K⁺, and Ca⁺⁺ for H⁺ ions.¹³⁻¹⁷ The simultaneous presence of oxygen and neutral-to-alkaline pH could also reduce the production of carboxylic acids (see Section 3.5).

Because of the existence of these opposing factors and the lack of a complete theoretical treatment of the glass-water interaction process, particularly under irradiation, John K. Bates et al. of Argonne National Laboratory designed and carried out appropriate laboratory experiments to study the glass behavior under saturated tuff conditions with gamma irradiation. Some of the results have been reported.^{18,19}

In order to apply these results to the prediction of glass behavior in a repository, it is necessary to understand the detailed mechanisms of the processes that occurred during the Bates et al. experiments. Therefore, using theory developed in earlier studies, in this paper we predict the radiation chemical effects that would be expected to occur in the experimental configuration used by Bates et al. and compare these predictions with parameters observed by them.

The purpose of this work is to contribute to the development of a detailed understanding of the behavior of nuclear waste glass in a tuff repository. The repository can then be designed and its performance projected in such a way that the required reasonable assurance can be provided that radionuclide releases will be below the limits established by the Environmental Protection Agency²⁰ and the Nuclear Regulatory Commission²¹ (40CFR191 and 10CFR60).

2. DESCRIPTION OF EXPERIMENTS AND RESULTS

Bates et al. performed two sets of experiments to study the influence of gamma irradiation on the reaction of actinide-doped Savannah River Laboratory 165-frit nuclear waste glass in a saturated tuff environment.^{18,19,22} These experiments consisted of irradiating small vessels containing various combinations of glass, tuff, water, and air with gamma rays for several time periods while maintaining an elevated temperature. The dissolved solutes and the glass surfaces were then analyzed.

The vessels were 304L stainless steel Parr reaction vessels, sealed with silicone rubber gaskets. They had a volume of 21.4 cm³. The nominal composition of 304L stainless steel is given in Table 1. The complete gasket composition was not measured. Bates found only Si in an examination by energy-dispersive x-ray analysis, which was sensitive only to elements of $Z \geq 11$.²² A later 150°C leaching experiment on the gasket material with HNO₃ solution revealed only Si as a major constituent, with traces of B, Mg, and Ca also released. The vessels were machined using Trimsol, a soluble oil-type cutting fluid manufactured by the Master Chemical Company. They were then polished using an aluminum oxide slurry. The vessels were ultrasonically cleaned in acetone, rinsed three times in high purity water, submerged in 90°C 1% HNO₃ solution for one hour, rinsed again three times with high purity water, and dried. The gaskets were heated to 90°C in high purity water for two hours, rinsed with high purity water, and dried.

The glass consisted of two types. The first was Savannah River Laboratory (SRL) 165 black frit to which U, Cs, and Sr had been added; it is referred to as SRL U glass. The second was SRL U glass to which ²³⁷Np, ²³⁹Pu, and ²⁴¹Am had been added; it is referred to as SRL A glass. In the first set of experiments, the glass was used both in the form of discs and powder. Discs, when used, were supported on 304L stainless steel stands. In the second set of experiments, only discs were used. The composition of the glass used in the first set of tests is given in Table 2; the actinide composition was slightly different in the second set.

The first set of experiments used crushed Topopah Spring tuff from a drill hole at Fran Ridge near the Yucca Mountain site in Nevada (UE-25 h #1, 173.0 to 173.6). We expect the major and minor element whole rock composition of this tuff to be similar to that reported by Zielinski²³ for drill hole

Table 1. Composition of AISI standard type 304L stainless steel.^a

Element	Weight %
Iron	Balance (at least 65)
Chromium	18.0-20.0
Nickel	8.0-12.0
Manganese	2.0 maximum
Silicon	1.0 maximum
Phosphorus	0.045 maximum
Sulfur	0.03 maximum
Carbon	0.03 maximum

^a From American Society for Metals, Metals Handbook (A.S.M., Metals Park, OH, 1980) 9th ed., vol.3, p. 5.

Table 2. Composition of SRL glasses used in first set of tests.^a

Component	Analysis (weight %)		
	SRL 165 U/A	Black Frit	
	ANL ^b	Ferro ^c	MCC ^d
Al ₂ O ₃	4.08	4.1	4.3
B ₂ O ₃	6.76	6.8	6.8
BaO	0.06		< 0.1
CaO	1.62	1.5	1.6
Fe ₂ O ₃	11.35	12.3	11.7
FeO	0.35		
K ₂ O	NA		0.2
Li ₂ O	4.18	4.7	4.8
MgO	0.70	0.8	0.6
MnO	2.27	2.9	2.8
Na ₂ O	10.85	10.3	10.8
NiO	0.85	0.9	0.8
P ₂ O ₅			0.3
SiO ₂	52.86	54.1	51.6
TiO ₂	0.14		0.2
ZnO	0.04		< 0.1
ZrO ₂	0.66	1.2	0.7
F	NA	0.06	
Cl	NA	0.05	
Pb	NA	0.05	
²³⁷ NpO ₂	0.008		
²³⁹ PuO ₂	0.022 ^e		
²⁴¹ Am ₂ O ₃	0.00036 ^e		
U ₃ O ₈	0.96		
Cs ₂ O	0.072		
SrO	0.11		
Others ^f			

NOTE: NA = not analyzed.

^aFrom J. K. Bates, D. F. Fischer, and T. J. Gerding, The Reaction of Glass in a Gamma Irradiated Saturated Tuff Environment. Part 1: SRL 165 Glass, Argonne National Laboratory, Argonne, IL, ANL-85-62 (1985).

^bOnly SRL U glass was analyzed for all components. SRL A glass was analyzed for ²³⁷Np, ²³⁹Pu, and ²⁴¹Am. The composition of both glasses are assumed to be the same, except for actinide elements.

^cBlack frit supplied to ANL by SRL, composition as determined by Ferro Corp.

^dBlack frit supplied by SRL to the MCC, composition as determined by MCC.

^eAnalysis by alpha spectrometry.

^fLa₂O₃, Nd₂O₃, CeO₂ < 0.05; MoO₃ < 0.01; and Cr₂O₃ < 0.01 weight %.

USW-G1, given in Table 3. The major mineral species present in this rock are quartz, cristobalite, and alkali and plagioclase feldspars. The second set of experiments used discs of tuff from USW-G1 (1235.1 - 5 ft.).

"Equilibrated J-13 water" was so-called because it was prepared by heating water from Well J-13 near Yucca Mountain, together with crushed tuff, in a closed Teflon bottle for two weeks at 90°C, filtering it, and storing it in a closed polypropylene container. Its composition should therefore be closer to what would exist in thermodynamic equilibrium with tuff at 90°C than the starting composition of J-13 water. The composition of the water used in the first set of experiments is shown in Table 4. The bicarbonate and potassium concentrations were not measured, so estimates were made based on anion-cation balance and previous analyses of solutions prepared in a similar way. The dissolved gas concentrations were calculated using Henry's Law, and the carbonate concentration was calculated assuming equilibrium (constants are given in Table 5). The water composition was slightly different for the second set of experiments. Measured pH values for the starting water used in both sets are shown in Table 6. The difference between the two measured values probably results from nonequilibrium concentrations of dissolved CO₂.

The air was ordinary laboratory air, the dry composition of which was probably near to that of standard dry air, as shown in Table 7. The humidity of the initial air was not controlled, but the air in the sealed capsules would have reached 100% relative humidity because there was excess liquid water present, and there was sufficient time to reach equilibrium vapor pressure.

The gamma irradiation was provided by ⁶⁰Co sources. In the first set of experiments, the dose rate (measured at the beginning of the experiments) was $2.0 \pm 0.2 \times 10^5$ rad/hour inside the vessels. In the second set of experiments, the dose rate was $1.0 \pm 0.2 \times 10^4$ rad/hour. The vessels were arranged relative to the sources to achieve essentially the same dose rates in all the vessels. (Additional experiments at lower dose rates are underway.)

The vessels were placed inside an oven, the temperature of which was controlled at $90.0 \pm 0.5^\circ\text{C}$. However, post-test measurements revealed that the actual vessel temperature was about 92°C for the first set of experiments. The vessels in the first set of experiments were run for time periods of 7, 14, 28, and 56 days. The vessels in the second set were run for periods of 14, 28, 56, 91, and 182 days. There were 66 vessels in each set of experiments.

Table 3. Composition of Topopah Spring tuff (whole rock)
from Hole USW-G1, expressed as oxides.^a

Species	Weight %
SiO ₂	75.2
Al ₂ O ₃	12.4
K ₂ O	4.8
Na ₂ O	3.1
Fe ₂ O ₃	1.8
CaO	0.5
MgO	0.2
TiO ₂	0.1
MnO	0.06
Loss on ignition	<u>1.0</u>
	99.16

^a From R. A. Zielinski, Evaluation of Ash-flow Tuffs as Hosts for Radioactive Waste: Criteria Based on Selective Leaching of Manganese Oxides, U.S. Geological Survey, Denver, CO, Open File Report 83-480 (1983).

Table 4. Composition of "Equilibrated J-13" water at 20°C
(first set of experiments).^a

Species	Weight ppm	mM
Na	46.5	2.02
Si	34.4	1.22
Ca	9.08	0.23
K (estimated)	6.	0.15
Mg	0.96	0.040
Al	0.63	0.023
B	0.16	0.015
Sr	0.045	0.0005
Li	0.044	0.006
Fe	0.01	0.00018
U	0.0024	0.00001
HCO ₃ ⁻ (estimated)	122.	2.00
SO ₄ ⁻²	17.3	0.18
NO ₃ ⁻	7.60	0.12
Cl ⁻	7.15	0.20
F ⁻	2.4	0.13
NO ₂ ⁻	not detected	-
CO ₃ ⁻²	1.9	0.032
CO ₂	0.57	0.013
N ₂	15.	0.53
O ₂	9.1	0.28

^a From J. K. Bates, D. F. Fischer, and T. J. Gerding, The Reaction of Glass in a Gamma Irradiated Saturated Tuff Environment. Part 1: SRL 165 Glass, Argonne National Laboratory, Argonne, IL, ANL-85-62 (1985).

Table 5. Parameters influencing composition of gas and liquid phases.

Parameter	Value at 20°C	Value at 90°C	Reference
Vapor pressure of water (kPa)	2.339	70.14	62
Specific volume of saturated liquid (m ³ /kg)	1.0018 x 10 ⁻³	1.036 x 10 ⁻³	62
Specific volume of saturated vapor (m ³ /kg)	57.791	2.361	62
Henry's Law constant of CO ₂ (M/Pa)	3.89 x 10 ⁻⁷	1 x 10 ⁻⁷	63,64
Apparent first dissociation constant of H ₂ CO ₃ (activity units)	4.1 x 10 ⁻⁷	4.0 x 10 ⁻⁷ (interpolated)	44
Second dissociation constant of H ₂ CO ₃ (activity units)	4.2 x 10 ⁻¹¹	7.3 x 10 ⁻¹¹	44
Ion product of water (M ²)	6.8 x 10 ⁻¹⁵	3.5 x 10 ⁻¹³	65
Henry's Law constant of N ₂ (M/Pa)	6.83 x 10 ⁻⁹	4.18 x 10 ⁻⁹	63
Henry's Law constant of O ₂ (M/Pa)	1.36 x 10 ⁻⁸	7.6 x 10 ⁻⁹	63

Table 6. Changes in compositions of gas and liquid phases due to heating, in vessels originally containing 16 ml of water.

	Temperature	
	20°C	90°C
<u>Gas phase</u>		
Volume ($m^3 \times 10^6$)	5.4	4.85
<u>Pressures (kPa)</u>		
N ₂	78.2	106.5
O ₂	21.0	28.6
Ar	0.9	1.3
CO ₂	0.03	0.42
H ₂ O	<u>1.1</u> (50% R.H.)	<u>70.1</u>
Total	101.23	206.92
<u>Liquid phase</u>		
Volume ($m^3 \times 10^6$)	16.0	16.55
pH (at temperature)	8.6 (calc.) $\left. \begin{matrix} 8.1 \\ 7.5 \end{matrix} \right\}$ (meas.)	8.06 (calc.)
<u>Concentrations of species that are affected (M)</u>		
CO ₂	1.3×10^{-5}	4.2×10^{-5}
HCO ₃ ⁻	2.0×10^{-3}	1.86×10^{-3}
CO ₃ ⁻²	3.2×10^{-5}	1.5×10^{-5}
N ₂	5.3×10^{-4}	4.4×10^{-4}
O ₂	2.8×10^{-4}	2.2×10^{-4}

Table 7. Composition of standard dry air.^a

Species	Volume %	Volume ppm
N ₂	78.084 ± 0.004	
O ₂	20.946 ± 0.002	
CO ₂	0.033 ± 0.001	
Ar	0.934 ± 0.001	
Ne		18.18 ± 0.04
He		5.24 ± 0.004
Kr		1.14 ± 0.01
Xe		0.087 ± 0.001
H ₂		0.5
CH ₄		2.
N ₂ O		0.5 ± 0.1

^a From R. C. Weast and M. J. Astle, Eds., CRC Handbook of Chemistry and Physics, 63rd ed. (CRC Press, Boca Raton, FL, 1982).

