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THE TRUPACT-II MATRIX DEPLETION PROGRAM

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ABSTRACT

Contact-handled transuranic (CH-TRU) wastes will be shipped and disposed at the Waste Isolation Pilot Plant (WIPP) repository in the Transuranic Package Transporter-II (TRUPACT-II) shipping package. A primary transportation requirement for the TRUPACT-II is that the concentration of potentially flammable gases (i.e., hydrogen and methane) must not exceed 5 percent by volume in the package or the payload during a 60-day shipping period. Decomposition of waste materials by radiation, or radiolysis, is the predominant mechanism of gas generation during transport. The gas generation potential of a target waste material is characterized by a G-value, which is the number of molecules of gas generated per 100 eV of ionizing radiation absorbed by the target material.

To demonstrate compliance with the flammable gas concentration requirement, theoretical worst-case calculations were performed to establish allowable wattage (decay heat) limits for waste containers. The calculations were based on the G-value for the waste material with the highest potential for flammable gas generation. The calculations also made no allowances for decreases of the G-value over time due to matrix depletion phenomena that have been observed by many experimenters. Matrix depletion occurs over time when an alpha-generating source particle alters the target material (by evaporation, reaction, or decomposition) into a material of lower gas generating potential. The net effect of these alterations is represented by the "effective G-value".

Based on existing allowable wattage limits, it is estimated that a large portion (approximately 34 percent) of the CH-TRU waste cannot be shipped. The TRUPACT-II Matrix Depletion Program (MDP) has been established with the objective to investigate the phenomena of matrix depletion to support more realistic, age-dependent effective G-values. The MDP is a cooperative effort involving the U.S. Department of Energy Carlsbad Area Office National TRU Program, the Idaho National Engineering Laboratory, the Los Alamos National Laboratory, and the Rocky Flats Environmental Technology Site. The MDP is comprised of experiments designed to examine the behavior of effective G-values over time for different waste materials and the effects of isotope, agitation, and heating. The experimental data will be evaluated in conjunction with waste container headspace gas sampling and theoretical and predictive modeling to formulate bounding effective G-values for each simulated waste material and time segment. This paper describes the objectives, scope, components and preliminary results of the MDP that are expected to provide the justification for greater wattage limits for CH-TRU waste containers. The increased wattage will ultimately allow shipment of a much greater portion of CH-TRU waste.

BACKGROUND

The inventory of contact-handled transuranic (CH-TRU) waste, currently in retrievable storage at U.S. Department of Energy (DOE) sites, is planned for shipment to, and disposal at, the Waste Isolation Pilot Plant (WIPP). The Transuranic Package Transporter-II (TRUPACT-II) is a reusable shipping package designed for the transportation of CH-TRU waste containers to WIPP. Waste containers are 55-gallon drums, standard waste boxes, and ten-drum overpacks.

The TRUPACT-II was designed in accordance with the requirements for Type B packaging found in Title 10, Code of Federal Regulations Part 71 (10 CFR 71). Upon completion of the design and the required testing, the TRUPACT-II Safety Analysis Report for Packaging (SARP) was submitted to the U.S. Nuclear Regulatory Commission (NRC) in 1989 . Based on the analyses presented in the SARP, the NRC issued Certificate of Compliance No. 9218 for the package in August of 1989 (NRC Docket No. 9218, 1994).

A major transportation requirement for the TRUPACT-II is that the concentration of potentially flammable gases must not exceed 5 percent (by volume) in the package or the payload during a 60-day shipping period after the TRUPACT-II is sealed. Decomposition of materials caused by radiation, or radiolysis, is the predominant mechanism of gas generation during transport.

CH-TRU waste is classified into four major types (I, II, III, and IV) based on chemical and physical characteristics and further subdivided into waste material types (I.1, I.2, I.3, II.1, II.2, and III.1) based on bounding flammable gas generation potential as shown in Tables 1-1 and 1-2 (NRC Docket No. 9218). The gas generation potential of a target material is characterized by its G-value, which is the number of molecular or ionic products (usually gaseous products) generated or consumed per 100 eV of ionizing radiation absorbed by the target material. Each CH-TRU waste container is assigned a TRUPACT-II shipping category, which is based on a combination of waste material type and the packaging (number and type of plastic layers of confinement) of the waste materials within the waste container. To demonstrate compliance with the flammable gas requirement, theoretical worst-case calculations were performed using G-values to establish allowable wattage (decay heat) limits for each TRUPACT-II shipping category.

