Gas Generation from Hanford Grout Samples

Final Report

by C. D. Jonah, S. Kapoor,
M. S. Matheson, W. A. Mulac, and D. Meisel

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C. D. Jonah, S. Kapoor, M. S. Matheson, W. A. Mulac, and D. Meisel

Chemistry Division

March 1994

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	1
SUMMARY	2
A. INTRODUCTION	3
B. RADIOLYTIC YIELDS OF GASES FROM GROUT	4
1. Introduction	4
2. Experimental	4
a. Radiation Source and Dosimetry	4
b. Sample Preparation and Handling	5
c. Temperature Measurements	8
d. Gas Measurements	11
Gas Chromatography	11
Total Pressure Measurements	11
Mass Spectrometry	12
3. Results and Discussion	12
a. H ₂ Yields from Irradiated Grout Samples	12
b. O ₂ and N ₂ Yields from Irradiated Grout Samples	16
c. N ₂ O Yields from Irradiated Grout Samples	18
d. Yields of CO and CH ₄ from Irradiated Grout Samples	18
e. Total Pressure and Mass Spectrometry Measurements	23
4. Conclusions	24
C. THERMAL GENERATION OF GASES FROM GROUT	27
1. Introduction	27
2. Experimental	27
3. Results and Discussion	27
4. Conclusions	32
D. MECHANISMS OF GAS GENERATION	33
REFERENCES	37
APPENDIX A. Grout Specimens and Their History	38

LIST OF FIGURES

<u>No.</u>		<u>Page</u>
B-1.	Description of the grout samples used for all experiments	6
B-2.	Photographs of sample No. 210 (Appendix A) before and after irradiation. The stamp is included as a color reference. Similar photographs for all samples are cataloged at ANL.....	7
B-3.	Weight (left-hand side) and weight distribution (right-hand side) of the virgin samples (top) and the preirradiated batch (bottom)	9
B-4.	Pyrex cell for grout samples. The same type of cell was used for all experiments except the total pressure measurements	10
B-5.	The amount of H ₂ generated from grout samples following various doses of irradiation at 130 krad/h. Squares are virgin samples and circles are preirradiated samples. Lines are linear least-squares fits to the corresponding data points; a and b are intercepts and slopes, respectively. G values calculated from the slopes using Equation B-1. Top scale is "Equivalent Grout Time" calculated assuming initial dose rate in the waste of 0.3 krad/h and half-life of 30 years	14
B-6.	The amount of H ₂ generated from grout samples following various doses of irradiation at 0.25 (circles) and 0.63 krad/h (triangles). Top part is for virgin samples and bottom for preirradiated samples. All other items are the same as in Figure B-5	15
B-7.	The amount of O ₂ generated from grout samples following various doses of irradiation at 130 (top), 0.63, and 0.25 krad/h (bottom, preirradiated only). Top part shows both virgin and preirradiated samples. All other items are the same as in Figure B-5.....	17
B-8.	The amount of N ₂ generated from virgin and preirradiated grout samples following various doses of irradiation at 130 krad/h. All other items are the same as in Figure B-5	19
B-9.	The amount of N ₂ generated from preirradiated grout samples following various doses of irradiation at 0.63 (top) and 0.25 krad/h (bottom). Note the high limits of error for the slopes of both least-squares fits. All other items are the same as in Figure B-5.....	20
B-10.	The amount of N ₂ O generated from virgin (circles) and preirradiated (triangles) grout samples following various doses of irradiation at 130 krad/h. All other items are the same as in Figure B-5.....	21
B-11.	The amount of CO generated from virgin (circles) and preirradiated (squares) grout samples following various doses of irradiation at 130 krad/h. The dashed line is the fit to the first four data points of the preirradiated samples. Note the positive intercept on the dose axis. All other items are the same as in Figure B-5	22
B-12.	The total amount of gas generated upon irradiation of virgin samples at 130 krad/h. Solid curve shows results from total pressure measurement; circles are the sum of the individual gases measured by gas chromatography	25

C-1.	Thermal release of H ₂ from virgin (empty circles) and preirradiated (solid circles) samples at 90 °C. Solid curve is exponential formation least-squares fit to the data from the virgin samples ($k = 1.7 \times 10^{-3} \text{ h}^{-1}$; $(\text{H}_2)_\infty = 1.8 \times 10^{-7} \text{ mole/g}$)	29
C-2.	Thermal release of N ₂ (circles) and N ₂ O (triangles) from virgin (solid data points) and preirradiated (empty data points) samples at 90 °C. Solid curves are exponential formation least-squares fit to the data from the virgin samples (for N ₂ : $k = 3.5 \times 10^{-3} \text{ h}^{-1}$; $(\text{N}_2)_\infty = 5.5 \times 10^{-7} \text{ mole/g}$; for N ₂ O: $k = 1.7 \times 10^{-3} \text{ h}^{-1}$; $(\text{N}_2\text{O})_\infty = 2.1 \times 10^{-6} \text{ mole/g}$)	30
C-3.	The sum of measured gases released from virgin (squares) and preirradiated (circles) samples at 90 °C. Solid curves are exponential formation least-squares fit to the data; fit parameters are shown in the figure.....	31
D-1.	Hydrogen generation from solution waste simulant. The composition of the solution is similar to the waste simulant that was added to the grout and is given in Table D-1. Irradiation dose rate was 2.54 krad/min	35

LIST OF TABLES

<u>No.</u>		<u>Page</u>
B-1.	Chemical composition of waste simulant solution taken from Ref. 2. Simulates Tank 102-AP waste; concentrations are as analyzed.....	6
B-2.	Yields of gases generated by radiolysis of the grout samples.....	16
B-3.	Mass spectrometric results for irradiated grout samples. All irradiations performed at a dose rate of 130 krad/h	26
C-1.	Mass spectrometric results for grout samples aged at 90 °C.....	32
D-1.	Test solution used for comparison with yields of H ₂ from grout samples (compare with Table B-1).....	33
D-2.	Comparison of yields of gases from grout and various waste simulants	36
AA-1.	Log of virgin grout sample history.....	39
AA-2.	Gases measured from virgin grout samples following irradiation or thermal aging	42
AB-1.	Log of preirradiated grout sample history	44
AB-2.	Gases measured from preirradiated grout samples following irradiation or thermal aging. Specimens labeled with a letter (a or b) were cut in half (i.e., 2" sample length) ...	47

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ABSTRACT

The radiolytic yields of H_2 , N_2 , O_2 , N_2O , and CO from two batches of WHC-supplied samples of grouted simulated waste have been γ irradiated at several dose rates (0.025, 0.63 and 130 krad/h for H_2 and 130 krad/h for all other gases). In one batch, the liquid waste simulant that was added to the grout included the original components that were added to Tank 102-AP (labeled "virgin" waste). The second batch included a similar liquid waste simulant that was preirradiated to 35 Mrad prior to incorporation into the grout. It is believed that the preirradiated samples more closely represent radioactive waste that was stored in the tank for several years. The lowest dose rate corresponds approximately to that expected in the grout; with the high dose rate, doses equivalent to about 85 years storage in grout vaults were achieved.

Most of the results on the batch of virgin samples have been reported recently (Report ANL 93/42). Here we report the results from the batch of preirradiated grout samples and compare the results from the two batches. The radiolytic yields of H_2 and N_2 are lower in the preirradiated than in the virgin grout; at 130 krad/hr ($G(H_2)_{(preirrad.)} = 0.041$ vs. $G(H_2)_{(virgin)} = 0.056$, and $G(N_2)_{(preirrad.)} = 0.058$ vs. $G(N_2)_{(virgin)} = 0.12$. On the other hand $G(O_2)$ is higher in the preirradiated samples: 0.078 vs. 0.026. The yield of nitrous oxide is essentially the same, $G(N_2O) \cong 0.010$, in both. The yields measured from both batches are significantly higher than previously reported values.

At 90 °C similar amounts of H_2 were generated thermally from both batches of grout, whereas the total amounts of N_2 and N_2O were larger for the preirradiated than for the virgin grout samples. At lower temperatures the rate of generation was hardly measurable. Mass spectrometric analysis suggests that NO is thermally (but not radiolytically) released from the grout samples.

SUMMARY

For long-term storage, the low-level radioactive liquid wastes in the tanks at Hanford can be blended with cement and other solids to form grout. Consequently, the rates of radiolytic and thermal generation of gases in the grout are of interest. For the experiments described here, WHC supplied two batches of samples of grout incorporating simulated waste. For the first batch (virgin), grout incorporating non-preirradiated simulated waste, the results were recently presented in an interim report.¹ For the second batch (preirradiated), the simulated waste solution was irradiated to 35 Mrad before it was mixed into the grout. In this final report we present our recent data on the preirradiated grout samples and compare these results with those for the virgin samples. The preirradiation of the samples was designed to simulate the consequences of storage of the waste in the tank for a period of several years. We have measured the G values (molecules of gas produced/100 eV absorbed) at 0.25 and 0.63 krad/hr for H₂, and at 130 krad/hr for H₂, N₂, O₂, CO, CH₄, and N₂O. The lowest dose rate is about that expected in the actual grout in the field, whereas the highest dose rate provides doses equivalent to more than 80 years storage in the grout.

The yield of H₂ at 0.25 krad/hr is ~70% that at 130 krad/hr for both virgin and preirradiated samples, a small change for such a large increase in dose rates. The G values measured at 130 krad/hr are: for virgin samples, $G(\text{H}_2)_v = 0.056$, $G(\text{N}_2)_v = 0.12$, $G(\text{O}_2)_v = 0.026$, $G(\text{N}_2\text{O})_v = 0.011$, $G(\text{CO})_v = 0.0042$, and $G(\text{CH}_4)_v \leq 1 \times 10^{-5}$; for preirradiated samples, $G(\text{H}_2)_p = 0.041$, $G(\text{N}_2)_p = 0.058$, $G(\text{O}_2)_p = 0.078$, $G(\text{N}_2\text{O})_p = 0.010$, $G(\text{CO})_p \leq 0.0028$, $G(\text{CH}_4)_p \leq 1 \times 10^{-5}$. Thus, $G(\text{H}_2)$ decreases about 25%, $G(\text{N}_2)$ decreases about 50%, whereas $G(\text{O}_2)$ increases about threefold, and $G(\text{N}_2\text{O})$ does not change following the preirradiation of the waste simulant. These differences can be rationalized based on the assumption (experimentally verified elsewhere²) that the concentration of organic solutes has decreased, and nitrite increased, upon preirradiation. Organics are required for the production of N₂ + N₂O; they inhibit O₂ production and they contribute to H₂ generation. Since catalysts may be required in the grout vault sump, to reduce H₂ and N₂O to acceptable levels, special effort was made to determine CO yields. An induction period in the production of CO for both batches of samples, and an actual decrease in yield above about 60 Mrad for the preirradiated samples suggest that CO is a secondary radiolytic product, and that CO eventually is also destroyed radiolytically.

Total pressure and mass spectrometry were used to show that no significant gas had been missed in the chromatographic results. The sum of the chromatographically determined yields (H₂, N₂, O₂, N₂O, and CO) agreed with the total pressure up to 50 Mrad for the virgin samples. Deviation at higher doses may be due to an accumulation of errors. Both the total pressure and the sum of rates of gas generation decreased above 60 Mrad. The mass spectrometric measurement found no unidentified gas.

Thermal rates of gas generation were also tested in the range 24-90 °C as the temperature of the grout may be higher than the ambient. Only at 90 °C were small amounts of gases definitely generated. For the virgin samples, the H₂, N₂, and N₂O yields at this temperature increased and then leveled off according to an exponential equation. For the preirradiated samples, the thermal yield of H₂ was about the same as for the virgin samples, whereas the N₂ and N₂O yields were greater in the preirradiated grout. An interfering product prevented measurement of O₂ in the thermal experiments and mass spectrometry suggests that NO is this product.

