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AN ASSESSMENT OF RADIOLYTIC GAS GENERATION IMPACTS FROM ROCKY FLATS PLANT RESIDUE ELIMINATION ALTERNATIVES

FINAL

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ACRONYMS

CDH	Colorado Department of Health
CH-TRU	Contact-handled transuranic
DOE	Department of Energy
EPA	Environmental Protection Agency
eV	electron volt
FFCA	Federal Facilities Compliance Agreement
IDC	Item Description Code
REP	Residue Elimination Project
RFP	Rocky Flats Plant
SNL-A	Sandia National Laboratory-Albuquerque
TRU	Transuranic
TRUCON	TRUPACT-II Content Codes
WIPP	Waste Isolation Pilot Plant

EXECUTIVE SUMMARY

This report evaluates the Sandia National Laboratory - Albuquerque analytical model that is used to support present wattage limit decisions for various matrix forms from the Residue Elimination Project for Waste Isolation Pilot Plant waste acceptability. This study includes (1) a comparison of the SNL-A model to Rocky Flats Plant models for consistency of assumptions and the phenomena considered in the models, and (2) an evaluation of the appropriateness of the Sandia National Laboratory - Albuquerque model to Rocky Flats Plant residues, considering that the original intent was to model wastes rather than residues.

The study draws the following conclusions: (1) only real-time gas generation testing of specific waste streams may provide a sound basis for an increase in the transportation wattage limit of specific waste streams, and (2) the radiolytic gas generation rate from Residue Elimination Project waste emplaced at Waste Isolation Pilot Plant, under worst-case conditions, is not a significant factor in comparison to the total gas generation rate due to radiolysis, microbial degradation, and corrosion.

1.0 INTRODUCTION

The purpose of this report is to evaluate the Sandia National Laboratory (SNL-A) analytical model that is used to support present wattage limit decisions for various matrix forms from the Residue Elimination Project (REP) for Waste Isolation Pilot Plant (WIPP) waste acceptability. This study includes (1) a comparison of the SNL-A model to Rocky Flats Plant (RFP) models for consistency of assumptions and the phenomena considered in the models related particularly to radiolytic gas generation, and (2) an evaluation of the appropriateness of the SNL-A model to RFP residues, considering that the original intent was to model wastes rather than residues.

The SNL-A analytical model and parameters related to wattage limit decisions for WIPP transuranic (TRU) waste acceptability are contained in Sandia Report SAND91-0893/3, "Preliminary Comparison with 40 CFR 191, Subpart B for the Waste Isolation Pilot Plant, December 1991" (Sandia National Laboratories, 1991). Volume 3 of this report contains the majority of information related to this study.

The RFP models for TRU waste from the REP consists of the spreadsheets developed to evaluate the options for disposition of residues in storage containing hazardous waste or hazardous waste constituents.

Comparison of the models for RFP residues focuses on the applicability of parameters used in the SNL-A model to determine consistency of assumptions and to evaluate whether inclusion of RFP residues will exceed limits set for waste acceptability at WIPP.

Additionally, this study addresses several issues related to established wattage limits associated with TRU waste transportation in the TRUPACT II.

2.0 BACKGROUND

The purpose of the REP is to eliminate plutonium residues in storage at the RFP. This section provides background information relevant to handling, transportation, and disposal of residues resulting from radiolytic gas generation.

2.1 Residue Handling

Residues in storage at RFP containing hazardous waste constituents (i.e., mixed waste) are required to be removed from the site in accordance with legal agreements, such as the Federal Facility Compliance Agreement (FFCA) between the Department of Energy (DOE), the Environmental Protection Agency (EPA), and the Colorado Department of Health (CDH). Specifically, mixed residues that do not have a permit or interim status per storage are required to be removed by January 1, 1999 in accordance with Compliance Order #91-07-31-01, date July 31, 1991. The residues requiring removal from storage are listed in the *Feed Study Report* (Department of Energy, 1991). The stored material contains approximately 3000 kilograms (kg) of plutonium.

Two alternatives for the removal of these residues from the RFP are currently being considered (Department of Energy, 1993). The first alternative is to ship the residues as waste, to an interim status or permitted disposal facility. The second alternative is to ship the residues to another DOE site for conversion into suitable waste or storage forms.

The first alternative listed above may include varying degrees of pretreatment for waste minimization purposes. The two bounding cases for pretreatment are: (1) minimal pretreatment to meet shipment packaging criteria, and (2) full implementation of pretreatment, including actinide separation or concentration. In order to account for the full range of consequences for the ship as waste alternative, we evaluated both of these bounding cases.

For the purpose of this study, three cases were evaluated. The names and descriptions of these three cases are:

1. Actinide Separation - the full pretreatment case for the ship as waste alternative. This case will include actinide separation and/or concentration via chemical or physical means, for the purpose of waste minimization.
2. Ship As Residue - the evaluation of the ship as residue alternative. This is the only case evaluation in this study for the ship as residue alternative. Once at another DOE site, the residues would be treated in a manner similar to that envisioned to take place at the RFP.
3. Ship As Waste - the minimal pretreatment case for the ship as waste alternative. This case will include repackaging and/or processing to meet transportation requirements and waste acceptance criteria.

Case 1 will require full implementation of the REP, which will consist of four major processes: (1) residue processing, (2) pyrochemical residue recovery, (3) miscellaneous recovery, and (4) volume reduction. Specifically for this report, the quantity of TRU waste generated from the processing of all residues was calculated to be 2,544 cubic meters (m^3) and is equivalent to 12,222 55-gallon (gal) drums. The physical, chemical, and radiological compositions, and the ratio of each waste form (consisting of a unique composition) of the resulting TRU waste, will be similar to the compositions and waste form ratios of existing TRU waste at the RFP.

Case 2 will require full implementation of a residue processing facility equivalent in function to the REP, with similar quantities of TRU waste generated. Additional TRU waste will be generated from the repackaging of residues for shipment to this equivalent facility.

Case 3 will require repackaging of the residues in order to meet waste transportation and disposal criteria. It is estimated that repackaging would produce 14,866 m³ of TRU waste, which is equivalent to 71,411 55-gal drums.

