LA-UR- 97-2934

Approved for public release; distribution is unlimited.

Title: **TRU Waste Transportation- The Flammable Gas Generation Problem**

CONF-970857--

Author(s): Michael J. Connolly,*Ph.D., and Stanley T. Kosiewicz* Ph. D.

*Idaho National Engineering and Environmental Lab
P.O. Box 1625, Idaho Falls, ID 83145-3875
208-526-0238

**Los Alamos National Lab
Los Alamos, NM 87545

Submitted to: Fourth Biennial Mixed Waste Symposium
August 18-21, 1997
Baltimore, MD

Los Alamos
NATIONAL LABORATORY

DISCLAIMER

TRU Waste Transportation - The Flammable Gas Generation Problem

Michael J. Connolly, Ph.D., Idaho National Engineering and Environmental Lab, P.O. Box 1625, Idaho Falls, ID 83145-3875, 208-526-0238, Stanley T. Kosiewicz, Ph.D., P.O. Box 1663, Los Alamos National Lab, Los Alamos, NM 87545, USA.

ABSTRACT

The Nuclear Regulatory Commission (NRC) has imposed a flammable gas (i.e., hydrogen) concentration limit of 5% by volume on transuranic (TRU) waste containers to be shipped using the TRUPACT-II transporter. This concentration is the lower explosive limit (LEL) in air. This was done to minimize the potential for loss of containment during a hypothetical 60 day period. The amount of transuranic radionuclide that is permissible for shipment in TRU waste containers has been tabulated in the TRUPACT-II Safety Analysis Report for Packaging (SARP,1) to conservatively prevent accumulation of hydrogen above this 5% limit. Based on the SARP limitations, approximately 35% of the TRU waste stored at the Idaho National Engineering and Environmental Lab (INEEL), Los Alamos National Lab (LANL), and Rocky Flats Environmental Technology Site (RFETS) cannot be shipped in the TRUPACT-II. An even larger percentage of the TRU waste drums at the Savannah River Site (SRS) cannot be shipped because of the much higher wattage loadings of TRU waste drums in that site's inventory.

This paper presents an overview of an integrated, experimental program that has been initiated to increase the shippable portion of the Department of Energy (DOE) TRU waste inventory. In addition, we will estimate the anticipated expansion of the shippable portion of the inventory and associated cost savings. Such projection should provide the TRU waste generating sites a basis for developing their TRU waste workoff strategies within their Ten Year Plan budget horizons.

INTRODUCTION

Hundreds of thousands of TRU waste drums are stored at the major Department of Energy (DOE) sites in the country. These will be shipped to the Waste Isolation Pilot Plant (WIPP) after the WIPP is certified as a disposal facility. Each drum of waste must be certified before it is shipped to WIPP for disposal. Large segments of the existing legacy and currently generated TRU wastes will not be certifiable for transportation to the WIPP because they exceed the permissible radionuclide contamination limits (referred to as the decay heat limits). These decay heat limits (1) are imposed to constrain radiolytically generated hydrogen to below 5% in the innnermost waste bag (down to 1-gallon size) inside a waste container. The potential of a waste to generate hydrogen gas from radiolytic decompostion (radiolysis) is characterized by a parameter called a "G" value for hydrogen. "G" is defined as the number of molecules of gas generated per 100 eV of energy deposited.

Two options currently exist to addess the drums which exceed the permissible shipping wattages. The first of these is gas generation testing of individual waste containers using the method described in the SARP. The second option is waste form modification by either repackaging with volume expansion and / or processing, e.g., vitrification, to destroy the hydrogenous waste matrix.

The Mixed Waste Focus Area (MWFA), in conjunction with the National TRU Program Office (NTPO), has initiated several activities as alternatives to these two options. These initiatives include determining "G" values for hydrogen, G(H2), that are more accurately representative of actual TRU waste than the extremely conservative ones used in the SARP.

In addition, investigation is underway into an alternate method for demonstrating compliance with the SARP hydrogen concentration limit. Finally, methods are under development to mitigate hydrogen gas accumulation within waste containers within the TRUPACT-II. We anticipate that this suite of activities constitutes a program (2) that will significantly reduce the rejection of drums at LANL, INEEL, RFETS, and SRS because of their potential to exceed the hydrogen limitation.

