A MODEL OF GAS GENERATION AND TRANSPORT
WITHIN TRU WASTE DRUMS

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ABSTRACT

A computer model has been developed to predict radiolytic gas generation and transport within Transuranic (TRU) waste drums. Gas generation from the radiolytic decomposition of organic material contaminated with plutonium is modeled. Concentrations of gas throughout the waste drum are determined using a diffusional transport model. The model accurately reproduces experimentally measured gas concentrations. With polyethylene waste in unvented drums, the model predicts that hydrogen gas can accumulate to concentrations greater than 4 mole % (lower flammable limit) with about 5 Ci of plutonium. Polyethylene provides a worst case for combustible waste material. If the drum liner is punctured and a carbon composite filter vent is installed in the drum lid, the plutonium loading can be increased to 240 Ci without generating flammable gas mixtures.

INTRODUCTION

Alpha radiation decomposes organic materials into gaseous products. Oxygen is consumed, and hydrogen, carbon monoxide, and carbon dioxide are produced by these radiolysis reactions. The objective of the model is to predict conditions that could lead to formation of flammable or explosive gas mixtures within TRU waste drums and to assess proposed gas venting methods.

The computer model calculates transient gas concentrations and total pressure as a function of waste composition and plutonium loading. The gas generation parameters in the model are based on experimental data on radiolysis from plutonium. Other isotopes could be included if gas generation data are available. Three volumes within the waste drum are modeled: Polyvinylchloride (PVC) bags containing the TRU waste, the volume between the bags and the drum liner, and the volume between the drum liner and the drum lid.

Radiolysis is assumed to occur at a constant rate within the PVC bags. Gas concentrations are calculated using a simple steady-state diffusion model of gas transport through drum barrier materials (PVC bag, polyethylene liner, and rubber gasket) and through free spaces within each barrier. The model is able to accurately simulate experimental data from the Savannah River Laboratory (SRL) and the Los Alamos National Laboratory (LANL) on measured gas concentrations in TRU waste drums.

All DOE sites generate TRU waste vent waste drums to prevent the accumulation of explosive gas mixtures. The Savannah River Plant (SRP) uses carbon composite filter beds 1.27 cm deep and 1.90 cm in diamater. The bed is contained in a galvanized carbon steel holder that is screwed into the drum lid and drum liner. The model allows the simulation of gas concentrations with or without the presence of filter vents in a waste drum.

GAS GENERATION MODEL

Gas generation is assumed to occur at a constant rate that is a function of the waste material composition, the level of the radioactivity in the waste, and the gas being considered. The molar gas generation rate (GR) may be expressed as:

$$GR(i) = (Ci\ Pu)*\ \Sigma_j\ g(i,j)*Mass(j)/\ \Sigma_j\ Mass(j) \quad (1)$$

In Eq. (1), g(i,j) is the radiolytic gas generation coefficient for gas i from material j in (moles/s-Ci Pu) and Mass(j) is the mass of material j in the waste mixture.

Equation (1) calculates gas generation as the summation of the generation from individual material components weighted by their mass fraction in the mixture. The gas generation coefficients reported by Kazanjian (1) were used in the model. When more than one coefficient could be applicable, the most conservative value was used to calculate the gas generation rate.

The model allows the user to specify a waste material composed of a mixture of cellulose, polyethylene, latex, polyvinylchloride, Plexiglas, and inert material in any relative proportion.

GAS TRANSPORT MODEL

Gas transport is assumed to take place by diffusion through the various barriers within the TRU waste drum. Gases are generated (or depleted) in the inner bag volume and diffuse through the PVC bag, the polyethylene liner, and the rubber drum gasket barriers. Any number of waste bags may be present in the drum. The model user specifies the surface areas of the PVC bags, the drum liner, and the drum gasket and the volumes enclosed by these barriers.