The volumes of "equilibrated J-13" water initially added to most of the vessels ranged from 12.5 to 16.4 ml. In order to study the effect of changing the air-water ratio, the water volumes in two vessels in each set of experiments (G-113 and G-114 in the first set, and G-265 and G-266 in the second set) ranged only from 4.6 to 6.2 ml.

In the first set of experiments, some vessels were found to be pressurized to above atmospheric pressure after the irradiations, while in the second set they were not. Most of the 182-day vessels in the second set were found to have closure nuts that could be loosened by hand. To reduce damage to the gaskets, the closures in the second set had not been tightened as much as those in the first set, so later gasket creep may have loosened the seal somewhat. In two experiments in the first set (numbers G-113 and G-114) and in three in the second set (G-208, G-247, and G-248), the water was found to contain a flocculent, rust-colored precipitate, and the stainless steel was visibly corroded. In these cases, high levels of chloride ion and lower-than-normal pH were also observed. Experiments G-113 and G-114 were run with deionized water, while the others used "equilibrated J-13" water. The solutions in G-208, G-247, and G-248 were found to be depleted in dissolved $\text{NO}_2^- + \text{NO}_3^-$ and SO_4^{2-} compared to initial values. In the second set of experiments, the solution was observed to be yellow in several other vessels. Films resembling oil films were observed in some vessels.

Analysis of the water was performed by inductively-coupled plasma optical emission spectroscopy, ion chromatography, and atomic fluorescence. In the second set, dissolved gas analysis was also performed, both by mass spectrometry of frozen samples and by the Van Slyke method, which involves gas chromatography of a stirred solution. The pH was measured for all solutions. Bates et al. have published some of the data.^{18,19}

3. DISCUSSION

3.1 OVERVIEW

In the experiments of Bates et al., two fluid media were in contact with each other: the gas phase, which started out as air, and the liquid phase, which started out in most cases as "equilibrated J-13" water having the dissolved species shown in Table 4. As time progressed, interactions occurred between the fluid phases and the other materials, namely the stainless steel, the glass, and the tuff. From a radiation chemistry standpoint, this is a very complex system. Radiation chemical experiments are usually performed on highly purified systems with a minimum number of constituents in essentially inert vessels. A precise theoretical analysis of this system would require a time-dependent computer model incorporating at least two compartments to represent the two fluid phases. Within each compartment, provision would need to be made for inputting the yields of the primary radiolytic species and calculating their reactions by means of coupled rate equations. The significant reactions and their rates would have to be known for both phases at the temperature of interest. Provisions would have to be made for transport of species between the two phases, and the equations governing such transport would have to be supplied. Significant interactions between the fluid and solid phases would also have to be understood well enough to be modeled mathematically.

At present, the capability to do all of this is not available, so far as I know. Researchers at Chalk River have made progress on understanding the irradiation of dry air and have published results of computer simulations.²⁴⁻²⁶ Tokunaga and Suzuki have qualitatively described the radiation chemistry of moist N_2-O_2 mixtures.²⁷ Busi et al. have presented a computer model for mixtures of N_2 , O_2 , H_2O , and CO_2 .²⁸ To my knowledge, however, modeling of the radiation chemistry of a gaseous system incorporating significant proportions of N_2 , O_2 , H_2O , and H_2 (from radiolysis), such as was present in the Bates et al. experiments, has not been performed.

Likewise, computer models of liquid water systems have been constructed by researchers from Argonne,²⁹ Harwell,³⁰ Chalk River,³¹ Riso,³² Battelle Pacific Northwest Laboratories,³³ and Battelle Columbus Laboratories.³⁴ However, these models have incorporated only a few solutes. To my knowledge,

modeling has not been performed on a bicarbonate water, although Swedish researchers have discussed the importance of bicarbonate as a scavenger in irradiated groundwater.³⁵

Provision for transport of H₂ and O₂ between a gas and a liquid phase has been made by some of these researchers. I am not aware of any computer models that have incorporated transport of oxides of nitrogen over time. Burns et al. have modeled the corrosion behavior of stainless and mild steels in the presence of irradiated air and demineralized or distilled water.³⁶ However, to my knowledge, interactions with nuclear waste glass and rock have not been modeled in a radiation chemistry code.

Since a thoroughgoing computer model of the system of interest was not available, I elected to perform an approximate analysis of the radiation chemistry, considering only the dominant reactions. In this report, I first present an overview of the major features and the expected observable results. I next consider the radiation chemistry in greater detail, beginning with the fluid phases in isolation. I then consider transport of species between the fluid phases and important interactions with the solid phases. With this background, I calculate specific observable parameter changes and compare them with the results of Bates et al. for cases in which corresponding measurements were made.

3.2 CHANGES IN COMPOSITION DUE TO HEATING

In this paper I take the irradiation temperature to be 90°C. Differences in behavior at 92°C, as actually used in the first set of experiments by Bates et al., are expected to be minor. When a closed system containing air and an aqueous solution such as "equilibrated J-13" water is heated from room temperature to 90°C, a number of changes occur that affect the composition of the two phases. The important parameters and their values at 20°C and 90°C were given in Table 5. The main effects of heating on the vessels that originally contained 16 ml of water and 5.4 ml of air are shown in Table 6. Note that: water evaporates to produce a higher vapor pressure; the remaining liquid water expands and reduces the gas space; a small amount of CO₂ moves from the liquid to the gas phase because of its reduced solubility; the bicarbonate and carbonate concentrations drop slightly to maintain equilibrium; the dissolved CO₂ concentration rises slightly because of the

increased vapor pressure; and the N_2 and O_2 concentrations drop slightly because of decreased solubility. My calculations of these values assumed constant concentrations for cations other than H^+ . I considered this valid because the water was previously "equilibrated" at $90^\circ C$. Ionization of silicic acid was not included; its effect would be to lower the pH only slightly. It should be noted that a small amount of gas leakage may have occurred from the 182-day vessels in the second set of experiments by Bates et al. This would have had the effect of reducing the relative concentrations of N_2 , O_2 , Ar, CO_2 , and later H_2 , with respect to water vapor, in the gas phase.

In the following discussion I focus first on the so-called "blank" experiments that started with 16 ml of water and did not contain rock or glass.

3.3 OVERVIEW OF MAJOR FEATURES AND EXPECTED OBSERVABLE RESULTS

Past research has shown that the stable products of low-dose-rate irradiation of moist air are gaseous nitric acid (HNO_3), nitrous oxide (N_2O), and a small amount of ozone (O_3).⁶ In a liquid water phase, the primary products of irradiation are OH , e_{aq}^- , H_3O^+ , H_2O_2 , H , H_2 , and HO_2 (Table 8).³⁷ If three conditions are met (i.e., if the water is of high purity, the container is inert and sealed, and only gamma irradiation is used), then the free radical products H , OH , e_{aq}^- , and HO_2 will react with the molecular products H_2 and H_2O_2 in such a way that the result is small steadystate concentrations of H_2O_2 , H_2 , and O_2 dissolved in the water, and there is no net decomposition of the water as a function of time. However, in the Bates et al. experiments there were several initially-dissolved species that have significant reaction rates with the primary free radical products. In addition, the species produced by irradiation of the gas phase would dissolve in the liquid phase, and could then also interact with the primary free radicals. Interactions would also take place between the free radicals and the stainless steel vessels. It appears from previous investigations that there would be four significant results of these processes:

1. A net decomposition (radiolysis) of water into H_2 and O_2 would occur as a function of time.
2. Nitrogen would be fixed and added to the liquid phase, appearing at the end of the experiments as nitrate (NO_3^-) and nitrite (NO_2^-) ions.

Table 8. Primary products of gamma irradiation of liquid water for pH 5 to 9.^a

Product	G
H ₂ O	-4.08
OH (hydroxyl radical)	2.72
e _{aq} ⁻ (hydrated electron)	2.63
H ₃ O ⁺ (hydronium ion)	2.63
H ₂ O ₂ (hydrogen peroxide)	0.68
H (hydrogen atom)	0.55
H ₂ (hydrogen molecule)	0.45
HO ₂ (perhydroxyl radical)	0.026

^a From J. W. T. Spinks and R. J. Woods, An Introduction to Radiation Chemistry (Wiley, New York, 1976), 2nd ed.

3. An equivalent amount of hydrogen ions would be produced in the solution, tending to lower the pH against the buffering action of the dissolved bicarbonate as well as that of the rock and glass, where present.
4. Colloidal Fe(III) iron-containing substances would become suspended in the solution as a result of vessel wall reactions.

3.4 GAS PHASE

If we use the gas composition at 90°C in Table 7 and assume that the gamma rays would interact with the species listed in proportion to their fractions of the total electron density (a valid assumption for Compton interactions, which are dominant here), we find that the energy should be absorbed in about the following proportions:

N_2 - 57%, H_2O - 26%, and O_2 - 17%, other gases negligible.

The production rates of the initial radiolytic products (ions, free radicals, excited molecules, and electrons) can be determined by weighting the yields, G , for the pure gases by these proportions. The yield (in radiation chemistry) is defined as the number of molecules of a particular species that are created or destroyed when 100 eV of energy is absorbed from radiation. G_X represents the primary yield of species X, i.e., the yield evaluated before any subsequent reactions take place. $G(X)$ represents the final or observed yield of species X in an experiment in which reactions may have occurred after the initial production of the species. $G(X)$ is measured, and G_X is inferred or measured in experiments designed such that G_X will be equal to $G(X)$.

Willis and Boyd have summarized available data to evaluate the yields for the various species formed in irradiation of inorganic gases.²⁵ For the gases that are important here, the species include N_2^+ , N^+ , N , N_2^* , O_2^+ , O^+ , O , O_2^* , H_2O^+ , H^+ , OH^+ , H , OH , H_2O^* , H_2 , and e^- . Some of these species are produced in more than one energy state, so the total description of the system becomes quite complex.

The ionic species produced in the irradiation would undergo a series of reactions with other species present.^{27,28} The results would be additional free radical and molecular species. The free radicals in turn would interact with each other and with other species to produce HNO_3 , N_2O , and O_3 , as observed by Jones.⁶ Intermediate species in this process are thought to include NO , NO_2 , and possibly N_2O_4 . (NO_3 and N_2O_5 are believed to be formed

in irradiation of dry air, but not moist air.) Further behavior is affected by interaction with the liquid phase.

3.5 LIQUID PHASE

For aqueous solutions with total solute concentrations less than about 0.1 M, interactions of the radiation only with the water need to be considered.³⁷ When gamma rays interact with water, they excite electrons and produce ionization by the photoelectric and Compton effects. The recoiling electrons deposit their energy by interacting with electrons in other molecules. The result is that excitation and ionization are produced in concentrated regions called spurs and tracks. This results in formation within these regions of the species H_2O^+ , e^- , and H_2O^* . Reaction of H_2O^+ with water molecules then produces H_3O^+ ions and OH. Dissociation of excited molecules produces H, OH, H_2 , and O. Some electrons are captured by H_3O^+ ions, producing H_2O and H. Some of the caged H and OH radicals recombine to form water. The electrons become solvated, forming e_{aq}^- . All of the above events occur within about 10^{-11} seconds of the initial interaction of the gamma ray with the water.

At about 10^{-10} seconds, the free radical species can diffuse far enough to undergo significant numbers of reactions with each other. This occurs first within the spurs and tracks, because of proximity. These reactions produce H_2O , H_2 , and H_2O_2 within the spurs and tracks within a total elapsed time of 10^{-8} seconds. So long as the concentrations of reactive solutes in the water are less than about 10^{-3} M, the solutes will not significantly interfere with the above processes.³⁷ As can be seen from Tables 4 and 6, the water in these experiments satisfies this criterion. At this stage, the products of the irradiation are called "primary products," and their yields are as shown in Table 8 for gamma irradiation of liquid water at room temperature in the pH range from about 5 to 9. At 90°C , the values might differ by as much as 10%, as deduced from the work of Hochanadel and Ghormley.³⁸

During the period between 10^{-6} sec and about 1 sec after an initial gamma interaction, the free radicals (OH, H, e_{aq}^- , and HO_2) and the molecular species (H_2 and H_2O_2) are able to diffuse from spurs and tracks into the bulk of the solution. There the free radicals interact with each other, with the

molecular species, or with reactive solutes, if present. In the case of gamma irradiation of very high purity (triply distilled) water in an inert, closed container, small concentrations of H_2O_2 , H_2 , and O_2 build up, the latter from decomposition of H_2O_2 . Since there are insignificant concentrations of solutes, the free radicals are able to react with the molecular species to reform water, and there is no net decomposition of water over time.

When reactive solutes are present in the water, as is the case with "equilibrated J-13" water, there is a competition for reaction with the free radicals. They undergo second order reactions, the rates of which are given by equations of the form

$$\text{Rate} \frac{\text{moles}}{\text{liter-sec}} = k \frac{\text{liter}}{\text{moles-sec}} \times [R_1] \frac{\text{moles}}{\text{liter}} \times [R_2] \frac{\text{moles}}{\text{liter}} \quad (\text{Eq.1})$$

where $[R_1]$ is the concentration of free radical R_1 , and $[R_2]$ is the concentration of another reactive species, either another free radical, a molecular product, or a solute.

