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RADIOLYTIC AND THERMAL GENERATION OF GASES FROM HANFORD GROUT SAMPLES

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Radiolytic and Thermal Generation of Gases from Hanford Grout Samples

INTERIM REPORT

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ABSTRACT

Gamma irradiation of WHC-supplied samples of grouted Tank 102-AP simulated non-radioactive waste has been carried out at three dose rates, 0.25, 0.63, and 130 krad/hr. The low dose rate corresponds to that in the actual grout vaults; with the high dose rate, doses equivalent to more than 40 years in the grout vault were achieved. An average $G(H_2) = 0.047$ molecules/100 eV was found, independent of dose rate. The rate of H_2 production decreases above 80 Mrad. For other gases, $G(N_2) = 0.12$, $G(O_2) = 0.026$, $G(N_2O) = 0.011$ and $G(CO) = 0.0042$ at 130 krad/hr were determined. At lower dose rates, N_2 and O_2 could not be measured because of interference by trapped air. The value of $G(H_2)$ is higher than expected, suggesting segregation of water from nitrate and nitrite salts in the grout.

The total pressure generated by the radiolysis at 130 krad/h has been independently measured, and total amounts of gases generated were calculated from this measurement. Good agreement between this measurement and the sum of all the gases that were independently determined was obtained. Therefore, the individual gas measurements account for most of the major components that are generated by the radiolysis.

At 90 °C, H_2 , N_2 , and N_2O were generated at a rate that could be described by exponential formation of each of the gases. Gases measured at the lower temperatures were probably residual trapped gases. An as yet unknown product interfered with oxygen determinations at temperatures above ambient. The thermal results do not affect the radiolytic findings.

SUMMARY

The low-level radioactive liquid wastes in the tanks at Hanford are to be mixed with cement and other solids for storage as grout. Consequently, it is important to determine the rate of radiolytic and thermal production of gases in the grout. In this interim report, we describe our results on these rates for WHC-supplied samples of grouted, simulated nonradioactive wastes. As we have shown elsewhere, ^{60}Co gamma radiation is equivalent to the radiation that is encountered in the actual waste (essentially no α emitters in the waste). Therefore, we have γ irradiated the grout samples at 0.25, 0.63, and 130 krad/hr and measured the G -values (molecules of gas produced/100 eV absorbed) for H_2 , N_2 , O_2 , CO , CH_4 , and N_2O . The lowest dose rate is about that expected in the grout vaults, at the highest dose rate we approach doses equivalent to more than 40 years in the grout.

The average $G(\text{H}_2) = 0.047$ molecules/100 eV was found to be independent of dose rate. There is, however, evidence that H_2 production decreases at doses above 80 Mrad. At the highest dose, about 0.01 moles of H-containing source molecules per kilogram of grout are destroyed; this comprises a negligible fraction of the water, but is a significant fraction of the total organics. For the other gases, $G(\text{N}_2) = 0.12$, $G(\text{O}_2) = 0.026$, $G(\text{N}_2\text{O}) = 0.011$, and $G(\text{CO}) = 4.2 \times 10^{-3}$ were determined at 130 krad/hr. At the lower dose rates, N_2 and O_2 could not be reliably measured owing to the scatter of data; probably a consequence of trapped air. No N_2O could be detected at the lower dose rates because of the lower sensitivity of the analytical procedure to this gas. No CH_4 was detected up to 100 Mrad, so a $G(\text{CH}_4) \leq 1.1 \times 10^{-5}$ was estimated.

The total pressure that is generated from irradiation of a grout sample at 130 krad/hr was determined independently. The total pressure measurements agree with the sum of the gases measured individually. This agreement indicates that the individual measurements account for essentially all major components in the gas. However, at high doses (>50 Mrad), the total pressure that was measured directly was somewhat higher than the sum of the individually measured gases.

The $G(\text{H}_2) = 0.047$ in the grout may be compared to the 0.04 we previously measured in a slurry of similar composition to the present waste solution prior to grouting. Because in the grout much of the radiation is absorbed by cementitious solids, we expected a lower G . This high yield suggests segregation of water from dissolved salts in the grout. Oxygen is usually destroyed radiolytically in the presence of organics, but in the grout it is generated. The origin of this O_2 is energy absorption by NO_3^- ; the generation of oxygen, therefore, again suggests segregation, this time organics from nitrate. The N_2 yields in the grout are larger, and the N_2O yields are smaller, than in the waste slurry. The ratio between N_2 and N_2O is known to be sensitive to the chemical composition of the irradiated system.

Friedman et al.⁶ used 800 krad/hr to γ irradiate grout-containing waste simulants for double-shell tank slurries. He found $G(\text{N}_2\text{O}) = 0.016$ (compare to 0.011 in this study) and $G(\text{H}_2) = 0.0062$ (compare to 0.047 in this study). The G values for N_2O are considered to be in reasonable agreement. The presently determined $G(\text{H}_2)$ is over sevenfold larger. The high doses (134, 192, and 211 Mrad) used by Friedman et al.⁶ may account for the difference (compare to our doses of ≤ 120 Mrad).

The thermal generation of gases at 24, 45, and 60 °C was very small. At the lower temperatures, most of the gas that was measured originates from trapped gases; the amount released increases with temperature. At 90 °C, H_2 , N_2 , and N_2O are generated at measurable but slow rates. An unknown thermal product interferes with oxygen determination. The thermal results do not affect the conclusions from the radiolytic studies.

A. INTRODUCTION

A long-term storage solution for the low-level liquid wastes in some of the tanks at the Hanford site might be large grout vaults. The wastes will be combined with dry ingredients to form a cementitious solid, commonly called grout. Any radiolysis that may occur in the grout is almost entirely by γ and β emitters; effectively equivalent to the radiation from a γ source such as ^{60}Co . It is conceivable that a potentially flammable combination of hydrogen with nitrous oxide and oxygen may be generated by this radiolysis. Relatively high temperatures may be encountered in the waste-containing grout, therefore, thermal reactions may also form these gaseous products. Earlier work¹⁻⁶ on simulated radioactive wastes in cement have shown that the gases are produced radiolytically. However, except for the cemented wastes examined by Friedman et al.,⁶ the compositions of these grouts were quite different from the one of current interest. The yields obtained by Friedman for double-shell tank slurries in grout were $G(\text{H}_2) = 0.0062$ and $G(\text{N}_2\text{O}) = 0.016$. Some N_2 and trace amounts of CH_4 were also produced.