A general equation for transient gas transport may be written (with the index i=1 to 3) as:

$$V(i)*d[C(i)]/dt = GR(i) + A(i-1)*J(i-1) - A(i)*J(i) \quad (2)$$

In Eq. (2), V(i) is the volume (m^3) of space i, C(i) is the gas concentration (moles/m^3) in space i, GR(i) is the rate of gas generation (moles/s) in space i, A(i) is the total surface area (m^2) of barrier i, and J(i) is the gas flux (moles/m^2-s) through barrier i. In Eq. (2), i=1 stands for the PVC bag volume and bag surface barrier, i=2 represents the polyethylene drum liner, and i=3 is used for the drum gasket. In the model calculations, gas generation occurs only in the PVC bags; therefore, GR(2) and GR(3) are equal to zero.

Assuming equilibrium between the gases in the drum volumes and within the barrier materials, expressions for the gas flux may be written as:

$$J(i) = Db(i)*(P(i) - P(i+1))/Xb(i) + Do(i)*(C(i) - C(i+1))*Y(i)/Xo(i) \quad \text{for } i=1,3 \tag{3}$$

In Eq. (3), Db(i) is the permeability coefficient (moles/m-s-Pa) for the gas in barrier i, Do(i) is the diffusion coefficient (m^2/s) for the gas in the barrier pores, P(i) is the gas partial pressure (Pa) in space i, Xb(i) is the transport path length (m) within barrier i, Xo(i) is the diffusion path length (m) through openings in barrier i, and Y(i) is the porosity of barrier i.

In writing Eq. (3), it is assumed that the gases within the drum are able to diffuse through the barrier materials and through openings that are present in the barriers. That is, gas transport takes place not only by gas permeation and diffusion directly through the material barriers, but also by free diffusion through large scale pores or holes in the barriers. As an approximation, the diffusion coefficient Do(i) is assumed to be equal to that for the gas in air.

Including the second term in Eq. (3) allows the model to simulate the presence of filter vents in the drum. However, it was also necessary to include this term to give realistic simulations of drum gas concentrations even when vents were not present. In this case, the term physically represents a lack of sealing or the presence of small holes in the barrier materials. Porosity in the seal on the neck of the PVC bags or around the liner and gasket seals is accounted for by this term. Since the porosities are not known, the model has a free parameter for each barrier that can be used to fit experimental data.

When applying Eq. (3), C(4) is the gas concentration in the ambient atmosphere surrounding the drum. The diffusion path length is taken to be equal to the barrier thickness. In reality the barrier pores will be irregular and tortuous paths. The squared porosity term is used to account for the effects of a random pore distribution and pore tortuosity.

The gases considered in this model are: Oxygen, nitrogen, carbon monoxide, carbon dioxide, and hydrogen. Oxygen is depleted in the PVC bags by the radiolysis reactions. Carbon monoxide, carbon dioxide, and hydrogen are all generated by the reactions. Nitrogen is a chemically inert species that simply diffuses through the material barriers. Equations (1), (2), and (3) are solved numerically for each gas present in the drum.

MODEL PARAMETERS

The basic parameters required for model simulations are: 1) Gas generation coefficients; 2) gas permeabilities through the barrier materials; 3) gas diffusion coefficients; and 4) waste drum physical characteristics.

Gas generation coefficients for the materials of interest are given in Table I. The values were obtained from Kazanjian (1) and converted to a basis of curies of plutonium.

The coefficients in Table I show that the primary radiolysis reactions are the consumption of oxygen and the production of hydrogen. Carbon monoxide and carbon dioxide are generally produced in smaller quantities. As hydrogen is generated, the gas composition in the waste drum may reach a flammable or explosive concentration. Table I also shows that polyethylene is the worst waste material, as it has both the highest hydrogen generation rate and smallest depletion rate.

Gas permeabilities through the barrier materials are listed in Table II (2). Hydrogen will diffuse through the barrier materials and the material pores more readily than the other gases. Styrene-butadiene rubber is assumed to be representative of drum gasket material.

The parameters used in the model calculations to specify the waste drum physical characteristics are listed in Table III. These parameters represent typical values for a 55-gallon waste drum having an overall void volume of 70%. The drum parameters can be changed to simulate other configurations.