2.2 Transportation

TRU waste will be transported in TRUPACT-II containers. Gas generation-related factors affecting TRUPACT-II transportation of TRU waste include the waste material type, composition, packaging, and type of payload container. During transportation, the generation of potentially flammable concentrations of hydrogen gas can be controlled by limiting the decay heat for a specific payload. *TRUPACT-II Content Codes (TRUCON)* (Department of Energy, 1989) set limits on the maximum allowable wattage for a given waste type and payload container identified by a content code. As defined in TRUCON, the content code is "a uniform system applied to waste forms to group those with similar characteristics for purposes of shipment in TRUPACT-II."

2.3 Disposal

The mechanisms contributing to gas generation after emplacement of TRU waste at WIPP are: (1) anaerobic corrosion, (2) microbial activity, (3) radiolysis, and (4) potential chemical or other synergistic interactions between mechanisms 1, 2, and 3 (Lappin et al., 1991). These mechanisms are affected by the following controlling waste-matrix

variables:

1. Cellulosic Materials,
2. Plastics,
3. Rubber Material,
4. Corroding Metal/Steels,
5. Corroding Metal/Aluminum,
6. Non-corroding Metals,
7. Solid Inorganic Materials,
8. Inorganic Sludge,
9. Cements,

10. Other Organic Material, and
11. Total Alpha Curie Content.

A twelfth category, Other Important Gas Generation Variables, categorizes unknown composition materials and water.

3.0 ANALYSIS

The approach used to assess the impacts of gas generation on TRU waste transportation and disposal at WIPP is based upon the evaluation of four wastes: (1) Graphite, coarse - Item Description Code (IDC) 312; (2) DB Filter Media - IDC 338; (3) Molten Salt (30 percent unpulverized) - IDC 409; and (4) Pulverized Incinerator Ash - IDC 420. These four wastes comprise approximately 50 percent of the total weight of plutonium in all residues in storage. Detailed analyses of options and resulting waste products for each IDC are presented in the IDC reports associated with the *Residue Analysis Study* (EG&G, 1992).

3.1 Evaluation of TRUCON Limits

The *Residue Analysis Study* (EG&G, 1992) estimates that IDCs 312, 338, 409, and 420 would contribute approximately 40 percent of the total volume of waste that would result under Case 3. Case 3 is assumed to exhibit the worst case in terms of maximum plutonium concentration and wattage per unit volume of waste, since it is expected that the Pu/Am concentration and wattage per unit volume of waste will be lower as a result of actinide separation (Cases 1 and 2). Under Case 3, the residue waste material would be repackaged and shipped as identified in Table 1.

Table 1
Listing of Select Residues by IDC

Waste Material	IDC	Shipping Category*
Graphite, Coarse	312	II.1A2
DB Filter Media	338	III.1A2
Molten Salt (30 percent unpulverized)	409	II.2AM or I.3A2
Pulverized Incinerator Ash	420	I.3A2

* Shipping Categories are listed in TRUPACT-II Content Codes (TRUCON) (DOE, 1989, Table 1)

In TRUCON, each shipping category is assigned a specific wattage limit based on the bounding effective G value, wherein the G value is a measure of the number of molecules of gas produced per 100 electron volts (eV) of decay heat. The bounding G values are upper limits for general categories of waste; hence, the actual gas generation and corresponding G value for a specific waste stream is subject to variation below this limit. For example, all waste types identified as *Waste Type III - Solid Organics* are categorized with the bounding G value of 3.4, which is an estimated maximum value based on a worst-case scenario for radiolytic gas generation in a solid organic-based waste matrix.

The gas generation rate and the specific activity are directly related, such that an increase in the alpha-emitting isotope will result in a linear increase in the gas generation rate. The gas generation rate is proportional to the G value. This relationship is evident from empirical studies and is associated with the type of material and cellulosic content in the waste.

Alpha radiolysis degradation studies have been conducted in the past at Los Alamos Scientific Laboratory to determine the effect on the G value over time (Molecke, 1979). At high Pu loadings, gas generation rates decreased as the elapsed time increased. This

decrease was attributed to localized organic material depletion adjacent to the Pu contaminated material and to the formation of degradation products that produce less gas. However, it was concluded that for low Pu loadings, the radiolytic gas generation rate is likely to be quite constant for hundreds of years. Thus, by assuming that the average Pu loading is relatively low for TRU waste at RFP, it can be assumed that the gas generation rate for RFP TRU waste forms will remain constant at least over a 10- to 50-year period.

Furthermore, since the transportation period (i.e., transportation of TRU waste from RFP to WIPP) cannot exceed 60 days, the time factor will be of minimal concern. Nonetheless, by assuming that the gas generation rate remains constant, our assessment will remain conservative for worst-case conditions.

Previous studies (Molecke, 1979) have proposed that the gas generation ratio relationship is represented in the following manner:

$$N_i = C_f * G_i * A_d * N_d \quad (1)$$

where,

- N_i = the number of moles of gas species i produced per year,
- C_f = a constant coefficient equal to 0.099,
- G_i = is the G value of gas species i produced for a given material/matrix in units of moles/(Curie-year),
- A_d = the activity of the waste (in units of Curies/drum), and
- N_d = the number of drums.

By assigning a constant value for alpha radioactivity in a drum, matrices of varied composition (radiologically, chemically, and physically) characterized by specific G values can be assessed. Assuming that the gas generation rate is linearly related to the activity given in equation 1, the gas generation rates from radiolysis for various waste materials/matrices can be normalized for a value of 1 Curie (Molecke, 1979).

Additionally, it is assumed that the Pu is evenly distributed throughout the waste material/matrix, and that the waste material/matrix can be modeled as a homogenous mixture. The modified gas generation rates normalized for a drum activity of 1 Curie are presented in Table 2.

