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Gas Generation From Transuranic Waste Degradation: An Interim Assessment

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Sandia Laboratories

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GAS GENERATION FROM
TRANSURANIC WASTE DEGRADATION:
AN INTERIM ASSESSMENT*

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ABSTRACT

A review of all available, applicable data pertaining to gas generation from the degradation of transuranic waste matrix material and packaging is presented. Waste forms are representative of existing defense-related TRU wastes and include cellulose, plastics, rubbers, concrete, process sludges, and mild steel. Degradation mechanisms studied were radiolysis, thermal, bacterial, and chemical corrosion. Gas generation rates are presented in terms of moles of gas produced per year per drum, and in G(gas) values for radiolytic degradation. Comparison of generation rates is made, as is a discussion of potential short- and long-term concerns. Techniques for reducing gas generation rates are discussed.

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GAS GENERATION FROM TRANSURANIC WASTE DEGRADATION:
AN INTERIM ASSESSMENT

INTRODUCTION

The generation of gases from the degradation of existing and potential forms of defense-related transuranic waste has received a considerable amount of study over the past several years.

This area of study, particularly under conditions to be expected for deep geologic terminal isolation, is a major segment of the Waste Isolation Pilot Plant (WIPP) Transuranic (TRU) Waste Experimental Characterization Program. This program, conducted by Sandia Laboratories and sponsored by the Department of Energy, is summarized elsewhere (1).

This paper contains a comprehensive review and assessment of all available, applicable gas generation data from published reports plus unpublished references such as office memoranda, internal laboratory documents, and personal communications. This review includes data on gas generation rates, degradation mechanisms, synergism between mechanisms, gas compositions, methods for reducing production rates, and intercomparisons between generation modes. Much of the data presented is preliminary and may be modified before the various studies are completed. This interim review and assessment was compiled for presentation to the Department of Energy Waste Acceptance Criteria Steering Committee (WACSC) in January 1979. An updated compilation will be presented in July 1979.

The mechanisms of TRU waste matrix and container degradation resulting in gas generation are summarized in Table 1. Also listed are the major gases produced in approximate order of abundance and significance.

The specific overall study areas for WIPP TRU waste characterization pertaining to gas generation and its significance are listed at the bottom of Table 1. The first three areas will be discussed in detail. Data from these endeavors will be coupled integrally with mathematical gas accumulation

TABLE 1
GAS GENERATION FROM TRU WASTES

Mechanisms of Waste Degradation, Gas Production:

1. Radiolysis
2. Thermal and Catalyzed Thermal
3. Chemical Corrosion
4. Bacterial

Primary Gases Produced:

H₂, C₂H₂, CO, CH₄, O₂, H₂O, NO_x, He

Concerns of Gas Generation:

Long-term: pressurization of repository
breach in containment integrity

Operational Phase:
flammable, explosive, toxic concentrations of gases
fuel for fire, with initiating event
particulate contamination carrier
effects on mine design, operation

Areas of WIPP Study:

1. kinetics, species, total extent of gas generation
2. predictive, analytical modeling of gas generation
3. techniques, additives for reducing generation rates
4. gas accumulation analysis
5. permeability studies on gas dissipation
6. mine response to gas accumulation
7. WIPP TRU waste acceptance criteria; to limit gas generation

analyses, measurements of gas permeability in WIPP rocksalt, and analyses of mine response to gas accumulation (areas 4,5, and 6). These areas are reviewed separately(2).

These studies are in progress at Sandia Laboratories and contractor facilities and are necessary to assess the potential consequences of gas generation from waste degradation on overall repository integrity and safety.

Specific Concerns of Gas Generation:

Concerns over gas generation in the WIPP or other (future) comparable waste repositories can be divided into two distinct phases: (1) the short-term or operational phase of the repository, and (2) the long-term phase, after the repository is filled, decommissioned, and ultimately sealed. Reference (1) describes these two phases in more detail including all identified concerns.

Long-term concerns are the driving force behind the majority of the WIPP-specific gas generation studies. Long-term potential gas-related consequences begin when the WIPP ventilation system is shut off to waste storage rooms just prior to their sealing. Waste storage rooms, backfilled with salt, have some residual void within the salt fill, but combustibility will no longer be a hazard because of insufficient oxygen. The major problem lies in eventual pressurization of the remaining void volume by gases still being produced via waste degradation. Although some modes of degradation may appear quite slow, significant effects may result over time periods of hundreds of years or longer:

SLOW RATES X LONG TIMES = POTENTIAL PROBLEMS

In the long term, generated gases are no longer removed by ventilation and concentration and potential pressurization could result--particularly if rates of gas dissipation (via formation permeability) are very low. The permeability of gases in WIPP rocksalt has been measured in the laboratory (2). If the temperature in the TRU waste isolation horizon increases from ambient (about 25°C) due to thermal fields arriving from heat generating

high-level waste or remote-handled TRU wastes stored on other horizons of the same facility, waste degradation can be accelerated. The increasing temperatures could result in further thermal waste degradation, gas generation, water (sorbed on waste matrix) vaporization, and higher pressures, all aggravating the long-term gas containment capacity of the facility.

If the pressure buildup is sufficient the overburden rock/salt/evaporate sequence may be fractured or a shaft seal may fail. This could lead to a release of potentially contaminated gases (aerosol or vapor entrained) to the surrounding geosphere, or provide a pathway for water intrusion into the repository. Much laboratory and in-situ experimental work remains to quantify the potential and credibility of these scenarios.

Experimental Conditions:

TEMPERATURE: Temperatures of interest for WIPP-specific studies of waste degradation range from 25°C, the approximate WIPP mine ambient temperature during its operational phase, up to 100°C, used for overtest purposes. While some of the conditions given here could not occur in the WIPP, conditions are postulated for more severe environments so that conservatism is maintained and results have more generic application.

If heat generating wastes (e.g., high-level wastes) were considered present at the lower horizon of the WIPP at a thermal density of 75 kW/acre (18.5 watts/m²), the calculated (3) maximum temperature obtained at the upper TRU horizon will be 43°C. The temperature will rise rapidly from ambient, reach its maximum at approximately 200 years (after sealing), then decrease slowly. This temperature versus time profile for the WIPP contact-handled TRU waste horizon is illustrated in Figure 1.

An upper boundary temperature of 70°C was investigated to assess the impact of collocation of contact-handled TRU and heat generating waste on the same horizon.

Laboratory analyses are being conducted at 20°C to 25°C, 40°C, 70°C, and 100°C for overtesting.

WIPP TRU CH LEVEL TEMPERATURE

FIGURE 1

PRESSURE: The pressure range of interest for experimental studies ranged from 1.3×10^5 to 1.5×10^4 kPa (1-150 atmospheres, 15-2100 psia). The lower pressure is the ambient pressure during the operational phase of the WIPP. The higher pressure is representative of the sealed repository lithostatic (rock overburden) pressure at the 646 m (2150 ft) water-handled TRU horizon.

WHEEL: Other variables, which may influence waste form degradation and gas generation rates, such as the *bedded salt mine geology/geochimistry*, or the presence or absence of an air atmosphere, will be described where applicable.