A. INTRODUCTION

For long-term storage, low-level radioactive liquid wastes that are now stored in tanks at Hanford could be mixed with dry ingredients to form a cementitious solid, commonly called grout. The radiolysis in the grout is almost entirely due to γ and β emitters, which are accurately simulated by ^{60}Co γ sources. This radiolysis may generate a mixture of gases of various adverse effects (flammability, environmental impact concerns, catalyst poisoning, etc.). Earlier work on simulated cemented wastes has shown that several gases are indeed produced radiolytically.³⁻⁵

Two batches of nonradioactive waste in grout samples were supplied to us by WHC. In the first batch, nonradioactive waste simulating the composition of the waste that was fed into Tank 102-AP was incorporated in the grout samples. Our results on these virgin samples were reported recently¹ and the present report is an extension of the previous one. During storage in the tanks, radiolysis has degraded the organic chelators and the initial composition of the waste has changed. Therefore, the second batch included the same simulated waste solution but it was preirradiated to 35 Mrad before mixing with the grout. These preirradiated samples should more closely represent Tank 102-AP wastes at present. We report here the results from that second batch and compare them to the earlier reported data on the virgin samples. To avoid confusion, we emphasize again that preirradiation refers to the liquid waste simulant only and not to the grout itself.

From the well-documented mechanistic understanding of the effects of ionizing radiation on aqueous solutions⁶ and, in particular, on waste simulants,⁷ the major two mechanisms for the radiolytic generation of H_2 are direct radiolysis of water and H-atom abstraction from organic solute in the solution. High concentrations of nitrate and nitrite reduce the generation of molecular H_2 via scavenging its precursors, H and e_{aq}^- . Commonly, in waste solutions the concentrations of these two scavengers are very high, so no additional scavenger could reduce significantly the yield of hydrogen. However, in the present simulant NO_x concentrations are relatively low. Other frequently found gases from the radiolysis of waste simulants are N_2O and O_2 . Organic compounds are required for the radiolytic generation of the former whereas they reduce the latter.⁷ We apply the same principles to the grouted waste simulant. However, we expect the solid grout components to modify the yields. Sequestering of water in pores, the presence of different materials, and the altered distribution of waste components between solid and aqueous phases could all alter the radiolytic yields.

For preirradiated grout we find that $G(\text{H}_2)$ (the yield in units of molecules per 100 eV) is about 25% lower, $G(\text{N}_2)$ is about 50% lower, $G(\text{O}_2)$ is about threefold higher than for the non-preirradiated samples, and $G(\text{N}_2\text{O})$ is about the same for both batches. Most of these results can be rationalized assuming partial destruction of the organic components during preirradiation. The high yield of H_2 in both batches is difficult to rationalize without invoking substantial change in reactivity patterns or migration of charge carriers from the solid to the water in the grout. Total gas yields, and individual yields of the various gases, measured in this study for both batches are significantly larger than previously reported.⁵ The composition of organics used by Friedman et al.⁵ is not known (probably only EDTA) so their lower yields might be due the different composition of organic components. It might also arise from the higher dose used in that study.

B. RADIOLYTIC YIELDS OF GASES FROM GROUT

1. INTRODUCTION

Determination of the radiolytic yields from the grout samples comprised the bulk of this study. Yields were determined at three dose rates, 0.25, 0.63, and 130 krad h⁻¹. The lowest dose rate reflects the dose rate expected in the waste-containing grout; the intermediate dose rate was studied to examine whether the yields depend on the dose rate in this low-dose-rate regime. The high dose rate was utilized in order to achieve the high doses expected during many years of storage. The highest dose utilized reached approximately 100 Mrad, equivalent to approximately 100 years of irradiation with ¹³⁷Cs at an initial dose rate of 0.3 krad/h.

Two batches of grout samples were tested. Most of the results from the first batch of virgin samples were reported previously.¹ The bulk of the new results comes from a batch of grout samples that was prepared with preirradiated waste simulant. The major difference between the two batches is the yield of oxygen; G(O₂) is significantly higher for the latter batch. We find little dose-rate effect, if any, on the yields of H₂. In both batches CO seems to require an induction period of irradiation before its generation starts but in the preirradiated samples it is also destroyed at high doses. The initial yield of CO in the "virgin" samples is about 50% higher than in the preirradiated ones. At a dose of 100 Mrad the CO is already being destroyed in the preirradiated samples and thus it is 4-fold lower than in the "virgin" batch of sample at that dose.

Three independent types of measurements were performed on the two batches. Individual yields of H₂, N₂, O₂, N₂O, CO, and CH₄ were determined by gas chromatography. The total pressure generated during the irradiation was measured in a specially designed cell linked to a pressure transducer. For the batch where this measurement was successful, the total pressure measurement agreed with the sum of the individual gas measurements within experimental error. A third type of measurement was designed to ensure that no major gas component escapes determination by the gas chromatographic procedure. For this test, the composition of the gases accumulated above the irradiated grout samples was determined by mass spectrometry. Except for NO in high-temperature thermal experiments, no unaccounted major component was observed in these measurements.

All of the data accumulated in these experiments are summarized in Appendix A. The yields of the individual gases are summarized in Table B-2.

2. Experimental

a. Radiation Source and Dosimetry

Irradiations were performed in a ⁶⁰Co γ-source chamber. Dosimetry was done using the "Fricke dosimeter".⁶ This chemical dosimeter contains 1 mM FeSO₄ in an air-saturated, 1 mM NaCl, 0.8 N H₂SO₄ solution. The test tubes containing the dosimeter solutions were positioned in the same locations that the grout samples were later placed. The product, Fe(III), was determined spectrophotometrically at 302 nm using $\epsilon = 2167 \text{ M}^{-1} \text{ cm}^{-1}$ at 23 °C and G(Fe(III)) = 15.6 molecules per 100 eV. The various dose rates were established by altering the distance from the source and by placing lead shielding between the sample and the source.

The gas measured from a sample (in units of μmole per sample and the dose in units of rad) can be converted to yields (commonly labeled G values, quoted in units of molecules per 100 eV) using equation B-1.

$$G \left(\frac{\text{molecules}}{100 \text{ eV}} \right) = \frac{\mu\text{mole from sample}}{(\text{weight of sample in g}) \cdot (\text{dose in rad})} \cdot 10^{-6} \frac{\text{mole}}{\mu\text{mole}} \cdot 1.602 \cdot 10^{-14} \frac{\text{rad}}{(\text{eV/g})} \cdot 6.02 \cdot 10^{23} \frac{\text{molecules}}{\text{mole}} \cdot 100 \frac{\text{eV}}{(100 \text{ eV})} ,$$

that is,

$$G \left(\frac{\text{molecules}}{100 \text{ eV}} \right) = \frac{\mu\text{mole from sample}}{(\text{weight of sample in g}) \cdot (\text{dose in rad})} \cdot 9.65 \cdot 10^5 . \quad (\text{B-1})$$

Whenever possible, the yield was determined from a series of measurements of the amount of gas at various doses and a constant dose rate (e.g., Figures B-5 through B-11). The amounts of gas were plotted vs. the dose; the slopes of these plots can be equated with the first term in the right-hand side of equation B-1. The intercept and slope (labeled as "a" and "b", respectively) of the linear least-square fits are given in the figures along with their probable uncertainties. The units for these parameters are identical to the units used for the axes in the corresponding figure. For example, in Figure B-5 for the virgin samples the intercept is $a = (2.6 \pm 1.7) \times 10^{-7} \text{ mole g}^{-1}$ and the slope is $(5.8 \pm 0.4) \times 10^{-7} \text{ mole g}^{-1} \text{ Mrad}^{-1}$.

b. Sample Preparation and Handling

Grout samples were supplied by WHC in two batches. The chemical composition of the waste liquid simulant, as provided by WHC, is given in Table B-1. These samples are labeled "virgin samples" for brevity and were the focus of an earlier report.¹ The second batch included the same waste simulant except that the liquid simulant was irradiated at WHC to 35 Mrad prior to incorporation in the grout. Thus, it is believed that this batch better simulates the liquid waste that will be incorporated in the grout because it accounts for some of the radiolytic degradation that the original waste undergoes during its storage in the tanks. This batch is labeled "preirradiated" in the following discussion. It has been proposed that most of the original chelators (EDTA, HEDTA, but not citrate) will be radiolytically degraded following these high doses of irradiation.⁷ Indeed, the chemical composition of the preirradiated waste simulant has been recently determined and it was shown that the original EDTA, HEDTA and glycolate have been largely degraded; formate was identified as the major degradation product.²

Details of the procedure that the samples of both batches underwent upon arrival at ANL have been given earlier.¹ This procedure was designed to minimize the variability among the samples that were eventually used in the tests. Briefly, the center parts of the cylindrical samples (~ 0.5 " diameter and 4" long out of the original 6" long rods) were used in all experiments. The cut parts of the grout cylinders are shown in Figure B-1. All the top ends and all the bottom ends were saved for further examination if needed. The two end pieces are visibly different from each other; the pieces that came from the bottom end appear grayish throughout their cross-section. The top pieces often had an off-white tint at their tips, probably due to some lighter material rising to the top before the grout was completely cured. The two $3/8$ " edge pieces appear similar to one another. Photographs of these pieces, and of the central 4" cylinder, were taken for all samples and are available at ANL. Photographs of all samples were taken after the irradiation as well. Figure B-2 shows photographs of the same sample, arbitrarily chosen, before and after the irradiation. During

the radiolytic experiments with the first batch it was found that the total amount of gases generated following radiolysis to high doses is higher than expected. Under these conditions the amount of gases that is pressurized into the Van Slyke apparatus is inconveniently high (>1 atm.) and requires high mercury levels when transferring the gases into the gas chromatograph. Therefore, some of the samples for the second batch were cut in half (2" long). To maintain the same dosimetry, a glass rod of the same dimensions as the missing grout length was added into the irradiation cells. These specimens are labeled with a letter a or b in the tables of Appendix A. Six samples were transferred to the Center for Cement at the University of Illinois, Urbana, as logged in Table AA-1 of Appendix A.

Table B-1. Chemical composition of waste simulant solution taken from Ref. 2. Simulates Tank 102-AP waste; concentrations are as analyzed.

Ion	Concentration mole L ⁻¹	Ion	Concentration mole L ⁻¹
Al	0.2882	Cl ⁻	0.0820
Bi	0.0006	CO ₃ ²⁻	0.3352
Cr	0.0098	NO ₂ ⁻	0.5360
K	0.0220	NO ₃ ⁻	0.9747
Na	6.687	OH ⁻	0.4247
NH ₄ ⁺	0.0338	PO ₄ ³⁻	0.1028
Pb	0.0018	SO ₄ ²⁻	0.0269
TOC	0.2317		
Species in TOC (as prepared)			
Na ₃ citrate	0.0110	Na ₃ HEDTA	0.0136
Na ₄ EDTA	0.0034	Na glycolate	0.0085

Figure B-1. Description of the grout samples used for all experiments.

Sample Number	Date opened	Pre-expt photo	Expt. started	Expt. ended	Post-expt photo
210	9/17/93	9/21/93	9/24/93	11/1/93	11/19/93

Post - experiment Photo

*Chemistry Division
Argonne National Laboratory*

[Redacted]

[Redacted]

29

Figure B-2. Photographs of sample No. 210 (Appendix A) before and after the irradiation. The stamp is included as a color reference. Similar photographs for all samples are cataloged at ANL.

All samples were marked with sample numbers, weighed, photographed, stored in test tubes, and placed in a chamber maintained at 100% humidity at 23 °C until taken for the experiment. Appendix A logs the grout samples and their history. The weight and weight distribution of the samples of the two batches, virgin and preirradiated samples, are shown in Figure B-3. As Figure B-3 shows, the average weight of the preirradiated batch is approximately 1 g smaller than of the virgin batch. Measurement of the diameter of the samples yielded 13.25 ± 0.18 and 12.91 ± 0.41 mm for the virgin and preirradiated batches of samples respectively. The average effective densities then were 1.54 ± 0.12 and 1.54 ± 0.19 g cm⁻³ for the two batches respectively. The larger standard deviation for the latter batch reflects the larger variability of the preirradiated batch that was also visibly evident. The variability in weight of both batches was larger than the that of the dimensions. The weight distributions of both batches show a small subgroup of samples that are ca. 2 g lighter than the average. There are also clear visual variations among the samples, as discussed in the results section, that also affect reproducibility of the experimental results.