The nonradioactive waste in the grout samples supplied to us by WHC simulates the radioactive waste in Tank 102-AP. The composition of the waste in 102-AP is similar to that in Tank 101-SY, but concentrations of the all-important nitrate and nitrite salts are somewhat lower. Our earlier studies⁷ on 101-SY waste simulants have established that:

- (1) H_2 is produced by the radiolysis of water and from the reaction of H with the chelators and their organic degradation products,
- (2) the high concentrations of NO_2^- and NO_3^- react so rapidly with H and e_{aq}^- (or the predecessor of e_{aq}^-) that the addition of other inhibitors of H_2 production will not have a significant effect,
- (3) the organic compounds reduce O_2 production, and
- (4) organic compounds are necessary for the production of N_2O , although the nitrogen in N_2O comes from the inorganic salts.

These results guide our thinking in the grout work, although one naturally expects the solid cementitious components to modify the radiolytic and thermal reactions due to sequestering of water in pores, the addition of different materials, and the altered distribution of waste components among solid and aqueous phases. Indeed, substantial differences were observed.

Our objective in this study was to determine the rate of production of gases, radiolytically and thermally, from WHC-supplied samples of grouted Tank 102-AP simulated waste. The waste in this tank is a combination of waste from Tank 106-AN and the heel from the first grout 101 campaign. This interim report describes the results for simulants that mimic the tank feed composition. The storage of the wastes in the tanks for many years certainly has led to changes in the composition. Therefore, another series of experiments is presently underway to measure rates and yields from waste simulants that were aged under radiolytic fields. The results from these experiments will be described in a separate report.

To date, we have measured the radiolytic generation rates at 0.25, 0.63 and 130 krad/hr. The yield of hydrogen, expressed as $G(\text{H}_2)$, the number of molecules produced per 100 eV absorbed, is about 0.05 and is essentially independent of dose rate. This is an unexpectedly high yield. To rationalize the high yield, we suggest segregation of water into pools of lower salt concentrations than in the original simulant. An independent measurement of the total pressure generated by the radiolysis corroborates the relatively high yield of gases. A measurable yield of N_2O ($G(\text{N}_2\text{O}) = 0.011$) has also been observed. The rate of the thermal generation of H_2 , relative to the radiolytic generation, even at 0.25 krad/hr, is negligible at 24 °C; it could be significant at lower dose rates. Substantial thermal generation of H_2 was found at 90 °C.

B. RADIOLYTIC YIELDS OF GASES FROM GROUT

1. INTRODUCTION

In this section we discuss the radiolytic processes for the generation of gases from the grout samples. The yields were determined at three dose rates, 0.25, 0.63, and 130 krad h⁻¹. The lowest dose rate closely reflects the dose rate expected in the grout vaults; the intermediate dose rate was studied to examine whether the yields depend on the dose rate in this low-dose-rate regime. The highest dose rate was utilized in order to achieve the high doses that will occur during many years of storage in the vaults. We find little dose-rate effect, if any, on the yields of the major gases. A small decrease in the yields was observed after extensive irradiation, but this change is an expected consequence of composition changes that occur with the high doses.

2. Experimental

a. Radiation Sources and Dosimetry

Irradiations were performed in a ⁶⁰Co γ-source chamber. Dosimetry was done using the "Fricke dosimeter"⁸. This chemical dosimeter contains 1 mM FeSO₄ in an air-saturated, 1 mM NaCl, 0.8 N H₂SO₄ solution. 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 $G(\text{Fe(III)}) = 15.6 \text{ molecules per } 100 \text{ eV}$. 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 per sample is reported in units of μmole. To convert these values into yields (commonly quoted in units of molecules per 100 eV), the following formula can be used:

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

i.e.,

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

b. Sample Preparation and Treatment

Grout samples were supplied by WHC. They arrived at ANL in HPVC cylindrical pipes, approximately 6" long and 0.5" o.d. The threaded caps were removed from the pipes. Because the grout was cast directly in the pipes, it often adhered to the inside surface as it hardened. Therefore the samples were removed from the pipes by cutting lengthwise through the wall in three or four places with a high-speed cutting wheel. Approximately 0.5" was removed from one end of the sample by using a hacksaw. The sample was then placed in a cutting jig and was cut on the

other end to 4.75". All the top ends and all the bottom ends were saved, in two separate bags, 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. It appears that the heavier black components of the grout settled to the bottom during the curing and shipping time periods. This observation is one, among many other indications, of the variability and heterogeneity of the samples. The elaborate procedure described here was intended to minimize the variability among the samples that were eventually used in the yield determinations.

The resulting 4.75" grout cylinder was cut to an operating length of 4.0" by cutting off pieces (0.375" less the saw kerf) on both ends. These end pieces appear similar to one another; photographs of these pieces and their parent cylinder were taken. All cuts except the first approximate cut were made using a cutting jig to ensure accurate lengths. Scheme I illustrates the process.

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. Appendix A logs the grout samples and their history. As Figure B-1 shows, the weights of the samples were quite consistent; however, there was a subgroup of samples that was of a considerably lower weight. The chemical composition of the waste liquid simulant, as provided by WHC, is given in Table B-1.

For irradiations, the samples were placed in cells shown in Figure B-2. 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 glass blowing 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-2.

Prior to the radiolytic or thermal experiments, the samples were evacuated by using 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. One sample was pumped for five minutes and another for ten minutes to determine the loss of water. The weight loss for five minutes was approximately 0.5 g (2-3%), for ten minutes it was approximately 0.8 g (4%). It is clear that the water is lost from the grout samples slowly and that the total weight loss depends on the pumping time. Furthermore, we found that the amount of air that remains trapped in the grout depends on the time of pumping (see Section C.3). 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 our efforts, some sample-to-sample variations must be expected from the unavoidable requirement of pre-evacuation. As noted above, there are clear visual variations among the samples that also necessarily affect reproducibility of the experimental results.

Table B-1. Chemical composition of waste simulant solution as provided by WHC. Simulates Tank 102-AP waste; concentrations are as analyzed.