Waste Form Characteristics:

The TRU contaminated waste matrices of primary interest for the WIPP TRU waste characterization program (1) consist of: cellulose (paper, cotton, cloth, wood, etc), plastics (polyethylene, polyvinyl chloride) rubbers (neoprene, Hypalon), a composite organic matrix of the above components, concrete-TRU ash, and process sludges. These wastes are usually contained in a 210 liter (55 gallon) mild steel drum.

For intercomparative purposes in this study, a defined "standard" TRU contaminated drum of waste is assumed to contain approximately 10 grams of weapons grade plutonium (^{239}Pu , primarily ^{239}Pu) or 0.77% of alpha emitters. The drum is assumed to contain 150 kg of waste matrix, regardless of its composition (i.e., cellulose or concrete). This weight represents the overall container weight of 210-liter waste drums temporarily stored at the Idaho National Engineering Laboratory (INEL) from September 1971 through December 1976 (4). Utilizing these defined contamination and weight values, the amount of gas generated by matrix degradation can be specified in terms of a "standard" unit matrix weight basis.

When a greater body of gas generation data has been accumulated (by July 1979), intercomparisons of gas generation will be made on a standard volume basis--the volume of a 210-liter drum. For this compilation (scheduled by July 1979), realistic values of contamination and matrix weight for existing drums of TRU contaminated wastes in temporary storage at INEL (4) will be utilized.

Degradation Study Participants:

The primary laboratories and experimenters who are conducting TRU waste degradation--gas generation studies are listed in Table 2.

TABLE 2

PRIMARY GAS GENERATION STUDY EXPERIMENTERS

1. Los Alamos Scientific Laboratory (LASL)
(S. Kozlowski, A. Zerkow, B. Barnhart)
2. Savannah River Laboratory (SRL)
(N. E. Bibler)
3. University of New Mexico (UNM)
(D. E. Caldwell)
4. Sandia Laboratories (SLA)
(J. W. Braithwaite)

Los Alamos Scientific Laboratories (LASL), Savannah River Lab (SRL), and the Rocky Flats Plant (RFP) are the only known laboratories to have studied the radiolysis of TRU wastes. The RFP studies were a part of the WIPP TRU waste characterization program. LASL is conducting the bulk of current studies of radiolytic, thermal, and catalyzed thermal degradation of organic waste matrices under WIPP specific conditions (5,6,7,8,9). LASL has been conducting similar non-WIPP-related radiolysis studies for over four years (10,11). SRL is conducting radiolytic and thermal degradation studies of concrete encapsulated TRU waste (calcined ash) (13,14) and has previously studied the radiolytic degradation of organic waste matrices (15) and HLW sludges in concrete (16). The UNM Biology Department is investigating bacterial action on organic waste matrices which can produce, consume, or transform gaseous products, plus other consequences of bacterial degradation (17,18). UNM is being assisted (under WIPP funding) by LASL (B. Barnhart). The generation of gas from the corrosion of mild steel TRU waste drums is

being entered in the actinide inventory at location and the location of actinide-containing packages for each drum is also in progress. (13,24,25,26)

The assistance of Dr. Kenneth G. LARSEN, N. Bible, of ORNL, Dr. Theodore J. AM, and Dr. Bruce Swartz of ORNL in preparing this document and in interpreting the data is greatly appreciated. Some of the supporting data and calculations have been incorporated directly.

RADIOLYTIC DEGRADATION DATA

A summary of the data on the gas generation rates from the radiolysis of liquid matrix PU contaminated waste, are summarized in Table 3. Values are tabulated in moles (total gas)/year/drum for a "standard" 50 liter, 1000 gram contaminated TRU package and also in terms of G (total gas) per gram of actinide, the number of atoms released per gram of actinide. The value of G is calculated, for example, for ^{239}Pu (5.1 MeV) yields 5.1×10^4 disintegrations/gram. The generation of "total gas" means the overall production of all of the gases, H_2 , H_2O , CO_2 , etc., plus the depletion of O_2 in moles O_2 per gram O_2 . This will be elaborated upon in subsequent sections.

Based on the definition of G(gas), the number of moles of gas produced per year per drum, the gas generation rate, can be calculated with the following equation:

$$\text{Moles of gas/year/drum} = (0.099 \text{ moles/G(gas)}) \text{G(gas/drum)}$$

This simplistic equation does not include any possible effects of pressure, temperature, or dose rate dependency on the gas generation rate. It assumes all alpha decay energy is deposited in the waste matrix. This equation is used, despite its possible shortcomings, to convert the measured G(gas) values in Table 3 to gas production rates.

for example: with G/drum = 0.77 (=10g ^{239}Pu)

G=1.0	yields	0.077 moles/year/drum
1.4	yields	0.11 moles/year/drum
1.9	yields	0.14 moles/year/drum

LASL Data:

The most extensive radiolysis studies now in progress are at LASL. Radiolytic gas generation rates are being measured as a function of:

1. Waste form--cellulosics (waxton and paper--ny, monol), polyethylene, PVC, and composite (81 percent cellulose, 12 percent polyethylene, 12 percent PVC, 15 percent neoprene, 17 percent Hypalon rubber);
2. Pu contamination level/drum loading (dose rate-equivalent to: 20 to 32,000g $^{239}\text{Pu}/\text{drum}$, or 1.94 to 2464 alpha Ci/drum, or 1.0×10^{-5} to 1.6×10^{-2} Ci/g (up to 150 kg) of waste, or 3.1×10^5 to 1.60×10^8 (where $x = 200$ g $^{239}\text{Pu}/\text{drum}$);
3. Temperature = 20°C, 40°C, 70°C, 100°C;
4. Time = 5 to 259 days (5); some at more than 4 years (10,11,12).

With the currently existing data base, dose rate (Pu loading) appears to have little effect (5) on resultant gas generation rates. Figure 2 illustrates the relative insensitivity for dose rates of 1×10^5 to 1.60×10^8 on a cellulosic matrix. *It appears justified, therefore, to extrapolate measured gas production rates at high Pu loadings down to defined "standard" contamination loadings of 0.77 Ci/drum.*

G(gas) was found to decrease as a function of time (integrated dosage) at high dose rates due to the localized depletion of organic matrix material adjacent to particles of Pu contaminant. Figure 3 illustrates the decrease of G(gas) for cellulose loaded to 40X for a period of over 4 years (12). These data were numerically fitted (5) to a regression equation of the form:

$$G(\text{gas}) = c_1 \exp(-c_2 t)$$

For a realistic average loading/dose rate of 10g of $^{239}\text{Pu}/\text{drum}$, the decrease of G(gas) with time would be slower by approximately three orders of magnitude. For a low dose rate, apparently, the effective gas generation rate should be quite constant for hundreds of years.