This paper will project the potential decay heat increases that the studies in the program may provide. We will discuss the chemical or physical basis for the individual studies and the technical reason for the expected expansion from the study. Lastly, we will provide an estimate of the potential cost savings from these studies.

DISCUSSION

I. Matrix Depletion Experiments

A. Basis

The first experimental study described is on matrix depletion (2). It has three distinct components. In the first, experiments are being conducted on simulated TRU wastes at the Los Alamos National Lab (LANL). In the second component, actual drums of TRU waste are being tested to determine their effective G values. Finally, a theoretical model for the matrix depletion effect is under development from a first principles basis. The matrix depletion program is intended to obtain more realistic values for $G(H_2)$ as well as aged $G(H_2)$ values that reflect the effect of depletion of the waste matrix.

Previous studies (3 - 6) have shown that lower $G(H_2)$ values can be expected from the matrix depletion experiments. Kosiewicz (3) showed approximately a threefold decrease in G(gas) for cellulosics with increasing dose. The basis for this phenomenon is that the chemical composition of a hydrogenous waste matrix in the immediate vicinity of a transuranic radionuclide particle changes with increasing deposited energy (dose). When alpha particles deposit their energy in the waste matrix, radicals form and may recombine in the alpha particle tracks. Some of these recombinations generate gases, e.g., hydrogen. Since alpha particles have high linear energy transfer (LET), their range in the waste matrix is very short, perhaps 50 microns. With increasing dose, the available hydrogen atoms become depleted and later alpha particles quench or deposit their energy in modes that do not generate as much gas. The degree of cross linking in the matrix may increase as well as the number of unsaturated carbon bonds.

B. Current Matrix Depletion Studies

The current matrix depletion studies (2) were initiated in 1996. They include monitoring radiolytically evolved gases from a variety of simulated waste matrices (polyethylene, polyvinyl chloride, cellulosics, and envirostone cement) contaminated with oxides of 238Pu or 239Pu. The materials are contaminated to the same dose rate with the two radioisotopes. Since 238Pu has a specific activity that is nearly 3oo times greater than that of 239Pu, a smaller mass of contaminant is used with the former radioisotope.

Some of the experiments are run at a higher temperature (60^0C) to observe potential temperature effects. Although Kosiewicz (7) observed thermal degradation of some waste materials at temperatures as low as 70^0C, it was not significant relative to the radiolytic degradation at the dose rates used in the experiments (3,5). However, some synergy was previously reported (3) that there was an increase in radiolytic gas evolution at higher experimental temperatures.

Although the potential for redistribution of radionuclides after radiolytic degradation was reported as a potential concern, it has not been observed (3,5,8). The current experiments will also study the effect of shaking on the gas evolution of materials after extended periods of exposure to the plutonium contaminants. This will be done to simulate the potential effects of transportation vibrations on the waste materials.

The gas generation testing done on actual drums of TRU waste (see II. below) will verify and support the matrix depletion studies.

Samples of the degraded materials will be examined by optical microscopy, scanning electron microscopy (SEM), and possibly other surface analysis methods to study the relationship of the radionuclide particle with the waste matrix.

Finally, all of the current activities will be used to calibrate a theoretical, mathematical model of the matrix depletion effect that is under development. The intent of this model is to provide the capability to predict and take credit for matrix depletion in waste matrices without having to do radiolysis experiments on each new waste matrix of interest.

C. Expected Expansion from Matrix Depletion Experiments

The matrix depletion studies are expected to produce $G(H_2)$ values that are more representative of: 1. the materials and conditions that exist for real TRU wastes, and 2. the reduced gas generation potential of aged, depleted waste matrices. In the SARP, very conservative (i.e., large) $G(H_2)$ values were used to calculate the permissible shipping wattages for the TRUPACT-II transporter. The initial G values reported by previous workers (3 - 6) whose experiments used plutonium contaminants are lower by 200 - 400% than those used in the SARP. The current studies are expected to provide data which will support increasing the permissible shipping wattages by as much as 400% on the assignment of G values. In addition, Shalek (9) offered a cogent explanation for his observation of a G value for hydrogen for cement that was about 500% lower than that assigned by the SARP.

