6870411

DP-1604
Distribution Category: UC-70

RADIOGENIC GAS ACCUMULATION IN TRU WASTE STORAGE DRUMS

JOHN P. RYAN

Approved by

E. L. Albenesius, Research Manager
Waste Disposal Technology Division

Publication Date: January 1982

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, SC 29808

PREPARED FOR THE U. S. DEPARTMENT OF ENERGY UNDER CONTRACT DE-AC09-76SR00001

INFORMATION ONLY

DISCLAIMER

ABSTRACT

A field experiment was conducted over a four-year time span to determine the effect of high-activity transuranic (TRU) waste on the atmosphere within TRU waste storage drums typical of those generated in Savannah River Plant operation. Routine gas composition analyses showed that a significant amount of hydrogen can accumulate in drums that contain high alpha activity, and that flammable gas mixtures could form in such drums in spite of the radiolytic consumption of oxygen. According to this study, gas pressure accumulation does not pose a threat to the integrity of the TRU waste containers that are now being stored at the Savannah River Plant. Therefore, the 20-year storage criterion is still viable. However, the continued avoidance of a perfectly gas-tight drum seal (e.g., epoxy, metal welding) is recommended. The test drums will continue to be monitored.

CONTENTS

687041

RADIOGENIC GAS ACCUMULATION IN TRU WASTE STORAGE DRUMS

INTRODUCTION

In 1970, the Atomic Energy Commission issued an Immediate Action Directive (IAD-0511-21) which defined the standards for transuranic (TRU) waste disposal that are presently in effect. This document mandated the retrievable storage of all solid waste containing more than 10 nCi of alpha-emitting radionuclides per gram, designated TRU waste, in containers with a minimum storage life of twenty years.

At the Savannah River Plant (SRP), TRU waste is normally stored in drums, which are then placed on specially engineered concrete pads in the burial ground. The drums that contain more than 0.5 Ci of alpha activity are placed in large concrete containers called culverts (fourteen drums per culvert) for additional containment security. When full, the culverts are placed on the pads beside the TRU waste drums. Finally, the pad (drums, culverts, and all) is covered with earth, a waterproof liner, and a layer of soil planted with shallow-rooted vegetation. This storage mode is designed to provide for retrieval of the drums, free of external contamination, for a period of twenty years. It is anticipated that these burial mounds will remain undisturbed until recovery procedures can be implemented. The waste will then be repackaged for continued extended storage onsite, or for shipment offsite to a federal repository. Alternatively, it will go into a proposed process that will combine the TRU species with SRP high-level waste for conversion to a form suitable for geologic storage offsite.

Safe loading limits for TRU waste drums are currently established by two separate criteria, the heat load limit and the limit based on nuclear safety considerations. The heat load limit is defined by a lower limit estimate of the amount of material which could cause the temperature of a waste storage drum to exceed the point of thermal stability for waste components contained by that drum. The maximum allowable temperatures are 190°F for drums that contain anion exchange resin, and 265°F for all others. The activity or mass of each radioactive contaminant that can be stored safely is calculated from these temperatures and from the power dissipation limits that have been calculated for the drums and culverts. The only material that is present in TRU waste at SRP that represents a significant heat load to the storage system is ^{238}Pu. Current loading limits of ^{238}Pu per container are given in Table 1.

TABLE 1

Heat Load Limits of ^{238}Pu

Waste Matrix	^{238}Pu/Drum, g	^{238}Pu/Culvert, g
Normal	32	110
With Anion Resin Present	1.1	62

The nuclear safety limit is defined only in terms of fissile isotopes, so it generally does not affect the amount of activity in the waste drums at SRP, which is due mostly to ^{238}Pu.

The distribution of activity in the TRU waste drums stored at SRP is given in Table 2. Less than 13% of all drums stored at SRP between 1974 and 1977 contained more than 3 Ci/drum of ^{238}Pu activity. Current and projected future TRU waste loading at SRP has been described in Reference 1.

TABLE 2

Distribution of ^{238}Pu in SRP Waste Drums
(July 1974 - June 1977)

Grams of ^{238}Pu	Number of Drums	Maximum Curies
0 - 5	657	85
5 - 10	36	170
10 - 15	24	255
15 - 20	14	340
20 - 25	9	425
25 - 30	4	510
30 - 35	3	595

The major purpose of the work described in this report was to obtain the basis for a critical appraisal of current TRU waste handling practices. Results showed that in terms of possible hazard the most important are the procedures for sealing the TRU waste drums, and the limits placed on the amount of radioactivity that may be stored in a given waste drum.

Experiments performed by the Savannah River Laboratory[2] and elsewhere[3-5] have indicated that gases produced by waste radiolysis, although not radioactive, could conceivably cause storage

drums to fail as a result of excessive internal pressure. In addition, potential buildup of flammable gases in the drums creates a risk of breach of containment should ignition occur.

Recognizing the dual hazard potential, for breach of containment as well as fire or explosion, an experiment was initiated in 1976[6] to acquire data on the drums as they exist under actual storage conditions. That experiment, which is reported here, was designed to measure the pressure buildup and gas composition within drums that contained TRU waste of high specific activity. To accomplish this, four drums were filled with a known inventory of highly contaminated material consisting of typical SRP waste. The waste was treated normally in all ways, except that special provisions were made to monitor the pressure, temperature, and gas composition in each drum at the storage site. Measurements were made and data were collected on a monthly basis for over four years.

RADIATION EFFECTS

Radiolysis

The effects of radiation on various waste matrices have been studied in some detail.[2-5] Radiation generally causes the decomposition of the absorbing matrix with the production of gas as a result. Gases can also be "consumed" in this process by reaction with the matrix. The rate at which energy is absorbed by the reacting substrate has proven to be the rate-determining factor, both in terms of the disintegration of that substrate, and in terms of the production or consumption of gases within the system.

The radiolysis of organic material in a closed system generally produces hydrogen, carbon dioxide, carbon monoxide, and light hydrocarbon gases. Oxygen is consumed, if present. In the absence of oxygen, the radiolysis products of hydrocarbons are simply hydrogen and small amounts of methane, ethane. and propane. Radiolysis of cellulosic material produces mostly hydrogen, carbon dioxide, and carbon monoxide. Nitrogen is generally unaffected by radiolysis.

The consumption of oxygen occurs as a result of the radiation-induced production of free radicals in the waste substrate. Oxygen, in its normal triplet ground state, reacts rapidly with radicals to form larger peroxy radicals. These, in turn, react to form either acidic functional groups on the waste substrate or carbon dioxide gas. These facts are reflected in the observations concerning the radiolysis of cellulosic waste. As mentioned previously, carbon dioxide is produced by the radiolysis of cellulosic material. In the absence of oxygen, carbon monoxide production

can exceed that of carbon dioxide. When oxygen is present, however, carbon dioxide production increases while carbon monoxide becomes almost negligible.[5]

Another factor that can influence radiolytic gas production is the dose (the energy absorbed per gram of waste). The alpha radiolytic production of gas may be somewhat less efficient after large doses of alpha radiation have been absorbed by the substrate surface.[3] Unfortunately, although it was known that the dose rates in this field study were fairly high, exact dose measurements could not be obtained because of the nonhomogeneous nature of the waste. Inspection of the data concerning gas generation rate, including drum pressurization rates and gas composition changes, indicated that the cumulative doses probably did not affect the radiogenic gas production rates during the four-year experimental period.

G Value

The measure of gas production efficiency in radiolytic processes is G. G is numerically equivalent to the number of molecules of the gaseous species in question that are produced per 100 eV of radiation absorbed by the substrate. Gas consumption is represented by a negative G value. All of the alpha radiation emitted by radioactive material in a waste matrix is considered to react with that matrix. For the purposes of this report, only alpha radiation will be considered.

Some typical values of G are listed in Table 3. The value of G for all gases produced and consumed by the radiolysis of cellulosic material (G_{TOTAL} for cellulose) is given as 1.9. However, it is important to realize this only represents the efficiency of a process carried out under specific conditions; G values are functions of gas composition, pressure, and dose rate. The usefulness of G values is that, if conditions are reasonably similar, a good estimate of gas production rates can be made with these numbers.

TABLE 3

The Radiolytic Decomposition of Various TRU Waste Matrices[3]

Matrix	G* (gas, total)	Approximate Molar Production Ratios H_2 :	CO_2 :	CO
Cellulosics	1.9	1.0	0.7	0.3
Polyethylene	1.9	1.0	0.05	
Pump Oil	2.0	1.0	0.25	
Octane	4.5	1.0	0.5	
PVC	8-11	1.0	0.05	0.05

* The G value represents the number of molecules of gas produced per 100 eV of absorbed alpha radiation, including the negative effects of oxygen consumption.

EXPERIMENTAL

Procedure

The experiment reported here consisted of monitoring four test drums, the concrete culvert that contained them, and outside air. Temperature, pressure, and gas composition measurements were made on a monthly basis from the 101st day after the drums were sealed. A detailed description of the experimental materials and procedures is given in Appendix A. Measurement and sampling techniques are described in Appendix B.

Drum Atmosphere Data

The data for all routine drum measurements, from Day 101 to Day 1538, are normalized and entered in Tables B-1 through B-4 in Appendix B. The concentrations of the radiogenic gases, hydrogen and carbon dioxide, are plotted for each drum with respect to time in Figures 1-4. The gases related to flammability considerations, hydrogen and oxygen, are also plotted for each drum in Figures 5-8. The approximate lower limit of explosivity,[4] 5 mole % of both H_2 and O_2, is indicated by the dotted lines in these figures. However, mixtures of hydrogen and air are considered flammable down to 4% hydrogen.[7] The total pressure in each of the four drums is plotted as a function of time in Figure 9.

