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# WASTE DRUM GAS GENERATION SAMPLING PROGRAM AT ROCKY FLATS DURING FY 1988

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U.S. DEPARTMENT OF ENERGY
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## DISCLAIMER

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# WASTE DRUM GAS GENERATION SAMPLING PROGRAM AT ROCKY FLATS DURING FY 1988

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SUBJECT DESCRIPTORS

G Values
Gas Generation
Hydrogen Permeability
TRU Waste

EG&G ROCKY FLATS, INC.
ROCKY FLATS PLANT
P. O. BOX 464
GOLDEN, COLORADO 80402-0464

PREPARED UNDER CONTRACT DE-AC04-90DE62349
FOR THE
ALBUQUERQUE OPERATIONS OFFICE
U.S. DEPARTMENT OF ENERGY

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# WASTE DRUM GAS GENERATION SAMPLING PROGRAM AT ROCKY FLATS DURING FY 1988

*D. K. Roggenthen, T. L. McFeeters, and R. G. Nieweg*


## ABSTRACT

Rocky Flats Plant Transuranic Waste Drums were sampled for gas composition. Combustibles, plastics, Raschig rings, solidified organic sludge, and solidified inorganic sludge transuranic waste forms were sampled. Plastic bag material and waste samples were also taken from some solidified sludge waste drums. A vacuum system was used to sample each layer of containment inside a waste drum, including individual waste bags. G values were calculated for the waste drums. Analytical results indicate that very low concentrations of potentially flammable or corrosive gas mixtures will be found in vented drums. $G(H_2)$ was usually below 1.6, while G(Total) was below 4.0. Hydrogen permeability tests on different types of plastic waste bags used at Rocky Flats were also conducted. Polyvinylchloride was slightly more permeable to hydrogen than polyethylene for new or creased material. Permeability of aged material to hydrogen was slightly higher than for new material. Solidified organic and inorganic sludges were sampled for volatile organics. The analytical results from two drums of solidified organic sludges showed concentrations were above detection limits for four of the 36 volatile organics analyzed. The analytical results for four of the five solidified inorganic sludges show that concentrations were below detection limits for all volatile organics analyzed.


## INTRODUCTION

Rocky Flats Plant (RFP) Transuranic (TRU) waste will be shipped in the TRUPACT-II container to the Waste Isolation Pilot Plant. The Nuclear Regulatory Commission must issue a Certificate of Compliance for TRUPACT-II to allow shipment of waste. In determining the RFP waste forms and potential shipping categories and characteristics, questions have arisen about: (1) gas generation (G value) of the waste material, (2) migration of gases through the packaging materials, and (3) volatile organic content of the sludge.

To answer questions related to gas generation of the waste material, actual gas compositions were analyzed to establish minimum and maximum values for hydrogen and organic solvents. Waste drums used in this study were either newly generated at RFP or RFP-generated waste drums stored at Idaho National Engineering Laboratory (INEL) and returned to RFP for examination. The waste forms are identified by item description code (IDC). Waste forms sampled contained wet combustibles, dry combustibles, plastics, Raschig rings, solidified organic sludge, and solidified inorganic sludge. Each containment layer inside the waste drum was punctured with a needle, and a sample of gas was collected in gas-tight bottles and analyzed by mass spectrometry for inorganic and organic gases. The G value was calculated, estimating the amount of gas generated per 100 eV of absorbed energy.

To investigate migration of gases through the packaging materials, the polyethylene (PE) and polyvinyl chloride (PVC) packaging materials used at RFP were tested for hydrogen permeability. The plastic material tested was recently purchased (new), new but bent (creased), or from waste drums stored more than five years (aged). Some aged plastic samples had been exposed to actinide activity. The permeation rates were determined by dynamic mass spectrometry.

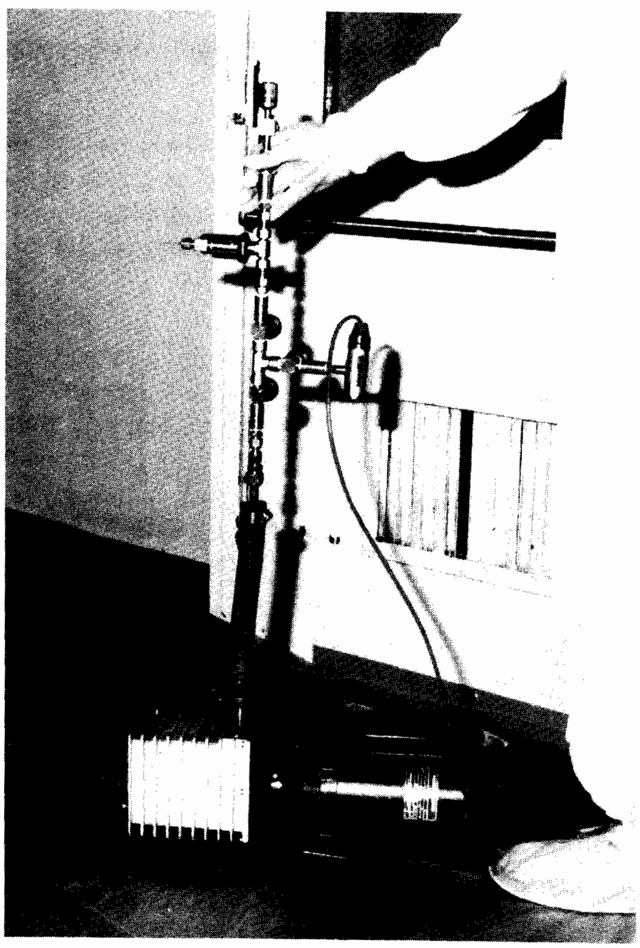
To explore the volatile organic concentrations, solidified organic and inorganic sludges were sampled and analyzed for flammable and nonflammable volatile organics. The solidified organic sludges were generated in 1984 and 1985. The solidified inorganic sludges were generated in 1983 and 1984 or in 1973.