Experiments at LASL have been initiated (5) in which highly contaminated cellulosics and polyethylene in test cylinders have been pressurized to approximately 1×10^4 kPa (1500 psi) with deuterium. These experiments will

TABLE 3

EXISTING RADIOLYTIC DEGRADATION DATAORGANIC MATRICES

Assumptions: 10g ^{60}Co /drum = 0.77 Ci average; 150 kg waste/drum.

	moles/yr/drum	G (total gas)
<u>IASL:</u> (20°C, PRELIMINARY)		
celluloses	9.11±0.03	1.4 ± 0.4
PVC	0.47	
polyethylene	--	
composite	--	
<u>SRL:</u> (20°C)		
celluloses	0.14	1.9
pump oil	0.15	1.0 (1.6-H ₂)
octane	0.34	4.5 (3.0-H ₂)
(concrete/TRU ash)	0.053-0.002	0.7-0.03
<u>RFP:</u>		
celluloses (dry)	0.05	(0.63)
celluloses (wet)	0.02	(0.31)
polyethylene	0.06	(0.73)
PVC	0.03-0.07	(0.43-0.96)
plexiglass	0.14	(1.9)
rubbers	0.03	(0.37)
oil	0.24	(3.1)
IX resins	0.008	(0.11)
cemented resins	0.16	
production wastes (resins and wet combustibles)	0.03-0.16	
<u>Alpha Decay:</u>		
He generation	1.5 X 10 ⁻⁶	

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DOSE RATE DEPENDENCY OF $G(\text{GAS})$

DECREASE OF $G(\text{GAS})$ WITH TIME

determine whether high pressures will inhibit or decrease further gas formation from radiolysis due to back reactions. This determination could have a significant impact on the total gas pressure to which a sealed repository is subjected. Similar experiments have been initiated (11, 14, 15) at SRP with concrete matrix wastes for the same purposes. Experimental and equipment difficulties have been encountered by both laboratories in this endeavor. Preliminary data on the effects of pressure on the gas generation rates from waste matrices are not yet available.

The gas from radiolysis of cellulose at 20°C was determined (5) to contain H_2 , CO_2 , CO , CH_4 , and O_2 , with H_2 making up about 50 mole percent of the total; the mole ratio $H_2:CO_2:CO$ was calculated to be 1.9:0.42:0.23. A similar SRP analysis on cellulosic radiolytic degradation (6) determined a $H_2:CO_2:CO$ ratio of 1.6:0.7:0.1. In both cases, O_2 was considered.

Experiments in progress at IASL are also investigating whether evolution of gases by radiolysis is temperature dependent. Preliminary results (5) for polyethylene and celluloses at high contamination levels (160X) indicate that more gas is generated at 70°C than at 20°C. Radiolytic gas generation data at 70°C plotted in Figures 4 (cellulose) and 5 (polyethylene) have been corrected to 20°C by using the ideal gas law. Consequently, the 70°C radiolysis data may be compared directly to the respective 20°C radiolysis data. The variations observed resulting from a temperature difference of only 50°C are somewhat surprising; thermal degradation is comparatively minor in this temperature range (16) to be discussed. Sommer and O'Donnell (23) found increases in the gas yield of low-density polyethylene upon gamma irradiation at higher temperature. Turner (21) did not feel that moderate temperature changes could be expected to exert such influence on the radiation chemistry of polymers.

Gas generation measurements in progress (5) at low, realistic TRU waste contamination levels (0.1X and 1X) and temperatures of 20°, 40°, and 70°C are either generating so little gas, or none at all, that their data cannot be considered reliable at this time.

As the temperature increases from ambient, the relative percentage of CO_2 and CO in the generated gas increases for cellulosic matrices. As the dose rate/contamination loading increases, the relative percentage of H_2

FIGURE 4

TEMPERATURE DEPENDENCE OF RADIOLYSIS OF CELLULOSE

FIGURE 5

TEMPERATURE DEPENDENCE OF RADIOLYSIS OF POLYETHYLENE

also increases for cellulosic matrices. At conditions expected in the WIPP, temperatures of approximately 40°C or less, gases generated by radiolytic/thermal mechanisms will consist primarily of H₂, CO₂, and CO.

SRL and RFP Data, Organic Waste Matrices:

The LASL G(gas) value for cellulose, 1.4 ± 0.4, compares quite well with the previously measured (15) G(gas) value for cellulose at SRL of 1.9 (see Table 1.).

Kazanjian, in (25) at RFP contaminated various common organic waste materials with either ²³⁹PuO₂ (2-20 microner particles) or ²³⁸PuO₂ (less than 30 microner particles). Dose rates varied by up to a factor of 50. Kazanjian also noticed a decrease in gas generation rates as a function of time due to localized matrix depletion. G(gas) values determined from his experiments are presented in Table 3. Discrepancies between the G(gas) values of Kazanjian and those of LASL and SRL are immediately apparent. The RFP G(gas) value for dry cellulose is approximately less than one half the LASL and SRL values. RFP also obtained lower gas yields for wet cellulose than from dry cellulose; this is contrary to similar work performed by Zerwekh at LASL (5,10,11). There remains a significant degree of doubt as to the validity of the RFP data considering these discrepancies between the RFP and concurring LASL and SRL data. It is possible that the lower G(gas) values/gas production rates determined by Kazanjian resulted from data collected after significant waste depletion had occurred.

Kazanjian (25) also postulated that depletion rates were dependent on contaminant particle size, with depletion times increasing as particle size decreases. Work by Bibler (14) on concretes comes to exactly the opposite conclusion regarding particle size.

Radiolysis Field Tests:

LASL (10,11), SRL (26), and RFP (27,28) have each conducted field tests on gases generated in drums of production wastes. LASL periodically sampled drums of hydrogenous wastes (contaminated with ²³⁸Pu) located in shallow trenches. No significant internal drum pressurization was detected due to gas diffusion through the standard gaskets; the gaskets are, however, liquid and particulate tight. Several explosive gas mixtures were detected, some

changed to non-explosive but combustible composition after a period of time. H_2 concentrations increased with time and the O_2 was depleted as a result of CO_2 and CO formation. It was also determined that oxygen (air) could diffuse into the drums while H_2 diffused out. Because the possibility of an explosible mixture exists, it was stated (10) that all drums of similar contaminated cellulose in temporary storage should be considered potentially explosible until the gaseous contents have been analyzed and/or replaced with an inert gas. This is a significant consideration when recovering or reprocessing stored wastes.

Other interesting observations were: Rags and paper suffered the most radiolytic (^{238}Pu) degradation, neoprene the least; CH_4 and traces of occasional hydrocarbons with molecular weights up to about 60 were detected; damp cellulose undergo more rapid radiolytic degradation than do dry cellulose (11), possibly due to the additional radiolysis of the sorbed water.

At SRL (26), four typical Savannah River Plant waste drums and one waste culvert were monitored for radiogenic gas composition and internal pressurization. Such monitoring covered a period of about 700 days. Drum internal pressures of up to 4 psi were detected; the drum gaskets permitted hydrogen and other gases to diffuse out while oxygen from the air diffused inward replacing some of the radiolytically depleted oxygen. Hydrogen concentrations in some of the drums approached 25 percent by volume; CO_2 similarly approached 20 percent by volume.