Matrix depletion curves previously published (3, 6) suggest that an additional 300% decrease in G value may be obtained for those materials which exhibit a matrix depletion effect. It is not expected that matrix depletion will be observed for cement. Bibler (10) did not observe decreases in gas evolution of cements with increasing gamma doses.

In summary, the combined effect of more representative $G(H_2)$ values and depleted $G(H_2)$ values may support higher wattage loadings for legacy TRU wastes of about an additional order of magnitude, i.e., 1000%, for materials which exhibit a matrix depletion effect.

II. TRUPACT-II Gas Generation Test

A. Basis

A second study is the TRUPACT-II Gas Generation Test Program (GGTP) (2). In the GGTP, the gas composition and gas generation rates from real drums of TRU waste are being measured at the Idaho National Engineering and Environmental Lab (INEEL)(11) and the Rocky Flats Environmental Technology Site (RFETS) (12). This provides the actual rate of hydrogen gas generation from the waste. Drums are qualified for shipment in the TRUPACT-II transporter if the concentration of hydrogen does not exceed 5% in a 60 day period. From these data and the amount of radionuclide in the drums, the effective

$G(H_2)$ values also can be estimated for the individual waste drums. These effective $G(H_2)$ values should support the matrix depletion experiments.

While the plutonium contaminant inside a waste drum may be distributed solely on a non-hydrogenous waste matrix, if the drum contains other waste materials in it, the SARP requires use of the largest $G(H_2)$ value for any waste material that is in the drum. Consequently, there is potential for the SARP to grossly over estimate the hydrogen gas generation rate, while the GGTP will measure the actual rate for individual drums.

In addition, since hydrogen gas may be measured more accurately than assay of the radionuclide mass, the error limits on measurement from gas generation testing will be smaller than that produced by measuring the drum's plutonium content. Consequently, hydrogen gas generation testing can provide for shipment of higher wattage drums because the error limits must be added to the measured plutonium content of a drum when calculating its wattage for comaprison against the SARP tabulations.

B. Current TRUPACT-II Gas Generation Test Studies

At the INEEL, the gas generation tests are conducted in an apparatus that closely resembles that suggested in the SARP. Up to 10 drums are expected to be tested at a time. The drums are configured with instruments and tubing to allow measurement of the rate of gas being generated within the individual drums. The hydrogen concentration in the evolved gas is determined by chemical analysis. With this experimental apparatus, the drums are heated to 60^0C. While the SARP test requires up to 42 days for testing, preliminary tests suggest that the drums stabilize within 2 weeks.

At the RFETS, test drums are placed inside an apparatus that is, in effect, a bell jar. Gas generated within the TRU waste drums diffuses through the lid filter and into the void space between the test drum and the bell jar. The initial gas composition is measured by mass spectometry and again two weeks later. These data are used to calculate the rate of hydrogen gas generation and then the effective $G(H_2)$ value for the waste drum. Preliminary data (12) estimate an average, effective $G(H_2)$ of 0.3. This compares to the SARP $G(H_2)$ value of 3.4. A request for certification from the WIPP will be made for this method of testing at the RFETS. The method will be done under an approved quality assurance project plan (QAPjP).

While the INEEL and RFETS experimental apparatus are somewhat different, the end goals of both studies are to measure actual hydrogen gas generation rates to qualify individual waste containers for transport to WIPP.

C. Expected Expansion from TRUPACT-II Gas Generation Test

It is expected that the GGTP will produce data that could increase the number of shippable drums at least as much as the matrix depletion experiments. However, this could only occur by gas testing each individual drum. This is not considered practical for a site with a large TRU waste inventory because of the time and cost involved in testing. However, for TRU waste drums that cannot be shipped because they: 1. are in the test category, or, 2. exceed the permissible SARP shipping wattages by 10X or less, this is a viable method for qualifying them for shipment in the TRUPACT-II. For sites that only have a small quantity of TRU waste, gas generation may be a very cost effective method for qualifying their TRU waste drums for shipment in the TRUPACT-II. Further, for a waste stream that is very consistent, an argument could be made that a random sampling process of some number of the waste containters could be extrapolated to the entire population. This could decrease the actual number of drums that require testing.