## EXPERIMENTAL PROCEDURE

### Gas Generation

Gas generation sampling was performed inside each layer of containment, including individual waste bags, in RFP-generated waste drums. The TRU waste was either newly generated at RFP or RFP-generated waste stored at INEL and returned for examination. The TRU waste consisted of wet and dry combustibles, plastics, Raschig rings, solidified organic sludges, and solidified inorganic sludges. All sampling was performed in the airlock of the Size Reduction Facility. A vacuum pump and sampling device (Figure 1) were used to obtain the samples. The properly tested sampling device was connected to the vacuum pump approximately 24 hours before beginning waste drum sampling.

FIGURE 1. Sampling Device

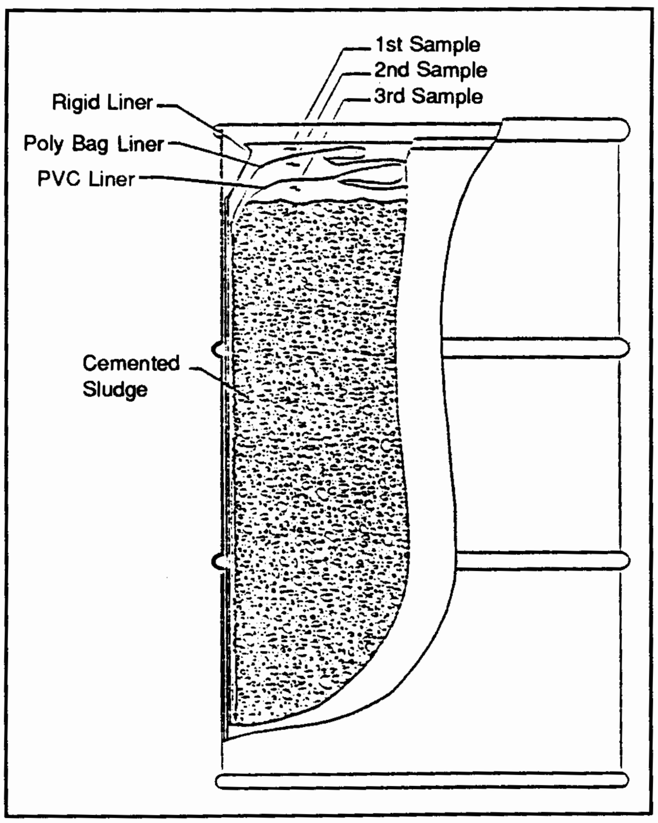


Sludge Waste Drum Sampling Procedure

The typical solidified sludge (IDC 001, 003, and 800) waste drum contains a rigid liner, a PE round-bottom bag, and a PVC bag. The sludge is placed inside the PVC bag. Figure 2 shows a sectioned diagram of a sludge drum and the sampling points. To sample the drum, two people wearing full-face masks and anti-contamination protective clothing stood inside the airlock. The waste drum was moved into the airlock and the drum lid removed. The lid of the PE rigid liner was punctured with an awl. The awl was removed as the needle on the sampling device was lowered into the same hole. A gas sample was then taken inside the rigid liner.

Next, the rigid liner lid was removed, exposing the round-bottom PE (outer) bag. The outer bag was

FIGURE 2. Solidified Sludge Waste Drum



pulled up and isolated, and a gas sample was taken between the outer bag and the PVC (inner) bag. The needle on the sampling device punctured the outer bag, and a gas sample was taken. Two-inch tape was placed over the needle puncture area to reseal the bag and prevent personnel contamination. The outer and inner bags were pulled up and isolated, and a gas sample was taken between the inner bag and the waste material. The needle on the sampling device punctured both bags, and a gas sample was taken. Two-inch tape was placed over the area of the needle puncture. The rigid liner lid and drum lid were replaced and the drum was sealed.

## Individual Waste Bag Sampling Procedure

The individual waste bag sampling procedure was used for all waste types except IDC 001, 003, and 800. The drums sampled were usually lined with a PE round-bottom (outer) bag and a PVC (inner) bag. The waste material was sealed inside smaller bags. For some waste forms, a rigid liner or cardboard liner was also installed outside the PE round-bottom bag. For some waste forms, a PVC bag was not used. The individual waste bag sampling procedure followed the sludge waste drum sampling procedure except the outer and inner bags were cut open after the gas sample was taken. With the outer and inner bags open, individual waste bags were removed from the drum one at a time. The waste was usually contained within two plastic bags. The plastic bag's material varied, depending on the origin of the waste.