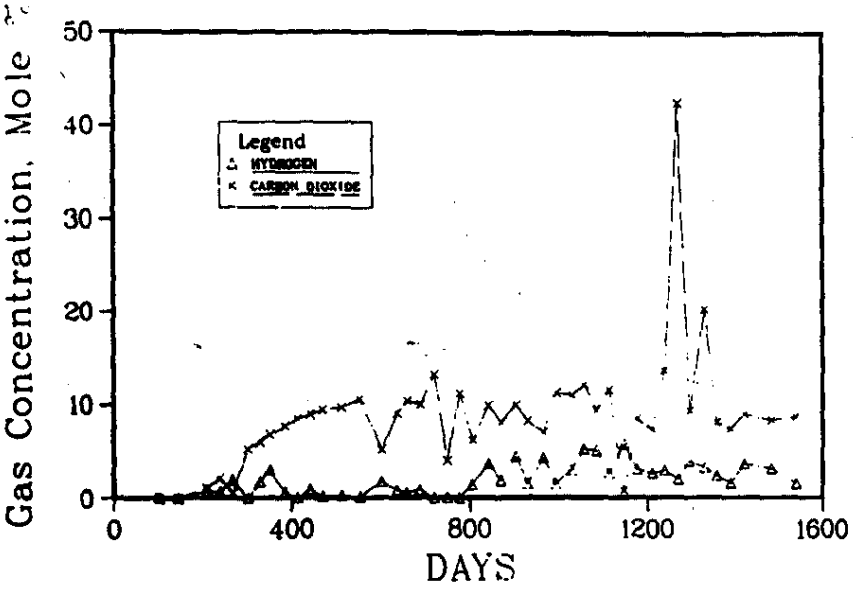

FIGURE 1. Radiogenic Gas Composition of Drum No. 119 (37 Ci Alpha) (Hydrogen and Carbon Dioxide Concentrations)

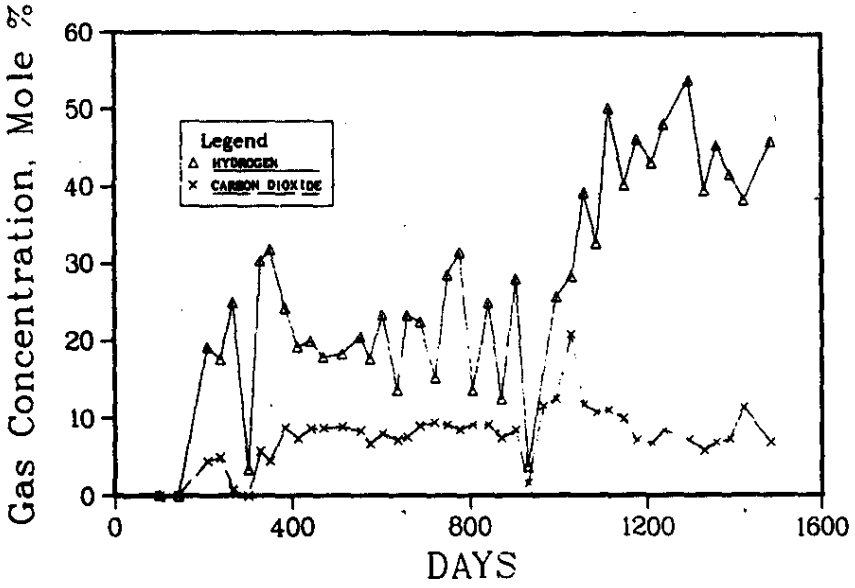

FIGURE 2. Radiogenic Gas Composition of Drum No. 120 (112.6 Ci Alpha) (Hydrogen and Carbon Dioxide Concentrations)

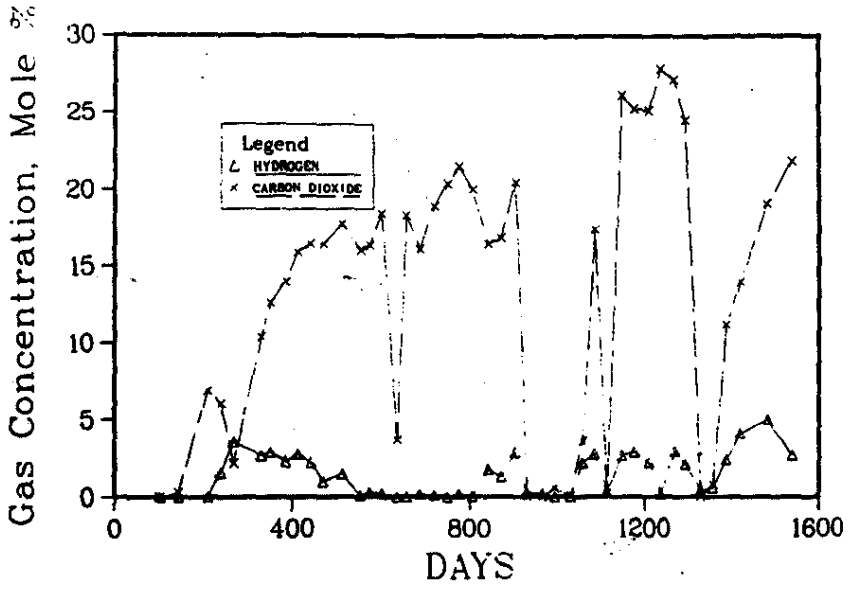

FIGURE 3. Radiogenic Gas Composition of Drum No. 121 (47.5 Ci Alpha) (Hydrogen and Carbon Dioxide Concentrations)

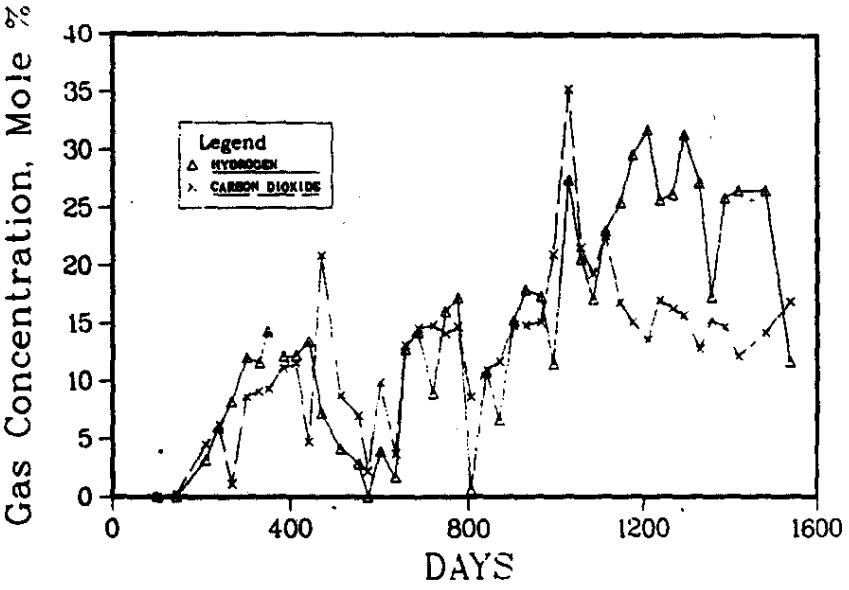

FIGURE 4. Radiogenic Gas Composition of Drum No. 122 (141.6 Ci Alpha) (Hydrogen and Carbon Dioxide Concentrations)

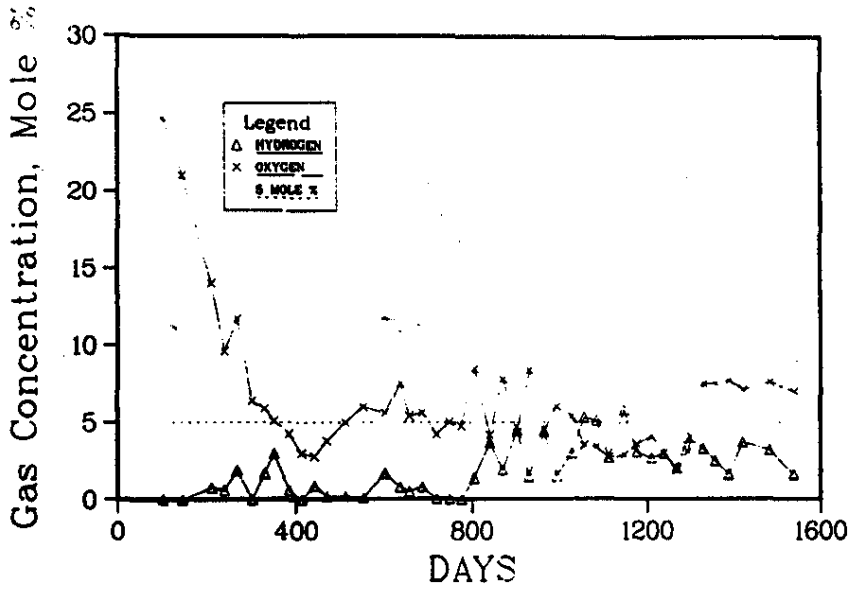

FIGURE 5. Flammable Gas Composition of Drum No. 119 (37 Ci Alpha) (Hydrogen and Oxygen Concentrations)

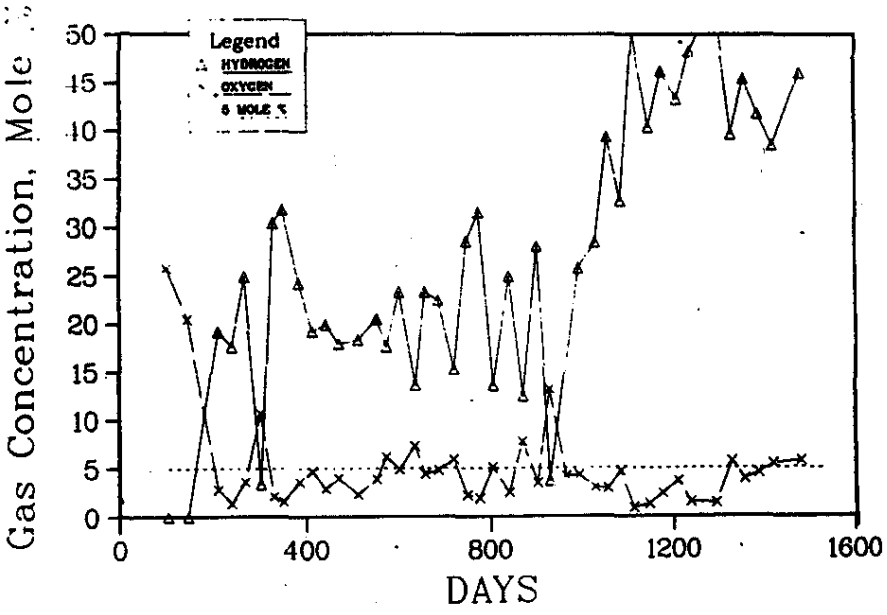

FIGURE 6. Flammable Gas Composition of Drum No. 120 (112.6 Ci Alpha) (Hydrogen and Oxygen Concentrations)

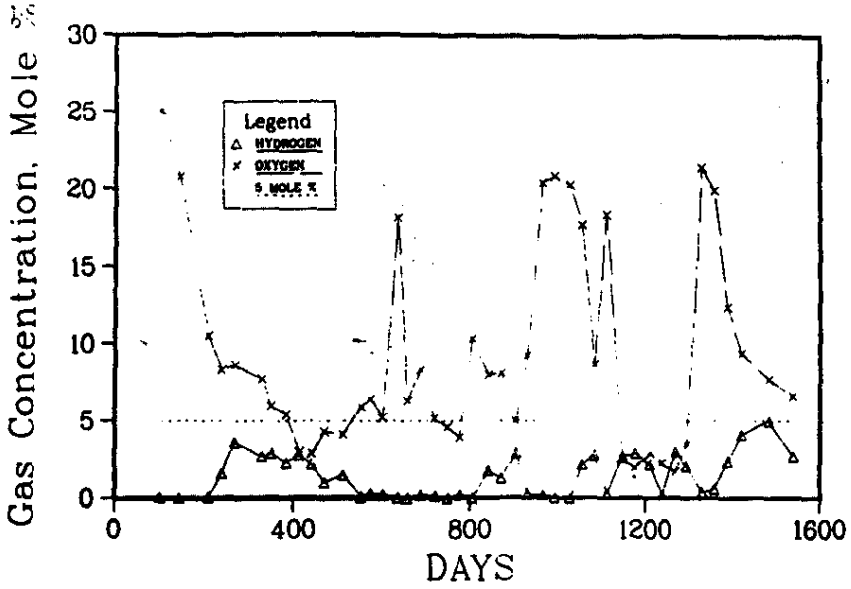

FIGURE 7. Flammable Gas Composition of Drum No. 121 (47.5 Ci Alpha) (Hydrogen and Oxygen Concentrations)