In summary, the expansion envelope from the GGTP could be greater than that from matrix depletion, but would be limited by the throughput capacity and cost of gas testing every TRU waste drum. If the matrix depletion experiments provide a 10X increase in shippable wattages, the benefits of the GGTP are greatly reduced. It would help those waste drums which are borderline shippable because of the uncertainty in measuring the plutonium content as well as those drums in which the plutonium is not actually in contact with higher $G(H_2)$ value waste matrices.

III. Alternate Method of Testing for Hydrogen Generation Rate

A. Basis

A study is being initiated (13) to develop an alternative method of testing for determining compliance with the requirement that 5% hydrogen is not exceeded in a 60 day period in a waste container. In this approach, a single measurement for hydrogen is made of the drum head space of an individual waste container. The number of layers of confinement must be known. In addition, it requires that the hydrogen concentrations across all layers of confinement within the drum be at steady-state, i.e., equilibrium, and that an estimate be made of the rate of loss of hydrogen from the drum. At equilibrium, the flow rates of hydrogen gas across all layers of confinement are the same and equal to the rate of generation of new hydrogen gas. The times required for equilibrium have been modeled for vented drums and are presented as the aspiration times in Appendix 3.6.11 of the SARP. If the drum is sampled after the drum aspiration time has elapsed, the hydrogen concentration in the drum headspace directly provides the rate of generation. If this rate will accumulate less than 5% hydrogen in a 60 day period, the drum is shippable in TRUPACT-II.

B. Current Alternate Method of Testing Studies

This method is currently under development at the INEEL (13). A supporting study on the diffusion of hydrogen through drum lid gaskets is also in progress at that site.

C. Expected Expansion from the Alternative Method of Testing for Gas Generation

If successful, this method would substantially increase the shippable TRU waste inventory over the GGTP since it could be done on all TRU waste drums in the inventory. An additional advantage it has over the GGTP procedure is that it can be done quickly and more cost effectively since it only requires a single measurement of the hydrogen concentration in the drum headspace. In addition, the error in measuring hydrogen is less than the assay error for plutonium. This translates into less restriction on the waste drum when the error limits are added to the measured value. This hydrogen analysis could be done when the headpsace analysis required by the WIPP WAC is performed. The cost savings would exceed that of the GGTP since this procedure would be applicable to a larger segment of the waste inventory and it is less expensive to perform.

IV. Hydrogen Getter Study

A. Basis

Hydrogen getters can potentially be used to eliminate or decrease accummulation of hydrogen gas in TRU waste containers. Getters are organic materials with unsaturated chemical bonds. Hydrogen gas reacts chemically and irreversibly across the unsaturated

bonds until the capacity of the material is exceeded. Getters have been successfully used in weapons applications for more than a decade. One getter material used is 1,4-bis(phenylethynyl)benzene (DEB).

To provide maximum utility for high Curie content TRU waste drums, the layers of confinement need to be pierced and a getter package placed within the drum. A getter package could also be placed within the inner containment vessel (ICV) of the TRUPACT-II to increase the permissible shipping wattages. However, if the getter is placed in the ICV of the TRUPACT-II transporter, its maximum increase in shippable wattages is limited to about 100%.

B. Current Hydrogen Getter Study

In mid-FY97, experiments were initiated at LANL (14) to study the use of hydrogen getters, and possibly recombiners, as a method for mitigating radiolytically-generated hydrogen. The primary focus of the current study is to assess the potential for gaseous components (e.g., volatile organic compounds (VOCs), hydrochloric acid, etc.) expected to be found in TRU waste to poison a specific getter material (DEB). Should the compounds decrease the effectiveness of the getter material, investigation will proceed on the use of foils and membranes that pass only hydrogen gas. These would potentially be used as encapsulants to protect the DEB getter material.

