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HYDROGEN CONTROL IN THE HANDLING, SHIPPING, AND STORAGE OF WET RADIOACTIVE WASTE

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1.0 INTRODUCTION

The production of flammable gases by the radiolysis of water and organic materials is fairly well understood. The gas produced is proportional to the amount of ionizing radiation absorbed by the water or the organic material. Therefore, in closed systems containing organic or wet radioactive materials, the buildup of flammable mixtures of gases can be expected and has been observed. Since the presence of flammable gases poses a number of potential hazards, particularly where concentrations might become detonable, careful evaluation and control of the handling, shipping, storage, and disposal of these materials is essential in ensuring an acceptable degree of safety.

The importance of flammable gas control was highlighted by the massive stabilization and cleanup operations subsequent to the Three Mile Island Unit 2 (TMI-2) loss-of-coolant accident (LOCA). During the first day of the LOCA, the metal-water reaction in the reactor core caused hydrogen to build up in the 5,700 m³ containment building. The hydrogen increased to the point where it ignited and burned (Henrie and Postma 1983). Even though the containment gas pressure increased to ~30 psig, and the average gas temperature increased to ~1200° F for a short period, the containment building with its design pressure of 60 psig easily maintained its integrity. Hydrogen-oxygen recombiners were used to remove most (122 kg) of the remaining hydrogen from the system/building.

Over one-half-million gallons of radioactive water accumulated in the containment building during and subsequent to the TMI-2 LOCA. To remove the bulk of the radioactive material, the water was circulated through a demineralizer system that was installed in the TMI-2 spent fuel pool. This "submerged" demineralizer system (SDS) collected the cesium and strontium by adsorption on mixed zeolites (Quinn et al. 1984). Radiolytic gas generation in several of the loaded SDS vessels was calculated and then verified (measured) to be between 0.5 and 1.0 L/h. To prevent the buildup of flammable gas mixtures during shipment and storage, the vessels were drained and vacuum pumped to remove the free, unbound water and a catalyst material was remotely added to form a hydrogen-oxygen recombiner in each vessel. A pressure relief system, consisting of a burst diaphragm and micropore graphite filter, was also added to each vessel to prevent the uncontrolled long-term buildup of nonrecombinable gas mixtures. Net hydrogen buildup can occur due to oxygen scavenging by various chemical reactions such as the formation of CO and CO₂ from the oxidation of organic materials (lubricating oils, etc.) trapped by the zeolites.

The canisters planned for the transport of the TMI-2 core debris will also be subject to radiolytic gas generation concerns. The calculated (probable-maximum) hydrogen-oxygen gas generation rate for these containers is 0.11 L/h for a canister loaded with fine, wet core debris (Henrie and Appel 1985). Studies show that the removal of enough water from the core debris to prevent significant hydrogen generation would not be cost effective (the radiolysis of 1 g of water produces 2 L of stoichiometric hydrogen and oxygen). Therefore, wet shipment and vented long-term storage prior to ultimate disposal is planned.

To ensure that flammable gas mixtures will not exist in these canisters, Rockwell Hanford Operations (Rockwell) conducted a demonstration test program in support of the U.S. Department of Energy (DOE), EG&G Idaho, Inc., and GPU Nuclear Corp., to determine which catalysts and bed configurations would be acceptable and near optimum under these wet conditions. These studies demonstrated the simplicity and effectiveness of catalytic recombination of hydrogen and oxygen, even under very wet conditions. The stoichiometric reaction of these gases in the container atmosphere maintains the minimum constituent (either hydrogen or oxygen) below 1%, and ensures that flammable mixtures (>4.1% H₂ and 5.0% O₂) will not be attained.

The U.S. Nuclear Regulatory Commission (NRC) Office of Inspection and Enforcement (I&E) has established requirements for the shipment of waste materials subject to hydrogen gas generation (Jordan 1984) (see appendix A). This I&E notice establishes a safe-shipping time period that is twice the expected shipping and handling period (from canister purging and closing to completion of shipment) to ensure safety during shipment. Hydrogen and oxygen concentrations "must be determined by tests and measurement or by analysis of a representative package." The concentration of hydrogen gas must be limited to 5% by volume (or 0.063 g-mol/ft³ when at pressures below one atmosphere), or the concentration of oxygen gas must be limited to 5% by volume.

This document is intended to convey the pertinent information concerning the handling and shipping of wet radioactive wastes which resulted (lessons learned) from the TMI-2 experience. It provides engineering tools, procedures, and precautions that are intended to ensure the safe handling, shipping and storage of wet radioactive wastes. A step-wise procedure is presented that permits the individual investigator to evaluate the potential for flammable gas generation, and to minimize potential hazards, with the intent of meeting the referenced NRC requirements.

2.0 EVALUATING SPECIFIC PROBLEMS

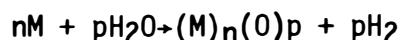
This section discusses factors to be considered in developing a course of action that will ensure safe storage and transport relative to radiolytic gas generation. Detailed mathematical predictions of radiolytic gas generation are reported in Flaherty et al. 1985, and are intentionally limited in the current treatment. Reliable empirical data or direct measurement, if available, should supersede a theoretical approach. A number of references to documents on theory and prior laboratory work are provided for further study as desired. The empirical approach usually simplifies the task and is especially valuable where a quick response to a situation is prudent. In a high percentage of containers of low-level waste, gas generation rates will be found to be low enough to allow shipment without any corrective action required. Conversely, wet high-level and abnormal waste may be expected to generate gases at potentially hazardous rates.

2.1 GAS SOURCES

There are two major sources of flammable gas generation: 1) reaction between metals and water, which takes oxygen from the water to oxidize the metal and releases the remaining hydrogen as gas; and 2) long-term exposure of water or organic materials to ionizing radiation (radiolysis), which provides the major source of flammable gases considered in this report.

2.1.1 Metal-Water and Other Reactions

Metal-water reactions follow the general equation:

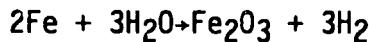


where

M = metal involved in the reaction

n and p = integer values based on the valence change in the metal.

This reaction is typified by the following reaction of iron:



Metal-water reactions occurring at near-ambient conditions are generally slow and self-limiting for most structural metals and become significant only at extreme temperatures. These reactions are not significant under most storage/transportation conditions and can usually be ignored. However, under certain (poorly defined) adverse conditions involving organic materials and corrosive metals, thermal/radiolytic degradation may result in exceptionally high gas production. Therefore, the investigator should be assured of the following conditions.

- o The container and contents have not been exposed to temperatures significantly in excess of ambient conditions during the sealed lifetime.
- o The waste package does not include finely divided or highly reactive metals such as sodium, magnesium, aluminum, lithium, zinc or zirconium, or corrosive liquids.

If these conditions are not met, some estimate of potential metal-water reactions or corrosive generation of gases should be made. If these conditions are met, it can be assumed that no significant corrosive reaction has occurred.

2.1.2 Radiolysis

The most important source of hydrogen-oxygen generation for typical wet radioactive waste storage and shipping is radiolysis. When water or organic materials are brought into prolonged contact or proximity to sources of alpha (α), beta (β), or gamma (γ) radiation, radiolysis will occur. These conditions are present in a significant fraction of radioactive waste containers. For further information concerning radiolysis, see section 3.0.

2.2 CONTAINER-BY-CONTAINER SOLUTION VERSUS GENERIC SOLUTION

An overview approach to the specific task should be taken to determine if a container-by-container solution is preferred to a generic solution. Many containers may require little evaluation and no corrective action to ensure that no flammable gas hazard exists. A limited number may require special care and design to ensure safety.

Conversely, economies of scale may apply. Where the containers and contents are similar, generic solutions can be safe and cost effective. Generic safety features should have conservative and redundant qualities that are forgiving of a wide range of conditions. The generic approach of a

gas purge, followed by the installation of a hydrogen-oxygen recombiner on all containers, may be less expensive than a case-by-case evaluation/action approach. For example, a simple catalyst bed and drum vent design (fig. 2-1) has been used successfully (2,000 per year) for several years for the storage of radioactive waste at Rockwell.

The approach selected will depend upon the specifics of each situation, the purpose of the evaluation (storage, shipping, or other), and the options open to the investigator. The following sections and references will aid in making these decisions.

2.3 EVALUATION

The radiolysis processes are shown in figure 2-2. A review of the specific case should indicate which of these reaction steps are predominate. Figure 2-3 is a functional logic diagram that describes the necessary steps for conducting orderly, detailed evaluations and for taking corrective actions prior to shipping.

The data collection and computation steps described in subsequent sections and outlined in figure 2-3 should be conducted iteratively to:

- Evaluate existing conditions and hazards
- Screen possible corrective actions that would reduce risk or eliminate hazards
- Evaluate selected corrective actions in detail
- Evaluate the results after taking the corrective action.

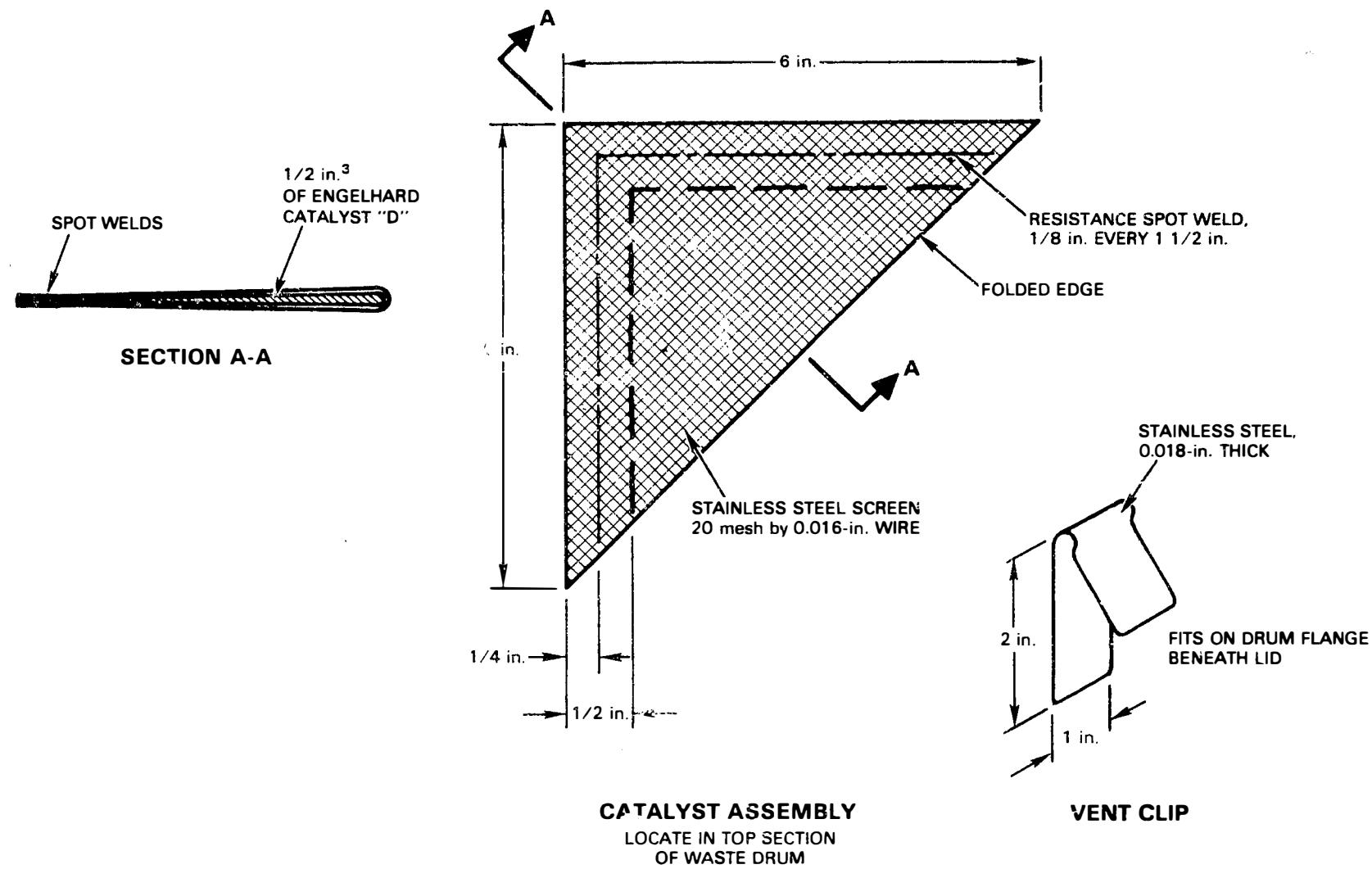
This iterative approach is especially important in performing calculations pertaining to the two key hazards, flammability and overpressurization. These two hazards are inseparably linked and correction of one may accelerate problems with the other. The investigator must provide assurance that both hazards have been corrected simultaneously.