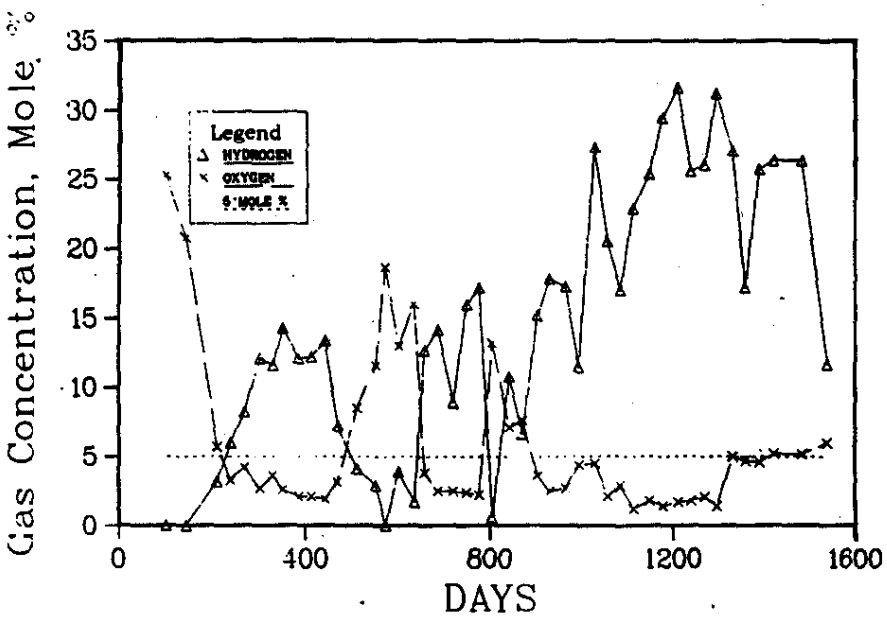

FIGURE 8. Flammable Gas Composition of Drum No. 122 (141.6 Ci Alpha) (Hydrogen and Oxygen Concentrations)

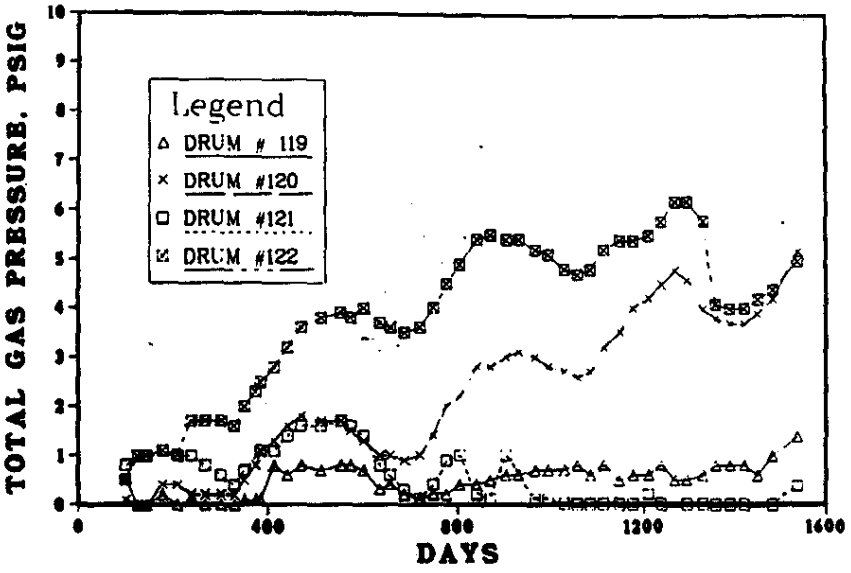

FIGURE 9. Drum Pressures Versus Time

Culvert Atmosphere Data

The lid of the culvert that contained the test drums was grouted and sealed, but hydrogen accumulation was almost negligible. The largest hydrogen concentration measured in a culvert air sample was about 0.7 mole %. Small amounts of NO_x and hydrocarbons were measured, and some oxygen depletion was also observed, but the pressure never exceeded 0.1 psig. The changes that were observed in measured pressures and concentrations in the culvert were too small to warrant graphical treatment, but the data are recorded in Table B-5 in Appendix B.

RADIOGENIC GAS PRESSURIZATION AND LEAKAGE RATES OF TRU WASTE DRUMS

Gas Production Rate

The best estimate of the total gas production rates within the experimental drums is based on laboratory experiments performed at SRL and elsewhere.[2-5] Under laboratory experimental conditions, the production rate for similar matrix compositions was approximately 0.01 mL/(min)(Ci), which corresponds to the G_{TOTAL} of about 2 (see Table 3). Using this value for the calculation, gas production rates ranged from 0.3 mL/min to 1.5 mL/min, depending on the activity in the drum. These rates should have diminished only slightly over the duration of the experiment and are essentially constant.

Since the purpose of the experiment was to measure pressure accumulation in actual TRU waste drums, no changes in the waste containment or drum closure procedures could be tolerated. Under these constraints it was not possible to measure the production rates of the radiogenic gases directly because a significant quantity of gas was escaping from the drums at all times.

A lower limit for the gas production rate was estimated based on the increases in gas pressure that were observed in the drums. The results are summarized in Table 4. The potential pressure accumulations listed in the table represent the pressures that would have been achieved if the drums had accumulated pressure for four years at the most rapid rate measured for each drum.

TABLE 4

Estimated Maximum Pressures After Four Years of Storage, psig

Extrapolated Value	Activity/Drum 37 Ci	47.5 Ci	112 Ci	147 Ci
Largest ΔpH_2	17 - 19	4 - 12	133 - 193	97 - 99
Largest ΔpCO_2	48 - 52	14 - 26	41 - 69	68 - 82
If G = 2.0	67	85	203	256
Largest Δp Total	33	24	29	33
Actual Pressure After 1482 Days	1.0	0	4.2	4.4

All numbers represent gas pressures in psig. The partial pressures of hydrogen and carbon dioxide in the test drums were calculated from each month's data. The largest two increases in these values were extrapolated to obtain an estimate of the potential pressurization rate for a closed system. A few of the largest apparent partial pressure increases were rejected, as noted in Tables B-1 through B-5. These were identified as intervals which included a data point on either side associated with:

1) A decreasing total drum pressure (>0.1 psig/month)

2) An excessively large or small partial pressure for the gas in question

3) A decrease in the partial pressure of the other radiogenic gas, either carbon dioxide or hydrogen.

The values that were used are believed to represent the highest pressurization rates that could be realized if the drums were perfectly sealed. The chosen values are noted in Tables B-1 through B-4. The pressurization rates so obtained are given in Table 4 in terms of pressure that would accumulate in each drum if that pressurization rate were realized over a four-year period.

Calculation involving G values are based on the free volume inside the drums rather than total containment volume. The free volume in the drums was estimated at 70% (see Appendix D).

All four of the drums demonstrated approximately the same maximum rate of total pressure accumulation, as measured directly by gauge. The monthly differences in partial pressure measurements, however, were strongly dependent upon the activity in each drum. And the potential pressure accumulations calculated from them were much greater than the extrapolated gauge pressure (total pressure) differences. This proves that gas must have been escaping the drums, and that the more highly loaded drums were losing gas at proportionately higher rates. Furthermore, the real gas production rates must have been greater than the rate indicated by the slope of the total pressure curve. Therefore, G_{TOTAL} is greater than or equal to 1.0. It is most likely about 2.0, as predicted by laboratory experiment.

Total Accumulated Pressures in TRU Waste Drums

As expected, the magnitude of the maximum pressure was proportional to the activity in each drum. The highest total pressure observed in an experimental drum was 6.2 psig, which occurred in Drum No. 122 (142 Ci) after 1,268 days of storage. The other three drums contained somewhat lower amounts of activity and reached correspondingly lower pressures. The maximum pressure measured in each drum is plotted as a function of activity in Figure 10. Considering the large uncertainty caused by inconsistencies in drum seal integrity and gas production efficiency, the linearity of the plot is surprising.

The plot of maximum pressures extrapolates to over 28 psig for a 600-Ci load in the same type of waste matrix. However, in separate experiments with the drum and gasket combination, drums leaked at least 1 cc/(min)(psig) at 10 psig no matter how tightly the lid was fastened. Since it takes 100 Ci of ^{238}Pu to produce gas at 1 cc/min, if the total G_{TOTAL} value is 2.0, even 600 Ci of alpha

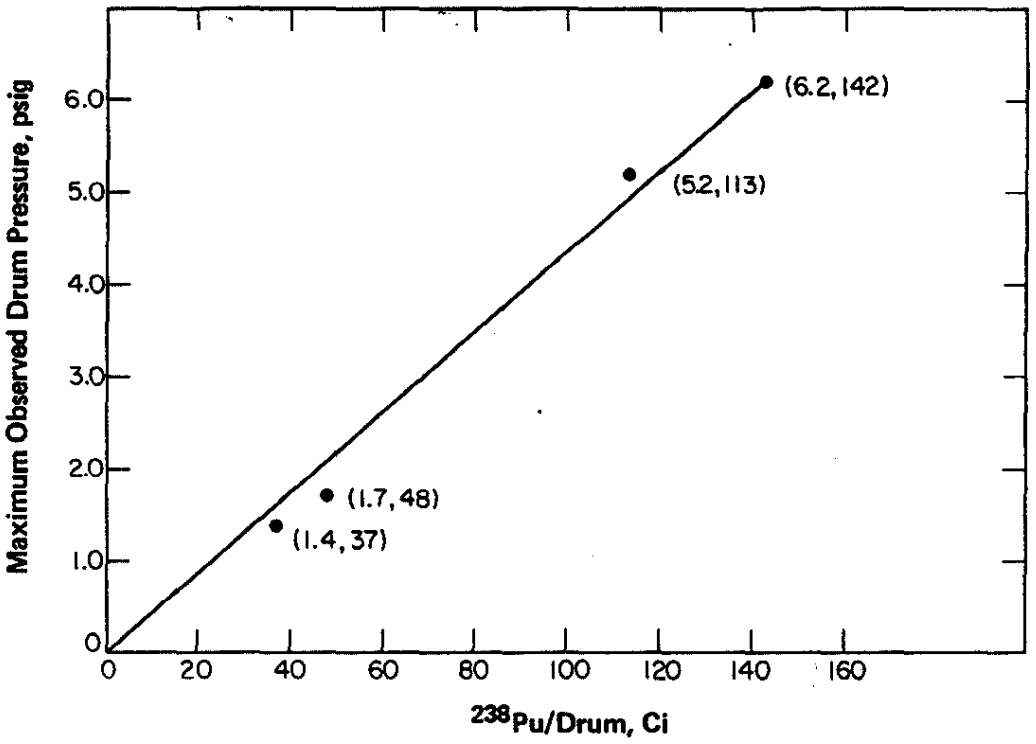

FIGURE 10. Relationship Between Curie Content and Drum Pressurization*

*The plot is drawn through the origin, but the slope, intercept, and correlation coefficient of the least squares fit for just the four data points are 0.048, −0.44, and 0.997, respectively. Ideally, the y intercept would be at the origin as drawn, so its magnitude (−0.44) is a measure of the non-ideal behavior of the system.

activity would not cause the pressure to reach 10 psig. Therefore, gas pressure should not affect the drums unless loading limits are violated or extraordinary sealing procedures are used.

