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TITLE: DETERMINING SITE-SPECIFIC DRUM LOADING CRITERIA FOR STORING COMBUSTIBLE ^{238}Pu WASTE

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DETERMINING SITE-SPECIFIC DRUM LOADING CRITERIA FOR STORING COMBUSTIBLE ^{238}Pu WASTE, R.S. Marshall, E.L. Callis, J.H. Cappis, J.M. Espinoza, E.M. Foltyn, and B.T. Reich (Los Alamos National Laboratory, Los Alamos, NM, and M.C. Smith (Benchmark Environmental Corp., 4501 Indian School Rd, Suite 105, Albuquerque, NM)

ABSTRACT

Waste containing hydrogenous-combustible material contaminated with ^{238}Pu can generate hydrogen gas at appreciable rates through alpha radiolysis. To ensure safe transportation of WIPP drums, the limit for ^{238}Pu-combustible waste published in the WIPP TRUPACT-II CONTENT (TRUCON) CODES is 21 milliwatts per 55 gallon drum. This corresponds to about 45 milligrams of $^{238}PuO_2$ used for satellite heat source-electrical generators. The Los Alamos waste storage site adopted a ^{238}Pu waste storage criteria based on these TRCUCON codes. However, reviews of the content in drums of combustible waste generated during heat source assembly at Los Alamos showed the amount of ^{238}Pu is typically much greater than 45 milligrams. It is not feasible to appreciably reduce Los Alamos ^{238}Pu waste drum loadings without significantly increasing waste volumes or introducing unsafe practices.

To address this concern, a series of studies were implemented to evaluate the applicability of the TRUCON limits for storage of this specific waste. Addressed in these evaluations were determination of the hydrogen generation rate (G_{eff}-H_2), hydrogen diffusion rates through confinement layers and vent filters, and packaging requirements specific to Los Alamos generated ^{238}Pu contaminated combustible waste. These evaluations generated G_{eff}-H_2 values and filter vent diffusion rates are very different than those used for the TRUCON limits. These studies also showed that the multiple-layer packaging practices in use at Los Alamos could be relaxed without significantly increasing the risk of contamination.

Based on a model developed to predict H_2 concentrations in packages and drum headspace, the site specific effective G_{eff}-H_2 and hydrogen-diffusion values, and revising the waste packaging practices, we were able to raise the safe loading limit for ^{238}Pu waste drums for on site storage to the gram levels typical of currently generated ^{238}Pu waste.

INTRODUCTION

United States space probes use ^{238}Pu heat sources in thermoelectric generators. The ^{238}Pu heat sources are fabricated at the Los Alamos National Laboratory from $^{238}PuO_2$ powder. Wastes generated during fabrication are placed in steel cans, removed from gloveboxes via PVC bag-out bags, and placed in steel, 55 gallon drums for storage. These drums typically contain tenths-of-a-gram to a few grams of ^{238}Pu. The drums are transferred to a Los Alamos storage site for above-ground storage.

Waste containing hydrogenous materials contaminated with ^{238}Pu typically generate hydrogen gas through alpha radiolysis. The safe transportation and storage of this waste must address the fire and explosion hazards posed by hydrogen-air mixtures. The Los Alamos waste storage site established a ^{238}Pu waste storage criteria based on the WIPP TRUPAC-II CONTENT (TRUCON) CODES . For ^{238}Pu combustible waste, the TRUCON code 55-gallon drum limit is 21 milliwatts (or about 45 mg of ^{238}Pu used for heat source fabrication). Fabrication of the heat sources in glove boxes typically generates waste during normal clean up and handling that greatly exceeds this limit. It is not feasible to significantly lower current loading levels without significantly increasing waste volumes or increasing risk of contamination release.

To resolve this problem, a task team was formed of persons representing the waste generator, waste management and the analytical laboratory. After review of studies used as the basis for the TRUCON codes, the team decided the materials, assumptions and conditions of these studies did not adequately represent the Los Alamos ^{238}Pu combustible waste. The team concluded that experiments with actual ^{238}Pu combustible waste were needed to establish site-specific hydrogen generation and diffusion rates.

EXPERIMENTS AND TESTS.

Hydrogen Generation.

