RADIOLYTIC GAS PRODUCTION FROM CONCRETE CONTAINING SAVANNAH RIVER PLANT WASTE

by

N. E. Bibler

M. L. Hyder, Research Manager
Separations Chemistry Division

Publication Date: January 1978

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or 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.

**E. I. DU PONT DE NEMOURS AND COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, SOUTH CAROLINA 29801**

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT AT(07 2) 1

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, 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 product, 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 any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

To determine the extent of gas production from radiolysis of concrete containing radioactive Savannah River Plant waste, samples of concrete and simulated waste were irradiated by ^{60}Co gamma rays and ^{244}Cm alpha particles. Gamma radiolysis simulated radiolysis by beta particles from fission products in the waste. Alpha radiolysis indicated the effect of alpha particles from transuranic isotopes in the waste.

With gamma radiolysis, hydrogen was the only significant product; hydrogen reached a steady-state pressure that increased with increasing radiation intensity. Hydrogen was produced faster, and a higher steady-state pressure resulted when an organic set retarder was present. Oxygen that was sealed with the wastes was depleted. Gamma radiolysis also produced nitrous oxide gas when nitrate or nitrite was present in the concrete. With alpha radiolysis, hydrogen and oxygen were produced. Hydrogen did not reach a steady-state pressure at <140 psi.

From these results, estimates of pressure in conceptual containers (cylinders 2 feet ID by 10 feet tall, 90% full) of SRP waste concrete were made. During the first 300 years of storage when radiolysis will mainly be from beta-gamma radiation (from ^{137}Cs and ^{90}Sr), hydrogen will reach a steady-state pressure of 8 to 28 psi, and oxygen will be partially consumed. These predictions were confirmed by measurement of gas produced over a short time in a container of concrete and actual SRP waste. The tests with simulated waste also indicated that nitrous oxide may form, but because of the low nitrate or nitrite content of the waste, the maximum pressure of nitrous oxide after 300 years will be <60 psi. After decay of these fission products, alpha radiolysis from ^{238}Pu and ^{239}Pu will predominate; the hydrogen and oxygen pressures will increase to >200 psi.

CONTENTS

Introduction	7
Composition of Simulated Wastes	9
Gamma Radiolysis of Concrete Containing Fe_2O_3 or MnO_2	9
High and Low Dose Rate Tests in Absence of Added NO_3^- or NO_2^-	9
Low Dose Rate Tests in Presence of Added NO_3^- or NO_2^- Ions	13
Gamma Radiolysis of Concrete Containing SRP Simulated Wastes	17
Gamma Radiolysis of Concrete Containing SRP Simulated Waste and an Organic Set Retarder	19
Experimental Procedures for Gamma Radiolysis Tests	21
Alpha Radiolysis of Concrete Containing SRP Simulated Wastes	22
Radiation Doses to Concrete from SRP Waste During Long-Term Storage	25
Measured Pressurization in Containers of Concrete and SRP Waste	28
Calculated Pressurization in Containers of Concrete and SRP Waste During Long-Term Storage	30
H_2 and O_2 Production	30
N_2O Production	33
He Production	34
Mechanism for Radiolytic Gas Production	34
References	38

LIST OF FIGURES

- 1 Conceptual Waste Solidification Process 7
- 2 Pressure from Gamma Radiolysis at 8.9×10^4 rads/hr of Concrete Containing Fe_2O_3 or MnO_2 as Simulated Waste 10
- 3 Pressure from Gamma Radiolysis at Two Dose Rates of Concrete Containing Fe_2O_3 11
- 4 Pressure from Gamma Radiolysis at 2.8×10^7 rads/hr of Concrete Containing Fe_2O_3 or MnO_2 as Simulated Waste 11
- 5 Effect of Dose Rate on Steady-State H_2 Pressures 12
- 6 Pressure from Gamma Radiolysis at 8.9×10^4 rads/hr of Concrete Containing Fe_2O_3 with Sorbed NO_3^- and NO_2^- Ions 14
- 7 Pressure from Gamma Radiolysis at 2.8×10^7 rads/hr of Concrete Containing Fe_2O_3 with Sorbed NO_3^- Ions 16
- 8 Pressure from Gamma Radiolysis at 8.9×10^4 rads/hr of Concrete Containing SRP Simulated Wastes 17
- 9 Pressure from Gamma Radiolysis at 1.4×10^7 rads/hr of Concrete Containing SRP Simulated Wastes 18
- 10 Pressure from Gamma Radiolysis at 8.9×10^4 rads/hr of Concrete Containing Fe-Al Simulated Waste and Ascorbic Acid Set Retarder 19
- 11 Pressure from Gamma Radiolysis at 1.4×10^7 rads/hr of Concrete Containing Fe-Al Simulated Waste and Ascorbic Acid Set Retarder 20
- 12 Pressure from Short-Term Alpha Radiolysis of Concrete Containing SRP Simulated Wastes 23
- 13 Pressure from Long-Term Alpha Radiolysis of Concrete Containing Fe-Mn Simulated SRP Waste 24

- 14 Calculated Dose Rates in Concrete Containing
Radioactive SRP Waste 25
- 15 Calculated Doses in Concrete Containing Radioactive
SRP Waste 26
- 16 Pressure from Concrete Containing Radioactive
SRP Waste 28
- 17 Estimate of Long-Term Pressurization from Concrete
Containing Radioactive SRP Waste 31
- 18 Effect of Bromide Ions on Pressurization from
Gamma Radiolysis of Concrete 36

LIST OF TABLES

- 1 Data for Gamma Radiolysis of Concrete Containing
 Fe_2O_3 or MnO_2 as Simulated Waste 10
- 2 Effect of Gas Volume and Water-to-Cement Ratio on
Steady-State H_2 Pressures 13
- 3 Data for Gamma Radiolysis of Concrete Containing
 Fe_2O_3 with Sorbed NO_3^- or NO_2^- Ions 15
- 4 Data for Gamma Radiolysis of Concrete Containing
SRP Simulated Wastes 18
- 5 Data for Gamma Radiolysis of Concrete Containing Fe-Al
Simulated Waste and Ascorbic Acid Set Retarder 20
- 6 Data for Alpha Radiolysis of Concrete Containing
SRP Simulated Wastes 23
- 7 Principal Isotopes Solidified in SRP Concrete Waste 27
- 8 Major Components in Washed, Dried Tank 15 Waste 30

RADIOLYTIC GAS PRODUCTION FROM CONCRETE CONTAINING SAVANNAH RIVER PLANT WASTE

INTRODUCTION

Savannah River Laboratory (SRL) is evaluating methods for solidifying and storing Savannah River Plant (SRP) high-level radioactive waste.¹⁻⁸ In one of several options, waste can be solidified as glass or concrete and stored in an onsite facility until it is shipped to a Federal repository. An earlier report¹ detailed the origins and characteristics of SRP wastes and the criteria for acceptable solid waste forms. One conceptual process based on that study is shown in Figure 1. Another conceptual process being considered is vitrification of the waste.