At RFP (27,28), the hydrogen production rate of several drums of contaminated production wastes was measured. The production wastes consisted of cemented ion exchange resins and cemented resins plus moist combustibles (including plastics and rubbers). "Cemented" ion exchange resin refers to layers of moist, organic ion exchange resins separated by layers of cement powder used to stabilize and soak up some of the moisture. For the cemented resins alone, a radiolytic H_2 generation rate of 5.8×10^{-4} moles/Ci/day was measured; for a "standard" drum containing 0.77 Ci, this rate is equivalent to 0.16 moles/yr/drum. For waste combinations of cemented resins and moist combustibles, the reported H_2 generation rates ranged from 1.1 to 6.1×10^{-4} moles/Ci/day, corresponding to 0.03-0.17 moles/year/drum for a "standard" drum.

SRL Data, Concrete Matrix TRU Waste:

Previous studies at SRL (13,16) have investigated the radiolytic degradation and gas generation rate of defense high-level waste sludges incorporated into concrete matrices. Current studies (13,14,15) are focused on the radiolytic gas generation of TRU waste when incorporated into a concrete matrix under conditions that such a waste form might encounter in the field. If the decision is eventually made to incinerate (or melt) the waste, the combustible, organic elements of defense TRU waste stored in a trench or in temporary surface or shallow-trench storage, concrete may be a suitable encapsulating matrix for the resultant ash (or other product).

The studies at SRL, funded by the WIPP project (1), are to determine the radiolytic gas generation capacity of concrete in organic waste matrices. Studies are also designed to determine additives or techniques which could significantly reduce the gas generation rate of the concrete. A significant amount of data has been reported and will be summarized (14,15).

Cement types investigated include high alumina cement (HAC), portland type I cement (I), and portland type I-pozzolan cement (I-P). The TRU waste ash simulant was made by the incineration of common laboratory-type waste (cane covers, rubber gloves, polyethylene tubing, etc.); this ash was incinerated at 800°C, yielding a low residual carbon content. The ash contained primarily CaO and TiO_2 , with a much smaller content of other oxides. A mixture of 10 weight percent ash in a dry cement mix gave sufficient workability of the resultant concrete paste. After curing, the total water/cement plus ash ratio was 0.1-0.4. ^{234}Pu in the form of a salt was added either as a solution (in 0.2M H_2SO_4 , to keep the Pu in solution) to the water used to make the concrete, or as $^{238}\text{PuO}_2$ particles added to the dry mix.

The gas generation capacity of the doped concrete was determined in terms of $G(\text{H}_2)$ and $G(\text{total gas})$ values. G values were determined from both changes in the sample-system pressure, or from the measured final gas composition and total dose.

G values determined (14) under various conditions for the concrete-TRU ash are summarized in Tables 4a and 4b.

TABLE 4a

RADIOLYSIS DATA OF CONCRETE-TRU ASH SAMPLES

4.gh Alumina Cement (HAC)

<u>Test Condition:</u>		<u>T°C</u> (<u>+2°C</u>)	<u>G (H₂)</u>	<u>G (total gas)</u>
without ash, Pu(L),	hdose	23	0.42	.33
with ash, Pu(L),	hdose	23	0.55	0.51
with ash, Pu(L),	ldose	23	0.48	0.24
with ash, Pu(S),	hdose	23	0.21+0.01	0.21+0.03
with ash, Pu(L),	hdose	23	0.13	0.15
		70sh	0.24	0.14
		70hs	0.15	0.11
with ash, Pu(L),	hdose	23	0.30	0.15
EDTA		70sh	0.19	---
		70hs	0.06	0.04
with ash, Pu(L),		23	0.08	0.43
1M Fe(NO ₃) ₃				
with ash, Pu(L),		23	0.63	0.43
2M Fe(NO ₃) ₃				
with ash, Pu(S),		23	0.08	0.03
3M NaNO ₂				

Note: Pu(L) = ²³⁸Pu in 0.2M H₂SO₄
 hdose = 10¹⁷ eV/min/g
 sh = sealed, then heated

Pu(S) = particulate ²³⁸PuO₂
 ldose = 10¹⁶ eV/min/g
 hs = heated, then sealed

G = 0.5 yields 0.04 moles/yr/drum ("standard" drum)
 G = 0.03 yields 0.002 moles/hr/drum (filled with 150kg concrete)

TABLE 4L

RADIOLYSIS DATA OF CONCRETE-TRU ASH SAMPLES

Portland Type 1 Cement (I)				
<u>Test Condition:</u>		T^{OC} ($\pm 2^{OC}$)	$G(H_2)$	<u>G(total gas)</u>
without ash, Pu(L),	hdose	23	0.43	0.48
with ash, Pu(L),	hdose	23	0.65	0.55
with ash, Pu(L),	ldose	23	0.63	0.61
with ash, Pu(S),	hdose	23	0.28	0.27
with ash, Pu(L),	hdose	70sh	0.46	0.46
		70hs	0.15	0.17
		100hs	0.11	0.05
with ash, Pu(L),	hdose	23	0.35	0.05
EDFA		70sh	0.11	0.03
		70hs	0.08	0.07
		100hs	0.05	0.03
with ash, Pu(L),		23	0.08	0.43
1M $Fe(NO_3)_3$				
with ash, Pu(L),		23	0.61	0.16
2M $Fe(NO_3)_3$				

Portland Type 1-Pozzolanic Cement (I-P)

without ash, Pu(L),	hdose	23	0.48	0.51
with ash, Pu(L),	hdose	23	0.68	0.73

For the HAC, I, and I-P contaminated concretes, H_2 was generally the only gas produced, O_2 was depleted, and N_2 was unaffected (deviations will be described). Hydrogen was not produced when concrete not containing Pu was heated to 70° and $100^\circ C$.

G(gas) values were higher (14,16) when the concrete contained the 30 percent ash than when it did not. G(gas) values with and without ash are 0.51 vs. 0.33, 0.55 vs. 0.48, and 0.73 vs. 0.51 for HAC, I, and I-P matrices, respectively. (The I-P matrix was eliminated after this test.) The increase of G(gas) with ash present is due to the association of some water with the ash.

A zero-order dose rate dependency was determined (14,16) for G(gas) in the concrete matrices, similar to the ion-effect described earlier (5). A maximum drum loading of $200 \text{ }^{238}\text{Pu}$ corresponds to $3.3 \times 10^{14} \text{ eV/min/g}$ in concrete. Dose rates utilized in the SRL study varied from $10^{16} - 10^{17} \text{ eV/min/g}$ of concrete.

The G(gas) value was lower (14) by approximately a factor of 2 when the ^{238}Pu was added as solid PuO_2 particles rather than being dissolved in H_2O to make the concrete. G(gas) of Pu(solution) vs. Pu(solid) are: 0.51 vs. 0.18, and 0.55 vs. 0.27 for HAC and I concretes, respectively. This reduction resulted (14) from some of the alpha energy being absorbed in the PuO_2 particle rather than in H_2O , yielding H_2 . In actual waste, Pu will be added as a solid with the ash and then water will be added to form the concrete. Therefore, tests using the Pu dissolved in acid can be expected to give the highest G(H_2) values. It was also determined (13) that changing the pH of added water (containing contaminant with an organic complexant agent) from 0.6 to 7 did not significantly alter G(H_2). This is consistent with the fact that G(H_2) is independent of pH for liquid water (29).