Calculated Leak Rates

Taking the production and leak rates as equal at any point of zero pressure increase, the leak rates can be estimated from G_{TOTAL} values that have been measured in the laboratory. The pressure maximum for each drum can therefore be considered the greatest amount of pressure that might be required to induce that leak rate. Even if G_{TOTAL} is only 1.0 for these systems, the average leak rates for the test drums were 0.3 to 1.5 cc/min (gas volume at ambient temperature and pressure) in the drum pressure range of 1.4 to 6.2 psig.

The largest actual leak rates (cc/min) that occurred in the experimental drums can not be calculated from the data, but the largest pressure losses can be used to obtain the highest average leak rate for the one-month interval. These calculations were based on an assumed gas production efficiency (G_{TOTAL} = 2.0) and on a free internal volume estimate of 70%. The results are given in Table 5.

TABLE 5

Maximum Estimated Leak Rates of Four Experimental TRU Waste Drums

Drum Number	Loading of ^{238}Pu, Ci	Pressure Range, psig	Highest Average Leak Rate for 30-Day Interval, cc/min
119	37	0.5 - 0.0	0.4
121	48	1.0 - 0.2	0.5
120	113	4.6 - 4.0	1.3
122	142	5.8 - 5.0	1.7

Seasonal Pressure Fluctuation

The total pressure in the drums at one time was quite variable, as each of the drums vented pressure periodically. The overall trend was toward gradually increasing pressures, with occasional losses, until a maximum pressure was reached. The more highly loaded drums were more stable in maintaining gas pressure, while those with less than 50 Ci of activity often vented completely, leaving only a slight positive pressure in the drum.

In addition to the random pressure fluctuation, there was a large sinusoidal variation in drum pressure on an approximately seasonal basis. The total pressure curves of the two more highly loaded drums are almost superimposable, with the lowest pressures observed routinely around February, and the highest around August. Calculations show that these pressure variations cannot be accounted for simply by gas expansion and contraction with temperature. Measurements, obtained through day 553, indicate that the temperature of the drums was always within about 5°C of ambient, so a complete inversion of the temperature gradient would represent a change of only 0.5 psig in total drum pressure. This would not account for the much larger and more gradual effects that were observed (Figure 9).

Temperature and humidity effects probably cause the sinusoidal shape of the pressure curves for the two drums with more than 100 Ci of alpha activity by inducing variations in the resistance of the drum gaskets to leakage. The cause may be as simple as expansion and contraction of the drum gasket itself.

GAS COMPOSITION IN TRU WASTE DRUMS

Relative Production Rates of Hydrogen and Carbon Dioxide

Hydrogen and carbon dioxide are the main products of waste radiolysis, and significant concentrations of these two gases were measured in the experimental drums (Figures 1, 3, 5, and 7). Although the semiclosed nature of the drums made it impossible to accurately determine absolute production rates, estimates of relative production rates were made based on the assumption of a diffusion-controlled mechanism.

Relative production rates were estimated by first taking the ratio of the averaged measured concentrations of hydrogen and carbon dioxide in the drums. Then, assuming the drums to be a diffusion-limited system approximately at equilibrium, Graham's law was invoked. Therefore, the ratios of the measured hydrogen and carbon dioxide concentrations were multiplied by the ratio of the square root of their masses (H_2 and CO_2) to obtain their relative leakage rates. These were then equated with relative production rates. NO_x, CO, and hydrocarbon production rates were considered negligible. The equation used for estimating CO_2:H_2 production ratio is:

$$\frac{[H_2]_{av}}{[CO_2]_{av}} = 4.7 \frac{[H_2]\ \text{prod}}{[CO_2]\ \text{prod}}$$

where 4.7 is $\sqrt{\frac{44}{2}} = \sqrt{\frac{\text{atomic weight of } CO_2}{\text{atomic weight of } H_2}}$

$[H_2]_{av}$ and $[CO_2]_{av}$ are the average observed concentrations (mole %) of H_2 and CO_2. The estimated relative production percentage of H_2 and CO_2 for each of the drums is given in Table 6.

TABLE 6

The Relative Production of H_2 and CO_2 in TRU Waste Drums

Drum No.	119	120	121	122
H_2, %	51	95	36	82
CO_2, %	49	5	64	18

These estimates are in reasonable agreement with the production ratios found in laboratory experiments. The radiolysis of matrices containing similar organic material has produced gases of approximately the same composition (References 2-5), although Drum No. 121 is somewhat low in hydrogen production. Therefore, the calculations support the assumption that the system is largely diffusion-controlled. This means that the drums leak slowly and continuously, probably from pores or small cracks in the gasket seal.

Hydrogen and Oxygen Concentrations

All four of the test drums exhibited significant oxygen depletion as hydrogen gas accumulated. This happened at slightly different rates [ΔpO_2/Ci(year)] because of the random nature of the waste, the differences in contact efficiency with the source of radioactivity, and the variability of the gasket seal. A point of crossover, where the hydrogen and oxygen concentrations were equal, was observed at least once in each drum (Figures 5-8). The concentration of the two gases at that point (Table 7) is a good indication of their corresponding reaction rates and the potential for the formation of flammable gas mixtures in the TRU waste drums. Gas mixtures with either oxygen or hydrogen concentrations below 5 mole % are considered nonexplosive, based on explosimeter experiments performed at Los Alamos National Laboratory with radiogenic gases.[4]

As the table shows, the two test drums that contained less than 50 Ci of ^{238}Pu had hydrogen-oxygen concentrations of less than 5% at the first crossover. However, each of the three most contaminated drums contained a potentially flammable or explosive gas mixture at least twice during the course of the experiment. The rates of the radiolysis processes were faster in the drums with higher loading. However, an exact relationship was not observed between oxygen depletion/hydrogen accumulation rates and the

radiation load because of the variable composition of the waste and the nature of the drum seal.

The two drums that contained more than 100 Ci of ^{238}Pu reached hydrogen-oxygen crossover points 175-220 days after the drums were sealed. The faster reacting system (Drum No. 120) contained a potentially explosive gas mixture during that period. Both drums contained flammable and potentially explosive gas mixtures a number of times during the experiment.

TABLE 7

Hydrogen and Oxygen Concentrations in TRU Waste Drums

Curies/drum	37	47.5	112	142
H_2 and O_2 at 1st crossover	45%	2.5%	13.5%	4.3%
Day of 1st crossover	900	425	175	220
Number of crossovers	7	4	1	9
Average H_2 and O_2 at crossover	2.9%	1.7%	13.5%	6.6%
Maximum estimated days with O_2 >5% and H_2 >4%	0	60	430	320
Days since O_2 >5% and H_2 >4%	-	30	now present	now present

For the most part, oxygen depletion is the mechanism that prevents the atmosphere in the more contaminated drums from being explosive. This process is counteracted by diffusion of oxygen back into the drums, something that was observed in all four drums, even against a pressure gradient of 6 psig.

The two drums that contained less than 50 Ci of ^{238}Pu usually did not retain hydrogen efficiently enough to form flammable or explosive gas mixtures, even if oxygen depletion had not occurred. Drum No. 119, which contained 37 Ci of ^{238}Pu, accumulated concentrations of hydrogen that exceeded 4 mole % in five different months, only two consecutively. The oxygen concentrations were 4.3 mole % or less during that time, making the mixture nonexplosive. The hydrogen concentration in Drum No. 121 (47.5 Ci) exceeded 4.0 mole % only after a storage period of 1420 days. The corresponding oxygen concentration was about 7.7 mole %. Hydrogen and oxygen appeared to diffuse out of and into this drum at a significant rate, and the intermittent venting of pressure was also observed.

GAS TRANSPORT

Waste Containment Bags and Drum Liner

There is experimental evidence that the waste containment bags function as gas concentration buffers for the drum atmosphere. Most of the bags contain a rich mixture of radiogenic gases, so that when the drums vent themselves, the induced pressure gradient causes the bags to leak more rapidly. This process tends to keep the gas concentrations fairly stable with respect to each other. It is also consistent with the observation that the concentrations of hydrogen and carbon dioxide are virtually independent of the total drum pressure. Correlation coefficients for plots of concentration versus pressure ranged approximately from -0.5 to +0.5.

The normal gas transport process from the waste bags is probably diffusion, which tends to favor the retention of carbon dioxide and the loss of hydrogen. However, simple slow leakage probably occurs also, and this is less selective.

Drum Gasket

Hydrogen escapes the drums more readily than carbon dioxide, especially at low pressures. There are apparently two mechanisms involved, one that operates approximately according to simple diffusion laws and one that is even more selective in retaining carbon dioxide. Oxygen seems to diffuse back into the drums as well.

The calculated production ratios of hydrogen to carbon dioxide were relatively low in the drums that contained less than 50 Ci of ^{238}Pu (Drums No. 119 and 121). In fact, laboratory measurements of the radiolysis products of materials similar to those in the waste matrix[5] are not consistent with the observation that hydrogen production was well below that of carbon dioxide in Drum No. 121. The erratic (nonequilibrium) nature of the seal does not account for this, since the venting of gas in bursts would tend to reduce the selectivity of the system for carbon dioxide rather than enhance it.

The retention of carbon dioxide relative to hydrogen was too great to account for by the difference in diffusion velocities. Therefore, it is logical to conclude that the mechanics of gas transfer (from the waste drums to open air) allowed hydrogen to pass selectively. The hydrogen pathway in this case is probably through pores in the gasket or gasket seal.

There appear to be two mechanisms by which gas can escape the drums. At low pressures, hydrogen escapes somewhat selectively.

But at slightly higher pressures some of this selectivity is lost. In both of the more highly loaded drums, the hydrogen concentrations increased in relation to the carbon dioxide concentrations as the pressure increased over the duration of the experiment. This probably means that the gaskets tend to separate far enough from the sealing surface to allow the simple diffusion of gas from the drums to become the predominant loss mechanism.

At times, the gaskets are probably forced far enough from the sealing surface to allow bursts of gas to escape. This is probably not the dominant pathway, however. For if it were, the carbon dioxide selectivity would be lost, and the hydrogen concentrations in the drums would be consistently higher than the carbon dioxide concentrations.

The theory of carbon dioxide enrichment by selective transport from the drums is also supported by the data from the sample volume tests (see Appendix C). In these tests, the carbon dioxide concentration decreased as larger and larger samples were removed from the drum. The hydrogen concentration increased simultaneously. These effects were caused by the influx of gas that was relatively rich in hydrogen from the waste containment bags. The apparent decrease in carbon dioxide concentration as gas was removed from the drums is further proof of a selective transport mechanism that made the gas outside the drum liner more concentrated in carbon dioxide (accountable to the loss of hydrogen) than the gas at the source.

CONCLUSIONS

The results of this field study indicate that the TRU waste storage drums are not likely to fail from overpressurization with radiogenic gas. The waste drums are not sealed tightly enough for them to accumulate destructive pressures under the normal loading conditions; and should exceptional circumstances be encountered, the most probable reaction to excessive stress would be the failure of a drum gasket. At worst, this could allow contaminated dust to escape the drum, but the associated activity would still be contained by the surrounding culvert.