The maximum allowable wattage limits for each shipping category and for the TRUPACT-II were based on the initial G-values observed during experiments on the irradiation of materials found in TRU waste. The wattage limit calculations assumed a constant G-value from the time the waste was packaged until emplacement at the WIPP facility. The calculations made no allowance for decreases of the G-value over time, a phenomenon observed by many experimenters (Kazanjian 1976, Kosiewicz 1981, Zerwekh 1979, Zerwekh and Warren 1986, Zerwekh et al. 1993, Smith et al. 1994, and Marshall et al. 1994). Because the majority of CH-TRU waste retrievably stored at DOE sites is 5 to 22 years old, wattage limits based on initial G-values are extremely conservative.

Taking into account the existing TRUPACT-II wattage limits, it is currently estimated that a large portion of the CH-TRU waste container inventory cannot be shipped. A joint effort was conducted at the Idaho National Engineering Laboratory (INEL), Los Alamos National Laboratory (LANL), and Rocky Flats Environmental Technology Site (RFETS) to determine the impact of existing wattage limits on the shippability of CH-TRU waste stored at those sites. Of the total volume certifiable CH-TRU waste (i.e., waste that meets the requirements of the *Waste Acceptance Criteria for the Waste Isolation Pilot Plant* [DOE 1991]), it was determined that approximately 34 percent of the waste would not be shippable based on its failure to meet the TRUPACT-II wattage limits. Although the effort was performed at the three named sites, the results are applicable to all DOE sites that plan to ship CH-TRU waste to WIPP. The TRUPACT-II SARP contains a Gas Generation Test Plan; however, implementing the plan for 34% of the CH-TRU waste would be prohibitively expensive and time consuming.

All TRU waste will ultimately have to be transported to the WIPP; therefore, a method to provide for its acceptance for shipment in the TRUPACT-II is needed. The solution may lie in determining effective G-values as a function of time and thus more realistic TRUPACT-II wattage limits, primarily by accounting for age-dependence of the waste. A cost-effective method for arriving at age-dependent G-values and revised TRUPACT-II wattage limits is matrix depletion testing.

Matrix depletion occurs over time when an alpha-generating source particle alters the target material (by evaporation, reaction, or decomposition) into a material of lower gas generation potential. The matrix depletion process decreases gas generation by reducing the availability of the target material, thereby resulting in a decrease in the G-value with time. The fraction of energy emitted that is absorbed by the target material varies with time and is related to the short mean free path of alpha particles. When the alpha-generating source is dispersed in or on the target material in a particulate form, it will affect only that target material in a small semi-spherical area around each source particle. Additionally, some energy will be lost in the source particle itself and in surrounding nonhydrogenous material, such as air, that is not available for the liberation of hydrogen. The net effect of these reactions is represented by the "effective G-value."

Two observations of CH-TRU waste over time support the concept of matrix depletion: (1) a consistent decrease in the effective G-value, and (2) darkening of plastic surfaces (i.e., charring of the waste matrix). The effective G-value has been found to decrease exponentially with time. In fact, within 2 years the effective G-value for Pu-238 contaminated materials was found to approach an asymptotic value several times lower than the initial effective G-value. Based on the available experimental and empirical results, matrix depletion acts to decrease the rate of flammable gas (specifically hydrogen and potentially methane) generation inside CH-TRU waste containers.

OBJECTIVES AND COMPONENTS

The Matrix Depletion Program (MDP) was established with the objective to investigate the phenomenon of matrix depletion and to arrive at age-dependent bounding effective G-values. The activities under the MDP include matrix depletion experiments, headspace gas sampling and analysis, data management and analysis, and documentation. In order to specify the quality of data from the data collection activities under the MDP, a formal procedure based on U.S. Environmental Protection Agency (EPA) guidance was used in formulating data quality objectives (DQOs). The DOE Carlsbad Area Office (CAO) is responsible for the overall management of the MDP. CAO is also responsible for performing audits of MDP activities at INEL.