2.4 ENGINEERING METHODS AND PROCEDURES

Methods for assessing potentially hazardous situations and specific procedures for corrective actions are required at facilities with potentially hazardous radioactive waste containers. These methods and corrective actions, which should be easy to understand and prioritized to ensure timely implementation, should include the following:

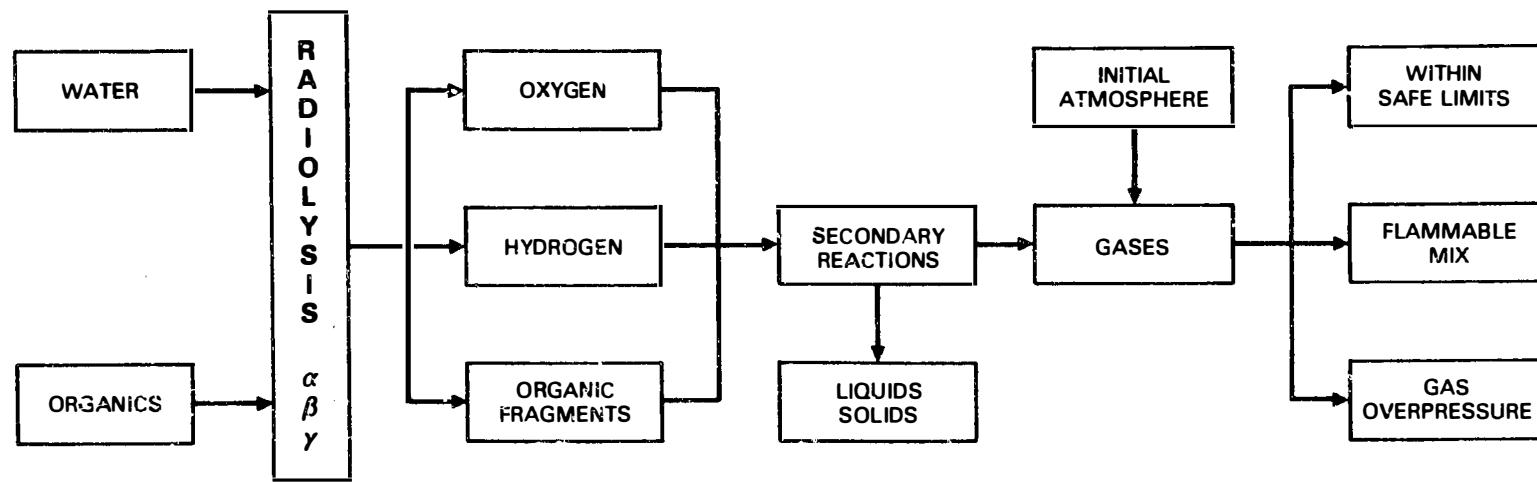
1. Screening procedures including:

- Methods of computing gas (H_2 , O_2) generation rates
- Methods of confirming gas generation rates.



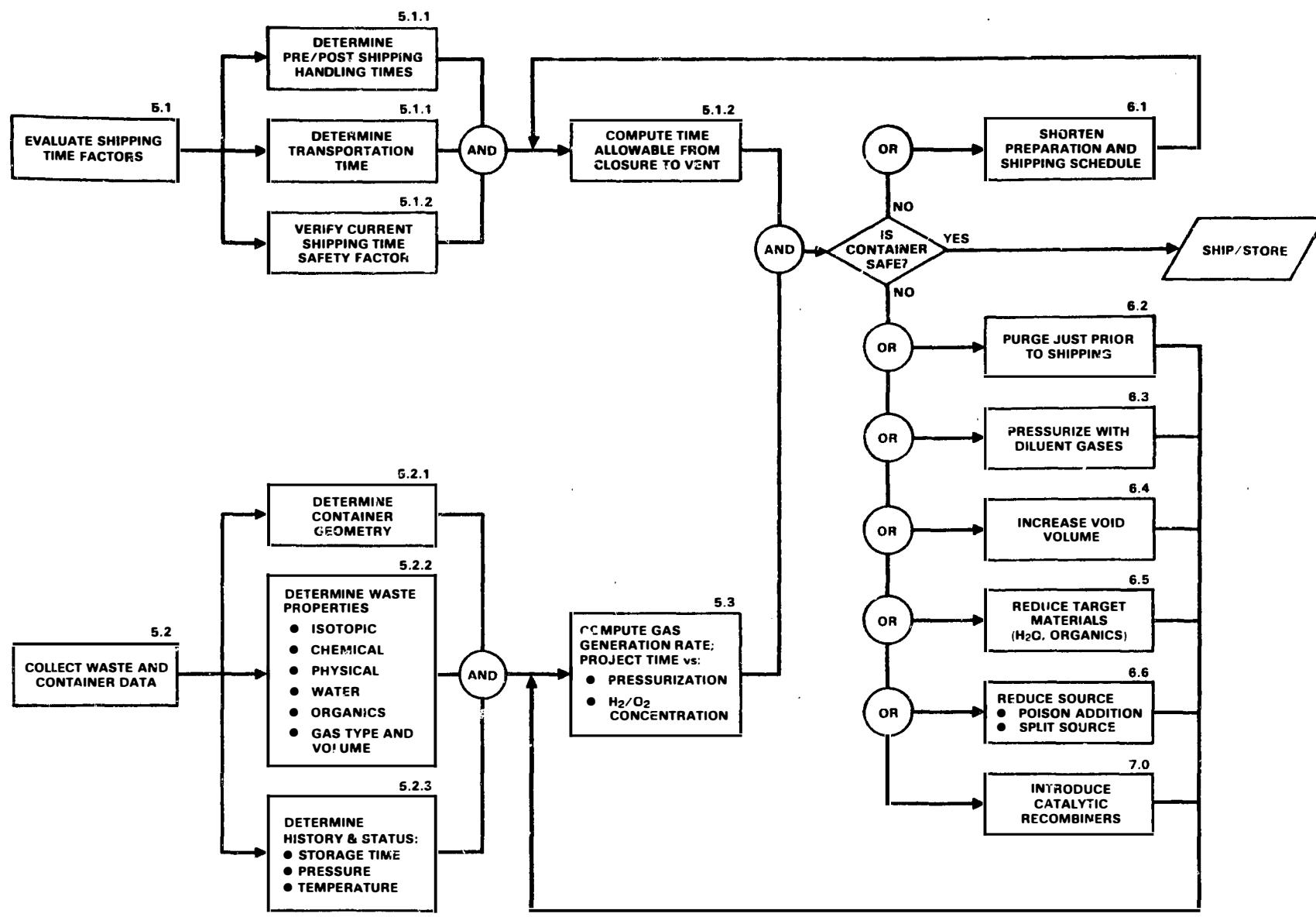
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Figure 2-1. Rockwell Hanford Operations Catalyst Bed and Vent for Drums of Radioactive Waste.



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Figure 2-2. Simplified Diagram of Radiolysis Effects in a Container of Radioactive Hydrogenous Wastes.



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Figure 2-3. Safety Logic Diagram for Shipping and Storing Containers of Radioactive Waste.

2. Corrective procedures including, as a minimum:

 - Venting the gases
 - Diluting with inert gases
 - Using hydrogen-oxygen recombiners.
3. Preventative actions including:

 - Reducing the existing gas generation rate
 - Providing administrative controls
 - Adding hydrogen-oxygen recombiners to new vessels prior to loading with wet wastes.
4. Confirming consultations which include a bibliography of related research and application reports and a listing of researchers and laboratories knowledgeable in specific control technologies.

3.0 RADIOLYTIC GAS GENERATION

The basic equation for computing radiolytic gas generation is:

$$\text{gas generated} = E \times F \times G \times C$$

where

E = the total ionizing radiation energy within the container,

F = the fraction of the total ionizing radiation that is absorbed by the target (hydrogen-containing material),

G = the number of molecules of gas generated per unit (100 eV) of ionizing radiation absorbed by the target material, and

C = a conversion factor based on the units of measurement.

In using this equation, the investigator should attempt to identify empirical data related to the specific conditions. Good storage records or measurements of the total ionizing energy (E) are of key importance. Frequently, all of the needed parameters are not known and some estimates (especially for the F factor and G value) must be made. Section 5.2 provides guides for obtaining, developing or estimating these parameters. Table 3-1 provides a listing of the available techniques for determining each of these values.

In addition, other parameters may be required or will be of value in determining the safety of each container and include the following items, which are discussed in detail in section 5.0:

- V = Void volume of the container (the volume occupied only by gases or vapor)
- P = Container pressure. Pressure measurements and pressure change over time can provide valuable information concerning actual gas buildup which has occurred, and the rate at which it is building up
- t = Time of storage and transport. During this period, the container is closed and gas pressure can increase
- T = Temperature. Measured temperatures may be used in conjunction with pressures and void volume to assist in determining gas generation rates. In some cases, calorimetry techniques may be the only source of radioactive waste loading estimates
- M = Total mass of waste in the container. Usually, mass data is part of the administrative records.

Table 3-1. Methods Table.

Factor	Units	Methods	Reference
Gas generated in time, t	Liters (L)	1. Physical measurement and analysis 2. Compute from E, F, and G data.	Section 5.2 Sections 5.2, 5.3
E, total ionizing energy in time, t	Watt-hour, joules (J), greys (Gy)	1. Compute from known isotopic content 2. Compute from measured source terms 3. Estimate from comparable cases 4. Estimate by calorimetry means.	Section 5.2.2.1 Section 4.4 Section 5.2.2.8
F, fraction of energy absorbed by target material	Unitless	1. Estimate based on comparable cases 2. Estimate based on radiation types, energies, waste particle size, quantities of target water or organic materials exposed, quantities of nonhydrogen-generating materials (absorbers), and waste container size and shape.	Section 4.0 Sections 4.0, 5.2.2.3
G, gas formed per unit of energy absorbed	Molecules/100 eV	1. Use previously verified (tested) values 2. Use values from comparable cases, with corrections for back reactions based on chemical makeup.	Section 4.0
C, conversion factor	Based on units of E	1 J = 1 watt-second 1 Gy = 100 rads = 1 J/kg 100 eV = 1.602×10^{-17} J 1 L = 2.688×10^{22} molecules	

4.0 EMPIRICAL GAS GENERATION DATA

This section presents TMI-2 and other available gas generation test data which are reduced to the F factors and G values discussed in section 3.0. In some instances, the data are presented only in the combined form, $F \cdot G(T)$, which represents the total net gas generation in molecules per 100 eV of ionizing radiation produced. This generally means that the test data is not complete enough to separate the F factor and G value and the total gas generated has not been divided into each of its constituents (H_2 , O_2 , CO , CO_2 , etc.).

