

CALCULATIONAL METHOD FOR PREDICTING RADIOLYTICALLY
GENERATED COMBUSTIBLE GAS CONCENTRATION AND SAFE STORAGE
AND SHIPMENT PERIODS FOR SEALED RADIOACTIVE WASTE CONTAINERS^a

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ABSTRACT

A cost-effective method, both in man-rem and dollars, has been developed to quantify hydrogen gas production in radioactive waste containers and aid utilities in compliance with U.S. Nuclear Regulatory Commission (NRC) requirements.

The production of combustible gases in sealed radioactive waste containers has been identified by the NRC as a significant safety concern relative to the handling, shipment, and storage of radioactive waste. The NRC acted on this safety concern in September 1984 by issuing Inspection Enforcement Information Notice No. 84-72: Clarification of Conditions for Waste Shipments Subject to Hydrogen Gas Generation, requiring waste generators to demonstrate with tests or measurements that combustible mixtures of gases are not present in radioactive waste shipments; otherwise the waste must be vented within 10 days of shipping.

Recently, the NRC modified these requirements allowing calculations, in addition to tests and measurements, as a means for determining combustible gas concentrations in sealed radioactive waste containers. These modifications were based primarily on the results of the work done by EG&G Idaho, Inc., in developing a calculational method for predicting hydrogen gas generation in sealed radioactive waste containers. That work is described in this paper.

INTRODUCTION

The potential exists for the production of combustible mixtures of gases in certain waste forms containing radioactive material e.g., resins, binders, sludge, and wet filters. Although the problem of hydrogen gas generation has been seen only in containers with greater than Type A quantities of waste, the same physical conditions exist in containers with Type A quantities of waste as well, even though the time to reach hazardous conditions is much longer.

Nuclear wastes subjected to ionizing radiation produces gas through the processes of radiolysis and waste degradation. The radiolytic decomposition of the residual water in the waste produces hydrogen and oxygen. In addition, the ionizing radiation acts as a catalyst for a chemical reaction between the oxygen, waste, and residual water in the container. Although hydrogen gas generation increases in a nearly linear relationship with increasing curie content, pressure does not increase in a sealed container, until the integrated dose is reached in which the oxygen inside the container is consumed by chemical reaction. The ongoing radiolytic process continues to produce gas. Pressure will increase in a sealed container and combustible concentrations of hydrogen

gas may result, thus presenting significant safety concerns relative to the handling, shipping, and storage of radioactive waste.

At Three Mile Island (TMI-2) organic ion exchange resin was used in the EPICOR II system to process more than 500,000 gallons of waste water, resulting in the generation of 72 prefilter liners with curie loadings ranging from 160 to 2200 Ci. Loadings in 22 of the liners were low enough to permit their disposal in a commercial low-level waste site, while the remaining 50 liners were stored at TMI-2. Subsequent preparations to ship these 50 liners revealed the presence of significant concentrations of hydrogen gas. As a result, the U.S. Department of Energy (DOE) sponsored research and development programs addressing gas generation and related safe management of radioactive ion exchange waste. The Nuclear Regulatory Commission (NRC) also sponsored technical studies on the effects of ionizing radiation on organic ion exchange resin and other radioactive wastes and surveyed operating nuclear power plants relative to actual resin usage and radionuclide loading.

It was determined from these efforts and actual TMI-2 on-site (EPICOR II) direct measurements that certain conditions and specific relationships exist, including:

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- Ion exchange media subjected to ionizing radiation generate a variety of gases (hydrogen, oxygen, carbon dioxide, carbon monoxide, and methane) from radiolysis and resin degradation.

- Hydrogen gas generation rates in radioactive waste containers increase at a nearly linear rate with increasing curie content.
- Pressure in a sealed wet radioactive waste container initially decreases due to oxygen depletion, masking hydrogen production. The pressure will continue to decrease until the delivered dose is sufficient to deplete the gaseous oxygen.
- Time to reach a given hydrogen gas concentration in a sealed radioactive waste container is predictable.
- U.S. commercial nuclear power generating plants typically ship radioactive wastes that are well below the present NRC permissible radionuclide loading limit (10 Ci/ft³); however a few have exceeded this limit.

The NRC's Inspection Enforcement (I&E) Information Notice No. 84-72 addresses most types of radioactive waste shipments from operating power plants. Basically, the requirements are as follows:

- During a period of twice the expected shipment time:
 1. Hydrogen gas concentration must be limited to no more than 5% by volume of the secondary container gas void, or
 2. The secondary container and cask cavity must be inerted to ensure that oxygen is limited to 5% by volume in those portions of the waste package that could have greater than 5% hydrogen gas.
- The above is not required if radioactivity concentration is less than that for low specific-activity material and shipped within 10 days of preparation (sealing) or venting.

Because of concerns expressed by radioactive waste generators (too conservative, too costly, venting problems, as-low-as-reasonably-achievable exposure rates, etc.) relative to the new NRC requirements, the Utility Nuclear Waste Management Group of the Edison Electric Institute (EEI) formed a Hydrogen Generation Task Force to study and evaluate the new NRC requirements. The task force used direct operational data and knowledge from the EPICOR experience of General Public Utilities Nuclear Corporation (GPU Nuclear) and technical assistance from the EG&G Idaho/DOE Technical Integration Office at TMI. These efforts resulted in the development of a calculational method to quantify hydrogen gas generation in sealed containers.

The Electric Power Research Institute (EPRI) demonstrated the use of this calculational method at TMI-2. A desktop computer with a spreadsheet program was used to compare the hydrogen concentration predicted using the EG&G Idaho calculational method with the hydrogen concentration actually measured when EPICOR II liners were vented during their preparation for shipment after three years of storage on site. On the average, the predicted hydrogen concentration was within 20% of the measured values.