Ion	Concentration mole L ⁻¹	Ion	Concentration mole L ⁻¹
Al	0.2882	Cl	.0820
Bi	0.0006	CO ₃	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	0.1028
Pb	0.0018	SO ₄	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

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. While 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, it was appropriate to measure the temperature rise of a grout sample under the radiolytic conditions.

To determine this temperature change, the Pyrex sample holder (Figure B-2) was modified by replacing the break-seal with a thick-walled capillary tube approximately 6" long. An iron-constantan(?) thermocouple wire was passed through the capillary into a ca. 1.25" deep × 1/16" diameter hole that was drilled into one of the grout samples. That particular sample did not contain the waste simulant. The thermocouple wire was sealed into the capillary using TorrSeal, a vacuum-resistant epoxy. The capillary was long enough that the epoxy seal could be lead-shielded from the irradiation. The reference junction of the thermocouple was maintained at room temperature.

Figure B-1. Weight of the grout samples as a function of sample number (bottom) and distribution of sample weights in the 4.00" grout cylinder (top). The solid line is a gaussian fit to the distribution of the population of larger weights.

Figure B-2. Pyrex cell for grout samples. The same cells were used for radiolytic, mass spectrometric and thermal measurements.

The cell was sealed off as for the other samples, including the addition of the glass-slug and the evacuation. The sealed sample with the thermocouple was arranged so that the grout sample was leaning on the thermocouple wire to ensure physical contact between the sample and the thermocouple. The thermocouple was calibrated against an ice bath and compared with a mercury thermometer. The temperature reading at room temperature based upon the thermocouple tables from Omega Engineering (a replacement for NBS Circular #561) was within 1 °C of the mercury thermometer, within the limit of accuracy cited by Omega Engineering.

Figure B-3. A recording of the temperature change during irradiation of a grout sample at 130 krad/h. Grout did not contain the waste simulant.

d. Gas Measurements

Gas Chromatography: H_2 , N_2 , O_2 , N_2O , CO , CH_4 . When a sample was ready for gas measurement, the cell (Figure B-2) was mounted on a Van Slyke apparatus. Details of the Van Slyke and its interface to the gas chromatograph can be found in an earlier report⁷. A small steel bar was inserted into the region above the break-off seal, which was then evacuated using a mechanical vacuum pump. The break-seal was then broken using a magnet. Gas was removed from the sample using the Van Slyke apparatus and transferred to a gas chromatograph equipped with a thermal conductivity detector. Samples were extracted 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 lasts approximately 10 minutes. Therefore, gas trapped within the grout (in pores or adsorbed on surfaces) may not be completely released during this time. Because of that possibility, the observed yields should 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. N_2O and CO (the latter together with CH_4) were determined in separate experiments using a molecular sieve 13X column; the column temperature was 175 °C for N_2O determinations and 38 °C for CO and CH_4 determinations. The signal from the gas chromatograph was integrated using a Spectra Physics Chromjet integrator for H_2 , O_2 , and N_2 and a Hewlett Packard 3390A integrator for the other gases.

Total Pressure and Mass Spectrometry Measurements. The system used to measure the total pressure of the gas as a function of time is shown in Figure B-4. It utilizes a differential pressure transducer (World Precision Instruments PNEU05, solid state, 0-5 psi pressure transducer). One sample is irradiated while the second sample is used as a reference. This differential measurement cancels most of the pressure that results from the vapor pressure of water. The fact that some pressure differential does develop even when none of the grout samples is irradiated (see below) indicates that the vapor pressure, as well as any other gases released from the grout, are not entirely identical for different samples. Furthermore, because both samples are located in the same room, any change in gas pressure due to ambient temperature change is compensated.

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 a RS-232 connection. Readings were taken to 5 1/2 digits with a full-scale reading of 100 mV. The voltage readings were hardware averaged over 20 cycles of the 60 Hz line. Each reading was saved to a hard disk. Maximum readings are expected (and so far observed) to remain in the range of ± 70 mV. 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 quadratic 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 higher pressures.

Before starting the measurements, the assembly was leak-checked using a helium leak detector; none was detected. The long-term stability of the instrument was determined by following the pressure changes over 3.5 days (evacuated grout samples on both sides, but no irradiation). The pressure changes observed during the 3.5 days prior to irradiation are given in Figure B-5. The drift rate was $1.02 \pm .05$ torr/day, and the corrected pressure (Figure B-5) was determined using this value. This drift is most probably due to a very small leak into the sample compartment. Note that the uncorrected pressure curve does not extrapolate to zero pressure. This is due to different vapor pressures of water and other gases over the two different samples. The whole assembly remained sealed after this determination to the end of the experiment.

Figure B-4. Cells arrangement for measurements of differential pressure build-up during irradiation of grout samples. The sample on the left side is shielded from the irradiation source; the sample on the right side is irradiated. The pressure transducer is connected to a digital multimeter, interfaced to a Macintosh computer.

After the irradiation period (37 days), the whole assembly was removed from the irradiation chamber, and the rate of pressure drift was redetermined without any change in the assembly (except for the irradiation; the total pressure in the sample compartment at this stage was approximately 250 torr higher than the reference). The rate of pressure change was now -0.30 torr/day. The system was then evacuated on both sides of the assembly and the drift in pressure was again measured; it was now 1.30 torr/day. These results suggest that there are very small pressure-

dependent leaks into both sides of the differential pressure system. As the pressure in the sample compartment increases, the rate of leak into this compartment decreases. Eventually, the leak into the reference compartment becomes faster than into the sample side; thus the change in sign of the drift rate. This hypothesis is confirmed by the fact that the rate returned essentially to the same level after the evacuation as prior to the irradiation.