Table 2
Modified Radiolytic Gas Generation Rates Based on Waste Matrices
Containing 1 Curie

Waste Material/Matrix	Gas Generation Rate* (moles/year/drum)		
	Lower Limit	Most Probable Range	Upper Limit
Cellulosics	0.051	0.13-0.28	0.31
Polyethylene	0.077	0.18	0.21
PVC	0.26	0.77-1.0769	2.1
Process Sludge	0.099		
Organic Composite	0.051	0.13	0.15
Asphalt	0.013	0.020-0.099	0.13
Concrete-TRU Ash (poured)	0.002	0.003-0.062	0.067
Concrete-TRU Ash (heated)	1.3E-5	3.3E-5-0.0023	0.0033

* Based on original data provided by Molecke, 1979

A review of the modified values in Table 2 indicates the gas generation rates can vary significantly depending upon the material/matrix. Thus, it would be expected that a drum of waste consisting of a high concentration of cellulosic materials, such as rags, plastic, and cloth from various processes (i.e., TRU Combustible Waste), would have a higher potential for gas generation than other organic waste, such as filter media from filter change operations (i.e., TRU Filter Media). These expected variations in gas generation rates are not reflected in the Shipping Categories in TRUCON for TRU Combustible Waste and TRU Filter Media. For example, in reference to TRUCON

Table 5 (Department of Energy, 1989), the wattage allowances for drums of waste identified by content codes RF116A and RF119A are each set at 0.0207 watts. Content code RF116A is for combustible waste consisting of paper, rags, cloth, coveralls, plastic, rubber, wood, and other similar items. Overall, this waste stream can be characterized as having a high cellulosic content, and cellulosic materials, in general, are expected to produce more gas than almost any other waste material (Molecke, 1979). Content code RF119A is for filter waste consisting of Absolute Drybox filters, HEPA filters, filter media, and Ful-flo filters. It is reasonable to assume that the TRUCON wattage limit should be higher for the filter waste than for the combustible waste since the filter waste would be expected to be more similar to organic composite waste materials for which the upper limit for the gas generation rate is equal to one-half that for cellulose (see Table 2).

It is understandable that the bounding G values incorporate a high degree of safety based on the high level of uncertainty associated with the limitations on the availability of precise gas generation rates for a given waste matrix. Also, recognizing that these limitations are further compounded by the variation of components within an actual waste matrix, the application of bounding G values is justified when actual gas generation rates, or G values, are not known. However, these uncertainties can be reduced through the accumulation of additional data from empirical studies. It is expected that many of the uncertainties related to G values can be removed on a waste form-specific basis if actual gas generation rates are measured and then G values are calculated.

TRUCON separates contact-handled transuranic (CH-TRU) waste into two major shipping categories: Analytical and Test Categories (Department of Energy, 1989).

The Analytical Category - Maximum Allowable Wattage provides the maximum allowable wattage derived from analytical calculations for each content code.

Maximum decay heat values are provided (where applicable) for a single drum, an

overpack of one or more drums in a Standard Waste Box, and a Standard Waste Box. Maximum decay heat limits are also given (where applicable) for a TRUPACT-II loaded with single drums, with overpacks of one or more drums in Standard Waste Boxes and with Standard Waste Boxes.

The Test Category - Maximum Allowable Wattage provides the maximum allowable wattage based on pre-transport test requirements for each content code. The maximum allowable wattage limits are given on a per drum and per TRUPACT-II basis.

The *TRUPACT-II Safety Analysis Report* (Nuclear Packaging, Inc., 1989) allows for waste of a specific content code to be placed into a test category to obtain real-time data on gas generation rates when:

"...the decay heat loading of the waste container exceeds the limit set for the shipping category of that payload container. Payload containers in Waste Types I, II, and III belong in this class (Section 1.2.3 of SAR)."

or when,

"...a waste process does not have a fully characterized bounding G value from previous sampling or waste stream analysis. Payload containers in Waste Type IV belong in this category."

Fully characterized TRU wastes are defined in Section 19 of TRUCON by content code. The complete characterization consists of identification of content code, content description, generating site, waste description, generating source, waste form, waste packaging, assay, free liquids, explosive/compressed gases, pyrophoric, corrosive, chemical compatibility, additional criteria, shipping category, analytical category - maximum allowable wattage, test category - maximum allowable wattage, and correlation table.

Thus, gas generation rates can be empirically determined for any TRU waste for which the decay heat loading exceeds the limit or for any TRU waste stream not fully characterized in TRUCON. Also, if the gas generation rate is below the established limit in TRUCON, then the wattage loading for that specific TRU waste is acceptable. Additionally, without knowing the actual gas generation potential for a specific TRU waste, there is no way to determine how conservative the bounding G value is of a shipping category in comparison to the specific TRU waste.

3.2 Evaluation of *WIPP Preliminary Comparison Boundaries*

The *WIPP Preliminary Comparison* (Sandia National Laboratories, 1991) was conducted based on a design volume of 175,565 m³. The design volume and distribution of waste for each major DOE site is calculated by totaling the volume of waste in storage and the volume of waste projected to be produced (termed the site-actual total volume). Then, for each of the following five DOE sites, Hanford, Idaho National Engineering Laboratory, Los Alamos National Laboratory, RFP, and Savannah River Site, the site-actual total volumes are scaled up so that the site-actual total volumes from all facilities, plus the additional waste volumes from scaling up, equals the design volume of 175,565 m³. Table 3 identifies the volume of TRU waste from the RFP. Because these volumes were not based on the explicit consideration of TRU wastes generated as a result of residue elimination, the primary objective of this section will be to assess whether the validity of the *WIPP Preliminary Comparison*, based on the original design criteria, is impacted by inclusion of TRU waste produced from residue elimination.