In the past, LANL has conducted a number of investigations of gas generation in CH-TRU waste to support the WIPP (Zerwekh 1979, Kosiewicz 1981, Zerwekh and Warren 1986, Zerwekh et al 1994). Recently, a limited number of experiments were conducted to determine the matrix depletion effects of Pu-238 on cellulose and polyethylene (Marshall 1994 and Smith et al. 1994). Because of this experience and the availability of the necessary equipment, LANL will be responsible for conducting the matrix depletion experiments. The experiments were designed to quantify the matrix depletion phenomenon using a variety of simulated TRU waste matrix materials (i.e., polyethylene [PE], dry cellulose, wet cellulose, polyvinyl chloride [PVC]), and solidified aqueous or homogeneous inorganic solids that contain water (i.e., cemented waste forms). The total duration of the MDP will be 2 years, with cylinder sampling occurring every 2 weeks. The sampling frequency was determined by the requirement for an adequate number of samples, so as to ensure accurate statistical analysis. Based on mechanistic arguments, the effective G-values for drums older than 2 years will be similar, but lower than those at 2 years; therefore, the value for 2 years will be conservative for older drums. The experiments will also quantify the effects of agitation and heating. Agitation levels to be used in the study are those that simulate transportation and handling events. The heating temperature is based on the highest values used in SARP analyses (140 °F ± 5 °F). Two isotopic sources of plutonium, a blend predominantly Pu-238 and a second blend predominantly Pu-239, will be used in the experiments because Pu-238 has higher decay heat production that causes many drums in the TRU waste inventory to exceed the established wattage limits and Pu-239 is the primary isotope present in TRU waste. The experiments will comprise 60 test cylinders split up into four groups: normal, heated, agitated, and heated/agitated. These groups are designed to simulate the range of conditions encountered during TRU waste transportation and handling operations. Effective G-values will be calculated for each test cylinder from the raw data derived from the experiments. The effect of each isotope, agitation, and heating will then be evaluated to formulate bounding effective G-values for each simulated waste material and time segment (Connolly et al, 1995a).

Headspace samples will be collected and analyzed from a representative subpopulation of existing TRU waste containers at ambient temperatures. Samples will be taken from both drum and inner confinement layer. These activities are being performed by the INEL and the RFETS under the WIPP Transuranic Waste Characterization Program (TWCP). Headspace sampling includes the drum headspace and the headspace of inner layers of confinement. In the TWCP, headspace gases of all CH-TRU waste drums will be sampled and certain drums will undergo innermost layers of confinement sampling. QA requirements specific to the MDP are described in the MDP QAPP, which is consistent with the TWCP requirements (Connolly et al, 1995b). Headspace gases will be analyzed for hydrogen and methane. The TWCP and MDP are coordinating efforts to make a variety of waste types and drum ages available to the MDP. A total of 740 drums will be examined prior to the completion of the matrix depletion experiments. Headspace gas sampling and analysis will be accomplished in accordance with the TWCP.

Drum headspace gas samples will be collected and analyzed from a limited number of existing TRU waste containers at elevated temperatures. This effort is being performed at the INEL under the TRUPACT-II Gas Generation Test Program (GGTP). The GGTP consists of controlled tests with actual containers of CH-TRU waste to determine gas generation rates under simulated transportation conditions. CH-TRU waste drums of waste types I, II, or III will be selected for testing if the decay heat loading of the container exceeds the TRUPACT-II wattage limit for the shipping category of the container. The drum must also meet other requirements before being tested, including having a fissile gram equivalents (FGE) less than 200 grams, weights less than 1,000 pounds, surface dose rates less than 200 mrem.

Data management and analysis involves several key elements. First, data obtained in each portion of the MDP must be validated to ensure that quality assurance requirements have been met and that the data are suitable for use in the MDP. Second, individual effective G-values must be calculated from raw data collected in the matrix depletion experiments. Third, the individual effective G-values must be summarized appropriately to formulate the bounding effective G-values. Fourth, the experimentally derived bounding effective G-values and drum headspace flammable gas (i.e., hydrogen and methane) concentrations predicted from the bounding values must be calculated and compared with respective actual waste drum values.

As noted above, data collected in matrix depletion experiments will be reduced to formulate bounding effective G-values. This first step involves calculating effective G-values for each sampling time and test cylinder. Second, individual effective G-values will be analyzed and used to formulate bounding values for each simulated waste material and time segment of interest; these values will be 95% upper confidence levels based on matrix depletion experimental effective G-values. A set of bounding effective G-values will be determined for PE, wet cellulose, dry cellulose, and cement for time segments of interest.

Existing mathematical models for predicting gas concentrations in waste containers will be finalized. The models are based on the aspiration model described in the TRUPACT-II SARP and simulate the time-dependent generation of flammable gas within the innermost confinement layer and subsequent time-dependent transport across the various confinement layers of TRU waste containers. The models will then be applied using the bounding effective G-values determined from the matrix depletion experiments to predict flammable gas concentrations within actual TRU waste containers up to the age of the container when sampled. A theoretical model that simulates matrix depletion effects in an idealized geometry will also be developed to further illustrate the phenomenon. Development of the models will be led by INEL. However, it is anticipated that the model development will be completed with a high degree of collaboration drawing on the expertise from the INEL, the LANL and the RFETS.

There will be two types of comparisons made using the bounding effective G-values derived from matrix depletion experiments. The first will compare the bounding values with the GGTP results and the second will compare hydrogen and methane concentrations predicted from the bounding values with hydrogen and methane concentrations measured in the TWCP.