The following procedure was applied to correct for the small leaks:

Let v_i designate the rate of drift in pressure (torr day⁻¹) at time t ; P_i is the pressure in compartment i . Then the rate of pressure change is:

$$v_o = \left(\frac{dP_{\text{sample}}}{dt}\right)_o - \left(\frac{dP_{\text{reference}}}{dt}\right)_o = 1.02 \text{ torr day}^{-1} \text{ before the irradiation and}$$

$$v_f = \left(\frac{dP_{\text{sample}}}{dt}\right)_f - \left(\frac{dP_{\text{reference}}}{dt}\right)_f = -0.30 \text{ torr day}^{-1} \text{ at the end of the experiment.}$$

Assume that the rate of change in the drift is linear with time (i.e., with dose and, thus, with increase in pressure in the sample compartment). The parameter $\alpha = \frac{v_f - v_o}{t} = -\frac{1.32}{37} = -0.035 \text{ torr day}^{-2}$, then, designates the rate of drift change. Also assume that, because the pressure in the reference compartment is small at all times, its change is negligible, i.e.,

$$\left(\frac{dP_{\text{reference}}}{dt}\right)_o = \left(\frac{dP_{\text{reference}}}{dt}\right)_f = \frac{dP_{\text{reference}}}{dt}.$$

The rate of drift at any time is then given by:

$$\frac{dP_{\text{sample}}}{dt} = \alpha t + \frac{dP_{\text{sample}}}{dt} = \alpha t + v_o$$

Integration gives:

$$P_{\text{sample}} = \frac{\alpha}{2} \times t^2 + v_o \times t = 1.02 \times t - 0.0175 \times t^2$$

This is the pressure in the sample compartment due to the small leaks at any time t (when t is in days). The results described in Section B3e were corrected for this drift by subtracting P_{sample} from the pressure readings. The maximum correction to the pressure is 10% at the lower total pressure measurements. The correction drops to approximately 5% at the end of the experiment, when the total pressure in the irradiated sample compartment rises to approximately 250 torr.

The volume of the system was determined using conventional vacuum line techniques. The volume of each side of the assembly shown in Figure B-4, and its associated tubing was approximately 45 ml; they were identical to one another within 3%. The absolute error in the volume determination is less than 5%.

The major interference expected 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 (approximately 2 °C rise in temperature, Figure B-3), 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 quite similar to 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

Figure B-5. Determination of the drift rate in the differential total pressure measurement. Both arms of the assembly were evacuated and contained grout samples; none irradiated.

in the cell, independent of head-space volume. The same temperature change will directly increase the gas pressure by only 0.7% (i.e., $\frac{303}{301}$). In order to minimize the latter effect, one prefers to work at low pressures, that is, under vacuum. On the other hand, working under vacuum increases the probability of gas leaks. We choose to work under vacuum, nonetheless, as we did for the measurements of the individual gas yields. The change in pressure due to the establishment of the water vapor - solid grout equilibrium is easily seen in the results shown in Section B3e.

3. Results and Discussion

a. H₂ Yields from 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-6 for samples irradiated at a dose rate of 130 krad/h. The same procedure was utilized whenever possible for the other G-value determinations. The yields were determined from the slope of the least-squares fits as shown in Figure B-6. In that particular figure, the point at highest dose seems to deviate significantly from the straight line and was not included in the least-squares analysis. It is common to observe such deviations at high doses as the changes in composition, due to the radiolytic processes, become significant. However, this deviation may also result from experimental error, as the total pressure in the highest dose experiment exceeded the atmospheric pressure. Also shown in Figure B-6 and other figures is an "Equivalent Grout Time" scale, which illustrates the time that the grout would have to be stored in the vaults to receive the same dose of irradiation. This scale was calculated assuming a constant dose rate of 0.3 krad/h in the vaults. Whereas the calculation assumes a constant dose rate, one should recognize that substantial decay of the major radionuclides in the grout will occur during the time shown and, thus, the dose rate will correspondingly decrease ($\tau_{1/2}=30.3$ and 28.1 years, for ¹³⁷Cs and ⁹⁰Sr, respectively).

Similar results are presented in Figure B-7 for hydrogen generation 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 N₂ and O₂ (because the samples were all equilibrated in air prior to irradiation). Nonetheless, the results of Figures B-6 and B-7 (also summarized in Table B-2) suggest that the yield of H₂ is independent of the dose rate; the average yield is 0.047 molecules/100 eV.

The reasonably good linearity obtained in the results shown in Figures B-6 and B-7 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 slope would have curved upward. 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(H₂)=0.6; by comparison the grout contains no more than 20% water and large concentrations of nitrate and nitrite, both efficient H₂ inhibitors).

b. N₂ and O₂ Yields from Grout Samples

The amounts of N₂ and O₂ that were extracted from the same samples of grout described in Section B3a, are shown in Figures B-8 through B-10. Only the high-dose-rate experiments provide G values for these two gases. These values are given in Table B-2. At the lower dose rates

Figure B-6. The amount of H₂ generated from the grout samples irradiated at 130 krad/h for various periods of time. Top scale is an "Equivalent Grout Time" required to get the same dose (assuming a constant dose rate of 0.3 krad/h). Also shown is the procedure to calculate the yield of H₂ in units of molecules per 100 eV.

Figure B-7. The amount of H₂ generated from the grout samples irradiated at 0.25 krad/h (top) and 0.63 krad/h (bottom) for various periods of time. Top scales assume constant dose rate of 0.3 krad/h.

(0.63 and 0.25 krad/h), both gases could be easily measured (see Figures B-9 and B-10). 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 gases originate 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. In support of this suggestion, we observe that the ratio of N_2/O_2 is not far from that in air. Also, the amount of these two gases decreases after longer periods of pumping (see Section C3 and Figure C-1). On the other hand there are slight differences between the amounts obtained at the two lower dose rates; the same amounts should be obtained if these are simply trapped gases. These differences are attributed to the scatter in the data and to slight temperature changes ($\pm 1^\circ C$). The large scatter in experimental points at low levels of gases has already been discussed in the Experimental Section and is mostly associated with the problem of reproducibly evacuating the samples prior to sealing off the cells.

c. N_2O Yields From 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 B2d. Preliminary results indicated that the amounts of N_2O generated by radiolysis with low dose rates (and thus, low doses) are below the detection limits of the analysis. Upper limits for the G values from these irradiations are shown in Table B-2. The results from the high-dose-rate experiments are shown in Figure B-11 and Table B-2.

d. Yields of CO and CH_4 From Grout Samples

The radiolytic yields of CO have been similarly determined. Figure B-12 shows the amount of CO determined at various doses, all at a dose rate of 130 krad/h. The slope yields $G(CO) = 4.2 \times 10^{-3}$ molecules per 100 eV, approximately 2% of the total gases. However, there is also a positive intercept at the dose axis. This indicates that the CO is a secondary radiolytic product, that is, it is generated by the radiolysis of a degradation product. In earlier reports, we showed smaller yields because of the distortion induced by this intercept.