C. Expected Expansion in Shipping Wattages from the Use of Getters

This study has the potential for the greatest increase in the permissible decay heat limits, especially for waste containers with no internal layers of packaging. Getters could be the most cost effective approach to making high Curie content TRU wastes shippable in TRUPACT-II. It is estimated that approximately 1 Kg of DEB is required to react the hydrogen generated during a 60 day period from a drum of TRU waste containing 40 g of heat source grade 238Pu. The current cost of that quantity of DEB is estimated at $2 - 3K. This could decrease if the DEB were produced in quantity.

Potential Cost Savings from Increased Shipping Wattages

I. Matrix Depletion

For the matrix depletion sudies, the potential cost savings from a 1000% increase in shipping wattages can be estimated for the legacy TRU waste inventory at LANL. The inventory at this site has undergone thorough evaluation (15) relative to the SARP thermal power restrictions. With an increase of 1000% in shipping wattages, an additional 6,300 drums of LANL TRU waste would be shippable. This represents an increase from 61% to 88% of the LANL inventory. Assuming that the 6,300 drums of waste would have had to be volume expanded to create a maximum of an additional 28,000 drums, a potential savings of roughly $100M would be incurred at this one DOE site. This assumes that the cost of certifying the volume expanded drums would be $4K per drum. In actuality, not all the wastes in this examined inventory will obtain a 1000% increase in shippable watage because some of them are cement which should not exhibit matrix depletion.

It is expected that a 1000% increase in shipping wattages would make most 239Pu contaminated waste in the DOE inventory shippable or, at worst, require only repackaging without volume expansion. High Curie content 239Pu contaminated wastes with many layers of confinement and very high Curie content 238Pu contaminated wastes would still exceed the permissible shipping wattages even with the 1000% increase in relief.

II. Gas Generation Testing - TRUPACT-II SARP Test

Assuming the throughput of an RFETS gas testing experimental arrangement is seven drums every two weeks with a duty time of 46 work weeks, about 160 drums per year could be tested. If each of these drums exceeded the permissible shipping wattages by 15X, about 2,400 volume expanded drums could be avoided at an estimated savings of about $10M. With the INEEL gas testing apparatus arrangement, about 220 drums per year could be tested. Cost savings from this apparatus could be estimated at $14M as was done done for the RFETS apparatus.

III. Gas Generation Testing - Alternate Method of Testing

The potential savings from the successful application of the Alternate Method of Testing for radiolytically generated hydrogen exceeds that from either matrix depletion or the TRUPACT-II SARP test methods. Even with a successful 1000% lowering of the G values from matrix depletion, high levels of conservatism are used to calculate the amount of hydrogen that could be produced within a waste package. This overstates the hydrogen concentration in the TRU waste inventory. The TRUPACT-II SARP gas generation test method requires two or more weeks to perform, and at present, can only qualify individual waste packages for shipment. Consequently, only a portion of a large site's inventory can be tested in this latter manner. The alternate method of testing could be applied to every drum of TRU waste when the mandatory headspace gas testing is done. Since it measures the actual hydrogen concentration in a drum, only the minimum amount of required safety conservatism is applied. In addition, this last test method is fairly inexpensive. Therefore, it is probably safe to assume that LANL alone would save in excess of $100M through application of the alternate method of testing (assuming no relief from matrix depletion).

IV. Hydrogen Gas Getters

To achieve maxaimal savings from application of hydrogen gas getters, the layers of waste confinement must be eliminated and the getter placed in direct communication with the hydrogen evolving source. This could require repackaging of legacy (i.e., already existing TRU wastes) or timing the placement of the getter into a newly generated waste package.

The only other viable alternative to the use of hydrogen gas getters for the high Curie 238Pu-contaminated waste is to perform waste form modification to destroy the hydrogenous matrix. The SRS estimated that a facility to process their 238Pu wastes would cost about $750M. If 30,000 drums in the SRS TRU waste inventory were processed, the unit cost would be $25K / drum. This compares to the maximum of $2 - 3K per drum estimated for the use of getters. Consequently, at the SRS alone, a potential savings exceeding $600M is estimated.