EEI task force representatives met with NRC Transportation Branch personnel and requested that the calculations be recognized as a means of satisfying the requirements set forth in NRC I&E Information

Notice No. 84-72 for determining hydrogen gas concentration in radioactive waste containers. Subsequently, the NRC approved calculations as acceptable and affected Certificates of Compliance were modified to allow the use of calculations for assessing gas generation, as well as tests and measurements.

CALCULATIONAL METHOD

The calculational method for predicting combustible gas generation in sealed radioactive waste containers described in this section is based on DOE and NRC research and GPU Nuclear's TMI EPICOR II experience. An effort has been made to extract pertinent findings from these resources and organize the information into a unified format. Data requirements and analytical capabilities of typical waste generators were evaluated and the format was modified to facilitate implementation by potential users of the model. Certain parameters that require mainframe computer computation have either been tabularized or are presented in graphical form. Presented below is a description of the calculational method developed to quantify combustible gas generation.

Formulas and Empirical Data

Combustible gas generation in sealed radioactive waste containers involves a combination of factors that can be addressed by considering the following:

- The production of gas in the waste form resulting from radioactive decay.
- The amount of energy resulting from the decay process that is retained in the waste container and absorbed by the waste.
- The free volume of the container, including interstitial voids inherent in the waste form.

These three factors and their interrelations are discussed below.

Production of Gas in the Waste Form Resulting from Radioactive Decay

The quantity of gas produced is a function of the amount of energy absorbed by the waste form. Gas formation is due primarily to radiolysis caused by the radioactive decay energy of nuclides present in the waste. NRC studies performed at Brookhaven National Laboratory indicate that the amounts of combustible gases formed by radiolysis are approximately linear with dose. The relationship between gas production and energy absorption is expressed as the waste's gas generation constant or G-value, which is described as the number of radicals or molecules formed or decomposed per 100 eV of energy absorbed. A number of G-values have been reported^{1,2,3,4}. Those of concern to typical waste generators are the G-values for dewatered, or swollen, resin and solidified waste. These gas generation constants range from 0.1 to 0.6 molecules per 100 eV (see Table I below). G-values for mixed resin bed systems can be approximated using the weight percent mix of the components.

Radioactive Decay Energy Absorbed by the Waste Form

The amount of energy absorbed by a waste form as a result of the radioactive decay process is a function of curie loading, waste properties and container geometry. The primary decay modes, for consideration, by typical waste generators are beta, Auger electron and x-ray emissions and gamma emission. For practical

TABLE I
HYDROGEN GAS GENERATION CONSTANTS (G_H)¹

| Resin | Ionic Form | G_H (Molecules/100 eV) ^b |
|--------------|------------|---------------------------------------|
| DOWEX 50WX10 | Li^+ | 0.11 |
| DOWEX 50W10 | H^+ | 0.095 |
| ZEO-KARB 215 | H^+ | 0.12 |
| IRN-77 | H^+ | 0.13 ± 0.02 |
| IRN-78 | OH^- | 0.6 |
| IRN-150 | HOH | 0.5 |
| IRN-77 | Na^+ | 0.2 |
| IRN-78 | Cl^- | 0.3 |
| IRN-150 | $NaCl$ | 0.3 |

The hydrogen gas generation yield for a mixed bed system is the sum of the yields of the individual components. For example, a mixed bed containing 0.40 resin 'A' and 0.60 resin 'B' by weight with 'A': $G_H = x$ and 'B': $G_H = Y$ is

$$G_H('A' + 'B') = 0.4x + 0.6Y$$

for beds of unknown composition use;

anion bed (OH^-); $G_H = 0.6$
cation bed (OH^-); $G_H = 0.13$
for solidified resin/cement; $G_H = 0.24$
for asphalt use $G_H = 0.41$

^b These values are the result of experimental analysis and appear as reported, for swollen (dewatered) resins from NUREG/CR-2830 and NUREG/CR-3383, cement values from NUREG/CR-2969, and values for asphalt from NUREG/CR-50617. The G-value is defined as the number of molecules formed or decomposed per 100 eV absorbed.

purposes, all beta and associated secondary radiation emission energies are assumed to be deposited in the waste. This is because of the relatively short travel length, or range (as compared with gamma rays), required for the beta particle to give up its energy in the waste material and the extremely low probability of a beta particle escaping the container. The gamma energy absorbed by the waste depends on the strength of the gamma emission, the amount of gamma ray energy absorbed by interaction (collision) with a waste particle and the number of particles the gamma ray interacts with. Because an interaction will either absorb or, more likely, attenuate an emission, the fraction of gamma energy absorbed depends on the number of interactions possible. Gamma energy absorption therefore increases with increasing numbers of waste particles. For this reason, gamma absorption is a function of container waste density and geometry.

The total energy absorbed in the waste is the sum of the beta and secondary radiation decay energy and that portion of the gamma ray energy retained in the waste's matrix. In order to calculate combustible gas generation, it is necessary to determine the absorbed energy at a specific time after the waste container is loaded and sealed. This is accomplished by use of

equations that consider nuclide loading curie content, and waste properties such as density, geometry, gamma ray attenuation, and absorption coefficients. The result of this exercise yields an absorbed energy dose in rads (radiation absorbed dose) for each nuclide in the waste at a time after sealing. The contributions of the beta, secondary, and gamma components of each nuclide are computed using the following equations:

$$\text{Beta absorbed dose (rads)} = D_i^\beta(t) = \frac{AC_i}{\lambda_i} (\bar{E}_i)(1 - e^{-\lambda_i t}) \quad (1)$$

$$\text{Secondary radiation absorbed dose (rads)} = D_i^x(t) = \frac{AC_i}{\lambda_i} (E_i^x)(1 - e^{-\lambda_i t}) \quad (2)$$

$$\text{Gamma absorbed dose (rads)} = D_i^\gamma(t) = \frac{AC_i}{\lambda_i} (E_i^\gamma)(1 - e^{-\lambda_i t}) \quad (3)$$

$$\text{Combining equations yields } D_i^{\beta,x,\gamma}(t) = \frac{AC_i}{\lambda_i} (\bar{E}_i + E_i^x + E_i^\gamma)(1 - e^{-\lambda_i t}) \quad (4)$$

where

- $D_i^{\beta,x,\gamma}(t)$ = total (beta plus secondary plus gamma) absorbed dose delivered by the i^{th} nuclide at time t , in rads
- t = the time after sealing the container in years
- A = a proportionality constant equal to $1.84 \text{ E}+10 \text{ rad-g ram/MeV-year-curie}$
- C_i = the specific activity of the i^{th} nuclide in Ci/g
- λ_i = the decay constant of the i^{th} nuclide in years^{-1}
- \bar{E}_i = average beta energy in MeV of the i^{th} nuclide
- E_i^x = the absorbed x-ray energy in MeV of the i^{th} nuclide
- E_i^γ = the absorbed gamma ray energy in MeV of the i^{th} nuclide