The volume listed under the drum liner is the void volume within the liner that is not occupied by the waste bags. The volume listed under the gasket is the volume between the rubber gasket and the drum lid. This volume is referred to as the drum head space in the following discussion. Porosity values represent the fractional part of the barrier material that is assumed to be free void space where the gas transport takes place by free diffusion rather than by permeation and diffusion. The porosity values are fractional parts that are open area.

SIMULATION RESULTS

The results of model simulations were compared to data collected on the gas composition within TRU waste drums at SRL and LANL. The SRL data (3) were collected during a four-year experimental study in which gas concentrations were monitored within four high-activity TRU waste drums. These were lined 55-gallon drums containing typical cabinet waste from a Pu-238 finishing facility. The drum gaskets were nonporous, and a caulking compound was used to seal the gaskets to the drum lids and to seal the drum liners. Gas samples were collected from the air space between the drum liner and the drum itself. Drums were monitored for: Temperature, pressure, oxygen, hydrogen, carbon monoxide, carbon dioxide, nitrogen, nitrous oxide, and total hydrocarbons. The SRL experiments represent a good source of long-term gas generation data on well-documented waste forms.

A model simulation was run for Drum No. 120 of the SRL study. This waste drum contained plastic, rubber, and metal contaminated with 112.6 Ci of Pu-238, 0.7 Ci of Pu-239, and 0.06 mCi of U-235. Figure 1 shows the model simulation of total pressure in the drum head space compared to experimentally measured values. Model predictions of the hydrogen and oxygen concentrations within the drum head space are shown in Fig. 2.

The simple diffusion model predicts a smooth pressure rise to about 4.5 psig at 1,500 days. Experimentally, an initial pressure decrease was observed followed by an irregular pressure rise. The data plotted in Fig. 1 have been corrected to 25°C to remove changes arising from temperature variation alone. However, much of the variation still apears to follow an annual pattern. The fluctuations may arise from variation in barrier permeabilities with ambient

TABLE I

Gas Generation Coefficients (Millimoles/Day-Curie Pu)

	Cellulose	Polyethylene	Latex	PVC	Plexiglas
Hydrogen	0.158	0.216	0.111	0.197	0.121
Carbon Dioxide	0.089	0.021	0.013	0.026	0.155
Carbon Monoxide	0.028	0.011	0.011	0.011	0.211
Oxygen	-0.199	-0.082	-0.557	-0.557	-1.150

TABLE II

Barrier Gas Permeabilities (Millimoles/Day-m-kPa) (Values Must be Multiplied by 10^{-10})

	Polyvinylchloride	Polyethylene	Styrene-butadiene Rubber
Hydrogen	588.5	3,648.5	5,796.3
Carbon Dioxide	40.6	753.2	1,447.6
Carbon Monoxide	55.9	7.2	43.5
Oxygen	13.5	844.4	868.0
Nitrogen	3.4	107.1	494.3

TABLE III

	PVC Waste Bag	Polyethylene Liner	Rubber Gasket
Number in Drum	17	1	1
Void Volume (m^3)	0.0057	0.028	0.021
Surface Area (m^2)	0.40	1.95	0.017
Thickness (mm)	0.51	2.29	9.53
Porosity	0.000125	0.00125	0.0060 - 0.0085

temperature or from pressure changes. No attempt was made to include such effects in the model.

As shown by the experimental data in Fig. 2, hydrogen gas accumulates rapidly in the drum head space while oxygen is depleted. These trends are reproduced by the model simulation. Both curves show essentially steady-state behavior after about one year of gas generation. Again, the strong fluctuations in the experimental data may be temperature or pressure dependent. At about day 1,000, the experimentally observed hydrogen gas concentration and total pressure suddenly increase. The integrity of a waste bag or the drum liner may have been compromised at this point.

The parameters given in Table III were used to obtain the model results plotted in Figs. 1 and 2. Using the higher gasket porosity gave the best fit to the SRL experimental data.