The individual waste bags removed from the drum had an outer and inner waste bag. The waste material was contained inside the inner-most bag. Figure 3 shows a sectioned diagram of the waste drum containing individual waste bags and the gas sampling points. A gas sample was collected between the outer waste bag and the inner waste bag using the sampling device. The needle of the sampling device punctured the outer bag, and a gas sample was taken. Two-inch tape was placed over the area of the needle puncture. A gas sample was also collected between the inner bag and the waste. The sampling device needle punctured both the

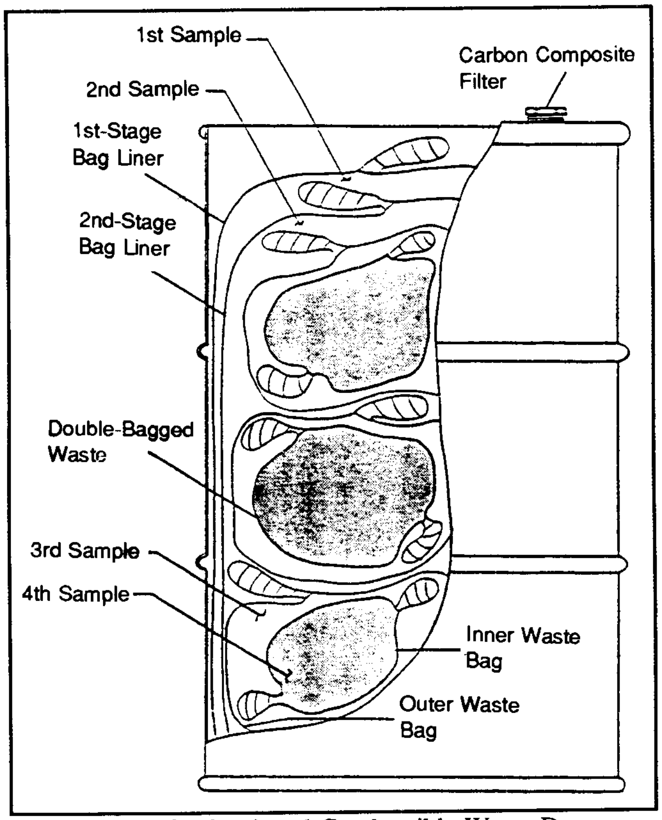


FIGURE 3. Sectioned Combustible Waste Drum

outer and inner waste bag (Figure 4). Two-inch tape was placed over the area of the needle puncture.

Each bag of waste was placed into a special 55-gallon drum for assay. This drum was prepared to position the small quantity of waste near its geometric center by placing a cardboard box and a round cardboard inside the plastic-lined drum (Figure 5). The special 55-gallon drum was closed and assayed at the passive/active neutron (PAN) counter. Positioning the waste in the center third of the drum provides the most reliable assay.

## Gas Sampling Procedure

A gas sample was collected inside a 10-mℓ evacuated sampling bottle. The sampling device shown in Figure 1 consisted of a Cajon VCO® connection to a 10-mℓ valved sampling bottle, a valved pressure gauge, a 0.5-micron sintered metal filter, a valve before entry into the vacuum pump,

FIGURE 4. Gas Sampling Individual Waste Bags

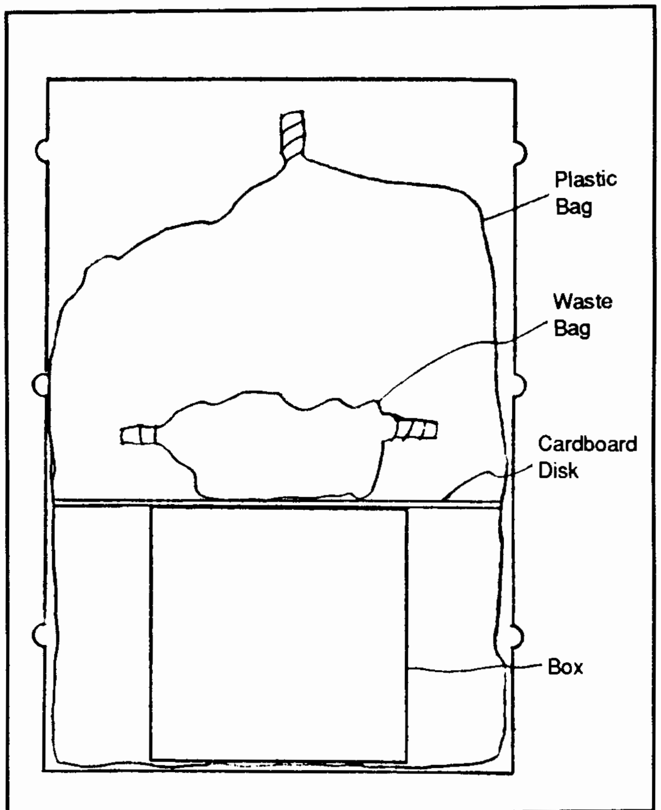



FIGURE 5. Specially Prepared 55-Gallon Drum

and a valved syringe needle. The sampling device was connected to the vacuum pump before sampling any drums and evacuating to less than 50 microns of mercury. The sampling device was evacuated to less than 80 microns of mercury between samples. The gas sample was taken using the needle of the sampling device to puncture the plastic bag.

The valves on the sampling manifold (Figure 1) were positioned in the following order for sampling:

1. Pressure gauge valve (V2) opened.
2. Vacuum valve (V3) shut.
3. Needle inserted through the plastic bag.
4. Needle valve (V4) opened.
5. Sample bottle valve (V5) opened.

The gas sample was collected once the sample bottle was filled. The valves were positioned in the following order to replace the filled sample bottle with an empty sample bottle:

1. Needle valve (V4) closed.
2. Sample bottle valve (V5) closed.
3. Vacuum valve (V3) closed.
4. Filled sample bottle removed.
5. Empty sample bottle attached.
6. Sample bottle valve (V5) opened.
7. Pressure gauge valve (V2) closed.
8. Vacuum valve (V3) opened.
9. Pressure gauge valve (V2) reopened approximately 1 to 2 minutes after opening V3.

The vacuum evacuated the sampling device and bottle to less than 80 microns of mercury. The sample bottle valve (V2) was closed. The sampling device was then prepared for the next sample.