For the HAC matrix, G(H_2) was not significantly affected (14) by temperature in the range of 23° to $70^\circ C$. Indeed G(gas) decreased by a factor of 3-4 at the higher temperatures of 70° and $100^\circ C$, resulting from the loss of free water from the concrete. This free, or capillary, water is not directly involved in the hydration reactions of the cement. Its loss does not adversely affect the strength of the cement. Once the free water is out, G(H_2) is independent of the temperature.

The G(gas) value of concrete-TRU ash waste can be significantly decreased not only by preheating to drive off free water, but by the addition of scavenging agents which react with the precursors of H_2 . Scavengers investigated include nitrate and nitrite ions, and EDTA. The organic complexing agent, 0.03M EDTA, was dropped after preliminary tests because it could potentially be responsible for enhanced actinide mobility if the waste were leached.

An example of scavenging agent action is:

Tests were run with 1-2M $Fe(NO_3)_3$ solutions; this compound was chosen because Fe^{+3} ions also have the ability of reacting with precursors of H_2 . The $Fe(NO_3)_3$ reduced $G(H_2)$ by a factor of about 20. However, oxygen was produced at a significant rate, $G(O_2) = 0.31-0.35$; the O_2 results from the radiolytic reduction of NO_3^- . The overall reduction of $G(gas) = G(H_2) + G(O_2)$ ranged from about 16 percent for HAC to over 300 percent for T type concrete.

A 3M $NaNO_2$ solution was added with the particulate PuO_2 contaminant as a scavenger. Nitrite is not stable in acid solution. Nitrite ions are less effective than nitrate ions for reducing $G(H_2)$, but are more effective for reducing the overall $G(gas)$ value. For HAC, the nitrite reduces $G(gas)$ from 0.32 ± 0.03 down to 0.03. The oxygen is consumed rather than produced with NO_2 addition. However, a small amount of nitrous oxide, N_2O was detected, indicating that some of the nitrite is radiolytically reduced. Possibly, some O_2 is utilized to oxidize some of the nitrite to nitrate.

Upcoming studies at SRL will concentrate on nitrite scavenging additions and the effect of high H_2 pressures on $G(H_2)$. In the past, no pressure dependency was assumed, but the linearity of pressure increase with time has been tested (16) only up to 200 psi. This was due to the difficulties and hazards of working with high-pressure apparatus in a radioactive contamination glove box.

The gamma radiolysis of concrete containing fission product sludges has also been studied at SRL (15,16). With gamma radiolysis, H_2 is the only significant product; H_2 reaches a steady-state pressure that increases with

increasing radiation intensities. Equilibrium H_2 pressures at realistic dose rates varied from 8-28 psi. When nitrate and nitrite ions were present, gamma radiolysis also produced oxygen and nitrous oxide.

Failure to reach a steady state pressure (at least up to 200 psi) reveals (16) a difference in mechanism between alpha and gamma radiolysis. This results from a difference in the spatial distribution of the H and OH radicals formed by the two types of radiation. Alpha particles lose energy in a much smaller volume than gamma rays, thus the reaction intermediates are formed much closer together.

THERMAL DECOMPOSITION DATA

The thermal degradation of organic TRU waste matrix materials is currently in the process of measurement at LASL (5,6,7,8,9). Waste matrices under study include: paper, cotton, and composite (dry and moist), plus polyethylene. Temperatures of interest are 20° , 40° , 70° , and 100° C. The 40° temperature is probably of most interest for the WIPP TRU waste repository once it is filled and sealed. A summary of available, preliminary gas generation rates from thermal waste decomposition is listed in Table 5a. Corresponding approximate measured gas composition at 70° C are also listed. Due to low generation rates, gas formation has been observed (5,6,7) at 100° C and 70° C only. Murphy (30) stated that cellulose decomposes even at room temperature at a very slow but finite rate. The LASL measured rates of gas generation at 70° C for cellulose (paper, cotton) are several orders of magnitude greater than that predicted by Murphy.

Utilizing Murphy's relation:

$$\log_{10} Q = 16.3 - 7.4 \times 10^3 / T^\circ K$$

where Q is the gas generation rate in cm^3 (STP)/year/g. The gas generation rate calculated for 40° C is about a factor of 100 less than that at 70° C. Based on LASL measured rates at 70° C for cellulose and polyethylene, this yields an approximate gas generation rate at 40° C of 0.2 moles/yr/drum (1.3×10^{-5} moles/year/gram). Utilizing a simplistic

TABLE 5a.

GAS GENERATION RATES FROM THERMAL DEGRADATION

(“Standard” drum = 150 kg of waste matrix)

Matrix:	<u>Gas Generation Rate (moles/year/drum)</u>		
	100°C	70°C	40°C*
Paper (dry)	94	20	--
Cotton (dry)	--	15	--
Composites (dry)	113	7-13	--
Polyethylene	--	18	--

*estimated at 0.4-2 mole/year/drum

TABLE 5b.

APPROXIMATE GAS COMPOSITIONS FROM THERMAL DEGRADATION: 70°C

	(Mole percent)				
	CO ₂	CO	H ₂	O ₂	CH ₄
Paper	80 %	19 %	--	1 %	--
Cotton	31%	11%	(1%)	58%	--
Composites (100°C)	76%	3%	14%	7%	(1%)
Polyethylene	3%	1%	3%	93%	--

chemistry relationship, that reaction rates double for every 10°C rise in temperature, the gas generation rates at 40°C for the organic waste matrices studied can be estimated/extrapolated at approximately 2 moles/yr/drum (1.3×10^{-4} moles/year/gram). The gas generation rate is, consequently, bounded at 0.2 to 2 moles/year/drum by the two methods of calculation.

Murphy (30) also postulated that thermal decomposition of celluloses should decrease exponentially as a function of time. He did not provide a relationship; assume $Q = c_1 \exp(-c_2 t)$. No data are yet available for the temperature range of primary interest, 40°C to 70°C, to use for estimating how much the gas generation rates will decrease, for example, in 100 years. No gas generation data from the degradation of organic matrices at temperatures of 100°C and below have been observed previously, due primarily to detection techniques. Still, no one had detected, much less expected, gas generation from thermal degradation at temperatures of 100°C or less until the current LASL results (5,6,7) were presented. Observation of accumulated gases via pressurization is a more sensitive indication of thermal waste degradation than is weight loss via thermal gravimetric analysis (TGA)--as used in earlier studies. For example, Tang and Bacon (31), in studies of pyrolysis of cellulose fibers at temperatures up to 500°C, reported that the gaseous decomposition products were water, CO₂, and CO, with only physical desorption of water occurring between 25°C and 150°C. Clearly, the current LASL data (5,6,7) do not corroborate the proposed decomposition mechanism of Tang and Bacon. Vershinskii and Pikaev (32) did find, however, that the rate of gas evolution for radiolysis increases sharply at the melting or softening point of polyethylene.