The total cumulative absorbed dose for all nuclei and decay modes at time (t) is found from

$$D_{\text{Total}} = \sum_i D_i^{\beta,x,\gamma}(t) \quad (5)$$

A discussion of various absorption parameters is presented below.

The beta absorbed dose \bar{E}_i in the waste is calculated using the value for average beta energy (E_i) for a nuclide. The average beta ray energy is approximately one-third of the sum of the possible beta emissions, multiplied by the relative abundance of the emission. For example, iodine 131 emits two beta particles, with 85% of the disintegrations result in a 0.608 MeV beta, while the remaining 15% are 0.315 MeV, then

$$\bar{E}_i = 1/3(0.85 \times 0.608 + 0.15 \times 0.315) \quad (6)$$

$$\bar{E}_i = 0.187 \text{ MeV}^c$$

These values have been tabularized and are available in standard health physics and nuclear engineering handbooks. The beta absorbed dose is then determined by

$$D_i^\beta(t) = \frac{AC_i}{\lambda_i} (A\bar{E}_i)(1-e^{-\lambda_i t}) \quad (7)$$

This is done for each beta emitting nuclide. Summing the beta dose for all nuclides at a time (t) yields the total beta absorbed dose for the waste.

Secondary radiations (E_i^x), such as x-rays and Auger electrons, result from the transition of a nuclide from an excited state to the ground state. All emissions with energies of 100 keV or less are considered to be totally absorbed by the waste form and participate in gas production.

Values for secondary radiations are available in standard handbooks⁵. The contribution to absorbed dose from secondary radiations for each nuclide in the waste is determined by

$$D_i^x(t) = \frac{AC_i}{\lambda_i} (E_i^x) (1-e^{-\lambda_i t}) \quad (8)$$

Summing the secondary radiation contribution for each nuclide present in the waste yields the total absorbed dose due to secondary radiations.

Determination of the gamma absorbed dose (E_i^γ) is more complex than calculating the beta absorbed dose because the total energy of the gamma emission may not be deposited in the waste form. The fraction of gamma energy deposited is a function of the waste's physical characteristics and waste container geometry. The gamma energy absorbed by the waste is calculated for each nuclide present using

$$E_i^\gamma = (\sum_j)(n_{ij})(f_{ij})(E_{ij}^\gamma) \quad (9)$$

where

E_i^γ = the gamma energy absorbed in MeV for the i^{th} nuclide

\sum_j = the summation of the fractions of the gamma ray energies absorbed

for all gamma emissions of the i^{th} nuclide.

n_{ij} = the abundance of the j^{th} gamma ray per decay of the i^{th} nuclide.

f_{ij} = the fraction of energy, of the j^{th} gamma ray of the i^{th} nuclide that is absorbed in the waste.

E_{ij}^γ = is the energy in MeV, of the j^{th} gamma ray of the i^{th} nuclide.

Example:

Cobalt 60 decays by emitting two gamma rays, 1.173 MeV and 1.332 MeV, both having an abundance of 1.0. The nuclide is present in waste with a density of 1 g/cm³ contained in a 55 gal. drum.

For the 1.173 MeV gamma ray

$$n_{ij} = 1.0, f_{ij} = 0.55, \text{ and } E_{ij}^\gamma = 1.173 \text{ MeV} \quad (10)$$

For the 1.332 MeV gamma ray

$$n_{ij} = 1.0, f_{ij} = 0.53, \text{ and } E_{ij}^\gamma = 1.332 \text{ MeV} \quad (11)$$

$$E_i^\gamma = (1.0)(0.55)(1.173 \text{ MeV}) +$$

$$(1.0)(0.53)(1.332 \text{ MeV}) = 1.351 \text{ MeV}$$

Therefore, of the 2.505 MeV emitted in the gamma decay of cobalt 60, 1.351 MeV is absorbed by the waste.

Values for n_{ij} and E_{ij}^γ were obtained from Ref. 5. Values for f_{ij} can be computed by the methods outlined in Appendix B and C⁶, or from Figures A-1 through A-4 in Appendix A⁶.

The contribution to absorbed dose from gamma ray emission for each nuclide in the waste is

$$D_i^\gamma(t) = \frac{AC_i}{\lambda_i} (E_i^\gamma)(1-e^{-\lambda_i t}) \quad (12)$$

Combining the beta, secondary, and gamma absorbed doses for each nuclide yields

$$D_i^{\beta+x+\gamma}(t) = \frac{AC_i}{\lambda_i} (\bar{E}_i + E_i^x + E_i^\gamma)(1-e^{-\lambda_i t}) \quad (13)$$

This is the absorbed dose in rads in the waste at time, t, due to the decay of the i^{th} nuclide. The process must be repeated for all nuclides present in the waste to arrive at the total absorbed dose at time t after sealing.

$$D_{\text{total}}(t) = \sum_i D_i^{\beta+x+\gamma}(t) \quad (14)$$

Free Volume of the Container

The free volume of the container is the sealed internal container volume not occupied by the waste

^c This is an approximate value, the value used is 0.1817 MeV from Ref. 5.

free volume = internal container volume - waste volume.