4.1 THREE MILE ISLAND UNIT 2 SUBMERGED DEMINERALIZER SYSTEM VESSELS

The data obtained from the cesium-and strontium-loaded TMI-2 SDS vessels, originally evaluated and reported in Quinn et al. 1984, has been reevaluated. The reevaluation utilizes new void-volume calculations that are based on canister weighings during the final dewatering and vacuum-drying process and indicate that the void volumes at the time the gas generation tests were made were 15% higher, on the average, than those calculated earlier. On this basis, generation rates reported in table 4-1 average 15% higher than those reported earlier.

Another potential correction, which could further increase generation rates, would compensate for the oxygen that was apparently consumed. An evaluation of all of the SDS gas analysis data available indicates that the total volume fraction of all of the other gases (mostly CO_2) generated was less than the oxygen which was depleted. It can be concluded that the $F \cdot G(T)$ values derived from the SDS data are on the low side and can also be considered to be $F \cdot G(H_2 + O_2)$ values, which are also on the low side. (In considering this conclusion, note also that since the tests were conducted at pressures above atmospheric, compensation for any leaks would be in the direction of further increasing gas generation rates.) Therefore, the $F \cdot G(T)$ values in table 4-1 are plotted in figure 4-1 as $F \cdot G(H_2 + O_2)$ values and are considered to be slightly on the low side of actual.

There are ~143 kg of zeolite (completely dry basis) in each of the SDS vessels. The amount of water in and around the zeolite during the radiolytic gas generation tests ranged from 28 to 103 kg. It appears that radiolytic gas generation rates are not highly dependent on the quantity of water in this range (see fig. 4-1). The three data points for vessel D10013 indicate essentially no reduction in F·G value even though the amount of water in the zeolite was reduced from 101 to 28 L by vacuum pumping. Of course, if the water is reduced to zero, the $F \cdot G(H_2 + O_2)$ value would be zero. Therefore, it is really the F factor (the fraction of the total ionizing radiation absorbed by the water) that goes to zero. The G ($H_2 + O_2$) value is considered to be a constant (0.66) for beta and gamma radiation under conditions where back reactions are not occurring. Back reactions are enhanced by the presence of excess hydrogen, chemicals such as nitrates, and particularly nitrites. For the SDS vessels, the average $F \cdot G(H_2 + O_2)$

Table 4-1. Radiolytic Gas Generation in Loaded Three Mile Island Unit 2 Submerged Demineralized System Vessels.

Vessel number	Date Test ended	Loading (kCi) (a)	Decay heat (W)	Water inventory (L)	Gas (void) (L)	Pressure rise rate (lb/in ² /h)	Gas generation rate		F·G(T) mol. 100 eV
							(cm ³ /h)	(cm ³ /h-kCi)	
D10011	January 12, 1982	88.2	223	81	129	0.059	481	5.5	.26
D10012	December 22, 1981	112.6	283	103	107	0.15	1,013	9.0	.43
D10012	December 26, 1981	112.6	283	103	107	0.11	744	6.6	.31
D10013	December 1981 (approx.)	97.2	246	101	109	0.069	475	4.9	.23
D10013	January 26, 1983	97.2	246	101	109	0.0861	593	6.1	.29
D10013	February 6, 1983	97.2	246	28	182	0.043	488	5.0	.24
D10015	December 1981 (approx.)	12.9	34	83	127	0.005	40	3.1	.14(b)
D10016	December 1981 (approx.)	112.6	283	66	144	0.061	555	4.9	.23
D20028	January 1982 (approx.)	86.3	216	64	146	0.042	378	4.4	.21
Average		85.0	214	77	133	0.061	475	5.6	.26

(a)Calculated at time of shipment and includes daughter products.

(b)No oxygen (chemically consumed).

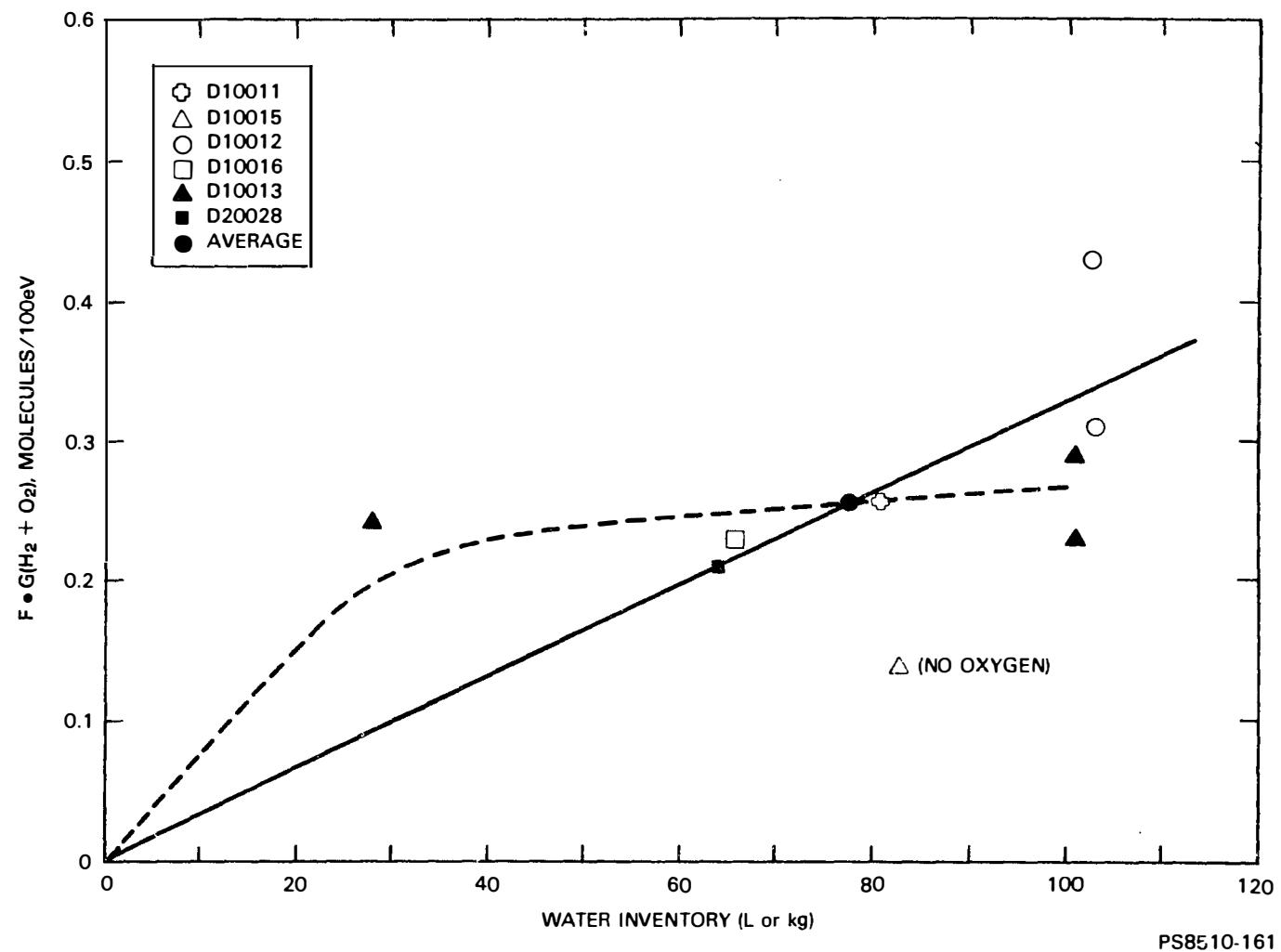


Figure 4-1. Total Gas Generation Rate Versus Water Inventory in SDS Vessels (beta-gamma radiation).

is 0.26. Assuming a G ($H_2 + O_2$) value of 0.66, the F factor would be ~0.40. Such a high value for F for the typical SDS vessel would not be intuitively assumed for the following reasons:

- Most of the ionizing radiation is 0.6 MeV gamma from ^{137}Cs . Therefore, some significant fraction would escape from the water and zeolite in the 0.6 m in dia. by 1.2-m-high vessel.
- The 143 kg of zeolite would be expected to absorb more beta and gamma radiation than the 77-kg average water inventory in an SDS vessel.

However, the dissolved radionuclides are in direct contact with the water on a molecular basis, and some of the ionizing radiation is beta and soft gamma. Apparently for these reasons, ~40% of the ionizing radiation is being absorbed by the water.

It is postulated that in the stored, upright condition of the SDS vessels, gas generation rates decrease significantly with time for the following reasons:

- Water is driven from the upper fraction of the zeolite, where most of the radioisotope source is located, as a result of thermal heating and evaporation. This water condenses on the relatively cold surfaces of the vessel and drains toward the bottom.
- Water in the high-radiation zone is also radiolytically decomposed. The resulting hydrogen and oxygen gases diffuse to the catalyst bed and are recombined back into water vapor that diffuses to cold surfaces, condenses and drains toward the bottom.

Therefore, even though no water is lost from the system, it is redistributed from where it was in close, molecular contact with a high concentration of radioisotopes to a lower radiation zone near the bottom of the vessel, thereby reducing the high initial F factor. However, there is a strong affinity of zeolites for water and the wicking and vapor transport of water back to the zeolite results in a relatively high equilibrium water content in the zeolite. Of course, the radioactive source energy, E, decreases with time as a result of the inherent decay characteristics of the radioisotopes.

4.2 GROUT MATERIALS

Recent experimental data have become available (Friedman et al. 1985; Bisco 1983) concerning radiolytic gas generation in grouts being developed for Hanford radioactive waste immobilization, and in grout being used for neutron moderation and absorption in the TMI-2 core debris shipping cask. These data are summarized in table 4-2.

Table 4-2. Radiolytic Gas Generation in Grout Materials Used for Waste Immobilization or Neutron Shielding.

Material	Test specimen no.	Radiation source	Total dose (rad.)	F·G(T) (mol./100 eV)
CAW(a,b)	1	Alpha	4.2 E+09	0.32
CAW(a,b)	2	Alpha	4.3 E+09	0.43
CAW(a,b)	3	Alpha	4.3 E+09	0.36
CAW(a,b)	4	Alpha	3.0 E+09	0.55
CAW(a,b,c)	5&6	Alpha	4.2 E+09	0.00
CAW(a,b)	7	Alpha	4.8 E+09	0.43
CAW(a,b)	8	Alpha	3.0 E+09	0.41
DSS(b,d)	9	Alpha	4.6 E+09	0.094
DSS(b,d)	10	Alpha	4.6 E+09	0.15
DSS(b,e)	1	Gamma	1.2 E+08	0.018
DSS(b,e)	2	Gamma	1.9 E+08	0.016
DSS(b,e)	3	Gamma	1.9 E+08	0.019
Bisco NS-3(f,g)	AV	Gamma	3.1 E+09	0.56
Bisco NS-3(f,g)	AV	Gamma	7.6 E+09	0.29
Bisco NS-3(f,g)	AV	Gamma	1.5 E+10	0.14

(a) Synthetic Hanford current acid waste (CAW) with curium added in solution form to act as the radiation source. Contains 0.16M NaNO₃.