During the same sequence of experiments, we also attempted to determine the yield of methane. In all of these experiments the amount of methane was below our detection limit, which places an upper limit of $G(CH_4) \leq 1.1 \times 10^{-5}$ molecules per 100 eV.

e. Total Pressure 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 will provide the relative ratio of the various gases. This sequence is still continuing and the results will be reported later. Preliminary observations reveal no major differences between the gas chromatography and the mass spectrometry. 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 this series of experiments are reported below.

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

Gas	Dose rate krad / hour	G molecules / 100 eV	Comments
H ₂	130	0.056	Up to app. 100 Mrad
	0.63	0.051	Up to app. 0.6 Mrad
	0.25	0.035	Up to app. 0.3 Mrad
		Average: G(H₂) = 0.047	
N ₂	130	G(N₂) = 0.12	
	0.25	Not measurable	Up to app. 0.3 Mrad
	0.63	(see text)	Up to app. 0.6 Mrad
O ₂	130	G(O₂) = 0.026	
	0.25	Not measurable	Up to app. 0.3 Mrad
	0.63	(see text)	Up to app. 0.6 Mrad
N ₂ O	130	G(N₂O) = 0.011	
	0.63	Below lower detection limit ^a	Up to app. 0.3 Mrad G(N ₂ O) ≤ 0.018
	0.25	Below lower detection limit ^a	Up to app. 0.05 Mrad G(N ₂ O) ≤ 0.14
CO	130	G(CO)=4.2×10⁻³	Up to app. 100 Mrad
CH ₄	130	Below lower detection limit ^b	Up to app. 100 Mrad G(CH ₄) ≤ 1 × 10 ⁻⁵

^a Detection limit is 0.125 μmole N₂O.^b Detection limit is 0.034 μmole CH₄.

Figure B-8. The amount of N₂ and O₂ generated from the grout samples irradiated at 130 krad/h for various periods of time. Top scale is an "Equivalent Grout Time" required to get the same dose (assuming a constant dose rate of 0.3 krad/h). Also shown are the calculations to obtain G(N₂) and G(O₂).

Figure B-9. The amount of N_2 (top) and O_2 (bottom) generated from the grout samples irradiated at 0.63 krad/h for various periods of time. Top scale is an "Equivalent Grout Time" (assuming a constant dose rate of 0.3 krad/h).

Figure B-10. The amount of N_2 (top) and O_2 (bottom) generated from the grout samples irradiated at 0.25 krad/h for various periods of time. Top scale is an "Equivalent Grout Time" (assuming a constant dose rate of 0.3 krad/h).

Figure B-11. The amounts of N_2O generated from the grout samples irradiated at 130 krad/h for various periods of time. Top scale assumes constant dose rate of 0.3 krad/h.

Figure B-12. Determination of the radiolytic yield of CO at 130 krad/h. Note the positive intercept at 11 Mrad. Top scale assumes constant dose rate of 0.3 krad/h.

The pressure changes in the grout sample during the first six days of irradiation at 130 krad/h are shown in Figure B-13. Data points were taken at intervals of approximately 300 sec., measured to an accuracy of $\frac{1}{60}$ th of a second. As Figure B-13 demonstrates, the pressure changes accurately track the movements of the γ source. The γ -source chronology is independently recorded and each abrupt pressure change that one detects in Figure B-13 was independently logged as a movement of the source. When the source is removed (downtime in Figure B-13), the pressure drops and when it is brought back up the pressure recovers. The drop in pressure is a reflection of the change in the equilibrium vapor pressure with temperature. When the irradiation is interrupted, the sample cools (by approximately 2 °C). The equilibrium vapor pressure then decreases and thus the drop in pressure. The reverse happens when the γ source is brought back into the irradiation chamber. Note that the temperature effect is on the vapor pressure equilibrium and not directly on the pressure as already discussed in Section B2d. We understand the kinetics of these pressure changes but will not discuss them here except to note that the "spikes" seen in the enlarged area of Figure B-13 represent two overlapping exponential curves, cooling and warming. We also note here that the water vapor pressure seems to equilibrate with the grout sample quite rapidly (faster than the cooling or warming). Our earlier experiments have shown that there is water in the grout that will not readsorb quickly once taken out (e.g., by high temperature). Clearly there are at least two "types" of binding interactions of the water with the grout. The results in Figure B-13 relate to the loosely bound water.

There are two long interruptions in the irradiation, easily recognizable in Figure B-13. Applying the same drift correction that was described in Section B2-d, one obtains the "corrected pressure" curve in Figure B-13. The fact that the latter curve is completely flat during the long "down" times is a strong indication that the drift correction is justified. When the sample is not irradiated, no pressure difference is generated between the reference and the tested samples. Furthermore, the similarity between the corrected and uncorrected curves indicates the drift correction is small in comparison to the pressure change that results from the gases generated by the radiolysis.

Figure B-14 displays the results that this experiment was designed to collect. The pressure changes were converted to μ moles of gas using the experimentally determined volume of the cell. The two long interruptions in the irradiation were subtracted but not the small "spikes." To allow comparison with other samples of earlier experiments, the results are presented on a "per gram of grout" basis. Several points need to be emphasized in the results of Figure B-14. First, the agreement between the amount of gas calculated from the total pressure measurements and the amount of gas calculated as the sum of the individual gas measurements is satisfactory. These are independent measurements conducted on different samples and utilizing several different techniques. The agreement between these measurements increases our confidence in either one of the results. Second, most of the gases are accounted for in the individual gas measurements (N_2 , O, H_2 , N_2O , and CO). At doses above 50 Mrad, the total pressure seems to increase faster than the sum of the individual gases. Preliminary mass spectrometry results reveal no other gases and, therefore, the discrepancy between the two measurements may simply indicate experimental scatter.

Close examination of the results in Figure B-14 reveals an apparent "induction period" during the first day of irradiation. This is emphasized in the enlargement at the bottom of Figure B-14 where the straight line depicts the initial rate; it clearly is slower than at the later times. This may be caused either by a dose-dependent process or by slow diffusion and migration of the gases out of the grout sample. It may take approximately this time period to achieve a steady state at which the rate of gas generation and the rate of its release to the head space are the same. On the other hand, a dose-dependent process may reflect a more efficient radiolytic generation of the gases by a degradation product than by the original waste components. We cannot reliably determine pressure changes during shorter times because of the changes in pressure arising from the warming of the

Figure B-13. Changes of pressure within the irradiated cell as a function of time. The bottom figure is an enlargement of the indicated time period. Each "spike" is a result of removing the γ source. Note the flat region in the corrected pressure curve when the source was removed for long periods of time.