In order to predict what the dominant reactions of each free radical will be, we need to know the concentrations of these other species and the reaction rate constants. The rate constants for the significant reactions that take place in pure water and common aqueous solutions have been measured and tabulated. The list given in Table 9 summarizes the reactions and rate constants presented by several authors. As can be seen, there is essential agreement between authors. The values shown are for 25°C. The free radical reaction rates are not expected to be significantly different at 90°C, because the free radicals in water radiolysis are highly reactive, having low energies of activation for their reactions.^{7,29} The reactions tend to be diffusion limited, rather than activation limited. The pK values for H_2O , HO_2 , and H_2O_2 do shift with temperature. The H_2O pK shift is the only significant one for our purposes, and it has been taken into account.

A measure of the relative importance of solutes compared to free radicals in reactions with free radicals can be obtained from a knowledge of the maximum concentrations that could be reached by the free radicals during a continuous irradiation of pure water, i.e., in the absence of reactive solutes. These concentrations are fixed by the reactions of free radicals with free radicals. For a maximum dose rate of 2×10^5 Mrad/hour, as used in these experiments, the upper limit to the free radical concentrations is in the range of 10^{-9} M.³⁷ Of the solutes found in "equilibrated J-13" water in

Table 9. Reactions and rate constants for pure water at 25°C.

Reaction	Rate Constant ($M^{-1} \text{ sec}^{-1}$ or sec^{-1}) ^a			
	Spinks and Woods ³⁷	Boyd et al. ³¹	Gordon et al. ²⁹	Burns et al. ³⁶
1. $e_{\text{aq}}^- + \text{H}_2\text{O} \rightleftharpoons \text{H} + \text{OH}^-$	16/-	20/-	16/-	16/2.0 x 10 ⁷
2. $e_{\text{aq}}^- + \text{H}^+ \rightarrow \text{H}$	2.35 x 10 ¹⁰	2.2 x 10 ¹⁰	2.3 x 10 ¹⁰	2.4 x 10 ¹⁰
3. $e_{\text{aq}}^- + \text{OH} \rightarrow \text{OH}^-$	3.0 x 10 ¹⁰	3.0 x 10 ¹⁰	3.0 x 10 ¹⁰	3.0 x 10 ¹⁰
4. $e_{\text{aq}}^- + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}^-$	1.2 x 10 ¹⁰	1.2 x 10 ¹⁰	1.3 x 10 ¹⁰	1.3 x 10 ¹⁰
5. $e_{\text{aq}}^- + \text{HO}_2 \rightarrow \text{HO}_2^-$	-	-	-	2.0 x 10 ¹⁰
6. $e_{\text{aq}}^- + \text{O}_2 \rightarrow \text{O}_2^-$	1.9 x 10 ¹⁰	1.9 x 10 ¹⁰	1.9 x 10 ¹⁰	1.9 x 10 ¹⁰
7. $(2 \text{H}_2\text{O}^+) e_{\text{aq}}^- + e_{\text{aq}}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$	5.4 x 10 ⁹	5.0 x 10 ⁹	5. x 10 ⁹	5.0 x 10 ⁹
8. $(\text{H}_2\text{O}^+) e_{\text{aq}}^- + \text{H} \rightarrow \text{H}_2 + \text{OH}^-$	2.5 x 10 ¹⁰	2.5 x 10 ¹⁰	2.5 x 10 ¹⁰	2.5 x 10 ¹⁰
9. $(\text{H}_2\text{O}^+) e_{\text{aq}}^- + \text{HO}_2^- \rightarrow \text{OH} + 2 \text{OH}^-$	-	3.5 x 10 ⁹ b	-	3.5 x 10 ⁹
10. $(\text{H}_2\text{O}^+) e_{\text{aq}}^- + \text{O}_2^- \rightarrow \text{OH}^- + \text{HO}_2^-$	1.3 x 10 ¹⁰	1.3 x 10 ¹⁰	-	1.8 x 10 ⁸
11. $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$	5.3 x 10 ⁹	5.5 x 10 ⁹	5.0 x 10 ⁹	4.5 x 10 ⁹
12. $\text{OH} + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}$	9. x 10 ⁹	1.2 x 10 ¹⁰	1. x 10 ¹⁰	1.2 x 10 ¹⁰
13. $\text{OH} + \text{O}_2^- \rightarrow \text{O}_2 + \text{OH}^-$	1.01 x 10 ¹⁰	9.0 x 10 ⁹	-	1.2 x 10 ¹⁰
14. $\text{OH} + \text{H} \rightarrow \text{H}_2\text{O}$	2.0 x 10 ¹⁰	2.0 x 10 ¹⁰	1.5 x 10 ¹⁰	2.0 x 10 ¹⁰
15. $\text{OH} + \text{H}_2 \rightarrow \text{H} + \text{H}_2\text{O}$	4.9 x 10 ⁷	3.6 x 10 ⁷	4.0 x 10 ⁷	4.5 x 10 ⁷
16. $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	2.7 x 10 ⁷	3.3 x 10 ⁷	2.25 x 10 ⁷	4.5 x 10 ⁷
17. $\text{OH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}^-$	1.2 x 10 ¹⁰	1.2 x 10 ¹⁰	-	-
18. $\text{OH} + \text{HO}_2^- \rightarrow \text{HO}_2 + \text{OH}^-$	-	5.0 x 10 ⁹	-	-
19. $\text{H} + \text{H} \rightarrow \text{H}_2$	1.3 x 10 ¹⁰	1.0 x 10 ¹⁰	1. x 10 ¹⁰	1.0 x 10 ¹⁰
20. $\text{H} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{H}_2\text{O}$	9. x 10 ⁷	9.0 x 10 ⁷	9. x 10 ⁷	9.0 x 10 ⁷
21. $\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	2.0 x 10 ¹⁰	2.0 x 10 ¹⁰	2. x 10 ¹⁰	2.0 x 10 ¹⁰
22. $\text{H} + \text{O}_2^- \rightarrow \text{HO}_2^-$	-	2.0 x 10 ¹⁰	-	2.0 x 10 ¹⁰
23. $\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	1.9 x 10 ¹⁰	1.8 x 10 ¹⁰	1.9 x 10 ¹⁰	1.9 x 10 ¹⁰
24. $\text{H} + \text{OH}^- \rightarrow e_{\text{aq}}^- + \text{H}_2\text{O}$	2.3 x 10 ⁷	2.1 x 10 ⁷	1.5 x 10 ⁷	-
25. $\text{HO}_2 \rightleftharpoons \text{H}^+ + \text{O}_2^-$	pK = 4.88	8.0 x 10 ⁵ / 4.5 x 10 ¹⁰	pK = 4.88	8.5 x 10 ⁵ / 5.0 x 10 ¹⁰
26. $\text{HO}_2 + \text{O}_2^- \rightarrow \text{O}_2 + \text{HO}_2^-$	4.4 x 10 ⁷	8.9 x 10 ⁷	-	1.5 x 10 ⁷

Table 9. Continued.

27. $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	2.5×10^6	2.0×10^6	1.6×10^6 (for pH=6.5)	2.7×10^6
28. $(2 \text{H}_2\text{O}^+) \text{O}_2^- + \text{O}_2^-$ $\rightarrow \text{O}_2 + \text{H}_2\text{O}_2 + 2 \text{OH}^-$.	-	-	0
29. $\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O}$	$1.43 \times 10^{11}/$	$1.43 \times 10^{11}/$	-	$1.438 \times 10^{11}/$
	-	2.6×10^{-5}	-	2.6×10^{-5}
30. $\text{OH}^- + \text{H}_2\text{O}_2 \rightleftharpoons \text{HO}_2^- + \text{H}_2\text{O}$	-	-	-	$1.0 \times 10^8/$ 1.022×10^4
31. $\text{H}^+ + \text{HO}_2^- \rightleftharpoons \text{H}_2\text{O}_2$	-	$2.0 \times 10^{10}/$ 3.56×10^{-2}	-	$2.0 \times 10^{10}/$ -
32. $\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}^-$	$(0.17 \text{ to } 2) \times 10^7$	1.7×10^6	-	-
33. $\text{O}^- + \text{O}_2 \rightarrow \text{O}_3^-$	2.9×10^9	3.0×10^9	-	-
34. $\text{O}^- + \text{H}_2 \rightarrow \text{H} + \text{OH}^-$	$8. \times 10^7$	8.0×10^7	-	-
35. $\text{O}^- + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2^-$	5.3×10^8	2.0×10^8	-	-
36. $\text{HO}_2^- + \text{O}^- \rightarrow \text{OH}^- + \text{O}_2^-$	-	8.0×10^8	-	-
37. $\text{O}_3^- + \text{H}_2\text{O}_2 \rightarrow \text{O}_2^- + \text{O}_2 + \text{H}_2\text{O}$	-	1.6×10^6	-	-
38. $\text{O}_3^- + \text{HO}_2^- \rightarrow \text{O}_2^- + \text{O}_2 + \text{OH}^-$	-	8.9×10^5	-	-
39. $\text{O}_3^- \rightarrow \text{O}_2 + \text{O}^-$	-	3.0×10^2 (pH = 13)	-	-
40. $\text{O}_3^- + \text{H}_2 \rightarrow \text{O}_2 + \text{H} + \text{OH}^-$	-	2.5×10^5	-	-
41. $\text{O}_2^- \rightarrow \text{products}$	-	6.0×10^{-2} (pH = 13)	-	-
42. $\text{O}_2^- + \text{O}_2^- \rightarrow \text{O}_2^{2-} + \text{O}_2$	5.0×10^7	-	-	-
43. $\text{OH} = \text{O}^- + \text{H}^+$	pK = 11.9	-	-	-

NOTE: Where two values are shown, the first is for the forward reaction and the second is for the reverse reaction.

^a Second order rates are given as $\text{M}^{-1} \text{sec}^{-1}$; first order rates as sec^{-1} , for k, not 2 k.

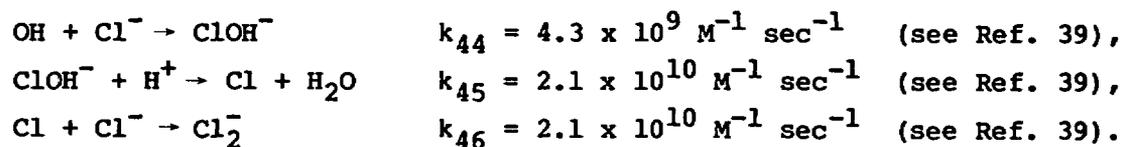
^b Reaction is actually given as $\text{e}_{\text{aq}}^- + \text{HO}_2^- \rightarrow \text{O}^- + \text{OH}^-$.

significant concentrations (Table 4), HCO_3^- , NO_3^- , Cl^- , CO_3^{2-} , CO_2 , and O_2 are known to have significant reaction rates (i.e., greater than $10^7 \text{ M}^{-1} \text{ sec}^{-1}$) with one or another of the free radical species. Since all these solutes have concentrations greater than 10^{-5} M , they can clearly dominate the free-radical/free-radical reactions in competing for free radicals.

In addition to reacting with dissolved solutes, the free radicals can also react with suspended colloids. Burns et al. found that Fe(III) iron oxide colloid formed upon gamma irradiation of distilled or deionized water and air in stainless steel vessels, and they believe that reactions between the free radicals and this colloid gave rise to the decomposition of water they observed.³⁶

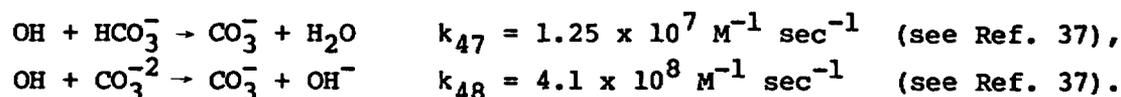
In the following discussion, I consider each of the free radical species in turn and determine what its dominant initial reactions with the solutes would be in the solution (described in Tables 4 and 6) using measured reaction rates reported in the literature. (Note that several solutes are present from the beginning, whereas the colloids form during irradiation.)

As can be seen in Table 8, the hydroxyl radicals (OH) are the products formed with the highest yield. Their initial reactions would primarily be with chloride ions:

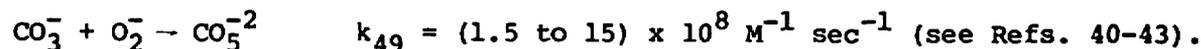


The product $k_{44}[\text{Cl}^-]$ would be $2 \times 10^5 \text{ sec}^{-1}$ initially.

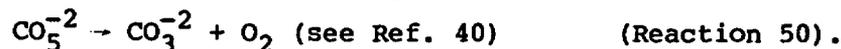
The hydroxyl radicals (OH) would also react with bicarbonate and carbonate ions:



The product $k_{47}[\text{HCO}_3^-]$ is $2.3 \times 10^4 \text{ sec}^{-1}$. For CO_3^{2-} , the product is 6.1×10^3 . The carbonate radical CO_3^- reacts with the superoxide ion O_2^- (the origin of which is discussed below), and the product is thought to be CO_5^{2-} (see Ref. 40):



This species in turn is thought to decay by a first order process:

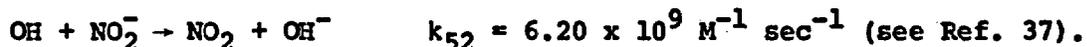


The carbonate ion would then associate to form bicarbonate at pH 8:



Since the O_2^- has originated as O_2 (see below), and one H_3O^+ ion is formed as a primary product for each e_{aq}^- radical formed in the irradiation, there would be no net chemical change from this sequence.