(b) Friedman et al. 1985.

(c) Dried by heating to 140 °C for 7 days.

(d) Synthetic Hanford double-shell slurry (DSS) with curium added in solution form to act as the radiation source. Contains 2M NaNO₃ and 1.6M NaNO₂.

(e) Synthetic Hanford double-shell slurry (DSS) subjected to gamma radiation from a ⁶⁰Co source. Contains 2M NaNO₃ and 1.6M NaNO₂.

(f) A boron-containing grout mix used primarily for neutron moderation and absorption in the TMI core debris shipping cask. The data shown are the average of 3 samples tested in a nuclear reactor. The radiolysis contribution from neutrons (6%) was subtracted from the total.

(g) Bisco 1983.

Grout test specimens 1 through 8 (table 4-2) contain synthetic Hanford current acid waste (C₆H₅COOH) and utilize ²⁴⁴Cm as the source of ionizing radiation. Curium is an alpha emitter and alpha particles have a high linear energy transfer (LET) type of ionizing radiation, which means it deposits energy at a high rate along a relatively short track. High LET radiation causes a high relative biological effect (RBE) and similarly, a high G value in water radiolysis. Since the curium is in the grout in solution rather than in particulate form, the alpha-emitting molecules are in direct contact with the water molecules. Under these conditions, the high LET alpha radiation results in a high F factor. With F and G both being high, the gas generation rates are high. The average F·G(T) for the alpha-bearing CAW solution in grout is 0.42. For F = 1, its highest possible value, G(T) = 0.42, its lowest value. For F = 0.5, which is likely even though the grout contains only 40% water by weight, G(T) = 0.84, which is reasonable for alpha. An analysis of the gas generated shows it is essentially all hydrogen and oxygen in the 2-to-1 ratio, and therefore G(H₂ + O₂) = G(T).

Grout test specimens 9 and 10 contain synthetic Hanford double-shell slurry (DSS) solution and also use ²⁴⁴Cm as the source of ionizing radiation. The information from these tests is not as conclusive as that from the alpha CAW tests. The data from each test run, except for the last test of specimen 10, indicate gas leaks from the test containments. Also, the gas analyses are inconsistent. Assuming that the last test of specimen 10 is valid, and it appears to be, F·G(T) is 0.15. Again assuming that the most likely F factor is ~0.5, the G(T) value would be 0.30. This lower G value is probably the result of the 1.6M sodium nitrite in the DSS solution.

The three gas generation tests of grouts utilizing synthetic Hanford DSS and gamma radiation from a ⁶⁰Co source are quite consistent in indicating an F·G(T) of ~0.020. The gas analyses show that oxygen is consumed and that N₂O is formed. Since the weight fraction of water in the grout is ~0.4, and the total absorbed gamma energy is obtained from mass-based calculations, it is reasonable to set F at 0.4. This results in a G(T) value of 0.05. It is believed that the presence of sodium nitrite in the DSS caused this depressed G value and was directly involved in the formation of the N₂O.

The data from three radiolytic gas generation tests of the Bisco NS-3 grout (used for neutron absorption in the TMI-2 core debris cask) are very consistent and therefore, only the average results were reported in table 4-2. These data show that the F·G(T) value decreased significantly with total-integrated dose. This reduction is much more than can be accounted for by loss of water. The gas analyses show that the oxygen is depleted and large quantities of carbon monoxide and smaller amounts of other gases are formed. At 10⁹ rad, the F·G(T) value is ~0.6. Since this grout is ~40% water on a weight basis, and the gamma dose calculations are on a mass basis, the appropriate value for F appears to be 0.4. On this basis, the G(T) value would be 1.5. This exceptionally high value and the gas analysis data indicate that organic materials are present which

radiolytically decompose and generate gas. The reduction in gas generation rate with accumulated dose may be the result of the depletion of the organic materials and water and back reactions caused by the increased hydrogen overpressure.

Only limited data was available from the literature on other grouts and are shown in figure 4-2 with $G(H_2)$ plotted against the water content. The dashed line represents only the general relationship for the grouts tested. Due to the wide variety of formulations, impurities, organic materials, potential back reactions, shielding densities, water-retention properties of the grouts, and differences between waste sources, the investigator should make conservative assumptions or generate test data specific to the grout/waste mix being used.

4.3 OTHER DATA

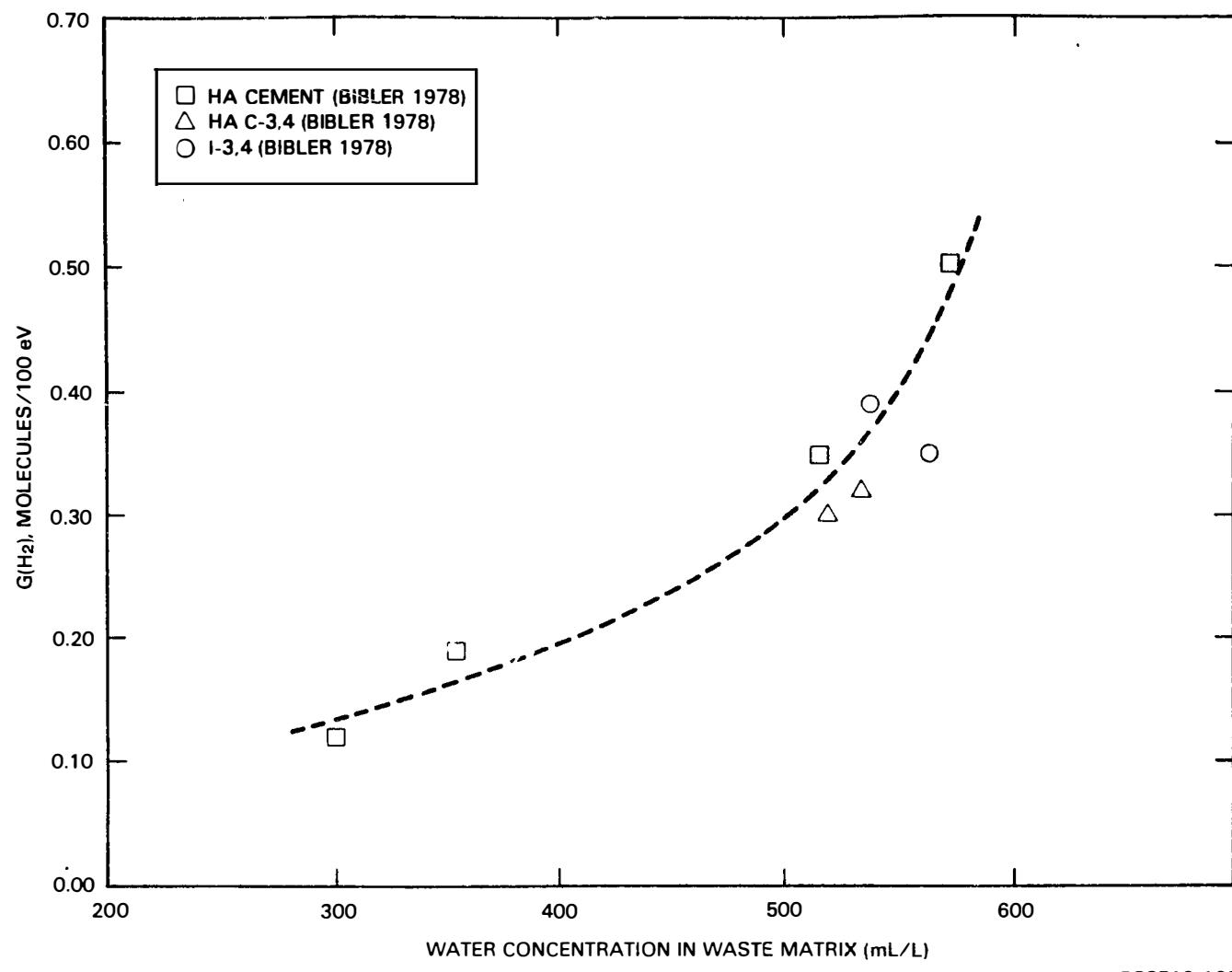
The data from the literature on hydrogen and oxygen generation and control have been grouped and plotted. The data were found to fall in families characterized by their chemical (inorganic or organic) and physical attributes. The $G(H_2)$ values for each family of tests, such as those for nitrate and nitrite salts, were found to cluster based on specific and easily measured parameters such as water content or density. Thus, these parameters can provide good initial estimates or ranges for $G(H_2)$ values.

4.3.1 Resins

Ion exchange resin bed data is presented in figure 4-3 with $G(H_2)$ plotted against specific gravity, and in figure 4-4 with the weight fraction of water in the various resins plotted as the X axis.

The grouping is apparent. In concentrations of water above 0.20, all resins tested fall in a fairly narrow range of $G(H_2)$ values. Below 0.20, there is a divergence of inorganic and organic resins, with the organics maintaining a higher level of hydrogen generation as the inorganic rate approaches zero. Also, specific metallic salts sorbed on the resin can reduce (through back reactions) the $G(H_2)$ values of organic resins to near those of the inorganics. The inorganics provide no hydrogen source other than the water content. The $G(H_2)$ of the saturated organic resins climbs beyond the 0.45 value for pure water, confirming the contribution of hydrogen from the resin itself.

Taking these factors into account, the clustering of the data permits a good first-cut estimate of $G(H_2)$ based on either of two rather easily determined parameters, specific gravity or water content.



PS8510-162

Figure 4-2. Hydrogen Gas Generation Rate Versus Water Concentration in Grouts (alpha radiation).