Table 3

**WIPP Performance Assessment Design Basis
Transuranic Waste Volumes from the Rocky Flats Plant***

RFP Transuranic Waste	Volume (m ³)
Stored	792
Projected	16,272
Scaled	25,869
Total (Design)	42,933

* Sandia National Laboratories, 1991, Table 3.4-4

Additional design criteria used to conduct the *WIPP Preliminary Comparison* includes the following relevant gas generation-related conditions for RFP waste:

Activity	8.016×10^4 Ci	Pu-239
Activity	6.2×10^5 Ci	All Radionuclides (U-235, Pu-239, Pu-240, Pu-241, Am-241)
Wattage	1.02 W/Drum	Average wattage loading per 55-gal drum (based on 10 kW/acre)

Without conducting a detailed analysis of the adequacy of the WIPP design volume for waste from RFP, it will be assumed that the maximum volume of waste generated from residue elimination can be accounted for in the *WIPP Preliminary Comparison* scaled volume (refer to Table 3). The scaled volume is equal to 25,869 m³, whereas the maximum volume of waste to be generated from residue elimination is 15,034 m³. Therefore, it will be assumed that the WIPP site will be capable of accepting all waste generated from residue elimination.

The total amount of Pu-239 estimated to be present in the stored residues at the RFP is approximately 3000 kg. This is equivalent to 1.84×10^5 Ci plutonium and is

approximately 2.3 times greater than the Pu-239 activity estimate used in the *WIPP Preliminary Comparisor*. The contribution of gas generated from the increased amount of Pu-239 after emplacement at the WIPP site is also a concern. Early indications from experimental data currently being collected suggest that the rate of gas generation from radiolysis of waste emplaced at WIPP is very small compared to that from corrosion and biodegradation (Sandia National Laboratories, 1991). However, these assessments are based on the initial assumption that the total design volume of waste from RFP contains 8.016×10^4 Ci of Pu-239 and 6.2×10^5 Ci for all radionuclides.

Existing gas generation rates from laboratory analysis for anaerobic corrosion, microbial activity, radiolysis, and other interactions are presented in Molecke (1990) and summarized in Table 4. The established gas generation rates will be used to assess the effects of overall gas generation based on simulated conditions.

In conducting these assessments, the following assumptions have been made:

1. The radiolytic gas generation rates vary linearly for a change in the activity of the waste as depicted by Equation 1.
2. The waste products from the four selected IDCs are representative, in terms of radiolytic gas generation potential, of all waste products that would be generated from elimination of RFP residues.
3. The gas generation rate per drum from anaerobic corrosion is constant. It will be assumed that the average gas generation rate from anaerobic corrosion is the same, whether it is from a 55-gal drum of stored, projected, or REP waste.

Gas generation rates using the design parameters in the *WIPP Preliminary Comparison* are used as the baseline. The estimated composition by volume of CH-TRU waste from RFP is presented in Table 5.

Table 4

**Laboratory-Measured Gas Generation Rates of Simulated
CH TRU Waste Materials Under Varying Conditions^a**

Mechanism	Waste Material/Matrix	Gas Production Limits (moles gas/year/drum)
MICROBIAL	Organic Composite, aerobic	0-(0.9-5.5)-12 ^c
	Organic Composite, anaerobic	0-(1.2-4.2)-32
	Plywood Box, aerobic ^b	0-(0.44-2.2)-3.0
	Plywood Box, anaerobic ^b	0-(1.1-3.7)-4.1
	(Plywood Box, aerobic, 3.2 m ³)	0-(2.8-14)-19
	(Plywood Box, anaerobic, 3.2 m ³)	0-(6.8-23)-26
	Asphalt, aerobic	0-(0.1-2.6)-8.4
	Asphalt, anaerobic	0-(0-1.9)-4.8
	Composite, aerobic, 1% water, 25°C ^d	1.3
	Composite, aerobic, 91% water, 25°C ^d	1.6
	Composite, aerobic, 91% water, 25°C ^d	---
	Composite, aerobic, 91% brine, 40°C ^d	5.2
	Composite, anaerobic, 1% water, 25°C ^d	2.4
	Composite, anaerobic, 91% water, 25°C ^d	4.2
	Composite, anaerobic, 91% brine, 25°C ^d	3.2
RADIOLYSIS	Cellulosics (0.039 Ci) ^e	0.002-(0.005-0.011)-0.012
	Polyethylene (0.039 Ci)	0.003-(0.007)-0.008
	PVC (0.039 Ci)	0.01-(0.03-0.042)-0.08
	Process Sludges (7.7 Ci)	0.76
	Organic Composite (0.039 Ci)	0.002-(0.005)-0.006
	Asphalt (7.7 Ci)	0.1-(0.15-0.76)-1.0
	Concrete-TRU Ash (poured, 15 Ci)	0.03-(0.045-0.93)-1.0
	Concrete-TRU Ash (heated, 15 Ci)	0.0002-(0.0005-0.035)-0.05
	Alpha decay, He generation (15 Ci)	0.000015
CORROSION	Mild Steel Drum ^b , anaerobic	0-2.0
	Mild Steel Drum ^b , aerobic	0
THERMAL	Organic Composite (25° C)	0
	Organic Composite (40° C)	0-(0.02-0.2)-0.4
	Paper (70° C)	0.5-(1.3)-2
OVERALL AVERAGE	Existing INEL TRU Wastes Aerobic	0.0005-(0.3-1.4)-2.8

a Molecke, 1990, Table 5.1

b drum volume - 0.21 m³

c lower limit - (most probable range) - upper limit. Low and upper limits include estimated uncertainties.

d Caldwell et al., 1987

e 0.039 Ci - 0.5 g ²³⁹Pu, 15.4 Ci - 200 g ²³⁹Pu (max/drum)

Table 5

**WIPP Performance Assessment
Estimated Composition by Volume of CH-TRU Waste
from Rocky Flats Plant***

Composition	Percent (by Volume)
Combustibles	34.24
Metal and Glass	34.31
Absorbed Liquids and Sludges	6.28
Concrete/Cemented Sludge	14.43
Dirt/Gravel/Asphalt	1.3
Filters/Filter Media	3.67
Other	5.77

* Sandia National Laboratories, 1991

For comparison, the volumes of waste for IDCs 312, 338, 409, and 420 were obtained from the *Residue Analysis Study* (EG&G, 1992) based on Cases 1 and 3. These values are presented in Table 6, which identifies the four original IDCs and the resulting wastes generated (by IDC) from primary and secondary activities. It is assumed that Case 2 (actinide separation at another facility) would result in the generation of waste similar in quantity and composition to that generated from Case 1 (actinide separation at RFP).