All samples were placed in the cells shown in Figure B-4. A piece of glass, approximately 3 cm long, was placed below the grout sample, and the end of the sample tube was sealed. Either nitrogen or argon was used during the glassblowing to avoid the addition of moisture to the sample. The glass slug was utilized to minimize the free volume of the cell and keep the end of the grout specimen away from the flame during seal-off. The procedure for seal-off is also depicted in Figure B-4.

Prior to the radiolytic or thermal experiments, the samples were evacuated on a glass-vacuum line. Only rough vacuum (approximately 1 torr) was used to evacuate the sample because the high moisture content of the sample prevented evacuation to a better vacuum. Water is lost from the grout samples slowly and the total weight loss depends on the pumping time. Furthermore, the amount of air that remains trapped in the grout depends on the time of pumping. This poses a significant problem in determining yields of N₂ and O₂. Therefore, the procedure for seal-off and evacuation was standardized to minimize sample-to-sample variations. The sequence that was used for all samples was then as follows: five samples were placed on the vacuum line and evacuated for one minute. The samples were then left to equilibrate for five minutes under vacuum but without pumping. They were again evacuated for one minute and then pumped-on individually as the vessels were sealed off (approximately 30 sec). Despite these efforts, some sample-to-sample variations must be expected from the pre-evacuation.

c. Temperature Measurements

Temperature rise, due to the absorption of the radiation energy by the grout samples, may profoundly affect the determination of yields of gases and the interpretation of the results. In particular, it may reflux water out of the grout and essentially lead to radiolysis of condensed water rather than grout. Although the heat load is not large (approximately 0.36 watt per kilogram at 130 krad/h), the loss of heat to the environment is difficult to evaluate because of uncertainties of the thermal contact between the grout sample and the evacuated Pyrex cell. Thus, the temperature rise of a grout sample under the radiolytic conditions was measured. Details of this measurement will not be repeated here (see Ref. 1); it was concluded that the temperature rise at 130 krad/h is ~2 °C above the ambient at the irradiation chamber, which was maintained at 28 °C. The half-life for warming is approximately one-half hour, and the profile is consistent with an exponential temperature rise; the temperature reaches a plateau level after approximately three hours and then remains constant.

Figure B-3. Weight (left-hand side) and weight distribution (right-hand side) of the virgin samples (top) and the preirradiated batch (bottom)

Figure B-4. Pyrex cell for grout samples. The same type of cell was used for all experiments except the total pressure measurements.

d. Gas Measurements

Gas Chromatography. For gas measurement, the cell shown in Figure B-4 was mounted on a Van Slyke apparatus. The Van Slyke is essentially a mercury gas pump utilized to transfer gases from the cell to the gas chromatograph. A description of the apparatus and its interface to the gas chromatograph can be found elsewhere.⁷ A small steel bar was inserted into the region above the break-seal, which was then evacuated. The break-seal was then broken using a magnet to manipulate the steel bar and any gas that was formed in the cell was removed and transferred to a gas chromatograph. Gases were repeatedly extracted from each sample until the ratio of gases from one extraction to the next was approximately constant. This ratio was then used to calculate the total amount of gas remaining in the sample, assuming a geometric series. Each extraction lasted approximately 10 minutes. Gas trapped within the grout (in pores or adsorbed on surfaces) may not be completely released during this time. Therefore, the reported yields may be considered to be lower limits.

Two gas chromatographs were used for these experiments (an Infotronics Model 15 C3 and a Varian Aerograph model 920); both were calibrated daily with authentic gas samples. Hydrogen, oxygen, and nitrogen were all determined in a single analysis by using molecular sieve 5 Å columns at ambient temperature. N₂O and CO (together with CH₄) were determined in separate experiments using a molecular sieve 13X column; the column temperature was 175 °C for N₂O determinations and 38 °C for CO and CH₄ determinations. The signal from the gas chromatographs was integrated using a Spectra Physics Chromjet integrator for H₂, O₂, and N₂ and a Hewlett Packard 3390A integrator for the other gases.

Total Pressure Measurements. The system used to measure the total pressure of the gas as a function of irradiation time has been described in detail.¹ It utilizes a differential pressure transducer (World Precision Instruments PNEU05, solid state, 0-5 psi pressure transducer). It includes two samples, one irradiated whereas the second is shielded from the radiation source and is used as a reference. This differential measurement cancels most of the pressure that results from the vapor pressure of water released from the samples. Furthermore, because both samples are located in the same room, any change in gas pressure due to ambient temperature changes will cancel out. The pressure transducer is connected to a Hewlett Packard digital multimeter (HP 34401A). Data were acquired using a Macintosh computer that was interfaced to the digital multimeter via an RS-232 connection. The differential pressure transducer was calibrated by comparison with a Barytron pressure gauge (MKS 270 capacitance manometer). The pressure as a function of voltage was fit to a cubic equation over the pressure range of ± 400 torr. The dominant terms in this function are the linear terms; the higher order term is of significance only at high pressures. The total pressure in the sample compartment at the end of the irradiation was approximately 250 torr higher than in the reference side. Small drifts and possible leaks in the system were determined before and after the irradiation and corrected for as previously described. The volume of the system was determined using conventional vacuum line techniques. The volume of each compartment of the assembly, and its associated tubing, was approximately 45 ml. The absolute error in the volume determination is less than 5%.

The major interference expected in this measurement is from water vapor pressure that develops above the grout samples. This vapor pressure will change as a function of temperature. The change in vapor pressure upon change in temperature results from two effects, the temperature dependence of the equilibrium water vapor pressure and the direct change of gas pressure with the

change in temperature. In the regime of temperature change relevant to the radiolysis experiments ($\sim 2^\circ\text{C}$ rise in temperature), the former is by far the dominant effect. To demonstrate the effect: the vapor pressure above liquid water (we do not know the vapor pressure above grout but it is somewhat lower than above free water) is 28.35 and 31.82 torr at 28 and 30°C , respectively. Thus, the change in the grout temperature due to the irradiation can lead to 3.5 torr pressure change in the cell, independent of head-space volume. The same temperature change will directly increase the gas pressure by only 0.7% (i.e., $\frac{303}{301}$).

Mass Spectrometry. Mass spectrometry was used primarily to ensure that no major gas product escapes identification. Therefore, it was decided to maximize sensitivity at the expense of accurate quantitative determination of individual gases. Total gas amounts injected into the mass spectrometer were, thus, relatively high, and cross reactions within the instrument were not eliminated. Samples for mass-spectral analysis were irradiated in the same vessels shown in Figure B-4. A differentially pumped 30 cm radius, 90° sector magnetic deflection mass spectrometer from Vg-Micromass (MM3001) of 7500 maximum resolving power and 10 kV maximum accelerating voltage was used for these studies.

3. Results and Discussion

Samples from the two batches, the virgin samples and the preirradiated ones, were visibly different. The most pronounced difference was the larger variability in consistency, tint, and hardness among the preirradiated samples. Of the 122 virgin samples, encased in pipes that arrived at ANL, 90 were opened and are logged in Appendix A. These samples were fairly soft (consistency of slightly damp chalk), uniform green-grayish in color, with white tops (removed during the sample preparation) and relatively uniform smooth surfaces. Only a few of these samples had a pitted appearance, probably a result of trapped gas bubbles. The preirradiated batch included 70 samples, all of which were removed from the HPVC pipes and used as detailed in Table AB-1 of the Appendix. These samples appeared much harder than samples from the previous batch; they adhered more to the plastic pipes, and many had large bubbles of gas entrapped in them. Some of the samples in this batch appeared to have been cast in two different periods of time (i.e., more material was added to a pipe after partial curing had occurred). At any rate, the obvious greater variability among samples of this batch reduced the reproducibility of the results and increased our experimental error significantly.

a. H_2 Yields from Irradiated Grout Samples

The amounts of hydrogen generated from the grout samples, following irradiation at three dose rates and various periods of irradiation (i.e., various doses), have been measured, and the yields have been calculated. The results are shown in Figure B-5 for samples irradiated at a dose rate of 130 krad/h. Samples from both the virgin and preirradiated batches are shown in Figure B-5. Yields were calculated from the slopes of the linear least-square fits of the data points using Equation B-1. The intercepts and slopes of these lines are shown in the figure labeled as a and b, respectively. $G(\text{H}_2)$ from the preirradiated samples is $\sim 25\%$ lower than from the virgin samples. Yields from these, and all other radiolytic experiments, are summarized in Table B-2.

The top scale in Figure B-5 (and the other figures as well) is an "Equivalent Time" scale for grout that would be irradiated with a γ or β source of initial intensity of 0.3 krad/h (typical dose rate for low-level waste) and by a radionuclide of 30 years half-life (for comparison, $\tau_{1/2} = 30.3$

and 28.1 years, for ^{137}Cs and ^{90}Sr , respectively). It was calculated using Equation B-2, which results from the integration of an exponential decay rate law:

$$t = -\frac{1}{k} \cdot \ln\left(1 - \frac{k \cdot D}{N_0}\right), \quad (\text{B-2})$$

where N_0 is the initial dose rate ($0.3 \text{ krad h}^{-1} = 2.628 \text{ Mrad y}^{-1}$), k is the decay rate constant ($= \frac{\ln 2}{\tau_{1/2}} = 0.023 \text{ y}^{-1}$), and D is the dose accumulated up to time t .

Similar results are presented in Figure B-6 for hydrogen generation from irradiation of the two batches at 0.25 and 0.63 krad/h. The amount of gas produced at these lower dose rates is much smaller than at the higher dose rate, and, therefore, the experimental uncertainty is larger. Furthermore, the results at these small amounts of gas are more sensitive to variations in the grout-gas phase equilibrium and are, thus, less reliable. Any hydrogen that may have remained trapped in the grout will strongly affect the results at low doses. This problem is particularly difficult in the determination of N_2 and O_2 because the samples were all equilibrated in air prior to irradiation. The results of Figures B-5 and B-6 (and summarized in Table B-2) indicate that the yield is somewhat lower at lower dose rates. The dependence, however, is rather weak. Upon ~500-fold reduction in dose rate, the yields decrease to ~65% of its value at the highest dose rate. At higher dose rates, radical-radical reactions are more significant than at lower dose rates. For H_2 generation, this suggests that reaction B-3 is a major contributor at high dose rates.

The main, non- H_2 -generating, competition for H atoms is from nitrite:

The other major contributor to the formation of H_2 is reaction B-5. This reaction will dominate at low dose rates.

This analysis may also rationalize the decreased yield of H_2 for the preirradiated samples. The preirradiation degrades the organic compounds in the waste, some of which are completely mineralized (CO_2 , carbonate, formate or oxalate). It also converts a significant amount of the nitrate to nitrite.² The former reduces the rate of the H_2 -generating reaction B-5, and the latter enhances the rate of the hydrogen-scavenging reaction B-4.

The reasonably good linearity obtained in the results shown in Figures B-5 and B-6 also suggests that the rate of release of hydrogen from the grout is faster than the rate of its generation. If hydrogen would have been retained for periods of time comparable to the time of these experiments (the shortest time was one day for the highest dose rate), then the curve would have developed an upward slope. Also, any retention of hydrogen within the grout would require higher yields than those given in Table B-2. Significantly higher yields would be very difficult to explain (100% water that contains no scavenger will give $G(\text{H}_2) = 0.6$; by comparison the grout contains no more than 20% water and large concentrations of nitrate and nitrite, both efficient H_2 inhibitors).

Figure B-5. The amount of H_2 generated from grout samples following various doses of irradiation at 130 krad/h. Squares are virgin samples and circles are preirradiated samples. Lines are linear least-squares fits to the corresponding data points; a and b are intercepts and slopes, respectively. G values calculated from the slopes using Equation B-1. Top scale is "Equivalent Grout Time" calculated assuming initial dose rate in the waste of 0.3 krad/h and half-life of 30 years.

Figure B-6. The amount of H₂ generated from grout samples following various doses of irradiation at 0.25 (circles) and 0.63 krad/h (triangles). Top part is for virgin samples and bottom for preirradiated samples. All other items are the same as in Figure B-5.