Model simulations were also made for several drums from a series of experiments conducted at LANL (4). Gas concentrations in eight drums of TRU waste

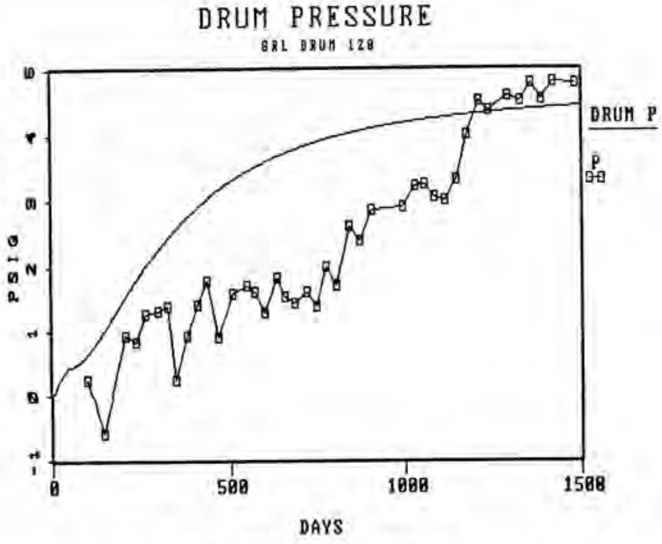

Fig. 1. Measured and Model-Predicted Pressures within the Drum Head Space for SRP TRU Waste Drum No. 120.

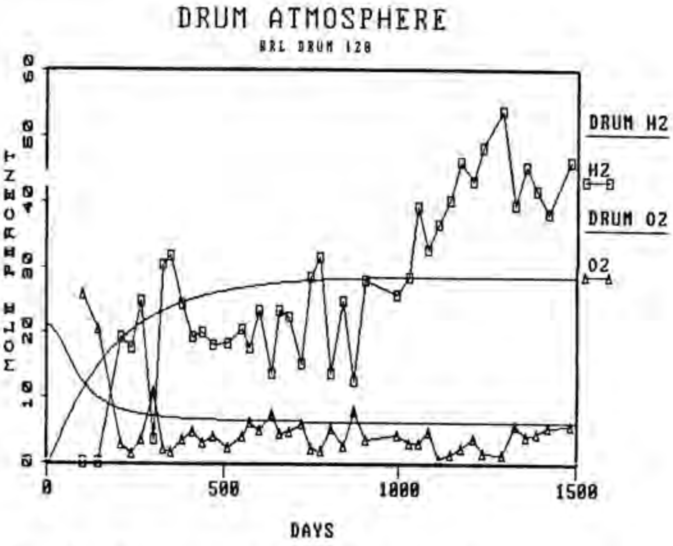

Fig. 2. Measured and Model-Predicted Concentrations of Oxygen and Hydrogen Gas within the Head Space for SRP TRU Waste Drum No. 120.

from plutonium heat-source production were monitored for about one. The isotopic composition of the waste is given in Table IV. As with the SRP drums, the drum lids and inner liners were sealed. The experiments were designed to evaluate the effectiveness of carbon composite filters in maintaining safe hydrogen gas concentrations within the drums. Drums were tested both with filter vents in place and without the vents. The filter vent that was tested is similar in design to the one in use at SRP.

TABLE IV

Isotopic Composition of LANL Heat Source Pu-238

Isotope	Weight Percent
Pu-238	80.0
Pu-239	16.3
Pu-240	3.0
Pu-241	0.6
Pu-242	0.1

Results from the simulation of waste drum BFB-114 are presented in Fig. 3 and Fig. 4. Experimental data are shown by lines connecting the plotted data points, while model predictions are indicated by smooth curves. Figure 3 shows model predictions of hydrogen and oxygen gas concentrations within the drum head space, while the same predictions for the drum liner are shown in Fig. 4. The waste drum was initially sealed and a filter vent in the drum lid was opened 112 days after preparation.

The waste drum contained 218.4 Ci (15.6 g) of Pu-238, which was the higest curie loading in the LANL study. The composition of the drum waste was not well defined. Therefore, the composition used in model calculations was adjusted to reproduce the reported total and hydrogen gas generation values. The drum parameter values listed in Table III were used. The lower gasket porosity improved the fit for the LANL data.

