A HIGH INTEGRITY PACKAGE FOR TRITIATED LIQUID WASTE

R. E. O'Brien, J. Krieger, G. Anderson, A. D'Urso
New England Nuclear
Boston, MA 02118

ABSTRACT

A high integrity container for the shallow land burial of concentrated tritiated liquid waste has been designed. Under worst case conditions the container will not rupture from radiolytically generated gas pressures, will not leak, will withstand corrosion from internal and external forces and will be structurally stable for >250 years.

INTRODUCTION

New England Nuclear Corporations's (NEN) manufacturing operations results in ~48,000 Ci/year of concentrated tritium waste in a liquid form. An extensive review[1] of NEN's waste forms by Brookhaven National Laboratories determined that NEN's present waste package for concentrated tritiated liquid waste would comply with the proposed Federal Regulation 10CFR61[2]; however, they expressed a number of concerns pertaining to containment. They suggested that radiolytically generated gas (HT) could be produced in sufficient quantities to cause rupture of the inner hermetically sealed bulb, possibly resulting in free access of radioactive materials to the environment. NEN has accepted these concerns and has developed a new package for concentrated liquid waste that accomplishes the implicit goals of 10CFR61 - - i.e. non-movement of radioactivity into the environment expressed as 300 year stability.

For the NEN package to be stable for >250 years, the time required to reduce the tritium radioactivity to 0.00037% of the original amount, the following requirements were identified. It must:

Not Rupture
Not Leak
Not Corrode (internally or externally) and maintain structural stability.

THE NEW PACKAGE

We propose that a waste bulb of 120 ml volume made from thick walled (47.6 mm) pyrex glass be used as an initial transfer container. This bulb will be hermetically sealed. Each bulb will be filled with the quencher/absorbent, Dri-Zit[a] (40 g) (Fig. 1).

a. Dri-Zit is an attapulgite clay product of Waverly Mineral Products Co.

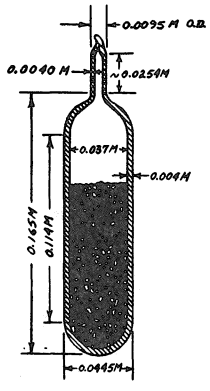

Fig. 1. Glass Container

The bulb will be contained in an aluminum (606IT-6) cannister (0.3175 cm wall thickness, 1809 ml volume) with T.I.G. welded end-caps. The cannister free space will be filled with Dri-Zit (951 g). The cannister will be considered the primary container for the waste (Fig. 2).

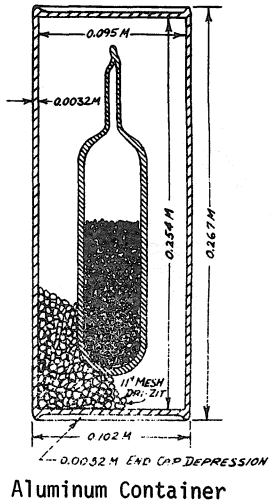

Fig. 2 Primary Aluminum Container

Sixty cannisters will be loaded into a 208 liter stainless steel (304 L, 62.5 mm wall thickness) drum with a welded lid.

The 208 liter drum will have an approximate radioactivity content of 3000 Ci and an approximate weight of 281.1 kg.

THE RATIONALE

Protection from Rupture

The package is designed for the worst case situation defined as 10 ml methanol containing 100 Ci of tritium. Experiments have shown (Table I) that this mixture, when sorbed onto Dri-Zit (40 g) will generate 8.28 MPa of pressure at infinite time (P_∞)

Table I - Total Radiolysis Pressures

Experiment	Mass Fraction	G total (molecules/ 100 ev)	$P_\infty tot^a$ (MPa)
1. 10 ml MeOH	1	4.4	21.4
2. 10 ml MeOH 15 g Dri-Zit	.344	2.9	14.5
3. 10 ml MeOH 40 g Dri-Zit	.164	1.5	7.6
4. 10 ml MeOH 60 g Dri-Zit	.116	1.7	8.3

a Normalized for 100 Ci and 100 ml void volume.