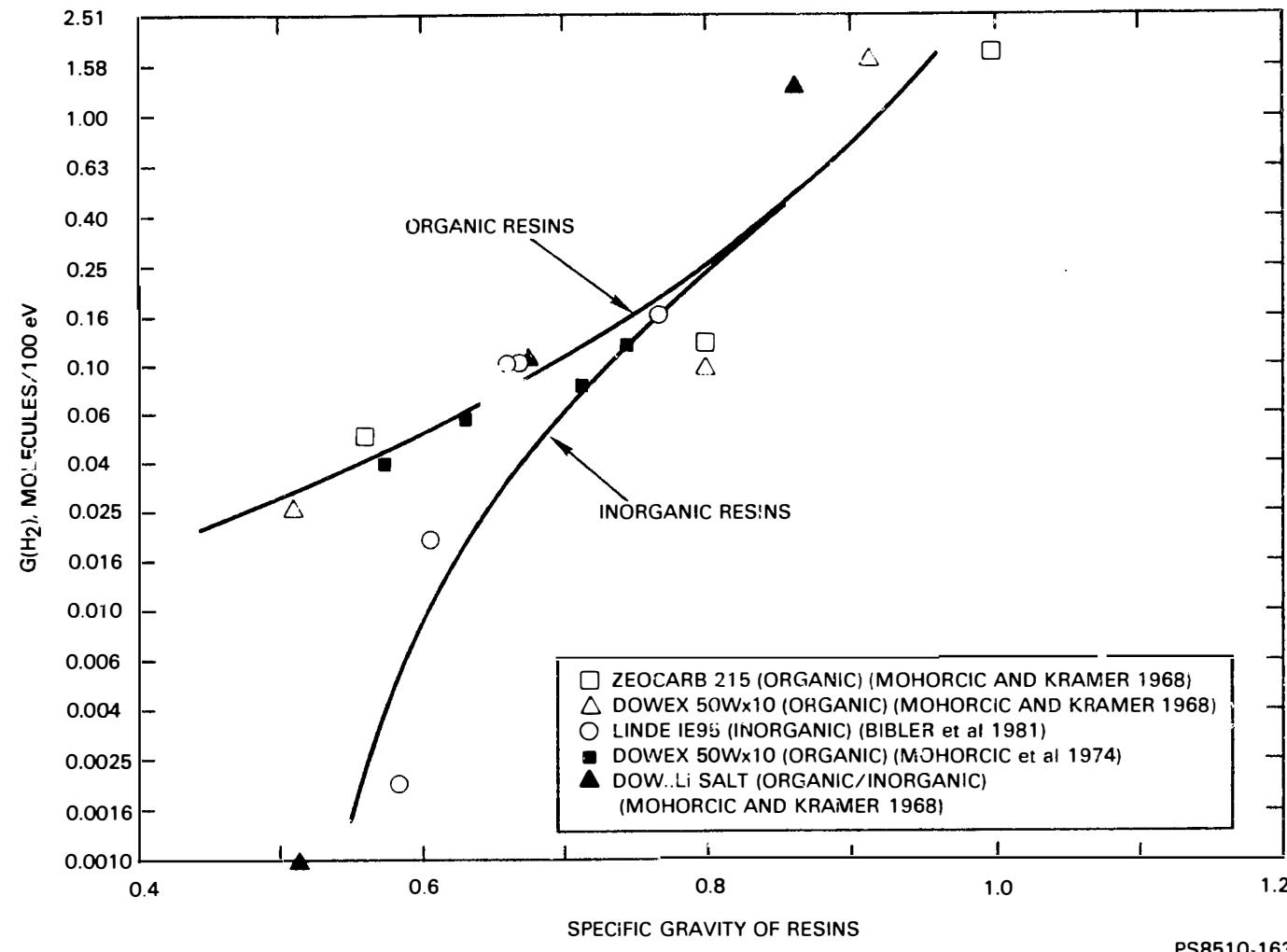


Figure 4-3. Hydrogen Gas Generation Rate Versus Specific Gravity of Resins (gamma radiation).

PS8510-163

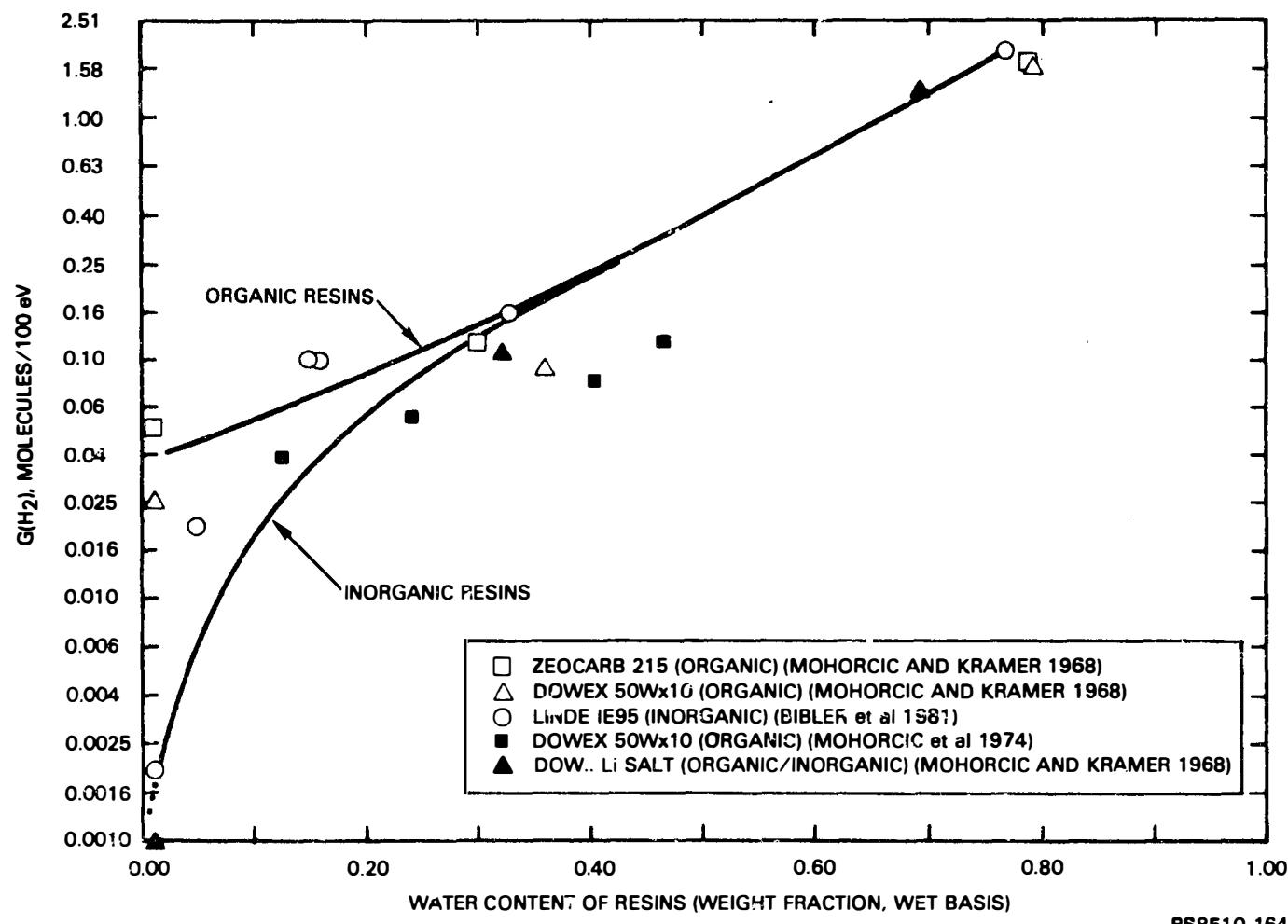


Figure 4-4. Hydrogen Gas Generation Rate Versus Water Content of Resins (gamma radiation).

PS8510-164

4.3.2 Solutions Containing Oxides of Nitrogen

Data from several reports on the $G(H_2)$ of various NO_x solutions are plotted against specific gravity and water concentration in figures 4-5 and 4-6.

The reports concentrate mostly on nitric acid, nitrates and nitrites, which are the materials of primary interest in the nuclear industry. Little data was found on other ligands. As with the resins, these plots are clustered together.

4.3.3 Organics, Liquids, and Solids

The results of tests conducted on a variety of organics versus the specific gravity of the organic is shown in figure 4-7. Water is included in the graph as a reference point. The $G(H_2)$ values for the pure organic materials are outlined in table 4-3.

The range of specific gravity values for aromatic compounds is very narrow, and gas generation rates are lower than for aliphatic materials. The lower generation rates are reportedly due to higher bond energies in these cyclic materials (Gauman and Hoigne' 1968). The test values for various pure aromatic compounds are listed in table 4-4.

The initial or direct hydrogen generation value, G_{H_2} , from the radiolysis of hydrogenous materials might be explained by the combination of two key parameters: vol% hydrogen and the bond strength of the hydrogen in the molecule. The latter is significantly less in organics than in water. Thus, the large organic molecules present both larger targets and more easily separated molecules and therefore exhibit higher G_{H_2} values. This initial or direct G_{H_2} value might then be altered (usually decreased) to a net $G(H_2)$ value by one or more of the many possible chemical back reactions such as $H\cdot + OH\cdot \rightarrow H_2O$. Also, the "interference" or energy absorption by nonhydrogen-producing salts in solution decreases gas generation rates. The effect of this nonhydrogen-producing energy absorption is often manifested by a reduced net hydrogen generation value, $G(H_2)$, for the material. However, its affect could also be treated as a reduction in the F factor. This leads to some confusion in the interpretation of reported test results. Where analyses of the gas are not made and F and G are not separated, the total gas generation value should be indicated as $F \cdot G(T)$. It is proposed for future research that F and G be separated by allocating the effects of organic materials and dissolved waste components to the G value and the undissolved materials to the F factor.