Table 6

Volumes of Waste Generated from Residue Elimination Cases 1 and 3

Final IDC	Case 1 Actinide Separation Volumes of Waste Generated (m ³)				Case 3 Ship as Waste Volumes of Waste Generated (m ³)			
	Original IDCs				Original IDCs			
	312	338	409	420	312	338	409	420
312					3065.78			
338					55.33	5726.15	26.9	316.56
339	9.9	2.89	0.44	45.4	12.36	90.04	248.26	
376	70.38	421.13	26.9					
409							13721.96	
438	1.9	0.15		5.41				
440	4.76	0.9	49.59	22.25				
806	114.59	8.02	1021.65	308.2				4125.64
807	13.97	4.02	42.02	68.76				
809	17.25	3.46	9.93	79.29				
821	7.32	3.53	0.5	357.04	5.75	1.44	0.5	26.9
824	7.42	16.43	17.21	35.14	6.01	12.	17.21	28.11
825	39.54				39.54			
831					15.47		198.6	72.36
832	112.65	61.66	1088.94	567.9	46.53		278.05	217.61
833		29.31	5.96	184.93		18.62	5.96	184.93

The number of moles of gas generated per year was calculated for each of three conditions: (1) Actinide Separation, (2) Ship as Waste, and (3) *WIPP Preliminary Comparison*, using the modified values (Table 2) derived from Molecke (1979) and estimated waste compositions as previously discussed. A summary of calculated gas generation values is presented in Table 7 on a per drum basis. Appendix A consists of calculations used to predict the total waste volume and gas generation rates.

Table 7
Calculated Gas Generation Rates by Mechanism
for Waste Emplaced at WIPP
(Based on maximum gas generation rate data)

Gas Generation Mechanism	Gas Generation (moles/drum-year)		
	Actinide Separation	Ship as Waste	WIPP Preliminary Comparison
Radiolysis	0.6453	0.2134	0.3893
Microbial	14.58	0.9671	11.28
Corrosion (anaerobic)	4.060	4.060	4.060
Total	19.33	5.240	15.73

The rate for radiolytic gas generation is calculated using Equation (1) such that,

$$N_{\text{tot}} = \sum_{j=1} 0.099 * G_{\text{tot},j} * A_{d,j} * N_{d,j} \quad (2)$$

where,

N_{tot} = total moles of all gases generated from radiolysis per year summed for all waste forms (by IDC) representing the total volume of waste,

$G_{\text{tot},j}$ = aggregate G value of all gases in units of moles/(Curie-year) for each waste form j,

$A_{d,j}$ = drum activity for each waste form j in units of Curie/year^p, and

$N_{d,j}$ = number of drums for each waste form j.

Gas generation from microbial degradation is calculated using the following equation:

$$N_{mtot} = \sum_{j=1} * G_{mtot,j} * N_{d,j} \quad (3)$$

where,

N_{mtot} = total moles of all gases generated from microbial degradation per year summed for all waste forms (by IDC) representing the total volume of waste,

$G_{mtot,j}$ = aggregate G value of all gases in units of moles gas/(drum-year) for each waste form j, and

$N_{d,j}$ = number of drums for each waste form j.

Gas generation from corrosion is calculated using the following equation:

$$N_{ctot} = \sum_{j=1} * G_{ctot,j} * N_{d,j} * SA_d \quad (4)$$

where,

N_{ctot} = total moles of all gases generated from corrosion per year summed for the total volume of waste,

$G_{ctot,j}$ = aggregate G value of all gases in units of moles gas/(year-m²) for each waste form j, and

$N_{d,j}$ = number of drums for each waste form j, and

SA_d = drum surface area in units of m²/drum.

In order to compare the gas generation rates on an equal basis, the *WIPP Preliminary Comparison* gas generation values were calculated based on a drum equivalent volume of waste generated under Case 1 (Actinide Separation) and Case 3 (Ship as Waste).

Activity concentrations were determined for each of three conditions: Ship as Waste, Actinide Separation, and *WIPP Preliminary Comparison*. For the Ship as Waste option,

the activity concentration for each IDC was calculated by dividing the total activity (based on an estimated 3000 kg of plutonium) by the estimated volume of waste to be produced. For both the Actinide Separation option and the *WIPP Preliminary Comparison* option, a value of 3.01 Ci/drum was used. This value was determined based on the design radionuclide inventory and the design volume for RFP waste (Sandia National Laboratories, 1991, Tables 3.3-5 and 3.4-4). This value is calculated by dividing the design radionuclide inventory of 6.2×10^5 Ci by the design volume of 42,933 m³. This value is equal to 14.44 Ci/m³ and converting the volume from cubic meters to drums (55-gal capacity), using the conversion factor of 3.785×10^{-3} m³/gal, results in an average drum activity of 3.01 Ci/drum. Since wastes produced from actinide separation are expected to be similar in composition (radiological, chemical, and physical) to waste compositions used in the *WIPP Preliminary Comparison*, this method is believed to be valid.

The predicted gas generation rates for Actinide Separation were higher than the *WIPP Preliminary Comparison* gas generation rates. The rates based on radiolysis and microbial gas generation are higher in the Actinide Separation option due to an estimated higher percentage of cellulosic materials and Pu concentrations. Additionally, a large increase in the amount of sludges, cements, and inorganic material in the waste resulted in a moderate increase in radiolytic gas generation. However, the total number of drums of waste produced was predicted to be only 12,222 as compared to the *WIPP Preliminary Comparison* design volume of 123,186 drums or the Ship as Waste predicted volume of 71,411 drums.

When comparing the Ship as Waste option to the *WIPP Preliminary Comparison*, total gas generation is greater for the latter. Radiolytic gas generation is less for the Ship as Waste option since this option results in a lower organic material content ratio (Table 6) even through the estimated concentration of Pu and Am is higher. Microbial gas generation is lower in the Ship as Waste option, also due to the lower estimated

percentage of organic (cellulosic) material. As a general observation, an increase in the percentage of cellulosic materials will result, as secondary treatment activities increase, since these activities result in the generation of large quantities of waste material such as paper, rugs, cloth, coverall, plastic, rubber, wood, and other similar items. This was the case observed for the Actinide Separation option. The gas generation due to corrosion is the same for both options because the rate is assumed to be constant per drum.