At the beginning of the experiments, there was no measurable nitrite in the solution, but some was found at the end, so I will consider its reactions. When nitrite was present, it would also have had a significant reaction rate with OH radicals:



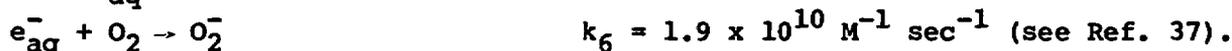
At the end of the "blank" experiments that received the highest doses, the nitrite concentration was 2.1×10^{-4} M. The product $k_{52}[\text{NO}_2^-]$ was then $1.3 \times 10^6 \text{ sec}^{-1}$, which means this reaction would dominate those mentioned above after NO_2^- had built up. The NO_2 thus formed would react with water to produce nitrate and nitrite⁴⁵:



As the irradiation proceeded, H_2 , formed as a primary product, would begin to build up and would compete with these other species for reaction with OH radicals. It would continue to build up until its rate of reaction with OH equaled its rate of formation. To achieve steadystate concentration, the H_2 would have to react with about one-sixth of the OH radicals, because G_{H_2} is about one-sixth of G_{OH} (see Table 8). To have had a reaction rate equal to one-fifth of the sum of the reaction rates of Cl^- and HCO_3^- , which were the competitors at the beginning of the experiment, the H_2 concentration would have had to have been 9.1×10^{-4} M, which requires an H_2 pressure above the solution of 130 kPa. Such a pressure would not have been reached before the NO_2^- concentration was observed to rise significantly, so H_2 would have continued to build up to higher pressures as competition increased for the OH. To have had a reaction rate equal to one-fifth that of the NO_2^- , Cl^- , and HCO_3^- , which were the solute competitors at the end of the experiment, the H_2 concentration would have had to have been 6×10^{-3} M, which would have required an H_2 pressure above the solution of about 850 kPa at 90°C . This means that relatively high H_2 pressures would have been required before the H_2 pressure would have leveled off. For comparison, Gray and Simonson found that gamma radiolysis of Permian Basin saturated brine at 75°C produced a total steadystate gas pressure (H_2 plus O_2) of about 10 MPa.⁴⁶ This is a much more concentrated solution than "equilibrated J-13" water.

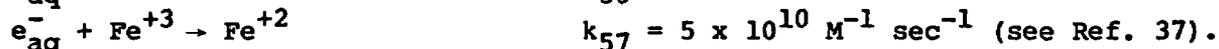
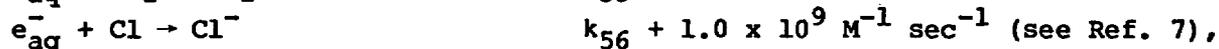
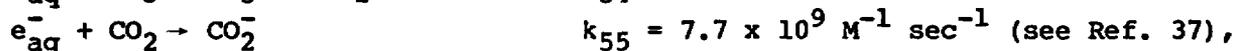
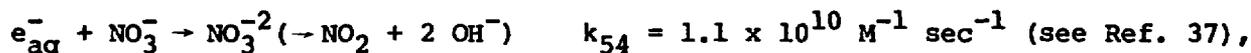
In their experiments mentioned earlier, Burns et al. found that gamma irradiation of air-saturated, triply distilled or demineralized water in stainless steel vessels at 30 to 50°C produced total steadystate pressures of 300 to 450 kPa, including H₂, O₂, and N₂.³⁶ As noted, they invoked the presence of a colloid to explain the results. If colloid-free radical reactions were significant in comparison to solute-free radical reactions at the end of the the Bates et al. experiments, then the H₂ pressure required for steadystate would have been significantly higher than 850 kPa.

The radical species produced with the next highest yield is the hydrated electron (e_{aq}⁻). In oxygenated solution, superoxide ions are formed:



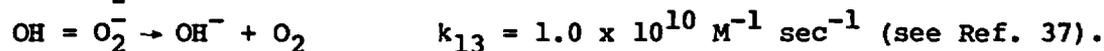
In the Bates et al. experiments that had 16 ml of water at the outset, the initial concentration of O₂ in the liquid phase would have been about 2.2 x 10⁻⁴ M (Table 6). The product k₆[O₂] would then have been about 4 x 10⁶ sec⁻¹ for this reaction.

Competing reactions would have been those with nitrate, dissolved CO₂, chlorine atoms, and ferric ions:



Using the initial NO₃⁻ concentration (Table 4), k₅₄[NO₃⁻] would have been 1.3 x 10⁶ sec⁻¹, and k₅₅[CO₂] would have been about 3.2 x 10⁵ sec⁻¹. The very low Fe⁺³ concentration would have made it a negligible contributor at the beginning of the experiments, and the pH buffering would have kept its concentration low. It is difficult to calculate the steadystate Cl concentration, but the maximum possible value of k₅₆[Cl] if only the initially dissolved Cl⁻ is considered would have been 2 x 10⁵ sec⁻¹. This indicates that nearly 70% of the e_{aq}⁻ would have reacted with O₂, about 22% would have reacted with NO₃⁻, and about 6% would have reacted with CO₂ at the outset. As the irradiation proceeded, the O₂ would have built up, taking a larger share of the e_{aq}⁻ reactions, and colloids also could have become important reactants.

As discussed above, the O₂⁻ produced would react with carbonate radicals, producing O₂. It would also react with OH by Reaction 13, again producing O₂:



Burns et al. predict that the O₂⁻ would also react significantly with the stainless steel vessel walls.³⁶

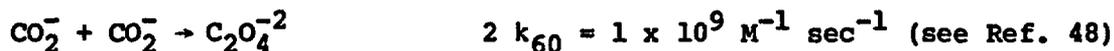
The HO₂ radicals produced as primary species would dissociate to O₂⁻ (at pH above about 5) and would react in these same ways. The NO₂ produced would react with water to form NO₂⁻ and NO₃⁻, as discussed earlier (Reaction 53). The carboxyl radicals (CO₂⁻) would remain dissociated at pH 8:



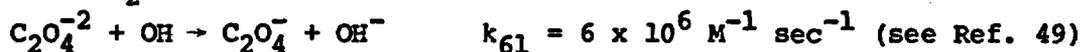
In oxygenated solution, the charge transfer reaction



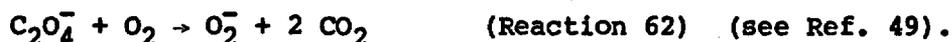
has been found to be fast,⁴⁷ and for [O₂] = 10⁻⁴ M, it would overwhelm the dimerization reaction to form oxalate:



so that very little oxalate would be formed. Furthermore, in solutions containing O₂, oxalate is destroyed by reactions with OH radicals

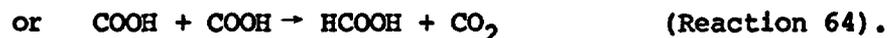
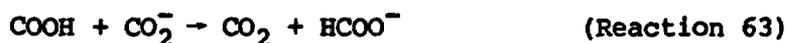


which are followed by reactions with oxygen:



In the presence of Ca⁺⁺ ions, as in "equilibrated J-13" water, oxalate (if present) would precipitate as calcium oxalate, which has a solubility of about 10⁻⁴ M (see Ref. 50). The fact that the observed Ca⁺⁺ concentration in solution did not decrease from its original value of 2.3 x 10⁻⁴ M supports the contention that little oxalate was formed. In the experiments of Hasselstrom and Henry, oxalic acid was produced by irradiation of bicarbonate and, necessarily, CO₂ solutions.⁵¹ Apparently there was insufficient oxygen to oxidize the carboxyl radicals, so that the dimerization to form oxalate was free to proceed. Their solutions were irradiated in polyethylene bags, and they did not perform gas analysis.

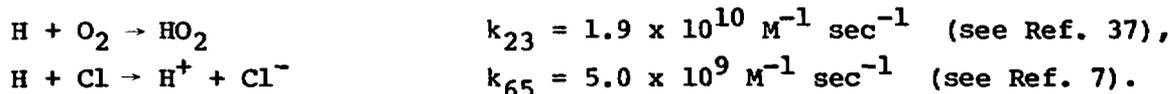
If the CO₂⁻ became associated to form COOH, it could react to form formate ions or formic acid⁴⁷:



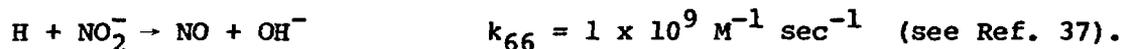
The formate and formic acid thus formed would remain soluble. Production of formate is not likely in the bulk of the liquid phase, because the pH there was buffered near 8, and the CO₂⁻ would not associate. However, it might have occurred in the liquid film around the top of the gas space, where nitric acid production and deposition could drive the pH down in the absence of buffering. It should be noted that past experiments in which formate was produced from dissolved CO₂ were either oxygen-free⁸⁻¹⁰ or were driven to low

pH by simultaneous formation of nitric acid.^{11,12} Either of these conditions would prevent the carboxyl radicals from transferring charge to oxygen, and thus make them available to form formate or oxalate.

The other primary free radical produced in the irradiation is the hydrogen atom. At the outset, its only significant reactions would be with dissolved oxygen and with Cl produced in the OH reaction mentioned earlier:



The HO₂ would dissociate to O₂⁻ and react as described earlier to produce O₂. The products k₂₃[O₂] and k₆₅[Cl] would be 4.2 x 10⁶ sec⁻¹ and 1 x 10⁶ sec⁻¹ (maximum), respectively. As the irradiation proceeded, nitrite would be formed as discussed earlier, and H atoms could react with it:

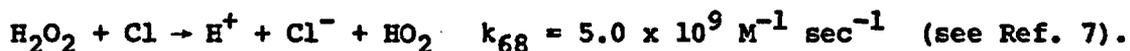


At the end of the highest dose experiments, k₆₆[NO₂⁻] was about 10⁵ sec⁻¹ for this reaction. In the Bates et al. experiments, the O₂ concentration as a function of time probably represents a balance between production by water radiolysis and loss to reaction with the stainless steel. Data from corrosion experiments indicate that reaction with the metal in these experiments would account for only a small part of the O₂ produced by radiolysis.⁵² This result was also found by Burns et al.³⁶ It therefore appears that the O₂ concentration would rise, and O₂ would dominate the H reactions during the entire experiment. The NO probably would react rapidly with an oxidizing species in the water to again form NO₂ and then would react with water to form NO₂⁻ and NO₃⁻.

Having discussed the fates of the primary free radical species, we turn now to the molecular species H₂ and H₂O₂. As discussed already, H₂ can be expected to rise in pressure to at least 850 kPa if the irradiation proceeds for a time long enough to reach steadystate conditions. In pure water, the H₂O₂ concentration is limited by reactions with e_{aq}⁻, H, and OH, as noted above. Where these were effectively scavenged by solutes, H₂O₂ could be expected to build up. We have observed this in room temperature irradiation corrosion experiments that included only a glass vessel, J-13 water, and a stainless steel electrode.⁵³ However, since H₂O₂ is thermodynamically unstable at all temperatures, it would thermally decompose at elevated temperatures and in the presence of materials that are catalytic for the decomposition reaction



Dissolved Fe^{+3} is known to be an effective catalyst, producing measurable effects at concentrations less than 0.1 ppm.⁵⁴ Solid materials found in the tuff and glass may also catalyze this decomposition. Manganese oxide, which is found in the tuff, is one example of a known effective catalyst.⁵⁴ H_2O_2 could also react with Cl:



It seems probable that the H_2O_2 concentrations in these experiments were limited to small values by these reactions. The decomposition of H_2O_2 would give rise to oxygen gas, and the amount would be essentially one-half the amount of hydrogen given off, since the stoichiometry of the solution must continue to correspond closely to H_2O .

3.6 GAS AND LIQUID PHASES CONSIDERED TOGETHER

Because gas and liquid phases are in contact in the experiments of Bates et al., we must consider exchange of gaseous species between them during the irradiation. As noted in Section 3.4, the stable products formed during irradiation of the gas phase would be gaseous HNO_3 , N_2O , and O_3 . In addition, there would be transient species such as NO , NO_2 , and probably N_2O_4 that could conceivably dissolve in the liquid phase before they reacted to form HNO_3 or N_2O . To determine which of these processes would be more rapid, we would need to calculate the lifetimes of these transient species by modeling the gas phase reaction sequence and then compare them to typical diffusion times to reach the liquid phase in the geometry used. This has not been done in this analysis because of the complexity of the system and the uncertainty of some aspects of the reaction sequence. However, even though the detailed mechanism is not established, experimental measurements have been performed on the two-phase air-water system.^{5,55}

Burns et al.⁷ have derived an equation describing the fixation of nitrogen as a function of time and other parameters for a sealed system:

$$N = 2 C_0 R [1 - \exp (-1.45 \times 10^{-5} \text{ GDt})] \quad (\text{Eq. 2})$$

where N is the concentration of HNO_3 in the water in moles/liter at time t ,

C_0 is the initial concentration of N_2 in the air in moles/liter,

R is the ratio of the volume of air to the volume of water,

G is the yield (= 1.9) (using Harwell data as interpreted by Burns et al.⁷),

D is the dose rate in Mrad/hr, and

t is the time in hours.