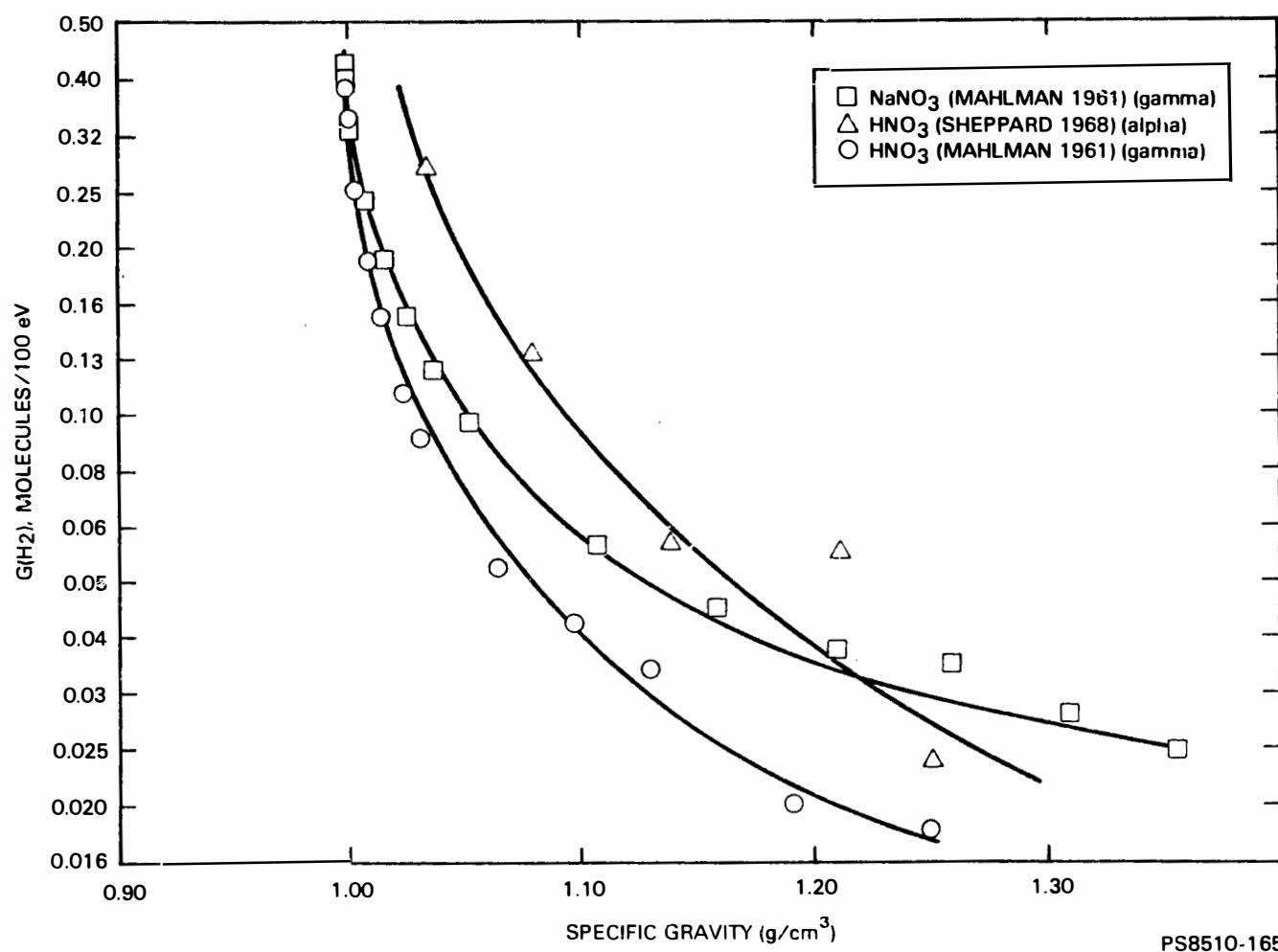
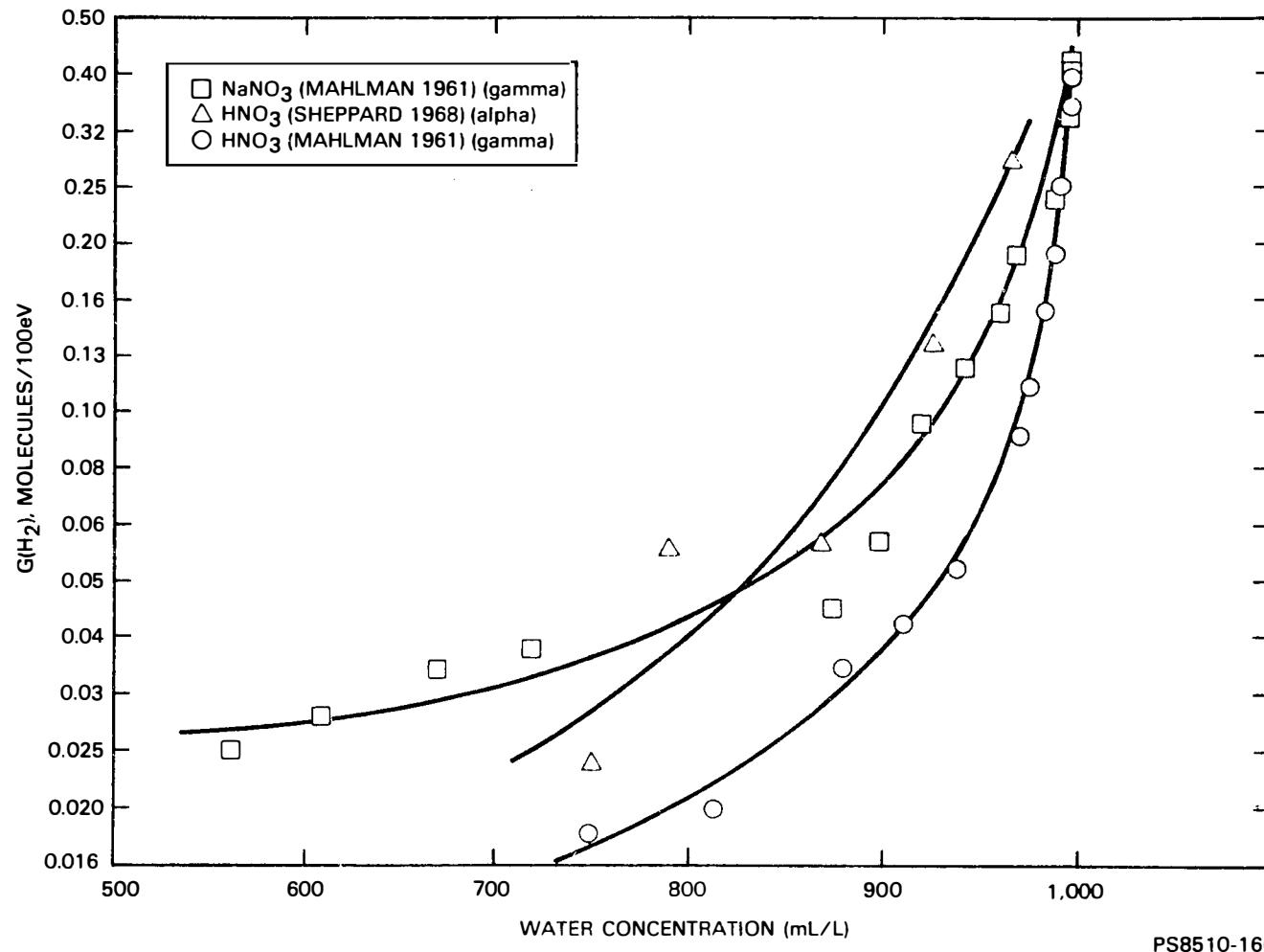


Figure 4-5. Hydrogen Gas Generation Rate Versus Specific Gravity for NO_x Solutions (alpha-gamma radiation).

PS8510-165



PS8510-166

Figure 4-6. Hydrogen Gas Generation Rate Versus Water Concentration in NO_x Solutions (alpha-gamma radiation).

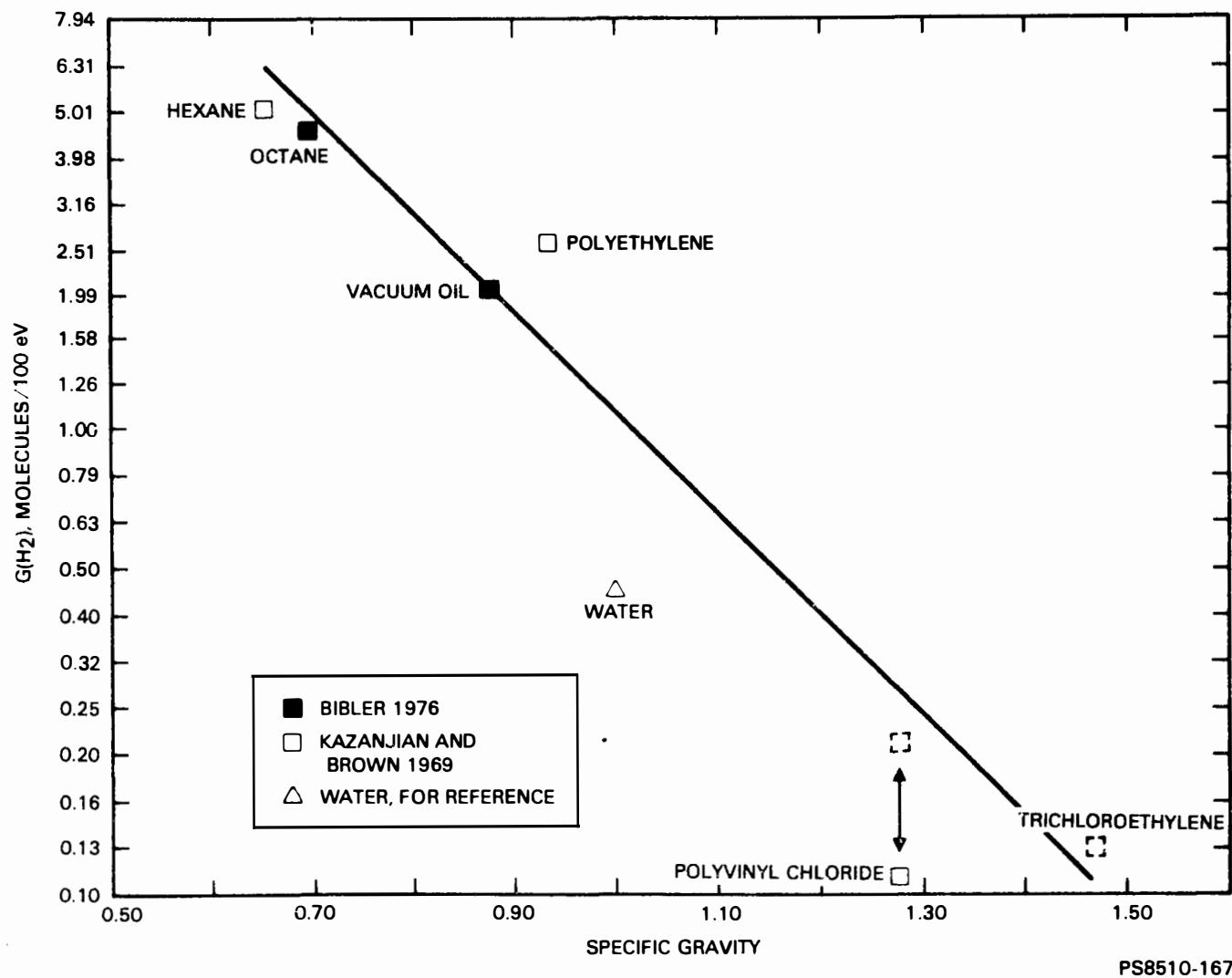


Figure 4-7. Hydrogen Gas Generation Rate Versus Specific Gravity of Organics (beta-gamma radiation).

Table 4-3. $G(H_2)$ Values for Paraffinic Hydrocarbons and Plastics
(beta-gamma radiation).

Hydrogenous material	$G(H_2)$
Water	0.45
Octane(a)	4.50
Vacuum oil(a)	2.00
Hexane(b)	5.00
Polyethylene(b)	2.2 to 3.1
Trichloroethylene(b)	0.0 (0.13)(c)
Polyvinyl Chloride(b)	0.11 (0.22)(d)

(a) Bibler 1976.

(b) Kanzanjian and Brown 1969.

(c) The author reports a zero $G(H_2)$ value for trichloroethylene, but reports a $G(HCl)$ of 0.25. (The nascent hydrogen is reacting with nascent chlorine, which is also a product of the radiolysis.) The value shown (0.13) represents the gross hydrogen produced and is thus actually G_{H_2} rather than $G(H_2)$. (See section 4.3.3.)

(d) The reported $G(H_2)$ value for polyvinyl chloride is 0.11. When adjusted for the reported $G(HCl)$ value of 0.21, the gross G_{H_2} value is $0.11 + 0.21/2$ or 0.22.

Table 4-4. $G(H_2)$ Values for Aromatic Hydrocarbons(a)
(low linear energy transfer radiation).

Hydrogenous material	$G(H_2)$
Benzene	0.012 to 0.039
Biphenyl	0.025 to 0.090
Terphenyl (paradiphenyl benzene)	0.005
Toluene (methyl benzene)	0.140
Xylene, o-	0.00235
p-	0.00184
m-	0.00205
Ethyl Benzene	0.158
Isopropyl Benzene	0.179 to 0.190
Ethyl Toluene, o-	0.190
m-	0.230
p-	0.230
Gaseous Benzene	0.140
Chlorobenzene	0.012
Cyclohexane(b)	5.600

(a) G  uman and Hoigne' 1978.

(b) Low bond strength, high hydrogen material

5.0 APPLYING THE TECHNOLOGY

Application of the technology for verifying the safe shipment and storage of radioactive waste containers is covered in two parallel presentations:

- The functional logic diagram (see fig. 2-3). The numbers shown above each of the functional blocks refer to the sections of this document where they are further discussed.
- A discussion of a step-wise procedure for determining the necessary parameters and making the required calculations (sections 5.1 through 7.0).

These presentations provide an overview and the detail required to independently conduct the initial evaluation of a radioactive waste container and the corrective actions necessary to ensure safe shipment and storage.

5.1 EVALUATING SHIPPING TIME ELEMENTS

There are two key elements used in establishing the shipping time (t) against which potential canister pressurization and hydrogen-oxygen concentrations must be measured:

- Overall handling, preparation and loading time period during which the container will be sealed
- Shipping safety factor regulated by the NRC.

