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ABSTRACT

David S. Lee. An Analysis of Hydrogen Gas Generation Specific to Dewatered Ion Exchange Resins in Radioactive Waste Shipment Containers. (Under the direction of Dr. James E. Watson, Jr.)

The analysis of hydrogen gas generation in radioactive waste containers considers the following areas: 1) the radiolytic reaction of water and dewatered ion exchange resins, 2) the parameters associated with the rate of hydrogen generation, and 3) the evaluation of an equation, which determines the rate of hydrogen generation, to aid in compliance with regulatory requirements. The two primary factors needed for the determination of the hydrogen gas generation rate are the total absorbed energy and the hydrogen generation constant, $G(H_2)$. The method developed by EG&G Idaho, Inc. adequately incorporates these two factors. However, there is a degree of uncertainty within this method. At present, the $G(H_2)$ values in the literature do not accurately represent typical resins used in the industry. Variables which affect the $G(H_2)$ have been identified. The degree to which these variables have an effect upon the $G(H_2)$ values is not known.

Studies addressing, 1) diffusion rates of gas from specific containers, and 2) G-values representing resins used within the industry, could lead to better quantification of the concentration of hydrogen gas in waste containers.

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INTRODUCTION

A) Purpose

The purpose of this study is to gain further insight into the subject of hydrogen generation in radioactive waste containers. Specific areas of study are as follows: 1) the radiolytic reaction of water and dewatered ion exchange resins, 2) the parameters associated with the rate of hydrogen generation, and 3) the evaluation of an equation, which determines the rate of hydrogen generation, to aid in compliance with regulatory requirements.

B) Radwaste Shipment Containers

The activity and type of radionuclides present within waste material are determining factors for the selection, preparation, and transportation of waste containers for burial. For example, ion exchange resins and filter media must be stabilized if they contain isotopes with greater than five year half-lives with a specific activity greater than or equal to one microcurie per cubic centimeter. This stabilization may be of two forms; 1) solidified or 2) dewatered in an approved high integrity container (HIC). A HIC is designed to contain waste for approximately 300 years while in a land burial environment. An NRC

approved shipping cask offers additional containment and shielding for a HIC during transport to the burial site. A Certificate of Compliance, which accompanies each type of cask, is certification by the NRC that a particular type of cask has undergone requirements as described in 10 CFR 71 (7) and 49 CFR 173.471 (8). These requirements include such performance tests for containment integrity under extremely low and high temperature, external pressure changes, vibration, water spray, free drop, compression, and penetration. These tests represent hypothetical accident conditions for each cask.

The majority of low-level radwaste does not warrant high integrity containers or heavy duty transport casks as described above. It is typically transported and buried in metal drums or metal boxes. Low-level radwaste in these containers may be further classified as dry active waste (DAW). DAW is unprocessed by-product material which is free of all free standing liquids. The mode of transport for DAW is usually a flatbed trailer for boxes and a closed van for drums.

Regulations governing the packaging, transport, and burial of radwaste are extensive. They are designed to address all aspects of radwaste disposal.

C) Identification of Gas Generation Concerns

The concern for hydrogen gas generation is a result of the detection of hydrogen gas in Epicor II liners used during the cleanup of contaminated water at Three Mile Island Unit 2. The waste within these liners contained much more activity than typical plant waste (Flaherty, 11). It was expected, with the radiolytic reaction in mind, that the activity would produce a hydrogen gas concentration that could possibly exceed the internal pressure capabilities of the liner. Although none of the liners erupted, hydrogen gas was detected by use of a gas chromatograph. The studies resulting from the sampling, preparation and shipping of these liners represent the only field data obtained from actual plant waste.

Organic ion exchange resins are used throughout the industry within the normal operations of a nuclear plant radwaste system. Resins function to control the purity of such liquid streams as the primary coolant, water in the spent fuel storage pools, and liquid radwaste resulting from normal plant operations. The resins filter radioactive ionic species and particulate matter from the various liquid streams. After maximum usage the resin is packaged in liners and transported in shipping casks to a burial site.

Hydrogen generation within liners containing organic ion exchange resins is the result of two processes. The first is the decomposition of the resin and the second is the radiolytic reaction within the resin/water media.

After considering these facts and reviewing technical studies by MacKenzie (21) and Barletta et. al. (3), the NRC determined that the issue of hydrogen generation in waste containers must be addressed.

EG&G Idaho is presently working on a calculational technique to predict the rate of hydrogen generation in sealed radioactive waste containers. The generation rates calculated from this technique are being compared to data obtained from the processing of the Epicor II liners at Three Mile Island (Flaherty, 11).

D) NRC Regulatory Implementation

The Nuclear Regulatory Commission has imposed changes within the Certificates of Compliance for certain waste shipping casks (NRC IE Information Notice No. 84-72, 33). These conditions pertain to those radioactive waste packages which may accumulate radiolytically generated gases over the shipping period. The conditions stem from preexisting regulatory requirements in 10 CFR 61.56 (6) with the intent to preclude the possibility of explosion which would significantly reduce the packaging effectiveness. The

conditions imposed may be divided into two categories:
1) tests and measurements and 2) shipping within ten days of preparation or within ten days after venting. The NRC IE Information Notice No. 84-72 (33) states the conditions as follows:

(1) For any package containing water and/or organic substances which could radiolytically generate combustible gases, determination must be made by tests and measurements or by analysis (sic calculational method) of a representative package such that the following criteria are met over a period of time that is twice the expected shipment time:

(a) The hydrogen generated must be limited to a molar quantity that would be no more than 5% by volume (or equivalent limits for other inflammable gases) of the secondary container gas void, if present, at STP (ie., no more than 0.063 g-moles/ft³ at 14.7 psia and 70°F) or

(b) The secondary container and cask cavity must be inerted with a diluent to ensure that oxygen must be limited to 5% by volume in those portions of the package that could have hydrogen greater than 5%.

For any package delivered to a carrier for transport, the secondary container must be prepared for shipment in the same manner in which determination for gas generation is made. The shipment period begins when the package is prepared (sealed) and must be completed within twice the expected shipment time.

(2) For any package containing materials with radioactivity concentration not exceeding that for low specific activity (LSA) material, and shipped within 10 days of preparation, or within 10 days after venting of drums or other secondary containers, the determination in (1) above need not be made, and the time restriction in (1) above does not apply.

Compliance by tests and measurements as described in section (1) above, would result in expensive container modifications for a sampling port or an expensive inerting program. Compliance, as described in section (2) above, is the best solution, if the package is shipped within 10 days of preparation. However, long-term on-site storage may soon be the norm with the implementation of the Low-Level Radioactive Waste

Policy Act of 1980. This act provides for the formation of interstate regional disposal facilities (compacts) to relieve the present burden of the three states with LLW disposal sites. After January 1, 1986 states with regional waste compacts will not accept LLW from nonmember states, thus requiring on-site storage for the affected utilities. Therefore, storing the containers, returning to vent, and then shipping within 10 days results in increased exposure to personnel. The practice of temporary on-site storage further enhances the problems associated with following good ALARA practices while maintaining assurance that the rate of hydrogen generation and other combustible mixtures is below explosive levels. Mechanical means of sampling and inerting yields excess disposal costs, while venting the containers periodically yields excess exposure to personnel.

An alternate approach is to utilize a calculational method which accurately determines the rate of hydrogen gas generation. This approach would be a type of analysis and would fulfill the criteria as stated in section (1) above. Exposure to personnel during tests and measurements would be eliminated and the frequency of container venting, while being stored on site, would be reduced.