4.0 CONCLUSION

An allowance has been made for waste of a specific content code to be placed into a test category. By doing so, real-time data can be obtained to identify the waste container's gas generation rates that exceed the limit set for the shipping category. These data also identify when a waste process does not have a fully characterized bounding G value from previous sampling or waste stream analysis. Testing is recommended for large-quantity waste streams for which the decay heat is a primary restricting parameter in terms of payload acceptability. The results from real-time gas generation rate testing may allow for a significant increase in the amount of decay heat allowed per drum during transportation. Otherwise, without a sound technical basis for increasing the wattage limit, the conservative wattage limits specified by the Analytical Shipping Categories (which are based on the bounding G values) must be used.

It is not expected that inclusion at WIPP of waste products from the REP will produce a significant perturbation in the overall gas generation rates due to the increased radiolytic gas generation rate. As discussed in the *WIPP Preliminary Comparison* (Sandia National Laboratories, 1991), early indications from experimental data currently being collected show the rate of gas generation from radiolysis is very small compared to that from corrosion and biodegradation. In all cases, radiolysis accounted for less than 4 percent of the gas generation rate. Therefore, unless future studies contradict current indications regarding gas generation due to radiolysis, the analyses conducted herein are consistent with existing data and the conclusion drawn should remain valid.

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APPENDIX A

The information in this appendix was developed for use in calculating the potential gas generation rates for the (1) Scaled Volume identified in the *WIPP Preliminary Comparison*, (2) volume of waste produced from the Ship as Waste case, and (3) volume of waste produced from the Actinide Separation case.

Table A-1, Calculation of Total Waste Volumes, was developed based on information obtained from the EG&G Residue Analysis Study. Predicted volumes of waste (on a drum basis) are tabulated for both the Ship as Waste and Actinide Separation cases to determine the predicted total volume of waste assuming that all residues are processed for a given case, multiply the Total Drums value by 2.5.

Table A-2 is a listing of G values for radiolysis, microbial, and corrosion mechanisms. These values were extracted from Table 2-3 in Rationale for Revised Bin-Scale Gas-Generation Tests with Contact-Handled Transuranic Wastes at the Waste Isolation Pilot Plant, 1991, SAND90-2481, UC-721, Sandia National Laboratories, Albuquerque, NM, and Livermore, CA.

Table A-1

CALCULATION OF TOTAL WASTE VOLUMES

SHIP AS WASTE VOLUMES (# of Drums) TRU and TRU Mixed

These four primary residues are used for all calculations of total gas generation.

	Graphite IDC 312	Filter Media IDC 338	Lead Gloves IDC 339	Molten Salt IDC 409	Cemented Ash IDC 806	Dry Comb IDC 821	Light Metal IDC 824	Plastic IDC 825	Dry Comb IDC 831	Wet Comb IDC 832	Plastic IDC 833	TOTAL DRUMS
1. IDC 312 Graphite Coarse	3065.78	55.33	12.36			5.75	6.01	39.54	15.47	46.53	18.62	3246.77
2. IDC 338 Filter Media		5726.15	90.04			1.44	12					5848.25
3. IDC 409 Molten Salt, 30%, Unpulverized		26.9	248.26	13721.96		0.5	17.21		198.6	278.05	5.96	14497.44
4. IDC 420 Pulverized Incinerator Ash		316.56			4125.64	26.9	28.11		72.36	217.61	184.93	4972.11
TOTAL DRUMS	3065.78	6124.94	350.66	13721.96	4125.64	34.59	63.33	39.54	286.43	542.19	209.51	28564.57

ACTINIDE SEPARATION VOLUMES (# of Drums) TRU and TRU Mixed

These four primary residues are used for all calculations of total gas generation.

	Lead Gloves IDC 339	Filter Media IDC 376	Insul IDC 438	Glass IDC 440	Cemented Ash IDC 806	Bypass Sludge IDC 807	Cemented Resin IDC 809	Dry Comb IDC 821	Light Metal IDC 824	Wet Comb IDC 825	Plastic IDC 832	Plastic IDC 833	TOTAL DRUMS
1. IDC 312 Graphite Coarse	9.9	70.38	1.9	4.76	114.59	13.97	17.25	7.32	7.42	38.54	112.65		399.68
2. IDC 338 Filter Media	2.89	421.13	0.15	0.9	8.02	4.02	3.46	3.53	16.43		61.66	29.31	551.5
3. IDC 409 Molten Salt, 30%, Unpulverized	0.44	26.9		49.59	1021.65	42.02	9.93	0.5	17.21		1088.94	5.96	2263.14
4. IDC 420 Pulverized Incinerator Ash	45.4		5.41	22.25	308.2	68.76	79.29	357.04	35.14		567.9	184.93	1674.32
TOTAL DRUMS	58.63	518.41	7.46	77.5	1452.46	128.77	109.93	368.39	76.2	39.54	1831.15	220.2	4886.64

NOTE: The four residues identified above account for approximately 40% of the total estimated waste to be generated.
To calculate the actual total number of drums of waste, multiply the "Total Drums" by 2.5.

