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# Contribution to Internal Pressure and Flammable Gas Concentration in RAM Transport Packages\*

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## INTRODUCTION

Various facilities in the U. S. operated by the U.S. Department of Energy generate wastes contaminated with transuranic (TRU) isotopes (such as plutonium and americium) that decay primarily by emission of alpha particles. The alpha particles lose energy in their passage through matter and change the material chemically in the process called radiolysis. The waste materials consist of a wide variety of commercially available plastics, paper, cloth, and rubber; concreted or sludge wastes containing water; and metals, glass, and other solid inorganic materials. TRU wastes that have surface dose rates of 200 mrem/hr or less are typically packaged in plastic bags placed inside metal drums or boxes that are vented through high efficiency particulate air (HEPA) filters. These wastes are to be transported from waste generation or storage sites to the Waste Isolation Pilot Plant (WIPP) in the TRUPACT-II, a Type B package.

Radiolysis of organic wastes or packaging materials, or wastes containing water generates gas which may be flammable or simply contribute to the internal pressure of the radioactive material (RAM) transport package. This paper discusses the factors that affect the amount and composition of this gas, and summarizes maximum radiolytic G values (number of molecules produced per 100 eV absorbed energy) found in the technical literature for many common materials. These G values can be used to determine the combination of payload materials and decay heats that are safe for transport. G values are established for categories of materials, based on chemical functional groups. It is also shown using transient diffusion and quasi-equilibrium statistical mechanics methods that hydrogen, if generated, will not stratify at the top of the transport package void space.

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## GAS GENERATION EQUATION

The rate,  $dn/dt$ , at which gas is generated by radiolysis, is given by:

$$dn/dt = F \times G \times E \times C$$

where

- $dn/dt$  = moles of gas generated (or consumed) per unit time
- $E$  = decay energy (eV)
- $F$  = fraction of decay energy absorbed by the gas generating material
- $G$  = number of gas molecules generated (or consumed) per 100 eV of energy absorbed
- $C$  = constant.

$F$  is determined by the materials being irradiated, the range of the radiation, and the proximity of the radioactive material to the waste material. For particulate contamination,  $F$  also depends on the particle size. The range of a 5 MeV alpha particle is about 4 cm in air, 50 micrometers in plastic or paper (Cember 1978), and about 11 micrometers in  $\text{PuO}_2$  (Bibler 1979). For a particle of  $\text{PuO}_2$  that is 10 micrometers in diameter, only about 80% of the alpha decay energy emerges from the particle. Because of the short range of alpha particles, all of the alpha decay energy is absorbed somewhere inside a drum or box of waste.

The parameter  $G$  is called the  $G$  value for the material.  $G$  values are experimentally measured in the laboratory for specific materials under controlled conditions, and have been reported in the technical literature for many solids and liquids (e.g., Dole 1973, Spinks 1976, Bolt 1963). Gases evolved are measured by pressure and gas composition changes. An effective  $G$  value is defined, where

$$G_{\text{eff}} = \sum_m (F_m \times F_p) \times G_m,$$

where

- $F_p$  = fraction of decay energy emerging from the particle
- $F_m$  = fraction of energy absorbed by a material  $m$
- $G_m$  =  $G$  value for material  $m$ .

For example, when surface-contaminated metal parts are wrapped in plastic, only about 1/2 of the decay energy emerging from particulate contamination is absorbed by the plastic. Then the value of  $G_{\text{eff}}$  is equal to 1/2  $G_{\text{plastic}}$ .

## FACTORS AFFECTING G VALUES

The amount and composition of the gas generated are functions of the chemical structure of materials being irradiated, temperature, atmosphere inside the RAM package, total absorbed dose, and linear energy transfer of the incident radiation.

### Chemical Structure

The controlling factor in the behavior of materials under irradiation, as under most other environmental influences, is the chemical structure. Chemical bonds are not broken randomly. Energy may be transferred from the location on a molecule where it is absorbed to another more reactive or sensitive chemical bond. Additives to improve physical or aging properties may affect changes produced by radiation.