Table B-2. Yields of gases generated by radiolysis of the grout samples.

gas	dose rate krad/hour	virgin samples	preirrad. samples	comments
		G (molecules) 100 eV	G (molecules) 100 eV	
H ₂	130	0.056	0.041	up to ~100 Mrad
	0.63	0.051	(0.024, large error)	up to ~0.6 Mrad
	0.25	0.035	0.028	up to ~0.3 Mrad
N ₂	130	0.12	0.058	up to ~100 Mrad
	0.63	not measurable	(1.06, large error)	up to ~0.6 Mrad
	0.25		(0.96, large error)	up to ~0.3 Mrad
O ₂	130	0.026	0.078	up to ~100 Mrad
	0.63	not measurable	not measurable	up to ~0.6 Mrad
	0.25			up to ~0.3 Mrad
N ₂ O	130	0.011	0.010	up to ~100 Mrad
	0.63			up to ~0.3 Mrad
	0.25	below detection limit ^a	below detection limit ^a	G(N ₂ O) ≤ 0.018 up to ~0.05 Mrad G(N ₂ O) ≤ 0.14
CO	130	0.0042	≤ 0.0028, see Figure B-11	up to ~100 Mrad ^b
CH ₄	130	below detection limit ^c	below detection limit ^c	up to ~100 Mrad G(CH ₄) ≤ 1 × 10 ⁻⁵
ΣX _i	130	0.217	0.190	sum of all gases at 130 krad/h

^a Detection limit is 0.125 μmole N₂O.^b Up to ~100 Mrad for the virgin samples and ~60 Mrad for the preirradiated samples.^c Detection limit is 0.034 μmole CH₄.

The radiolytic yield of H₂ in the virgin grout samples, G(H₂) = 0.056, is lower than the yield we find for the liquid waste simulant (prior to grouting, Figure D-1), G(H₂) = 0.087. Similarly, the yield obtained by Powell² for 102-AP simulant is 0.07, averaged over 35 Mrad. The reduction in yield is smaller than the expected reduction based on simple dilution ratio of the solution in grout. Possible explanations for that are discussed in Section D. As noted above, the original chelators have largely degraded after 35 Mrad dose² so the lower yield for the preirradiated sample is to be expected. The 0.041 yield obtained for the preirradiated samples involve only a small contribution to H₂ generation by reactions (e.g. reaction B-5) of the organics.

b. O₂ and N₂ Yields from Irradiated Grout Samples

The amounts of O₂ that were extracted from the same samples of grout described in the previous section, are shown in Figure B-7. Only the high-dose-rate experiments provide data from which G values could be calculated for both batches. These values are given in Table B-2. At the

Figure B-7. The amount of O₂ generated from grout samples following various doses of irradiation at 130 (top), 0.63, and 0.25 krad/h (bottom, preirradiated only). Top part shows both virgin and preirradiated samples. All other items are the same as in Figure B-5.

lower dose rates (0.63 and 0.25 krad/h), O_2 could be easily measured (see bottom of Figure B-7 for the preirradiated batch). However, the scatter in the data and the absence of a clear increase in the amount of gas upon increasing the irradiation time lead us to believe that these amounts are not generated radiolytically (or thermally). Rather, this behavior indicates that the oxygen originates from air trapped within the grout; it is pertinent to note that the grout is placed under vacuum once it is sealed in the sample cells. Similar observations for O_2 , as well as N_2 , were reported and discussed earlier for the virgin samples batch.

The top part of Figure B-7 shows the yields of oxygen from both the virgin and preirradiated samples following irradiation at the high dose rate. These results represent the most pronounced difference between the preirradiated and virgin samples. $G(O_2)$ for the preirradiated batch is approximately three times larger than for the virgin samples. The increased O_2 yield is expected if the yield of organic radicals (which inhibit the generation of O_2) is reduced in the preirradiated samples due to degradation of the organic component in the simulant.

The situation for the yield of N_2 is reversed. As can be seen in Figure B-8, following irradiation at 130 krad/h, $G(N_2)$ for the virgin samples is twice that for the preirradiated samples.

The mechanism for the generation of N_2 is not clear but it has been shown to be very sensitive to the composition of the irradiated solution. Often the yield of N_2 increases at the expense of N_2O . However, in the present system, the yield of N_2O for both batches is essentially the same. Again, determination of N_2 yields at the lower dose rates and doses is susceptible to a large experimental error (Figure B-9). It was concluded earlier¹ from the results of the virgin samples at low dose rates that although nitrogen is released during the irradiation period, its release is not a result of radiolytic (or thermal) generation but due to the vacuum in the sample cells.

c. N_2O Yields from Irradiated Grout Samples

The sequence of irradiations that was used for the determinations of H_2 was repeated to determine the yield of N_2O . The procedure was identical except for the gas chromatographic details, which were described in Section B-2d. The results from the experiments on both batches are given in Figure B-10 and Table B-2. Both the virgin and preirradiated samples give essentially the same yield, $G(N_2O) = 0.01 \pm 0.002$. Close examination of the data for the preirradiated samples indicates that the amount of N_2O that is generated tends to level off at the high dose limit. Samples from both batches were also tested for the generation of N_2O at the lower dose rates (e.g., see Appendix A); the amounts of N_2O generated were all below the detection limits of the analysis. Upper limits for the G values from these irradiations are shown in Table B-2.

d. Yields of CO and CH_4 from Irradiated Grout Samples

The radiolytic yields of CO have been determined as described above. Figure B-11 shows the amount of CO obtained following various doses of irradiation, all at a dose rate of 130 krad/h. For the virgin samples, a linear dependence on dose is observed. The slope yields $G(CO) = 0.0042$ molecules per 100 eV, approximately 2% of the total gases. However, as is clearly seen in Figure B-11, CO starts to appear only after the samples (both virgin and preirradiated) received approximately 11 Mrad of irradiation. This indicates that CO is a secondary radiolytic product. It is generated by the radiolysis of a radiolytic degradation product. A similar positive intercept is also observed for the preirradiated samples. However, the amount of CO obtained from the preirradiated samples decreases upon continued irradiation above a dose of ~50 Mrad. It is emphasized that the absolute amount of CO, and not just the yield, decreases with increased irradiation. This must mean that CO itself

Figure B-8. The amount of N₂ generated from virgin and preirradiated grout samples following various doses of irradiation at 130 krad/h. All other items are the same as in Figure B-5.

Figure B-9. The amount of N₂ generated from preirradiated grout samples following various doses of irradiation at 0.63 (top) and 0.25 krad/h (bottom). Note the high limits of error for the slopes of both least-squares fits. All other items are the same as in Figure B-5.

Figure B-10. The amount of N_2O generated from virgin (circles) and preirradiated (triangles) grout samples following various doses of irradiation at 130 krad/h. All other items are the same as in Figure B-5.

Figure B-11. The amount of CO generated from virgin (circles) and preirradiated (squares) grout samples following various doses of irradiation at 130 krad/h. The dashed line is the fit to the first four data points of the preirradiated samples. Note the positive intercept on the dose axis. All other items are the same as in Figure B-5.

enters into some reaction that leads to its destruction. This destructive reaction occurs concurrent with the generation reaction and the net result is the amount monitored. It is conceivable that a similar destructive reaction will be observed when the dose delivered to the virgin sample will match the total dose delivered to the preirradiated samples (including the dose of the preirradiation period). This destruction may be irrelevant to the situation in large grout vaults if CO is allowed to rapidly escape the grout. Because of this destruction of CO, the definition of "yield" is not straight-forward. We arbitrarily chose in Figure B-11 and Table B-2 to report the least-squares fit to the first four data points from the preirradiated samples.

During the same sequence of experiments, we also attempted to determine the yield of methane. In all of these experiments on samples from both batches, the amount of methane was below our detection limit. This places an upper limit of $G(\text{CH}_4) \leq 1.1 \times 10^{-5}$ molecules per 100 eV.

e. Total Pressure and Mass Spectrometry Measurements

The yields of the various gases described above were measured individually by gas chromatography. There is no *a priori* reason to believe that these are *all* the gases that are generated by the radiolysis. Two experiments were devised in order to determine whether the gas chromatographic measurements account for all, or a fraction, of the gases generated. One is a mass spectrometric series of experiments, which provides the relative ratio of the various gases. The second approach is to measure the total pressure generated during the irradiation. From the pressure and the volume of the cells, the amount of gases can be determined (assuming an ideal gas behavior). These can then be compared with the sum of the individual gas measurements. The results of both series of experiments are reported below.

Experimental details, calibration procedures, and corrections required for the total pressure measurements were reported recently.¹ Figure B-12 displays the results from the total pressure measurements conducted on virgin samples. Similar experiments on the preirradiated samples failed because of calibration difficulties. Due to time limitations, these experiments could not be repeated. The pressure changes were converted to μmoles of gas using the experimentally determined volume of the cell as described in Section B-2d. Several points may be noted in the results of Figure B-12. First, the amount of gas calculated from the total pressure measurements and the amount of gas calculated from the sum of the individual gas measurements agree to within 10% up to a dose of ~ 80 Mrad. At larger doses (last point in Figure B-12) the deviation is larger; the sum of the individual gases drops much faster than the total pressure measurement. Second, most of the gases are accounted for in the individual gas measurements (N_2 , O_2 , H_2 , N_2O , and CO). The results from the mass spectrometry experiments reveal no unaccounted gaseous product and, therefore, the discrepancy between the two measurements may simply indicate accumulation of experimental scatter in the sum of the individual gases. As can be seen in Figure B-12, both types of measurements show a decrease in the yield of the gases after approximately 60 Mrad of irradiation. The yield is expected to decrease as the composition of the waste in the grout changes with radiolytic degradation. This observation of a decreased yield at high doses may provide an explanation for the discrepancy in H_2 yields between our results and those of Friedman et al.⁵ The lowest dose at which Friedman et al. have determined yields was 134 Mrad (Table 10, Ref. 5). The sum of the yields of the various gases is also given in Table B-2. Although there are significant differences between the virgin and preirradiated samples in the yield of individual gases, the sum of the yields is only 12% smaller for the preirradiated than for the virgin batch.

Mass spectrometry results from irradiated samples of both batches, virgin and preirradiated samples, have been conducted and are summarized in Table B-3. They were intended primarily to search for otherwise unidentified gaseous products and, therefore, were optimized for high sensitivity. As described in the experimental section, these results were designed merely for qualitative determination, and they are prone to high experimental error, especially for O_2 and N_2 , because of possible leaks during the transfer of the gases from the cells to the mass spectrometer. The sample cell (Figure B-4) was connected to the mass spectrometer via a cold trap (dry ice / acetone). This minimizes the amount of water that is transferred to the spectrometer but allows transfer of ammonia, if any is present. Identification, and even more so - quantification, of the various gases are not unambiguous in these experiments (e.g., both N_2 and CO appear at $m/e =$

28). In the experiments described here, a species that appears at $m/e = 30$ is a major source of ambiguity, especially in the thermal experiments described in Section C (e.g., see Table C-1). Because of these difficulties, all of the data are given in Table B-3. The sensitivity coefficients in Table B-3 were determined earlier, in a separate sequence of experiments, on genuine samples of the corresponding gas. Sensitivities in the tested mixtures, however, may depend on other components present and, therefore, quantities of gases may be distorted in these experiments. For the same reason, the gases are normalized to $H_2 = 100$ (third column for each sample), rather than the common presentation as a percentage of the total amount of gas.

As mentioned above, the $m/e = 30$ presents a problem because essentially any NO_x will appear at this value. For example, N_2O loses a nitrogen atom in the mass spectrometer to appear at this m/e value. We, therefore, also provide in Table B-3 the ratio of the intensities at $m/e = 44$ (unambiguously N_2O) to $m/e=30$ (see footnote e in Table B-3). As can be seen in the table, this ratio in all the radiolytic experiments is within 10% equal to 7.8, indicating that no other product appears at this m/e value. This can be contrasted with the thermal results in Section C.