Figure B-14. Comparison between the amounts of gas measured from total pressure and from the sum of the individual gases determined by gas chromatography. The bottom figure is an enlargement of the early time irradiations. The dotted straight line emphasizes the initial slower gas release. Top scale assumes constant dose rate of 0.3 krad/h.

sample. It is also clear from Figure B-14 that the yield of the gases decreases after approximately 60 Mrad of irradiation. This was already suspected during the measurements of the individual gases but is more evident when the yields of all gases are combined. The yield is indeed expected to decrease as the composition of the waste in the grout changes with the 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. We note that the lowest dose at which Friedman et al. have determined yields was 134 Mrad (Table 10, ref. 6).

In Figure B-15 we show several fits to the data of Figure B-14. The line calculated from $\Sigma G(X_i)$ seems to deviate significantly from the experimental points. This results from the intercept that was commonly observed in the G-value determinations (e.g., Figures B-6 and B-7). This intercept reflects the thermal release of gases into the cell. It was not considered in the calculation of Figure B-15. This intercept is not expected and was not seen in the total pressure measurements because they were designed to measure only differential pressure changes. Nonetheless, the slope of that line is only ~20% lower than that determined from the total pressure measurement. The two lines that are nearly superimposed on one another in Figure B-15 are least-squares best fits to the linear portions of the total pressure measurement and to the sum of the individual gas measurements. They are essentially indistinguishable.

4. Conclusions

The only gas for which reliable yields could be determined at low and high dose rates is hydrogen. For this gas, there seems to be little dependence of the yield on the dose rate. The G values obtained for H_2 are higher than expected and higher than the yields obtained by Friedman et al.⁶ For comparison, a slurry containing a similar composition of waste (prior to grouting) produced $G(H_2) \approx 0.047$; because the percentage of water in the grout is significantly smaller than in the waste slurry and because water is the major source for H_2 , one expects a decrease in the yield upon grouting. The fact that such a large yield is observed indicates that the concentration of hydrogen scavengers in the water in the grout is smaller than in the slurries. This may result from segregation of water from the dissolved salts. If, indeed, regions of water of a relatively low concentration of scavengers (mostly nitrite and nitrate) are created within the grout, then the yield of H_2 may exceed that of an equivalent solution prior to grouting.

Nitrogen yields from the grout are much higher than from the waste slurries, whereas N_2O yields are smaller. This, however, is not surprising because the ratio between these two gases is sensitive to the exact composition of the irradiated slurry. Both of these gases are believed to have a common origin, probably hydroxylamine.

Although oxygen is usually destroyed when irradiated in the presence of organic compounds, in the present systems it is being generated. Generation of oxygen is commonly attributed to direct absorption of the radiation energy by nitrate:

Because the yield of O_2 is quite significant, one may conclude that the organic molecules do not reside in the vicinity of nitrate within the grout. This is another indication of segregation of the waste components in the grout. We note that the ratio $G(O_2)/G(N_2)$ resembles the composition of the gases in air, but we believe that it is a coincidence.

The yield of hydrogen seems to level off at the high doses. This happens when significant changes in the composition of the grout occur due to radiolytic degradation. At the highest dose,

Figure B-15. Same experimental results as in Figure B-14. Added are three calculated lines: Solid line: least mean squares fit to the section between 10-30 Mrad. Dashed line: least mean squares fit to the first four points from the ΣX_i data. Dotted line: linear dependence using the sum of the measured G values.

approximately 5 μmole of H_2 is produced per g grout. This corresponds to destruction of 1×10^{-2} moles (two molecules per one H_2) of hydrogen-containing source molecules per kg grout. This is negligible relative to the initial concentration of water, if water is the source of H_2 . A common H_2 -producing reaction (reaction 3) requires one water (to give H atom) and one organic (RH)

molecule. From Table B-1 one may conclude that a significant amount of the initial organic material will degrade if reaction 3 is the source for H_2 .

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 at 24, 45, 60, and 90 $^\circ\text{C}$. The temperature range was chosen to span the range of conceivable temperatures to be encountered in the vaults. At higher temperatures, the mechanical integrity of the grout may be compromised. The rate of gas generation at these temperatures, with the possible exclusion of 90 $^\circ\text{C}$, is hardly measurable. We conclude that the thermal conditions do not lead to the 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-2) 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 $^\circ\text{C}$) or in an oven (90 $^\circ\text{C}$). Room temperature was maintained at 24 $^\circ\text{C}$. All samples were brought to room temperature before the gas measurement. Approximately an hour was allowed to equilibrate the sample 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 re-equilibrate rapidly with the grout. Furthermore, in the samples that were kept at 90 $^\circ\text{C}$, some gray-white material was observed to coat the cell walls. Either a reaction product or an unidentified original component leaches out at that temperature. Because of these observations, we sealed the samples in the cells very carefully to avoid temperature increases of the grout specimen during the torch-seal procedure. For the same reason, the samples were not cooled during evacuation to avoid a temperature gradient that would lead to irreversible water condensation. Because of the large G value of H_2 in liquid water, it is important to avoid the presence of water during irradiation.

Figures C-1 through C-4 show the amounts of H_2 , N_2 , and O_2 collected at the four different temperatures. We encountered difficulties in determining the amounts of O_2 released at ≥ 45 $^\circ\text{C}$ because of an overlapping (negative) peak that appears in the gas chromatograms from these samples. This thermal product has not been identified yet, but the mass spectrometric measurements

should establish its identity. It was not observed in any of the radiolytic experiments. Because of this interference, we will not discuss the results for oxygen any further. The lines shown in Figures C-1 through C-4 are intended to connect the points only and not to provide any interpretation. As already mentioned several times, when the amounts of gas are small, the absolute values will have large errors. The problem under these circumstances is trapped gas that remains in the grout. This is especially severe for nitrogen and oxygen because of the large amounts of trapped air in the grout. An illustration of this effect is given in Figure C-1.

One of the specimens was subjected to a longer than usual (ten minutes instead of two minutes) evacuation before it was sealed off. That sample showed much less N_2 and O_2 , as highlighted in Figure C-1. Clearly, equilibration between the grout and the gas phase is not fast and depends on the pumping procedure.