E) Scope

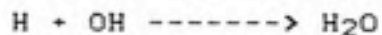
Within the scope of this study are the following objectives:

- ^ To describe the radiolytic reaction of dewatered ion exchange resins by means of a literature review.
- ^ To describe parameters which influence the rate of hydrogen generation. The literature review will identify these parameters.
- ^ To evaluate an equation which determines the rate of hydrogen generation. This evaluation will consider those parameters described above.

MECHANISM OF HYDROGEN GENERATION

A) The Radiolysis of Water

The radiolysis of water is the chemical decomposition of water molecules by the action of radiation. Orekhov et. al. (27) report that according to approximate calculations the number of radiolyzed water molecules reaches a value of 10 to 12 per 100 eV during the passage of ionizing particles through water. This number includes both ionized and excited water molecules. The ionization of water molecules, accounting for about half of the absorbed energy, leads to the formation of chemically active products of a radical character (H^\bullet and OH^\bullet). Subsequent recombinations between the H^\bullet and OH^\bullet radicals produce hydrogen (H_2), hydrogen peroxide (H_2O_2), and water (H_2O). Carswell (5), in a simplified form, presents the following reactions for the production of the radical and molecular products:



Those molecules raised to an excited state may possess electrons raised to different levels depending upon the amount of energy absorbed. As these molecules return to the ground state energy will be released. However, the contribution of excited molecules to the radiolysis of water and aqueous solutions is generally insignificant (Denaro, 10).

The photoelectric effect and Compton scatter are the two photon interactions considered concerning the radiolysis of water. The probability of pair production, per gram of absorber, is directly proportional to the atomic number (Z) (Gollnick, 13). Therefore, hydrogen with an atomic number of one and oxygen with an atomic number of eight are not expected to have substantial interactions via the pair production process.

A full energy transfer to an inner shell electron is the result of photon interaction by the photoelectric effect. The photoelectric interaction is directly proportional to the cube of the atomic number, Z , and inversely proportional to the cube of the energy of the photon.

A Compton scatter interaction results in a recoil electron and a secondary photon with an energy less than the incident photon. The probability of a Compton scattering event is inversely proportional to the

energy of the incident photon, but is independent of the atomic number of the absorber.

The resulting ionizations from those ejected electrons from photon interactions are termed "indirect" ionizations. Those ionizations resulting from a particle emission are termed "direct" ionizations. Subsequent indirect and direct ionizations depend upon both the probability of the interaction and the amount of energy transferred from each event. As each ionization occurs, the energy of a moving electron is decreasing. Since the probability of an event increases the longer the electron remains in the presence of the water molecule, more events will occur as the moving electron decreases in velocity. Since secondary electrons have less energy than the primary electrons, the probability of an event along the secondary electron track will be greater than the probability of an event along the primary electron track.

Similar to this concept is the parameter, linear energy transfer (LET). As defined by Lapp and Andrews (18), LET is represented by the equation:

$$\text{LET} = \frac{dE}{dX}$$

where dE is the energy removed from the particle and

imparted to the medium at or near the site of the track.

Areas of ionization are produced as energy is transferred along this track. In water the free radicals H^\bullet and OH^\bullet will be formed as a result of these ionizations. The concentration of these ionized areas will differ between low and high LET tracks. Therefore, the irradiation of water molecules producing the free radicals H^\bullet and OH^\bullet will yield differing radical concentrations for differing LET radiations.

The ionization of water molecules leads to the formation of the molecular products H_2 (hydrogen) and H_2O_2 (hydrogen peroxide). These molecular products are formed by the recombination of the radicals H^\bullet and OH^\bullet , produced along the particle track. The differing radical concentrations will yield different radical recombination probabilities. The higher the concentration the higher the probability of recombination. Therefore, low and high LET tracks vary in the probabilities for radical recombination. An example of these two types of tracks is illustrated in Figure 1.

Both low and high LET tracks exhibit localized areas of ionization or "spurs". A "spur" is best described as a very localized area in which radicals are formed by the incident radiation. The dimensions of the spur, or the initial distance traveled by the

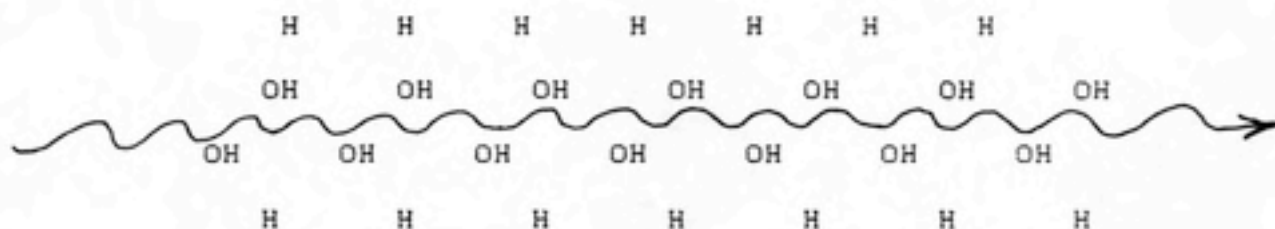
radicals, is dependent upon the energy of the incident radiation.

Figure 1. The formation of free radicals from low and high LET tracks.

LOW LET



HIGH LET



Denaro (10) discusses in greater detail these "spurs" or areas of ionization. If the ionizing particle has a low LET, the spurs formed by the track are about 500 nm apart. Since the minimum distance traveled by an electron ejected from the parent molecule with an energy of 10 eV would be about 5 nm

before thermalization, it will still be within the spur. If the ionizing particle has a high LET, the spurs themselves are only about 1 nm apart and therefore overlap from the moment of formation. This produces a columnar track with a high concentration of radicals.

With the spurs being isolated with low LET radiation, the radicals may diffuse so that radical concentration decreases quite rapidly. After diffusion the radicals are available to react with materials in the solution. Since H is a strong reducing agent and OH a strong oxidizing agent, oxidation - reduction reactions are common in irradiated solutions (Allen et. al., 1). It is expected in this situation that the amount of H_2 and H_2O_2 formed along the track will be small versus the number of radicals escaping into the solution or recombining to form water.

High LET radiation forms overlapping spurs in the form of a densely packed columnar track. In this situation, many radicals recombine with each other with only a few escaping into the solution. A slow moving heavy particle will have a relatively straight track, remaining in the presence of water molecules for a relatively long period. This increases the probability of an event and forms a concentrated columnar track of free radicals. This high concentration increases the

recombination probabilities producing the molecular products H_2 , H_2O_2 , and H_2O (Carswell, 5). Therefore, with high LET radiation, greater quantities of H_2 , H_2O_2 , and H_2O would be expected to form than in the case of low LET radiation (for the same total energy deposited per unit mass).

Another factor within this scope of recombination properties is the influence of radical scavengers. These scavengers bond with radicals, preventing their reaction with other products. Iodine, oxygen, palladium, and bromide are several examples of radical scavengers (Denaro, 10). Experimentally, scavengers may be introduced to reduce the large number of species formed in some reactions. Extraction of these species allows a more accurate measurement of a desired reaction (Carswell, 5).

The presence of bromide ions, which are readily oxidized, is a good example of radical scavengers. Allen et. al. (1) give the following probable reactions occurring with bromide ions:



Here the bromide ions act as catalysts for the recombination of radicals to water.

The final molecular yield of H_2 is denoted by a G-value. The G-value for hydrogen, $G(H_2)$, is the number of hydrogen molecules formed per 100 eV absorbed. Several factors affecting this yield are water purity, temperature, and LET of the incident radiation (Martin, 20).

Allen et. al. (1) state that an increase in the amount of water decomposition occurred with an increase in added impurities. Since photons ionize indirectly, added impurities with a density greater than that of water will increase the probability of secondary ionizations. These additional ionizations will increase the total amount of energy deposited. Therefore, if water decomposition depends upon the energy deposited (via the radiolysis of water) added impurities will increase the probability of water decomposition.