Conclusions

It is fully anticipated that this suite of studies, individually or in aggregate, will support substantially increasing the shippable wattages of the DOE TRU waste inventory. At the LANL alone, the matrix depletion component of this experimental program has the potential for saving an estimated $100M by eliminating volume expansion of drums which exceed the permissible decay heat limits. At the SRS, successful application of getters to react hydrogen could save about $600M through the avoidance of an expensive facility that would be built to process 238Pu contaminated wastes.

Even though these studies will provide technical support for increasing the shipping wattages for TRU wastes, such an increase must be petitioned for and received from the

NRC. The rigor of quality assurance in these experiments will support the petition to the NRC.

References:

1. TRUPACT II Safety Analysis Report for the TRUPACT-II Shipping Package (SARP) (NRC Docket No. 9218 1994).

2. Connolly, M.J., Djordjevic, S.M., Banjac, V. and Loehr, C.A., "TRUPACT II Matrix Depletion Program Test Plan," INEL-95/0360, Lockheed-Martin Techncologies Company, Idaho Falls, ID (1995).

3. Kosiewicz, S.T., "Gas Generation from Organic Transuranic Wastes. I. Alpha Radiolysis at Atmospheric Pressure," Nuclear Technology V.54, pp. 92 - 99 (July 1981).

4. Kosiewicz, S.T., "Gas Generation from the Alpha Radiolysis of Bitumen," Nuclear and Chemical Waste Management V.1, pp. 139 -141 (1980).

5. A. Zerwekh, "Gas Generation from Radiolytic Attack of TRU-Contaminated Hydrogenous Waste," Los Alamos Scientific Laboratory report LA-7674-MS, Los Alamos, NM 87545 (1979).

6. Marshall, R.S., Callis, E.L., Cappis, J.H., Espinoza, J.M., Foltyn, E.M., and Reich, B.T., "Determining Site-Specific Drum Loading Criteria for Storing Combustible 238Pu Waste, Los Alamos National Laboratory unclassified release LA-UR-94-409 submitted for presentation at WM'94 Conference, Tucson AZ (1994).

7. Kosiewicz, S.T., "Cellulose Thermally Decomposes at 70^{0}C," Thermochimica Acta, pp. 319 - 326 (1980).

8. Zerwekh, A., Warren, J., and Kosiewicz, S., " The Effect of Vibration on Alpha Radiolysis of Transuranic (TRU) Waste," Proceedings of WM'93, pp. 927 - 929, Tucson, AZ (1993).

9. Internal Los Alamos National Laboratory memorandum NMT-2-PROC-92-140, P. Shalek, "Meeting TRUPACT-II Wattage Requirements for Shipping Cemented TRU Wastes to WIPP," Dec. 22, 1992.

10. Bibler, N., Savannah River National Laboratory, personal communication with S. Kosiewicz (Feb. 1997).

11. Edinborough, C.R., Idaho National Engineering and Environmental Lab report INEL-94/0109, INEEL TRU Waste Program, "Quality Assurance Project Plan for the Gas Generation Testing Program at the INEEL," (Sept. 1996).

12. Schierloh, J. B., "Gas Generation Testing - Interim Technical Report for FY96," Rocky Environmental Technology Site report RS-090-026, Safe Sites, RFETS, Golden, CO (Oct. 1996).

13. Idaho National Engineering and Environmental Lab White paper, "Certifying Containers for TRUPACT-II Shipment Using Flammable Gas Headspace Measurement: A White Paper," INEEL, TRU Waste Programs, Idaho Falls, ID, 83415 (July 9, 1996).

14. Mroz, E.J., Liebman, C.P., and Kosiewicz, S.T., "Increasing TRUPACT-II Wattage Limits: Two Technical Approaches," Proceedings of WM'97 Conference, Tucson, AZ (March 1997).

15. Kosiewicz, S.T., Triay, I.R., Rogers, P.S.Z., and Christensen, D.V., "Los Alamos National Laboratory Accelerated Transuranic Waste Workoff Strategies," Proceedings of WM'97 Conference, Tucson, AZ (March 1997).