The waste itself may contain interstitial voids that can be included in the free volume. The interstitial voids can be expressed as a void fraction of the waste. The void fraction can be determined from the bulk and true densities of the waste. Values for these properties are available for organic resins from vendor-supplied information

$$\text{void fraction} = \frac{\text{true density} - \text{bulk density}}{\text{true density}}$$

Void fractions for mixed systems, such as cation and anion resins, can be approximated using weight percentages of each component

$$\text{free volume} = (\text{internal container volume} - \text{waste volume}) + (\text{waste volume} \times \text{void fraction})$$

The free volume for solidified waste is the internal container free space over the solidified waste. Credit for internal voids can be taken if the porosity of the solidified mixture is known or can be calculated.

Gas Generation Constants, Absorbed Dose, and Allowable Hydrogen Concentration

The three components of the combustible gas generation calculation can be assembled to predict hydrogen volume at a given time. Combining the equations developed in previous sections yields

hydrogen volume = G-factor x total absorbed dose x mass of waste x constant.

This equation is expressed mathematically as

$$V_H = G_H \times D_{\text{total}} \times M_W \times 2.33 \text{ E-06 eV, cm}^3/\text{rad gram molecule} \quad (15)$$

The proportionality constant, 2.33 E-06 eV, cm³/rad gram molecule is determined from

$$\frac{100 \text{ Erg/gram}}{\text{rad}} \times \frac{6.25 \text{ E+11 eV}}{\text{Erg}} \times \frac{1 \text{ gram mole}}{6.02 \text{ E+23 molecules}} \times \frac{22.4 \text{ liters}}{\text{gram mole}} \times \frac{1000 \text{ cm}^3}{\text{liter}} = 2.33 \text{ E-06 eV, cm}^3/\text{rad gram molecule} \quad (16)$$

The total absorbed dose is a function of time.

NOTE: The G-factor, G_H , is expressed as $\frac{\text{molecules}}{100 \text{ eV}}$

The hydrogen concentration is obtained by dividing the hydrogen volume (V_H) by the free volume of the waste container (V_F).

SAMPLE PROBLEM

The sample problem presented below uses data from NUREG/CR-2830³ on a high level reactor cleanup resin shipped from the Vermont Yankee Plant in 1980, for isotopic activity density values.

Worksheets 1 and 2 below have been completed from the data and information in the tables and graphs included in this paper. For actual utility application, the plant records and vendor information would be used. This method is valid for both dewatered resins and solidified wastes.

Gamma Fraction Absorbed

The graph presented below in Fig. 2 is for a 55-gal. drum, which expresses the gamma absorbed energy fraction as a function of container geometry, waste density and gamma ray energy. Graphs for other typical size containers are included in Ref. 6, Appendix A. This graph provides the values for Worksheet 2, Column e. The gamma ray energy(s) for column c of Worksheet 2, were obtained from data tables in Ref. 5. Use this energy (column c) to find the gamma fraction absorbed by intercepting the density line closest to the waste's density^a from Step 5 Worksheet 1. Read the fraction on the y axis and place value in column e Worksheet 2. In the example problem, the waste density from Worksheet 1, Step 5 is 0.78 g/cm³ so the 0.8 g/cm³ line is used. For example, a 1-MeV gamma would be 0.48 absorbed. This graph is valid for both resin and solidified wastes.

Absorbed Dose Calculation

The absorbed dose is calculated for each nuclide (individually) using the information from Worksheets 1 and 2. The calculation is performed for several chosen times after sealing the container. The dose to the waste from each nuclide at a chosen time is then summed to give a total absorbed dose at that time. For low-level waste, good choices for time intervals are 5 = 1, 5, 10, and 20 years. If the calculated total dose for a time interval exceeds the value of step 12, Worksheet 1, the 5% hydrogen concentration level has been exceeded.

For each nuclide, the absorbed dose equals

$$\frac{AC_i}{\lambda_i} (\bar{E}_i + E_i^x + E_i^y) (1 - e^{-\lambda_i t}) \quad (17)$$

In the columnar notation of Worksheet 2

$$\frac{Aa}{\lambda_i} (g + h + f) (1 - e^{-bt}) \quad (18)$$

where the constant $A = 1.86 \text{ E+10} \frac{\text{rad gram}}{\text{MeV/year/curie}}$

$$\text{From } \frac{\text{rad}}{(100 \text{ erg/g})} \times \frac{1.6 \text{ E-12 erg}}{(\text{eV})} \times \frac{\text{E+06 eV}}{(\text{MeV})} \times$$

$$\frac{3.7 \text{ E+10 D/s}}{(\text{curie})} \times \frac{3.15 \text{ E+07 s}}{(\text{year})} \quad (19)$$

WORKSHEET 1

| Step | Variable | Value |
|------|--|-----------------------------------|
| 1. | Volume of waste container (ft ³ x 2.83 E+04 cm ³ /ft ³) | 1.83 E+05 cm ³ |
| 2. | Heights (interior) of waste container | 72 cm |
| 3. | Radius (interior) of waste container | 27 cm |
| 4. | Volume of waste (ft ³ x 2.83 E+04 cm ³ /ft ³) | 1.65 E+05 cm ³ |
| 5. | Bulk density of waste (lbs/ft ³ x 1.6 E-02 g cm ³ /lb/ft ³) | 0.78 g/cm ³ |
| 6. | True density (specified gravity) of waste | 1.3 g/cm ³ |
| 7. | Mass of waste (Step 4 x Step 5) | 1.29 E+05 g |
| 8. | Radiolytic hydrogen generation constant, G _H (See attached Table 1) | 0.3 molecules/100 eV ^a |
| 9. | Waste void space (expressed as a decimal) (Step 6 - Step 5)/Step 6 | 0.40 |
| 10. | Free volume (Step 1 - Step 4) + (Step 9 x Step 4) | 8.4 E+04 cm ³ |
| 11. | Maximum allowable hydrogen volume (0.05 x Step 10) | 4.2 E+03 cm ³ |
| 12. | Absorbed Dose for Step 11 (Step 11/(Step 8 x Step 7 x 2.33 E-06)) | 4.7 E+06 RAD |

a 0.65 percent cation G_H = (0.65 x 0.13 + 0.35 x 0.6)
 0.35 percent anion G_H = 0.3