For total doses much less than 3.6×10^4 Mrad, this equation reduces to
$$N = 2.90 \times 10^{-5} C_0 \text{ RGDt.} \quad (\text{Eq. 3})$$

In the Bates et al. experiments, the maximum dose was 269 Mrad, so this form of the equation is adequate. As can be seen, the production of fixed nitrogen is directly proportional to R and to the dose Dt.

Although Equation 2 appears to have been derived using unbuffered, initially neutral water, I have applied it to the Bates et al. data on the grounds that the total fixed nitrogen concentration does not appear to be very sensitive to pH under oxidizing conditions.⁵⁵ This probably results from the facts that the oxidation occurs in the gas phase and that once the nitrogen is fixed as nitrate or nitrite in the solution, it tends to remain in the solution, because to escape, it would have to be reduced to NO, and this species is rapidly oxidized in an irradiated solution regardless of the pH, forming NO₂ and then NO₂⁻ and NO₃⁻. The movement of fixed nitrogen is thus a one-way process under these conditions.

The N₂O produced in the gas phase may dissolve in the liquid phase and be destroyed by reactions with e_{aq}⁻:



Ozone rapidly decomposes upon dissolution in water at high temperatures and neutral or high pH. The mechanism is not completely understood, but the formation of OH radicals is a significant aspect of it.⁵⁶

The gases generated in the liquid phase in excess of their solubilities must move to the gas phase. These include H₂, O₂, and the N₂ resulting from the above N₂O reaction.

3.7 INTERACTIONS WITH THE SOLID PHASE

As mentioned earlier, we expect that some oxidation of the stainless steel will occur, although it should be limited by the formation of a protective layer under the pH and redox conditions of most of these experiments. Dissolution of iron and chromium should be slight, so long as the pH remains near 8.⁵⁷ Nickel and manganese do have some solubility under these conditions, but their dissolution should be limited by the protective layer.

Burns et al. have gamma irradiated sealed cylinders made of Types 304 and 321 stainless steel, containing air and either triply distilled or

demineralized water.³⁶ Temperatures in their experiments ranged between 30 and 50°C, and dose rates were between 0.15 and 2 Mrad/hour, with doses extending up to 1000 Mrad. They analyzed the gases inside the cylinders and monitored their pressures. The amount of corrosion occurring was calculated from the deficit in oxygen gas observed compared to one-half the observed hydrogen. They explained their gas composition results on the basis of the formation of an Fe(III) iron-oxide colloid, which they observed at the end of some of their experiments.

As noted in the description of the Bates et al. results in Section 2, yellow solutions were found in several vessels, and rusty precipitates were found in others. It seems clear that an iron-containing colloid was formed in the Bates et al. experiments as well. Flocculation of the colloid may account for the anion depletion.

Stainless steel is not a very efficient catalyst for the decomposition of H₂O₂. The stainless steel surface could act as a substrate for precipitation of species from the solution that may have dissolved from the glass or tuff and later become less soluble because of changing solution conditions or changes in the chemical form or oxidation state of the species. The stainless steel could also affect the nitrite-nitrate ratio in the solution, because of the ability of iron to reduce nitrate to nitrite. In unirradiated open system corrosion experiments with J-13 water and stainless steel, we have observed the gradual disappearance of fixed nitrogen from the water completely, over a period of a few months.⁵⁸ We presume that this disappearance results from the reduction of nitrate to nitrite and then to N₂O, which is a relatively inert gas and could diffuse out of an open system.

The tuff rock would serve as a powerful pH buffer for the solution by exchanging Na⁺, K⁺, or Ca⁺² ions for H⁺ ions. This has been observed extensively in the past with feldspar minerals, as mentioned in the Introduction (Section 1). The manganese oxide and iron in the tuff could serve as catalysts for H₂O₂ decomposition, as mentioned in Section 3.5. Transient primary radical species formed near the surface of the tuff could react with it directly, particularly with species such as iron, which has more than one possible oxidation state. Dissolution of some minerals from the tuff could be expected, as well as precipitation of others.

Reports by Bates and Oversby¹⁸ and Bates et al.¹⁹ describe the behavior of the glass. This behavior includes dissolution and precipitation of various

species. As is true for the tuff, we expect that the iron and manganese oxide in the glass could serve as decomposition catalysts for H_2O_2 , and the iron could also enter into reactions with primary free radical species.

In the Bates et al. experiments, the SRL A glass was doped with actinides (as noted in Section 2), and the resulting alpha emission necessarily delivered ionizing radiation to the liquid in contact with the glass surface. However, approximate calculations indicate that the dose rate would have been less than 10^3 rad/hour at the interface for the doping level used, compared to the 10^4 and 2×10^5 rad/hr gamma dose rates absorbed by the solutions in the experiments. When one considers in addition that only a layer of liquid of the order of 10^{-3} cm thick received the alpha dose, it is clear that the alpha contribution to the bulk irradiation of the solution was small compared to the gamma contribution in these experiments. However, near the surface of the glass in the lower dose rate experiments, the alpha irradiation could have caused a significant increase in the concentrations of the molecular products H_2 and H_2O_2 , since their yields are considerably higher in alpha radiolysis than in gamma radiolysis.³⁷ Bates noted that in both sets of experiments the SRL A glass reacted slightly faster than the SRL U glass.^{18,19,22} This may have been a consequence of alpha radiolysis.

3.8 DECOMPOSITION OF WATER

As has already been alluded to in Section 3.5, one effect of gamma irradiation on an aqueous solution containing solutes that can react with the primary free radical species is decomposition of water into H_2 and O_2 .

In the Bates et al. experiments, it appears that the solutes present initially were in high enough concentration to prevent the radicals from reacting significantly with the molecular products in the bulk of the solution, but they would not have been so high as to interfere with the formation of the molecular products in the tracks and spurs. It thus appears that the initial water decomposition yield $G(-H_2O)$ should have been approximately equal to G_{H_2} , i.e., 0.45. Applying this value to the "blank" experiments irradiated at 2×10^5 rad/hr for the maximum time of 56 days, giving a total dose of 269 Mrad, the exposure of 16 grams of water would have led to the decomposition to H_2 and O_2 of 3.6×10^{-2} grams, or 2 millimoles, assuming no back reactions occurred. Using the ideal gas law and a gas space (at room temperature) of

5.4 ml, this amount of gas would have developed a pressure increase of over 1.3 MPa after cooling to room temperature. As noted in Section 3.5, the back reaction of H_2 with OH radicals would actually limit the H_2 pressure to about 850 kPa at $90^\circ C$, if reactions with colloids are not considered. Adding an O_2 pressure equal to half this value would produce a total of about 1.28 MPa at $90^\circ C$. This would be equivalent to 1.03 MPa at $20^\circ C$. This indicates that at the highest dose in the Bates et al. experiments steady-state gas pressures should have been achieved. The total pressure, including the original air, would have been 1.13 MPa at $20^\circ C$. Bates et al. observed pressurization of the higher dose vessels (as noted in Section 2), although the pressures were not measured.¹⁹

In their second set of experiments, Bates et al. applied a maximum dose of about 43.7 Mrad, or less than one-sixth of that in the first set. This would help to account for the lack of observed pressurization in the second set. It should be noted also that some loss of gases through or around the silicone rubber gasket may have occurred in this set, as mentioned in Section 2, and some reaction of oxygen with the stainless steel also occurred; both of these processes would have reduced the pressure. The time available for these processes to occur was over three times as long for the longest duration irradiations in the second set of experiments as for those in the first set. Although calibrated dissolved gas analyses were not complete at the time this paper was written, Bates reports that considerable amounts of hydrogen were found (in addition to nitrogen, oxygen, and carbon dioxide) in the second set of experiments, and that the relative amounts found were consistent with the hypothesis that some gas leakage occurred in the second set.²²

3.9 FIXATION OF NITROGEN

As noted in Section 3.6, Equation 2 (Burns et al.⁷) predicts that the amount of radiation-fixed nitrogen should be linear with dose in this range. The equation also predicts that the amount should be proportional to R, the ratio of gas to liquid volume. Since R varied between vessels, it is necessary to correct for this in making comparisons. Before such a correction can be applied, the value of the initial total fixed nitrogen concentration must be subtracted from the measured fixed nitrogen data.

An initial plot of the data for the 2×10^5 rad/hour experiments showed that there was considerable scatter and that subtraction of the reported initial value (7.6 ppm or 1.22×10^{-4} M NO_3^-) did not result in a best fit line passing through the origin. Nevertheless, it was assumed that such a line must obtain, and that the points at 28 and 56 days were the most reliable, being highest above the initial value. Consequently, the value chosen for the initial total fixed nitrogen concentration was that which resulted in a straight line passing through the origin and the average values at 28 and 56 days, uncorrected for R value. This turned out to be 1.65×10^{-4} M (or 10.2 ppm) NO_3^- . This initial value was subtracted from the data, and the correction for R was then applied.

The resulting data for the 2×10^5 rad/hour experiments are plotted in Fig. 1, normalized to $R = 0.337$, which was the value at room temperature for the vessels containing water and air only. The solid line represents the prediction of the Burns et al. equation, indicating 1.6×10^{-4} M of additional fixed nitrogen concentration for a dose of 269 Mrad. The agreement is satisfactory, considering the uncertainties in the data and in the yield. Each data point is an average from two replicate experiments. In some cases replicates differed by more than 15% in reported total fixed nitrogen concentrations.

Bates et al. give the precision of anion analyses as $\pm 5\%$, and the accuracy also as $\pm 5\%$. The uncertainty in dose was $\pm 10\%$. The uncertainty in G value was not given by Burns et al.,⁷ but a value of $\pm 15\%$ would not be unreasonable, based on the dose uncertainty in the reference they cite.⁵⁵ Because of these uncertainties, it is not possible to determine whether there were significant differences in nitrogen fixation rates among the various vessels. All that can be said is that the rates were essentially as predicted by the Burns et al. equation.

For the second set of experiments, the dose was less than one-sixth as great as it was for the first set. The predicted increase in fixed nitrogen concentration would thus be 2.6×10^{-5} moles/liter for those vessels having low gas-to-liquid volume ratios. The observed total fixed nitrogen concentration does not show a significant increase over the course of the experiments, and the scatter in values is of the order of 1 to 3×10^{-5} moles/liter. As can be seen from Fig. 1, the predicted increase is less than the precision of the data and would therefore not be expected to be seen.

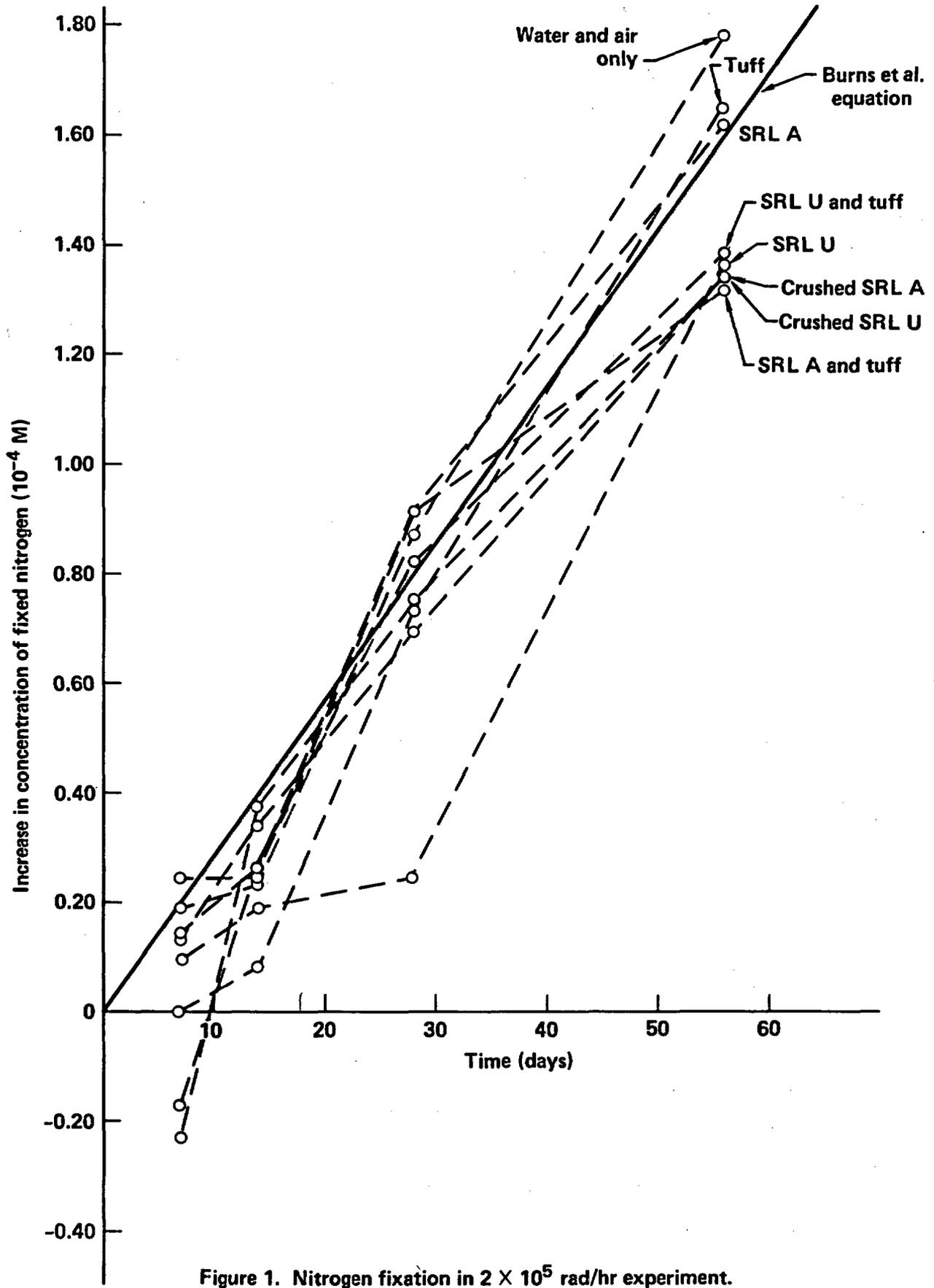


Figure 1. Nitrogen fixation in 2×10^5 rad/hr experiment.