5.1.1 Determining Total Handling Time

The total handling time, t_H , is the time required from canister closure to canister venting and is represented by the following equation:

$$t_H = t_p + t_T + t_v$$

where

t_p = the total preparation time after vessel closure, and includes the time from purging and closure of all container vents through preparation of the canister for shipping, up to the point of departure,

t_T = the estimated transportation time as planned by the cask handling service,

t_v = the estimated handling time after receipt of the vessel, through offloading, lag storage and venting, or safe disposal of the container.

Each of these estimated times should include an allowance for potential delays to provide a conservative estimate of t_H .

The purpose for the separation of the three time factors is to delineate the responsibilities of each group. Total t_H and t_p are controlled by the shipper, t_T is controlled by the carrier, and t_y is the responsibility of the receiver. Responsibility for all canister handling steps should be carefully spelled out between these three parties, whose cooperation is assumed. Preparation of or concurrence with the time estimates and any changes thus have clearly defined respondents.

5.1.2 Computing Allowable Shipping Time

At present, the NRC requires an overall shipping safety factor of 2 times the estimated handling and shipping time (see appendix A). Thus the safe shipping time, t , is represented by the following equation:

$$t = 2t_H$$

This safe shipping time represents the minimum length of time that the investigator must ensure the safety of the canister and shipping cask against container overpressurization or flammable gas mixtures.

5.2 COLLECTING RADIOACTIVE WASTE AND CONTAINER DATA

The overall purpose of the following activities is to collect the best data available relative to hydrogen-oxygen gas generation. Three major groupings of data exist:

1. Physical characteristics of the canister, shipping cask and related equipment or instrumentation (i.e., equipment that may be subject to or measure radiolysis effects)
2. Sources of radiolysis: the radioactive waste and target materials that have the potential for generating various gases
3. Past and present status information, particularly any previous instrumented storage of the waste/canister assemblage or of an assemblage typical of the one in question.

The purposes of these data are to establish a baseline of conditions at the initiation of the shipping sequence.

Whenever practical, data should be verified by using more than one valid approach to determining the required values, then using the more conservative value.

5.2.1 Determining Canister Geometry

Sections 5.2.1.1 through 5.2.1.3 discuss canister geometry.

5.2.1.1 Container Size. The physical dimensions of the container should be determined by measurement or from verified drawings of the container. Of specific interest is the total interior volume of the canister.

5.2.1.2 Ports. The availability of all access ports including filling ports, instrumentation ports, vents, drains, etc., should be determined from inspection and/or drawings, and should include present status and serviceability of each port. (Ports in loaded canisters should not be opened prior to completion of the initial analysis. Valuable data can often be obtained during the venting process. See section 5.2.2.6.)

5.2.1.3 Instrumentation. The availability and serviceability of instrumentation, specifically temperature and pressure measurement devices, should be determined. If such instruments are not installed, but ports are available, installation may be advisable or necessary, as part of the analysis or testing procedure.

5.2.2 Analyzing Contents

Complete sampling and laboratory analysis of container contents is not always necessary or feasible, but the investigator should take steps to provide as much verifiable data as practicable. The engineer should use care and be conservative in making predictive evaluations, and testing should be used whenever practical.

5.2.2.1 Isotopic Inventory. The investigator should collect available radiological data on each container being evaluated. Historical data on the loading of the canister may provide detailed isotopic data. Any valid data in this area should be integrated into the analysis. Measurement of dose rates through canister walls may be practicable, however, such measurements are often expensive and subject to errors resulting from nonhomogeneity.

5.2.2.2 Chemical Inventory. The chemical nature of the contents should be determined. Historical records, laboratory analysis and analogous or synthetic waste data should be reviewed. If it is necessary to avoid overly conservative gas generation estimates, it is important to understand the chemical species present. Soluble isotope concentrations in the liquid portion of the waste is important, since hydrogen-oxygen generation is controlled in significant part by the proximity of the ionizing radiation source (radioisotopes) to the target (water, organic or other hydrogenous) molecules. Similarly, the presence of dissolved nonradioactive materials "dilutes" the target water, decreasing the radiolysis effects. Further, the presence of nitrates, nitrites, and certain other chemicals contribute to back reactions that decrease the net gas generation.

5.2.2.3 Physical Inventory. The F factor is primarily a function of the materials in the container, including the distribution type and energy of the ionizing radiation, the distribution of target materials and other materials which can act as a "shield" between the source and target materials, and the physical size and shape of the container. An F factor of 1.0 would consider that all source and target materials are in intimate contact (i.e., in solution or fine dispersion) and that no radiation escapes from the vessel contents. The total volume of solids and liquids in the container should be determined. The bulk density and specific gravity of various components of the waste should be determined when practicable.

Again, independent approaches should be used to provide verification. Knowledge of the average density of the waste coupled with the total and tare weight of each container should provide one estimate. A second estimate should be available from the results of the void volume testing as identified in section 5.2.2.7.

Source distribution is also a key factor in gas generation. Dissolved or fine particulate source and target materials provide the maximum potential for radiolysis, whereas solid, clad, or coarse particulate source materials are less productive. A solution of source and target material produces a higher gas generation rate than a particulate dispersion of an equal quantity of the same material. In the consideration of materials not directly involved in the radiolysis (nonsource, nontarget materials), the opposite is true: increased dispersion tends to provide more inhibition to gas generation.

A conservative approach (high-side generation rates) would thus consider conditions that would result in an F factor of 1.0 and for water radiolysis, a $G(H_2)$ value of 0.45.

If this conservative approach produces marginal safe shipping time requirements, consult section 4.0 and conduct a more detailed evaluation of the various factors.

5.2.2.4 Water. Being the primary target material for hydrogen-oxygen generation in most radioactive waste disposal situations, water volume and water chemistry are of key importance. Water "location" in the canister should also be determined (i.e. what fraction of the water is "hydrated," "interstitial," or free?). Is the water saturated with chemical constituents? Are soluble, radioactive isotopes present? Can excess water be removed if necessary?

5.2.2.5 Organic Materials. The organic materials present in the waste must be determined. Are these materials liquid or solid? What radiolysis products would be expected in addition to hydrogen-oxygen? What hazards might be associated with those decomposition products? Will these materials consume oxygen by the creation of CO, CO₂, or other oxides, leaving an excess of hydrogen?

5.2.2.6 Gases. The pressure increase over a specific time period provides a valuable measure of total gas generation rate. To ensure conservatism when test pressures are above atmospheric, leak tightness of the system must be verified (see section 5.2.3.1). As a result of such test information, it may be determined that many containers require no corrective action, or simply a purge with inert gas prior to shipment. For canisters with unverified contents, measurement of gas pressure increase with time, followed by gas sampling and analysis may be the key in verifying shipping conditions. For this reason, a thorough "paper evaluation" should be made of the expected gaseous contents prior to opening or venting the container. If this evaluation indicates the need for gas sampling, then the gas may be sampled prior to or as part of the venting operation. For some containers, tests which include recording pressure and/or gas sampling and analysis over time may be the only accurate way of determining gas generation values. Care must be taken to avoid the accumulation of hazardous gas mixtures (see section 8.0).

Without gas analysis, pressure increases in container are not necessarily valid indications of hazardous H₂/C₂ buildup. Other gaseous materials can be produced by radiolysis of organic materials, and oxygen can be consumed in various chemical reactions, forming solids, liquids, or other gases. Flammability requires both a minimum amount of hydrogen (or other fuel such as methane) and a minimum amount of oxygen (or other oxidizing agents). Careful sampling and analysis provides the best assurance of the type of radiolysis products generated. Care must be taken to avoid any inleakage or gas outleakage and air contamination during gas sampling and analysis.

5.2.2.7 Void Volume. The void volume or gas/vapor space in the container is a key parameter in projecting pressure buildup and H₂/O₂ concentrations. Small void volumes permit the rapid buildup of potentially hazardous conditions, whereas large void volumes delay the effects of such buildup. One of the key remedies for high flammable gas concentration or overpressure potential is to increase the void volume by either 1) removing excess water, 2) removing waste, or 3) increasing the void volume by venting the canister to the shipping cask (assuming that the cask provides the necessary containment).

In determining void volume, three major approaches can be used. The first is by computation based on canister interior dimensions and the waste loading data. The second, assuming a full canister initially, is to measure the amount of water removed during the dewatering process by collecting and measuring the volume of water, or by weighing the canister and contents (in air or underwater) when full and after dewatering. This was the key procedure used to determine void volume in the TMI-2 SDS vessels (Quinn et al. 1984) and is planned for the TMI-2 core debris canisters. This methodology is discussed in detail for the core debris canisters in Henrie and Appel 1985. The third method involves a measurement procedure based on changing the pressure in the canister by removal or addition of a known volume of gas using a gas bomb attached to the canister (detailed in appendix B). The pressure change procedure should be used in marginal cases where void volume is in doubt.

Where canisters of waste are stored underwater, it is important to ensure that the void volume is not inadvertently decreased by water intrusion. This can be ensured by adding an inert gas to the container at a pressure greater than the external hydraulic pressure and monitoring for gas outleakage. Weighing after dewatering and just prior to shipment provides an even more positive assurance against inadvertent water intrusion.

5.2.2.8 Thermal Data. Energy balance calculations indicate that the radiolysis process is very inefficient. Of the total ionizing radiation absorbed by water, only ~1% goes into the production of hydrogen and oxygen. The remaining 99% of the absorbed radiation energy degrades to heat. Since some of the ionizing radiation is absorbed by non-gas-producing materials, the fraction of the ionizing radiation energy that is converted into chemical energy in the form of hydrogen-oxygen gas is usually less than 1%, and can be ignored when measuring the total ionizing energy by calorimetric means. The measured thermal energy being lost from a container of radioactive material can thus provide verification of the reported isotopic energy. In cases where records or analyses are incomplete, thermal data may provide the only measure of total energy being produced by the system.

The American Society of Testing Materials provides details on a range of thermal measuring devices and procedures (ASTM 1985). In addition, a considerable number of commercial devices are available to measure heat output and heat flux. However, for containers of low-level waste with low heat generation rates, this approach may be impractical.

The measured heat generation rate can be multiplied by the time, t , and used directly in the gas generation equations as the E term. The E term is independent of the type of radionuclides present; however, the F factor and G value do vary with the type of radiation.

5.2.3 Determining History and Current Status

Historical data collection is not so much a separate activity as it is one of selecting specific data, such as dewatering, canister pressure, and pressure rise rates from the overall data set collected or discovered in the investigation.

5.2.3.1 Container Pressure History. If the container has been stored for a period of time in a sealed mode with a pressure gauge attached, pressure change over time provides a valuable index of the total gas buildup rate. If the container is vented through an accessible independent line, closure of the vent for a period of time and careful measurement of the pressure rise over that time can provide direct evidence of this key parameter.

However, precautions must be taken when determining container pressure history. First, the investigator must confirm the integrity of the container and associated equipment. This is best accomplished by leak testing following assembly, loading, and closure of the vessel. If the vessel is pressurized, it can be submerged in water and monitored for gas

bubbles. Leaky fittings, a leak in the container, or faulty pressure-measuring devices could invalidate any conclusions from subsequent test data. Due to the possibility of leaks, the lack of excessive pressure buildup may not ensure the absence of flammable H₂/O₂ mixtures. One way to ensure against error from leakage is to conduct pressure rise tests starting both below and above atmospheric pressure. If the same gas generation rate is measured in both tests, a nonleaking system is assured. If different generation rates were measured, the leak rate can be calculated from the data and appropriately added or subtracted to determine the actual generation rate. Direct verified pressure measurements constitute some of the most valuable data available for determining gas generation rates.