The amounts of H_2 collected from the grout samples at 24 °C are rather small. It is completely negligible relative to the amounts formed in the radiolytic experiments at high dose rates. It may account for up to 50% of the amounts measured at the lowest dose rate. However, its effect on the radiolytic determinations is not severe as the G values were determined from the slopes of the dose dependence (e.g., Figures B-6 and B-7). Furthermore, there is no clear time dependence of the amount of H_2 obtained in the thermal experiments. This indicates that the hydrogen measured reflects equilibration of the grout with the gas phase and not a thermal chemical reaction. The source of this hydrogen can only be a chemical reaction that generated the gas over time (a couple of months) in the grout. At 90 °C there seems to be an increase in the amounts of H_2 and N_2 with time (Figure C-4). The results at this temperature may reasonably be described by an exponential generation as shown by the solid curves in Figure C-4. The parameters for that function are given in the figure. The plateau levels for both H_2 and N_2 are very small.

The average amounts of nitrogen are the same, within a factor of two, for all the temperatures (Figures C-1 to C-4). The amounts of hydrogen, on the other hand, increase with increasing the temperature. The release of hydrogen seems, therefore, to increase with increasing temperature. However, it should be noted that the gases were measured after the samples were cooled to room temperature. The hydrogen that is released on increasing the temperature does not readsorb into the grout within the time required for the sample temperature to reach the ambient. Therefore, the amounts measured cannot reflect equilibrium conditions.

Other parallel experiments were performed to determine the amounts of N_2O generated thermally from the grout samples. No N_2O could be detected (<0.125 μmole per sample) from samples aged at 24 and 45 °C. At 60 °C some N_2O was detected after two weeks (0.067 $\mu\text{mole/g}$); none could be detected after one-week aging at that temperature. The results from the thermal studies at 90 °C are shown in Figure C-5 along with the least-squares fit to exponential growth. These amounts are similar (coincidentally) to the amounts obtained from the radiolytic generation at 130 krad/h at room temperature.

4. Conclusions

Determination of the rates of thermal generation of gases from the grout are more difficult than the determination of radiolytic yields. This is because the amounts of gases, particularly at the lower temperatures, are very small. Determination of rates of thermal generation of the gases is further hampered by the variability of the samples and by the difficulty of reproducibly evacuating the samples while minimizing water losses from the grout. Taking into account the rather large scatter in the results at 25-60 °C, we conclude that no measurable amounts of H_2 or N_2 (and perhaps O_2) were generated in that temperature range. The gases that were apparently trapped in the grout were released upon evacuation. Nitrogen and oxygen obviously remain from trapped air, and small amounts of hydrogen were probably generated over a period of several months of grout existence. The situation for N_2O is similar; it could hardly be detected after two weeks at 60 °C.

Figure C-1. Amounts of H_2 , N_2 , and O_2 at 24 °C as a function of time. Note the low point after prolonged pre-evacuation; the same relative decrease was observed for O_2 . The lines are shown only to connect the points.

Figure C-2. Amounts of H_2 , N_2 , and O_2 at 45 °C as a function of time. The lines are shown only to connect the points. The results for oxygen are distorted by another product (see text).

Figure C-3. Amounts of H_2 and N_2 at 60 °C as a function of time. The lines are shown only to connect the points. Oxygen was impossible to measure because of overlapping peak (see text).

Thermal Generation of Gases at 90 °C

Figure C-4. Amounts of H₂ and N₂ at 90 °C as a function of time. The line for H₂ is a least-squares best fit using the parameters shown.

Figure C-5. Amounts of N_2O at 60 and 90°C as a function of time. The line is a least-squares best fit using the parameters shown.

At 90 °C, H₂, N₂, and N₂O are all generated at slow but measurable rates. The activation energy for thermal generation is clearly high, however, in order to determine this parameter one needs to measure the rate at several temperatures. None of these observations affects the determination of the radiolytic yields given in Section B.

Finally, it should also be noted that the investigation of the thermal process is still incomplete. There is at least one product that is generated thermally and not radiolytically. This product interferes with the determination of oxygen, and its identity is still unknown.

D. MECHANISMS OF GAS GENERATION

Any mechanistic description of the processes that generate gases in the grout will be rather speculative because of a lack of information on the microscopic state of the grout and the waste that it contains. There seem to exist three phases, solid (mostly the original grout components and much of the waste salt compounds), liquid (mostly nearly pure water), and gas. The equilibration between these phases is rather slow, presumably because of the slow diffusion and migration of ions and molecules within the grout pores. Therefore, one may analyze the system as the sum of three essentially isolated systems. It should be emphasized that the time scale of relevance in this context is the time that it takes for the reaction to occur. The time scale for a hydrogen atom to react and produce a hydrogen molecule is very fast (nanoseconds to milliseconds, depending on composition). During this time no exchange between the phases could occur. The hydrogen atom, for example, can react with another molecule (e.g., an organic molecule or water molecule that may serve as a donor molecule for the second hydrogen atom) only if that molecule is present in its vicinity at the time that the hydrogen atom is generated. This general description allows one to understand the unexpectedly high yield of radiolytically generated H₂ that was observed in this study.

The description of slow interphase exchange should not be confused with the description of the migration of the gases out of the grout samples. Concerns were raised at the planning stage of this study as to whether or not the gas measurement technique actually measures all of the gas because some may remain trapped in the grout. In this context, the relevant time is the time of irradiation. Preliminary results (not presented in this report) indicate that the time for migration of the gases out of the grout is several hours at room temperature. The shortest irradiation time during this study was approximately one day and, therefore, we believe that most of the generated gases were collected. We were also concerned about whether or not the rate of generation or the rate of release is the rate-determining step in our measurements. The same argument leads to the conclusion that the former is the rate-determining step. The results in Section B are in agreement with this conclusion.