No major new component in the mixture of gaseous products can be observed in the results of Table B-3. The m/e scale was scanned up to $m/e = 250$ but no signal was observed at $m/e \geq 47$. Trace amounts of ammonia and hydrogen sulfide could be observed in some of the specimens. The former is a commonly observed product in the radiolysis of waste simulants.⁷ The latter probably arises from radiolysis of the fly ash in the grout. The relative ratios between the various components determined by mass spectrometry is different from those determined by gas chromatography. In particular, nitrogen and nitrous oxide for the preirradiated samples appear higher in the mass spectrometry results than in the gas chromatography. The latter results are far more reliable than the former.

4. Conclusions

Only for hydrogen could reliable yields be measured at the low dose rates (0.25 and 0.63 krad/hr). $G(H_2)$ at 0.25 krad/hr is about two-thirds that at 130 krad/hr for both virgin and preirradiated samples, indicating little dependence of yield on dose rate. At 130 krad/hr, $G(H_2)$ is 0.056 and 0.041 for the virgin and preirradiated yields, respectively. These yields are higher than expected. One would expect a lower yield in the grout, because the percentage of water (a major source of hydrogen) is lower in the grout than in the waste simulant alone. However, if the NO_3 and NO_2 inhibitors are partially segregated from the water and organics (or are less effective as a radical scavenger), and if some of the radiation absorbed by the solids is effective in generating H_2 from water or organics on solid surfaces, the high grout yield could be explained.

The preirradiation of the waste simulant should result in a solution that better represents the waste, now present in the tanks, where radiolysis has degraded organics and converted some nitrate to nitrite. As seen above, in the preirradiated grout the hydrogen yield is about 25% smaller than in the virgin grout. Further, $G(N_2)$ is about 50% lower and $G(O_2)$ is about threefold higher in the preirradiated grout, whereas $G(N_2O)$ is about the same in both. Lower organic content and higher nitrite concentration in the preirradiated samples can account for all of these differences.

Figure B-12. The total amount of gas generated upon irradiation of virgin samples at 130 krad/h. Solid curve shows results from total pressure measurement; circles are the sum of the individual gases measured by gas chromatography.

Table B-3. Mass spectrometric results for irradiated grout samples. All irradiations performed at a dose rate of 130 krad/h.

gas	m/e (sens.) ^a	virgin samples						preirrad. samples		
		irradiated to 110 Mrad			irradiated to 22 Mrad			irradiated to 65 Mrad		
		I ^b	I/S ^c	norm. (from GC) ^d	I ^b	I/S ^c	norm. ^d	I ^b	I/S ^c	norm. (from GC) ^d
H ₂	2 (13.5)	670	49.6	100 (100)	597	44.22	100	57.3	4.24	100 (100)
CO	12 (0.6)	1.01	1.7	3.4 (7.5)						
NH ₃	17 (48)	1.58	0.03	0.07	1.70	0.04	0.08	3.75	0.08	1.84
N ₂	28 (45)	1755	39.0	78.6 (214)	1758	39.07	88	1495	33.22	783 (141)
NO (?)	30 (45)	19.34 (7.9) ^e			16 (6.8) ^e			133 (8.7) ^e		
O ₂	32 (36)	728	20.2	40.7 (46)	360	10.00	23	1.5	0.04	0.98 (190)
H ₂ S	34 (42)	2.95	0.07	0.14						
N ₂ O	44 (40)	152	3.8	7.7 (20)	108	2.70	6.11	1154	28.85	680 (24)

^am/e is the mass over charge at which the molecule was analyzed; for all except CO it is identical with its molecular weight; sensitivity coefficient in parentheses.

^bSignal intensity at m/e.

^cSignal intensity divided by sensitivity coefficient, proportional to concentration.

^dI/S normalized to H₂ = 100. In parentheses are results from gas chromatography also normalized to H₂ = 100.

^eRatio of I at 44 to I at 30 to show that no contribution from NO is observed for the irradiated samples.

Nitrogen and N_2O are believed to have a common origin, probably hydroxylamine or oxime. The ratio of the two gases depends on the compositions of the slurry and the grout. The sum of both, N_2 and N_2O , in the preirradiated samples is approximately half of the sum in the virgin samples. The generation of N_2O has been shown to require the presence of organic molecules.⁷ It is reasonable to assume the rate of its generation will decrease if the concentration of organic molecules decreases. Organic compounds are also known to destroy oxygen via the reaction of organic radicals with molecular oxygen (Ref. 7, p. 16). Partial oxidative degradation of the organic compounds during the preirradiation period can, therefore, explain the increase in O_2 yield.

The rates of formation of all gases, for both the virgin and preirradiated grout, decrease at dose rates above about 50 Mrad. Also, the sum of initial G values is lower for the preirradiated than for the virgin grout (last line, Table B-2). Both observations are to be expected as the radiolysis degrades the chelators. As can be deduced from Equation B-2, 50 Mrad corresponds to approximately 25 years of irradiation of the waste at its native dose rate. Therefore, the dose rate in the grout in the field will decay to nearly half its original value and the rate of gas generation can then be expected to decrease even more than shown in the present study.

Carbon monoxide is generated in small, but significant, amounts in the virgin and the pre-irradiated samples. It is a secondary product in radiolysis and eventually is destroyed by radiolysis. Analysis of its implication to catalytic converters of H_2 is beyond the scope of this study.

C. THERMAL GENERATION OF GASES FROM GROUT

1. Introduction

The yields of gases that were generated under identical conditions but without irradiation were also measured. These measurements were conducted in the 24-90 °C range. The temperature range was chosen to span the range of conceivable temperatures that the grout may encounter. At higher temperatures, its mechanical integrity may be compromised. The rate of gas generation at these temperatures, with the possible exclusion of 90 °C, is hardly measurable. We conclude that thermal reactions do not lead to significant generation of gas. Rather, it seems that gases trapped in the grout are released from the grout, and the amount of gases released increases on increasing the temperature. This thermal release of the gases seems irreversible, and the gases do not easily reabsorb into the grout.

2. Experimental

Procedures for the measurement of the thermal generation of gases were identical to those used for the radiolytic experiments. Identical cells (Figure B-4) were used and the techniques for gas measurement were also identical in the two types of experiments. Once the cells were sealed, they were placed either in water baths (45 and 60 °C) or in an air-circulated oven (90 °C). All samples were brought to room temperature (24 °C) before the gas measurement. Approximately an hour was allowed for each specimen to equilibrate with the ambient before measurement.

3. Results and Discussion

In all the experiments that were performed above room temperature, water condensed on the walls of the cell upon cooling to room temperature. This indicates that water that is released from the grout as a result of temperature gradients will not reequilibrate rapidly with the grout.

Furthermore, in the samples that were kept at 90 °C, some gray-white material was observed to coat the cell walls.

It was shown in our recent report¹ that the small amounts of H₂, N₂, and O₂ collected from virgin samples at all temperatures other than 90 °C were not generated by a chemical reaction but were released from the grout by the increased temperature. The argument to support this conclusion was the lack of time dependence of the amount of gas collected during digestion at a given temperature. Essentially the same results were obtained for the preirradiated samples as well. The amounts of gases collected at 24 °C are negligible relative to those produced by the radiolysis at the high dose rate. However, they may reach 50% of the amount collected after irradiation at the lowest dose rate for the same period of time. Nonetheless, the effect of the thermally released gases on the radiolytic determinations is not severe because the G values were determined from the slopes of the dose dependence (e.g., Figures B-5 through B-11). As the data in the tables of Appendix A show, the amount of H₂ released from the preirradiated samples are not significantly different from those obtained from the virgin samples. Nitrogen and oxygen were somewhat higher, perhaps indicating weaker binding of these gases to the grout batch that was prepared with the preirradiated waste simulant.

It was not possible to determine the amount of O₂ released at and above 45 °C because of an overlapping (negative) peak that appears in the gas chromatograms from samples aged at these temperatures. This thermal product was not observed in any of the radiolytic experiments but was observed in the thermal experiments of both batches. The mass spectrometric results, described below, suggest that it is NO.

At 90 °C, the amounts of H₂ released from the batch of virgin samples increase with time (Figure C-1). For this batch, the results at 90 °C may reasonably be described by an exponential generation (Equation C-1) as shown by the solid curve in Figure C-1. The least-squares parameters

$$[X_2] = [X_2]_{\infty} \{ 1 - \exp(-kt) \} \quad (C-1)$$

for this fit are $k = 1.7 \times 10^{-3} \text{ h}^{-1}$ and $(H_2)_{\infty} = 1.8 \times 10^{-7} \text{ mole/g}$. For the preirradiated samples, little increase with time could be discerned even though the amounts of H₂ released are similar for both batches. Similar results from N₂ and N₂O measurements are shown in Figure C-2. The scatter of the data from the preirradiated samples does not allow meaningful evaluation of the time correlation. The total amounts of all gases (dominated by N₂ and N₂O) obtained at 90 °C are shown in Figure C-3. They are larger for the preirradiated than for the virgin samples. The least squares fit to exponential formation rate law, with the fit parameters for these gases, are also given in the figures.

Mass spectrometry on samples from both batches that were aged at 90 °C were conducted in an effort to identify unaccounted products. In particular, the interfering product that prevents measurement of O₂ at the higher temperature range was the focus of this effort. The results are summarized in Table C-1. Comparing the relative intensities of $m/e = 44$ to $m/e = 30$ in Table C-1 with those in Table B-3, one can recognize that an additional product is obtained from the thermally aged virgin samples. The natural candidate for this product is NO. The results for the virgin samples are consistent with those from the gas chromatography but those for the preirradiated sample are not. In particular, the relative abundance of nitrogen and oxygen are very different in the two measurements. It should be recognized that for lack of time, only one experiment was performed on a preirradiated sample and any measurement of this kind will include all gases released from the sample (rather than only those generated by a chemical reaction).

Figure C-1. Thermal release of H₂ from virgin (empty circles) and preirradiated (solid circles) samples at 90 °C. Solid curve is exponential formation least-squares fit to the data from the virgin samples ($k = 1.7 \times 10^{-3} \text{ h}^{-1}$; $(\text{H}_2)_\infty = 1.8 \times 10^{-7} \text{ mole/g}$).

Figure C-2. Thermal release of N_2 (circles) and N_2O (triangles) from virgin (solid data points) and preirradiated (empty data points) samples at 90 °C. Solid curves are exponential formation least-squares fit to the data from the virgin samples (for N_2 : $k = 3.5 \times 10^{-3} \text{ h}^{-1}$; $(N_2)_\infty = 5.5 \times 10^{-7} \text{ mole/g}$; for N_2O : $k = 1.7 \times 10^{-3} \text{ h}^{-1}$; $(N_2O)_\infty = 2.1 \times 10^{-6} \text{ mole/g}$).

Figure C-3. The sum of measured gases released from virgin (squares) and preirradiated (circles) samples at 90 °C. Solid curves are exponential formation least-squares fit to the data; fit parameters are shown in the figure.

Table C-1. Mass spectrometric results for grout samples aged at 90 °C.

gas	m/e (sens.) ^a	virgin samples						preirradiated samples		
		3 weeks at 90 °C			1 week at 90 °C			3 weeks at 90 °C		
		I ^b	I/S ^c	norm. ^d	I ^b	I/S ^c	norm. ^d	I ^b	I/S ^c	norm. ^d
H ₂	2 (13.5)	122	9.01	100	77.8	5.76	100	574	42.52	100
NH ₃	17 (48)	63	1.31	14.53	65.1	1.36	24	1.4	0.03	0.07
N ₂	28 (45)	1300	28.89	321	1431	31.80	552	829.8	18.44	43
NO (?)	30 (45)	900 (1.91) ^e	14.92	166	1348 (1.02) ^e	25.88	449	9.97 (7.20) ^e	0.01	0.02
O ₂	32 (36)	41	1.14	12.61	34.5	0.96	16.64	796.3	22.12	52
H ₂ S	34 (42)							3.2	0.07	0.17
N ₂ O	44 (40)	1715	42.88	476	1375	34.38	597	71.8	1.80	4.22

^am/e is the mass over charge at which the molecule was analyzed; for all except CO it is identical with its molecular weight; sensitivity coefficient in parenthesis.

^bSignal intensity at m/e.