It has also been determined (Table II) that the 120 ml, thick walled pyrex flask will tolerate up to 6.97 MPa of pressure (called burst pressure).

Table II -

Burst Pressure Determination of Heavy Walled Flask

Flask	MPa
1	7.76
2	5.00
3	5.70
4	8.80
5	7.59
Ave.	6.97 ± 1.29

Inspection of the fragments after bursting showed breakage at the Kovar seal - glass to metal fusion.

Accepting a 7/1 relationship to adjust for stress fatigue rupture pressures of 1.04 MPa are calculated to appear in 2.5 years.

Experiments have shown that the aluminum cannister has a burst pressure of 3.90 MPa (Table III).

Table III

Burst Pressure Determination of Aluminum Cannister

Cannister	Burst Pressure MPa
1	4.14
2	3.80
3	3.80
Ave.	3.9 ± 0.15

Inspection of the fragments showed destruction only at the welds on the end-caps.

In the event of free access of the gas into the cannister either by rupture or leak, the pressure in the cannister is calculated to be 0.72 MPa at P_∞. An approximate 5 fold excess capacity exists, then, between the burst pressure of the cannister and the P_∞.

A bulb pressurized to rupture inside a specially constructed aluminum cannister (Fig. 3) showed that the cannister withstood the force of the rupture (Table IV), and that, after a brief pressure stabilization period, no gas leakage occurred.

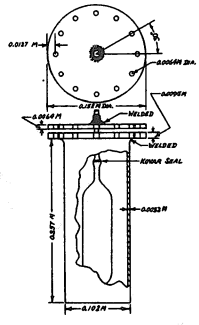

Fig. 3. Areas marked A & B filled with Dri-Zit as described.

Table IV

Cannister Integrity After Internal Rupture of Bulb

Run #	Burst Pressure (MPa)	Visual Inspection
1	5.87	Pressure dropped to 0.28 MPa. In 5 mins. it fell to 0.18 MPa. No visible damage to aluminum.
2	9.67	Pressure dropped to 0.69 MPa then in 5 mins. to 0.28 MPa. No visible damage to aluminum.
3	6.90	Pressure dropped to 0.58 MPa then in 5 mins. to 0.21 MPa. No visible damage to aluminum.
	Ave. 7.48 ± 1.79	

This latter experiment demonstrates that the cannister can accept this type of rupture without escape of the contents.

Protection from Permeation

Aluminum and stainless steel have been shown to have a low permeability to tritium gas[3]. Two mechanisms for release to the environment are envisioned. These are by a sequential diffusion first through the aluminum and then the steel or by leakage through cracks in the welds in both containers. Any combination of these events can potentially result in release to the environment.

The permeation (f) of gas[3] through the aluminum cylinder walls, in the absence of weld cracks, is given by

$$f\ (cc/yr.) = \frac{A}{t}\left[(P\infty(1-e^{-\lambda t}))^{1/2}-1\right]p \cdot \frac{}{3.15 \times 10^{7}\ sec./yr.} \qquad (A)$$

Where: p = permeability of hydrogen through aluminum

$(cc \cdot cm^{-1} \cdot s^{-1} \cdot atm^{-1/2})$

A = Area (cm^2)

t = Thickness (cm)

P∞ = Maximum pressure of gas generated (Atm.)

λ = Tritium decay constant

Permeation by tritium gas (Φ) can be expressed by conversion of the equation to:

$$\Phi\ (curies/yr.) = \frac{A}{t}\left[(P\infty(1-e^{-\lambda t}))^{1/2}-1\right] \cdot p \cdot 3.15 \times 10^{7}\ sec./yr. \cdot 2 \cdot 4e^{-\lambda t} \cdot Co \qquad (B)$$

where Co is a conversion factor for the specific activity of the radiolytically generated gas.