Table A-2

CALCULATION OF GAS GENERATION RATES

G VALUES

(moles/level of radioactivity*yr)

RADIOLYSIS

Controlling Variable

1. Cellulosic Materials (0.039 Ci)*	0.002	0.005	0.011	0.012
2. Plastics (0.039 Ci)*	0.003	0.007	0.007	0.008
3. Rubber Materials (0.039 Ci)*	0.001	0.03	0.042	0.08
4. Corroding metal/steels	0	0	0	0
5. Corroding Metal/aluminum	0	0	0	0
6. "Non-Corroding" metals	0	0	0	0
7. Solid Inorganic Materials	0	0	0	0
Asphalt (7.7 Ci)*	0.1	0.15	0.76	1
8. Inorganic Sludges (7.7 Ci)*			0.76	0.76
9. Cements (15 Ci)*	0.03	0.045	0.93	1
10. Other Organic Materials (Composite 0.039 Ci)	0.002	0.005	0.005	0.006
11. Total Alpha Curie Content **	0	0	0	0
12. Water **	0	0	0	0

** G-values for these variables are assumed to be accounted for in Controlling Variables 1-6

** G-values for these variables are assumed to be accounted for in Controlling Variables 1-10

(moles/drum-yr)

MICROBIAL (assumes anaerobic condition)

Controlling Variable

Material	Volume (m³)	Weight (kg)	Volume (m³)	Weight (kg)
1. Cellulosic Materials	0	1.2	4.2	32
2. Plastics	0	0	0	0
3. Rubber Materials	0	0	0	0
4. Corroding metal/steels	0	0	0.005	0.005
5. Corroding Metal/aluminum	0	0	0	0
6. "Non-Corroding" metals	0	0	0	0
7. Solid Inorganic Materials (plywood box 0.21 m2)	0	0	0	0
Asphalt	0	1.1	3.7	4.1
8. Inorganic Sludges	0	0	1.9	4.8
9. Cements	0	0	4.2	4.2
10. Other Organic Materials (Composite)	0	0	0	0
11. Total Alpha Cune Content	0	0	0	0
12. Water	0	0	0	0

CORROSION (assumes anaerobic condition)

(moles/m²-yr)

Controlling Variable

Material	0	0	0	0
1. Cellulosic Materials	0	0	0	0
2. Plastics	0	0	0	0
3. Rubber Materials	0	0	0	0
4. Corroding metal/steels	0	0	0	0
5. Corroding Metal/aluminum	0	0	2	2
6. "Non-Corroding" metals	0	0	2	2
7. Solid Inorganic Materials (plywood box 0.21 m2)	0	0	0	0
Asphalt	0	0	0	0
8. Inorganic Sludges	0	0	0	0
9. Cements	0	0	0	0
10. Other Organic Materials (Composite)	0	0	0	0
11. Total Alpha Curie Content	0	0	0	0
12. Water	0	0	0	0

Tables A-3 through A-5 consist of the calculations of the gas generation rates based on each gas generation mechanism (i.e., radiolysis, microbial, corrosion). These values are reported in total moles per year based on the total number of drums estimated from calculations performed on Table A-1.

Table A-3

CALCULATION OF GAS GENERATION RATES

GAS GENERATION RATES
(total moles/yr)

SCALED VOLUME (No. of Drums 123,186)

RADIOLYSIS

Controlling Variable

1. Cellulosic Materials (0.039 Ci)*

2. Plastics (0.039 Ci)*

3. Rubber Materials (0.039 Ci)*

4. Corroding metal/steels

5. Corroding Metal/aluminum

6. "Non-Corroding" metals

7. Solid Inorganic Materials

Asphalt (7.7 Ci)*

8. Inorganic Sludges (7.7 Ci)*

9. Cements (15 Ci)*

10. Other Organic Materials (Composite 0.039 Ci)

11. Total Alpha Curie Content **

12. Water **

** G-values for these variables are assumed to be accounted for
in Controlling Variables 1-10

LOWER LIMIT	LOWER RANGE	UPPER RANGE	UPPER LIMIT
6553.97	16384.92	36046.82	38323.81
0.00	0.00	0.00	0.00
63.00	94.50	478.80	630.00
		2313.57	2313.57
107.72	161.58	3339.40	3580.75
702.49	1756.23	1756.23	2107.48
TOTAL	7427.18	18397.24	43934.83
			47965.61

(total moles/yr)

MICROBIAL (assumes anaerobic condition)

Controlling Variable

1. Cellulosic Materials

2. Plastics

3. Rubber Materials

4. Corroding metal/steels

5. Corroding Metal/aluminum

6. "Non-Corroding" metals

7. Solid Inorganic Materials (plywood box 0.21 m2)

Asphalt

8. Inorganic Sludges

9. Cements

10. Other Organic Materials (Composite)

11. Total Alpha Curie Content

12. Water

LOWER LIMIT	LOWER RANGE	UPPER RANGE	UPPER LIMIT
0.00	50614.80	177151.80	1349728.00
0	0	0	0
0.00	0.00	3041.90	7684.80
		32491.20	32491.20
0	0	0	0
TOTAL	0	50614.8	212684.9
			1389904

(total moles/yr)

CORROSION (assumes anaerobic condition)

Controlling Variable

1. Cellulosic Materials

2. Plastics

3. Rubber Materials

4. Corroding metal/steels

5. Corroding Metal/aluminum

6. "Non-Corroding" metals

7. Solid Inorganic Materials (plywood box 0.21 m2)

Asphalt

8. Inorganic Sludges

9. Cements

10. Other Organic Materials (Composite)

11. Total Alpha Curie Content

12. Water

LOWER LIMIT	LOWER RANGE	UPPER RANGE	UPPER LIMIT
0	0	500135.16	500135.16
TOTAL	0	0	500135.16
			500135.16

Table A-4

CALCULATION OF GAS GENERATION RATES

GAS GENERATION RATES
(total moles/yr)

SHIP AS WASTE VOLUME (No. of Drums 71,411)

RADIOLYSIS

Controlling Variable

	LOWER LIMIT	LOWER RANGE	UPPER RANGE	UPPER LIMIT
1. Cellulosic Materials (0.039 Ci)*	97.72	244.30	537.45	586.31
2. Plastics (0.039 Ci)*	39.89	93.09	93.09	106.38
3. Rubber Materials (0.039 Ci)*	22.48	674.35	944.08	1798.26
4. Corroding metal/steels	0	0	0	0
5. Corroding Metal/aluminum				
6. "Non-Corroding" metals				
7. Solid Inorganic Materials				
Asphalt (7.7 Ci)*	0	0	0	0
8. Inorganic Sludges (7.7 Ci)*				
9. Cements (15 Ci)*	247.252056	370.878084	7664.813736	8241.7352
10. Other Organic Materials (Composite 0.039 Ci)	1502.91	3757.27	3757.27	4508.72
11. Total Alpha Curie Content **				
12. Water **				