^cSignal intensity divided by sensitivity coefficient, proportional to concentration.

^dI/S normalized to H₂ = 100.

^eRatio of I at 44 to I at 30. Compare to footnote e in Table B-3.

4. Conclusions

Thermal generation of gases was studied in the range 24-90 °C. The amounts of gas measured were very small, especially in the 24-60 °C range. Because of the variability of the samples and the presence of trapped gases, in particular N₂ and O₂, significant data could be obtained only at 90 °C. Despite these uncertainties, we believe that no measurable amounts of H₂, N₂, or O₂ were generated in the 24-60 °C range. N₂O could barely be detected after two weeks at 60 °C.

The gases, H₂, N₂, and N₂O, are generated at slow but measurable rates at 90 °C. For virgin samples the rate could be fitted to an exponential rate law that levels off after several weeks. The total amount of H₂ is about the same for the virgin and preirradiated samples, whereas for N₂ and N₂O the amounts are about a factor of two larger in the preirradiated ones. Owing to scatter, the data from preirradiated samples could not be fitted to an analytical equation. Also, owing to a thermally generated product (perhaps NO), O₂ could not be measured at 90 °C. The thermal rates are small even at 90 °C and do not affect the radiolytic results of Section B.

D. MECHANISMS OF GAS GENERATION

The general, and much simplified, mechanism for the generation or inhibition of hydrogen production in irradiated solutions is given in reactions D-1 through D-4.

Recombination of H atoms (reaction D-1) and hydrogen abstraction (D-2) can be minimized on addition of nitrite, due to the competing reaction D-3, and nitrate (due to scavenging of e^-_{aq} , which is the basic form of H atoms). Essentially all of the experimental observations of this study could be rationalized by the effect of one parameter or another on these reactions. We may also note that the concentrations of NO_3^- and NO_2^- in the simulant used here are relatively low (e.g., it is $\sim 1/4$ th their combined concentration in tank 101-SY). Increasing their concentration will most probably reduce radiolytic H_2 generation rates.

Table D-1. Test solution used for comparison with yields of H_2 from grout samples (compare with Table B-1).

inorganic		organic	
compound	concentration mole L^{-1}	ion	concentration mole L^{-1}
NaNO_3	0.975	Na_3 HEDTA	0.014
NaNO_2	0.536	Na_3 citrate	0.011
NaOH	0.425	Na glycolate	0.010
H_2O	86.6% w	Na_4 EDTA	0.003
(density = 1.09 g cm^{-3})			

The yield of hydrogen from the grout samples seems relatively high. To verify experimentally that it is indeed higher than expected, we measured $G(\text{H}_2)$ from a liquid solution of composition similar to that of the waste simulant that was mixed into the grout during its preparation (see Table B-1). The composition of this test solution is given in Table D-1. Components that appear in Table B-1 but not in Table D-1 are known to have no effect on yields of H_2 at the concentrations given in that table. The results from the irradiation of this solution are given in Figure D-1.

The yield, calculated from Figure D-1, is $G(\text{H}_2) = 0.087$, nearly twice that from the grout samples and approximately the value that could be predicted from previous studies.⁷ There are only two sources for hydrogen in all the compositions utilized in this study, water and organic compounds. Direct absorption of the radiation by organic compounds can be neglected because of their small quantities. The water content in the grout is $\leq 20\%$, as compared to 87% in the test solution. The absorption of radiation energy is proportional to the density of the material. Therefore, the

energy absorbed by water in the grout is only $\leq 23\%$ (i.e., $\leq 20/87$) the amount absorbed by water in the solution. If the composition of the aqueous phase in the grout is the same as that of the solution, and if only irradiation absorbed by the aqueous phase leads to H_2 , then the amount of H_2 generated by the grout would have been 23% of the solution. It is, in fact, $\sim 50\%$ of the yield from the solution.

Table D-2 compares the yields obtained in this study for the two grout batches with several waste simulants. The waste simulant recently reported by Powell² is very similar in its composition to the one used for Figure D-1. The yield reported by Powell is 0.07 H_2 molecules per 100 eV. The difference between the value obtained from Figure D-1 ($G(H_2)=0.087$) and Powell's value is perhaps due to the much larger dose utilized in the latter experiment (35 Mrad vs. 0.4 Mrad). As repeatedly emphasized along this report, at this dose most of the original organic additives have been degraded. For comparison, a previously studied simulant for tank 101-SY waste is also included in Table D-2. The yield of H_2 in this simulant is half as high as in the presently studied simulant because of the significantly higher NO_3^- and NO_2^- concentrations (see footnote a Table D-2). There is little doubt that increasing the concentration of these two anions, especially nitrite, in the presently studied simulant will reduce $G(H_2)$. Our earlier studies on the 101-SY waste simulant showed that in the absence of organics the $G(H_2)$ would be 0.03 for that simulant. The lower concentrations of nitrite and nitrate in the 102-AP simulant will lead to an increase in $G(H_2)$, approximately to twice this value. Thus we conclude that at the lower concentration in that simulant, the major contributor to H_2 generation is direct radiolysis of water. Nonetheless, the relatively small decrease in $G(H_2)$ upon grouting is unexpected.

Two mechanisms may explain the observation of the relatively high H_2 yields from the grout. Either the radiation energy that is absorbed by grout components other than water finds its way to the water component, or the radiation energy that is absorbed by the water in the grout is more efficient at H_2 generation than that of the water in the solution. Probably both mechanisms apply here. To allow for the radiation energy that is absorbed by the nonaqueous components in the grout to migrate to the water in the grout one will need to invoke high efficiency of charge migration (electrons and/or holes, that result from the deposition of the energy in the other grout components) to the water. Partial transfer of these charge carriers to the water probably does occur but the extent that this happens is not known. The other mechanism requires higher efficiency of H_2 generation from the energy that was deposited in the water phase. Possible causes for this higher efficiency might be lower nitrate or nitrite concentrations or higher concentration of organic solutes in the water pools of the grout. The former intervene in the generation of H_2 via reactions D-3 and D-4 whereas the latter generates H_2 via reaction D-2.

The nitrogen-containing gases, N_2 and N_2O , are believed to originate from a common degradation product but the ratio of the two is strongly affected by other components in the system. For the virgin samples $G(N_2)_v + G(N_2O)_v = 0.13$, and $G(N_2)_{pre} + G(N_2O)_{pre} = 0.068$. Because organic compounds are required for the generation of these gases, the lower yield in the preirradiated samples may reflect the reduction in their concentration. For comparison,⁷ standard solutions containing four times higher $NO_2^- + NO_3^-$ concentrations yield $G(N_2) + G(N_2O) = 0.50$. Considering the lower concentration of the NO_x components in the presently used simulant, and the fact that less than 20% of the grout weight is that simulant, lead one to expect a smaller yield than that observed in the virgin samples. This again suggests that some of the radiation energy absorbed by the solids is also effective in N_2 and N_2O generation.

Figure D-1. Hydrogen generation from solution waste simulant. The composition of the solution is similar to the waste simulant that was added to the grout and is given in Table D-1. Irradiation dose rate was 2.54 krad/min.

Table D-2. Comparison of yields of gases from grout and various waste simulants. Shown are G values in units of ($\frac{\text{molecules}}{100 \text{ eV}}$)

Gas	Grout (from Table B-2)		102-Ap Simulant (from Ref. 2)	Simulants	
	virgin samples	preirrad. samples		102-Ap Simulant (Table D-1)	101-SY Simulant (from Ref. 7 ^a)
H ₂	0.056	0.041	0.0695	0.087	0.045
N ₂	0.12	0.058	0.0639		0.014
O ₂	0.026	0.078	Loss		Loss
N ₂ O	0.011	0.010	0.131		0.49
CO	0.0042	≤ 0.0028	2.3×10 ⁻⁴		
CH ₄	≤1×10 ⁻⁵	≤1×10 ⁻⁵			
ΣX _i	0.217	0.190	0.265		0.55

^a Solution contained 2.3 M NaOH, 2.8 M NaNO₃, 2.2 M NaNO₂, 0.86 NaAlO₂, 0.065 M HEDTA and EDTA, 0.1 M Citrate labeled solution POC in Ref. 7.

No oxygen is radiolytically generated from waste simulants that contain organic compounds, even though its yield in the absence of organics is significant, $G(\text{O}_2) = 0.08$.⁷ In the virgin grout samples, $G(\text{O}_2)_v = 0.026$, and it rises to $G(\text{O}_2)_{\text{pre}} = 0.078$ in the preirradiated samples. Oxygen is produced by reactions D-5 and D-6 (or an equivalent sequence with NO₂⁻):

The inhibiting effect of the organic compounds is via destruction of O₂ by organic radicals and not prevention of reactions D-5, D-6. The high yield of O₂ may again indicate segregation of nitrate and nitrite to zones of high concentration away from the location of the organic components.

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APPENDIX A**Grout Specimens and Their History**

The following pages provide a complete chronology of all grout samples received at ANL during this interim period. Table AA-1 includes a log of all the specimens and their fates. Table AA-2 presents a full accounting of all gas measurements. Tables AB-1 and AB-2 provide the same information, respectively, for the batch of preirradiated samples.

Table AA-1. Log of virgin grout sample history.

ANL no.	date open	pre- expt. photo	expt. start	expt. end	post expt. photo	initial wt (g)	comments	dose rate (krad/h)	rad. time (hrs)	temp °C	therm time (h)	gases measured				ANL no.
												H ₂ O ₂ &N ₂	CO	CH ₄	N ₂ O	
001	7/6/93	7/8/93	7/12/93	8/2/93	9/3/93	22.55	2 pcs	0.253	647.45			✓				001
002	7/6/93	7/8/93	7/12/93	7/20/93	9/3/93	19.36		0.253	198			✓				002
003	7/6/93	7/8/93	7/12/93	8/2/93	9/3/93	20.86	2 pcs	0.253	499.25			✓				003
004	7/6/93	7/8/93	7/12/93	7/26/93	9/3/93	20.91	2 pcs cracked	0.253	335.45			✓				004
005	7/6/93	7/8/93	7/12/93	8/16/93	9/3/93	22.52		0.253	813.25			✓				005
006 ^a	7/6/93	7/8/93	7/12/93	8/2/93	9/3/93	22.38		130	499.25			✓				006
007	7/6/93	7/8/93	7/12/93	8/9/93	9/3/93	22.77	scored	130	647.45			✓				007
008 ^a	7/6/93	7/8/93	7/12/93	8/16/93	9/3/93	21.93	scored	130	813.25			✓				008
009	7/6/93	7/8/93	7/12/93	7/20/93	9/3/93	21.88		130	198			✓				009
010	7/6/93	7/8/93	7/9/93	8/3/93	9/3/93	21.79	2 pcs cracked			23.8	594	✓				010
011	7/6/93	7/8/93	7/12/93	7/26/93	9/3/93	21.90		130	335.45			✓				011
012	7/6/93	7/8/93	7/26/93	8/16/93	9/3/93	22.53				45	502	✓				012
013	7/6/93	7/8/93	7/26/93	8/23/93	9/3/93	20.32	scored			45	668	✓				013
014	7/6/93	7/8/93	7/26/93	8/2/93	9/3/93	22.19	scored			60	166.75	✓				014
015	7/6/93	7/8/93	7/26/93	8/2/93	9/3/93	21.61	2 pcs cracked			45	166.75	✓				015
016	7/6/93	7/8/93	7/26/93	8/16/93	9/3/93	22.76	lightly scored	0.625	477.8			✓				016
017	7/6/93	7/8/93	7/26/93	8/2/93	9/3/93	18.65		0.625	163.8			✓				017
018	7/6/93	7/8/93	7/26/93	8/9/93	9/3/93	23.11	lightly scored	0.625	312			✓				018
019	7/6/93	7/8/93	7/26/93	8/24/93	9/3/93	22.13		0.625	669.35			✓				019
020	7/6/93	7/8/93	7/26/93	8/30/93	9/3/93	21.97	lightly scored	0.625	808.3			✓				020
021	7/6/93	7/8/93	7/26/93	8/30/93	9/3/93	22.93	lightly scored			45	836.5	✓				021
022	7/6/93	7/8/93	7/26/93	8/9/93	9/3/93	20.24	pitted			60	333.5	✓				022
023	7/6/93	7/8/93	7/26/93	8/16/93	9/3/93	22.57	scored			60	502	✓				023
024	7/6/93	7/8/93	7/26/93	8/23/93	9/3/93	23.18	scored			60	668	✓				024
025	7/12/93	7/14/93	7/26/93	8/9/93	9/3/93	21.59				45	333.5	✓				025
026	7/12/93	7/14/93	7/26/93	8/30/93	9/3/93	22.06	2 pcs cracked			60	836.5	✓				026
027	7/12/93	7/14/93	8/2/93	8/9/93	9/3/93	22.09				90	166.5	✓				027
028	7/12/93	7/14/93	8/2/93	8/23/93	9/3/93	22.32	2 pcs cracked			90	501	✓				028
029	7/12/93	7/14/93	8/2/93	8/16/93	9/3/93	21.13				90	335	✓				029
030	7/12/93	7/14/93	8/2/93	8/30/93	9/3/93	19.00				90	669.5	✓				030
031	7/12/93	7/14/93	8/2/93	9/7/93	10/22/93	21.92	2 pcs cracked			90	862	✓				031
032	7/12/93	7/14/93	8/9/93	8/16/93	9/3/93	21.40	2 pcs/sawing	130	165.8						✓	032
033 ^a	7/12/93	7/14/93	8/9/93	8/24/93	9/3/93	20.47		130	357.35						✓	033
034 ^a	7/12/93	7/14/93	8/9/93	8/30/93	9/3/93	22.40		130	496.3						✓	034