Preliminary thermal degradation studies at LASL (8,9) utilizing thermal gravimetric analysis determined threshold decomposition temperatures in air ranging from 175°C to 205°C for celluloses, 150°C to 210°C for plastics (excluding Teflon), and 165°C to 195°C for rubber materials commonly found in laboratory waste. A previous study at the Battelle Pacific Northwest Laboratory (33) determined the endothermic starting point (pyrolysis, in nitrogen, utilizing differential thermal analysis) for similar waste matrix materials. Polyethylene had the lowest decomposition (melting) temperature of 80°C; almost all other materials had

decomposition starting points at greater than 250°C. These results (33) confirm earlier work done at LASL (12) where rags, paper, polyethylene, PVC, latex, bitasol, and neosol did not begin to decompose (in air) up to 150°C, although both polyethylene and PVC began to soften. At 200°C, all test specimens began to char and decompose.

Considering that oxygen in TRU contaminated waste drums would be consumed by radiolysis (10), LASL (8) repeated threshold decomposition studies using TGA in an anaerobic (nitrogen) atmosphere for cellulose, polyethylene, lucite, and hypalon rubber. In addition, the potential effect (on threshold temperatures) of catalysts which could be found or formed by storing drums of TRU waste in a salt mine (the WIPP) were investigated. Catalysts included: none, NaCl, Fe₂O₃, FeCl₂, and Fe powder, with loadings ranging from 2 to 38 weight percent. Threshold decomposition temperatures (compared to those measured in air, ranging from 150 to 210°C) changed by approximately plus/minus 30°C.

Returning to the primary objective, measurement of gas generation rates, LASL (7) has started new tests to evaluate the effects of possible mine catalysts on thermal degradation. Paper and polyethylene were (separately) catalyzed with NaCl and FeCl₂ at 2 weight percent loading, in air atmosphere, at 40°C. Gas detection techniques are being utilized, but insufficient data have been gathered from these analyses.

Other pertinent data gathered from the LASL thermal studies include:

1. All "dry" cellulose tested (9) evolved approximately 2 weight percent water (sorbed) when heated from 40°C to 110°C.
2. Dewatering of LASL process sludges was determined (17) at 25°C, 40°C, 70°C, and 100°C as a function of time. These sludges are primarily ferric hydroxide precipitant containing about 30 percent solids. Experimental conditions included flowing dry nitrogen over gram-size samples of sludge contained in a thermobalance. This arrangement should be somewhat representative of a (corrosion) breached waste drum in a salt repository, with the salt acting as a desiccant for released water vapor. Times for 100 percent dewatering of the sludge samples ranged from 1 hour at 100°C to 35 hours at 25°C. In conclusion, drums containing sludge waste could be expected to release essentially all their water on a very short (geological) time scale due simply to attainment of equilibrium water vapor pressure.

3. Cement paste has been used at LASL (5) for immobilization of certain waste materials. Currently, it comprises the second-ranked contributor (by volume) to the LASL waste inventory. Rates of thermal dewatering of cement paste at 40°C and 100°C were performed for comparison to the process sludge material. The cement paste samples utilized (dating from 1974, contained no lower than 10 weight percent water (as determined by heating to 400°C) and may be considered more similar to concrete than to "paste." From preliminary data, it appears that cement paste-concrete is much more difficult to dewater than process sludge. Cement paste-concrete may not dewater completely at the credible boundary temperature of 70°C in the WIPP TRU waste horizon.

The potential fates of water thermally volatilized, or that possibly produced by pyrolysis (but as yet unmeasured,, are summarized below:

- a. Dissolution of salt yielding brine pools or lenses
- b. High humidity in mine, pumped out via ventilation system during working phase of facility
- c. Potential enhanced corrosion of metallic waste canisters, instrumentation, and mining-engineering equipment
- d. Hydrolysis, hydration of minerals (anhydrite, clays, etc.) with potential swelling effects
- e. Leaching or dissolution of waste materials resulting in the potential water/brine mobilization of radionuclides as true solutions, colloidal solutions, or as entrained particulate material.

BACTERIAL DEGRADATION DATA

Organic matrix TRU contaminated wastes (unprocessed) will most probably contain bacteria or fungi prior to isolation in a terminal waste repository. It is assumed that any kind of microorganism may survive and adapt to the existing environment, potentially resulting in significant microbial degradation. This could lead to several consequences including gas generation. Overall concerns of microbial degradation

pertinent to radioactive waste have been summarized elsewhere (17,34). A WIPP-specific (and funded) laboratory study of microbial waste degradation concerns conducted by the University of New Mexico Biology Department with support by EASL (B-1 division) has been in progress since May, 1978. A description of individual studies and techniques is found elsewhere (17,18).

The production, consumption, and transformation of gases by microorganisms have been studied extensively; a recent review was made by Cole (15). Gases can be produced by bacterial decomposition, by the metabolic processes of anaerobic or aerobic respiration, fermentation, denitrification, sulfate reduction, methanogenesis, etc. Examples of microbial consumption of gases produced abiotically (primarily H_2) are as follows:

An example of microbial transformation of gases in the anaerobic reaction:

The main topic of both concern and laboratory study is which of these types of reactions will occur under WIPP-specific conditions and at what rate. There is no question that CO_2 will be produced regardless of the conditions present (17).

The preliminary gas generation data measured at UNM (18) are summarized in Table 6. Initially, only the oxygen concentration (air atmosphere and anaerobic), temperature (25° , 49° , 50° , 60° , $70^\circ C$), and organic substrate have been varied. Samples consisted of 1g of substrate inoculated with 20mg of soil mixture containing bacteria. Subsequently, either 10 or 1000 microliters of phosphate buffer, 0.01 M, pH 7.0, were added to each sample vial. Only results obtained with the 1000 microliter of buffer addition are presented in Table 6; insufficient data have been obtained with the 10 microliter addition.

TABLE 6

PRELIMINARY GAS GENERATION RATES FROM BACTERIAL DEGRADATION(moles CO₂/yr/drum; drum = 150 kg of waste)

Matrix:	T ^o	Aerobic	Anaerobic
LASL composite	25 ^o	2.6	3.6
	40 ^o	22	5.0
	50 ^o	36	94
	60 ^o	46	11
	75 ^o	8.4	0.4
asphalt	25 ^o	1.3	0.3

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Gas produced by bacterial action was analyzed with an automated gas chromatograph with a thermal conductivity detector. Detection sensitivity for the potential gases of interest, H_2 , CO_2 , CO , CH_4 , H_2S , SO_2 , etc., is 6×10^{-10} g./cc.; minimum detectable level for CO_2 is 2×10^{-8} moles/100 microliter sample.

The only major gas detected (18) as a degradation product of LASL composite waste (35 percent cellulose, 23 percent polyethylene, 12 percent PVC, and 30 percent of various rubbers) was CO_2 . From the preliminary data (18), the rate of CO_2 evolution is temperature dependent, reaching a maximum at 55°C. Data measured in the 40°C to 60°C temperature range may be the most applicable for geologic isolation conditions. Bacterial action occurring inside a drum may raise the drum temperature higher than the mine ambient temperature.

A comparison of the rates of CO_2 evolution from LASL composite waste with that from carboxymethyl-cellulose (not presented) indicates some correlation. This suggests (18) that the cellulose component of the composite waste is the substrate utilized for CO_2 evolution. A series of samples containing composite waste minus the cellulosic component will be tested to determine if other organic matrices contribute to the gas generation.