3.10 HYDROGEN ION PRODUCTION

The production of nitrite and nitrate in the aqueous solution was accompanied by an equimolar production of hydrogen ions. For the experiments with 16 ml of water and a dose of 269 Mrads, the total added H^+ would therefore have amounted to 1.6×10^{-4} moles/liter. Since the initial bicarbonate concentration was more than 10 times this level, we would expect it to have buffered the added H^+ and thus to have prevented a large pH change. This is in fact what is observed in the Bates et al. data. By contrast, experiments performed by others using deionized or distilled water have shown shifts of pH into the 3-4 range.² The changes in pH due to nitrogen fixation for the second set of experiments by Bates et al. should be even less significant, since the maximum dose was one-sixth as large.

3.11 NITRITE-NITRATE RATIO

Most past experiments involving irradiation of two-phase air-water systems that have been reported in the literature have made use of deionized or distilled water. In such cases the solution is unbuffered, and generation of nitric acid drives the pH so low that any nitrite present tends to associate with H^+ to form nitrous acid, HNO_2 ($pK_a = 5.22$ at $25^\circ C$).⁴⁵ This acid is thermally unstable and decomposes according to the reaction:



It also reacts with H_2O_2 :

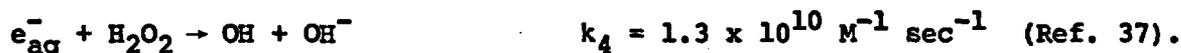


NO is rapidly oxidized in irradiated solution to NO_2 . The NO_2 reacts with the water to form equimolar amounts of NO_2^- and NO_3^- . The NO_2^- then associates and repeats the cycle. The result is that any NO_2^- initially formed is converted to NO_3^- , and this is the only nitrogen species observed at the end of the experiment.

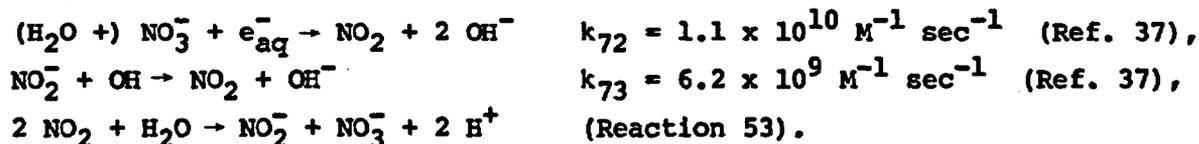
Linacre and Marsh reported some experiments in which nitrogen gas and water containing KOH were irradiated.⁵⁵ In these cases, only nitrite was observed in solution after irradiation. The explanation they gave was that the nitrogen was fixed first as NO_2^- , which did not associate because of the alkaline pH, and was therefore stable. Conditions in these experiments would have been less oxidizing than in the Bates et al. experiments, because of the absence of oxygen at the start of the experiments.

The pH in most of the Bates et al. experiments was also buffered above the pK of HNO₂. However, oxygen was present in addition to the nitrogen. A balance would therefore have been achieved between NO₂⁻ and NO₃⁻ that reflected the oxidation conditions in the solution. Figures 2 and 3 show the nitrite-nitrate ratios for the two sets of experiments. It can be seen that the higher dose rate (Fig. 3) generally produced lower ratios of nitrite to nitrate. At the lower dose rate (Fig. 2), the ratios were lowest for the vessels containing water and air only. In the higher rate experiments, those with either tuff or crushed glass present had higher ratios than the others at the end of the irradiation.

These results can probably be explained in part by the balance between production of H₂O₂ in the solution by irradiation and its catalytic decomposition by materials such as manganese oxides in the tuff and the glass. The higher dose rate would have produced a higher steadystate H₂O₂ concentration. In the water-only vessels, there would have been less catalytic material, so that higher H₂O₂ concentrations would have existed. The vessels with either tuff or crushed glass would have had high catalytic surface areas, tending to decompose the H₂O₂. Although H₂O₂ does not react directly with NO₂⁻ to produce NO₃⁻, it can affect the relative concentrations of e_{aq}⁻ and OH radicals by the reaction:



These two free radicals in turn can affect the nitrite-nitrate balance according to the reactions:



In summary, the greater catalytic activity of the tuff and/or crushed glass would reduce the H₂O₂ concentration. This in turn would raise the ratio of e_{aq}⁻ to OH concentrations. The result of this would be to raise the ratio of NO₂⁻ to NO₃⁻ concentrations. In addition, H₂O₂ would tend to oxidize any trace organics present, thus decreasing the concentrations of these other possible reducing agents. The oil-like films observed in some experiments may be evidence for the presence of organics.

At the end of the lower dose rate experiments, it appears that the nitrite-nitrate ratios were influenced strongly by the types of solid materials present. SRL A glass produced higher ratios than SRL U glass, and

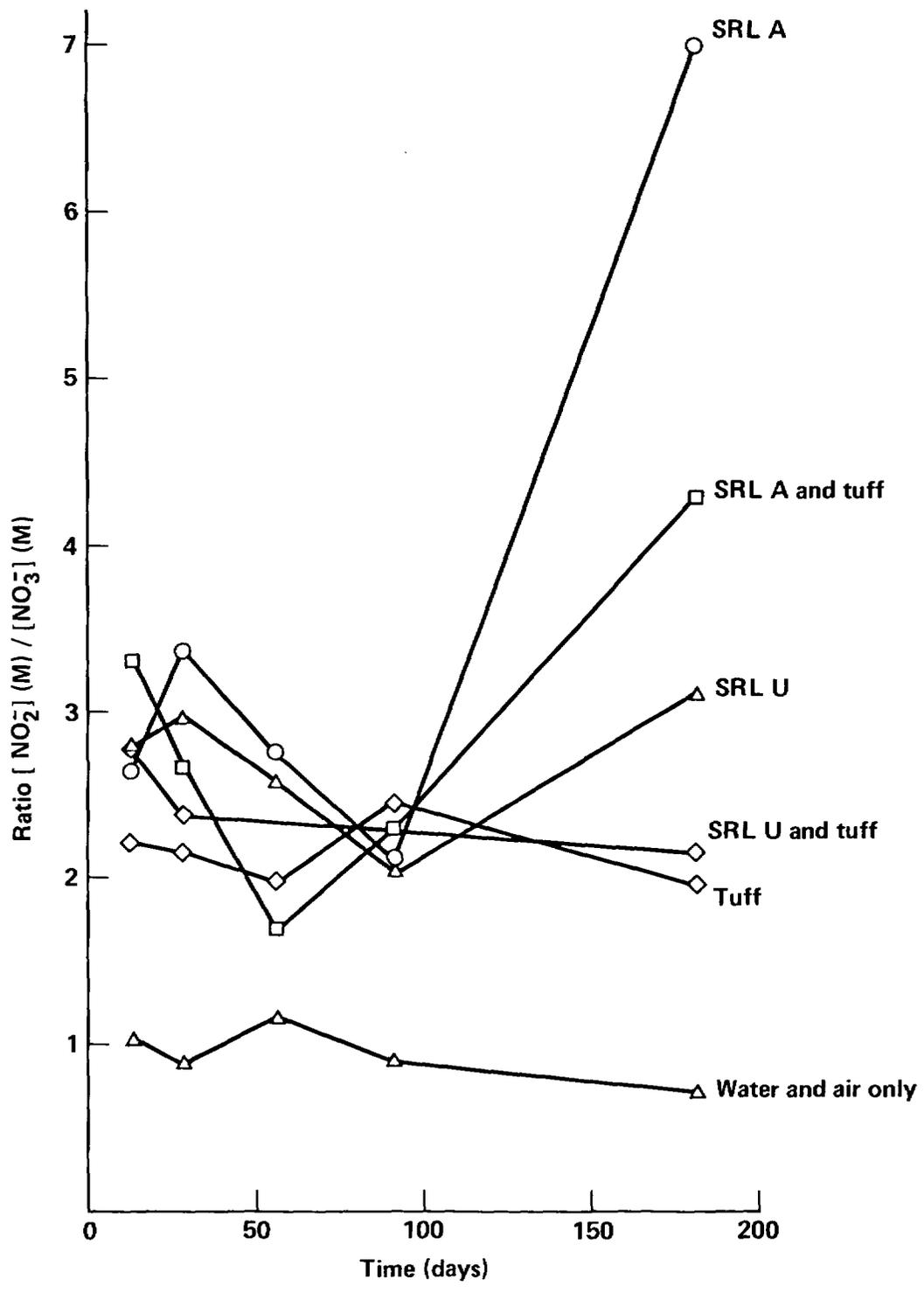


Figure 2. Nitrite-nitrate ratios in 10^4 rad/hr experiments.

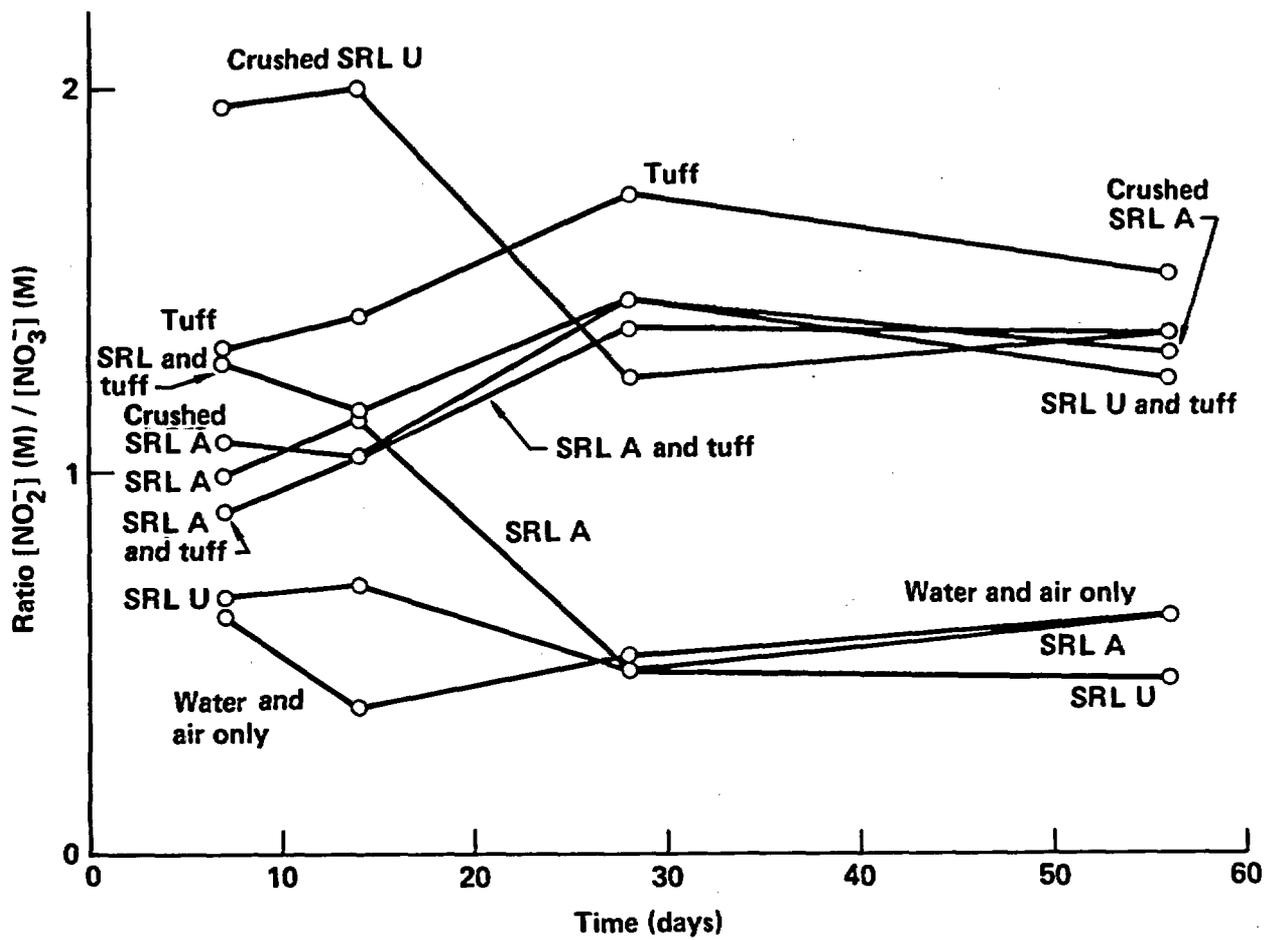


Figure 3. Nitrite-Nitrate ratios in 2×10^5 rad/hr experiments.

the tuff appeared to be lowering the ratios that these glasses would otherwise produce. I do not currently understand the mechanisms behind this behavior. Lower dose rate experiments now in progress should help us to understand this behavior better.