Table AA-1. Log of virgin grout sample history. (Cont'd)

ANL no.	date open	pre- expt. photo	expt. start	expt. end	post expt. photo	initial wt (g)	comments	dose rate (krad/h)	rad. time (hrs)	temp °C	therm time (h)	gases measured				ANL no.
												H ₂ O ₂ &N ₂	CO	CH ₄	N ₂ O	
035	7/12/93	7/14/93	8/9/93	9/8/93	10/22/93	22.20		130	691						✓	035
036 ^a	7/12/93	7/14/93	8/9/93	9/13/93	10/22/93	21.92	scored	130	828.9						✓	036
037	7/12/93	7/14/93	8/9/93	8/17/93	10/22/93	19.04		0.625	165.8						✓	037
038	7/12/93	7/14/93	8/9/93	8/31/93	10/22/93	20.92	scored	0.625	469.3						✓	038
039	7/12/93	7/14/93	8/9/93	9/15/93	10/22/93	19.01		130/0.63	17/834						✓	039
040	7/12/93	7/14/93	8/9/93	9/17/93	10/22/93	22.43	3 score lines	130/0.63	70/829						✓	040
041	7/12/93	7/14/93	8/9/93	10/15/93		21.06		130/0.63	798/829			m. spec				041
042	7/12/93	7/14/93	8/9/93	8/16/93	10/22/93	18.99		0.253	165.8						✓	042
043	7/12/93	7/14/93	8/9/93	9/1/93	10/22/93	22.67		130/0.25	191/357				✓	✓		043
044	7/12/93	7/14/93	8/9/93	9/21/93	10/22/93	21.64	cracked in 2	130/0.25	307/691				✓	✓		044
045	7/12/93	7/14/93	8/9/93	9/27/93	10/22/93	21.85	3 score lines	130/0.25	445/691				✓	✓		045
046	7/12/93	7/14/93	8/9/93	10/12/93	10/22/93	22.19	2 pcs cracked	0.25/130	691/776				✓	✓		046
047	7/12/93	7/14/93	8/6/93	8/16/93	9/3/93	21.69	3 scars			23.4	234.17	✓				047
048	7/12/93	7/14/93	8/6/93	8/23/93	9/3/93	21.08	2 scars			22.6	400.17	✓				048
049	7/12/93	7/14/93	8/6/93	8/30/93	9/3/93	22.47				23	569.25	✓				049
050	7/12/93	7/14/93	8/6/93	9/13/93	10/22/93	22.29	scored			24.2	908	✓				050
051	7/12/93	7/14/93	8/6/93	9/7/93	10/22/93	22.50	2 pcs cracked			22	761.25	✓				051
052	7/12/93	7/14/93	8/23/93	9/7/93	10/22/93	22.72				90	356				✓	052
053	7/12/93	7/14/93	8/23/93	9/27/93	10/22/93	22.26				90	836				✓	053
054	7/12/93	7/14/93	8/23/93	9/20/93	10/22/93	21.76				90	668				✓	054
055	7/12/93	7/14/93	8/23/93	9/13/93	10/22/93	21.38				90	502				✓	055
056	7/12/93	7/14/93	8/23/93	8/30/93	9/3/93	20.96				90	163.5				✓	056
057 ^a	7/12/93	7/14/93	9/13/93	10/16/93	10/29/93	21.05	scored	130	789.2			m. spec				057
058	7/12/93	7/14/93	9/24/93	10/18/93		21.86	end pcs crumb			90	868.8	m. spec				058
059	7/12/93	7/14/93	9/24/93	10/18/93	10/29/93	21.81	end pcs crumb			90	868.8	m. spec				059
060	7/12/93	7/14/93	9/13/93	9/20/93	10/22/93	20.64	cracked in 2			60	163.75				✓	060
061	8/24/93	8/26/93	9/13/93	10/4/93	10/22/93	21.39				60	500.3				✓	061
062	8/24/93	8/26/93	9/13/93	10/11/93	10/22/93	22.32				60	668				✓	062
063	8/24/93	8/26/93	9/13/93	10/18/93	10/29/93	21.79				60	835.5				✓	063
064	8/24/93	8/26/93	9/13/93	9/27/93	10/22/93	22.12				60	332				✓	064
065	8/24/93	8/26/93	9/13/93	9/14/93	10/22/93	22.98		130	17			✓				065
066	8/24/93	8/26/93	9/13/93	9/17/93	10/22/93	21.40		130	70.2			✓				066
067	8/24/93	8/26/93				22.06										067
068	8/24/93	8/26/93				21.93										068

Table AA-1. Log of virgin grout sample history. (Cont'd)

ANL no.	date open	pre- expt. photo	expt. start	expt. end	post expt. photo	initial wt (g)	comments	dose rate (krad/h)	rad. time (hrs)	temp °C	therm time (h)	gases measured				ANL no.
												H ₂ O ₂ &N ₂	CO	CH ₄	N ₂ O	
069	8/24/93	8/26/93	10/8/93	10/15/93	10/29/93	22.34		130	159.9			m. spec				069
070	8/24/93	8/26/93	10/11/93	10/18/93	10/29/93	21.78				90	162.3	m. spec				070
071	8/24/93	8/26/93	X	X	X	21.79	not used	X	X	X	X					071
072	8/24/93	8/26/93				22.89										072
073	8/24/93	8/26/93				22.01										073
074	8/24/93	8/26/93				21.30	2pcs									074
075	8/24/93	8/26/93				22.77										075
076	8/24/93	8/26/93	X	X	X	21.17	not used	X	X	X	X					076
077	8/24/93	8/26/93				22.69	2pcs									077
078	8/24/93	8/26/93				22.37										078
079	8/24/93	8/26/93				22.39	2pcs									079
080	8/24/93	8/26/93				22.30										080
081	8/24/93	8/26/93				19.12										081
082	8/24/93	8/26/93				19.82	2pcs									082
083	8/24/93	8/26/93				19.28	2pcs									083
084	8/24/93	8/26/93	X	X	X	20.37	not used	X	X	X	X					084
085	8/24/93	8/26/93	X	X	X	21.18	not used	X	X	X	X					085
086	8/25/93	8/26/93				22.47										086
087	8/25/93	8/26/93				22.17										087
088	8/25/93	8/26/93				21.32	2pcs									088
089	8/25/93	8/26/93				22.39										089
090	8/25/93	8/26/93				22.68										090

*These specimens were transferred on 11/29/93 to Prof. F. Young, Center for Cement, University of Illinois, Urbana.

Table AA-2. Gases measured from virgin grout samples following irradiation or thermal aging.

Radiolytic H₂, N₂, O₂

ANL #	dose rate krad/hr	irrad. time h	total dose Mrad	gases extracted μmoles per sample		
				H ₂	O ₂	N ₂
002	0.253	198	0.050	0.18	0.46	2.37
004	0.253	335	0.085	0.27	0.53	1.97
003	0.253	499	0.126	0.24	0.33	2.00
001	0.253	647	0.164	0.300	0.29	2.19
005	0.253	813	0.206	0.33	0.72	4.49
017	0.625	164	0.102	0.11	0.57	6.75
018	0.625	312	0.195	0.41	0.29	5.57
016	0.625	478	0.299	0.36	0.30	4.01
019	0.625	669	0.418	0.59	1.55	9.47
020	0.625	808	0.505	0.63	0.56	5.58
065	130	17	2.21	5.64	2.23	8.49
066	130	70	9.10	12.80	8.09	23.94
009	130	198	25.7	45.84	20.27	88.89
011	130	335	43.6	63.80	29.11	135.30
006	130	499	64.9	90.90	42.77	168.60
007	130	647	84.1	108.00	51.76	226.10
008	130	813	105.7	111.00	66.86	213.60

Radiolytic CO and CH₄

ANL #	dose rate krad/h	irrad. time h	total dose Mrad	gases extracted μmoles per sample	
				CO	CH ₄
043	0.25/130	357/191	24.90	0.987	≤ 0.034
044	0.25/130	691/307	40.00	2.925	≤ 0.034
045	0.25/130	691/445	58.00	4.880	≤ 0.034
046	0.25/130	691/776	101.00	8.480	≤ 0.034

Radiolytic N₂O

ANL #	dose rate krad/h	irrad. time h	total dose Mrad	μmoles N ₂ O per sample
042	0.253	165.80	0.04	≤ 0.125
037	0.625	165.80	0.10	≤ 0.125
038	0.625	496.30	0.31	≤ 0.125
039	0.63/130	834/17	2.73	0.46
040	0.63/130	829/70	9.65	3.13
032	130	166	21.55	5.77
033	130	357	46.46	12.56
034	130	496	64.52	21.25
035	130	691	89.83	21.43
036	130	829	107.76	28.20

Table AA-2. Gases measured from virgin grout samples following irradiation or thermal aging.
(Cont'd)

Thermal N₂O

ANL #	°C	(hrs)	µm N ₂ O
060	60	163.75	≤ 0.125
064	60	332.00	1.48
061	60	500.25	2.66
062	60	668	6.18
063	60	835.5	7.53
056	90	163.50	5.86
052	90	356.00	20.51
055	90	502.00	30.14
054	90	668.00	34.40
053	90	836.00	31.68

Thermal H₂, N₂, O₂

ANL #	temp. °C	time (h)	µmole per sample		
			H ₂	O ₂	N ₂
047	23	234.20	0.0400	1.7660	8.0100
048	23	400.20	0.0443	0.6350	7.3600
049	23	569.25	0.0267	0.5280	7.3450
010	24	594.00	0.0607	0.3330	1.8070
051	22	761.25	0.0241	0.6920	6.5300
050	24	908.00	0.0279	0.4790	6.4900
015	45	166.75	0.0860	3.1510	5.5760
025	45	333.50	0.0730	0.2040	4.3330
012	45	502.000	0.1160	0.1380	4.8200
013	45	668.000	0.1280	could not measure	3.7100
021	45	836.500	0.1460	could not measure	4.7800
014	60	166.75	0.1350	0.4810	4.4910
022	60	333.50	0.2350	0.1010	3.2750
023	60	502.000	0.1710		6.2900
024	60	668.000	0.1980	could not measure	5.9800
026	60	836.500	0.2160	could not measure	5.4200
027	90	166.50	0.6530		4.0230
029	90	335.00	1.9260	could not measure	10.2600
028	90	501.00	2.1230		8.7100
030	90	669.50	2.6800		9.9100
031	90	862.00	2.8600		9.9700

Table AB-1. Log of preirradiated grout sample history.