Once we accept the picture of a three-phase system, we can address the processes in each of the phases separately. It is easy to show that the irradiation dose that is absorbed by the gas phase is negligible. The absorbed dose is directly proportional to the density of the material and is negligible for the gas phase when compared to the density of the solid grout. The density of liquid water is comparable to that of the grout, but it constitutes no more than 30% of the total weight of the sample. Nonetheless, if this liquid water phase contains smaller concentrations of dissolved scavengers than the original waste solution, then the yield of gases (we focus on H₂) from this phase will be very high. To demonstrate this point, assume small water pools in the grout that contain no nitrate or nitrite (or any other dissolved material). The radiation absorbed by these water pools alone (i.e., by pure water) will generate H₂ with a yield of $G(\text{H}_2)_{\text{water}} = 0.45$. In the composite material only 20% of the radiation energy will be absorbed by these water pools (assume 10% is still strongly bound and does not segregate) and, therefore, the maximum theoretical yield may be $G(\text{H}_2)_{\text{grout}}^{\text{max}} = 0.45 \times 0.2 = 0.09$. If the water pools contain organic compounds,

the yield may increase due to reaction 3. Our observations give $G(H_2)=0.05$, well below the theoretical maximum and probably indicate that these water pools do contain an amount of nitrate and nitrite that could be estimated from existing models of radiation chemistry.

It is also possible, but less likely, that some of the energy that was deposited in the solid grout created ionization events. Charges (electrons) generated by these events may find their way to the water molecules and generate hydrogen there. These charges, however, are most likely to be trapped by the large variety of electron acceptors in the solid before they reach the water molecules. Once the concept of segregation of water in the grout is accepted, there is no difficulty in rationalizing the relatively high yields of hydrogen. It should be noted that Friedman et al.⁶ obtained a value that is an order of magnitude smaller than that observed here. A possible explanation to this discrepancy is the difference in waste composition (lower nitrate and nitrite concentrations) and the lower dose in the presently studied system.

The radiolytic generation of oxygen is easy to understand. It is often produced by the direct absorption of radiation by nitrate, as described in Section B4, reactions 1 and 2. In aqueous solutions oxygen molecules will be scavenged by organic radicals. Oxygen will be destroyed, rather than generated, under such conditions. In the grout samples oxygen is generated in spite of the presence of organic molecules. This observation can also be rationalized on the basis of spatial separation of the nitrate from the organic molecules.

Nitrogen and nitrous oxide are often generated during the radiolysis of nitrate- and nitrite-containing solutions in the presence of organic molecules. Several processes and several intermediates are known to generate both of these gases, often one at the expense of the other. The intermediates invoked in order to rationalize the generation of these two gases are often long-lived (albeit very reactive) substances of high vapor pressure (e.g., hydroxylamine, hyponitrous acid, etc.) They could conceivably live long enough to allow diffusion to an organic molecule in the grout.

Thermal reactions seem to be relatively unimportant in the grout. No significant thermal reaction was observed except for samples that were kept at 90 °C. This is not surprising and was predicted to be the case in our statement of work. Diffusion of molecules, especially large organic molecules, is very slow in the grout and, therefore, the only reactions that could significantly lead to gas generation are unimolecular reactions. These reactions require large activation energies and, therefore, might be expected to be slow at the lower temperatures.

REFERENCES

1. Mockel, H. J., Koster, R. H., "Gas formation during the γ -radiolysis of cemented low- and intermediate-level waste products", *Nuclear Technology* (1982), 59, 494-497.
2. Bibler, N. E., "Radiolytic Gas Production from Concrete Containing Savannah River Plant Waste," Savannah River Lab., E. I. du Pont de Nemours and Co. Inc., Aiken, SC., 1978.
3. Bibler, N. E., "Scientific Basis for Nuclear Waste Management", C. J. M. Northrup, Jr., Ed.; Plenum Publishing: NY (1980), Vol. 2, pp. 585-592.
4. Lewis, M. A., Warren, D. W., Material Res. Soc. Symp., Proceedings, (Scientific Basis Nuclear Waste Management) (1985), 44, 257-264.
5. Lewis, M. A., Warren, D. W., Ceramic Trans., Nuclear Waste Management (1990), 3, 97-111.
6. Friedman, H. A., Dole, L. R., Gilliam, T. M., Rogers, G. C., "Radiolytic Gas Generation Rates from Hanford RHO-CAW Sludge and Double Shell Slurry Immobilized in Grout," ORNL Report TM-9412, 1985.
7. a. Meisel, D., Jonah, C. D., Kapoor, S., Matheson, M. S., Sauer, M. C., "Radiolytic and Radiolytically Induced Generation of Gases from Synthetic Wastes," ANL Report, in clearance, 1993.

b. Meisel, D., et al., "Radiolytic Generation of Gases from Synthetic Waste", ANL report No. ANL-91/41, December, 1991.
8. Spinks, J. W., Woods, R. J., An Introduction to Radiation Chemistry, J. Wiley & Sons: New York (1976) pp. 97-101.

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 fate. Table AA-2 presents a full accounting of all gas measurements. The tables were last updated on October 30, 1993.

Table AA-1. Log of Grout Sample History

04

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	2pcs	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	2pcs	0.253	499.25			✓				003
004	7/6/93	7/8/93	7/12/93	7/26/93	9/3/93	20.91	2pcs 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	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	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	2pcs 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	scarred			45	668	✓				013
014	7/6/93	7/8/93	7/26/93	8/2/93	9/3/93	22.19	scarred			60	166.75	✓				014
015	7/6/93	7/8/93	7/26/93	8/2/93	9/3/93	21.61	2pcs 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	2pcs 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	2pcs 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	2pcs cracked			90	862	✓				031
032	7/12/93	7/14/93	8/9/93	8/16/93	9/3/93	21.40	2pcs/sawing	130	165.8						✓	032
033	7/12/93	7/14/93	8/9/93	8/24/93	9/3/93	20.47		130	357.35						✓	033
034	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 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	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			mass 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	scarred			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	7/12/93	7/14/93	9/13/93	10/16/93	10/29/93	21.05	scarred	130	789.2			mass spec				057
058	7/12/93	7/14/93	9/24/93	10/18/93		21.86	end pcs crumb			90	868.8	mass 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	mass 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

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[illegible]

Table AA-2: Gases Measured from Grout Samples Following Irradiation or Thermal Aging

Radiolytic H₂, N₂, O₂

ANL#	dose rate krad/hr	irradiation time h	tot. 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. T. h	tot. dose Mrad	CO CH ₄ 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. t. h	tot. 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 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		3.7100
021	45	836.500	0.1460		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		5.9800
026	60	836.500	0.2160		5.4200
027	90	166.50	0.6530		4.0230
029	90	335.00	1.9260		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

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