WORKSHEET 2

| Column | | a | b | c | d | e | f ^a | g | h |
|-------------------|--------|------------------|----------------|---|---|--|--|---|--|
| Nuclide | Curies | Activity Density | Decay Constant | Gamma Energy | Abundance | Percent Absorption | E _i ^γ | E _i | E _i ^x |
| Mn-54 | 0.770 | 5.98 E-06 | 0.809 | 0.835 | 1.0 | 0.51 | 0.430 | 0.0 | 0.0052 |
| Co-58 | 0.757 | 5.88 E-06 | 3.575 | 0.811 1.675 0.511 | 1.0 0.0054 0.299 | 0.51 0.44 0.53 | 0.410 0.0040 0.081 | 0.0290 -- -- | 0.0053 -- -- |
| Co-60 | 3.93 | 3.05 E-05 | 0.1315 | 1.173 1.332 | 1.0 1.0 | 0.48 0.47 | 0.560 0.630 | 0.0958 -- | -- -- |
| Zn-65 | 2.61 | 2.03 E-05 | 1.036 | 1.115 0.511 | 0.508 0.0283 | 0.48 0.53 | 0.270 0.0077 | 0.0020 -- | 0.0077 -- |
| Cs-134 | 2.29 | 1.78 E-05 | 0.336 | 0.475 0.567 0.605 0.797 1.039 1.168 1.365 | 0.0146 0.238 0.976 0.941 0.0100 0.0180 0.0304 | 0.53 0.52 0.52 0.51 0.49 0.48 0.47 | 0.0037 0.070 0.307 0.382 0.005 0.010 0.020 | 0.157 -- -- -- -- -- -- | 0.0055 -- -- -- -- -- -- |
| Cs-137/ Ba-137 | 6.24 | 4.84 E-5 | 0.023 | 0.662 | 0.8998 | 0.52 | 0.310 | 0.171 | 0.0657 |

^a f = c x d x e.
 a = Ci/mass of Waste (Worksheet 1 Step 7).

b, c, d, g, h; Table A-1⁶
 e, Figure A-1 through A-4⁶, fraction of a gamma energy absorbed. (Fig. 2-this paper).

GAMMA ABSORPTION

(55 Gal-7.5 CuFt Drum)

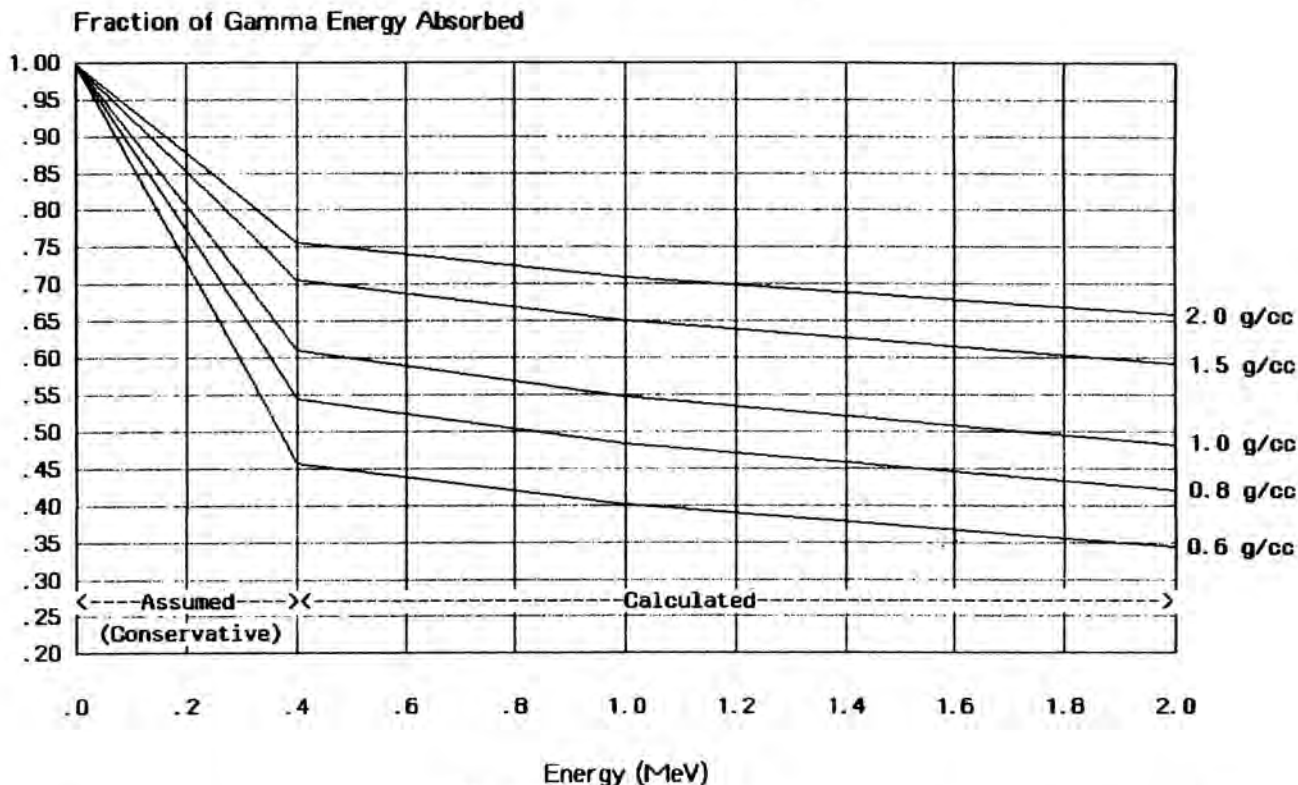


Fig. 2. Gamma Absorption.