3.12 LIKELY EFFECTS ON GLASS REACTION

Gamma irradiation has been found to affect glass dissolution in deionized water in two ways: 1) indirectly through promotion of an acid pH, which increases the solubility of some elements and makes H^+ ions available for attack of the glass structure and for ion exchange and 2) production of free radicals such as OH, which can attack the glass directly. It appears that both these effects would be somewhat ameliorated in "equilibrated J=13" water. The presence of bicarbonate in the solution serves to buffer the pH, so that the solution remains near neutral. In addition, the initial presence of Cl^- and HCO_3^- , and NO_2^- after some irradiation, serves to lower the OH concentration in solution. We would therefore not expect as large an effect on glass dissolution from irradiation with this solution as is observed with deionized or distilled water.

Bates has noted, however, that the solubilities of actinides are highly pH-dependent in the pH range of these experiments, so that even the small changes caused by irradiation may account for the observed differences in the actinide behavior.²² Nash et al. have discussed the effects of irradiation on actinide behavior during reaction of glass with high purity water.⁶⁰ Bates et al. are planning to publish a more complete discussion of the glass behavior they observed in their experiments, at a later date.

3.13 HIGH GAS-TO-LIQUID VOLUME RATIO EXPERIMENTS

As noted in Section 2, four vessels were irradiated with a smaller initial liquid volume, which produced a larger gas-to-liquid volume ratio. In the first set of experiments, test no. G-113 began with 4.60 ml of deionized water, while test no. G-114 began with 5.16 ml of deionized water. These two vessels also contained a stainless steel waste form holder, but no tuff or glass. They were irradiated for 28 days at 90°C and a dose rate of 2×10^5 rad/hour, producing a total dose of 134 Mrad. At the end of the irradiation,

the vessels were found to contain a flocculant, rust-colored precipitate, and the vessels and waste form holders were visibly corroded. The solutions were very acidic, with the pH values being 1.82 and 2.58 for G-113 and G-114, respectively. The solutions in both vessels contained significant amounts of elements known to be in stainless steel (Cr, Cu, Fe, Mn, Ni, and Si). They also contained 27.2 and 25.6 ppm of nitrate, respectively, and no detectable nitrite. The solutions also contained 589 and 103 ppm of chloride, respectively. The precipitate was found to consist of amorphous material, high in Fe, Cr, and Si.

Tests G-265 and G-266 in the second set of experiments had comparable amounts of "equilibrated J-13" (rather than deionized) water. They were irradiated for 182 days at 90°C and a dose rate of 1×10^4 rad/hr, producing a total dose of 44 Mrad. They were found to have pH values of 6.94 and 6.88, respectively, and normal "equilibrated J-13" water concentrations of the anions F^- , Cl^- , and SO_4^{2-} . The nitrate concentrations were 4.4 and 2.1 ppm, respectively, and the nitrite concentrations were 10.8 and 7.5 ppm, respectively. No corrosion or rust-colored precipitate was evident. A small amount of formate was detected in the solutions.

In test G-113, the predicted concentration of nitrate from Equation 2 (Burns et al.⁷) is 8.3×10^{-4} M, taking account of the water expansion and contraction and the space occupied by the holder. The observed concentration was 4.4×10^{-4} M, almost a factor of two less. If the calculated amount of nitric acid had formed, the pH would have dropped to 3.1. Thus several anomalous results appeared in tests G-113 and G-114: the fixed nitrogen concentration was much lower than calculated; the pH was also much lower; and large concentrations of chloride appeared, the source of which was unknown. Bates performed leach tests on the gasket material at 150°C in deionized water for seven days and found no chloride release.²² He also performed leach tests at 150°C for seven days on a stainless steel vessel using deionized water and a pH 2 HNO_3 solution. In these tests he found 14.2 micrograms of Cl^- released into the deionized water and 33.7 micrograms released into the HNO_3 solution. These results led us to suspect that the Cl^- in tests G-113 and G-114 came from the vessels.

A brief study of the chemistry of steel making and consultation with several steel chemists convinced us that chloride should not be present in significant amounts in bulk steel, because of the high vapor pressure of

chlorides at the melting temperature of steel (see Section 3.14 for results of stainless steel analysis). We then looked into the composition of the cutting fluid used to fabricate the vessels and learned that Trimsol consists of an emulsion of a chlorinated oil in water. The chlorine composition of the concentrated emulsion sold by Master Chemical Company for water dilution by users is about 10.5 wt%. Some of this material may have been buried in the surface during machining and may have survived the cleaning process.

In view of these observations, it appears that the following processes took place in vessels G-113 and G-114. Irradiation produced nitric acid in the solution. The pH dropped, because there was no buffering. The acid conditions accelerated the corrosion of the stainless steel and formed a positively-charged Fe(III)-containing colloid. The corrosion released some form of chlorine that had been buried in the surface of the stainless steel. The chlorine was either initially present in the surface as chloride ions or was reduced to chloride ions by the H and e_{aq}^- radicals, forming H^+ as well. This led to more rapid corrosion. Some of the anions were attracted and adsorbed by the colloid, which then coagulated and removed them from the solution, forming the rust-colored precipitate. The absence of NO_2^- in the solution resulted from the acid pH, as discussed in Section 3.11.

The behavior of tests G-265 and G-266 was more similar to the tests with lower ratios of air to water than was the behavior of G-113 and G-114. The predicted increase in fixed nitrogen concentration was 2.7×10^{-4} M, compared to the observed values of 1.8×10^{-4} M and 7.5×10^{-5} M. The agreement is not very close, but it is noteworthy that these two tests showed the only measurable increases in fixed nitrogen in the second set of tests. The differences are probably accounted for by the uncertainties discussed in Section 3.9. The fact that all these values, both calculated and measured, are below the bicarbonate concentration in "equilibrated J-13" water explains why the pH remained near neutral and no significant corrosion occurred.

3.14 ANOMALOUS TESTS

Three tests in the second set of experiments (out of a total of 66) also showed anomalous results: G-208, G-247, and G-248. In all three cases, the irradiation lasted for 91 days. At the end of the tests, the pH values were found to be between 3.6 and 4.8; a flocculent, rust-colored precipitate was

observed; the chloride levels were high (between 73 and 287 ppm); and other anion concentrations were generally lower than usual. The fixed nitrogen had been lost, rather than added to the solutions.

As mentioned in Section 2, other tests in this series produced solutions that were yellow in color, while other parameters were normal. The explanation of these results is probably the same as for the tests described in Section 3.13. Apparently enough chlorine was accessible to produce the effects even though a buffered solution, rather than deionized water, was present. Analysis of the stainless steel of vessel #90, used in test G-247, revealed 0.2 ppm Cl by weight in the bulk and a range of 0.5 to 300 ppm at the surface, with an average of 5 ppm on the surface.²²

4. CONCLUSIONS

It appears from this analysis that the observable radiation chemical changes that would have been expected in those vessels of Bates et al. that contained 16 ml of water at the outset of the experiments are the following:

1. Decomposition of a small fraction of the water to hydrogen and oxygen, resulting in an observable pressure increase in the highest dose experiments.
2. Fixation of a small amount of nitrogen from the air as nitrite and nitrate ions in the solution. The increase in total fixed nitrogen should have been measurable in the highest dose experiments.
3. Addition of an equivalent amount of hydrogen ions to the solution, which would be well within the bicarbonate buffering capacity, and which should therefore lower the pH only slightly from what it would be without irradiation.
4. Variation in the nitrite-nitrate ratio, depending on the presence of materials catalytic to the decomposition of hydrogen peroxide. A higher ratio should be observed when catalysts are present.
5. Formation of Fe(III)-containing colloidal material from vessel wall reactions.

It does not appear that measurable amounts of carboxylates (formate or oxalate) should have been formed. The pH changes, though subtle, could influence actinide solubility so that even the small changes caused by irradiation could produce changes in the amounts of actinides in solution. It appears from an examination of the Bates et al. data that these expectations are largely borne out, except in a few tests that showed anomalously high chloride levels. This chloride most likely came from residues from chlorinated oil cutting fluid buried under the surface of the vessel walls. This emphasizes the need to carefully specify the cutting fluids and cleaning procedures to be used for waste packages.

5. APPLICATION TO THE REPOSITORY

The repository system is expected to differ in a number of ways from the configuration used in the Bates et al. experiments. This is to be expected, since the Bates et al. experiments were designed to represent saturated conditions and to permit control of variables and convenience of operation and analysis, while other engineering considerations apply to the repository case. In applying the experimental results, one must keep these differences in mind:

1. As noted in the Introduction, we expect that most of the nuclear waste glass in the repository would remain dry during the first 300 to 1000 years when significant gamma ray fluxes would be present. Under these conditions, aqueous dissolution of the glass would not occur.
2. The repository would be a physically open system, because of the permeability of the rock. Therefore, gases could escape from the irradiated region, and the total gas pressure would remain at about 0.1 MPa. In addition, any liquid present would be free to migrate through the rock, subject to the constraints of capillarity, permeability, and other factors.
3. The ratio of gas to liquid volume after cooling to below the boiling point could be considerably higher in the region near the containers in the repository than in these experiments, particularly if there were only a thin liquid film on the solid surfaces in contact with a relatively large gas space in the annular region around each package.
4. The tuff would have a relatively larger effective surface area in the repository in relation to the areas of metal and glass surfaces than it did in these experiments.
5. The tuff surface in the repository would be essentially in contact with the gas phase (perhaps through a thin liquid film) rather than being submerged under bulk water.
6. The times of interest for the repository would be much longer than those used in the experiments (100,000 years versus a few months), but the gamma dose rates would decrease substantially with time (initially with a 30-year half-life) and with distance away from the packages (becoming negligible in tens to hundreds of centimeters).

7. The temperatures in the repository would vary over space and time, rather than being held at a fixed value.
8. The physical dimensions of the waste containers would be much larger than those of the experimental vessels.
9. The repository design may incorporate hole liners made of carbon steel to facilitate retrievability, as required in NRC regulations. This material was not present in the experiments.

These differences and the uncertainties currently surrounding them make the repository a more difficult case to analyze. Nevertheless, the main features seen in the experiments should also be present in the repository:

1. Nitrogen in the gas phase would be fixed in the form of NO at the highest temperatures, then NO₂ and N₂O₄ at lower temperatures, and finally as HNO₃ at temperatures near the boiling point of water. Some of this gas would migrate to moist rock, dissolve, and undergo ion exchange with the feldspars to produce nitrate and nitrite salts in the tuff. Some would react with the metal surfaces to increase their oxidation rates. When the surfaces had cooled so that a liquid film could exist on them, some of the nitrogen oxide gases could dissolve in the film; at that time, the gamma dose rates would be less than a few rad/hr for most of the packages. For those that cooled to below the boiling point while the gamma dose rate was still relatively high, the concentration of fixed nitrogen in the liquid film could increase measurably, particularly if the ratio of gas to liquid volume were large.
2. An equivalent amount of hydrogen ions would be produced in the liquid film. If this amount did not exceed the buffering capacity of the bicarbonate, the pH would not change significantly. If it did, the pH would move in the acid direction, increasing the corrosion rates of the metals.
3. The ratio of nitrite to nitrate would vary, depending on the surface upon which the liquid film rested.
4. Carboxylates (formate and oxalate) should not form in liquid films in contact with tuff or in those which had well-buffered pH due to dissolved bicarbonate in concentrations in excess of those of radiation-produced hydrogen ions. However, small amounts of carboxylic acids could be expected to form in liquid films that reached low pH as a result of excess

nitric acid formation. If they formed, they could increase corrosion rates by chelation.

5. The spatial variation of temperature coupled with the large physical size of the packages could give rise to transport and concentration of corrosive species by evaporation and condensation. However, the volume of the resulting liquid is expected to be small.
6. A carbon steel hole liner, if present, could be expected to scavenge a good share of the corrosive species.
7. Where liquid water containing dissolved species was irradiated, decomposition to hydrogen and oxygen would occur. The rate would depend on the radiation dose rate and would not be constrained by buildup of gas pressure.

As the design parameters of the repository become more firmly fixed, it will be possible to make estimates that are more quantitative of the radiation chemical effects to be expected. In the meantime, the experiments of Bates et al. have provided a number of significant insights.