The alpha radiolysis generation rate for hydrogen is calculated from $G\text{-}H_2$ ie. the number of hydrogen molecules produced from 100 eV of alpha decay energy. Studies by Kosiewicz and Zerwekh[1] show that of the waste materials commonly generated at Los Alamos, cellulose and polyethylene

had high G-H_2 values. Literature values for G-H_2 for these materials vary from 0.75 to 5.5. The TRUCON code G-H_2 for ^{238}Pu combustible waste is 3.4. The Team recognized that an important variable affecting G-H_2 measurements was the coupling or contact between the ^{238}Pu source and the matrix material. To properly relate this variable to the Los Alamos waste, G-H_2 needed to be measured using actual waste or with synthetic waste very closely matching actual waste.

Three experiments were performed to determine G-H_2 using both cellulose and polyethylene matrices. To distinguish G-H_2 values determined in these specific experiments from theoretical G-H_2 values wherein the total emitted alpha energy is deposited in the matrix material, a term G-effective (G_{eff}) is used. Each experiment was conducted by inserting a ^{238}Pu contaminated waste matrix inside a 2.1 liter stainless steel test chamber equipped with a gas sampling port and a Baritron pressure transducer. At approximately 30 day intervals, 5 milliliter gas sample were withdrawn and analyzed with a Finnigan-MAT model 271 mass spectrometer.

Heat source fabrication personnel prepared the test chambers as follows: For each of three test chambers approximately 20 milligrams of $^{238}PuO_2$ powder was distributed on cotton cheesecloth and paper (the combination referred to as a cellulosics matrix). The PuO_2 used for all the experiments was a fine powder with a volumetric mean diameter of 3.61 microns. The diameter of the largest fraction of particles (31%) occurred in the range of 1-2 microns. After addition of the PuO_2, the cheesecloth was loosely wrapped in the paper and sealed in a test chamber.

Three similar test chambers were prepared using polyethylene as the matrix. In one chamber, approximately 20 milligrams of $^{238}PuO_2$ powder was placed inside a polyethylene bottle and distributed on the inner walls by rolling the bottle. A hole in the bottle cap allowed the gaseous radiolysis products to vent into the test chamber. For the 2nd and 3rd polyethylene tests, the $^{238}PuO_2$ powder was distributed over the surface of strips of 8 mil polyethylene bags which were rolled up and placed inside test chambers.

Figure 1 shows the observed test chamber gas composition history for a cellulose matrix. Note the expected increase of H2 and CO_2 with time

along with a concomitant decrease of O_2 to zero in about 200 days. The gas concentrations are shown as ratios relative to N_2. The N2 component in the test chambers remains effectively constant throughout the tests. Recognize that the test chambers were sealed; the gas composition in a vented drum will be influenced by the back diffusion of air into the drum and the diffusion of headspace gases out of the drum.

Place Fig. 1 here

Figure 2 shows the sequential G_{eff}-H_2 values calculated from the observed H_2 generation rates in the cellulosics matrix tests. The sequential G_{eff} is the G for the individual periods between the taking of samples. Note that the G_{eff}-H_2 for all three tests start between 0.83 and 1.17, then decreases steadily, approaching an equilibrium value between 0.2 and 0.4 after about six months. The decrease in H_2 generation rate with time has been previously reported by Zerwekh[2].

Place Fig. 2 here

Figure 3 shows the gas composition history for a test chamber with a polyethylene matrix. Notice that when the test chamber O_2 is depleted CO_2 generation ceases. The test chambers containing the polyethylene bottle and the second polyethylene bags demonstrated essentially the same gas generation and depletion patterns, however the rates of generation and depletion are much different between the three chambers. The differences seen with the bottle used in the first test and the polyethylene strips in tests two and three are probably the effect of the ^{238}Pu coupling with the matrix. The discrepancy between the two polyethylene strips has not been explained.

Place Fig. 3 here

Figure 4 shows the sequential G_{eff}-H_2values for the polyethylene matrix tests. Initial G_{eff} values varied from 0.77 to 1.55 and leveled at <0.1-0.45 after about 6 months.

Place Fig. 4 here

Note that the G_{eff}-H_2 values for both cellulosics and polyethylene are

much smaller than the 3.4 TRUCON code value for ^{238}Pu combustible waste.