With decreasing temperature, the quantity of water decomposed decreases (Martin, 20). At lower temperatures, close to freezing, the dissipation of radicals formed is restricted by ice molecules. Therefore, recombination of radicals will occur with higher probability. This recombination will increase the yield of water molecules, while decreasing the yield of hydrogen gas or hydrogen peroxide molecules.

As defined above, the number of hydrogen molecules formed is proportional to the amount of absorbed

energy. Foremost in variation of the absorbed energy is the type of emissions incident upon the absorbing media. The entirety of the emission energy is assumed to be absorbed in the media for alpha and beta emissions, while absorption for gamma emissions may be from zero to one hundred percent, depending on the absorption coefficient and the geometrical dimensions of the media. After ionization of the water molecule, direct for alpha and beta and indirect for gamma, the LET affects the recombination probabilities of the radicals formed. High LET radiation produces a higher concentration of radicals. A higher concentration of radicals produces an increased probability for recombination, yielding higher G-values for the molecular products formed.

B) The Radiolysis of Dewatered Ion Exchange Resins

The exact mechanisms to explain the interaction of radiation with different types of organic ion exchange resins have not been determined due to the complexity of the polymer systems (Gangwer, 12). However, the kinds of chemical bonds attacked and the relative degrees to which different types of chemical reactions occur are known (MacKenzie, 21).

The types of bonds attacked in resin molecules

are: the C-C bonds in the polymer structural framework, the bonds linking the functional groups to the carbon framework, and the C-H bonds (MacKenzie, 21). Breaking of C-H bonds leads to the formation of hydrogen gas and to a certain amount of cross linking. The hydrogen gas is formed by the recombination of two H atoms, freed by the breaking of the C-H bond. MacKenzie (21) states that this cross linking is constructive rather than destructive, which may mitigate to some extent the damage done by other processes. However, the overall effect of radiation is deterioration of the resin, particularly in the presence of water and air. McFarland (22) irradiated cation and anion exchangers to high doses in an experiment where buildup of gas pressure was followed. The sum of the G-values calculated for several gases, at 7.9×10^8 rad, were 0.09 and 0.69 for cation and anion exchangers, respectively (MacKenzie, 21). Of these G-values, $G(H_2)$ represented 41% for cation exchangers and 53% for anion exchangers. These data show that the anion exchanger exhibits a rate of gas production eight times that of the cation exchanger. MacKenzie (21) reports that in terms of total pressure a threshold for gas production exists around 5×10^7 rad.

A gas analysis after the irradiation of two types of commercial resins under various conditions was

performed by Mohorcic (23). Table 1 presents this data for hydrogen gas.

Table 1. Hydrogen gas evolved from Dowex 50W and Zeo-Karb 215. $G(H_2)$ = # H_2 molecules formed per 100 eV absorbed.

<u>Resin</u>	<u>G(H₂)</u>
Dowex dry	0.026
Dowex 6 moles H ₂ O/eq. resin	0.095
Dowex 41 moles H ₂ O/eq. resin	1.7
Dowex Li salt dry	0.001
Dowex Li salt 5.1 moles H ₂ O/eq. resin	0.11
Dowex Li salt 24 moles H ₂ O/eq. resin	1.3
Zeo-Karb dry	0.051
Zeo-Karb 9.2 moles H ₂ O/eq. resin	0.12
Zeo-Karb 80 moles H ₂ O/eq. resin	1.7

These resins were irradiated in three forms, a dry state, swollen with water, and embedded under water. As evident in these data, an increase in hydrogen generation is a function of increasing water content.

The dose rate from a Co-60 source was 2.5×10^5 rad/hr. with irradiation times from 10 to 30 days. This

represents a dose range from 6×10^7 rad to 1.8×10^8 rad.

MacKenzie (21) reports the properties and the differences in susceptibility (these are generalizations with expected exceptions) of different types of resins with respect to degradation and hydrogen gas production as follows:

- Most cation exchangers begin to show significant damage at a dose of around 1×10^8 rad, while most anion exchangers are damaged noticeably at a somewhat lower dose.

- A greater increase in resin degradation is observed when resins are irradiated in the presence of water than when they are irradiated dry.

- Results of investigations reported in the literature support a nearly linear increase in gas generation with dose. McFarland (22) found an apparent threshold for gas production from both cation and anion resin of about 5×10^7 rad.

- Although irradiation of resin leads to net formation of gaseous products, there is a marked depletion of any oxygen present during the irradiation.

- In general, generation of gases is greater from anion than from cation resins. Of these gases, hydrogen seems always to be formed in the largest amount. Some of this hydrogen is a result of radiolysis of water in the resin matrix in moist resins, but in dry resins it obviously must come from the resin itself.

PARAMETERS ASSOCIATED WITH HYDROGEN GENERATION

A) Total Absorbed Energy

Factors determining the total absorbed energy within the resin/water media are as follows: 1) radionuclide composition, 2) density of absorbing media, and 3) container geometry.

The radionuclides present within the media are determinants as to the type of radiation and quantity of energy incident upon the media. Particle emissions below a particular energy may be absorbed 100% except in the exterior layer of media. The depth of this layer will depend upon the range of the particle in the media. Those particles with a range greater than their depth of emission from the nearest surface of the container will not transfer their total energy. The percent of photon absorption will depend upon the energy of the photon and the mass absorption coefficient of the media.

The linear absorption coefficient is the factor representing the fraction of a beam of photons absorbed per unit thickness of material. The mass absorption coefficient is the linear absorption coefficient per unit absorber density. Therefore, photon absorption is dependent upon the density of the absorbing media.

The more dense the media the greater the probability for an event. Most events will either be a photoelectric or a Compton scatter event. The energy of the photon and the atomic number of the absorber affect the probability for each of these events.

Assuming a uniform distribution of nuclides within the waste media, the geometry of the container affects the energy absorbed by the media. For example, waste in a spherical container will have a higher percentage of self-absorption than an equal volume of waste in a long, flat container. Although these geometries are hypothetical they demonstrate the effect of container geometry upon absorbed energy.

B) G-value for Hydrogen Gas, $G(H_2)$

Two factors which affect the $G(H_2)$ are; 1) the LET of the incident radiation, and 2) the specific characteristics of the waste media.

As described previously, the LET dependence of $G(H_2)$ is established by the variation of net hydrogen formation between low and high LET radiations. High LET radiation produces greater quantities of hydrogen gas than low LET radiation.

Specific characteristics of the waste media which affect $G(H_2)$ are: the percent water content, the type of resin, the impurities within the media, the presence of radical scavengers, and the concentration of

hydrogen peroxide.

The two mechanisms for hydrogen gas production in dewatered ion exchange resins are the radiolysis of water and resin degradation. Of the two, the radiolysis of water is the predominant mechanism. Therefore the percent water content within the waste media is an important variable in the production of hydrogen gas (Refer to Table 1).

Differing resin types, whether anion, cation or manufactures' brands, yield different values of $G(H_2)$. Gas generation is generally greater from anion than from cation resins. If the polymer structural framework differs between different manufactures' resins, the hydrogen generation values may differ also.

Added impurities within the waste media will increase the number of available "targets" for an ionizing event. Ionizations produce those radicals which later recombine to form hydrogen gas. Therefore, with an increase in the probability of an ionizing event comes an increase in the probability of radical formation. The probability of radical recombination for particular molecular formation is dependent upon the LET of the incident radiation and the radical scavengers present within the media.

Radical scavengers bond to radicals preventing them from reacting with other products. The presence of scavengers bonding to either the H or OH radical will

affect the formation of the molecular products H_2 , H_2O_2 and H_2O .