A graphical representation of both equations is shown in Fig. 4.

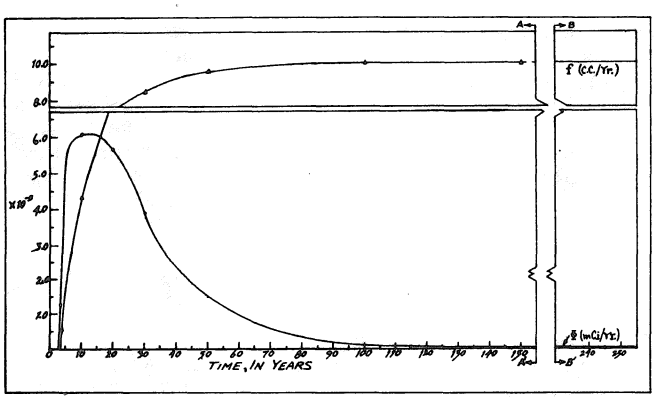

Fig. 4. Permeation of gas through aluminum cylinder walls.

For the worst case situation, 100 Ci Tritium in 10 ml methanol, the specific activity of the Tritium is 100 mCi/mAtom of hydrogen (Co = 0.003) and, assuming complete mixing of tritium and hydrogen, the total amount of tritium permeating each cannister for >250 years is 2.2 μCi's. Sixty cannisters, the total number in a barrel, will permeate 132 μCi's in this period of time.

The stainless steel barrel constitutes the second barrier to environmental release. The maximum volume of gas added to the barrel by permeation from 60 containers is 7×10^{-4} ml. Since the contribution of permeated gas to the void volume of the barrel (105L) is small, negligible quantities of gas are expected to permeate the barrel, and, thus, there should be negligible release to the environment by permeation.

It is the integrity of the welds, then, that is the significant factor in assuring no release to the environment. Of the welded configurations shown in Fig. 5, C and D are considered[4] the most readily inspectable by ultrasound techniques.

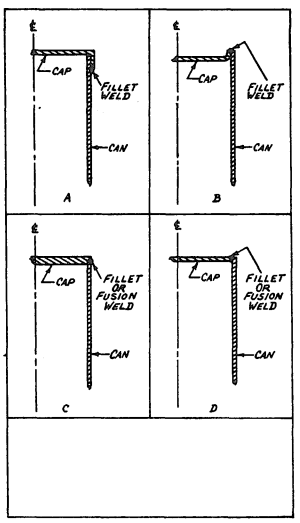

Fig. 5. Possible Weld Configurations

A & B - Not Inspectable
C & D - Inspectable by ultrasonic techniques

Imperfections in the weld can be of 2 types. These are pores through which gas can diffuse and cracks or holes which, under stress and over time, can deteriorate to separate the weld. The critical flaw size, the diameter of a hole which stress will cause to deteriorate, for configuration D, Fig. 5, has been calculated[5] to be equal to the thickness of the weld (3.18 mm). The sensitivity of ultrasound inspection of the weld has been determined to be 0.79 mm in hole diameter. However, to ensure no pores or plastic deformation, ultrasound inspection will be used to evaluate and signal for repair those welds having imperfections prior to acceptance. Also it is considered unlikely[4] that pores <0.79 mm will extend 3.18 mm in length; the thickness of the weld.

Protection from Corrosion

Considerable evidence exists in the literature to justify 304L stainless steel (62.5 mm) as a suitable material for use as a water impenetrable barrier. This information is thoroughly reviewed in a report[3] by E. P. Gause and co-workers at Brookhaven National Laboratories. It is their conclusion that AISI 304L, 625 mm thick stainless steel constitutes an effective barrier to water penetration with an expected lifetime of >250 years at which time the radioactivity would be at 0.00037% of the original amount. Welded seals acceptable by ultrasound inspection will assure noninvasion through cracks or holes.