Diffusion Measurements.

Two types of carbon filters, NucFil 13 and NucFil 30, manufactured by the Nuclear Filter Technology Co. of Denver Colorado, were tested. The NucFil 13 filter was mounted in a threaded steel housing designed to screw into 55 gallon drum lids. The NucFil 30 filter was mounted in a two-part plastic housing designed to snap together through a plastic bag. Diffusion coefficients for each filter type were measured by sealing a filter to the lid of a vacuum chamber identical to those used for the test chambers. The chambers were filled to 1 atmosphere pressure with a 6%H_2-argon mixture. The rate of H_2 loss was measured by withdrawing 5 ml samples at regular intervals and measuring the gas sample constituents with a Finnigan-MAT model 271 mass spectrometer. Four tests performed on NucFil 13 filters showed a mean diffusion coefficient of 8.5E-6 mole/sec/mole fraction, with a relative standard deviation of 3.2% and a range of 7.2%. This diffusion coefficient is approximately three times greater than that reported in the TRUPACT-II SARP (NuPac 1992) for the same filter type. Twelve tests were performed on NucFil 30 filters. The mean diffusion coefficient was 1.12E-5 mole/sec/mole fraction with a relative standard deviation of 3.4% and range of 14%. There are no previously performed studies on the NuFil 30 filter in the literature for comparison.

Hydrogen diffusion tests were also performed on 12 mil PVC bag-out bag ends. The ends were either heat sealed by the manufacturer or "*horse-tail*" sealed by Los Alamos technicians. The open end of the bag was stretched over, and sealed, to an aluminum disk. The disk had valving for introducing H_2-argon gas and removing samples. As with the filters, a 6% H_2-argon gas mixture was added to 1 atmosphere pressure and 5 ml gas samples removed at intervals for analysis in a mass spectrometer. Two tests have been performed on factory heat-sealed bag ends. The area of the bag end was about 2800 square centimeters. The average diffusion coefficient of the bags was 2.8E-7 moles/sec/mole fraction, which is approximately one half of the value reported in the TRUPAC-II SARP (NuPac 1992) for similar bags. Five tests were performed with bag ends sealed with "*horsetails*". The seals were prepared by three different technicians. A mean diffusion coefficient of 3.6E-7 moles/sec/mole fraction with a one standard deviation of 51% and range of 127% was obtained. These values are on the order of one-half the value reported in

the TRUPAC-II SARP (NuPac 1992).

GAS GENERATION AND DIFFUSION MODEL.

At the request of Los Alamos, Benchmark Environmental Corp. developed a computational model which is capable of predicting the equilibrium hydrogen concentration within waste packages and drums. Because TRU waste is packaged at Los Alamos with multiple confinement layers, the model was designed to predict H_2 concentration within each packaging layer within a waste drum. The model determines the concentration in each confinement layer by first calculating the H_2 generation for each package within the container, using the G_{eff}-H_2 value and ^{238}Pu content. Fick' first law of diffusion is then used to calculate the diffusion rate across the various confinement layers, and an equilibrium concentration derived. The model is also used to calculate the transient H_2 concentration for all confinement layers given initial H_2 concentration, volumes, generation rates, diffusion rates, temperature and pressure.

WASTE PACKAGING.

Using the G_{eff}-H_2 values and diffusion coefficient data from Los Alamos tests, and the Benchmark model, we calculated the H_2 concentration in 55 gallon drums assuming various packaging strategies. It became apparent that H_2 diffusion through slip-lid steel cans, 12 mil PVC bag-out bags, and two layers of sealed drum liners was sufficiently low as to generate undesirable H_2 concentrations (>10%) in packages and drums thereby limiting drum loadings to less than 1 gram ^{238}Pu. By simply folding over and not sealing drum liners, the model predicts that the drum headspace H_2 concentrations is considerably reduced. More importantly, by installing NucFil 30 filters to all slip-lid cans and bag-out bags, the model predicts H_2 concentration can be maintained <10% in inner containers and higher drum loadings can be achieved. The model also shows that the headspace H_2 concentration is relatively insensitive to the H_2 concentration in the inner layers because the drum headspace H_2 concentration is mainly influenced by the diffusion rate out of the drum lid carbon filter.