One circumstance that could conceivably cause a drum gasket to fail would be the containment of a large quantity of easily decomposable material together with the maximum allowable ^{238}Pu activity. Except for unstable chemicals like peroxides, the one common material that may constitute a hazard in this respect is polyvinylchloride (PVC). G values as high as 11.0 have been measured for this substrate.[3] This means that if 550 Ci of ^{238}Pu were intimately mixed with PVC, gases (H_2, CO_2, CO, etc.) would be produced at a rate of about 28 mL/min. The pressure that a sealed

drum would attain before achieving an equivalent leak rate is not known, but it may exceed 10 to 15 psig. A "blown" or deformed gasket might result from this kind of overloading.

There is no doubt that some of the TRU waste storage drums at SRP contain flammable gas mixtures, which could burn explosively. The drums that contain the most activity have the highest gas generation rates and are also the most likely to contain explosive gas mixtures. The depletion of oxygen is an important mechanism in preventing the atmosphere in the higher-activity drums from being flammable, but it is not dependable since the oxygen concentrations in the experimental drums intermittently approached explosive levels. Furthermore, the waste containment bags can hold significant volumes of hydrogen at gas pressures at least slightly elevated with respect to the surrounding drum atmosphere. This could cause a flammability hazard during recovery operations because the bags could ignite very easily, even though all of the excess pressure might have been vented from the drum.

Another important consideration is that heavily loaded drums react so quickly that explosive gas mixtures can build up in less than six months after the drums are sealed. The four years of observation reported here give no indication that loaded TRU waste drums become safer to handle with time. Therefore, once sealed, drums that contain more than 100 Ci should be interred within one month.

The present containment facility is more than adequate to store TRU waste safely. The culverts will eventually be moved, with the drums still inside, to a recovery facility where the fire and explosion hazards can be minimized and the TRU waste safely recovered.

APPENDIX A

EXPERIMENTAL MATERIALS

Waste Drums

Throughout this experiment, the drums and waste were handled according to routine procedures. The drums were standard SRP TRU waste containers, 55-gallon drums (DOT 17C). They were hot-dip galvanized to greater than 3-oz zinc/ft^2, inside and out. and they contained 90-mil-thick high-density polyethylene liners. The waste itself was contained in plastic bags which were placed within the liner. The liner was sealed with Rayco (Raycon Instrument Company, Boulder, CO) sealing compound adhesive (MOR AD B-31, Morton Salt Company, is now used at SRP). The drum lids were locked on over a neoprene-butadiene O-ring gasket, with a galvanized ring bolt and 90 ft-lbs of torque.

The neoprene-butadiene gaskets that are used at SRP are specified to be nonporous, 3/8-inch-thick, endless tubular gaskets. Sealing compound is also used to hold the gasket in place on the drum lid, but adhesive is not applied to the lower surface of the gasket.

For the purposes of this experiment, valves and airtight bulkhead fittings were connected to each drum wall prior to the introduction of waste. These could then be used to take samples and make pressure measurements of the gases formed in drums. The pressure and sampling taps (bulkhead fittings) were located at a point inside the drum wall but outside the drum liner (Figure A-1). The valves were kept closed until they were connected to the sampling and testing lines in the storage culvert.

Waste

The experimental drums were filled with typical cabinet waste from the SRP ^{238}Pu finishing facility. The waste was enclosed in plastic bags, which were then placed in the 90-mil polyethylene drum liners. An inventory was made of all the waste material contained by each of the four test drums. This is shown in Table A-1.

Culverts

Like all SRP solid waste drums that contain more than 0.5 Ci of alpha activity, the test drums were placed in concrete culverts. These are large (7 ft high x 7 ft diameter) cylindrical containers, the bottom and side being cast of 6-inch-thick concrete in a single piece. They are designed to contain fourteen 55-gallon waste drums, in two tiers of seven. Once filled, the culverts are covered with equally thick concrete lids, which are grouted in place and sealed with epoxy.

The culvert used in this experiment was equipped with an airtight port before the drums were placed. Two thermocouple wires and five 1/4-inch sampling and testing lines were then sealed into the port so that, once connected to the test drums, they could be used for taking samples and measurements from a station located a few yards from the culvert. All of the test drums were located in the second tier of drums in the culvert to simplify the sample line connection scheme.

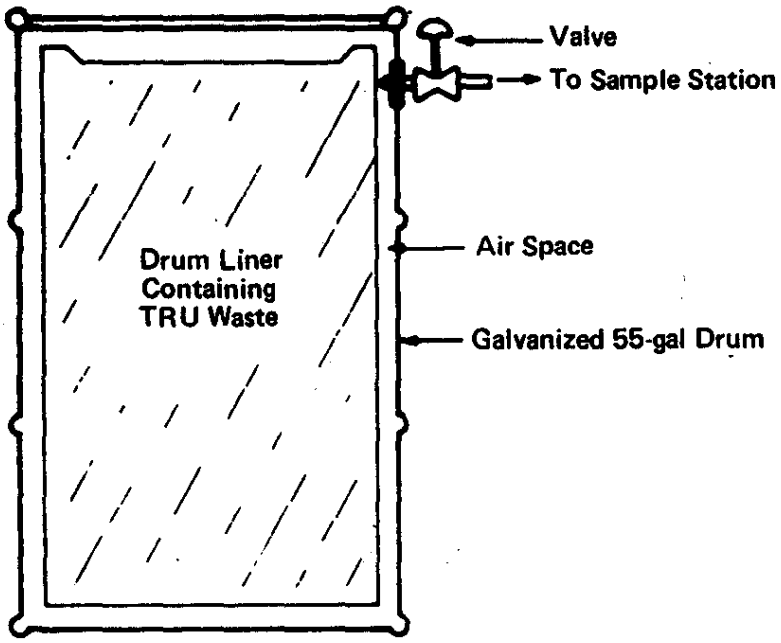

FIGURE A-1. DOT 17C Waste Storage Drum

TABLE A-I

Isotopic Abundance and Item Description of Waste in Test Drums

Drum Number	Analysis Number	Isotopic Content, g ^{238}Pu	^{235}U	^{239}Pu	Item
119	629	0.08	0.54	-	2 gloves
	630	0.02	0.13	-	1 glove, 1 can opener
	631	0.03	1.32	-	1-qt tin can
	632	0.78	0.93	0.37	1-qt tin can
	633	0.35	0.05	-	2"-dia x 18"-long pipe
	634	0.08	0.49	0.11	1-qt tin can
	635	0.57	0.04	-	agitator motor (1/4 HP)
	636	0.05	0.14	-	1 glove, SS bolts
	637	0.05	1.31	0.16	1-qt tin can
	638	0.12	0.26	0.13	1-qt tin can
	639	0.02	0.34	0.10	1-qt tin can
	640	0.05	0.50	0.11	1-qt tin can
	Total, g	2.20	6.05	0.98	
	Total, Ci	37	1.3×10^{-5}	0.06	
120	599	0.01	0.53	-	2 gloves
	600	0.01	1.44	0.29	1 glove, 1 tin can
	601	0.05	10.96	4.00	plastic
	602	0.31	3.61	1.50	tin can
	603	1.72	-	0.25	2 gloves
	604	0.03	0.36	-	1 can opener, 1 SS bolt
	605	0.03	0.36	-	1 pr triple beam scales
	613	0.09	0.07	2.15	plastic bottle
	614	0.01	7.08	0.05	tin cans
	615	0.05	0.60	-	1 beaker, 1 sponge
	616	2.01	0.87	-	2 gloves, tin cans
	617	0.17	-	-	SS tools, plastic
	618	0.62	-	0.99	2 gloves
	619	1.52	-	0.61	2 gloves
	621	0.05	-	-	tin can
	623	0.01	-	1.08	3"-dia x 20"-long SS pipe
	624	0.03	-	-	3"-dia x 20"-long SS pipe
	Total, g	6.70	25.88	10.92	
	Total, Ci	112.6	5.5×10^{-5}	0.67	
121	641	0.76	0.04	-	tools and plastic
	642	0.28	0.07	-	hot plate
	643	0.04	-	-	2 gloves, SS bolts
	644	0.07	-	0.19	tin cans and plastic
	645	0.08	0.71	0.10	tin cans and plastic
	646	0.59	-	0.39	2"-dia x 20"-long SS pipe
	647	0.13	-	-	2"-dia x 20"-long SS pipe
	648	0.34	-	-	2 gloves and pipe
	649	0.33	-	-	2 gloves and pipe
	650	0.02	-	0.07	tin cans and plastic
	651	0.06	0.60	-	2 gloves and pipe
	652	0.13	-	-	2 gloves and pipe
	Total, g	2.83	1.42	0.75	
	Total, Ci	47.5	3×10^{-6}	0.05	
122	654	0.55	-	-	2"-dia x 20"-long SS pipe
	656	0.49	-	-	3 sponges
	659	2.07	-	-	2 gloves
	660	2.03	-	-	2 sponges
	661	0.81	-	-	tin cans
	662	0.05	-	-	1 glove
	663	0.66	-	-	2 gloves
	664	0.05	-	-	2 gloves
	665	1.68	-	-	2 gloves
	667	0.04	-	-	2"-dia x 20"-long pipe
	Total, g	8.43			
	Total, Ci	141.6			

APPENDIX B

EXPERIMENTAL PROCEDURE

Drum Placement

Approximately 100 days after the experimental drums had been filled with waste and sealed according to standard procedure, they were taken to the burial ground. There they were placed in the specially modified culvert and connected via 1/4-inch tubing through the culvert port to a remote sampling and testing station. The valves on the test drums were opened after the lines and the culvert port had been thoroughly tested for leaks. One of the thermocouple wires that were sealed into the culvert port was attached to the drum that contained the greatest amount of radioactivity (Drum No. 122), and the other was left suspended in the culvert. The culvert lid was then grouted and sealed in place. The burial procedure was completed 208 days after the drums were sealed, when the culvert was covered with earth. Figure B-1 is a schematic drawing of the experimental setup.

Gas Analyses

Samples of the gas in the TRU waste drums were taken for analysis approximately every thirty days, starting 101 days after the drums were sealed. Samples were generally drawn in the morning, and the pressure and temperature readings were obtained simultaneously. The pressure and temperature readings are recorded, along with the results of the gas analyses, in Tables B-1 through B-5. Observations and measurements began 101 days after the drums were sealed.

The samples were taken with standard 185-mL gas samplers. These had stopcocks on either end and a septum-plugged outlet in the middle. They were evacuated in the laboratory and then filled by simply connecting one end to the sampling valve at the remote sampling station, and opening the stopcock on the sampler. Once up to pressure, as monitored by the gauges at the sampling station, the stopcock and sampling valve were both closed and the connection removed.

Samples were analyzed by gas chromatography. A Hewlett Packard 5750 GC, equipped with thermal conductivity (TC) and flame

ionization detectors (FID) was used. Radiogenic gases were separated on a molecular sieve 5A column 6-ft x 1/4-inch OD, and they were analyzed with TC detection. Hydrocarbons were analyzed with the FID.

The gases in ambient air were determined as part of the standardization of each gas analysis. The results of 45 analyses were N_2 : 79.0% by volume, σ = 1,44%; O_2 : 20.9% by volume, σ = 1.47%. Carbon dioxide averaged 0.11% overall with a standard deviation (σ) of 0.9%.