** G-values for these variables are assumed to be accounted for
in Controlling Variables 1-10

TOTAL 1910.25 5139.88 12996.71 15241.41

(total moles/yr)

MICROBIAL (assumes anaerobic condition)

Controlling Variable

	LOWER LIMIT	LOWER RANGE	UPPER RANGE	UPPER LIMIT
1. Cellulosic Materials	0.00	2589.60	9063.60	69056.00
2. Plastics	0.00	0.00	0.00	0.00
3. Rubber Materials	0.00	0.00	4.38	4.38
4. Corroding metal/steels	0	0	0	0
5. Corroding Metal/aluminum				
6. "Non-Corroding" metals				
7. Solid Inorganic Materials (plywood box 0.21 m2)				
Asphalt				
8. Inorganic Sludges				
9. Cements	0	0	0	0
10. Other Organic Materials (Composite)	0.00	0.00	0.00	0.00
11. Total Alpha Curie Content				
12. Water				

TOTAL 0 2589.6 9067.98325 69060.38325

(total moles/yr)

CORROSION (assumes anaerobic condition)

Controlling Variable

	LOWER LIMIT	LOWER RANGE	UPPER RANGE	UPPER LIMIT
1. Cellulosic Materials				
2. Plastics				
3. Rubber Materials				
4. Corroding metal/steels	0	0	289930.284	289930.284
5. Corroding Metal/aluminum				
6. "Non-Corroding" metals				
7. Solid Inorganic Materials (plywood box 0.21 m2)				
Asphalt				
8. Inorganic Sludges				
9. Cements				
10. Other Organic Materials (Composite)				
11. Total Alpha Curie Content				
12. Water				

TOTAL 0 0 289930.284 289930.284

Table A-5

CALCULATION OF GAS GENERATION RATES

GAS GENERATION RATES
(total moles/yr)

ACTINIDE SEPARATION VOLUME (No. of Drums 12,222)

RADIOLYSIS

Controlling Variable

1. Cellulosic Materials (0.039 Ci)*
2. Plastics (0.039 Ci)*
3. Rubber Materials (0.039 Ci)*
4. Corroding metal/steels
5. Corroding Metal/aluminum
6. "Non-Corroding" metals
7. Solid Inorganic Materials
Asphalt (7.7 Ci)*
8. Inorganic Sludges (7.7 Ci)*
9. Cements (15 Ci)*
10. Other Organic Materials (Composite 0.039 Ci)
11. Total Alpha Curie Content **
12. Water **

** G-values for these variables are assumed to be accounted for
in Controlling Variables 1-10

	LOWER LIMIT	LOWER RANGE	UPPER RANGE	UPPER LIMIT
1. Cellulosic Materials (0.039 Ci)*	854.46	2136.15	4699.53	5126.76
2. Plastics (0.039 Ci)*	151.27	352.96	352.96	403.38
3. Rubber Materials (0.039 Ci)*	11.42	342.62	479.67	913.66
4. Corroding metal/steels	0.00	0.00	0.00	0.00
5. Corroding Metal/aluminum				
6. "Non-Corroding" metals				
7. Solid Inorganic Materials Asphalt (7.7 Ci)*	0.00	0.00	0.00	0.00
8. Inorganic Sludges (7.7 Ci)*	0.00	0.00	96.30	49.43
9. Cements (15 Ci)*	23.67	35.51	733.78	789.01
10. Other Organic Materials (Composite 0.039 Ci)	201.38	503.45	503.45	604.14
11. Total Alpha Curie Content **				
12. Water **				
TOTAL	1242.20	3370.68	6865.68	7886.38

(total moles/yr)

MICROBIAL (assumes anaerobic condition)

Controlling Variable

1. Cellulosic Materials
2. Plastics
3. Rubber Materials
4. Corroding metal/steels
5. Corroding Metal/aluminum
6. "Non-Corroding" metals
7. Solid Inorganic Materials (plywood box 0.21 m2)
Asphalt
8. Inorganic Sludges
9. Cements
10. Other Organic Materials (Composite)
11. Total Alpha Curie Content
12. Water

	LOWER LIMIT	LOWER RANGE	UPPER RANGE	UPPER LIMIT
1. Cellulosic Materials	0.00	6598.80	23095.80	175968.0
2. Plastics	0.00	0.00	0.00	0.00
3. Rubber Materials	0.00	0.00	0.74	0.74
4. Corroding metal/steels	0.00	0.00	0.00	0.00
5. Corroding Metal/aluminum				
6. "Non-Corroding" metals				
7. Solid Inorganic Materials (plywood box 0.21 m2) Asphalt	0.00	233.20	784.40	869.20
8. Inorganic Sludges	0.00	0.00	1352.40	1352.40
9. Cements	0.00	0.00	0.00	0.00
10. Other Organic Materials (Composite)	0.00	0.00	0.00	0.00
11. Total Alpha Curie Content				
12. Water				
TOTAL	0	6832	25233.335	178190.335

(total moles/yr)

CORROSION (assumes anaerobic condition)

Controlling Variable

1. Cellulosic Materials
2. Plastics
3. Rubber Materials
4. Corroding metal/steels
5. Corroding Metal/aluminum
6. "Non-Corroding" metals
7. Solid Inorganic Materials (plywood box 0.21 m2)
Asphalt
8. Inorganic Sludges
9. Cements
10. Other Organic Materials (Composite)
11. Total Alpha Curie Content
12. Water

	LOWER LIMIT	LOWER RANGE	UPPER RANGE	UPPER LIMIT
1. Cellulosic Materials				
2. Plastics				
3. Rubber Materials				
4. Corroding metal/steels	0	0	49621.32	49621.32
5. Corroding Metal/aluminum				
6. "Non-Corroding" metals				
7. Solid Inorganic Materials (plywood box 0.21 m2) Asphalt				
8. Inorganic Sludges				
9. Cements				
10. Other Organic Materials (Composite)				
11. Total Alpha Curie Content				
12. Water				
TOTAL	0.0	0.0	49621.3	49621.3

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