DISCUSSION

The proposed package has 3 components which are a) a hermetically sealed, thick walled glass bulb which will act as a temporary vehicle for transferring the waste from the point of generation to the primary container; b) which is a 606IT 31.8 mm aluminum cylinder with ultrasound tested welded end-caps. Sixty aluminum cylinders are fitted into a 62.5 mm 304 L stainless steel 208 liter drum with an ultrasound tested welded lid as the secondary container acting also as a barrier to corrosion. This package will release negligible tritium to the environment by permeation or leakage, will not corrode, and will maintain structural stability.

EXPERIMENTAL SECTION

Tritium Radiolysis Studies of Methanol Containing Waste

The total hydrogen pressure resulting from the radiolysis of 10 ml methanol containing 100 Ci of tritium in 50 ml aste bulbs has been estimated as 39.7 MPa[1] using a G value for hydrogen generation from methanol of 5.4[6] molecules per 100 ev of radiation absorbed. The radiolysis of organic waste, in particular octane and pump oil, absorbed on vermiculite has been measured under conditions of γ and α-radiation and these values extrapolated to estimate gas generation from tritium β-radiolysis of absorbed organics[7].

The total pressure of hydrogen generated is directly proportional to the dose rate I, the initial activity present Ci, and the G value for hydrogen generation G (H_2) and inversely proportional to the void

$$P\ (H_2)\ \text{atm} = \frac{RT.}{NV} \cdot \frac{G\ (H_2)}{100} \cdot \frac{Ci^{\circ}\ I}{\lambda} \qquad (C)$$

volume of the bulb V. The gas generated in the β-radiolysis of methanol under conditions simulating the waste package is comprised primarily of hydrogen with contributions from methane and carbon dioxide as well. The relative percentages of the gaseous components have been determined. The quantity of interest, however, is the total gas pressure, regardless of the nature of the gas. Consequently the G values for total gas production, rather than just hydrogen, have been derived experimentally.

Results & Discussion

The pressure of radiolysis normalized for a volume of 100 ml and 100 Ci are presented in Table I. Pressure decreases are observed in the presence of Dri-Zit. Bibler and Overbaugh[7] have observed a linear dependence between the G values resulting from γ-radiolysis of organics and the mass fraction of organics radiated. The physical significance of the linear dependence is that only the energy absorbed by the organics leads to gas generation. The energy absorbed by the inert absorbent is quenched. In the experiments conducted with simulated tritium waste a decrease in G value (and pressure) is observed with decreasing mass fraction. The apparent high G value in experiment 4 we attribute to the observation that the methanol is not evenly distributed throughout the entire mass of absorbent. Consequently, only a fraction of the absorbent is available to intercept the radiation.

The total gas mixture has been separated into its constituent components by gas chromatographic analysis. These results are tabulated in Table V.

Table V

Gas Composition

Run	Percent Composition		
	H_2	CH_4	CO_2
1. 10 ml MeOH	91	9	
2. 10 ml MeOH 15 g Dri-Zit	92	8	
3. 10 ml MeOH 40 g Dri-Zit	62	5	33

Mixtures of hydrogen, methane and, in one case CO_2 were observed. Carbon dioxide was detected from the run in which water-^3H was used as the source of the tritium.

Apparatus & Pressure Measurements

A manifold with a known void volume and a sealed in mercury manometer was used to conduct the radiolytic gas generation experiments. All experiments were conducted in an evacuated system and allowed to continue until atmospheric pressures were reached. Periodically gaseous samples were removed for gas chromatographic analysis. Pressure measurements were made at 24 hr. intervals and are corrected for the vapor pressure of methanol and temperature.

[Carbon-T] methanol was used for runs 1 and 2 and methanol and T_2O for run 3.

Gas composition was determined by gas chromatography on a 8' x 1/4" Porapack Q column at 70 ml/min. flow, temperature programmed at 50°C for 2 min., 32°C/min. to 150°C.