## Drum Assay and G Value Calculation Requirements

To calculate the drum assay and the G value for each waste drum, the following information was required. If the waste form was a sludge or did not contain individual bags of waste, the entire waste drum was assayed in the PAN counter. The individual waste bags were weighed. Individual waste bag dimensions were also taken. If the waste drum contained individual waste bags, they were sampled and repackaged into a 55-gallon drum for assaying at the PAN counter. Any unsampled waste bags in the original waste drum were also repackaged and assayed in the PAN counter. The PAN drum counter gives results in passive and active mass (grams). The active mass value was usually used in the drum assay calculations. Sludge drums were measured for the amount of free space available inside the rigid liner. The type of rigid liner was also determined. For filtered drums, the carbon composite filters have a minimum diffusion coefficient of $1.9 \times 10^{-6}$ moles/sec/mole fraction of hydrogen. The minimum diffusion coefficient for hydro-carbons was six orders of magnitude lower and considered insignificant. The minimum diffusion coefficient was determined at standard pressure and 23 °C.[1]

The drum assay was calculated using the above information. The drum assay is the total alpha activity from inside a drum or the sum of all individual waste bags inside a drum. The total alpha activity was calculated by multiplying the specific activity of each radioactive element by the weight of each radioactive element. The specific activity (curie per gram) is a constant. The specific activity values were taken from the Solid Waste Information Management System data base. The weight of each radioactive element was calculated from the active mass value reported by the PAN counter. The active mass value was assumed to be only plutonium unless an analysis of the waste form or the origin of the waste gave additional information on americium or uranium content.

The waste drum void volume was also calculated. The total drum void volume includes:

1. Space between the rigid liner and the 55-gallon drum.

2. Inside the rigid liner. Space above the sludge or outside of the individual waste bags.

3. Void space inside the individual waste bags.

RFP specifications were used to obtain dimensional information for the rigid liners and the 55-gallon drum. Knowing the type of rigid liner, the void space between the inside of the 55-gallon drum and the outside of the rigid liner was calculated. The three types of rigid liners have approximately the same outside volume, but the method of lid closure varied. The inside dimensions of each rigid liner type were obtained for calculating the void space outside the individual waste bags or above the sludge.

When individual waste bags were combined into one drum for assay, the average package dimension was used. The solidified sludge waste was assumed to contain no void space. The void space for the individual waste bags was determined by subtracting the volume of the individual waste bag from the volume of waste. Individual waste bags were assumed to be right circular cylinders for volume calculations. The volume of waste was determined by dividing density of the waste into the weight of an individual package or the net weight of the drum. Densities of 1.0 kg/ℓ for combustibles and plastics and 2.8 kg/ℓ for the Raschig rings were assumed.

Using information from above, the G value was calculated. The G value is the number of molecules of gas formed or consumed per 100 electron volts (eV) of energy absorbed by the system. All calculations used standard pressure and room temperature (23 °C or 74 °F). The moles of gas generated were calculated from the ideal gas law based on the void volume of the drum, the diffusion rate of hydrogen out of filtered drums, and the analytical results. The moles of gas were calculated for hydrogen, carbon dioxide, and the total of all nonchlorinated compounds except nitrogen, argon, and oxygen. Except for individual waste bags, the highest total analytical results were used. Changes in oxygen concentration were not accounted for in these calculations. The absorbed energy is calculated from the total alpha activity calculations and the length of time since the drum had been sealed. The G values for each drum were calculated from the following equation:

$$G = \frac{\text{moles gas} \times (6.02 \times 10^{23}\ \text{molecules/mole})}{[(\text{curie Pu}) \times (5.23 \times 10^{4}\ 100\ \text{eV/dist}) + (\text{curie Am}) \times (5.64 \times 10^{4}\ 100\ \text{eV/dist})] \times (\text{days drum sealed}) \times (3.7 \times 10^{10}\ \text{dist/s-Ci}) \times (8.64 \times 10^{4}\ \text{s/day})}$$

## Hydrogen Permeability

The hydrogen permeability values were obtained for bag material samples by dynamic mass spectrometry measurements. The PE and PVC plastic material was obtained from recently purchased bags (new or creased) and from bags that had been in waste drums since 1984 or 1973 (aged). The creased bag material was recently purchased material that had been bent repeatedly until perpendicular creases in the plastic material were permanent. The 1984 and 1973 waste drum plastic material was taken from areas in contact with either (1) the headspace gas or (2) the sludge waste. The aged plastic samples were taken from waste drums sampled for gas generation. The permeability coefficient values are arithmetic means obtained from ten-flowrate determination at six pressure points ranging from 16 to 600 torr for new or creased material and three pressure points ranging from 150 to 600 torr for aged material.

The dynamic mass spectrometry measured hydrogen flowrates at nominal pressure points by recording spectral peaks. The analytical plastic samples are held in a modified screen-supported sample holder located in the manifold between a hydrogen reservoir and the mass spectrometer. The analytical samples were 1 sq. cm. cut from 6-inch squares of bag material. Before measurements were taken, the manifold was evacuated and the hydrogen reservoir pressurized to one of the nominal pressures. The permeability coefficient values are obtained after normalizing background corrected values for area (1 sq. cm.), pressure (1 torr), and sample thickness (1 in.).

## Sludge Sampling

Solidified organic and inorganic sludges were sampled and analyzed for potentially flammable and nonflammable volatile organics. The solidified organic and inorganic sludge waste drums were initially examined for gas generation. Then, the drums were moved into the vault where sludge (approximately five grams) was sampled from the side of the waste. The sludge samples were then analyzed by Gas Chromatography/Mass Spectrometry (GC/MS) for 34 target compounds (EPA List) and two alcohol compounds commonly used at RFP (Table 1). RFP Production Support Laboratory performed the analytical work.