ANL no.	date open/ recut	pre- expt. photo	expt. start	expt. end	post expt. photo	initial wt (g)	comments	dose rate (krad/h)	rad. time (hrs)	temp °C	therm time (h)	gases measured				ANL no.
												H ₂ O ₂ &N ₂	CO	CH ₄	N ₂ O	
201	9/17/93	9/21/93	9/24/93	10/4/93	10/29/93	21.40				90	168.5	✓				201
202	9/17/93	9/21/93	9/24/93	10/11/93	10/29/93	20.17				90	336	✓				202
203	9/17/93	9/21/93	9/24/93	10/18/93	10/29/93	18.17				90	503.75	✓				203
204	9/17/93	9/21/93	9/24/93	10/25/93	10/29/93	21.87				90	671.25	✓				204
205	9/17/93	9/21/93	9/24/93	11/1/93	11/19/93	21.94				90	912.75	✓				205
206	9/17/93	9/21/93	9/24/93	10/4/93	10/29/93	18.64				90	168.5				✓	206
207	9/17/93	9/21/93	9/24/93	10/11/93	11/19/93	20.72				90	336				✓	207
208	9/17/93	9/21/93	9/24/93	10/18/93	10/29/93	18.94	2 pcs			90	503.75				✓	208
209	9/17/93	9/21/93	9/24/93	10/25/93	10/29/93	18.53	2 pcs			90	671.25				✓	209
210	9/17/93	9/21/93	9/24/93	11/1/93	11/19/93	19.01				90	912.75				✓	210
211	9/17/93	9/21/93	9/27/93	10/5/93	10/29/93	19.78	2 pcs	130	161.1			✓				211
212	9/17/93	9/21/93	9/27/93	10/5/93	10/29/93	21.47	2 pcs	130	161.1						✓	212
213	9/20/93	9/21/93	9/28/93	10/15/93	10/29/93	18.48		130	330.5			mass	spec			213
214	9/20/93	9/21/93	9/28/93	10/18/93	10/29/93	18.75				90	967.5	mass	spec			214
215	9/20/93	9/21/93	9/28/93	10/18/93	10/29/93	19.32	2 pcs			90	967.5	mass	spec			215
216	9/20/93	9/21/93	10/11/93	10/19/93	10/29/93	19.35	2 pcs	0.625	159.9			✓				216
217	9/20/93	9/21/93	10/11/93	10/25/93	10/29/93	21.93	short pc, ok	0.625	326.6			✓				217
218	9/20/93	9/21/93	10/11/93	11/2/93	11/19/93	20.27		0.625	471.3			✓				218
219	9/20/93	9/21/93	10/11/93	11/8/93	11/19/93	20.30	dble cast, hard	0.625	637			✓				219
220	9/20/93	9/21/93	10/11/93	11/15/93	11/19/93	21.47	2 pcs dble cast	0.625	802.7			✓				220
221	9/20/93	9/21/93	10/11/93	10/19/93	11/19/93	18.41	dble cast	0.625	159.9						✓	221
222	9/20/93	9/21/93	10/11/93	11/2/93	11/19/93	21.77	dble cast	0.625	471.3						✓	222
223	9/20/93	9/21/93	10/11/93	11/15/93	11/19/93	21.83		0.625	802.7						✓	223
224	9/20/93	9/21/93	10/11/93	12/20/93		20.70		.625/130	803/825				✓			224
225	9/20/93	9/21/93	10/11/93			22.09		0.625							✓	225
226	9/20/93	9/21/93	10/11/93	10/19/93	11/19/93	21.36		0.253	159.9			✓				226
227	9/20/93	9/21/93	X	X	X	X	not used	X	X	X	X	X	X	X	X	227
228	9/20/93	9/21/93	10/11/93	10/25/93	11/19/93	19.77	2 pcs	0.253	326.6			✓				228
229	9/20/93	9/21/93	10/11/93	11/2/93	11/19/93	19.72	2 pcs, pocked	0.253	471.3			✓				229
230	9/20/93	9/21/93	X	X	X	X	not used	X	X	X	X	X	X	X	X	230
231	9/20/93	9/21/93	10/11/93	11/8/93	11/19/93	19.24	3 pcs, good	0.253	637			✓				231
232	9/20/93	9/21/93	10/11/93	11/15/93	11/19/93	21.66		0.253	802.7			✓				232
233	9/20/93	9/21/93	10/11/93	10/19/93	11/19/93	21.12		0.253	159.9						✓	233
234	9/20/93	9/21/93	10/11/93	12/13/93		18.72		.253/130	1132/329.2				✓			234

Table AB-1. Log of preirradiated grout sample history. (Cont'd)

ANL no.	date open	pre- expt. photo	expt. start	expt. end	post expt. photo	initial wt (g)	comments	dose rate (krad/h)	rad. time (hrs)	temp °C	therm time (h)	gases measured				ANL no.
												H ₂ O ₂ &N ₂	CO	CH ₄	N ₂ O	
235	10/4/93	10/5/93	10/11/93	12/20/93		21.29	2 pcs	.253/130	967/967				✓			235
236	10/4/93	10/5/93	10/11/93	12/6/93		19.00		.253/130	1132/162				✓			236
237	10/4/93	10/5/93	10/11/93	12/13/93		22.16		.253/130	967/495				✓			237
238	10/4/93	10/5/93	10/18/93	11/1/93	11/19/93	19.16				60	331.5	✓				238
239	10/4/93	10/5/93	10/18/93	11/15/93	11/19/93	21.15				60	671.5	✓				239
240	10/4/93	10/8/93	X	X	X	X	not used	X	X	X	X	X	X	X	X	240
241	10/4/93	10/5/93	10/18/93	11/15/93		18.80				60	671.5				✓	241
242	10/4/93	10/5/93	10/15/93	10/25/93	11/19/93	18.73				21.8	234.5	✓				242
243	10/4/93	10/5/93	10/18/93	11/1/93	11/19/93	18.83				60	336				✓	243
244	10/4/93	10/5/93	10/15/93	11/1/93	11/19/93	18.82				22.2	404.5	✓				244
245	10/4/93	10/5/93	10/15/93	11/8/93	11/19/93	22.64				22	571.5	✓				245
246	10/4/93	10/5/93	10/15/93	11/15/93	11/19/93	20.85				22	739	✓				246
247	10/4/93	10/5/93	10/15/93	11/22/93		20.58	2 pcs			22	907.5	✓				247
248	10/4/93	10/5/93	10/15/93	11/22/93		19.59				22	910				✓	248
249	10/4/93	10/5/93	11/10/93	12/8/93		20.43		130	568.8			✓	pressure			249
250	10/4/93	10/5/93	11/10/93	12/8/93		23.52		?	568.8				pressure			250
251	10/4/93	10/5/93				21.44										251
252	10/5/93	10/5/93	X	10/8/93	X	21.85	cut in half	X	X	X	X	X	X	X	X	252
252a	10/8/93	10/8/93	10/18/93	11/8/93	11/19/93	10.60		130	477.1			✓				252a
252b	10/8/93	10/8/93	10/18/93	11/15/93	11/19/93	11.03		130	642.8			✓				252b
253	10/5/93	10/5/93	X	10/8/93	X	21.17	cut in half	X	X	X	X	X	X	X	X	253
253a	10/8/93	10/8/93	10/18/93	10/25/93	11/19/93	10.41		130	166.7			✓				253a
253b	10/8/93	10/8/93	10/18/93	11/22/93		10.48		130	807.2			✓				253b
254	10/5/93	10/5/93	X	10/8/93	X	21.44	cut in half	X	X	X	X	X	X	X	X	254
254a	10/8/93	10/8/93	10/18/93	11/1/93	11/19/93	10.64		130	311.4			✓				254a
254b	10/8/93	10/8/93	11/1/93	12/6/93		10.57		130	823						✓	254b
255	10/5/93	10/5/93	X	10/25/93	X	19.06	cut in half	X	X	X	X	X	X	X	X	255
255a	10/25/93	10/28/93	11/1/93	11/29/93		9.51		130	661.1						✓	255a
255b	10/25/93	10/28/93	11/8/93	11/29/93		9.28		130	495.4						✓	255b
256	10/5/93	10/5/93	X	10/25/93	X	21.16	cut in half	X	X	X	X	X	X	X	X	256
256a	10/25/93	10/28/93	11/22/93	12/6/93		10.56		130	327.2						✓	256a
256b	10/25/93	10/28/93	11/15/93	11/22/93		10.26		130	164.4						✓	256b
257	10/5/93	10/5/93				21.32										257

Table AB-2. Gases measured from preirradiated grout samples following irradiation or thermal aging. Specimens labeled with a letter (a or b) were cut in half (i.e., 2" sample length).

Radiolytic H₂, N₂, O₂

ANL #	dose rate krad/hr	irrad. time h	total dose Mrad	gases extracted μmoles per sample		
				H ₂	O ₂	N ₂
226	0.253	159.9	0.0405	0.0489	1.205	8.440
228	0.253	326.6	0.083	0.0982	2.998	15.39
229	0.253	471.3	0.120	0.142	0.194	6.839
231	0.253	637.0	0.161	0.149	5.590	17.04
232	0.253	802.7	0.203	0.157	1.453	12.02
216	0.625	159.9	0.099	0.118	0.767	3.930
217	0.625	326.6	0.204	0.345	2.921	9.380
218	0.625	471.3	0.295	0.383	1.111	9.109
219	0.625	637.0	0.398	0.304	1.370	16.90
220	0.625	802.7	0.502	0.416	1.100	12.10
211	130	161.1	20.94	41.78	38.25	51.41
253a	130	166.7	21.67	14.20	16.40	39.94
254a	130	311.4	40.48	18.60	18.63	41.74
252a	130	477.1	62.02	31.20	43.50	67.10
249	130	568.8	73.94	59.50	98.77	166.3
252b	130	642.8	83.56	47.40	67.39	85.99
253b	130	807.2	104.9	52.15	86.17	73.25

Radiolytic CO and CH₄

ANL #	dose rate krad/h	irrad. time h	total dose Mrad	μmoles per sample	
				CO	CH ₄
236	0.253+130	1132.4+161.9	21.33	0.4718	below detection limit
234	0.253+130	1132.4+329.2	43.08	1.626	
237	0.253+130	967.1+494.5	64.53	4.412	
235	0.253+130	967.1+660.5	86.11	3.832	
224	0.625+130	802.7+824.9	107.7	1.789	

Radiolytic N₂O

ANL #	dose rate krad/h	irrad. time h	total dose Mrad	μmoles N ₂ O per sample
233	0.253	159.9	0.0405	0.294
221	0.625	159.9	0.0999	0.294
222	0.625	471.3	0.295	0.110
223	0.625	802.7	0.502	1.262
212	130	161.1	20.94	7.526
256b	130	164.4	21.37	3.150
256a	130	327.2	42.54	5.473
255b	130	495.4	64.40	8.179
255a	130	661.1	85.94	10.04
254b	130	823.0	107.0	9.723

Table AB-2. Gases measured from preirradiated grout samples following irradiation or thermal aging. Specimens labeled with a letter (a or b) were cut in half (i.e., 2" sample length). (Cont'd)

Thermal N₂O

ANL #	°C	(hrs)	μm N ₂ O
248	22	910.00	0.111
243	60	336.00	2.200
241	60	671.50	5.681
206	90	168.50	28.48
207	90	336.00	48.77
208	90	503.75	19.50
209	90	671.25	53.20
210	90	912.75	66.44

Thermal H₂, N₂, O₂

ANL #	temp. °C	time (h)	μmole per sample		
			H ₂	O ₂	N ₂
242	23	234.50	0.0089	2.260	8.0100
244	23	404.50	0.0058	air leak	—
245	22	571.50	0.0340	2.540	21.971
246	22	739.00	0.0287	1.605	13.290
247	22	907.50	0.0328	1.433	8.7390
238	60	336.00	0.1210	0.243	14.340
239	60	671.50	0.2000		15.610
201	90	168.50	0.6800	could not measure	15.130
202	90	336.00	3.0600		43.430
203	90	503.75	2.4800		45.200
204	90	671.25	2.6300		40.110
205	90	912.75	2.7600		101.00

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