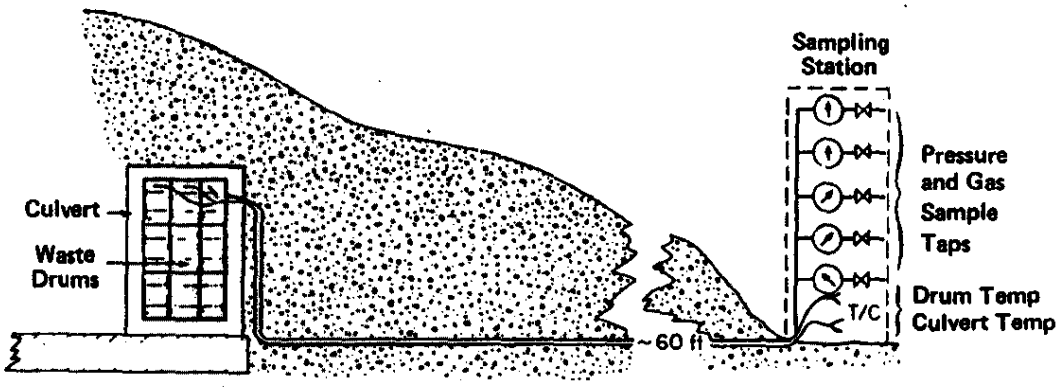

FIGURE B-1. Physical Arrangement of Radiogenic Gas Experiment

TABLE B-1

Routine Measurements of Drum No. 119*

Date	Day	O_2	H_2	CO	CO_2	Hydrocarbons, ppm	N_2	N_2O	T, °C**	psig
6/24	101	24.7	0.03	0	0.07	0	74.7	0	20/22	0.5
7/19	126†	-	-	-	-	-	-	-	-	0.0
8/6	144	21.0	0	0	370 ppm	1	78.8	0	39/37	0.0
9/10	179†	-	-	-	-	-	-	-	28/26	0.2
10/11	210	14.0	0.8	0	1.0	21	84.2	0.01	20/15	0.1
11/9	239	9.6	0.6	0.2	2.1	493	87.1	0.4	11/13	0.1
12/8	268	11.7	1.9	0	0.5	414	85.1	0.6	9/5	<0.1
1/11	302	6.4	0	0	5.3	391	88.2	0	4	0.0
2/8	330	5.9	1.7	0	6.0	233	85.8	0.6	3	<0.1
3/1	351	5.1	3.0	0.3	6.8	195	84.2	0.6	26/30	0.1
3/25	375†	-	-	-	-	-	-	-	22/28	0.1
4/4	385	4.3	0.6	0.2	7.7	211	86.5	0.7	16/28	0.1
5/2	413	3.0	-	0.3	8.5	700	87.7	0.5	21/23	0.8
5/31	442	2.8	0.9	0.3	9.0	548	86.5	0.5	21/22	0.6
6/28	470	3.8	0.2	0.3	9.5	728	86.1	0.4	38/42	0.8
8/9	512	5.0	0.2	0.2	9.7	590	84.8	0.3	27	0.7
9/19	553	6.0	0.1	0.2	10.5	244	83.0	0.3	27/25	0.8
10/10	574	18.4	0	0	1.9	89	79.7	0.4	23	0.8
11/8	602	5.6	1.7	0.3	5.2	306	86.9	0.3	25	0.7
12/12	636	7.5	0.8	0.2	9.1	120	83.1	0.2	10	0.3
1/3	658	5.4	0.5	0.3	10.4	1746	83.8	0.1	15	0.4
2/1	687	5.6	0.8	0.3	10.0	693	83.9	0.3	15	0.2
3/6	720	4.2	0	0.2	13.3	468	82.0	0.3	14	0.1
4/4	749	5.0	0	0	4.0¶	1193	90.1	0.9	25	0.2
5/1	776	4.7	0	0	11.3¶	1204	83.9	0.1	25	0.2
5/30	805	8.5	1.4	0.3	6.2	15	83.5	0.1	34	0.4
7/5	841	4.2	3.7	0	9.9	1273	82.0	0.1	28	0.4
8/3	870	7.8	1.9¶	0	8.2	1390	82.0	0.1	32	0.5
9/5	903	4.3	4.5¶	0	10.0	1088	81.0	0.1	27	0.6
10/2	930	8.4	1.5	0	8.3	874	81.4	0.4	35	0.6
11/6	965††	4.5	4.4	0	7.1	1045	83.8	0.1	26	0.7
12/4	993	6.0	1.5	0	11.3	520	79.5	1.7	23	0.7
1/8	1028	5.4	3.0¶	0	11.1	1550	80.4	0.1	16	0.7
2/5	1056	3.5	5.3¶	0	12.2	2584	78.9	0.1	14	0.8
3/5	1084	3.4	5.1	0	9.4	1395	82.0	0.1	19	0.6
4/2	1112	2.7	2.7	0	11.7	656	82.0	1.6	28	0.8
5/7	1147††	2.9	5.8	0	0.8	817	90.4	0.1	28	-0.5
6/5	1176	3.6	3.1	0	8.5	327	84.7	0.2	25	0.6
7/9	1210	4.1	2.7	0	7.4¶	384	85.7	0.2	20	0.6
8/6	1238	3.0	3.0	0	13.7¶	545	80.1	0.1	27	0.8
9/5	1268††	1.9	2.0	0	42.6	205	53.4	0.06	21	0.5
10/1	1294	3.1	4.0	0	9.4	271	83.4	0.09	25	0.5
11/5	1329††	7.5	3.3	0	20.3	203	68.9	0.03	17	0.6
12/3	1357	7.5	2.5	0	8.1	394	79.4	0.09	10	0.8
1/3	1388	7.7	1.6	0	7.5	354	83.2	0.09	12	0.8
2/4	1420	7.1	3.7	0	9.0	550	80.2	0.07	8	0.8
3/5	1449†	-	-	-	-	-	-	-	12	0.6
4/7	1482	7.6	3.2	0	8.4	363	80.8	0.04	16	1.0
6/2	1538	7.0	1.6	0	8.7	289	82.3	0.03	23	1.4

* Gas compositions are given in mole percent or in parts per million by volume.

** Temperature data were taken from Drum No. 122, the culvert, and outside air. Drum temperatures are listed first; outside air temperatures are listed second. Single values are for outside air.

† No measurements were made of gas composition.

†† Measurements for gas composition are considered anomalous, and are not included in gas production calculations (see footnote to Table 4).

¶ Values used for radiogenic gas partial pressure calculations.

TABLE B-2

Routine Measurements of Drum No. 120*

Date	Day	O_2	H_2	CO	CO_2	Hydrocarbons, ppm	N_2	N_2O**	T, °C†	psig
6/24	101	25.8	0.03	0	0.01	0	74.2	0	20/22	0.1
7/19	126††	-	-	-	-	-	-	-	-	0.0
8/6	144	20.5	-	-	771 ppm	26	78.0	0	39/37	0.0
9/10	179††	-	-	-	-	-	-	-	28/26	0.4
10/11	210	3.6	19.5	2.5	3.8	115	62.6	0.6/8.3	20/15	0.4
	210	2.0	18.8	1.7	4.9	100	60.8	0.6/11.1	20/15	0.4
11/9	239	1.4	17.6	0.75	4.9	1430	60.6	0.5/15.0	11/13	0.2
12/8	268	3.6	24.9	0.91	0.73	2190	69.2	0.64	9/5	0.2
1/11	302	10.7	3.4¶	0	0¶	1350	84.0	0	4	0.2
2/8	330	2.1	30.4¶	0.9	5.7¶	1273	60.4	0.5	3	0.2
3/1	351	1.6	31.8	1.0	4.4	981	60.7	0.5	26/30	0.5
3/25	375††	-	-	-	-	-	-	-	22/28	0.8
4/4	385	3.5	24.2	1.1	8.7	1781	67.8	0.5	16/28	1.1
5/2	413	4.7	19.2	1.0	7.3	3170	67.3	0.5	21/23	1.3
5/31	442	2.9	19.9	1.2	8.6	3190	67.0	0.4	21/22	1.6
6/28	470	4.0	17.9	1.1	8.7	3092	67.8	0.4	38/42	1.8
8/9	512	2.3	18.3	1.1	8.8	3620	68.5	0.4	27	1.7
9/19	553	3.9	20.5	1.2	8.3	1260	65.7	0.4	27/25	1.7
10/10	574	6.2	17.6	0.8	6.6	1890	68.5	0.3	23	1.5
11/8	602	4.9	23.3	1.1	7.9	1178	62.4	0.4	25	1.3
12/12	636	7.3	13.6	1.1	7.1	897	70.0	0.3	10	1.0
1/3	658	4.4	23.3	1.1	7.5	7125	63.5	0.2	15	1.0
2/1	687	4.8	22.4	1.3	8.9	3498	62.3	0.3	15	0.9
3/6	720	5.9	15.2	1.3	9.4	1825	68.0	0.2	14	1.0
4/4	749	2.1	28.5	1.2	9.2	5635	58.8	0.3	25	1.4
5/1	776	1.9	31.5	1.1	8.5	6860	56.9	0.1	25	2.0
5/30	805	5.1	13.6	1.2	9.1	3862	70.9	0.1	34	2.2
7/5	841	2.5	24.9	1.2	9.2	8956	62.2	0.1	28	2.8
8/3	870	7.8	12.5¶	0.9	7.4	3751	71.3	0.1	32	2.8
9/5	903	3.5	28.0¶	1.1	8.4	6853	58.9	0.1	27	3.0
10/2	930¶¶	13.2	3.7	0.6	1.5	4265	80.8	0.07	35	3.1
11/6	965¶¶	4.2	0	1.5	11.6	8666	82.7	0.1	26	3.0
12/4	993	4.3	25.7	1.1	12.5¶	100	56.4	0.1	23	2.8
1/8	1028	3.0	28.4	1.0	20.8¶	11420	46.6	0.2	16	2.7
2/5	1056	2.9	39.3	0.9	11.8	19140	45.0	0.1	14	2.6
3/5	1084	4.6	32.7	1.0	10.7	19780	50.9	0.05	19	2.7
4/2	1112	0.7	36.7	0.5	11.1	6920	50.9	0.04	28	3.2
5/7	1147	1.3	40.3	0.7	10.0	11970	47.7	0.08	28	3.5
6/5	1176	2.4	46.2	0.4	7.1	3550	43.9	0.02	25	4.0
7/9	1210	3.7	43.2	0.4	6.8	3183	45.9	0.02	20	4.2
8/6	1238	1.5	48.2	0.5	8.4	7445	41.4	0.03	27	4.5
9/5	1268¶¶	5.6	-	0.5	10.0	6237	-	0.03	21	4.8
10/1	1294	1.4	53.9	0.5	7.2	2928	37.0	0.02	25	4.6
11/5	1329	5.7	39.6	0.3	5.8	2407	48.5	0.02	17	4.0
12/3	1357	3.9	45.4	0.3	6.8	7205	43.6	0.01	10	3.8
1/3	1388	4.5	41.7	0.3	7.3	4017	46.1	0.01	12	3.7
2/4	1420	5.4	38.4	0.3	11.4	5725	44.6	-	8	3.7
3/5	1449††	-	-	-	-	-	-	-	12	3.9
4/7	1482	5.7	46.0	0.3	6.9	3528	48.3	-	16	4.2
6/2	1538††	-	-	-	-	-	-	-	23	5.2

* Gas compositions are given in mole percent or in parts per million by volume.