# RESULTS AND DISCUSSION

## Waste Drum Sampling

### <u>Gas Generation</u>

Sixteen drums of waste were sampled for gas generation composition, including one drum each of wet combustible (IDC 336), dry combustible (IDC 330), plastic (IDC 337), and Raschig rings (IDC 442), four drums of organic solidified sludge (IDC 003), and eight drums of inorganic solidified sludge (IDC 001 and 800). G values were not calculated for a dry combustible drum, an organic solidified sludge, and three inorganic solidified sludge drums because of incomplete assay or package size information.

Because of a 5 vol % hydrogen limit inside drums to be shipped in TRUPACT-II, one drum would not have been shippable. Drum 741203492, containing solidified inorganic sludge, was pressurized, exceeded the 5 vol % hydrogen limit, and had a potentially flammable internal mixture of gases. However, if it had been vented, potentially flammable mixture of gases would have been unlikely and it would be shippable in a TRUPACT-II container.

Table 1. Volatile Organic Analysis of Sludge Samples[a]

| Volatile Compounds(ppm) | Drum Number 7411-2808 | 7412-02917 | 7412-03492 | 7412-03850 | 7411-2578 | 7431-6930 | 250-0484 |
|---|---|---|---|---|---|---|---|
| 1,1-Dichloroethene | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 80[b] |
| 1,2-Dichloroethene(Total) | 7.8 | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U |
| Chloroform | 1.8 | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U |
| 1,1,1-Trichloroethane | 8.8 | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U |
| Tetrachloroethene | 1.7 | 0.1U | 0.1U | 0.1U | 0.1U | 1.2 | 40[b] |
| 1,1,2,2-Tetrachloroethane | 4.7 | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U |
| Toluene | 0.9 | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U |
| Ethylbenzene | 5.3 | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U |
| Styrene | 9.6 | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U |
| Total Xylenes | 19.0 | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U |
| Carbon Tetrachloride | 0.1U | 0.1U | 0.1U | 0.1U | 0.1U | 2.2 | 700[b] |
| Freon TF | 0.2U | 0.2U | 0.2U | 0.2U | 0.2U | 4.0 | 0.2U |

U Analyzed, not detected

a. Other volatile organic compounds analyzed for but not detected include:

| | | |
|---|---|---|
| propanol | butanol | chloroethane |
| methylene chloride | acetone | carbon disulfide |
| 1,1-dichloroethane | 1,2-dichloroethane | 2-Butanone |
| vinyl acetate | bromodichloromethane | 1,2-dichloropropane |
| cis-1,3-dichloropropene | trichloroethene | dibromochloromethane |
| 1,1,2-trichloroethane | benzene | trans-1,3-dichloropropene |
| bromoform | 4-methyl-2-pentanone | 2-hexanone |
| chlorobenzene | chloromethane | bromomethane |

All detection limits are 0.2 or 0.1 ppm for above compounds.

b. Concentrations in ppb.

G value limits have been proposed for the materials being shipped inside TRUPACT-II. The upper bounding G values for flammable gas are 3.1 and 4.1 for the TRUPACT-II.[2] The flammable gas G value includes hydrogen, methane, and ethane. The maximum G (Flam Gas) calculated was 3.1 for solid organic materials packaged in cardboard and plastic. Materials with a calculated G (Flam Gas) greater than 4.1 are not allowed in quantities greater than 1 wt % for TRUPACT-II shippable waste.

The $G(H_2)$ and G(Total) values for the inorganic solidified sludge ranged from 0.005 to 1.6 and 0.006 to 4.0, respectively (Table 2). The $G(H_2)$ and G(Total) values for the organic solidified sludge range from 0.02 to 0.5 and 0.04 to 0.6, respectively (Table 2). The $G(H_2)$ and G(Total) values for the individual waste bag drums ranged from 0.08 to 5.4 and 1.1 to 10.8, respectively (Table 3). Except for one high G value drum, the G value would not prevent the shipment of these drums, even though most were not vented.

The high G value drum had been closed less than 10 days when the gas sampling was performed. Drum 41450 (IDC 336) had a $G(H_2)$ and G(Total) of 5.4 and 10.8, respectively. It would have had acceptable G values if it had been sampled later. The drum is discussed below.

Drum 41450, a wet combustible, had a $G(H_2)$ and G(Total) of 5.4 and 10.8. Five factors contributed to the high G values.

1. Analytical results from inside the individual waste bags were used for all of the void space in the moles of gas-generated calculation. In such a short period, the drum probably had not established equilibrium. Therefore, a lower hydrogen concentration inside the rigid liner void space could have lowered the G values significantly.

2. Length of time that the drum had been closed (nine days). The G value calculation was influenced by how long it had been closed

based on the moles of gas generated. If the moles of gas generated have been generated over 90 days, the G values would have been lowered to a tenth (0.54 and 1.1) of the calculated values (5.4 and 10.8).

3. Analytical error. The detection limit for hydrogen is 200 ppm. The analytical results are reported to the nearest 100 ppm from 200 to 500 ppm. Above 500 ppm, the analytical results are reported to the nearest tenth of a volume percent.

4. Individual waste bags had accumulated inside the drum for several days before the drum was closed.

5. Drum was not vented.

Possible assumptions that could introduce some error into the G value calculation are:

1. Gases remained inside a non-filtered, sealed drum with semi-permeable gaskets.

2. Gas composition remains the same from the day the drum is closed until it is sampled.

3. Individual waste bags were accumulating in the drum before closing.

4. Radiological decay on the waste inside individual waste bags contacted the plastic material[3].

Error can also be introduced into the G value calculation because of analytical and PAN drum assay error.