The chemical interaction of hydrogen peroxide with the resin will cause some C-H bonds to break, thus freeing the hydrogen atoms. As more bonds are broken more hydrogen atoms may recombine to form hydrogen gas. This type of reaction is not radiolytic., However, over time the amount of H_2 produced may contribute significantly to the total hydrogen gas generated.

Evaluation of a Computational Technique
for Determining the Rate of Hydrogen Generation

A) Background

The Utility Nuclear Waste Management Group (UNWVG) of the Edison Electric Institute formed a "Hydrogen Generation Task Force" to evaluate those requirements stated in the NRC IE Information Notice No. 84-72. The Task Force requested technical assistance from EG&G Idaho, Inc. As a result, EG&G developed a calculational method to quantify hydrogen gas generation in sealed containers (Flaherty, 11).

B) Equation

The following is the method presented by Flaherty (11) to determine the time to reach a hydrogen gas concentration equal to 5% of the free volume within a container:

Step 1) Determine the absorbed dose necessary to generate a 5% hydrogen gas concentration (D₅) by the following equation:

$$D_5 \text{ (5\% H}_2 \text{ conc.)} = \frac{(.05)FV}{(GC)(m)(K)} \quad (\text{Eq. 1})$$

where: FV = free volume of the container (cc)

GC = G(H₂) H₂ generation constant
(molecules/100 eV absorbed)

m = mass of waste (grams)

K = $2.33 \times 10^{-8} \frac{\text{eV-cc}}{\text{rad-gm-molecule}}$

The free volume (FV) of the container is the container volume minus the waste volume plus the interstitial free volume. The interstitial free volume is the interstitial void space ratio times the waste volume. The interstitial void space ratio is the difference between the true and bulk density divided by the true density of the resin. The true and bulk density may be obtained from the resin manufacturer.

Flaherty (11) reports from the literature G(H₂) for the several types of resins. These values are reported as Table 2.

Table 2. Hydrogen gas generation constants, $G(H_2)$,
by resin type and ionic form.

Resin	Ionic Form	$G(H_2)$
Dowex 50Wx10	Li^+	0.11
Dowex 50Wx10	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	Ni^+	0.2
IRN-78	Cl^-	0.3
IRN-150	NaCe	0.3

Flaherty (11) states that the hydrogen gas generation yield for a mixed bed system is the sum of the yields of the individual components. For example, a bed with 30% resin "A", and 70% resin "B", by weight, with $G(H_2)$ for "A" and "B" equal to x and y, respectively, the $G(H_2)$ to be used equals:

$$0.3(x) + 0.7(y) = G(H_2)$$

Flaherty (11) recommends for beds of unknown composition the use of 0.6 and 0.13

for the $G(H_2)$ values for anion and cation resins, respectively, and for solidified resin/cement the use of a value of 0.24. The constant (K) is derived as follows:

$$K = (22.4 \text{ l/mole}) (1000 \text{ cc/l}) (100 \text{ ergs/gm-rad}) \\ (\text{eV}/1.6 \times 10^{-12} \text{ ergs}) \text{ divided by } 6.02 \times 10^{23} \text{ molecules/mole}$$

This gives a value of 2.33×10^{-6} eV-cc/rad-gm-molecule. Since the $G(H_2)$ is defined as # molecules/100 eV absorbed and that value is reported as that integer (for example, a value of 0.3 molecules/100 eV absorbed is reported as 0.3) the incorporation of this factor of 100 produces the value of 2.33×10^{-8} eV-cc/rad-gm-molecule.

Step 2a) Determine the absorbed dose for each radionuclide at time intervals (at least three) using the following equation:

$$D(n,t) = \frac{(a)A(E_{\beta} + E_{\gamma})(1 - e^{-\lambda t})}{\lambda} \quad (\text{Eq. 2})$$

where: $D(n,t)$ = dose from nuclide, n, at time, t.

a = specific activity (Ci/gm)

A = $1.86 \times 10^{10} \frac{\text{rad-gm}}{\text{MeV-yr-Ci}}$

E_{β} = average beta energy (MeV/dis)
 E_{γ} = (gamma energy)(% abundance)
 x (% gamma absorption) See Figure 2.
 (MeV/dis)
 h = radiological decay constant (yrs.⁻¹)
 t = time (years)

The specific activity (a) may be recorded from data obtained by normal plant procedures.

The constant (A) is derived as follows:

$$\begin{aligned}
 &(3.7 \times 10^{10} \text{ dis/s/Ci})(1.6 \times 10^{-6} \text{ ergs/MeV}) \\
 &(1 \text{ rad-gm/100 ergs})(3.15 \times 10^7 \text{ s/yr})
 \end{aligned}$$

The average beta energy for each nuclide, it's decay constant, and it's gamma energy and abundance, are easily obtainable from numerous tables (eg. in radiological handbooks).

The gamma energy absorption is the fraction taken from Figure 2. The fraction of gamma energy absorbed was calculated by evaluating the energy received at up to 200 detector sub-volumes as a result of irradiation by a maximum of one million source sub-volumes. The total absorbed gamma energy is the sum of the absorbed gamma energy from each detector sub-volume (Flaherty, 11). This value is dependent upon the energy of the

Gamma % Absorption

(6'x6'—170 CuFt Liner)