** The second numbers represent measured concentrations of NO.

† Temperature data were taken from Drum No. 122, the culvert, and outside air. Drum temperatures are listed first; outside air temperatures are listed second. Single values are for outside air.

†† No measurements were made of gas composition.

¶ Values used for radiogenic gas partial pressure calculations.

¶¶ Measurements for gas composition are considered anomolous, and are not included in gas production calculations (see footnote to Table 4).

TABLE B-3

Routine Measurements of Drum No. 121*

Date	Day	O_2	H_2	CO	CO_2	Hydrocarbons, ppm	N_2	N_2O**	T,°C†	psig
6/24	101	25.1	0.03	0	0.008	0	74.9	0	20/22	0.8
7/19	126††	-	-	-	-	-	-	-	-	0.8
8/6	144	20.8	0	0	2,600 ppm	13	78.5	0	39/37	1.0
9/10	179††	-	-	-	-	-	-	-	28/26	1.1
10/11	210	10.5	0.007	0	6.9	70	79.1	0.008/2.8	20/15	1.0
11/9	239	8.3	1.6	0	6.1	1800	75.0	4.5	11/13	1.0
12/8	268	8.6	3.6	0	2.16	1200	85.4	0.22	9/5	0.8
1/11	302††	-	-	-	-	-	-	-	4	0.6
2/8	330	7.7	2.7	-	10.4	413	79.2	-	3	0.4
3/1	351	6.0	2.9	0.2	12.6	304	78.2	0.1	26/30	0.7
3/25	375††	-	-	-		-	-	-	22/28	0.8
4/4	385	5.4	2.3¶	0.2	14.0¶	249	78.0	0.1	16/28	1.1
5/2	413	3.0	2.8¶	0.2	15.9¶	1006	77.9	0.2	21/23	1.1
5/31	442	2.9	2.2	0.3	16.4	728	78.0	0.2	21/22	1.4
6/28	470	4.3	1.0	0.2	16.4	709	77.9	0.2	38/42	1.6
8/9	512	4.1	1.5	0.3	17.7	750	76.2	0.2	27	1.6
9/19	553	5.9	0.1	0.3	16.0	192	77.5	0.3	27/25	1.7
10/10	574	6.4	0.3	0.2	16.3	444	76.8	0.3	23	1.6
11/8	602	5.2	0.2	0.3	18.4	168	75.8	0.2	25	1.4
12/12	636¶¶	18.2	0	0	3.7	12	78.0	0.1	10	0.8
1/3	658	6.3	0	0.2	18.3	926	74.9	0.2	15	0.6
2/1	687	8.3	0.2	0	16.1	355	75.4	0.1	15	0.3
3/6	720	5.2	0.1	0	18.9	182	75.8	0.1	14	0.1
4/4	749	4.6	0	0	20.4	206	75.0	-	25	0.4
5/1	776	3.9	0.2	0	21.5	567	74.6	0.1	25	0.9
5/30	805	10.3	-	0	20.0	251	69.6	0.1	34	1.0
7/5	841	8.0	1.8	0	16.4	860	73.7	0	28	0.2
8/3	870	8.1	1.3¶	0	16.8¶	440	71.3	0.1	32	0.1
9/5	903	5.0	2.9¶	0	20.5¶	929	71.7	0	27	0.1
10/2	930	9.3	0.3	14.6	0	598	74.1	0	35	<0.1
11/6	965	20.5	0.2	0	0	0	79.1	0.4	26	0.1
12/4	993	20.9	0	0	0.6	0	78.4	0	23	0.1
1/8	1028	20.4	0	0	0.1	0	79.5	0	16	<0.1
2/5	1056	17.8	2.2	0	3.6	330	76.4	0	14	<0.1
3/5	1084¶¶	8.7	2.8	0	17.4	692	71.1	0.02	19	0
4/2	1112¶¶	18.5	0.3	0	0.2	12	81.3	0	28	0
5/7	1147¶¶	2.6	2.7	0	26.2	714	68.4	0.07	28	0
6/5	1176¶¶	2.0	2.9	0	25.3	366	69.8	0.04	25	0
7/9	1210¶¶	2.9	2.2	0	25.2	344	69.8	0.02	20	0.2
8/6	1238¶¶	2.3	0.2	0	27.9	786	69.8	0	27	0
9/5	1268¶¶	1.7	3.0	0	27.2	381	68.1	0	21	0
10/1	1294¶¶	3.5	2.1	0	24.6	278	69.7	0	25	0
11/5	1329¶¶	21.5	0.4	0	0.04	0	78.5	0	17	0
12/3	1357¶¶	20.0	0.6	0	0.8	43	79.2	0	10	0
1/3	1388¶¶	12.4	2.4	0	11.2	236	74.1	0	12	0
2/4	1420¶¶	9.4	4.1	0	14.0	413	72.5	0	8	0
3/5	1449††	-	-	-	-	-	-	0	12	0
4/7	1482¶¶	7.7	5.0	0	19.1	334	68.2	0	16	0
6/2	1538¶¶	6.6	2.7	0	21.9	343	68.8	0	23	0.4

* Gas compositions are given in mole percent or in parts per million by volume.

** The second number represents measured concentrations of NO.

† Temperature data were taken from Drum No. 122, the culvert, and outside air. Drum temperatures are listed first; outside air temperatures are listed second. Single values are for outside air.

†† No measurements were made of gas composition.

¶ Values used for radiogenic gas partial pressure calculations.

¶¶ Measurements for gas composition are considered anomalous, and are not included in gas production calculations (see footnote to Table 4).

TABLE B-4

Routine Measurements of Drum No. 122*

Date	Day	O_2	H_2	CO	CO_2	Hydrocarbons, ppm	N_2	N_2O**	T, °C†	psig
6/24	101	25.3	0.03	-	0.008	-	74.7	0	20/22	0.5
7/19	126††	-	-	-	-	-	-	-	-	1.0
8/6	144	20.8	0	0	2,600 ppm	13	78.5	0	39/37	1.0
9/10	179††	-	-	-	-	-	-	-	28/26	1.1
10/11	210	5.7	3.2	2.3	4.5	65	77.7	1.5/7.5¶	20/15	1.0
11/9	239	3.3	6.0	0.6	6.2	1250	70.5	1.7/11.8¶	11/13	1.7
12/8	268	4.2	8.2	0.8	1.1	2250	82.3	3.2	9/5	1.7
1/11	302	2.7	12.1	0	8.7	2000	74.6	1.7	4	1.7
2/8	330	3.6	11.6	0	9.1	1098	74.4	1.3	3	1.6
3/1	351	2.6	14.3	0.6	9.3	824	71.9	1.3	26/30	2.0
3/25	375††	-	-	-	-	-	-	-	22/28	2.3
4/4	385	2.1	12.1	0.6	11.1	256	72.6	1.5	16/28	2.5
5/2	413	2.1	12.2	0.5	11.5	2737	72.4	1.3	21/23	2.8
5/31	442	1.9	13.4	0.6	4.7	2276	78.0	1.4	21/22	3.2
6/28	470¶¶	3.1	7.2	0.5	20.9	1781	67.2	1.1	38/42	3.6
8/9	512	8.5	4.1	0.3	8.7	1570	77.5	0.8	27	3.8
9/19	553	11.6	2.9	0.3	7.0	432	77.6	0.7	27/25	3.9
10/10	574	18.7	0	0	2.2¶	240	78.9	0.2	23	3.8
11/8	602	13.0	3.9	0.4	9.8¶	473	86.8	0.2	25	4.0
12/12	636	16.0	1.7¶	0.1	3.7¶	156	78.1	0.3	10	3.7
1/3	658	3.8	12.7¶	0.5	13.1¶	4136	68.9	1.1	15	3.6
2/1	687	2.5	14.2	0.5	14.6	1866	67.2	1.0	15	3.5
3/6	720	2.5	8.9	0.6	14.8	1011	72.4	0.9	14	3.6
4/4	749	2.4	16.0	0.4	14.1	2840	66.3	0.8	25	4.0
5/1	776	2.2	17.2	0.4	14.7	3980	64.9	0.7	25	4.5
5/30	805	13.2	0.6¶	0.1	8.6	702	77.6	0.4	34	4.9
7/5	841	7.1	10.8¶	0	11.0	3368	70.6	0.4	28	5.4
8/3	870	7.6	6.6	0	11.7	1829	73.7	0.5	32	5.5
9/5	903	3.6	15.2	0	14.8	-	65.8	0.6	27	5.4
10/2	930	2.5	17.9	0.4	14.8	4470	63.9	0.6	35	5.4
11/6	965	2.7	17.3	0	15.1	3870	64.3	0.6	26	5.2
12/4	993¶¶	4.4	11.5	0.4	21.0	4379	62.1	0.6	23	5.1
1/8	1028¶¶	4.5	27.4	0.7	35.2	9133	31.1	1.1	16	4.8
2/5	1056	2.1	20.6	0.2	21.6	9015	54.9	0.6	14	4.7
3/5	1084	2.9	17.1	0.5	19.3	4584	59.7	0.5	19	4.8
4/2	1112	1.2	23.0	0	22.6	3297	52.9	0.3	28	5.2
5/7	1147	1.8	25.5	0	16.8	4099	57.6	0.3	28	5.4
6/5	1176	1.4	29.6	0	15.1	1337	53.6	0.2	25	5.4
7/9	1210	1.7	31.8	0.1	13.6	1787	52.5	0.3	20	5.5
8/6	1238	1.8	25.7	0.2	17.0	3536	55.0	0.3	27	5.8
9/5	1268	2.1	26.2	0	16.3	1713	55.2	0.3	21	6.2
10/1	1294	1.4	31.4	0	15.7	1416	51.1	0.4	25	5.8
11/5	1329	5.0	27.2	0	12.8	1205	54.8	0.2	17	5.0
12/3	1357	4.7	17.3	0	15.3	3250	62.4	0.3	10	4.1
1/3	1388	4.6	25.9	0	14.7	1957	54.6	0.2	12	4.0
2/4	1420	5.2	26.5	0	12.2	3107	55.0	0.2	8	4.0
3/5	1449††	-	-	-	-	-	-	-	12	4.2
4/7	1482	5.2	26.5	0	14.2	2215	54.0	0.2	16	4.4
6/2	1538	6.0	11.7	0	16.9	1335	62.5	0.2	23	5.0

* Gas compositions are given in mole percent or in parts per million by volume.

** The second numbers represent measured concentrations of NO.

† Temperature data were taken from Drum No. 122, the culvert, and outside air. Drum temperatures are listed first; outside air temperatures are listed second. Single values are for outside air.

†† No measurements were made of gas composition.

¶ Values used for radiogenic gas partial pressure calculations.

¶¶ Measurements for gas composition considered anomalous, and are not included in gas production calculations (see footnote to Table 4).