The model is able to accurately simulate hydrogen and oxygen concentrations within both volumes over the entire experimental time period. Gas concentrations within the drum liner are only slightly different from those in the drum head space. With a sealed drum, the hydrogen gas concentration exceeds 4% within 20 days, while oxygen is rapidly depleted. Opening the drum lid vent significantly reduces the hydrogen gas concentration; however, flammable gas concentrations persist. The filter was modeled as a carbon bed 1.9 cm in diameter and 1.27 cm long with a 0.1 bed porosity.

APPLICATION TO SRP TRU WASTE

The experimental studies discussed in the preceding sections show that flammable and explosive gas mixtures can accumulate in TRU waste drums with relatively low plutonium loads. To ensure adequate conservatism in safety analysis, a limit of 4% (lower flammable limit) is placed on the hydrogen gas concentration allowed within waste drums. Limiting the curie loading in waste drums such that flammable gas mixtures will not accumulate places severe restrictions on the management of SRP TRU waste. Therefore, the use of vented drums has been proposed as a method of reducing hydrogen gas concentrations in stored waste to allow greater amounts of plutonium to be safely placed in TRU waste drums.

Model simulations were run to assess the effect of venting on SRP TRU waste drums. Figure 5 presents a plot of model predictions of the steady-state hydrogen gas concentrations within the drum liner (Liner) and drum head space (Drum) for an unvented drum containing polyethylene waste. Figure 5 shows that a plutonium loading of 5 Ci in the waste material yields concentrations of hydrogen gas exceeding 4 mole % in both the liner and drum. The hydrogen concentrations shown in Fig. 5 are similar to the values observed during the SRP experimental study (3). The experiments and simulations demonstrate that high concentrations of hydrogen can be realized in actual waste drums.

With a loading of 10 Ci in an unvented drum, a flammable gas accumulates inside the drum liner in 163 days and inside the head space within 185 days. The drum becomes potentially dangerous in a relatively short time.

SRP has begun the routine use of drum vents for newly generated waste in 1986. The carbon composite filter was selected as a vent for SRP drums because of its high efficiency for particulate removal, rugged

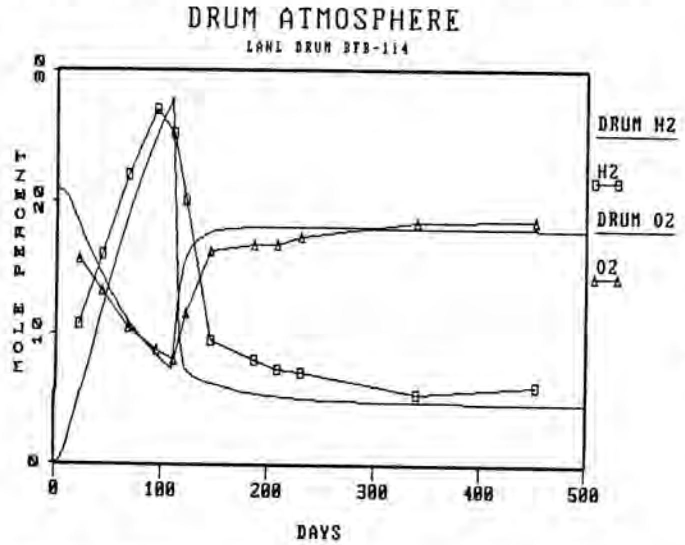

Fig. 3. Measured and Model-Predicted Concentrations of Oxygen and Hydrogen Gas within the Head Space for LANL TRU Waste Drum BFB-114.