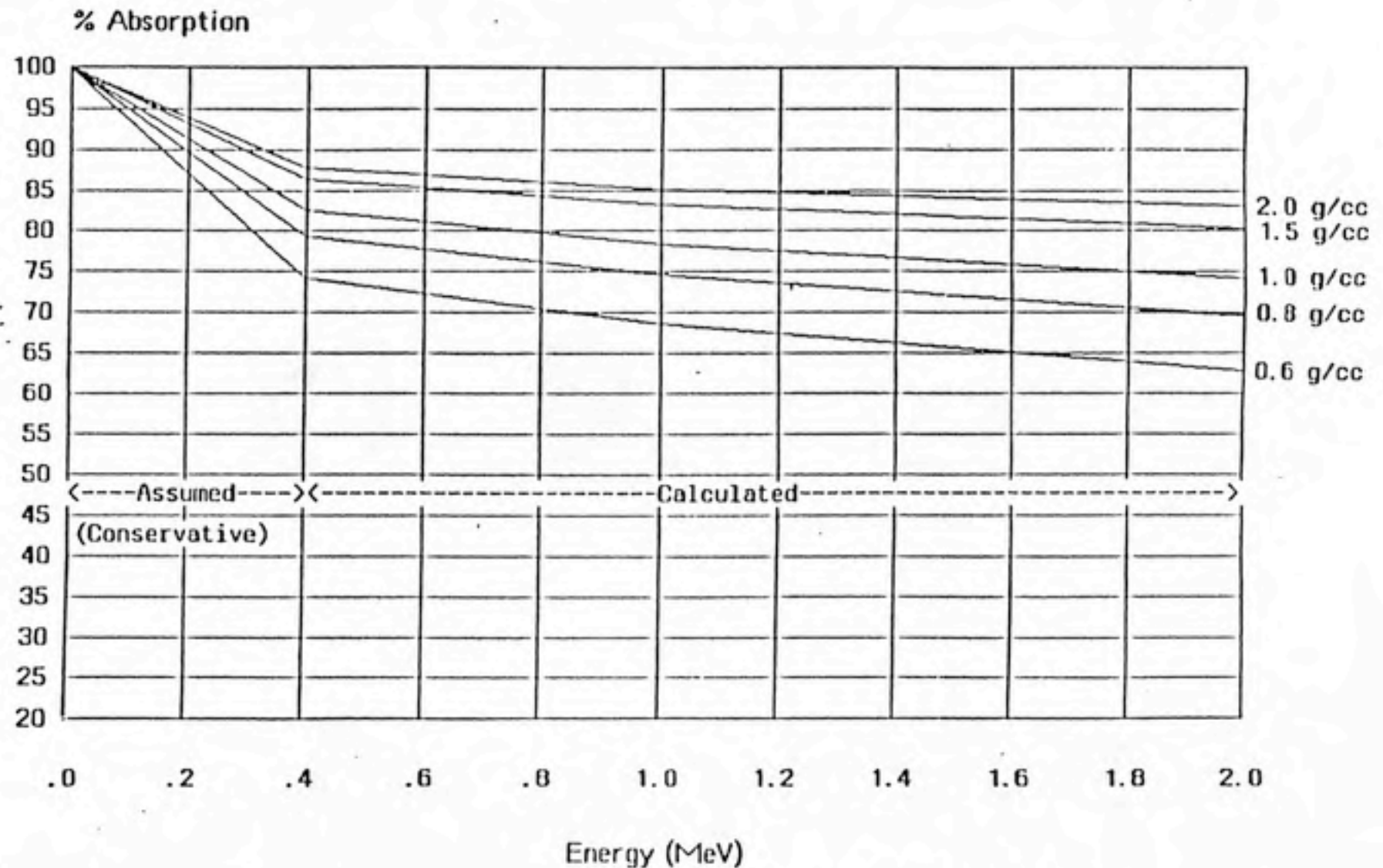


Figure 2. Percent Gamma Absorption dependent upon the gamma energy and the density of the absorbing media (Taken from Flaherty, 11).

photon, the density of the absorbing media and the volume and geometry of the absorbing media. Similar figures, yielding the gamma energy absorbed fraction, have been calculated by EG&G, Idaho, Inc., for other volumes/geometries (eg. 98 ft³/5' in height by 5' in diameter).

Step 2b) Determine the total absorbed dose, D_t . D_t is the sum of the doses contributed by radionuclides, n at time, t .

$$D_t = \sum_n D(n,t) \quad (\text{Eq. 3})$$

Step 3) Determine the percent hydrogen concentration for each time interval using the following equation:

$$\%H_2 \text{ at time}(t) = \frac{(D_t)(m)(GC)(K)100}{FV} \quad (\text{Eq. 4})$$

where: D_t = total absorbed dose
(Eq. 3)

Using Eq. 1; $\%H_2$ at time, t (Eq. 4), becomes

$$\%H_2 \text{ at time, } t = \frac{5}{D_5} D_t \quad (\text{Eq. 5})$$

Step 4) Determine the time to reach a 5% hydrogen concentration by one of two methods:

A) Plot on semi-log paper the values determined in Eq. 4 (%hydrogen versus time).

B) Use a computer to iterate Eq. 2 for each radionuclide for values of time, t , until the total absorbed dose, D_t equals the dose, D_5 determined in Eq. 1.

C) Parameter Considerations Within Equation

The formulation of the method presented by Flaherty (11) is correct. He considers the three factors affecting the total absorbed energy, previously discussed. They are the radionuclide composition, the density of the absorbing media and the container geometry.

However, the use of an inaccurate $G(H_2)$ would produce an incorrect value for, 1) the dose necessary to reach a 5% hydrogen concentration (Eq. 1), and 2) the %5 hydrogen at time, t (Eq. 5). Because of this there is an uncertainty associated with the calculational method.

The $G(H_2)$ presented by Flaherty (11), Table 2, were empirically determined by the irradiation of glass ampules, filled with resin and water, by a single external source. The dose rate incident upon the resin/water media was 2.5×10^5 rad/hr. Irradiation times

were from one hour to thirty days. The ampules were immediately sampled for hydrogen gas after the irradiation period. The amount of H_2 was then converted to a G-value with units of the number of H_2 molecules per 100 eV absorbed.

The following variables, previously discussed, are identified as having an affect upon empirically derived $G(H_2)$:

- 1) percent water content
- 2) the type of resin
- 3) the impurities within the media
- 4) the presence of radical scavengers
- 5) the concentration of hydrogen peroxide

In order for the $G(H_2)$ to be accurately applied in an equation, these variables must remain constant throughout each application. This obviously can not be the case. For example, the percent water content of typical plant resin will, in most cases, never exactly equal that of resins experimentally irradiated for the determination of the present $G(H_2)$. This inconsistency between practical and experimental applications will be the case for all of the variables with the exception of the type of resin. The resin type variable will only be consistent if one of the nine resin types listed in Table 2 is used.

D) Application of Method

A computer program has been developed for the utilization of step 4(B). Step 4(B) necessitates the use of a computer to iterate Eq. 2 for each radionuclide for values of time, t , until the total absorbed dose, D_t equals the dose, D_5 determined in Eq. 1. The program incorporates all of the steps necessary for the completion of the method. The program is included as Attachment A.

Sample data were entered into the program as follows:

container volume	5.52 E 6 cc
waste volume	4.81 E 6 cc
bulk density	0.19 g/cc
true density	1.12 g/cc
mass of waste	9.25 E 5 g
G(H ₂)	0.4
radionuclide:specific activity	Co60: 1.5 E -4 Ci/g
	Cs137: 2.6 E -6 Ci/g
	Mn54: 1.7 E -4 Ci/g

(note: These data were obtained from a radioactive waste shipment from a BWR)

The computer program gives the time to reach the specified hydrogen concentration (5% of the free volume) as 8.43 years. The dose necessary to reach

this concentration (D_5) equals $2.72 \text{ E } 7$ rads.

Input of the sample data into step 4(A) yields the following:

Eq. 1 $D_5 = 2.64 \text{ E } 7$ rad

Eq. 2	Nuclide	Time (years)		
		1	5	15
	Co60	$4.9 \text{ E } 6$	$1.9 \text{ E } 7$	$3.4 \text{ E } 7$
	Cs137	$2.9 \text{ E } 4$	$1.4 \text{ E } 5$	$3.7 \text{ E } 5$
	Mn54	$1.3 \text{ E } 6$	$2.2 \text{ E } 6$	$2.3 \text{ E } 6$
	D_t Total	$6.2 \text{ E } 6$	$2.1 \text{ E } 7$	$3.7 \text{ E } 7$

Using Eq. 5; % Hydrogen at: 1 year = 1.2

5 years = 4.1

15 years = 7.1

These data, plotted as Figure 3, reveal that the time to reach a 5% hydrogen concentration is equal to approximately 9 years.

In order to evaluate how a range of $G(H_2)$ values affect the method, differing values were used with all other variables remaining constant. The results are illustrated in Figure 4.

SEMI LOGARITHMIC
4 CYCLES X 10 DIVISIONS PER INCH

MADE IN U.S.A.