TABLE B-5

Culvert Atmosphere Data*

Date	Day	O_2**	H_2	CO	CO_2**	Hydrocarbons, ppm*	N_2**	N_2O	T,°C†	psig
6/24	101	19.1/18.9	0.04	0	0.009	-	80.9/76.4	0	20/22	0.2
7/19	126††	-	-	-	-	-	-	-	-	0.0
8/6	144	20.5/21.2	0	0	414 ppm	1	77.5/78.8	0	39/37	0.0
9/10	179††	-	-	-	-	-	-	-	26/26	0.0
10/11	210	19.7/20.7	0	0	0	6.5	80.3/79.3	0	20/15	0.1
11/9	239	18.7/20.6	0	0	0	20	81.3/78.6	0	11/13	<0.1
12/8	268	24.5/25.5	0	0	<0.1	6	75.5/74.5	0	9/5	0.1
1/11	302	18.3/20.9	0	0	0	0	81.7/79.1	0	4	<0.1
2/8	330	19.0/20.5	0	0	0	0	81.0/79.5	0	3	0.1
3/1	351	19.1/21.7	2500 ppm	0	.03	14	80.8/78.3	0.1	26/30	0.1
3/25	375††	-	-	-	-	-	-	-	20/28	0.1
4/4	385	19.8/21.3	0	0	0	22	80.1/78.7	0.1	14/28	0.1
5/2	413	18.2/21.3	0	0	0	55	81.5/78.7	0.3	20/23	0.1
5/31	442	17.2/21.0	0	0	0.03/.03	35	82.7/79.0	0.1	21/22	<0.1
6/28	470	15.9/21.6	0	0	0.02/0.1	51	84/78.3	0.09	38/42	0.1
8/9	512	14.7/21.1	0	0	0	60	85.2/78.8	0.1	27	<0.1
9/19	553	12.8/21.4	0	0	0.1/0.1	29	87.0/78.6	0.1	27/25	<0.1
10/10	574	14.7/21.4	0	0	0	31	85.2/78.5	0.1	23	<0.1
11/8	602	13.0/20.6	0	0	0.1/0.2	20	86.8/79.2	0.2	25	0.1
12/12	636	15.4/20.5	0	0	0.2/0.1	8	84.3/79.4	0.1	10	0.1
1/3	658	16.2/20.4	0	0	0.1/0.1	77	83.7/79.5	0	15	0
2/1	687	16.9/20.3	0	0	0/0.1	44	82.7/79.5	0.3	15	0.1
3/6	720	17.7/20.4	0	0	0.1/0.1	9	82.1/79.5	0.2	14	0.1
4/4	749	18.0/20.3	0	0	0.4/0.4	35	81.5/79.3	0.1	25	0.1
5/1	776	18.0/20.3	0	0	0.1/0.1	50	81.7/79.5	0.1	25	<0.1
5/30	805	19.4/20.3	0	0	0.1/0.1	0	80.4/79.6	0.1	34	<0.1
7/5	841	17.2/20.5	0	0	0.1/0.3	173	82.5/79.3	0.1	28	<0.1
8/3	870	18.3/20.5	0	0	0.05/0.09	29	81.5/79.5	0.1	32	<0.1
9/5	903	14.7/20.7	0	0	0.1/0.1	0	85.1/79.2	0.1	27	<0.1
10/2	930	17.0/20.7	0	0	0.29/0.04	45	82.6/79.2	0.1	35	<0.1
11/6	965	14.4/20.4	0	0	0.2/0.2	120	85.3/79.3	0.1	26	<0.1
12/4	993	15.6/21.0	0.3	0	0.1/0.3	138	84.3/78.7	0	23	<0.1
1/8	1028	15.7/20.7	0.3	0	0.1/0.2	135	84.0/79.0	0.2	16	<0.1
2/5	1056	17.5/20.8	0.66	0	0.3/0.3	175	82.1/79.0	0.1	14	<0.1
3/5	1084	17.9/20.4	0.52	0	0.07/0.09	98	81.8/79.5	0.2	19	0
4/2	1112	11.6/14.7	0.50	0	0.07/0.03	47	88.3/85.2	0.09	28	0
5/7	1147	10.7/13.0	0.51	0	0.06/0.06	91	89.0/86.9	0.2	28	0
6/5	1176	13.2/13.3	0.27	0	0.2/0.1	29	86.6/86.6	0	25	0
7/9	1210	11.3/14.0	0.09	0	0.05/0.06	43	88.5/86.0	0.2	20	0.2
8/6	1238	11.2/19.5	0	0	0.05/0.2	90	88.7/80.3	0.1	27	0
9/5	1268	11.1/14.3	0.17	0	0.2/0.1	42	88.7/85.6	0	21	0
10/1	1294	14.0/15.7	0.12	0	0.09/0	12	85.8/84.3	0.07	25	0
11/5	1329	11.3/13.9	1.3	0	0.03/0.04	24	87.3/86.1	0.09	17	0
12/3	1357	11.1/13.9	0.26	0	0.05/0.07	50	88.7/86.0	0.1	10	0
1/3	1388	11.6/15.0	0.34	0	0/0.16	34	88.3/84.8	0.14	12	0
2/4	1420	12.7/14.7	0.40	0	0.2/0.1	53	87.0/85.2	0.1	8	0
3/5	1449††	-	-	-	-	-	-	0	12	0
4/7	1482	10.1/12.3	0.54	0	0.07/0	22	89.7/87.7	0.08	16	0
6/2	1538	11.6/15.0	No data	0	0.06/0.09	17	88.2/84.9	0.08	23	0

* Gas compositions are given in mole percent or in parts per million by volume.

** Measured value in culvert/ambient air.

† Temperature data were taken from Drum 122, the culvert, and outside air. Drum temperatures listed first; outside air temperatures are listed second. Single values are for outside air.

†† No measurements were made of gas composition.

APPENDIX C

SAMPLING AND TRANSFER LINES

The volume of gas in the transfer lines from the experimental drums to the sampling station was estimated to be about 500 mL. However, the transfer lines were airtight, so the gas in them is approximately at equilibrium with the gas contained in the drums themselves.

An experiment was performed to determine the homogeneity of the gas mixture in the drum and transfer line system. The two drums that had accumulated the most pressure, Drums No. 120 and 122, were sampled as usual. The transfer lines were then flushed by venting two or more liters of gas through each line from the corresponding drum.

The sampling process was then repeated. Drum No. 120 was simply flushed once with a 7.5-liter volume of vented gas, while Drum No. 122 was flushed three times with approximately 2-liter volumes. Samples were taken each time. The results of this experiment are reported in Table C-I.

TABLE C-I

The Effect of Sample Volume on Gas Composition Measurements

Drum Number	Total Volume of Vented Gas, L	Measurements, mole %					
		O_2	N_2	Co_2	H_2	CO	NO
120	0	7.8*	50.8	13.9	27.1	0.5	-
120	7.5	8.0	53.7	6.5	31.2	0.1	-
122	0	6.6	64.8	21.8	6.4	-	0.5
122	2	5.9	63.0	20.0	10.7	-	0.3
122	4	4.9	51.6	16.3	26.9	-	0.3
122	6	4.8	52.0	16.8	25.4	-	0.5

* Mole % of gas sample component.

The data indicate that samples taken directly from the transfer lines do not correspond exactly to the overall composition of the gas contained in the drums. The composition of the gas in the transfer lines is representative of the gas at the sampling port of the drums, which is very close to the drum lid. Of course, one would expect hydrogen to be less concentrated near the drum lid than inside the individual sample containment bags and drum liner.

A gradual but pronounced change was observed in the composition of the gas as it was released from Drum No. 122. It became less concentrated in oxygen and nitrogen, and the hydrogen concentration was significantly higher. Therefore, the plastic waste containment bags must have contained hydrogen at relatively high concentrations. Then, when the loss of gas through the transfer lines caused the pressure to drop, hydrogen-rich radiogenic gas escaped from the drum liner to mix with the rest of the gas in the drum and in the transfer lines.

Measurements of the samples obtained after the transfer lines were flushed are well within the range of all values acquired without flushing (see Tables 4, B-2, and B-4). The advantage of not flushing the transfer lines was that unnecessary pressure drops were avoided, so the system was disturbed less and pressure measurements would have more validity. Also, the gas samples that were taken directly from transfer lines most closely represented the composition of the atmosphere inside, near the lid of the drums. This is important in terms of flammability considerations. Therefore, it was concluded that the sampling procedure without gas venting best served the purpose of the experiment.

APPENDIX D

GAS VOLUME IN DRUMS

The volume of free space in the drums must be known so that gas production rates and potential pressure accumulations can be calculated. The free volume in Drums No. 120 and 122 were determined using the pressure drop caused by venting a measured volume of gas from the drum. The vented gas was measured over water, and the change in gas pressure was read from the gauge at the sampling station. This experiment was part of the transfer line experiment, which was performed after the other data in this report were taken, so pressure and composition data were not affected in any way. The following equation is derived from the ideal gas law:

$$V = V_c \cdot \frac{T_c}{T_i} \cdot \frac{P_c}{(P_i - P_f)}$$

where P_c = Atmospheric pressure, less the partial pressure of water at T_c,

P_i = Initial pressure inside the drum

P_f = Final pressure inside the drum

T_c = Temperature of collection

T_i = Temperature inside the drum (°K)

V = Internal gas volume

V_c = Collected gas volume.

The total volume of the drums was known to be about 218 liters. Two trials resulted in estimates of 181 and 159 liters for the total atmospheric volume in Drum No. 120. The average of these two values, 170 liters, was used in subsequent calculations. The gas volume in Drum No. 122 was estimated at 145 liters, based on a single trial. The precision of the pressure measurements limit accuracy, probably to ±10% in the total gas volume estimate. These results show that only about 30% (22% in Drum No. 120 and 34% in Drum No. 122) of the total volume of the drums is actually filled with solid waste.

REFERENCES

1. Supplemental Alternatives for Long-Term Management of Defense Transuranic Waste at the Savannah River Plant. USDOE Report SR-WM-79-1 (August 1980).

2. N. E. Bibler. Radiolytic Gas Production During Long-Term Storage of Nuclear Wastes. CONF-761002-3, Savannah River Laboratory (1976).

3. M. A. Molecke. Gas Generation from Transuranic Waste Degradation: Data Summary and Interpretation. USDOE Report SAND-79-1245, Sandia National Laboratories, Albuquerque, New Mexico (December 1979).

4. A. Zerwekh. Gas Concentration from Radiolytic Attack of TRU-Contaminated Hydrogenous Waste. USDOE Report LA-7674-MS, Los Alamos National Laboratory, Los Alamos, New Mexico (June 1979).

5. A. R. Kazanjian. Radiolytic Gas Generation in Plutonium Contaminated Waste Materials. USDOE Report RFP-2469, Rockwell International, Rocky Flats, Colorado (October 1976).

6. J. E. Hoy. Radiogenic Gases and Drum Pressures Associated with TRU Waste Storage. Du Pont-SRL Internal Report DPST-78-245, E. I. du Pont de Nemours & Co., Savannah River Laboratory, Aiken, South Carolina (February 1978).

7. H. F. Coward and G. W. Jones. Limits of Flammability of Gases and Vapors. Bulletin 503, Bureau of Mines, U. S. Government Printing Office (1952).