### Organic Concentration of Sludge

Two IDC 003 organic solidified sludge drums were sampled for headspace gas composition and for organic compounds in the sludge. Both were originally generated at RFP, stored at INEL, and returned to RFP for examination. Drum 74316930 was generated in 1984. Drum 2500484 was generated in 1985. Both contained some organic compounds in the sludge at total concentrations less than 8 ppm. Only Drum 2500484 contained organic compounds in the headspace, and the total concentration was only 5.1 vol %.

Five IDC 001 inorganic sludge drums were sampled for headspace gas composition and for organic compounds in the sludge. They were originally generated at RFP, then stored at INEL, and returned to RFP for examination. Three of the five were filled in 1983 or 1984. The remaining two were filled in 1973. Only one (7411-2808) of the five drums contained sludge with organic compounds above the detection limits. The analytical results are shown in Table 1. Waste in Drum 7411-2808 was generated at RFP in 1973 and had a filter vent (INEL filter - installed in October 1987) in the lid. The sludge contained nine organic compounds (ppm concentrations) of the 36 compounds analyzed. The gas samples of the same drum showed no trace of the organic compounds within the layers of containment (Table 2). Therefore, the sludge has retained volatile organic compounds.

## Hydrogen Permeability

The hydrogen permeability study used PVC and PE plastic material cut from new bags or from bags used in packaging waste at RFP. The plastic material samples were approximately 6 inches square. New and creased plastic materials had ten permeation rate measurements made at six pressure points ranging from approximately 16 to 600 torr. Aged plastic material had ten permeation rate measurements made at three pressure points between 150 and 600 torr.

The hydrogen permeability results show no statistically valid differences in the permeability coefficient values between new and creased plastic material. The permeability coefficient values below were obtained at pressures between 150 and 600 torr. The data obtained at 75 torr and below contain significant levels of variation. Reasons for the inaccuracy are not completely understood. Therefore, the lower permeability coefficient values (pressures between 150 and 600 torr) are reported and provide a margin of safety. Permeability

| | DRUM NUMBER | IDC CODE | SAMPLING DATE | DATE DRUM CLOSED | GROSS WEIGHT (KG) | DRUM VENTED | DRUM ASSAY Pu (GM) | Am (GM) | U (GM) | CALCULATED DRUM ASSAY (Ci/DRUM) | CO2 (VL%) | GENERAL COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| INORGANIC SLUDGE | 62542 | 800 | 7-18-88 | 6-21-88 | 219 | NO | 2.6 | 0.0 | | 0.245 b | | |
| | | | | | | | 3. | | | | | :IGID LINER LID HAD A GASKET |
| | | | | | | | | | | | 400 c | |
| | | | | | | | | | | | 200 c | |
| | 59728 | 800 | 7-18-88 | 6-20-88 | 200 | NO | 1.7 | 0.07 | 0.6 | 2.233 | | |
| | | | | | | | 2. | | | | 0.1 | :IGID LINER LID HAD A GASKET |
| | | | | | | | | | | | 300 c | |
| | | | | | | | | | | | 450 c | |
| | 62815 | 800 | 7-18-88 | 7-10-88 | 236 | NO | 1.7 | 0.0 | 1.7 | 0.145 | | |
| | | | | | | | 2. | | | | 600 c | :IGID LINER LID HAD A GASKET |
| | | | | | | | | | | | 500 c | |
| | | | | | | | | | | | 200 c | |
| | 74112808 | 001 | 9-14-88 | 4-9-73 | 238 | YES a | 4.7 | 0.8 | | N/A | | |
| | | | | | | | | | | | 0.3 | ID LINER |
| | | | | | | | | | | | 0.1 | |
| | | | | | | | | | | | 0.1 | IPLED |
| | 74112578 | 001 | 9-14-88 | 2-9-73 | 251 | YES a | 2.5 | 0.4 | | N/A | | |
| | | | | | | | | | | | 0.3 | ID LINER |
| | | | | | | | | | | | 0.1 | |
| | | | | | | | | | | | 0.1 | RED SLUDGE = FLY ASH; SLUDGE SAMPLED |
| | 741203850 | 001 | 9-14-88 | 8-2-84 | 229 | NO | 6.41 | 2.41 | | N/A | | |
| | | | | | | | | | | | 0.1 | IL IN SAMPLE, TYPE II RIGID LINER |
| | | | | | | | | | | | 0.1 | IL IN SAMPLE |
| | | | | | | | | | | | 0.1 | IL IN SAMPLE; SLUDGE SAMPLED |
| | 741202917 | 001 | 9-15-88 | 9-7-83 | 231 | NO | 3.4 | 1.6 | | 22.13 | | |
| | | | | | | | 3. | | | | 0.1 | GID LINER |
| | | | | | | | | | | | 0.1 | |
| | | | | | | | | | | | 0.1 | PLED |
| | 741203492 | 001 | 9-15-88 | 3-9-84 | 212 | NO | 11.1 | 2.31 | | 23.07 | | URIZED |
| | | | | | | | 11. | | | | 0.1 | WEEN BAGS, TYPE II RIGID LINER |
| | | | | | | | | | | | | IL IN SAMPLE |
| | | | | | | | | | | | 0.1 | PLED |
| ORGANIC SLUDGE | 74316881 | 003 | 10-4-88 | 4-3-84 | 196 | NO | .035 | | | N/A | | |
| | | | | | | | | | | | TRACE | NER |
| | | | | | | | | | | | TRACE | WAS YELLOW COLORED |
| | 74317069 | 003 | 10-4-88 | 12-5-84 | 184 | NO | 7.66 | | | 0.164 b | | |
| | | | | | | | 8. | | | | 0.1 | NER |
| | | | | | | | | | | | 0.1 | WAS YELLOW COLORED |
| | | | | | | | | | | | 0.1 | LORED SLUDGE |
| | 74316930 | 003 | 1-27-89 | 5-25-84 | 184 | NO | 2.0 | 0.0 | | 0.167 b | | |
| | | | | | | | 2. | | | | 0.1 | INER |
| | | | | | | | | | | | 0.1 | BREACHED; GREENISH COLORED SLUDGE SAMPLED |
| | 2500484 | 003 | 1-27-89 | 4-17-85 | 200 | NO | .036 | 0.0 | | 0.74 b | | |
| | | | | | | | 0 | | | | TRACE | GANICS INSIDE TYPE III RIGID LINER |
| | | | | | | | | | | | 0.1 | AG; GREENISH COLORED SLUDGE SAMPLED |