Solving for t = 1 year

$$\text{Mn-54: } D_{\text{abs}} = (1.86 \text{ E}+10)(5.98 \text{ E}-06)(0.0052 + 0.430)(1-\exp-0.809)/0.809 = \underline{3.32 \text{ E}+04 \text{ rad}} \quad (20)$$

$$\text{Co-58: } D_{\text{abs}} = (1.86 \text{ E}+10)(5.88 \text{ E}-06)[0.029 + 0.0053 + (0.410 + 0.004 + 0.081)](1-\exp-3.575)/3.575 = \underline{1.57 \text{ E}+04 \text{ rad}} \quad (21)$$

$$\text{Co-60: } D_{\text{abs}} = (1.86 \text{ E}+10)(3.05 \text{ E}-5)(0.0958 + 0.560 + 0.630)(1-\exp-0.1315)/0.1315 = \underline{6.84 \text{ E}+05 \text{ rad}} \quad (22)$$

$$\text{Zn-65: } D_{\text{abs}} = (1.86 \text{ E}+10)(2.03 \text{ E}-05)(0.0020 + 0.0077 + 0.270 + 0.0077)(1-\exp-1.036)/1.036 = \underline{6.75 \text{ E}+04 \text{ rad}} \quad (23)$$

$$\text{Cs-134: } D_{\text{abs}} = (1.86 \text{ E}+10)(1.78 \text{ E}-05)(0.157 + 0.0055 + 0.0037 + 0.070 + 0.307 + 0.382 + 0.005 + 0.010 + 0.020)(1-\exp-0.336)/0.336 = \underline{2.70 \text{ E}+05 \text{ rad}} \quad (24)$$

$$\text{Cs-137/Ba-137: } D_{\text{abs}} = (1.86 \text{ E}+10)(4.84 \text{ E}-05)(0.1708 + 0.0657 + 0.31)(1-\exp-0.023)/0.023 \quad (25)$$

The total absorbed dose at 1 year after sealing is

$$D(1 \text{ yr}) = 3.32 \text{ E}+04 + 1.57 \text{ E}+04 + 6.84 \text{ E}+05 + 6.75 \text{ E}+05 + 2.70 \text{ E}+05 + 4.86 \text{ E}+05 \text{ Total} = \underline{1.55 \text{ E}+06 \text{ rad}} \quad (26)$$

Solving in the same manner for t = 5 years

| | |
|----------------|---------------|
| Mn-54: | 5.88 E+04 rad |
| Co-58: | 1.62 E+04 rad |
| Co-60: | 2.67 E+06 rad |
| Zn-65: | 1.04 E+05 rad |
| Cs-134: | 7.70 E+05 rad |
| Cs-137/Ba-137: | 2.32 E+06 rad |

(27)

The total absorbed dose 5 years after sealing is

$$D_{\text{Total}}(5 \text{ yrs}) = \underline{5.94 \text{ E}+06 \text{ rad}} \quad (28)$$

^c If the waste density differs from the plotted values use the density line that is greater but closest to the actual waste density. More exact values for the gamma fraction absorbed as a function of density can be obtained using the methods outlined in Appendix C, 6.

To find the approximate time when 5% hydrogen concentration occurs, a graphical technique using Worksheet 1 and the calculated absorbed dose is used.

Hydrogen Concentration Graphical Solution

Hydrogen concentration is graphed versus time using the 1- and 5-year doses with the values from the steps in Worksheet 1.

$$H_2 = \frac{D_{\text{Total}} \times \text{Step 7} \times \text{Step 8} \times 2.33 \text{ E-06} \times 100\%}{\text{Step 10}} \quad (29)$$

For 1 year: percent $H_2 = (1.56 \text{ E+06})(1.29 \text{ E+05})$
 $(0.3/100)(2.33 \text{ E-06})(100\%)/8.4 \text{ E+04} = 1.67\%$

For 5 years: percent $H_2 = (5.93 \text{ E+06})(1.29 \text{ E+05})$
 $(0.3/100)(2.33 \text{ E-06})(100\%)/8.4 \text{ E+04} = 6.38\%$

These values are plotted on a graph shown in Fig. 3. The graph predicts 3.7 years to produce 5% hydrogen. To verify, set $t = 3.7$ years and calculate D_{Total} . The value is found to be 4.73 E+06 rads, slightly higher than the total Step 12 value of 4.7 E+06 rads.

Calculating the percentage $H_2 = (4.73 \text{ E+06})(1.29 \text{ E+05})(0.3/100)(2.33 \text{ E-06})(100\%)/(8.9 \text{ E+04})$
 $= 5.08\%$

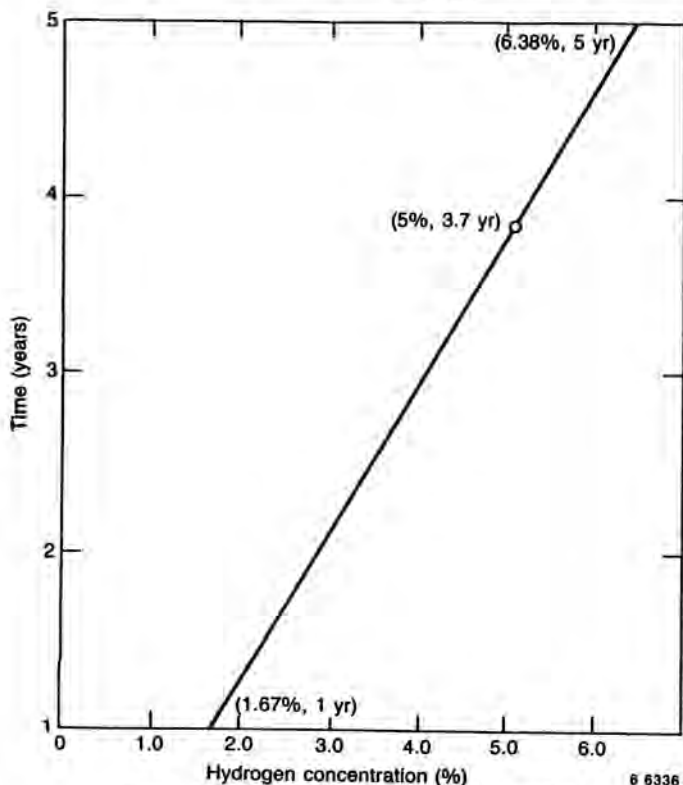


Fig. 3. Hydrogen Concentration Values.
COMPUTER APPLICATION

The most desirable approach to solving this type of problem is through the use of computers. The information from Worksheet 2 is placed in the computer