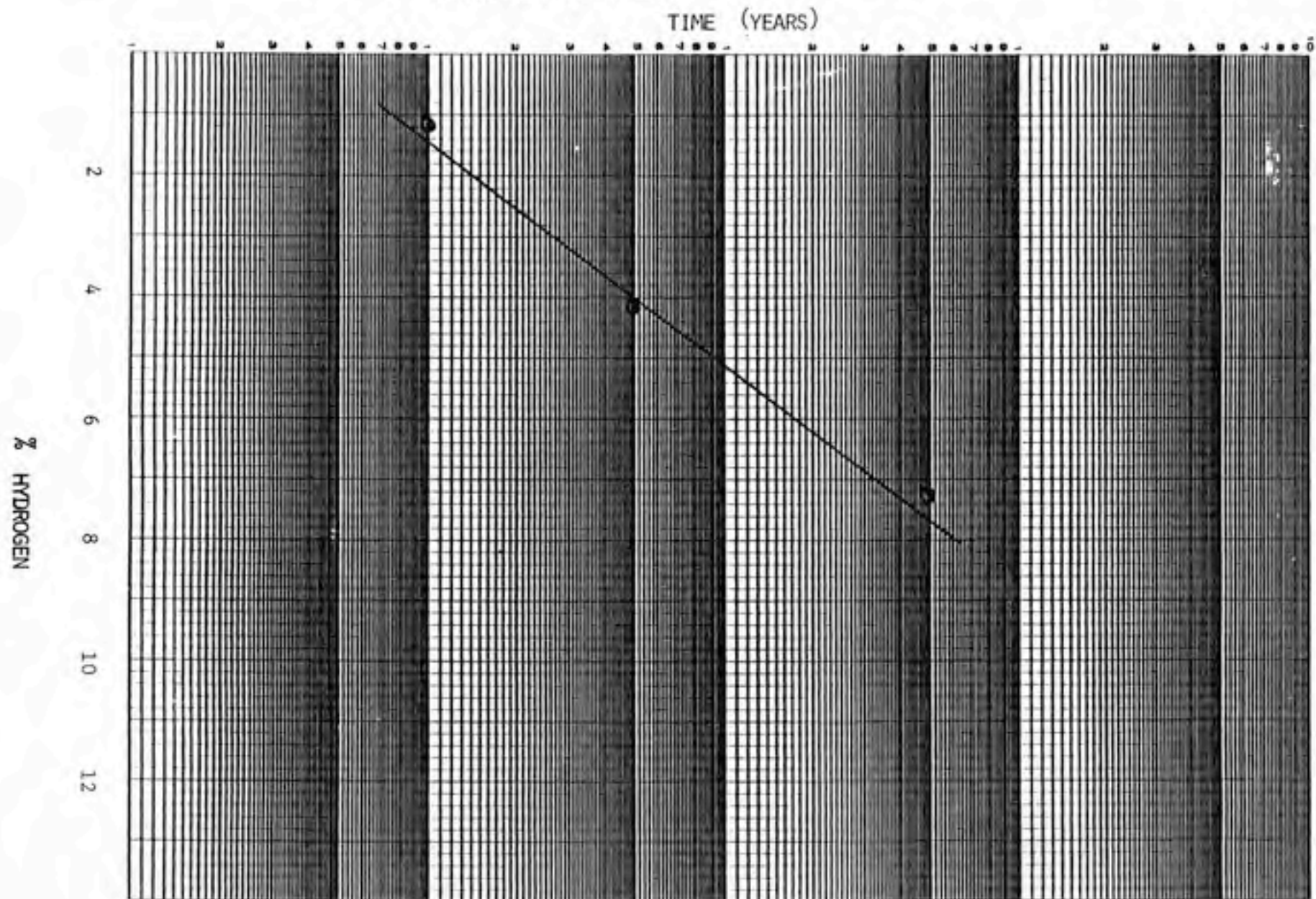
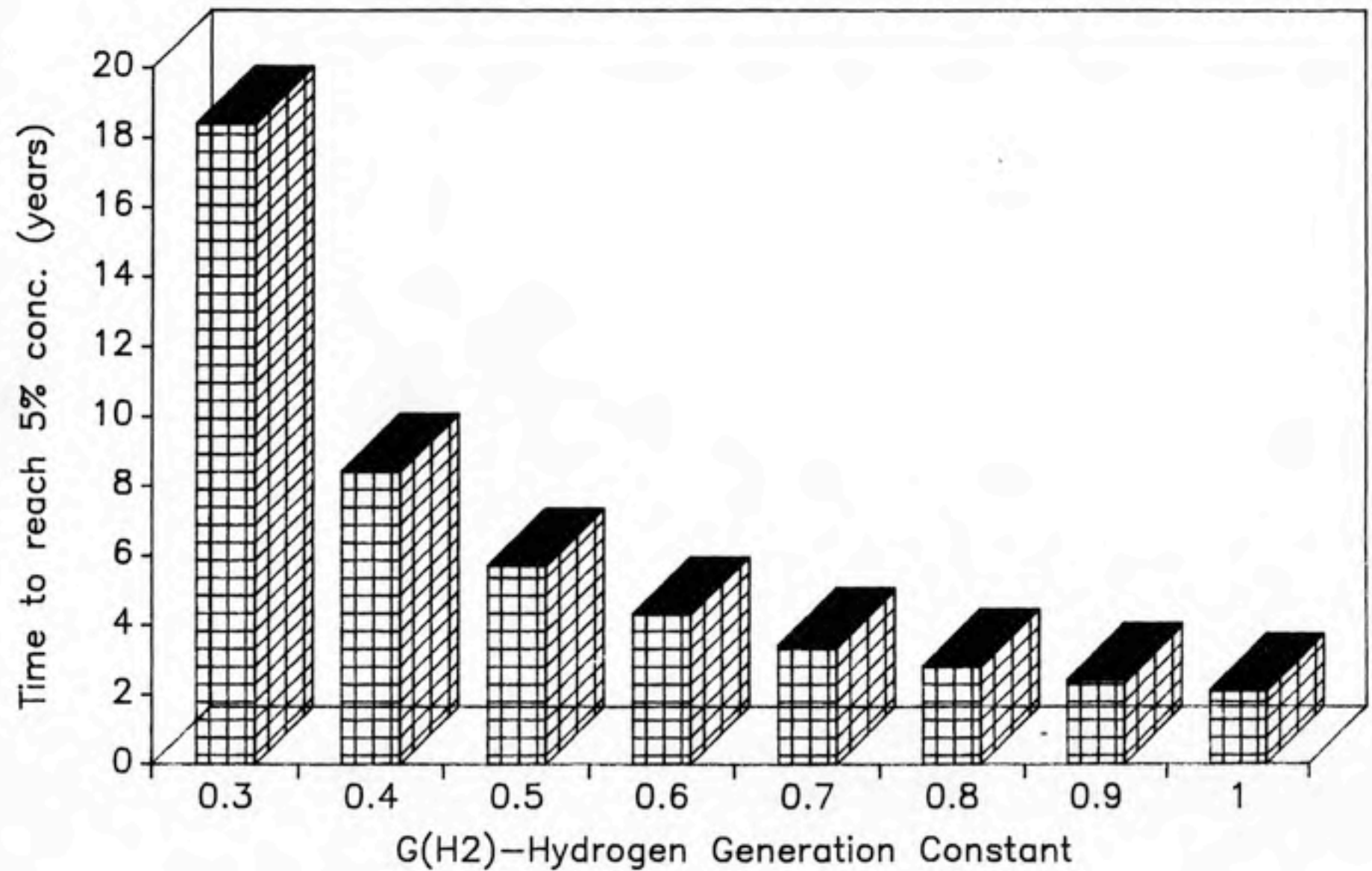


FIGURE 3. TIME VS. PERCENT HYDROGEN CONCENTRATION

Figure 4. Time to Reach 5% Hydrogen Concentration as a Function of $G(H_2)$



CONCLUSIONS

The calculational technique developed by EG&G Idaho, Inc. has the potential to provide an adequate analysis of the hydrogen gas concentration in waste containers. It's accuracy is questionable because of the use of what may be non-representative $G(H_2)$ values. It has been determined in this report that several variables affect these values. At present, data are not available to determine the extent to which these variables alter the $G(H_2)$.

Considering the very small molecular size of hydrogen gas, diffusion from a sealed container is far from improbable. Diffusion may occur through the container walls or through very small molecular spaces existing within a sealant media. A sealant media typically is used between removable lids and may be in the form of a gel or rubber stripping. MacKenzie (21) supports this theory and goes further to state that it would constitute a mitigating effect in the case of a limiting dose to be set on the basis of gas generation. At present, studies for the determination of the rate of diffusion for specific containers have not been carried out.