Experimental techniques are being modified and an expanded test matrix utilized to include variations in pH and salinity, and to determine gas production rate as a function of time. Data should be obtained prior to October 1979. These data should better reflect long-term microbial activity in organic TRU waste matrices in bedded salt geologic isolation. Data now available indicate that bacterial degradation yielding gas generation is quite significant and must be taken into account.

CHEMICAL CORROSION DATA

The generation of H_2 gas from the corrosion of the mild steel alloy used in TRU waste containers, 210 l (55 gallon) drums, is the only long-term chemical degradation mechanism of significance yielding gaseous reaction products.

The aqueous corrosion rate of most mild (carbon) steels, e.g. 1018 steel, is controlled by diffusion of dissolved oxygen to the steel surface. This is followed by the cathodic reduction of oxygen (19):

If O_2 is kept from the metal surface, then the cathodic reaction is the reduction of H_2O in neutral solutions or hydrogen ions in acid solution, yielding gaseous H_2 :

The anodic reaction is the oxidation and dissolution of Fe:

Reaction a) always proceeds preferentially over reaction b) when oxygen is present and is 10 to 100 times faster.

For mild steel, the aqueous corrosion rate (in aerated water) at $25^\circ C$ would be approximately 0.3 mm/yr for the first year, dropping off to 0.05 to 0.08 mm/yr thereafter. This rate doubles for each $30^\circ C$ rise in temperature. With no oxygen present, the aqueous corrosion rate would be about 0.005 mm/yr, with this rate doubling with each increase of $10^\circ C$.

Braithwaite (20) measured the rate of corrosion of 1018 mild steel in inundated saturated NaCl brine at $25^\circ C$ by measuring the quantity of hydrogen produced or oxygen consumed. These corrosion rates and gaseous quantities are:

aerated - 0.05 mm/yr (in oxygenated brine)
5.4 moles O_2/m^2 year consumed

deaerated - 0.003 mm/yr (in deaerated brine)
0.5 moles H_2/m^2 year produced

These rates are quite similar to the corresponding corrosion rates in water.

Since a 210 l drum has a total surface area (inside and out) of 4 m^2 , the appropriate gas generation/consumption rates, assuming inundation, are:

aerated - 22 moles/yr drum O_2 consumed,

de-aerated - 2 moles/yr drum H_2 produced.

Once all available oxygen is consumed in a sealed salt repository, the cathodic reduction of water, yielding H_2 , will commence assuming water is available. Remember, however, that the 2 moles/yr drum of H_2 is a maximum credible rate of gas production under brine inundated conditions and with absolutely no protective coating such as paint on the drum surface.

Measurements are in progress at Sandia (21) to measure the gas generation of 1018 mild steel in more probable WIPP environments of dry salt (with 1/2 weight percent of water) and various relative humidities, at temperatures of 25°C and 70°C . Sensitive gas detection measurements are being made with a system coupled mass spectrometer. Preliminary gas measurements with these conditions are not yet available; however, after 5 months, superficial surface corrosion of the dry salt-steel system at 70°C was visually evident; after approximately 8 months, visual observation of superficial surface corrosion was made in the corresponding 25°C system.

Detailed corrosion data for other alloys, at temperatures up to 250°C , and under various environmental conditions pertinent to a salt high-level waste repository are summarized elsewhere (36).

For the WIPP environment, the following points about hydrogen gas generation can be made (21):

1. Any oxygen present will substantially reduce the amount of hydrogen produced.
2. Overall, if the oxygen is depleted and water is present, a total of 672 moles of H_2 can theoretically be produced from the complete corrosion of a 210 l drum.
3. No hydrogen will be produced if moisture does not contact the steel drum (dry salt); the only reaction, which will be extremely slow, is:

Anti-Corrosion Coating Study:

The use of coatings to significantly reduce corrosion of TRU waste metal drums, and potential resulting gas generation (or consumption), is also being studied at Sandia Laboratories (20). Anti-corrosion coatings under study are limited to various classes of paint, primarily because of recognized cost and ease of application considerations. The driving force behind this particular study is the prevention of significant corrosion on waste containers during the limited initial storage period (estimated at 5 to 25 years) when such waste might be required to be retrievable (1).

Accelerated aging testing of selected coatings (on a 1018 mild steel substrate) utilize an alternate immersion in brine then air drying procedure. This type of exposure was severe and led to localized failure of all the paints evaluated (22). The time to failure is a measure of the durability of the paints and decreased in the following order: coal tar epoxy, chlorinated rubber, polyamide epoxy, acrylic enamel, lacquer (22). Acrylic enamel is the coating currently used on waste drums stored at the Transuranic Storage Area pads at the Idaho National Engineering Laboratory. Other coatings previously evaluated (20) included vinyl latex, silicone rubber, polyester resin, asphalt epoxy, and polyimide dip. The alternate immersion test results (22) should only be used for the rank ordering of the coating durability and do not indicate that the coatings will fail under more realistic conditions. For this reason, future evaluations will be conducted in more benign environments (salt fog, high humidity, crushed salt, etc.) in order to assess the long-term durability of these candidate paints.

SUMMARY AND INTERCOMPARISONS

The generation of gases from the degradation of existing and potential forms of defense-related transuranic (TRU) contaminated wastes has received a considerable amount of attention over the past several years. This area of study, particularly under environmental conditions to be expected for deep geologic terminal isolation, is a major segment of the Waste Isolation Pilot Plant Transuranic Waste Experimental Characterization Program (1). A comprehensive review and assessment of all available, applicable waste degradation-gas generation data is presented herein.

Waste Matrices Studies:

CELLULOSICS
PLASTICS
RUBBERS
COMPOSITE (above organics)
CONCRETES
MILD STEEL

Gas generation rates of the above matrices have been measured in terms of moles gas/year/drum of waste. The following waste degradation mechanisms have been studied:

Waste Degradation Mechanisms:

RADIOLYTIC
THERMAL & CATALYZED THERMAL
BACTERIAL
CHEMICAL CORROSION
ALPHA DECAY (He Generation)

Synergistic effects between temperature (in the range of 20^o to 70^oC, and 100^oC, for overtesting) and the other mechanisms have also been studied.

Assumptions are made regarding a "standard" reference waste form and container so that intercomparisons between different degradation mode results can be made. These are:

Assumptions:

1. "Standard" Drum Contains 0.77 alpha Ci or 10g ^{wg}Pu/drum
2. "Standard" Drum Contains 150 kg of Organic Matrix Waste
3. Standard 210 l Drum : wt. = 25 kg, surface area = 4 m²

An intercomparison of total gas generation rates measured for various mechanisms and several matrices is presented in Table 7, in terms of moles gas/yr/standard drum.