Data Treatment

Calculation of G-values

G-values, the number of molecules of gas produced per 100 ev of energy absorbed, were calculated from the slope of pressure - time plots in accord with eq. E.

$$G_{atm}\ (total) = \frac{S \cdot V \cdot N \cdot 100}{R \cdot T \cdot 760 \cdot I \cdot Ci_0} \qquad (E)$$

where $= \frac{1.8 \times 10^2 \cdot V \cdot S}{Ci_0}$

S = initial slope in mm (hg) per day

V = void volume in l

N = Avogadro's number = 6.02×10^{23} mol cules·mole^{-1}

R = Gas constant=8.16×10^{-2} atm.l·mole^{-1} ·K^{-1}

T = Temperature in degrees kelvin = 298

760 = Conversion factor for mm (Hg) to atm.

I = dose rate=3.7×10^{10} dis. sec^{-1} Ci^{-1}

·8.64×10^4 sec. day^{-1}

·5.69×10^3 ev

= 1.8×10^{19} ev·day^{-1}.Ci^{-1}

and

Ci_0 = initial radioactivity present in Curies

G values calculated in this manner are dependent upon the mass fraction of organics, but independent of the initial activity and void volume. The G values represent the aggregate molecules of gas produced per 100 ev of radiation.

Determination of Final Pressure

The total pressure is calculated from eq. F

$$P^{\infty}_{atm}/total = \frac{RT}{NV} \cdot \frac{G\ (total)}{100} \cdot \frac{Ci_0\ I}{\lambda} \qquad (F)$$

$$= \frac{4.85 \times 10^{-2} \cdot Ci^{\circ} \cdot G\ (total)}{V}$$

where

λ = tritium decay constant = 1.5×10^{-4}/day

Other constants defined above.

The pressure as a function of time is calculated by including the effects of tritium decay as shown in equation (G).

$$P^{t}_{atm} = P^{\infty}_{atm}\ (1 - e^{-\lambda t}) \qquad (G)$$

Burst Pressure Determinations

Burst pressure determinations were conducted by attaching the container through a suitable attachment, a Kovar seal for glass bulb to metal union or 62.5 mm MPT aluminum fitting welded to one end-plate of the aluminum cannister, to a tank of air (13.8 MPa) and continuously applying pressure until rupture. Pressures were recorded from a suitable guage.

Fragments were inspected to determine rupture points. In the case of glass, rupture occurred at the Kovar seal, and for the aluminum cannister, at the welds.

Acknowledgements

The authors gratefully acknowledge the guidance and assistance of Evelyn Gause and Emil Veakis at Brookhaven National Laboratories. We also thank Jane Flaherty of New England Nuclear Corp. for help with the permeation calculations.

REFERENCES

1. E. P. Gause, E. Veakis, and J. Smalley, "Characterization of the Class B Stable Radioactive Waste Package of the New England Nuclear Corporation", NUREG/CR-3018 BNL-NUREG-51607, Oct. 1982.

2. 10CFR Part 61.55 and 61.56.

3. For a comprehensive review on permeation see: E. P. Gause, B.S. Lee, D.R. Mackenzie, and R. Wiswall, Jr. "Alternative Containers for Low-Level Wastes Containing Large Amounts of Tritium", May 1981, BNL-NUREG-29566.

4. Personal Communication, D.A. Wells, Material Engineer, E.I. DuPont de Nemours, Wilmington, Delaware.

5. Personal Communication, E. Perez, Materials Stress Engineer, E.I. DuPont de Nemours, Wilmington, Delaware.

6. G. R. Freeman, "Radiolysis of Alcohols", Actions Chimiques et Biologiques des Radiations, Quartorzieme Serie, M. Haissinsky, Ed. Masson et Cie, Paris P. 73 (1970).

7. N. E. Bibler and E.G. Overbaugh, Savannah River Laboratory, "Radiolytic Gas Production From Tritiated Waste Forms, Gamma and Alpha Radiolysis Studies", DP-1459, July, 1977.