memory along with the waste density (Step 5 of Worksheet 2) the container type, and constant $A = 2.33 \text{ E-06}$. The computer iterates the equation

$$\text{Absorbed dose} = \frac{Aa}{b} (g + h + f)(1 - e^{-bt}) \quad (30)$$

For values of time (t) until the absorbed dose of Step 12 Worksheet 1 is reached, yielding the time to produce a 5% hydrogen concentration.

Considering the number of variables and the complexity of the calculation, a shielding computer code (QAD-FN) was used to determine the absorbed dose in different container geometries with various waste forms. The code was modified to calculate the waste's internal absorbed dose. This was accomplished by locating the modeled detector points inside the container waste matrix.

The computer calculates the absorbed gamma dose by evaluating the dose received at up to 200 detector subvolumes as the result of irradiation by a maximum of 1 E+06 source subvolumes. The detector subvolume gamma absorbed doses are summed to yield the wastes total absorbed gamma dose. Several assumptions are made:

- The container is full to the normal fill point
- The waste is of uniform density
- Gamma absorption constants are generated using energy absorption coefficients for water
- The nuclides are uniformly distributed in the waste matrix.

A more detailed description of the computer code model and its application is provided in Appendix C of Ref. 6, and is the subject of a companion paper and presentation.

EPICOR GAS MEASUREMENTS VERSUS CALCULATIONAL METHOD RESULTS

An important element in the overall program to justify use of a calculational technique to predict radiolytic gas generation was the need to benchmark theoretical predictions against actual gas measurements in representative waste packages. Although there has been considerable research in this area (nearly all published by the NRC), most of the published work in the U.S. has been directed toward laboratory scale investigations to determine the constants for gas generation as a function of deposited energy (e.g., the G-value), or to assess the effects of organic resin degradation under high integrated radiation doses. There has been little study, however, of actual size and similarly configured waste packages representative of nuclear utility wastes.

The exception to this was the work done by EPRI at TMI-2 with the experience gained during shipment of the EPICOR II prefilters and submerged demineralizer system (SDS) zeolite liners. Although the hydrogen generation characteristics for each of these waste forms had been evaluated and published (Refs. 1, 2, 3, 4), the applicability of the reported hydrogen generation rates were questioned due to the higher curie loading in relation to normal power plant resin waste. The SDS liners were considered to be too highly loaded with Cs and Sr for direct use in benchmarking the EG&G Idaho model, however, it was

felt that the EPICOR II prefilters might offer sound operational data on hydrogen generation rates for use by EG&G Idaho in validating the current calculational technique.

Consequently, it was determined that an in-depth review of actual gas measurement data from TMI-2 dewatered resin waste, particularly the EPICOR II prefilters, would be undertaken with the following objectives:

1. Assess the reported EPICOR II hydrogen generation data
2. Determine, if possible, the hydrogen generation rate in EPICOR II prefilters by methods independent of the techniques used in Preparations to Ship EPICOR II Liners (Ref. 7)
3. Assess the linearity of long-term average hydrogen generation rates as a function of deposited curies in order to extrapolate to curie loadings more representative of utility wastes
4. Summarize the available measurements of hydrogen gas in EPICOR II prefilters for use to benchmark the EG&G calculational model
5. Develop a simple computer program that could accurately predict the generation of gases in representative waste containers.

EPRI demonstrated the use of this calculational method at TMI-2. EPRI used a desk top computer with a spreadsheet program to compare the predicted hydrogen concentration from the EG&G Idaho calculational method to the hydrogen concentration actually measured when the EPICOR II liners were vented during their preparation for shipment, after nearly three years of storage on site. It was suspected that many of the 50 EPICOR II prefilters would be unable to completely contain the buildup of internal gases, due to small leaks in gasket materials, penetration seals, etc. In order to differentiate between leaking and nonleaking liners for the purpose of performing hydrogen correlation studies, an opening gas pressure of 0.2 psig was used to define a nonleaking liner. Using this definition, 28 liners were considered to be nonleaking and therefore suitable for detailed investigation. On the average, the predicted hydrogen gas concentrations were within 20% of the measured values.

A more detailed description of the work done with the actual EPICOR II gas measurements and validation of the calculational method is the subject of a companion paper and presentation.

CONCLUSIONS

There have been numerous discussions as to whether the combustible gas generation problem is applicable to typical commercial nuclear power plant radioactive wastes, as with the TMI-2 EPICOR experience. Recent information has indicated that although the total absorbed dose is higher for EPICOR type waste, the energy deposition rates for typical nuclear power plant primary system resin wastes and similar to the TMI-2 EPICOR waste. Thus, the same degree of accuracy can be achieved in predicting gas production in nuclear power plant waste. (See Figs. 4 and 5.)

The acceptance of the calculational method by the NRC to comply with I&E Notice No. 84-72 requirements will not only satisfy safety concerns, but will also provide nuclear power utilities with savings both in dollars and manrem.