a INEL filter
b Only Pu content in calculation
c VALUE OF UNITS IN PPM
d AT DETECTION LIMITS
e TCA = 1,1,1-Trichloroethane
f FRN = FREON TF

3. Individual Waste Bag Drum Gas Sampling

| ATED SAY b RUM) | CO2 (VL%) | N2 (VL%) | Ar (VL%) | O2 (VL%) | H2 (VL%) | NOx (VL%) | CH4/ C2H6 (VL%) | CALCULATED G VALUE G(H2) | G(CO2) | G(TOT) | SAMPLE LOCATION | INDIVIDUAL WASTE BAG CONTENTS | GENERAL COMMENTS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| ].488 | | | | | | | | 5.4 | 5.4 | 10.8 | | | |
| ].146 | 0.1 | 78.3 | 1.0 | 20.6 | 0.1 | | | | | | WASTE BAG | PLASTIC BOTTLES | TYPE III RIGID LINER |
| ].151 | 700 d | 77.3 | 0.9 | 21.7 | 200de | | | | | | WASTE BAG | PLASTIC BOTTLES | WASTE BAG REPACKAGED |
| ].191 | 0.1 | 77.7 | 0.9 | 21.2 | 0.1 | | | | | | WASTE BAG | PLASTIC | |
| | | | | | | | | | N/A | | | | 24 INDIVIDUAL WASTE BAGS |
| 10-3 | 3.6 | 77.1 | 0.9 | 18.4 | | | | | | | WASTE BAG | PLASTIC, PINT CONT | DRUM ASSAY SHEET DIFFICULT TO READ, TYPE III LINER |
| 10-5 | 9.0 | 85.1 | 1.0 | 4.8 | 500 d | | | | | | WASTE BAG | PAPER, GLOVES | |
| 10-3 | 2.6 | 77.5 | 0.9 | 19.0 | 200de | | | | | | WASTE BAG | PINT CONTAINERS | |
| 10-3 | 8.8 | 81.5 | 1.0 | 8.7 | | | | | | | WASTE BAG | PLASTIC GLOVES | |
| 10-3 | 0.3 | 78.2 | 1.0 | 8.7 | | | | | | | WASTE BAG | PINT CONT, GLOVES | |
| 10-3 | 3.9 | 79.2 | 0.9 | 16.0 | 200de | | | | | | WASTE BAG | PINT CONT, GLOVES | |
| 10-3 | 2.9 | 78.0 | 1.0 | 18.1 | 400 d | | | | | | WASTE BAG | PINT CONT, GLOVES | |
| 10-3 | 2.2 | 78.1 | 0.9 | 18.8 | | | | | | | WASTE BAG | PINT CONT, GLOVES | DRUM NO. WRONG ON ASSAY SHEET-USED TID TO MATCH |
| 10-4 | 4.0 | 86.2 | 1.0 | 8.5 | | 0.3 | | | | | WASTE BAG | PLASTIC GLOVES | |
| | | | | | | | | | | | | | CONTAINED 15 WASTE BAGS OF UNKNOWN CONTENT |
| ].062 | | | | | | | | 0.16 | 0.9 | 1.1 | | | DRUM RETRIEVED FROM INEL STORAGE 1983 |
| | 1.4 | 80.6 | 1.0 | 16.9 | 0.03 | | 0.08 | | | | RIGID LINER | | TYPE I RIGID LINER LID CONCAVE BEFORE SAMPLING |
| | 1.2 | 81.6 | 1.0 | 16.1 | | | 0.06 | | | | OUTER BAG | | FILTER INSTALLED IN OCT 1987 AND EXAMINED IN INEL |
| | 1.2 | 79.9 | 1.0 | 17.8 | 0.04 | | 0.02 | | | | INNER BAG | | SWEPP IN JULY 1988 |
| 10-3 | 0.6 | 77.7 | 1.0 | 20.7 | 0.04 | | 0.04 | | | | OUTER WASTE | | |
| | 0.9 | 79.1 | 0.9 | 19.0 | 0.05 | | 0.05 | | | | INNER WASTE | PLASTIC BOTTLE | REPACKAGED |
| ].013 | 0.1 | 77.4 | 0.9 | 21.4 | 0.04 | | 0.06 | | | | INNER WASTE | PLASTIC BOTTLE | OUTER BAG BREACHED & PLASTIC COLOR IS DARK BROWN |
| ].010 | | | | | | | | | | | | 5 PLASTIC BOTTLES | ALL INDIVIDUAL WASTE PACKAGES BREACHED |
| ].035 | | | | | | | | | | | | 8 PLASTIC BOTTLES | ALL INDIVIDUAL WASTE PACKAGES BREACHED |
| ].029 | | | | | | | | D.08 | 1.5 | 1.8 | | | |
| | 0.4 | 79.1 | 1.0 | 19.4 | 0.02e | | 0.06 | | | | RIGID LINER | | TYPE III RIGID LINER |
| | 0.4 | 78.7 | 0.9 | 19.9 | | | 0.08 | | | | OUTER BAG | | WET VERMICULITE BETWEEN BAGS |
| | 0.4 | 78.8 | 0.9 | 19.8 | | | 0.08 | | | | INNER BAG | RASCHIG RINGS | 3 INDIVIDUAL WASTE BAGS UNSEEN THROUGH INNER BAG |