FIGURE 1. Conceptual Waste Solidification Process

SRP wastes consist of an alkaline salt solution, a solid salt cake (mostly nitrate and nitrite), and an insoluble sludge containing most of the radioactivity and large amounts of iron, aluminum, manganese, uranium, and other elements. Principal sources of radiation are ^{90}Sr , ^{137}Cs , ^{238}Pu , and ^{239}Pu . In the conceptual process, sludge is separated from the salt cake and solution, is washed to remove residual nitrate and nitrite ions sorbed from the solution, and is then dried. Soluble ^{137}Cs is removed from the solution by ion exchange^{3,4} and mixed with the sludge. These materials can then be solidified in a glass or concrete matrix and sealed inside steel containers for long-term storage. If solidified in glass, the dried sludge and ^{137}Cs from ion exchange can be mixed with a glass frit and melted. If solidified in concrete, the ^{137}Cs can be transferred to zeolite and mixed with the dried sludge. This mixture can then be used as aggregate for making concrete.

Glass and concrete as solidification matrices for SRP wastes have been studied extensively at SRL.⁵⁻⁸ These forms are attractive for radioactive waste storage because they are compatible with SRP wastes and have high compressive strengths and low leachabilities for ^{90}Sr , ^{137}Cs , and the transuranic isotopes ^{238}Pu and ^{239}Pu . The effects of gamma and alpha radiation on glass forms have been evaluated.⁵⁻⁸ Radiolysis does not produce gaseous products, nor does it affect the leachabilities of overall appearances of the forms. With concrete, only the effects of radiation on compressive strengths and leachabilities have previously been evaluated.⁵ No detrimental effects were detected.

This report presents results of a study to determine if radiolysis of concrete waste during long-term storage will produce significant amounts of gases. Large gas pressures could breach the waste container. In this study, samples of simulated SRP wastes were mixed with a high-alumina cement to make concretes. These samples were then irradiated with ^{60}Co gamma rays or ^{244}Cm alpha particles. Previous study has shown that high-alumina cement is superior for solidification of SRP waste.⁵ Nominal composition (wt %) of this cement is Al_2O_3 , 41; CaO , 37; SiO_2 , 9; Fe_2O_3 , 6; and MgO , 2 with small amounts of other oxides. Radiolysis with ^{60}Co gamma rays simulated beta radiolysis from the fission products ^{90}Sr and ^{137}Cs in the waste. Radiolysis with ^{244}Cm alpha particles simulated alpha radiolysis by the transuranic isotopes. Samples were irradiated in gas-tight steel containers. Each container had a pressure gage and a sampling valve. During radiolysis, the pressure was monitored; and after radiolysis, the gas was sampled. Its composition was determined by gas chromatography. Results of these tests were used to estimate radiolytic pressurization in containers of concrete and SRP radioactive waste during long-term storage.

COMPOSITION OF SIMULATED WASTES

The main components of SRP radioactive wastes are hydrous oxides of Al, Fe, and Mn. For initial radiolysis tests, reagent-grade Fe_2O_3 or MnO_2 was used as simulated waste. Al_2O_3 was not tested individually because it was always present as one of the components of the cement. Tests were also performed with concrete containing materials that were specially prepared to simulate SRP waste sludges. These materials were equimolar mixtures of hydrous oxides of Fe^{3+} and Al^{3+} or of Fe^{3+} and Mn^{4+} . The mixtures were prepared by hydroxide precipitation of the ions from neutral nitrate solutions.⁵ After precipitation, each mixture was washed several times and then dried. For all tests, the simulated wastes were 40 wt % of the dry cement-waste mixture.

GAMMA RADIOLYSIS OF CONCRETE CONTAINING Fe_2O_3 OR MnO_2

Concrete containing 40 wt % (dry basis) reagent-grade Fe_2O_3 or MnO_2 as simulated waste was irradiated to determine the effects of radiation dose and intensity on the rate of gas production. Also, the effect of added NO_3^- or NO_2^- ions was investigated in the presence of these reagents. NO_3^- or NO_2^- may be present in the washed and dried radioactive SRP waste because this waste is presently stored in a NO_3^- or NO_2^- solution. Another study⁹ has shown that direct radiolysis of NO_3^- leads to O_2 formation. This O_2 formation could be another source of radiolytic pressurization.

High and Low Dose Rate Tests in Absence of Added NO_3^- or NO_2^-

Both high and low dose rate tests established that H_2 was the only gas produced. The initial production rate of H_2 was dependent upon the dose rate; but, as the H_2 pressure increased, a reaction removing H_2 was initiated. Eventually, H_2 reached a steady-state pressure. This steady-state pressure was also dependent upon the dose rate. At higher dose rates, higher steady-state pressures were achieved. Gas volume and the water-to-cement ratio did not affect this steady-state pressure. Gas composition at the end of the tests showed that O_2 from the air sealed with the concrete was consumed and N_2 was unaffected.

Pressure changes from gamma radiolysis at different dose rates are shown in Figures 2, 3, and 4. Data for these tests are shown in Table 1. The final gas compositions indicate that N_2 was not significantly affected and that O_2 was 60 to 80% consumed. This consumption accounts for the initial pressure

TABLE 1

Data for Gamma Radiolysis of Concrete Containing Fe_2O_3 or MnO_2 as Simulated Waste

<i>Materials Irradiated, g</i>				<i>Gas Volume, mL</i>	<i>Final Gas Composition, %</i>		
<i>Oxide</i>	<i>Cement</i>	<i>H₂O</i>			<i>H₂</i>	<i>O₂</i>	<i>N₂</i>
Fe_2O_3^a	300	451	306	105	16.3	6.7	77.0
MnO_2^a	369	554	228	112	6.9	4.9	88.2
Fe_2O_3^b	96	144	99	124	82.2	6.8	11.0
Fe_2O_3^c	94	130	96	135	83.8	4.7	11.6
Fe_2O_3^c	93	139	95	141	85.9	6.6	9.8
MnO_2^c	117	177	82	135	80.2	2.3	17.8

a. Dose rate = 8.9×10^4 rads/hr. Irradiation temperature = 40°C .

b. Dose rate = 1.4×10^7 rads/hr. Irradiation temperature = 45°C .

c. Dose rate = 2.8×10^7 rads/hr. Irradiation temperature = 45°C .

FIGURE 2. Pressure from Gamma Radiolysis at 8.9×10^4 rads/hr of Concrete Containing Fe_2O_3 or MnO_2 as Simulated Waste

FIGURE 3. Pressure from Gamma Radiolysis at Two Dose Rates of Concrete Containing Fe_2O_3

FIGURE 4. Pressure from Gamma Radiolysis at $2.8 \times 10^7 \text{ rads/hr}$ of Concrete Containing Fe_2O_3 or MnO_2 as Simulated Waste

decreases observed in the test at 8.9×10^4 rads/hr (Figure 2). O_2 was consumed faster than H_2 was produced; however, O_2 was not completely consumed because of the long, small ID tube separating the irradiation container from the pressure gage and sampling valve. This small-diameter tube prevented O_2 from diffusing into the radiation field where it could react. In a test where the entire gas volume was in the radiation field, 95% of the O_2 was consumed.