Statistical comparisons will be made of bounding effective G-values derived from the matrix depletion experiments with the measurements from actual TRU waste drums (i.e., TWCP and GGTP) in order to show that the effective G-values from the matrix depletion experiments are in fact bounding. Because of the simulated waste materials used in the MDP, it is expected that headspace flammable gas concentrations predicted from the MDP bounding effective G-values will be greater than measured drum headspace flammable gas concentration at ambient temperatures. It is also expected that the bounding effective G-values measured in the MDP will be greater than the effective G-values calculated from sampling TRU waste containers at elevated temperatures.

In both cases, MDP effective G-values are expected to be greater due to the nature of the target material and the geometry of the cylinder contents. While other non hydrogen-generating materials are present in actual CH-TRU waste, these are not included in the MDP. In addition, the target material will be directly sprinkled with plutonium, allowing it to be embedded in the target. In actual CH-TRU waste, the plutonium is dispersed and not always in such direct contact with hydrogen-generating materials.

Assuming the data justifies an application for higher TRUPACT-II wattage limits, the documentation to support an application to the NRC will be prepared and submitted to the CAO and National TRU Program.

PRELIMINARY RESULTS AND CONCLUSIONS

[Note to Reviewer: Preliminary results will be included in the final version of the paper.]

Quantification of the time-dependent behavior of the effective G-values (i.e., flammable gas generation rates within waste containers) is expected to support justifications for greater wattage limits for CH-TRU waste. The increased wattage limits will allow for shipment of a much greater portion of certifiable TRU waste without increased risk.

REFERENCES

10 CFR Part 71. September 1994. "Packaging and Transportation of Radioactive Material." *Code of Federal Regulations*, Washington, D.C., Office of the Federal Register National Archives and Records Administration.

Connolly, M.J., S.M. Djordjevic, V. Banjac, and C.A. Loehr. 1995a. *TRUPACT-II Matrix Depletion Program Test Program,* INEL-95/0360. Idaho Falls, Idaho, Idaho National Engineering Laboratory.

Connolly, M.J., G.R. Hayes, T.J. Krause, and J.S. Burt. 1995b. *TRUPACT-II Matrix Depletion Quality Assurance Program Plan*, INEL-95/0361. Idaho Falls, Idaho, Idaho National Engineering Laboratory.

DOE. 1991. *Waste Acceptance Criteria for the Waste Isolation Pilot Plant*. WIPP-DOE-068, Revision 4. Carlsbad, New Mexico, Waste Isolation Pilot Plant, U.S. Department of Energy.

DOE. 1995a. *Transuranic Waste Characterization Quality Assurance Program Plan, Revision 0.* CAO-94-1010, Carlsbad, New Mexico, U.S. Department of Energy.

Kazanjian, A.R. 1976. *Radiolytic Gas Generation in Plutonium Contaminated Waste Materials.* RFP-2469, Golden, Colorado, Rocky Flats Plant, Rockwell International.

Kosiewicz, S. T. 1981. "Gas Generation from Organic Transuranic Wastes. I. Alpha Radiolysis at Atmospheric Pressure." *Nuclear Technology* 54: pp. 92-99.

Marshall et al. 1994. *Determining Site-Specific Drum Loading Criteria for Storing Combustible 238Pu Waste*. LA-UR-94-409, Los Alamos, New Mexico, Los Alamos National Laboratory.

NRC Docket No. 9218. 1994. *Safety Analysis Report for the TRUPACT-II Shipping Package*. Revision 14, NRC Docket No. 9218, U.S. Nuclear Regulatory Commission, Washington, D.C.

Smith, M.C., R. Marshall, E.L. Callis, J.H. Cappis, J.M. Espinoza, and E.M. Foltyn. 1994. *Hydrogen Generation and Release in Stored 238Pu Waste at Los Alamos National Laboratory*. In preparation.

Zerwekh, A. 1979. *Gas Generation from Radiolytic Attack of TRU-Contaminated Hydrogenous Waste*. LA-7674-MS, Los Alamos, New Mexico, Los Alamos National Laboratory.

Zerwekh, A. and J. L. Warren 1986. *Gas Generation and Migration Studies Involving Recently Generated Pu-238-Contaminated Waste for the TRU Waste Sampling Program*. LA-10732-MS, Los Alamos, New Mexico, Los Alamos National Laboratory.

Zerwekh, A., J. Warren, and S.T. Kosiewicz. 1993. "The Effect of Vibration on Alpha Radiolysis of Transuranic (TRU) Waste." *Waste Management '93*, Tucson, Arizona, Waste Management Symposia, Inc.