The potential for a polymer to generate flammable gas through radiolysis is primarily determined by its chemical functional group(s), in common with other chemical reactions. Organic functional groups found in common polymers, in the approximate order of high to low G values for flammable gas, include (1) saturated carbon-carbon bonds, (2) alcohol groups, (3) ether groups, (4) unsaturated carbon-carbon bonds, (5) ester groups, and (6) aromatic groups (resonant structures containing carbon and hydrogen or carbon and nitrogen atoms). Examples of maximum G values for polymers at room temperature are shown in Table 1. Polymers with saturated carbon-carbon bonds, or alcohol or ether functional groups, have the greatest potential to generate flammable gas. Polyethylene, with a maximum value of  $G(\text{flam gas}) = 4.1$ , provides the upper bound for most commercial materials.

Polymers containing chlorine are stabilized to reduce the catalytic effect of HCl generated by radiolysis or thermal degradation. Plasticizers are added in some cases to increase flexibility. The strong effect of the plasticizers and stabilizers on the radiolysis of PVC is demonstrated by the differences in the volume percent of HCl measured (8, 14, and 85%) by the same experimenter for three different formulations of PVC (Arakawa 1986). In addition, pure PVC has G values (in vacuum) reported at about 10 at room temperature, while  $G(\text{HCl})$  values for formulations with plasticizers and stabilizers range from not detectable to 1.7 (Szymanski 1976).

### Temperature

The rates of chemical reactions, as well as the movement of gas molecules inside solids, increase with increasing temperature. For these reasons, measured G values also increase with increasing temperature. The activation energy for the Arrhenius equation for radiolysis is about 1 kcal/mole for polyethylene (Chapiro 1962). This would cause a 17% increase in the measured G value if the temperature is increased from 25°C to 55°C.

### Atmosphere

Oxygen, if present in the surrounding atmosphere, participates in the chemical reactions, so that G values can be quite different for experiments conducted in air versus experiments conducted under vacuum.

Table 1. Maximum G values for polymers at room temperature from the technical literature

Functional Group	Polymer	G(H <sub>2</sub> )	G(flam gas)	G(net gas)
saturated carbon-carbon	polyethylene	4.0	4.1	4.1
alcohol	polyethylene glycol	3.5	3.5	3.5
ether	cellulose	3.2	3.2	10.2
unsaturated carbon-carbon	polyisoprene	0.7	0.9	0.9
ester	polymethyl methacrylate	0.4	2.0	4.1
aromatic	polystyrene	0.2	0.2	0.2

\*Net gas includes depletion of oxygen, when applicable, and generation of flammable and nonflammable gases.

### Total Absorbed Dose

Radiation chemically changes the irradiated material, so that G values and corresponding gas generation rates also change with absorbed dose. G values typically decrease as absorbed dose increases. The absorbed dose for alpha radiation is limited to the track of the alpha particle, and is about 20 Mrad for a single 5 MeV alpha particle in plastic or paper (National Academy of Sciences 1976). Gamma and alpha data appear comparable for solids, provided the gamma dose is at least 20 Mrad.

### Linear Energy Transfer

The chemical reactions are also affected by the density of ions formed in the track of the ionizing particle. The G(H<sub>2</sub>) values for alpha and gamma radiation of liquid water are quite different: 1.4-1.6 for alpha radiation and 0.45 for gamma radiation (Spinks 1976). These effects appear to be much weaker in solids, based on the few measurements that have been reported on irradiation of the same material by radiation having different LET.

### DISTRIBUTION OF HYDROGEN IN TRANSPORT PACKAGES

The SARP (Safety Analysis Report for Packaging) must address the flammability of gases which are present or are generated during transport. Hydrogen has a lower density than that of air. The question then arises, "Does hydrogen generated by radiolysis mix with the air in the void spaces of the package or does it stratify at the top of the package"?

Basic chemistry textbooks contend that two or more different gases will mix completely and uniformly when put in contact with one another. The primary reason for this is that gas molecules are in constant rapid motion. They are far apart (unlike liquid or solid molecules) and behave as if the other gas molecules were not there (they are not attracted or repelled by the other molecules). The answer to the stratification question can be shown analytically using a simple diffusion model and quasi-equilibrium statistical mechanics.