Achievement of a steady-state pressure is evident from the tests at 1.4×10^7 and 2.5×10^7 rads/hr (Figures 3 and 4). Results indicate that the value of this final pressure is dependent upon the dose rate (Figure 3) and the composition of the wastes (Figure 4). The dose rate dependency of this steady-state pressure was examined at two lower dose rates, 8.9×10^4 and 3.9×10^5 rads/hr. At these lower intensities, the irradiation time necessary to generate enough H_2 to reach a steady-state pressure was several months. Thus, to achieve steady state in a shorter time, H_2 was pressurized into the irradiation container until radiolytic pressurization ceased. Steady-state pressures determined at the four dose rates are shown in Figure 5.

FIGURE 5. Effect of Dose Rate on Steady-State H_2 Pressures

Data in Table 2 show that gas volume and water-to-cement ratios (by weight) from 0.29 to 0.77 did not significantly affect the steady-state pressure. Because of the lack of an effect of gas volume, smaller amounts of H₂ were produced in containers with smaller gas volumes. The water-to-cement ratios bracket those that give workability to the concrete.

TABLE 2

Effect of Gas Volume and Water-to-Cement Ratio
on Steady-State H₂ Pressures^a

<i>Materials Irradiated, g</i>			<i>Free</i>	<i>Equilibrium</i>
<i>Cement</i>	<i>H₂O</i>	<i>W/Cb</i>	<i>Volume,</i> <i>mL</i>	<i>H₂ Pressure,</i> <i>psi</i>
244	67	0.27	144	100
199	55	0.28	167	105
132	36	0.27	223	96
225	95	0.40	138	102
225	173	0.77	125	108

a. Dose rate = 2.8×10^7 rads/hr. Irradiation temperature = 45°C.

b. Water-to-cement ratio.

Low Dose Rate Tests in Presence of Added NO₃⁻ or NO₂⁻ Ions

Low dose rate tests (8.9×10^4 rads/hr) showed that added NO₃⁻ or NO₂⁻ did not lead to additional pressurization. O₂ was still consumed, and H₂ was still produced. However, small amounts of N₂O were produced. At the high dose rate (2.8×10^7 rads/hr), however, O₂ was a product indicating a different radiolytic mechanism at this intensity. Also, a steady-state pressure was not achieved as it was when NO₃⁻ or NO₂⁻ was absent. N₂O was also a product at this dose rate. The amount of N₂O formed could be significantly decreased by lowering the amount of NO₂⁻ present.

Pressure changes resulting from gamma radiolysis of concrete containing Fe₂O₃ and 5 wt % NO₃⁻ or 5 wt % NO₃⁻ and 2.5 wt % NO₂⁻ at 8.9×10^4 rads/hr are shown in Figure 6. Pressure change data in the absence of these ions are also included (Table 3). Data from gas analyses show that in all three tests, 80 to 90% of the O₂ was consumed, and N₂ was not significantly affected. Lower amounts of H₂ were produced in the tests with NO₃⁻ or with NO₃⁻

and NO_2^- present. The ions scavenge the precursors of H_2 . These precursors are H atoms formed by radiolysis of the water. This scavenging process leads to chemical reduction of the NO_3^- or NO_2^- . Sufficient reduction would form N_2O , the other gaseous product observed. A larger amount of N_2O formed when NO_2^- was present suggests that this ion is significant in the mechanism for N_2O formation. Separate tests showed that lowering the NO_2^- content by a factor of 5 lowered the N_2O production rate by a factor of about 2.5.

FIGURE 6. Pressure from Gamma Radiolysis at 8.9×10^4 rads/hr of Concrete Containing Fe_2O_3 with Sorbed NO_3^- and NO_2^- Ions

TABLE 3

Data for Gamma Radiolysis of Concrete Containing Fe_2O_3 with Sorbed NO_3^- or NO_2^- Ions^a

<i>Materials Irradiated, g</i>					<i>Gas Volume, mL</i>	<i>Final Gas Composition, %</i>			
<i>Cement</i>	<i>Fe₂O₃</i>	<i>H₂O</i>	<i>NO₃⁻</i>	<i>NO₂⁻</i>		<i>H₂</i>	<i>O₂</i>	<i>N₂</i>	<i>N₂O</i>
451	300	306	0	0	105	20.3	6.7	73.1	0.0
467	312	297	15	0	85	8.5	2.3	88.8	0.4
474	316	280	15	8	71	4.4	7.6	86.9	1.1

a. Dose rate = 8.9×10^4 rads/hr. Irradiation temperature = 41°C.

In the two tests which contained NO_3^- or NO_2^- and NO_3^- ions, radiolytic pressurization was stopped by pressurizing the system with about 30 psi H_2 . This pressure agrees with that predicted in Figure 5 at this dose rate. Because pressurization was stopped by H_2 addition, NO_3^- and NO_2^- ions did not significantly affect the backreaction leading to steady-state pressures. Achievement of a steady-state pressure indicates that O_2 was not a radiolytic product at 8.9×10^4 rads/hr. Finally, achievement of the steady-state pressure showed that N_2O production was stopped by the presence of H_2 . Apparently, the intermediate leading to N_2O formation can be scavenged by large pressures of H_2 .

Results of a test at a much higher dose rate (2.8×10^7 rads/hr) with concrete containing 1 wt % NO_3^- are shown in Figure 7. Data obtained in the absence of NO_3^- are also presented. At the end of the test with NO_3^- present, the gas composition was 64% H_2 , 25% O_2 , 11.5% N_2 , and 0.5% N_2O . Similar results were obtained with concrete containing 1 wt % NO_3^- and 1 wt % NO_2^- , except that in presence of NO_2^- , more N_2O was produced. The gas composition data indicated that O_2 was now a product of the radiolysis along with H_2 and N_2O . Based on the initial and final O_2/N_2 ratios, the ratio of evolved O_2 to H_2 was 0.3. These results are in contrast to those at the lower dose rate (8.9×10^4 rads/hr), where O_2 was consumed rather than produced. O_2 production suggests a different radiolytic mechanism at the high dose rate.

Another difference caused by NO_3^- in the high dose rate test is that a steady-state pressure is not reached. This difference (Figure 7) also suggests that a different radiolytic mechanism occurred at the high dose rate. A final test was performed to determine whether O_2 was an initial product or a secondary product

resulting from the large radiation dose (3.8×10^9 rads). Two samples of concrete and Fe_2O_3 , one with 5 wt % NO_3^- and one without added NO_3^- , were irradiated at the high dose rate (2.8×10^7 rads/hr) in containers with small void volumes. The concrete samples were irradiated to 8×10^6 rads. This dose caused about 80% O_2 consumption at the low dose rate (Figure 6). Analysis of the resulting gases showed that O_2 was 92% consumed in the absence of NO_3^- , but O_2 was increased by 43% when NO_3^- was present. The data establish that O_2 , at the high dose rate, resulted from the presence of NO_3^- rather than from the large radiation dose.