REFERENCES

1. R. G. Baxter, Description of Defense Waste Processing Facility Reference Waste Form and Canister, E. I. duPont de Nemours and Co., Savannah River Plant, Aiken, SC, DP-1606 Rev. 1 (1983).
2. L. R. Pederson and G. L. McVay, "Influence of Gamma Irradiation on Leaching of Simulated Nuclear Waste Glass: Temperature and Dose Rate Dependence in Deaerated Water," J. Am. Ceram. Soc. 66, 863 (1983).
3. W. Primak and L. H. Fuchs, "Transportation of Matter and Radioactivity by Ionized Air Corrosion," Physics Today 7, 15 (1954).
4. W. Primak and L. H. Fuchs, "Nitrogen Fixation in a Nuclear Reactor," Nucleonics 13, 38 (1955).
5. J. Wright, L. K. Linacre, W. R. Marsh, and T. H. Bates, "Effect of Radiation on Heterogeneous Systems of Air or Nitrogen and Water," in Proc. 1st Int'l. Conf. Peaceful Uses Atomic Energy, Geneva, 1955 (United Nations, Geneva, 1956), vol. 7, p. 560.
6. A. R. Jones, "Radiation-Induced Reactions in the $N_2-O_2-H_2O$ System," Radiation Research 10, 655 (1959).
7. W. G. Burns, A. E. Hughes, J. A. C. Marples, R. S. Nelson, and A. M. Stoneham, "Effects of Radiation on the Leach Rates of Vitrified Radioactive Waste," J. Nucl. Mater. 107, 245 (1982).
8. W. M. Garrison, D. C. Morrison, J. G. Hamilton, A. A. Benson, and M. Calvin, "Reduction of Carbon Dioxide in Aqueous Solutions by Ionizing Radiation," Science 114, 416 (1951).
9. N. Getoff, G. Scholes, and J. Weiss, "Reduction of Carbon Dioxide in Aqueous Solutions under the Influence of Radiation," Tetrahedron Letters 18, 17 (1960).

10. N. Getoff, "Synthese organischer Stoffe aus Kohlensäure in wässriger Lösung unter Einwirkung von Co^{60} Gamma-Strahlung," Int'l. J. Appl. Radiation and Isotopes **13**, 205 (1962).
11. Aaron Barkatt, Alisa Barkatt, and W. Sousanpour, "Effects of Gamma Radiation on the Leaching Kinetics of Various Nuclear Waste-form Materials," Nature **300**, 339 (1982).
12. Aaron Barkatt, Alisa Barkatt, and W. Sousanpour, "Gamma Radiolysis of Aqueous Media and Its Effects on the Leaching Processes of Nuclear Waste Disposal Materials," Nucl. Technol. **60**, 218 (1983).
13. O. Tamm, "Experimentelle Studien über die Verwitterung und Tonbildung von Feldspaten," Chem. Erde **7**, 420 (1930).
14. C. W. Correns and W. von Engelhardt, "Neue Untersuchungen über die Witterung des Kalifeldspates," Chem. Erde **12**, 1 (1938).
15. C. W. Correns, "Die Chemische Verwitterung der Silikate," Naturw. **28**, 369 (1940).
16. V. E. Nash and C. E. Marshall, "The Surface Reactions of Silicate Minerals - Part II. Reactions of Feldspar Surfaces with Salt Solutions," Res. Bull. **614**, Univ. of Missouri, Agric. Expt. Station, Columbia, MO (1956).
17. R. M. Garrels and D. F. Howard, "Reactions of Feldspar and Mica with Water at Low Temperature and Pressure," in Proc. of the Sixth Nat. Conf. on Clays and Clay Minerals, Berkeley, CA, Aug. 19-23, 1957 (Pergamon Press, New York, 1957), p. 68.
18. J. K. Bates and V. M. Oversby, "The Behavior of Actinide Containing Glasses during Gamma Irradiation in a Saturated Tuff Environment," in Proc. of the Materials Research Society Symposium on the Scientific Basis for Nuclear Waste Management VIII, Boston, MA, Nov. 26-29, 1984, C. M. Jantzen et al., Eds. (Materials Research Society, Pittsburgh, PA, 1985), p. 257.

19. J. K. Bates, D. F. Fischer, and T. J. Gerding, The Reaction of Glass in a Gamma Irradiated Saturated Tuff Environment. Part 1: SRL 165 Glass, Argonne National Laboratory, Argonne, IL, ANL-85-62 (1985).
20. Environmental Protection Agency, "Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes; Final Rule," in Code of Federal Regulations, Title 40, Part 191, Federal Register Vol. 50, No. 182, p. 38066 (September 19, 1985).
21. Nuclear Regulatory Commission, "Disposal of High-Level Radioactive Wastes in Geologic Repositories," in Code of Federal Regulations, Title 10, Part 60 (U.S. Government Printing Office, Washington, D.C., 1984).
22. J. K. Bates, Argonne National Laboratory, Argonne, IL, private communication (1985).
23. R. A. Zielinski, Evaluation of Ash-flow Tuffs as Hosts for Radioactive Waste: Criteria Based on Selective Leaching of Manganese Oxides, U.S. Geological Survey, Denver, CO, Open File Report 83-480 (1983).
24. C. Willis, A. W. Boyd, and M. J. Young, "Radiolysis of Air and Nitrogen-Oxygen Mixtures with Intense Electron Pulses: Determination of a Mechanism by Comparison of Measured and Computed Yields," Can. J. Chem. 48, 1515 (1970).
25. C. Willis and A. W. Boyd, "Excitation in the Radiation Chemistry of Inorganic Gases," Int'l. J. Radiat. Phys. Chem. 8, 71 (1976).
26. R. G. Macdonald and O. A. Miller, "Low Dose-Rate Radiolysis of Nitrogen: Yield of Nitrogen Atoms, $N(^4S)$ and $N(^2D, ^2P)$," Radiat. Phys. Chem. 26, 63 (1985).
27. O. Tokunaga and N. Suzuki, "Radiation Chemical Reactions in NO_x and SO_2 Removals from Flue Gas," Radiat. Phys. Chem. 24, 145 (1984).

28. F. Busi, M. D'Angelantonio, Q. G. Mulazzani, V. Raffaelli, and O. Tubertini, "Radiation Treatment of Combustion Gases: Formulation and Test of a Reaction Model," Radiat. Phys. Chem. **25**, 47 (1985).
29. S. Gordon, K. H. Schmidt, and J. R. Honekamp, "An Analysis of the Hydrogen Bubble Concerns in the Three-Mile Island Unit-2 Reactor Vessel," Radiat. Phys. Chem. **21**, 247 (1983).
30. W. G. Burns and P. B. Moore, "Water Radiolysis and Its Effect upon In-Reactor Zircaloy Corrosion," Rad. Effects **30**, 233 (1976).
31. A. W. Boyd, M. B. Carver, and R. S. Dixon, "Computed and Experimental Product Concentrations in the Radiolysis of Water," Radiat. Phys. Chem. **15**, 177 (1980).
32. H. Christensen and E. Bjergbakke, "Radiolysis of Ground Water from Spent Fuel," Svensk Karnbransleforsorjning AB/Avdelning KBS, Stockholm, Sweden, SKBF KBS Report No. 82-18 (1982).
33. S. A. Simonson and W. L. Kuhn, "Predicting Amounts of Radiolytically Produced Species in Brine Solutions," in Proc. of the Mater. Research Soc. Symp. on the Sci. Basis for Nucl. Waste Management, Boston, Mass., Nov. 14-17, 1983, G. L. McVay, Ed. (Elsevier, New York, 1984), p. 781.
34. S. L. Nicolosi, "A Generalized Model for the Analysis of Groundwater Radiolysis," in Proc. of the Mater. Res. Soc. Symp. on the Sci. Basis for Nucl. Waste Management VIII, C. M. Jantzen et al., Eds. (Materials Research Society, Pittsburgh, PA, 1985), p. 631.
35. T. Eriksen and A. Jacobsson, "Radiation Effects on the Chemical Environment in a Radioactive Waste Repository," Svensk Karnbransleforsorjning AB/Avdelning KBS, Stockholm, Sweden, SKBF KBS Report No. 83-27 (1983).

36. W. G. Burns, W. R. Marsh, and W. S. Walters, "The Gamma Irradiation-Enhanced Corrosion of Stainless and Mild Steels by Water in the Presence of Air, Argon, and Hydrogen," Radiat. Phys. Chem. 21, 259 (1983).
37. J. W. T. Spinks and R. J. Woods, An Introduction to Radiation Chemistry (Wiley, New York, 1976), 2nd ed.
38. C. J. Hochanadel and J. A. Ghormley, "Effect of Temperature on the Decomposition of Water by Gamma Rays," Radiat. Res. 16, 653 (1962).
39. G. G. Jayson, B. J. Parsons, and A. J. Swallow, "Some Simple, Highly Reactive, Inorganic Chlorine Derivatives in Aqueous Solution," J. Chem. Soc. Faraday Trans. I 69, 1597 (1973).
40. D. Behar, G. Czapski, and I. Duchovny, "Carbonate Radical in Flash Photolysis and Pulse Radiolysis of Aqueous Carbonate Solutions," J. Phys. Chem. 74, 2206 (1970).
41. G. E. Adams, J. W. Boag, and B. D. Michael, "Transient Species Produced in Irradiated Water and Aqueous Solutions Containing Oxygen," Proc. Roy. Soc. London, Ser. A 289, 321 (1965).
42. E. Hayon and J. J. McGarvey, "Flash Photolysis in the Vacuum Ultraviolet Region of SO_4^{2-} , CO_3^{2-} , and OH^- Ions in Aqueous Solutions," J. Phys. Chem. 71, 1472 (1967).
43. T. E. Eriksen, J. Lind, and G. Merenyi, "On the Acid-Base Equilibrium of the Carbonate Radical," Radiat. Phys. Chem. 26, 197 (1985).
44. K. V. Baczko, Ed., Gmelin Handbuch der Anorganischen Chemie, System-Nummer 14, Part C, Number 3, "Kohlenstoff" (Verlag Chemie-GMBH, Weinheim/Bergstrasse, Germany, 1973), p. 123.
45. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry (Wiley, New York, 1980).

46. W. J. Gray and S. A. Simonson, "Gamma and Alpha Radiolysis of Salt Brines," in Proc. of the Materials Research Society Symp. on the Sci. Basis for Nucl. Waste Management VIII, Boston, Mass., Nov. 26-29, 1984, C. M. Jantzen et al., Eds. (Materials Research Society, Pittsburgh, PA, 1985), p. 623.
47. A. Fojtik, G. Czapski, and A. Henglein, "Pulse Radiolytic Investigation of the Carboxyl Radical in Aqueous Solution," J. Phys. Chem. **74**, 3204 (1970).
48. J. P. Keene, Y. Raef, and A. J. Swallow, "Pulse Radiolysis Studies of Carboxyl and Related Radicals," in Pulse Radiolysis, Proc. of the Int'l. Symp., Manchester, England, April, 1965 (Academic, New York, 1965), p. 99.
49. I. G. Draganic and O. Gal, "Radiation Chemistry of Oxalic Acid and Oxalates," Rad. Res. Rev. **3**, 167 (1971).
50. H. Stephen and T. Stephen, Solubilities of Inorganic and Organic Compounds, Vol. 1, Binary Systems, Part 1 (Macmillan, New York, 1963), p. 251.
51. T. Hasselstrom and M. C. Henry, "New Synthesis of Oxalic Acid," Science **123**, 1038 (1956).
52. M. C. Juhas, R. D. McCright, and R. E. Garrison, Behavior of Stressed and Unstressed 304L Specimens in Tuff Repository Environmental Conditions, Lawrence Livermore National Laboratory, UCRL-91804 (1985) (presented at Corrosion '85, National Association of Corrosion Engineers Annual Meeting, Boston, MA, March 25-29, 1985).
53. R. S. Glass, R. A. Van Konynenburg, and G. E. Overturf, "Corrosion Processes of Austenitic Stainless Steels and Copper-Based Materials in Gamma-Irradiated Aqueous Environments," Lawrence Livermore National Laboratory, UCRL-92941 (1986) (presented at Corrosion '86, National Association of Corrosion Engineers Annual Meeting, Houston, Texas, March 17-21, 1986).

54. W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, Hydrogen Peroxide (Reinhold, New York, 1955).
55. J. K. Linacre and W. R. Marsh, "The Radiation Chemistry of Heterogeneous and Homogeneous Nitrogen and Water Systems," Chemistry Division, AERE Harwell, England (1981), AERE-R10027.
56. J. A. Roth and D. E. Sullivan, "Solubility of Ozone in Water," Ind. Eng. Chem. Fundam. 20, 137 (1981).
57. M. Pourbaix, Atlas of Electrochemical Equilibria in Aqueous Solutions (Pergamon, New York, 1966).
58. R. A. Van Konynenburg, Lawrence Livermore National Laboratory, unpublished data discussed in internal memorandum entitled "Water Chemistry Results from Corrosion Experiment No. 11 (General Corrosion of Stainless Steels in Hot, Unirradiated J-13 Water)," October 22, 1985.
59. W. L. Jolly, The Inorganic Chemistry of Nitrogen (W. A. Benjamin, New York, 1964).
60. K. L. Nash, S. Fried, A. M. Friedman, N. Susak, P. Rickert, and J. C. Sullivan, "Radiation Effects in Solution and on the Solid/Liquid Interface," Nucl. Technol. 60, 257 (1983).
61. R. C. Weast and M. J. Astle, Eds., CRC Handbook of Chemistry and Physics (CRC Press, Boca Raton, FL, 1982), 63rd ed.
62. J. H. Keenan, F. G. Keyes, P. G. Hill, and J. G. Moore, Steam Tables (Wiley, New York, 1978).
63. J. A. Dean, Ed., Lange's Handbook of Chemistry (McGraw-Hill, New York, 1979), 12th ed.
64. A. M. Amorosi and J. R. McDermet, "The Calculation of the Distribution of Carbon Dioxide Between Water and Steam," ASTM Proc. 39, 1204 (1939).

65. P. Cohen, Water Coolant Technology of Power Reactors (American Nuclear Society, La Grange Park, IL, 1969).

Technical Information Department • Lawrence Livermore National Laboratory
University of California • Livermore, California 94550