MODEL AND PARAMETER EVALUATION.

A 55 gallon test drum was prepared to evaluate, and hopefully validate, the Benchmark model and the Los Alamos derived G_{eff}-H_2 values and the diffusion coefficients. The drum was loaded with eight waste items, each contained in a slip-lid steel can and bag-out bag. The cans and bags were

fitted with NucFil 30 filters. Each can contained cheesecloth and polyethylene waste and was assayed using calorimetry to obtain accurate ^{238}Pu loading values. The amount of ^{238}Pu in each can ranged from 0.04 grams to 5.66 grams and the drum total loading was 7.05 grams. For use in the model a G_{eff}-H_2 of 0.24 is used. This value approximates the equilbrium G_{eff}-H_2 in the cellulosics test chambers. Coupled with the diffusion coefficients described in this paper and G_{eff}-H_2 of 0.24 , the model was used to predict H_2 concentrations from the time the drum lid, fitted with a NucFil 13 filter, was secured to the drum. Gas samples were withdrawn and analyzed periodically over a 5 month period. Figure 5 shows the predicted and measured head space H_2 concentrations. The model predicted an equilibrium H_2 concentration in the drum headspace of 0.98%. The final 6 samples taken from the drum headspace had an average H_2 concentration 0.96% and a standard deviation of 0.28%. Of interest is the relatively wide variation of measured H_2 concentration of the final 6 samples. The variations are not believed to be sampling or analysis errors, but are thought to be linked to variations in diffusion rates of H_2 through the drum lid filter caused by varying barometric pressure.

Place Fig. 5 here

In addition, the H_2 concentrations in the drum headspace of three existing drums of ^{238}Pu waste was measured. The measured and predicted hydrogen concentrations (G_{eff}-H_2 of 0.24 used) were 0.12% and 0.18%, 0.36% and 0.35%, and 0.71% and 0.19%, respectively. The ^{238}Pu content of these drums was determined by the less accurate segmented gamma counter or neutron counter methods. The difference between predicted and measured H_2 concentrations is probably related to inaccurate ^{238}Pu measurements. More importantly, while sampling the drum headspace for the third drum, the distinct odor of an organic was noted. Subsequent qualitative measurements of the head space gas failed of isolate the compound causing the odor. If ^{238}Pu was in contact with an organic liquid, the G_{eff}-H_2 value used would understate the actual value.

CONCLUSIONS.

Experiments were conducted on cellulosics and polyethylene contaminated with known quantities of heat-source type $^{238}PuO_2$ to determine G_{eff}-H_2 values specifically applicable to Los Alamos ^{238}Pu waste. The measured G_{eff}-H_2 values embrace the variables specific to Los

Alamos ^{238}Pu waste generated during heat source production and are significantly smaller than those commonly reported in the literature and much smaller than the TRUCON code value for ^{238}Pu -combustible waste.

Measurements were made to determine the H_2 diffusion coefficients for packaging materials used at Los Alamos: carbon drum, can and bag filters, PVC bag-out bag material, and "horsetail" bag seals. Diffusion coefficients for the carbon filters were found to be greater than those reported in the literature whereas the PVC bagout bags and horsetail seals demonstrated lower diffusion coefficients.

A model, developed by Benchmark Environmental Corp., was used to predict H_2 concentration in the individual packages and 55 gallon drum headspace of ^{238}Pu waste. The model, the selected G_{eff}-H_2 value, and the diffusion coefficients were evaluated by preparing a test drum of well characterized ^{238}Pu waste items. The drum was periodically sampled and the predicted and measured H_2 were in good agreement.

The work presented here is encouraging in that the model and parameters used seem to predict drum headspace H_2 with sufficient accuracy to ensure safe storage of ^{238}Pu waste drums. Further, by modifying the packaging configuration for removing waste from gloveboxes to include the use of carbon filters on interior cans and bagout bags, the enhanced diffusion of H_2 will allow combustible waste containing several-gram quantities of ^{238}Pu to be stored safely.

Los Alamos is in the process of implementing a ^{238}Pu waste acceptance criteria based on model-predicted headspace and inner container H_2 content rather than on a fixed ^{238}Pu mass or heat loading criteria.

References.

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