FIGURE 7. Pressure from Gamma Radiolysis at 2.8×10^7 rads/hr of Concrete Containing Fe_2O_3 with Sorbed NO_3^- Ions

GAMMA RADIOLYSIS OF CONCRETE CONTAINING SRP SIMULATED WASTES

Concrete containing material that simulated SRP waste sludges was irradiated. This material contained equimolar mixtures of hydrous oxides of Fe^{3+} and Al^{3+} or hydrous oxides of Fe^{3+} and Mn^{4+} . The oxides were prepared by hydroxide precipitation of the respective metal ions from NO_3^- solutions. These simulated wastes were identical to those used in other studies evaluating concrete⁵ or glass⁶ as solidification matrices. Results of irradiation of samples containing 40 wt % (dry basis) of the simulated wastes at both low- (8.9×10^4 rads/hr) and high (1.4×10^7 rads/hr) dose rates were not significantly different from those with concrete containing reagent-grade Fe_2O_3 with added NO_3^- and NO_2^- ions.

At the low dose rate (Figure 8, Table 4), the pressure initially decreased because almost 80% of the O_2 was consumed. Hydrogen and a trace of N_2O were produced. Nitrogen was not affected. With both types of simulated wastes, pressurization could be stopped by adding 36-psi hydrogen.

FIGURE 8. Pressure from Gamma Radiolysis at 8.9×10^4 rads/hr of Concrete Containing SRP Simulated Wastes

At the high dose rate (Figure 9, Table 4), a steady-state pressure was not achieved as it was with concrete containing only Fe_2O_3 or MnO_2 . Also, O_2 was a significant product. The evolved gas was 34% oxygen and 66% hydrogen. These results suggest that NO_3^- ions were present in the simulated wastes. The presence of these ions is not unexpected because the simulated wastes were prepared by precipitation of Fe-Al or Fe-Mn ions from nitrate solutions.

TABLE 4

Data for Gamma Radiolysis of Concrete Containing SRP Simulated Wastes^a

<i>Materials Irradiated, g</i>				<i>Gas Volume, mL</i>	<i>Final Gas Composition, %</i>			
	<i>Wastes</i>	<i>Cement</i>	<i>H₂O</i>		<i>H₂</i>	<i>O₂</i>	<i>N₂</i>	<i>N₂O</i>
Fe-Mn ^a	228	432	273	110	11.8	5.0	82.9	0.3
Fe-Al ^a	317	476	313	123	9.1	5.4	85.5	0.0
Fe-Mn ^b	88.0	132	89	148	77.1	13.8	9.2	0.0
Fe-Al ^b	88.5	133	91	140	60.8	32.9	6.3	0.0

a. Dose rate = 8.9×10^4 rads/hr. Irradiation temperature = 41°C.

b. Dose rate = 1.4×10^7 rads/hr. Irradiation temperature = 45°C.

FIGURE 9. Pressure from Gamma Radiolysis at 1.4×10^7 rads/hr of Concrete Containing SRP Simulated Wastes

GAMMA RADIOLYSIS OF CONCRETE CONTAINING SRP SIMULATED WASTE AND AN ORGANIC SET RETARDER

If concrete is used to solidify SRP wastes, a set retarder may be added to the cement-sludge mixture. The set retarder will lengthen the time for the concrete to harden and will allow more time for pouring the paste from a mixing tank into a final storage container. Several set retarders have been evaluated.¹⁰ Many are organic compounds that may generate H_2 or CO_2 when irradiated. To determine if an organic set retarder would produce gases when irradiated in concrete, samples of concrete containing Fe-Al simulated waste and ascorbic acid ($C_6H_8O_6$) as a typical organic set retarder were irradiated. In a low dose rate test (Figure 10, Table 5), O_2 was consumed; and H_2 was produced as in the tests without a set retarder. However, pressurization could not be stopped as it was in absence of set retarder. In fact, addition of 60 psi H_2 , the maximum tested, did not affect the pressurization rate.

In a high dose rate test, the initial pressurization was faster than that when the retarder was absent (Figure 11, Table 5). A steady-state pressure of about 150 psig was achieved when the retarder was present. Also, gas composition data (Table 5) show that O_2 was not a product.

FIGURE 10. Pressure from Gamma Radiolysis at 8.9×10^4 rads/hr of Concrete Containing Fe-Al Simulated Waste and Ascorbic Acid Set Retarder

TABLE 5

Data for Gamma Radiolysis of Concrete Containing Fe-Al
Simulated Waste and Ascorbic Acid Set Retarder^a

Dose Rate, rads/hr	Materials Irradiated, g				Gas Volume, mL	Final Gas Composition, %		
	Oxide	Cement	H ₂ O	C ₆ H ₈ O ₆		H ₂	O ₂	N ₂
8.9×10^4	329	493	294	5.3	60	10.8	4.7	84.5
8.9×10^4	300	451	306	0.0	105	7.3	9.7	83.0
1.4×10^7	85	128	83	1.5	140	89.8	0.8	9.0
1.4×10^7	84	126	84	0.0	156	76.7	14.4	8.9

a. Irradiation temperature = 40 to 50°C.

FIGURE 11. Pressure from Gamma Radiolysis at 1.4×10^7 rads/hr of Concrete Containing Fe-Al Simulated Waste and Ascorbic Acid Set Retarder

The low dose rate results show that if an organic set retarder is used in the waste solidification process, an additional source of H₂ pressurization will be present at low dose rates. The high dose rate results indicate that a steady-state pressure may be reached in containers of SRP concrete waste forms, but the pressure may be about 150 psig.

EXPERIMENTAL PROCEDURES FOR GAMMA RADIOLYSIS TESTS

Samples were irradiated at 8.9×10^4 rads/hr with a Gammacell*-220 ⁶⁰Co source at an ambient temperature of 40°C. The irradiation containers were 500-mL glass bottles. In a separate container, water was added to the cement-simulated waste mixture (40 wt % waste) until good workability was attained (water-to-cement ratios about 0.3 by weight). The mixture was then poured into the glass bottle and allowed to cure for at least 20 hours.

During irradiation, the bottle was attached to 5 feet of 1/8-inch copper tubing that extended out of the radiation field to a sampling valve, a mercury manometer, and a recording strain gage pressure transducer. Sensitivity of the transducer was 0.43 torr/mm of chart response. Dose rates in the concrete were measured with the Fricke dosimeter.¹¹ Minor corrections for differences between the electron densities of the solution and concrete were not applied.