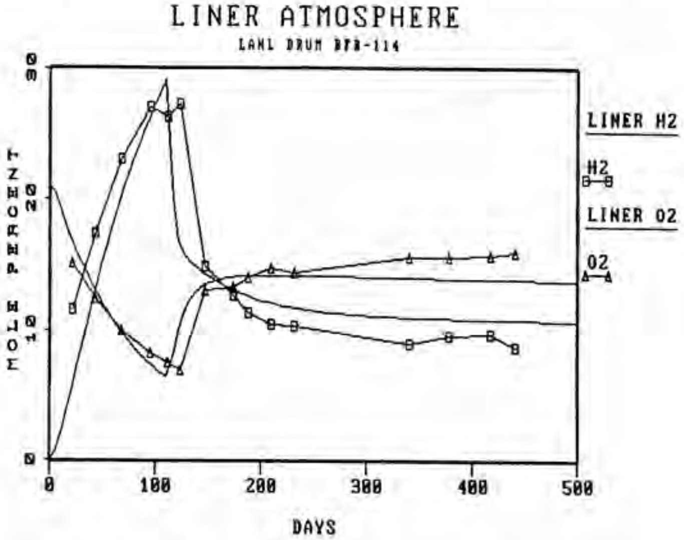

Fig. 4. Measured and Model-Predicted Concentrations of Oxygen and Hydrogen Gas within the Drum Liner for LANL TRU Waste Drum BFB-114.

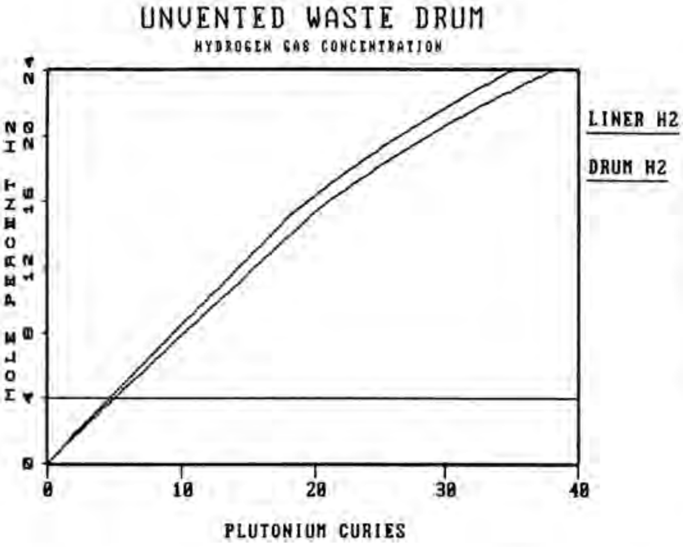

Fig. 5. Model Predictions of the Steady-State Hydrogen Gas Concentration within the Drum Liner and Head Space for an Unvented TRU Waste Drum Containing Polyethylene Waste.

construction, low cost, and ready availability. The filter will effectively prevent the dispersal of contaminated particulate matter from the waste drum while allowing gases to freely escape.

Experiments to evaluate different designs of the carbon filter case have been conducted by the Science Applications International Company (SAIC). The best venting was obtained with a filter housing having 0.95-cm-diameter inlet and 0.32-cm-diameter outlet ports with no cap over the case. Assuming that the primary barrier to gas transport is through the filter bed, the SAIC experimental results can be used to determine an effective bed porosity. Model simulations of six SAIC experiments (5) using a bed porosity of 0.51 are presented in Fig. 6. The computer model is able to closely reproduce the experimental data. Therefore, using the experimentally determined porosity, model simulations of filter vent performance can be conducted with confidence.

Model predictions of steady-state hydrogen gas concentrations within the drum liner and the drum head space when filter vents are present in both the liner and drum lid are shown in Fig. 7. Compared to an unvented drum, the hydrogen gas concentrations are significantly lower. With venting, up to 133 Ci of plutonium can be placed in a drum of polyethylene waste before the hydrogen flammable limit is exceeded. However, if 200 Ci are inadvertently placed in the drum, a flammable hydrogen concentration occurs within the drum liner after only 44 days. Therefore, careful monitoring of the waste content is required.

The drum curie loading is limited by the hydrogen concentration within the drum liner. If the liner is punctured by a hole several centimeters in diameter, the liner will be fully vented. The curie loading then becomes limited by the performance of the filter vent in the drum lid. As Fig. 7 shows, the curie loading could be increased to about 240 Ci before a flammable gas concentration develops. Of course, the barrier to particulate transport between the drum liner and head space has been removed.