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(10 Ci/Ft³ Co-60 vs. 30 Ci/Ft³ Cs-137)

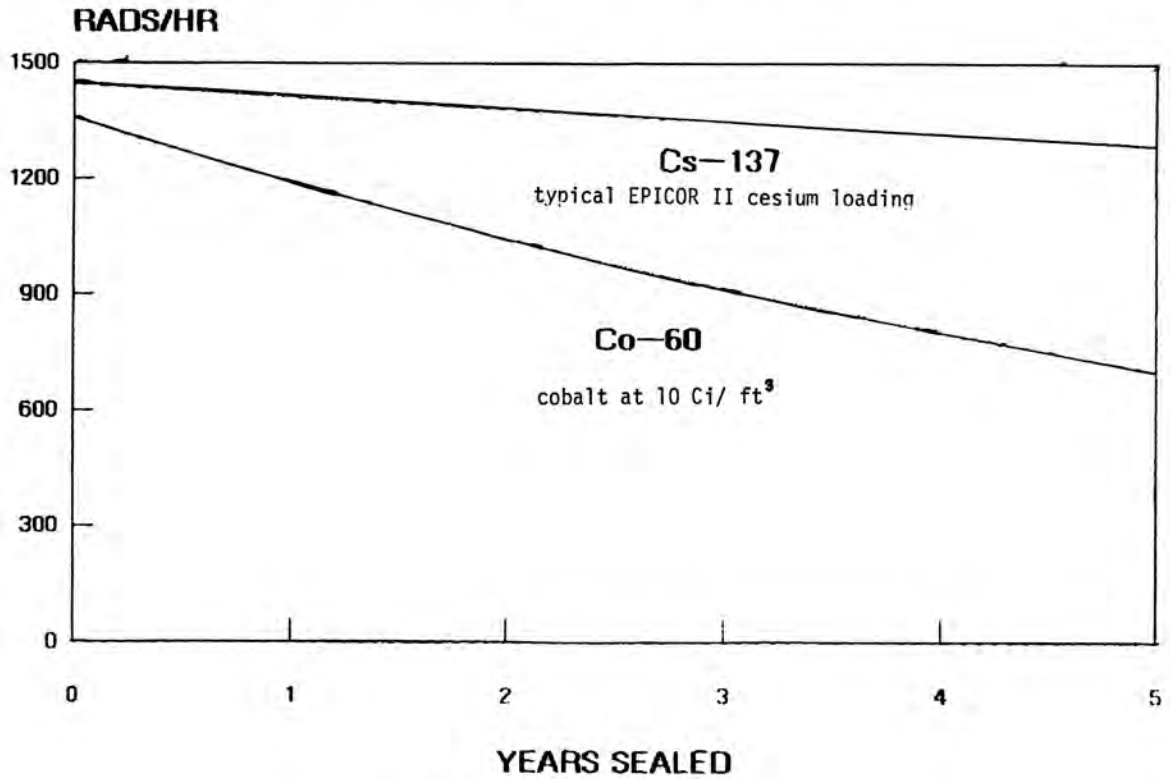


Fig. 4. Dose Rate Comparison.

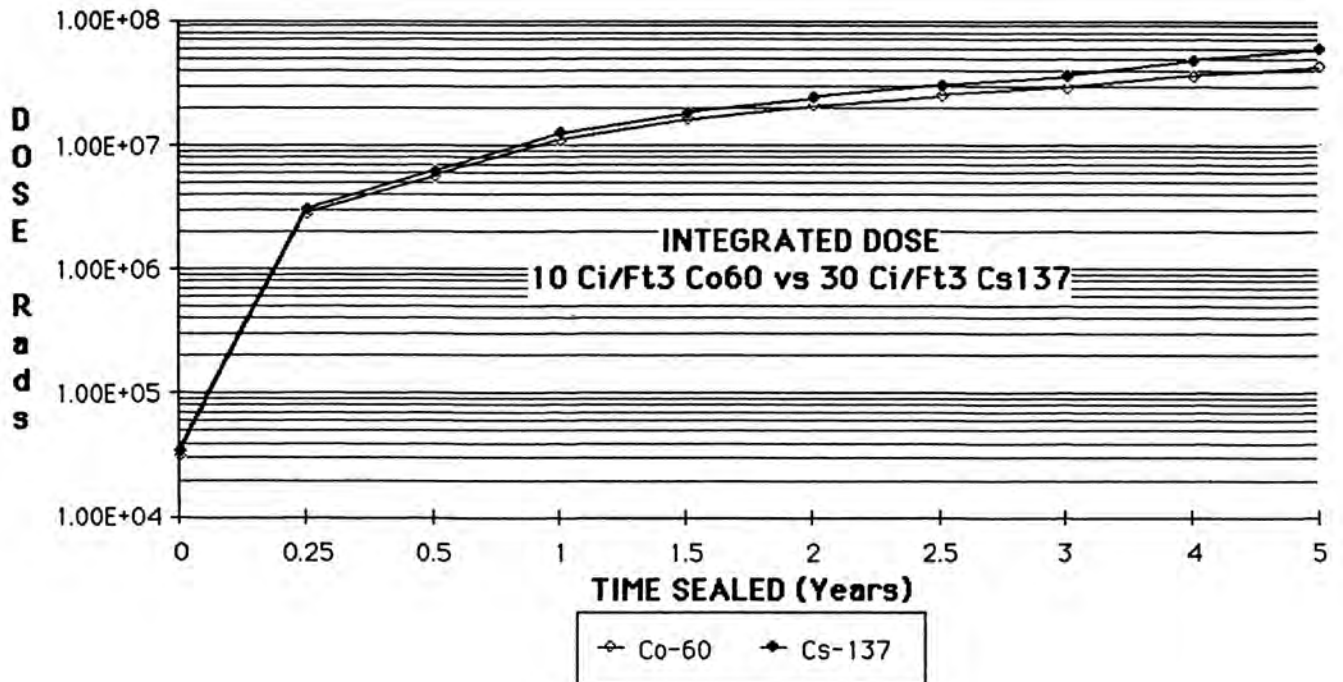


Fig. 5. Integrated Dose.