After irradiation, the gas was sampled for analysis by expanding it into an evacuated sampler that had a much larger volume than that of the irradiation container and associated equipment. This expansion ensured that almost all the gas was removed, and a representative sample was obtained for analysis. Preliminary tests had shown that the copper tubing prevented complete mixing of the evolved gas with the air already present in the system. The gas in the sampler was compressed to atmospheric pressure and analyzed by gas chromatography. Free volume in the radiolysis container and associated equipment was determined by expanding a known amount of air into the volume and measuring the resulting pressure.

* Atomic Energy of Canada, Ltd., Ottawa, Canada.

Samples were irradiated at 1.4×10^7 rads/hr and 2.8×10^7 rads/hr with a ^{60}Co source submerged in 20 feet of water. Temperature during irradiation was 40 to 50°C. These samples were cast into 3.5-cm-ID $\times$ 18.5-cm-tall glass test tubes. Again, minimum set time was 20 hours. During irradiation, the glass tubes were in a steel container that was attached to about 25 feet of 1/8-inch-OD steel tubing. The tubing extended above the water to a sampling valve and pressure gage. Dose rates to the samples were determined by irradiating film dosimeters in a small tube in the concrete.¹² Methods for sampling and analyzing the gas and for determining the free volume were identical to those described previously.

ALPHA RADIOLYSIS OF CONCRETE CONTAINING SRP SIMULATED WASTES

Radioactive SRP wastes contain alpha emitters, such as ^{238}Pu and ^{239}Pu . Because alpha radiolysis can produce different effects than gamma radiolysis, concrete samples were irradiated with alpha particles. ^{244}Cm was used as the radiation source. Concrete samples containing 40 wt % (dry basis) SRP simulated wastes and ^{244}Cm were prepared in steel tubes that could be sealed to pressure gages and sampling valves. The range of the alpha particles in concrete is about 0.01 mm; thus, all the alpha energy was absorbed by the sample. In all the tests, 7.2 g of cement and 4.8 g of simulated wastes were used. A known amount of ^{244}Cm dissolved in the water was used to make the concrete. The significant results were that both O_2 and H_2 were products (O_2/H_2 ratio varied from 0.2 to 0.5), and that a steady-state pressure was not achieved up to 200 psi, which was the maximum pressure tested. These results agree with those observed in alpha radiolysis of another type of concrete in another study.¹³

Results of three alpha radiolysis tests are shown in Figure 12 and Table 6. For these tests, a known amount of ^{244}Cm was dispersed as a $\text{Cm}_2(\text{SO}_4)_3$ solution in a mixture of cement and Fe-Mn or Fe-Al waste. Mixing was performed in a steel test tube (0.9 cm ID $\times$ 10 cm long). After the concrete had cured 20 hours, the tube was sealed to a pressure gage and sampling valve. At the end of the test, the gas was sampled and analyzed, and the gas volume determined as previously described for the gamma radiolysis tests. Partial pressures before and after the test were compared. The pressures showed that N_2 did not change, and O_2 and H_2 were produced. The ratio of evolved O_2 to H_2 for the three tests was 0.4.

FIGURE 12. Pressure from Short-Term Alpha Radiolysis of Concrete Containing SRP Simulated Wastes

TABLE 6

Data for Alpha Radiolysis of Concrete Containing SRP Simulated Wastes^a

²⁴⁴ Cm, mg	Material Irradiated, Wastes	Material Irradiated, g			Dose Rate, eV/hr	Gas Volume, mL	Final Gas Composition, %		
		Cement	Water				H ₂	O ₂	N ₂
4.5	Fe-Al	4.8	7.2	b	2.8×10^{20}	12.0	18.2	21.9	59.9
4.5	Fe-Mn	4.8	7.2	b	2.8×10^{20}	11.9	19.2	22.1	58.7
2.6	Fe-Mn	4.8	7.2	b	1.6×10^{20}	8.1	15.6	21.4	63.0

a. Irradiation temperature = 23°C.

b. The amount of water was not measured. Sufficient water was added to get a paste with good workability.

To determine the effect of higher pressures on the pressurization rate, the test with Fe-Mn waste and 4.5 mg ^{244}Cm was monitored for a much longer time. Over a period of about 4.5 months, the pressure increased almost linearly to 200 psi (Figure 13). This increase indicated little effect of pressure on the pressurization rate. The dose rate in this test which was 4×10^5 rads/hr was calculated by using 5.8 MeV as the energy of the alpha particle and 1.8×10^{11} alpha/(min-mg) for the specific activity of ^{244}Cm .¹⁴ For gamma radiolysis, a steady-state pressure of about 50 psi is predicted at this dose rate (Figure 5). Failure to achieve a steady-state pressure reveals a difference between gamma and alpha radiolysis.

Steady state was not reached with alpha radiolysis because of an increase in the efficiency of the H_2 production reaction and a decrease in that for the H_2 removal reaction. Gas composition at the end of the long-term test was 62% H_2 , 32% O_2 , and 6% N_2 . The respective partial pressures before and after the test showed that N_2 did not change, and O_2 and H_2 were produced in the ratio of 0.5 to 1. Alpha radiolysis decomposed water in the concrete to stoichiometric quantities of H_2 and O_2 . The reason for less than a stoichiometric amount of O_2 being produced in the other tests is not known.

FIGURE 13. Pressure from Long-Term Alpha Radiolysis of Concrete Containing Fe-Mn Simulated SRP Waste

RADIATION DOSES TO CONCRETE FROM SRP WASTE DURING LONG-TERM STORAGE

Principal sources of radiation in SRP waste in concrete waste forms for long-term storage will be the fission products ^{90}Sr and ^{137}Cs and the transuranic isotopes ^{238}Pu and ^{239}Pu .¹ Based on data for the conceptual waste solidification process, initial dose rates to the forms will be 5.4×10^4 rads/hr for beta-gamma radiation and only 300 rads/hr for alpha particles. As the isotopes decay, these dose rates decrease (Figure 14). After about 700 years when >99% of the ^{90}Sr , ^{137}Cs , and ^{238}Pu have decayed, the dose rate is only about 7 rads/hr, mainly due to ^{239}Pu . This dose rate corresponds to 630 nCi of ^{239}Pu /g of concrete waste form. Accumulated doses to the forms are shown in Figure 15. The final beta-gamma dose from ^{90}Sr and ^{137}Cs is about 100 times larger than the alpha dose from ^{238}Pu and ^{239}Pu .