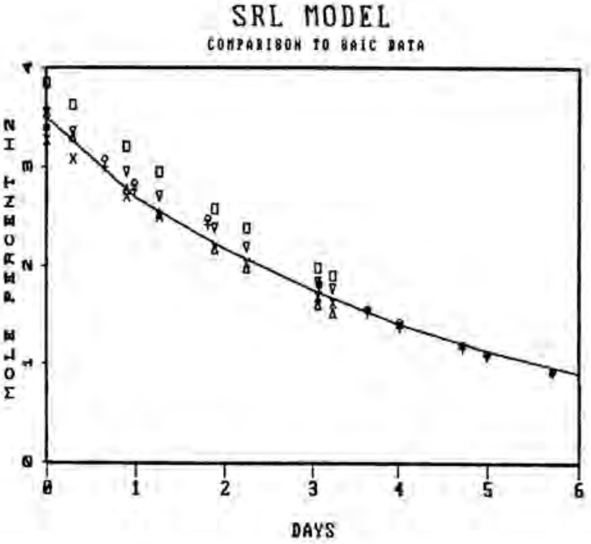

Fig. 6. Model Simulation of SAIC Diffusion Experiments on a Carbon Composite Filter Vent without a Ridged Cap.

CONCLUSIONS

A model of radiolytic gas generation and gas transport within TRU waste drums has been developed. The model assumes a combination of gas transport through permeation of the barrier materials and by free diffusion through large scale pores in the barrier materials. The model was tested by simulating experimental data collected at SRL and LANL over a wide range of conditions. These data were used to determine typical porosity values for waste bags, drum liners, and drum gaskets. Using a consistent set of parameters, the model is able to predict gas concentrations in TRU waste drums within the accuracy of the experimental data. The model can be used to evaluate the effectiveness of filter vents in controlling the atmosphere within TRU waste drums.

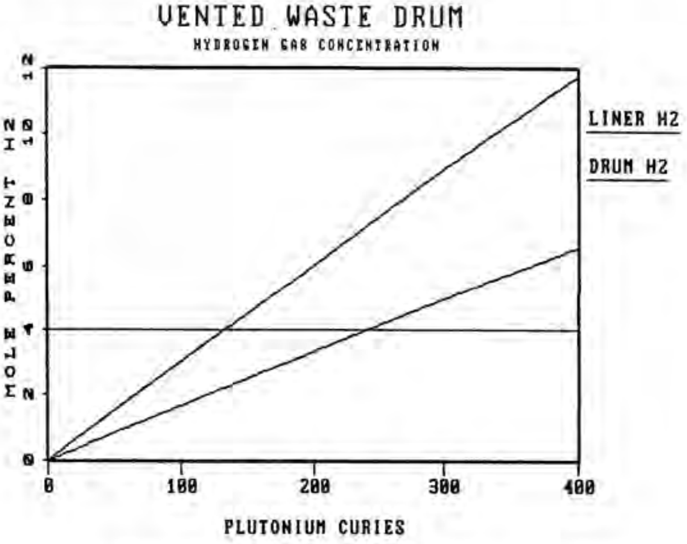

Fig. 7. Model Predictions of the Steady-State Hydrogen Gas Concentration within the Drum Liner and Head Space for a Vented TRU Waste Drum Containing Polyethylene Waste.

The model has been applied to SRP TRU waste to predict a maximum plutonium loading that can be safely placed in newly generated waste drums without the accumulation of explosive gas mixtures. In the worst case, a plutonium inventory of less than 5 Ci is sufficient to generate hydrogen gas concentrations greater than the 4 mole % limit. This curie loading limit would be too restrictive for SRP operations. Therefore, drums vented through carbon composite filters will be used at SRP. With vents in both the drum liner and the drum lid, it should be possible to safely store from 133 to 240 Ci of plutonium without accumulating explosive gas mixtures.

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