From the measured total gas generation rates in Table 7, it can be seen that the only insignificant generation made is alpha decay yielding He. Representative, realistic conditions to be expected in a repository include a temperature range of about 25-40^oC; a very small amount of water present

TABLE 7

INTERCOMPARISON OF MEASURED GAS GENERATION RATES

(0.77 Ci, 150 kg matrix, per drum)

<u>Mechanism:</u>	<u>Material:</u>	<u>Total Gas Rate:</u> (moles/yr/drum)	<u>Comments:</u>
RADIOLYSIS	Cellulosics	0.13±0.03	LASL, SRL
	PVC	0.47	LASL
	HAC Concrete/Ash	0.04-0.002	SRL
THERMAL	Cellulosics	(0.2-2)	40 ^o , calc.
	Cellulosics	15-20	70 ^o , LASL
	Composite	(0.2-2)	40 ^o , calc.
	Composite	7-13	70 ^o , LASL
	Polyethylene	(0.2-2)	40 ^o , calc.
	Polyethylene	18	70 ^o , LASL
Aerobic/Anaerobic			
BACTERIAL	Composite	2.6//3.6	25 ^o , UNM
	Composite	22// 5.0	40 ^o , UNM
	Composite	36//94	50 ^o , UNM
CORROSION	Mild Steel	2.0	de-aerated brine inundation, SLA
ALPHA DECAY	He Generation	1.5 x 10 ⁻⁶	

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in drums, from moist cellulose primarily; and, an aerobic in-drum environment changing to anaerobic. Under such conditions, we can rank the gas generation mechanisms in order of significance as follows:

Gas Generation Mechanism Rank Ordering:

1. BACTERIAL
2. THERMAL
3. RADIOLYSIS
4. CORROSION (dry conditions)

In order to put the above mechanisms into perspective, the total amount of gas generated per drum of existing organic matrix waste for a 100-year degradation period is shown in Table 8 and Figure 6, and is based on extrapolation of initial observed rates. The maximum and minimum amounts of gas generated are indicated and reasons for such will be described. For comparative purposes only, the theoretical maximum number of gas moles generated-- if all waste form materials and container were degraded into gaseous species in an air atmosphere by a combination of probably incredible mechanisms (i.e., high temperature combustion)--is listed in Table 9.

Radiolytic degradation of organic materials yielding gas has been found to decrease as a function of time due to matrix depletion at high dose rates. However, for a low dose rate of 0.77 Ci/drum, the rate of radiolysis should presumably remain constant for 100 years. If localized depletion should occur, intimate contaminant-organic matrix contact with fresh matrix materials could recur if TRU waste drums are eventually crushed by the lithostatic pressure in a sealed repository. The maximum and minimum moles of gas generated by radiolysis for organics are therefore specified as identical.

If organic matrix TRU contaminated wastes are processed (incinerated, slagged, digested, etc.) and the byproducts (e.g. ashes) immobilized in a non-organic matrix, the gas generation rate can be reduced by approximately two orders of magnitude (with concrete) to a relatively insignificant value. The minimum gas value listed in Table 8 for concrete encapsulated TRU ash can be achieved by preheating the concrete matrix during processing to drive off the free water. It can also be achieved by adding scavenging agents such as NaNO_2 to the concrete mix to react with the radiolytic precursor products which form hydrogen.

TABLE 8

EXTRAPOLATED GAS GENERATION FOR 100 YEARS, Per DRUM

(150 kg matrix)

<u>Mechanism:</u>	<u>Materials:</u>	<u>Minimum:</u> (moles/drum)	<u>Maximum:</u> (moles/drum)
RADIOLYSIS	Cellulose	13+3 *	13+3 *
	PVC	47 *	47 *
	HAC Concrete/Ash	0.2	4
THERMAL	Composite (40°C)	20 *	200 *
BACTERIAL	Composite	260 *	9400 *
CORROSION	Mild Steel	0	200
ALPHA DECAY	Helium	0.00015	0.00015

*(essentially eliminated if organic waste processed)

TABLE 9

THEORETICAL GAS GENERATION/DRUM

(in air atmosphere)

210 : Drum	25 kg	--
Polyethylene Drum Liner (C ₂ H ₄) _n	8.6 kg	616 moles CO _x
		616 moles H ₂
Cellulosic Waste Matrix (C ₆ H ₁₀ O ₅) _n	141.4 kg	5,240 moles CO _x
		<u>4,360 moles H₂</u>
Total =		10,800 moles/drum

FIGURE 8

Waste processing of the organic matrix wastes could also essentially eliminate gas generation by thermal and bacterial degradation mechanisms.

The thermal degradation maximum and minimum gas values are dependent on boundary value calculations made for 40°C degradation, based on measured values at 70°C. The decrease in thermal degradation rates as a function of time has not been determined for organic wastes in the 40° to 70°C range. The effect of mine catalysts, NaCl and Fe Cl₂, on thermal degradation of celluloxics and polyethylene at 40°C is still being measured at LASL. The effect of thermal dewatering of waste forms such as TRU process sludges (up to 70 percent by weight of water) has not been included in the maximum thermal gas value shown in Table 8, but it has been measured. The bacterial degradation of organic waste matrices provides the greatest potential for gas generation in a repository, but also has the greatest uncertainty in value, depending on environmental conditions in individual drums. The bacterial minimum gas value is based on measured aerobic degradation data at 25°C. The maximum gas value, 9400 moles/drum, is based on measured anaerobic gas generation values. However, based on the theoretical total amount of gas which could be generated per drum, 10,800 moles (Table 8), the value of 9400 moles seems excessively high--or overly optimistic. The rate of bacterial degradation as a function of time is not presently known. It is quite possible that the bacteria would deplete their source of nutrients in a drum of organic waste long before 9400 moles of gas (CO₂, predominantly) are generated. Nonetheless, the total quantity of gas which can be generated by bacterial degradation appears more significant than that from any other mechanism.

Corrosion of the mild steel used in construction of 210 l (55 gallon) drums could release a maximum of 200 moles/drum in 100 years if it was inundated with deaerated NaCl brine at all times. This is not very probable. During the period of time when air is still present in the waste storage room, corrosion will consume oxygen and not generate hydrogen. In a dry salt environment, with oxygen present, no gaseous corrosion products would be generated.

Additional Work in Progress:

In order to finalize the necessary data base on gas generation from waste degradation, several topics of investigation are still in progress. The topics of greatest significance are listed in Table 10.

TABLE 10

MOST SIGNIFICANT GAS GENERATION STUDIES IN PROGRESS

1. Determine effects of high pressure on gas generation rates; equilibrium pressure.
 2. Make final determination of radiolysis rates as a function of several variables.
 3. Determine bacterial survival under salt mine environment.
 4. Obtain further data on bacterial generation, transformation, and consumption rates.
 5. Determine thermal and bacterial degradation rates as a function of time.
-

The gas generation quantities listed in Table 8 for various mechanisms are not additive. For instance, if organic waste is degraded to gas by radiolytic and thermal decomposition, the remaining material may not be suitable as further bacterial nutrient. The values in Table 8 are meant to provide measured, reasonable limits on quantities of gas to be generated in order to provide input data for consequence assessment studies. Calculations of total gas accumulation in a sealed repository (room) are being coupled with data on gas dissipation via rock salt permeability. Results of such calculations may be useful for further studies on mine response to gas accumulation and pressure buildup. All of these analyses are now in process, and are reported on elsewhere (2,37).

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