FIGURE 14. Calculated Dose Rates in Concrete Containing Radioactive SRP Waste

FIGURE 15. Calculated Doses in Concrete Containing Radioactive SRP Waste

Nuclear properties of the principal radioactive isotopes irradiating the concrete wastes are shown in Table 7. ^{90}Sr and ^{137}Cs are in secular equilibrium with their beta decay products ^{90}Y and $^{137\text{m}}\text{Ba}$; thus, these isotopes irradiate the concrete at the same rate as their parent isotopes. All of the energy of the alpha and beta particles will be sorbed by the concrete because of the short ranges of these particles (about 0.004 cm). The fraction of gamma ray energy absorbed can be estimated from the equation for energy transmitted from a cylinder by homogeneously distributed radiation sources.¹⁶

TABLE 7

Principal Isotopes Solidified in SRP Concrete Waste¹⁵

Isotope	Half-Life	<u>Decay Heats, w/kilocurie</u>		
		Alpha	Beta	Gamma
⁹⁰ Sr	28 yr	-	1.18	-
⁹⁰ Y	64.2 hr	-	5.59	-
¹³⁷ Cs	26.6 yr	-	1.23	-
^{137m} Ba	2.6 m	-	-	3.61
²³⁸ Pu	88 yr	32.5	-	-
²³⁹ Pu	24,400 yr	31.0	-	-

The concrete forms in the conceptual process are 10 × 2-ft-OD cylinders. The linear absorption coefficient for ^{137m}Ba gamma rays (E = 0.66 MeV) in concrete is estimated to be 0.18/cm.¹⁷ With these values, about 9% of the gamma energy is transmitted; thus, about 91% is absorbed. In the conceptual process, 2 × 10⁸ Ci of ⁹⁰Sr, 2 × 10⁸ Ci of ¹³⁷Cs, 4 × 10⁵ Ci of ²³⁸Pu, and 10⁴ Ci of ²³⁹Pu will be solidified in 1.7 × 10⁴ tons of concrete. The initial dose rate from a specific isotope is given by

$$I_0 = \frac{(Ci)_0 (H) (K)}{M} \quad (1)$$

where

I_0 = the initial rate in rads/hr

$(Ci)_0$ = the curies of the isotope

H = its decay heat in watts/Ci

M = the mass of concrete in g

K = a conversion factor, 2.8×10^{-9} (rads/hr)/(watt/g)

Because of radioactive decay, the initial dose rate decreases according to the equation

$$I = I_0 e^{-\lambda t} \quad (2)$$

where λ is the decay constant ($0.693/t_{1/2}$) for the isotope being considered. Integration of this equation gives the dose D as a function of time.

$$D = \frac{I_0}{\lambda} (1 - e^{-\lambda t}) \quad (3)$$

To calculate the results in Figures 14 and 15, all of the gamma energy was assumed to be absorbed.

MEASURED PRESSURIZATION IN CONTAINERS OF CONCRETE AND SRP WASTE

Samples of concrete containing actual SRP waste had been prepared for another program⁵ in which other properties of concrete as a waste solidification matrix were evaluated. To measure radiolytic pressurization, two of these samples were sealed in containers that had attached pressure gages. The pressure was monitored for about 1 year. Results (Figure 16) were completely consistent with those expected from low-dose rate gamma radiolysis of concrete containing simulated SRP waste. The pressure initially decreased to less than atmospheric and then increased. In one test, a steady-state pressure of 7 psi was achieved.

FIGURE 16. Pressure from Concrete Containing Radioactive SRP Waste

The dose rate from the radioactive isotopes in these samples was calculated by methods described in the previous section. The result was 3×10^4 rads/hr. At this dose rate, a steady-state pressure from 4 to 20 psi is indicated by Figure 5. The observed steady-state pressure of 7 psi is within the 4 to 20 psi range. This agreement supports the conclusion that steady-state pressures from gamma radiolysis of concrete containing simulated waste can be used to estimate steady-state pressures that will occur in containers of concrete and actual SRP waste.

As indicated in Figure 14, one of the gages indicated that initially the pressure decreased to less than atmospheric. Previous results indicated that this decrease in pressure was caused by O_2 depletion. Although the other gage could not measure pressures less than atmospheric, evidence for such a decrease is indicated by extrapolation of the curve to zero time. Both containers had 165 g of concrete; therefore, the difference between pressurization rates in the two systems was due to differing void volumes in the containers and pressure gages. After about 1 year, both containers leaked, possibly because of radiation damage to a gasket below the pressure gage.

The two concrete samples contained 37.5 wt % of washed, dried wastes from SRP waste tank 15. Also, 2.5 wt % ^{137}Cs -loaded zeolite from removal of ^{137}Cs from the waste supernate was present.⁵ Major components of this waste are listed in Table 8. The ^{137}Cs content of the zeolite was 45 mCi/g,⁴ and the water-to-cement ratio of the concrete was 0.8.⁵ The beta dose rate, calculated from the ^{90}Sr , ^{144}Ce , and ^{137}Cs content was 3×10^4 rads/hr. The alpha-dose rate was only 0.04×10^4 rads/hr. The most significant alpha emitter was assumed to be ^{238}Pu . The gamma-dose rate was negligible because of the small amount of ^{137}Cs present and the small size of the samples (1 inch OD $\times$ 5 inches tall).

TABLE 8

Major Components in Washed, Dried Tank 15 Waste¹⁵

<i>Chemical Composition</i>		<i>Radionuclide Content</i>	
<i>Element</i>	<i>Wt %</i>	<i>Isotope</i>	<i>mCi/g</i>
Al	33.5	⁹⁰ Sr	25.6
Fe	3.1	¹⁴⁴ Ce	16.9
Mn	2.3	¹⁰⁶ Ru	1.7
Na	1.2	¹²⁵ Sb	1.3
Hg	0.9	¹⁵⁴ Eu	1.2
U	0.9	Gross Alpha	0.14
NO ₃ ⁻	5.0		
NO ₂ ⁻	0.04		

CALCULATED PRESSURIZATION IN CONTAINERS OF CONCRETE AND SRP WASTE DURING LONG-TERM STORAGE

To estimate the long-term pressurization in sealed containers of concrete and SRP waste, data from gamma and alpha radiolysis tests of concrete containing simulated wastes were used. The gases H₂, O₂, and N₂O produced by radiolysis and He produced by neutralization of alpha particles were considered.

H₂ and O₂ Production

During the time period when the beta and gamma dose rate from ⁹⁰Sr and ¹³⁷Cs is larger than the alpha dose rate from ²³⁹Pu and ²³⁸Pu, the H₂ pressure will be a steady-state value between 8 and 28 psi; the O₂ pressure will decrease to almost zero. The range for the H₂ pressure is based on extrapolation of data in Figure 6 to 5.4×10^4 rads/hr, the combined beta-gamma dose rate calculated for the concrete. This time period is about 300 years. After ⁹⁰Sr and ¹³⁷Cs decay, ²³⁸Pu and ²³⁹Pu alpha radiolysis will become dominant; and the H₂ and O₂ pressures will increase. The H₂ pressure will increase twice as fast as the O₂. These increases will be nearly linear, to at least 200 psig, and are shown in the solid lines in Figure 17. If the increases continue linearly until the ²³⁹Pu completely decays (in about 2×10^5 years). The final pressures in conceptual waste containers (2 × 10 feet tall with 10% free volume) will be 1400 psi for H₂ and 700 psi for O₂. These increases are shown in the dashed line in Figure 17. Estimates of pressures as a function of storage time are shown in Figure 17.