RECOMMENDATIONS

It is recommended that more studies be performed to accurately determine $G(H_2)$. A study design for the determination of $G(H_2)$ values should include the following steps;

- A) determine the free volume within the experimental container.
- B) determine the hydrogen gas diffusion rate of the container.
- C) determine the radionuclide concentration, density of the media, and geometry of the container, yielding the energy absorbed in the waste media. Quantify/address the following variables for the;

- A) Energy absorbed

- 1) LET of radiation

- B) Waste media

- 1) water content
 - 2) resin type
 - 3) impurities within the media
 - 4) presence of radical scavengers
 - 5) concentration of hydrogen peroxide

- D) determine the concentration of hydrogen gas

- E) determine the sensitivity and efficiency of the instrument (eg. mass spectrometer) to measure the hydrogen gas concentration.
- F) determine the number of hydrogen gas molecules from the concentration of hydrogen gas (Step D).
- G) determine the $G(H_2)$ value (number of hydrogen molecules formed per 100 eV absorbed) by dividing the number of hydrogen molecules (Step F) by the energy absorbed (Step C).

It is also recommended that H_2 gas diffusion rates for specific containers be studied.

The above mentioned studies may determine that the $G(H_2)$ presently in the literature do not accurately represent resins used in the industry. However, until this is shown, the present values should be used in the calculational method.

The determination of the most appropriate $G(H_2)$ for a resin type should consider the form of stabilization, either solidified in cement or dewatered. If solidified in cement, Flaherty recommends a $G(H_2)$ value of 0.24. If the resin is dewatered, the type of resin must be considered. If a $G(H_2)$ has not been measured for a particular type, the $G(H_2)$ of the type most similar in physical and chemical composition, should be used.

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ATTACHMENT A

```

10 REM
20 REM  HYDROGEN GENERATION CALCULATION
30 REM
40 REM
100 CLS: DIM A(50), F(50), L(50), T(50), N$(50), G(5), P(5)
200 INPUT "VOLUME OF CONTAINER (CUBIC FEET) "; CV
205 CV = CV * 28300!
210 INPUT "VOLUME OF WASTE (CUBIC FEET) "; WV
215 WV = WV * 28300!
220 INPUT "BULK DENSITY OF WASTE (POUNDS PER CUBIC FOOT) "; BD
225 BD = BD * .01602
230 CLS: PRINT "VOLUME OF CONTAINER (CM3)"; CV
235 PRINT "VOLUME OF WASTE (CM3)"; WV
237 PRINT "BULK DENSITY OF WASTE (GRAMS PER CM3)"; BD
240 LINE INPUT "SPECIFIC GRAVITY OF RESIN (GRAMS PER CM3)"; TD$
241 TD = VAL(TD$)
245 WM = WV * BD: PRINT "MASS OF WASTE (GRAMS)"; WM
250 LINE INPUT "HYDROGEN GENERATION CONSTANT"; GC$
251 GC = VAL(GC$)
255 IV = (TD - BD) / TD: IF BD > TD THEN IV = 0
260 PRINT "INTERSTITIAL VOID SPACE (FRACTION)"; IV
265 FV = (CV - WV) + (IV * WV)
270 PRINT "FREE VOLUME (CM3)"; FV
275 MH = .05 * FV
280 PRINT "MAXIMUM ALLOWABLE HYDROGEN VOLUME (CM3)"; MH
285 AD = MH / (GC * WM * 2.33E-08)
290 PRINT "ABSORBED DOSE FOR ABOVE (RADS)"; AD
300 PRINT: PRINT: INPUT "PRESS ENTER WHEN READY TO CONTINUE"; Z
500 CLS: PRINT: INPUT "HOW MANY NUCLIDES ARE PRESENT"; N
505 C = 1.86E+10
509 X = 0
510 X = X + 1
520 CLS: PRINT: PRINT "NUCLIDE # "; X: INPUT "NUCLIDE "; N$(X)
525 RESTORE: GOSUB 1000
530 PRINT: PRINT "ENERGY ABSORBED PER DISINTEGRATION "; F(X)
542 IF S$ = "S" THEN S = 3.156E+07 ELSE IF S$ = "M" THEN S = 526000! ELSE IF S$ = "Y" THEN
S = 8766 ELSE IF S$ = "D" THEN S = 365.24 ELSE IF S$ = "Y" THEN S = 1
543 IF S = 0 THEN 520
544 L(X) = LOG(2) / (HL / S)
545 PRINT: PRINT "HALF-LIFE OF NUCLIDE : "; HL; S$
547 PRINT: INPUT "SPECIFIC ACTIVITY (MICROCURIES PER GM) "; SA
548 A(X) = SA / 1000000!
550 IF X < N THEN 510

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555 PRINT:PRINT:PRINT"CALCULATING ...":T=1
560 PRINT" H2":
570 TT=0:FOR X=1 TO N
575 A1=A(X)*C*F(X):A2=EXP(-L(X)*T):A3=1-A2
576 T(X)=A1*A3/L(X)
580 TT=TT+T(X)
590 NEXT X
599 P=TT*WM*GC*2.33E-08*100/FV
600 Z%=INKEY$:IF Z%="P" THEN 651
610 IF P<4.99 THEN T=T*1.1:GOTO 560
620 IF P>5 THEN T=T*.9:GOTO 560
625 PRINT:PRINT:PRINT"TOTAL DOSE FOR":T;" YEARS = ";TT
626 PRINT"PERCENTAGE OF MAXIMUM ";P
630 PRINT:INPUT"DO YOU WANT HARDCOPY":A$
640 IF A$="Y" OR A$="YES" THEN 680
650 END
651 PRINT T,P:GOTO 610
680 PRINT:LINE INPUT"ENTER SHIPMENT NUMBER : ";SN$
720 CLS:PRINT"PRINTING DATA ....."
750 LPRINT"                HYDROGEN GENERATION CALCULATION"
760 LPRINT:LPRINT:LPRINT:LPRINT"SHIPMENT NUMBER : ";SN$
770 LPRINT:LPRINT"SHIPPING WINDOW : ";USING "##.##":T/2:LPRINT" YEARS"
780 LPRINT:LPRINT:LPRINT:LPRINT
790 LPRINT"VOLUME OF CONTAINER (CM3) -----> ";USING "##.##~~~~~":CV
791 LPRINT:LPRINT
800 LPRINT"VOLUME OF WASTE (CM3) -----> ";USING "##.##~~~~~":VW
801 LPRINT:LPRINT
810 LPRINT"BULK DENSITY OF WASTE (GRAMS PER CM3) -----> ";BD
811 LPRINT:LPRINT
820 LPRINT"SPECIFIC GRAVITY OF RESIN (GRAMS PER CM3) --> ";TD
821 LPRINT:LPRINT
830 LPRINT"MASS OF WASTE (GRAMS) -----> ";USING "##.##~~~~~":MW
831 LPRINT:LPRINT
840 LPRINT"HYDROGEN GENERATION CONSTANT -----> ";GD
841 LPRINT:LPRINT
850 LPRINT"INTERSTITIAL VOID SPACE (FRACTION) -----> ";IV
851 LPRINT:LPRINT
860 LPRINT"FREE VOLUME (CM3) -----> ";USING "##.##~~~~~":FV
861 LPRINT:LPRINT
870 LPRINT"MAXIMUM HYDROGEN VOLUME (CM3) -----> ";USING "##.##~~~~~":MH
871 LPRINT:LPRINT
880 LPRINT"ABSORBED DOSE FOR 5% H2 GENERATION (RADS) --> ";USING "##.##~~~~~":AD
881 LPRINT:LPRINT
890 LPRINT:LPRINT:LPRINT
910 LPRINT"TIME FOR " USING "##.##":P;
915 LPRINT:LPRINT:LPRINT
920 LPRINT"% HYDROGEN GENERATION = " USING "##.##":T;
930 LPRINT" YEARS"
940 LPRINT"      ";:FOR X=1 TO N:LPRINT N*(X),;:NEXT
950 LPRINT
999 END
1000 FOR Z=1 TO 41:READ N$,G(1),G(2),G(3),G(4),G(5),BETA,P(1),P(2),P(3),P(4),P(5)
),HL,S$

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1010 IF N$(X)=N$ THEN Z=0:GOTO 1050
1020 NEXT Z:PRINT:PRINT"NUCLIDE NOT FOUND IN LIBRARY ..."
1025 FOR XX=1 TO 1500:NEXT XX:GOTO 520
1040 END
1050 Y=0
1051 IF (WV=(28300#*98#) THEN C$="1"
1052 IF (WV)28300#*98#) THEN C$="2"
1053 EGAMMA=0
1054 FOR D = 1 TO 5
1055 IF G(D) < .4 THEN 1250
1056 IF C$="1" THEN 1200
1060 IF BD<=.6 THEN Y=-.105*G(D)+.79
1070 IF BD>.6 AND BD<=.8 THEN Y=-.075*G(D)+.82
1080 IF BD>.8 AND BD<=1! THEN Y=-.075*G(D)+.855
1090 IF BD>1! AND BD<=1.5 THEN Y=-.058*G(D)+.88
1100 IF BD>1.5 AND BD<=2! THEN Y=-.04*G(D)+.9
1110 GOTO 4000
1200 IF BD<=.6 THEN Y=-.1*G(D)+.72
1210 IF BD>.6 AND BD<=.8 THEN Y=-9.000001E-02*G(D)+.78
1220 IF BD>.8 AND BD<=1! THEN Y=-.075*G(D)+.815
1230 IF BD>1! AND BD<=1.5 THEN Y=-.06*G(D)+.86
1240 IF BD>1.5 AND BD<=2! THEN Y=-.05*G(D)+.875
1245 GOTO 4000
1250 IF C$="1" THEN 1350
1260 IF BD<=.6 THEN Y=-.65*G(D)+1
1270 IF BD>.6 AND BD<=.8 THEN Y=-.525*G(D)+1
1280 IF BD>.8 AND BD<=1! THEN Y=-.438*G(D)+1
1290 IF BD>1! AND BD<=1.5 THEN Y=-.338*G(D)+1
1300 IF BD>1.5 AND BD<=2! THEN Y=-.3*G(D)+1
1310 GOTO 4000
1350 IF BD<=.6 THEN Y=-.8*G(D)+1
1360 IF BD>.6 AND BD<=.8 THEN Y=-.65*G(D)+1
1370 IF BD>.8 AND BD<=1! THEN Y=-.55*G(D)+1
1380 IF BD>1! AND BD<=1.5 THEN Y=-.4*G(D)+1
1390 IF BD>1.5 AND BD<=2! THEN Y=-.35*G(D)+1
4000 IF Y=0 THEN PRINT "BULK DENSITY OUT OF RANGE"
4010 EGAMMA=EGAMMA+(Y*G(D)*P(D)):NEXT D
4020 F(X)=EGAMMA+BETA
4030 RETURN
5000 DATA CO60,1.173,1.332,0,0,0,0.094,1,1,0,0,0,5.26,Y
5010 DATA CR51,.32,0,0,0,0,0,.09,0,0,0,0,27.8,D
5020 DATA MN54,.835,0,0,0,0,0,1,0,0,0,0,303,D
5030 DATA SR90,0,0,0,0,0,.2,0,0,0,0,0,27.7,Y
5040 DATA SR89,0,0,0,0,0,.583,0,0,0,0,0,52.7,D
5050 DATA FE59,1.292,1.095,.192,.143,0,.116,.44,.56,.028,.08,0,45.6,D
5060 DATA CO58,.511,.810,.865,1.67,0,0,.3,.99,.014,.006,0,71.3,D
5070 DATA ZN65,.511,1.115,0,0,0,0,.034,.49,0,0,0,245,D
5080 DATA AG110M,.658,.885,.937,1.384,1.505,.07,.96,.71,.32,.21,.11,255,D
5090 DATA CS137,.662,0,0,0,0,.195,.85,0,0,0,0,30,Y
5100 DATA CS134,.57,.605,.796,1.168,1.365,.152,.23,.98,.99,.019,.034,2.246,Y
5110 DATA NI63,0,0,0,0,0,.017,0,0,0,0,0,92,Y
5120 DATA PU241,0,0,0,0,0,.005,0,0,0,0,0,13.2,Y