## Diffusion Model

A simple one-dimensional diffusion equation can be used to calculate the hydrogen concentration as a function of distance and time and is given by:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (1)$$

where  $c$  is the concentration ( $\text{g/cm}^3$ ),  $D$  is the diffusivity of hydrogen in air ( $\text{cm}^2/\text{sec}$ ),  $x$  is the distance along a path ( $\text{cm}$ ), and  $t$  is the time ( $\text{sec}$ ). The initial condition is that the concentration of hydrogen is zero at time zero. The boundary conditions are a constant flux of hydrogen coming in at one end ( $x=L$ ) and insulated (no hydrogen leaving) at the other end ( $x=0$ ). The solution to this equation (Arpaci 1966) is given by:

$$c = \frac{jL}{D} \left[ \frac{Dt}{L^2} + \frac{1}{2} \left( \frac{x}{L} \right)^2 - \frac{1}{6} - 2 \sum_{n=1}^{\infty} \frac{(-1)^n}{(n\pi)^2} e^{-D \frac{n^2 \pi^2}{L^2} t} \cos \frac{n\pi}{L} x \right] \quad (2)$$

The characteristic time from this equation, ignoring  $n>1$  terms, is:

$$t = \frac{L^2}{D\pi^2} \quad (3)$$

This equation represents the time it will take to have a fairly uniform concentration of hydrogen throughout the total length and the problem approaches a pseudo-steady state. As indicated, this term is dependent on the path length and diffusivity. The diffusivity, in turn, is dependent on pressure and temperature. High pressure and/or low temperature inhibit diffusion while low pressure and/or high temperature favor it.

### Example Case

The TRUPACT-II Type B transport package is used as an example for predicting the mixing time of hydrogen and air. The path length for this example is 3 meters, the distance from the center drum, up the side of the transport package, and around the head. For the highest design pressure ( $4.5 \times 10^5 \text{ N/m}^2$ ) and lowest design temperature (244 K), the diffusivity is calculated to be  $0.1168 \text{ cm}^2/\text{sec}$  (Treybal 1980). Thus, the characteristic (mixing) time, from Eq. 3, is 22.4 hours. After this time the hydrogen inside TRUPACT-II will be mixed uniformly with the air (it will not stratify). This is the most conservative case. For ambient conditions ( $1.013 \times 10^5 \text{ N/m}^2$ , 293 K) the diffusivity is  $0.6916 \text{ cm}^2/\text{sec}$  and the characteristic time is 3.8 hours. Both of these times are short in comparison to the 60 day maximum

expected transport time during which the TRUPACT-II package is sealed and cannot be vented.

### Statistical Mechanics

Statistical mechanics, which apply to molecules in thermal equilibrium, can be used to estimate the stratification of molecules in the atmosphere. The density of a gas as a function of height (Feynman et al. 1963) is given by

$$n = n_0 e^{-mgh/kT} \quad (4)$$

where  $n$  is the gas density (molecules/volume),  $n_0$  is the gas density at  $h=0$ ,  $m$  is the molecular weight (g/mole),  $g$  is the gravitational acceleration ( $\text{cm}/\text{sec}^2$ ),  $h$  is the height (cm),  $k$  is Boltzmann's constant ( $\text{g}\cdot\text{cm}^2/\text{sec}^2/\text{K}$ ) and  $T$  is absolute temperature (K). For TRUPACT-II with  $h = 3$  meters and  $m = 2$  g/mole for hydrogen, the ratio of  $n$  to  $n_0$  is 0.99997. This implies that the hydrogen density at  $h=3\text{m}$  is very nearly the same as at  $h=0$ . It can therefore be concluded that hydrogen does not stratify in the TRUPACT-II.

### CONCLUSIONS

Factors that affect gas generation from the radiolysis of organic materials or water have been presented that permit upper bound calculations to be performed for internal pressure and flammable gas concentration during transport. Hydrogen generated inside the vented waste containers does not stratify at the top of the transport package but quickly mixes with the air present initially.

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