FIGURE 17. Estimate of Long-Term Pressurization from Concrete Containing Radioactive SRP Waste

- Calculated from $G(\text{H}_2) = 0.21$ molecules/100 eV and $G(\text{O}_2) = 0.1$ molecules/100 eV for alpha radiolysis
- Calculated, assuming $G(\text{H}_2)$ and $G(\text{O}_2)$ for alpha radiolysis independent of H_2 or O_2 pressure

The H_2 and O_2 pressures in the containers from alpha radiolysis were calculated by using the ideal gas law, the alpha radiolysis dose, and the value for the number of molecules of H_2 or O_2 produced per unit energy absorbed by the concrete. This latter quantity in terms of 100 eV of energy absorbed is termed the G-value and was calculated from data in Table 6 and Figures 12 and 13 by using the equation

$$G = \frac{FSVN100}{RTI} \quad (4)$$

Here,

F = fraction of evolved gas that is H₂ or O₂

S = total rate of pressure increase (slopes in Figure 12)
(psi/hr)

V = gas volume (mL)

R = gas constant (1205 psi mL/mole K)

T = temperature (296 K)

N = number (6.02×10^{23} molecules/mole)

I = dose rate (eV/hr)

For the four alpha radiolysis tests, G(H₂) was 0.21 ± 0.01 molecules/100 eV. G(O₂) was 0.1 molecules/100 eV from the long-term radiolysis data in Figure 13. Pressure in the container at any time was calculated from

$$P_t = \frac{G(X)RTMK'D}{100NV} \quad (5)$$

In this case,

V = gas volume in a container (mL)

M = mass of cement in a canister (g)

K' = conversion factor 6.24×10^{13} eV/g rad

D = alpha dose at time t from ²³⁹Pu

The container was assumed to be a 2-foot-ID cylinder, 10 feet tall and to hold 1.5 tons of concrete waste. A 10% free volume was assumed, and the concrete was assumed to have 10% porosity. The dose D was calculated from Equation 3 with I₀ equal to the initial dose rate due to ²³⁹Pu (7 rads/hr). Alpha radiation from ²³⁸Pu remaining after decay of the ⁹⁰Sr and ¹³⁷Cs (in 300 years) contributes only 0.6% of the total dose from ²³⁹Pu and was thus neglected. For this calculation, the rate of pressurization was assumed to be independent of H₂ pressures up to 1400 psi and independent of O₂ pressures up to 700 psi. In the experiments with simulated wastes, pressurization rate was tested to only 200 psig because of hazards associated with working

with high pressures in radioactive-containment glove boxes. Further experiments would be necessary to determine if the pressurization rate was affected by higher H₂ and O₂ pressures.

N₂O Production

The possibility of N₂O production in the containers must also be considered even though it was not produced in all the radiolysis tests. It was detected only in the gamma radiolysis of concrete containing Fe-Mn simulated waste or containing reagent-grade Fe₂O₃ and NO₃⁻ or NO₂⁻ ions. If these ions are present in the SRP waste, N₂O may be produced in the storage containers. However, it will probably not reach appreciable pressures because, as indicated by the gamma radiolysis tests where NO₃⁻ and NO₂⁻ were added and also by the tests with simulated sludge, the H₂ generated can stop N₂O pressurization. Also, N₂O production can be reduced by washing sorbed NO₃⁻ and NO₂⁻ ions from the waste. If no effect of H₂ on N₂O production is assumed, the estimated maximum N₂O pressure in the actual canisters is <60 psi based on the measured NO₃⁻ and NO₂⁻ content of the actual wastes.¹⁴

The maximum N₂O pressure was calculated with Equation 5 by assuming that N₂O production was linear with dose. In this calculation, D was the total beta-gamma dose from decay of ⁹⁰Sr and ¹³⁷Cs. G(N₂O) was calculated with data from the radiolysis at 8.9 × 10⁴ rads/hr of concrete containing Fe₂O₃ with added NO₃⁻ and NO₂⁻ ions (see Table 3 and Figure 7). The equation for calculating G(N₂O) is

$$G(N_2O) = \frac{F_{N_2O} P_f^{VN100}}{RTK'MD_f} \quad (6)$$

where

F = fraction of the gas that is N₂O

P_f = final pressure of the gas

M = mass of concrete (including H₂O) that was irradiated

D_f = dose in rads at the end of radiolysis

For the test with 5% NO₃⁻ present (see Table 5 and Figure 7), G(N₂O) was 0.001 molecules/100 eV. With the final calculated beta-gamma dose of 1.9 × 10¹⁰ rads for D in Equation 5, a final

pressure of 60 psi is calculated. When 2.5 wt % NO_2^- was present, $G(\text{N}_2\text{O})$ increased significantly to 0.008 molecules/100 eV. In this case, the final calculated N_2O pressure would be about 400 psi. However, the actual NO_2^- content of the waste is much lower; thus, much lower pressures would be predicted. Measured values for NO_2^- are 0.03 to 0.09 wt %; and for NO_3^- , measured values are 0.5 to 5 wt %.¹⁷ Based on these values and the measured effect of NO_2^- on N_2O production (lowering the N_2O content by a factor of 5 lowered the N_2O production rate by a factor of 2.5), a maximum pressure of about 60 psi is predicted. This pressure would occur in a container containing concrete and waste that is 5 wt % NO_3^- and <0.2% NO_2^- . Lower pressures would be generated with waste of lower NO_3^- and NO_2^- content.

He Production

Helium will also form in the containers from neutralization of alpha particles from ^{238}Pu and ^{239}Pu . Because the amounts of these isotopes are small, the He pressure after decay of the $^{238},^{239}\text{Pu}$ will only be 0.2 psi and thus negligible.

Helium pressurization in a canister was calculated from the initial ^{238}Pu and ^{239}Pu content (29 Ci for ^{238}Pu and 1 Ci for ^{239}Pu) and the ideal gas law.

MECHANISM FOR RADIOLYTIC GAS PRODUCTION

Almost all the data from this study are consistent with the free radical mechanism for radiolytic decomposition of water developed from many studies on the radiolysis of liquid water.¹⁸ This mechanism can qualitatively explain H_2 production and O_2 consumption; attainment of an equilibrium pressure and its dose rate dependence, the effect of added NO_3^- ions or organic set retarders, and the differences between gamma and alpha radiolysis.

In this mechanism, the radiation interacts with water in concrete and produces H atoms and OH radicals by excitation and dissociation or by ionization followed by neutralization. These reactions are

There is no reason to assume that these reactions cannot occur when the water molecules are incorporated into concrete, a rigid metal oxide framework. Once formed, the H atoms and OH radicals can migrate until they react with other radicals to form H₂ and H₂O₂, or water.

Production of H₂O₂ by radiolysis was indicated by positive tests obtained from treating irradiated samples of neat cement and of concrete containing Fe₂O₃ or Fe-Al waste with reagents sensitive to H₂O₂.¹⁹ These reagents were a neutral solution of Fe(Cl)₃-Fe(CN)₄⁻ and an acidic solution of KI containing stabilized starch.