coefficient values of $1.67 \times 10^{-15}$ and $1.64 \times 10^{-15}$ (moles/sec)-inch/cm$^2$-torr were obtained for new and creased PE, respectively. Values of $2.84 \times 10^{-15}$ and $2.82 \times 10^{-15}$ (moles/sec)-inch/cm$^2$-torr were obtained for new and creased PVC, respectively.

The hydrogen permeability results for 16-year-old PVC and PE plastic materials show an increase in the permeability coefficient. The permeability coefficient for 5-year-old PVC and PE plastic showed no significant change from new or creased material. The permeability coefficient for PVC showed no variation between the material exposed to air mixtures or sludge. Permeability coefficient values of $1.9 \times 10^{-15}$ and $5.4 \times 10^{-15}$ (moles/sec)-inch/cm$^2$-torr were obtained for 5- and 16-year-old aged PE, respectively. Values of $2.8 \times 10^{-15}$ and $7.8 \times 10^{-15}$ (moles/sec)-inch/cm$^2$-torr were obtained for 5- and 16-year-old aged PVC, respectively.

Although permeabilities vary with age, the permeability coefficient ratio (PVC/PE) was fairly consistent. The permeability coefficient ratio (PVC/PE) was slightly lower for the aged material at 1.47 and 1.46 for 5-year-old and 16-year-old plastic, respectively, and was 1.70 for new or creased material. Based on the small data base, the effects of aging are consistent for PE and PVC materials. Therefore, the data indicate PVC material should not allow as much hydrogen accumulation inside the waste bags.

## CONCLUSIONS AND RECOMMENDATIONS

The three separate areas discussed in this report are: gas generation by RFP-generated waste, hydrogen permeability of various plastics, and ability of the solidified sludges to retain volatile organic compounds.

RFP-generated waste showed varying concentrations of hydrogen, carbon dioxide, various hydrocarbons, and nitrogen oxides in the headspace and individual waste bags from the 16 drums sampled. The calculated G(Total) values for these drums did not exceed any bounding G Value. Only one exceeded the bounding G(Flam Gas) value of 3.1.

Various G Value ranges calculated are as follows:

| Sludge | G(Total) | G(Flam Gas) |
|---|---|---|
| Organic solidified | 0.04 to 0.06 | 0.02 to 0.5 |
| Inorganic solidified | 0.006 to 4.0 | 0.005 to 1.6 |
| Individual waste bag drums | 1.1 to 10.8 | 0.08 to 5.4 |

The drum with high G values had been closed for nine days and was not vented. One inorganic solidified sludge drum was pressurized, exceeded the 5 vol % hydrogen limits allowable in TRUPACT-II, and had a potentially flammable mixture of gases inside the drum. If the drum had been vented, potentially flammable mixture of gases or the 5 vol % hydrogen concentration would have been unlikely.

Possible assumptions that could introduce some error into the G value calculation are that:

1. All gases remained inside a non-filtered, sealed drum with semi-permeable gaskets.
2. Gas composition remains the same from the day the drum is closed until it is sampled.
3. Individual waste bags accumulated in the drum before closing.
4. All radiological decay on the waste inside individual waste bags contacted the plastic material.[3]

The hydrogen permeability of the various plastics used on plantsite was tested using new (recently purchased) and old (in waste drums 5 and 16 years) materials. Some of the old material had been exposed to radioactivity. The hydrogen permeability tests show the plastic material's permeability may be slightly affected by age but not by radiological exposure. The PVC material was more permeable to hydrogen than the PE material.

Both of the organic solidified sludges sampled showed detectable amounts of volatile organic compounds. The concentration levels ranged from 40 ppb to 4.0 ppm for four organic compounds. Organic compounds were also detected in the headspace of one drum with a total concentration of 5.1 vol %.

Four of the five inorganic solidified sludges sampled showed no detectable volatile organic compounds or alcohols in the sludge. One of the five sludges did show concentrations ranging from 0.9 to 19 ppm for nine organic compounds. Because organic compounds were not detected in the headspace gas sampling, the inorganic solidified sludges retained low concentrations of organic compounds.

Recommendations based on data in this report include:

1. Additional gas sampling on RFP-generated waste. (This has been performed and will be reported in later publications.)
2. Additional gas sampling for other waste forms (also planned).
3. Venting all TRU waste drums.
4. Establishing a minimum time period at RFP before the drums can be shipped in TRUPACT-II containers.

## REFERENCES

1. "Safety Analysis Report For The TRUPACT-II Shipping Package Docket Number 71-9218," Appendix 3.6.9 - Gas Release Assessment, February 1989, Nuclear Packaging, Inc., Seattle, WA.
2. "Safety Analysis Report For The TRUPACT-II Shipping Package Docket Number 71-9218," Appendix 3.6.7 - Effective G Values for TRUPACT-II Waste Forms, February 1989, Nuclear Packaging, Inc., Seattle, WA.
3. "Safety Analysis Report For The TRUPACT-II Shipping Package Docket Number 71-9218," Appendix 3.6.8 - Radiolytic G Values For Waste Materials, February 1989, Nuclear Packaging, Inc., Seattle, WA.

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