```

5130 DATA I129,.04,0,0,0,0,.04,.09,0,0,0,0,1.7E7,Y
5140 DATA Y90,0,0,0,0,0,.931,0,0,0,0,0,64,H
5150 DATA NP237,.03,.086,.145,0,0,0,.14,.14,.01,0,0,2.14E6,Y
5160 DATA H3,0,0,0,0,0,.005,0,0,0,0,0,12.26,Y
5170 DATA C14,0,0,0,0,0,.049,0,0,0,0,0,5730,Y
5180 DATA FESS,0,0,0,0,0,0,0,0,0,0,0,2.6,Y
5190 DATA C057,.014,.12,.136,.692,0,0,.09,.87,.11,.0014,0,270,D
5200 DATA NB95,.765,0,0,0,0,.046,1,0,0,0,0,35,D
5210 DATA ZR95,.724,.756,0,0,0,.115,.49,.49,0,0,0,65.5,D
5220 DATA TC99,0,0,0,0,0,.085,0,0,0,0,0,2.12E5,Y
5230 DATA RU106,0,0,0,0,0,.009,0,0,0,0,0,368,D
5240 DATA RH106,.512,.622,1.05,1.13,1.55,1.415,.21,.11,.015,.005,.202,30,S
5250 DATA SB124,.603,.644,.72,1.69,1.31,.385,.97,.07,.14,.5,.03,62.4,D
5260 DATA SB125,.176,.43,.46,.59,.63,.084,.06,.31,.1,.24,.11,2.7,Y
5270 DATA I131,.08,.28,.36,.64,.72,.18,.026,.05,.82,.068,.016,8.05,D
5280 DATA BA140,.03,.163,.31,.44,.54,.282,.11,.06,.06,.05,.34,12.8,D
5290 DATA LA140,.33,.48,.82,.92,1.596,.49,.2,.4,.19,.1,.96,40.22,H
5300 DATA CE141,.145,0,0,0,0,.144,.48,0,0,0,0,32.5,D
5310 DATA CE144,.08,.134,0,0,0,.081,.02,.11,0,0,0,284,D
5320 DATA PR144,.695,1.487,2.19,0,0,1.208,.015,.003,.007,0,0,17.27,M
5330 DATA PU242,0,0,0,0,0,0,0,0,0,0,0,3.79E5,Y
5340 DATA PU238,0,0,0,0,0,0,0,0,0,0,0,86.4,Y
5350 DATA PU239,.052,0,0,0,0,0,.0002,0,0,0,0,24390,Y
5360 DATA PU240,0,0,0,0,0,0,0,0,0,0,0,6580,Y
5370 DATA AM241,.06,.101,0,0,0,0,.36,.0004,0,0,0,458,Y
5380 DATA CM242,.044,0,0,0,0,0,.00041,0,0,0,0,162.5,D
5390 DATA CM243,.209,.228,.278,0,0,0,.04,.12,.14,0,0,32,Y
5400 DATA CM244,.043,.1,.15,0,0,0,.0002,.000015,.000013,0,0,17.6,Y