The H and OH radicals are also capable of reactions with sorbed stable molecules or ions.

Reaction 5 accounts for H₂ production, and Reaction 11 accounts for O₂ consumption. The HO₂ radicals react as follows:

Reaction 12 accounts for NO₃⁻ lowering the rate of H₂ production. Reaction 8 accounts for the steady-state H₂ pressures. Once the H₂ pressure is such that the rates of 5 and 8 are equal, steady-state equilibrium is attained.

An experiment was performed to test the hypothesis that Reaction 8 is significant in affecting the steady state. A concrete containing 7 wt % Br⁻ was prepared by adding NaBr solution to the cement. This sample and one not containing Br⁻ were irradiated at 1.4 × 10⁷ rads/hr in a ⁶⁰Co source. Bromide was added to scavenge OH radicals.

This reaction lowers the rate of Reaction 8 and thus, steady state should not be achieved when Br^- ions were present. As shown in Figure 18, steady state was not achieved, indicating that Reaction 8 is significant in causing the steady state. At the end of the tests, gas compositions were 79% H_2 , 16% O_2 , and 6% N_2 in the presence of Br^- and 83% H_2 , 2% O_2 , and 16% N_2 in its absence. In the presence of Br^- , O_2 was a product; in the absence of Br^- , O_2 was depleted. O_2 resulted from reduction of Br by HO_2 or H_2O_2 .

Reactions 9 through 12 also affect the steady-state pressure but not as significantly as Reaction 8. The dose-rate effect on the steady-state pressure (Figure 4) results from the dose-rate effect on Reactions 5 and 8. As the dose rate increases, the rates of both reactions increase; however, Reaction 5 increases faster because it is second order with respect to the radical concentration, and Reaction 8 is first order.²⁰ To compensate for the faster increase of Reaction 5, higher H_2 concentrations (or pressures) are necessary.

FIGURE 18. Effect of Bromide Ions on Pressurization from Gamma Radiolysis of Concrete

Reaction 11 accounts for O_2 depletion. This reaction may also occur with organic radicals produced when an organic set retarder is present. Reaction 12 accounts for the lowering of H_2 production by NO_3^- ions. The NO_2 could eventually be reduced to NO_2^- or be reoxidized by OH to HNO_3 . An explanation of the failure of steady state to be achieved at high-dose rates when NO_3^- ions were present is not immediately apparent.

When an organic set retarder is present, H_2 may be formed in a one-step process by radiolysis of the organic molecule.²¹ Also, the organic radical cannot react with H_2 ;²¹ thus, steady state is not achieved by pressurizing the system with H_2 . However, no immediate explanation of why steady state was achieved at high-dose rates is evident (Figure 12). Perhaps a secondary product formed by the large doses in this test caused steady state.

Differences between alpha and gamma radiolysis result from differences in the spatial distribution of the H and OH radicals formed by the two types of radiation. Alpha particles lose energy in a much smaller volume than gamma rays; thus, the intermediates are formed much closer together. The efficiencies of Reactions 5, 6, and 7 are therefore increased. Reaction 8 cannot compete sufficiently to cause steady state. Oxygen may result from the reaction of OH with H_2O_2 accumulated in the concrete (Reaction 9). O_2 would then recombine with the HO_2 radicals, and the probability of Reaction 8 would decrease if OH radicals were removed.

REFERENCES

1. R. M. Wallace, H. L. Hull, and R. F. Bradley. *Solid Forms for Savannah River Plant High-Level Waste*. USAEC Report DP-1335, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1973).
2. G. H. Thompson. *Evaluation of Mineralization Processes for SRP Waste*. USERDA Report DP-1389, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1975).
3. J. R. Wiley and R. M. Wallace. *Removal of Cesium from Savannah River Plant Waste Supernate*. USERDA Report DP-1388, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1975).
4. J. R. Wiley. *Decontamination of Savannah River Plant Waste Supernate*. USERDA Report DP-1436, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1976).
5. J. A. Stone. *Separation of SRP Waste Sludge and Supernate*. USERDA Report DP-1441, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1976).
6. J. A. Kelley. *Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste: Nonradioactive and Tracer Studies*. USERDA Report DP-1382, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1975).
7. J. A. Kelley. *Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste Radioactive Studies*. USERDA Report DP-1397, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1975).
8. J. A. Kelley and N. E. Bibler. *Effects of Internal Alpha Radiation on Borosilicate Glass Containing Savannah River Plant Waste*. DOE Report DP-1482, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (to be published).
9. M. L. Hyder. "The Radiolysis of Aqueous Nitrate Solutions." *J. Phys. Chem.* 69 (1965).

10. J. A. Stone and P. D. d'Entremont. *Measurement and Control of Cement Set Times in Waste Solidification*. USERDA Report DP-1404, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1976).
11. H. Fricke and E. J. Hart. *Radiation Dosimetry*, Vol. 2 (2nd Edition), p 185. F. H. Attix and W. C. Roesch, editors. Academic Press, New York, NY (1969).
12. N. E. Bibler. *Calibration of Intense ^{60}Co Gamma Ray Sources at the Savannah River Plant*. USERDA Report DP-1414, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1976).
13. N. E. Bibler and E. G. Orebaugh. *Radiolytic Gas Production from Tritiated Waste Forms, γ - and α -Radiolysis Studies*. USERDA Report DP-1459, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1977).
14. J. A. Stone, J. A. Kelley, and T. S. McMillan. *Sampling and Analyses of SRP High-Level Waste Sludges*. USERDA Report DP-1399, Savannah River Laboratory, E. I. du Pont de Nemours and Company, Aiken, SC (1976).
15. E. D. Arnold. *Handbook of Shielding Requirements and Radiation Characteristics of Isotopic Power Sources for Terrestrial, Marine, and Space Applications*. USAEC Report ORNL-3576, Oak Ridge National Laboratory, Oak Ridge, TN (1964).
16. B. T. Price and K. F. Spinney. *Radiation Shielding*. p 228, Pergamon Press, New York, NY (1957).
17. C. W. J. Wende. *The Computation of Radiation Hazards*. AECD Report 3661, E. I. du Pont de Nemours and Company, Wilmington, DE (1944).
18. I. G. Dragnic' and Z. D. Draganic'. *The Radiation Chemistry of Water*. Academic Press, New York, NY (1971).
19. F. Feigl. *Spot Tests in Inorganic Analysis*. p 354, Elsevier Publishing Company, New York, NY (1958).
20. W. G. Burns and R. Barker. "Dose Rate and Linear Energy Transfer Effects in Radiation Chemistry." *Progress in Reaction Kinetics*, 3, 305 (1965).
21. J. W. T. Spinks and R. J. Woods. *An Introduction to Radiation Chemistry*. p 309, John Wiley and Sons, Inc., New York, NY (1964).