5.2.3.2 Prior Sampling and Analysis. Changes of gaseous composition over time provides confirmation of H₂/O₂ buildup rates. As with pressure history data, changing gas composition data should be verified to avoid errors due to leaking equipment or sampling and analysis problems.

5.2.3.3 Current Status. The current pressure, temperature, ventilation hookups, access to ports, and general physical status of the container and its environment should be determined. This information may limit the available measurement techniques or direct the selection of a specific sequence of evaluation and/or corrective action steps.

The current container pressure may indicate the system integrity and the lack of significant leaks versus probable significant leaks. Current pressure coupled with other storage data may provide good empirical data on gas generation rates. (The precautions noted in section 5.2.3.1 also apply here.)

Conservative (maximum) gas generation rate values will be determined when canister pressures (initial and final) remain below ambient. Leakage in such containers will be in-leakage, and errors in calculating generation rates from pressure histories will be on the high side. In containers stored at ambient or higher pressures, leakage would result in the underestimation of gas generation rates.

The temperature of the container wall may be of significance if it is well above ambient. This condition could imply high loading of heat-producing radioisotopes or chemical reactions. A measurement or estimate of internal temperatures can be used to "temperature correct" the pressure data.

5.2.3.4 Changes in Container Status. Alterations of the current canister conditions should be made only after deliberation to minimize the loss of potential valuable information as changes are induced.

5.3 CONDUCTING ANALYSES

Once the data have been collected, the investigator conducts a series of analyses and evaluations to 1) assess the gas generation rate, 2) assess the pressure increase, 3) determine the gas mix that will exist during the shipping cycle for each container (or the worst case container), and

4) determine the allowable safe shipping time. These calculations are then compared to determine if the container can be safely shipped as planned or if changes are required prior to shipping.

Using the data collected in section 5.2 and the information in section 4.0, the investigator uses the method discussed in section 3.0 to calculate the gas generation rate and projects the times to the unsafe conditions such as overpressurization (t_o) and flammability (t_f). If these projected times exceed the safe shipping time, ($t_f > t$) and ($t_o > t$), the container can be safely shipped. If the time to flammability or the time to overpressurization is less than the shipping time, corrective measures must be taken prior to shipment.

In computing the overpressurization and flammability times, the investigator should use a conservative and redundant approach. That is, the worst case analysis should be made first, predicting the earliest possible time to reach the unsafe condition. If, under these conditions, there is still a safety margin, then justification exists for shipping the container without further analysis or modification.

This approach should identify a good percentage of the containers as being safe and permit concentration of efforts on the remainder. Handling of the marginal, potentially hazardous containers is discussed in further detail in sections 6.0 and 7.0.

6.0 CORRECTIVE PROCEDURES

The evaluation process of section 5.0 will have identified containers that can be safely shipped and containers that will require some other action prior to shipment. This section discusses the corrective procedures listed in boxes 6.1 through 6.6 of the radiolysis safety logic diagram (fig. 2-2). These procedures are presented in the order of increasing difficulty or cost. Treated iteratively, these procedures should provide the optimum route to safe shipping conditions.

For a given set of containers, one or more of these procedures may be preferred over the others, and the investigator may elect to bypass the simpler options for a generic approach to be used on all containers in the set. For example, it may be determined to use catalytic recombiners (described in section 7.0) in all containers. This approach ensures safe shipping conditions in cases where hydrogen-oxygen gases are generated in stoichiometric mixtures of H₂/O₂. Applied as a generic change over many containers, the design costs, procedure preparation, and installation may prove less costly than the one-by-one evaluation of the steps presented in sections 6.1 through 6.6.

6.1 SHORTENING THE PREPARATION AND SHIPPING SCHEDULE

As primarily an administrative task, this corrective step may provide the least expensive action to achieve the desired results. Where time to flammability or time to overpressurization exceeds allowed shipping time by a small margin, it may be possible to accelerate handling activities to accommodate a safe shipping schedule. The primary precaution here is that a realistic schedule must be maintained.

6.2 PURGING/EVACUATING PRIOR TO SHIPPING

The canister preparation time is reduced if a vent-purge (inert gas, if appropriate) step is performed as close to the shipping point as practical.

In containers where the net gas produced is not stoichiometric (usually oxygen deficient), an overpressurization problem might be solved by a vent-evacuation step, since lowering the initial canister pressure would increase the time to reach the established pressure limit. However, lowering the canister's initial pressure will reduce the time to flammability, if the net gas produced includes both hydrogen and oxygen, and no hydrogen-oxygen recombiner (see section 7.0) is provided.

6.3 PURGING AND PRESSURIZING WITH DILUTENT GASES

The flammable limits for hydrogen and oxygen are given in volume or molar percent. By increasing the pressure of inert gases within the canister from one atmosphere to two atmospheres, the time to flammability is effectively doubled. The limitation on this procedure is canister/cask overpressure.

6.4 INCREASING VOID VOLUME

The time to flammability and time to overpressurization are both dependent on the void volume of the container. Two approaches to increasing the void volume are removal of liquids and venting.

6.4.1 Removal of Liquids

Water or other liquid inside the container may be removed by draining or vacuum pumping to provide more vapor space. Removal of this liquor will have the added beneficial effect of reducing gas generation due to the partial reduction of the radiolysis target and the possible reduction of the radioactive source (see sections 6.5 and 6.6).

6.4.2 Venting to Cask

The cask design may permit the direct venting of the atmosphere of the radioactive material container to the atmosphere of the cask (inner containment vessel of a cask providing double containment). Assuming reasonable diffusion rates, this effectively increases the void volume to that available in both the canister and the cask. This volume increase may be adequate to solve either flammability or overpressurization problems.

6.5 REDUCING TARGET MATERIALS

This step is similar to section 6.4.1 except that the purpose is to reduce the amount of water or organic material available as a target or producer of hydrogen-oxygen gases.

6.6 REDUCING SOURCE TERMS

The reduction of radioactive source terms is possible by either removal of some of the source or by poisoning of the source.

6.6.1 Source Removal

Source removal parallels the target removal in section 6.5, and is most easily accomplished if the source is dissolved in the liquid portion of the waste. The effect of reducing the loading in each canister reduces gas generation and increases void space. The added costs for the effort required to remove the material and the additional containers and shipments may be high.

6.6.2 Chemical Poisoning

The value of $G(H_2)$, the net hydrogen generation rate, is affected (reduced) by the presence of several soluble species and by the concentrations of a given species. The addition of salts (nitrites, etc.) to increase back reactions, or otherwise act as radiolysis inhibitors, is a potential in cases where weak solutions exist in the liquid portion of the waste.

This approach must be tailored to the specific chemistry of each set of containers. Results should be verified by careful measurement of generation rates after the modification.

6.7 USING CATALYTIC RECOMBINERS

The use of catalyst beds is discussed in detail in section 7.0. This approach provides solutions where procedures previously discussed are inadequate or not cost effective.

7.0 CATALYTIC RECOMBINERS

Catalytic recombiners provide the benefits of passive, maintenance-free hydrogen-oxygen control. The action of the recombiners is dependent upon the presence of the reactive gases. Catalysts of the type used in TMI-2 studies provide continuous control of the concentration of those gases (or the minimum constituent gas, usually oxygen in initially inerted systems) to levels well below flammable concentrations.

Catalytic recombiners remove hydrogen-oxygen gases in the stoichiometric 2-to-1 ratio. Where nonstoichiometric net gas generation occurs, such as in cases where the oxygen is being scavenged by waste components, the hydrogen can build up in excess. If the oxygen is sufficiently limited, there is little hazard from flammability; however, the excess hydrogen can cause overpressurization of the container and provides a potential for ignition upon venting to the atmosphere or in-leakage to the container.

Long-term storage conditions may require other means of controlling this type of buildup. Active or passive venting systems can be used. Active systems require administrative control, but allow releasing/purging of the gas at the most favorable times and conditions. Passive filtered vents on the container require no administrative controls, assuming that they vent into an open area. The filter units can be selected to prevent the escape of radioactive particulates, but would of course allow radioactive gases, such as xenon and krypton, to escape and air to enter.

7.1 CATALYSTS

Recent progress has been made in the development of passive catalytic recombination systems. In the passive system, the hydrogen-oxygen gases diffuse to the catalyst and are recombined to form water vapor, which then diffuses to and condenses on the colder surfaces in the system. Pilot plant work at Rockwell related to the shipment of the TMI-2 SDS ion exchange vessels and the TMI-2 core debris canisters has identified an effective catalyst blend for use under very wet conditions (Henrie and Appel 1985). A mixture of 80% Engelhard Deoxo D (nuclear-grade A 16430) and 20% silicone-coated AECL (Atomic Energy of Canada Limited) catalysts was found to be a very effective recombiner and strongly synergistic under very wet (not submerged) conditions. The Engelhard catalyst, particularly under reasonably dry conditions, provides highly efficient recombination of hydrogen-oxygen gas while the AECL catalyst provides rapid recovery of the entire catalyst bed from very wet conditions.

7.2 CATALYST BED DEVELOPMENT

Canister design features related to size and shape of the catalyst bed were developed for use in the TMI-2 core debris canisters. A highly effective design utilizes thin (approximately 1-cm thick), disk-shaped beds of catalyst. Beds at each end of the cylindrical canister hold about 100 g of catalyst. This design provides a safety margin several times the minimum quantity of catalyst required for gas control in the core debris canister.

Other bed shapes and sizes were also tested. Cylindrical shapes of varying inlet area and bed depths were used. Each design utilized a screened container for the catalyst and performed adequately as long as minimum bed sizes and open screen areas were maintained.

Several screen mesh sizes were tested for gas diffusion effects, with no significant reduction in catalyst performance unless the gas flow path was severely restricted. An 8-mesh (8 wires/in.), stainless steel screen utilizing 0.035-in.-dia. wire is recommended. This size screen provides adequate containment of the catalyst pellets (1/8-in.-minimum size), heavy wire construction for maximum bed protection, and a large, effective open area for gas diffusion.

7.3 CATALYST BED LOCATION FEATURES

Catalyst beds were built symmetrically into both ends of new TMI-2 core debris canisters to ensure gas-exposed (nonsubmerged) catalysts in any canister position. This design (Henrie and Appel 1985) thus prevents radiolytic gas buildup even under postulated accident (upside down) scenarios.

Other designs, where most of the water is removed, may require only a single bed, placed such that submersion is not possible. The TMI-2 SDS vessels utilized such a single bed arrangement, but required vacuum pumping to remove the free water.

7.4 CATALYST BED RETROFITS

The engineer assigned to provide a catalyst system for a specific container can readily evaluate the specific features of the container and review the minimum requirements for the catalyst bed(s). The best approach will become readily apparent and the design will usually be a matter of selection between options. See Quinn 1984 for a specific example.

7.5 CATALYST BED DESIGN CRITERIA

Specific design features for catalytic recombiner units will depend upon the physical form of the waste, the size, design and porting of the container, and the intended purpose (i.e., storage or shipping). However, each catalytic unit located in a canister of wet radioactive material for flammable gas control should meet the following criteria.

- One catalyst bed must be exposed to the gas/vapor space at all times.
- Very wet systems should contain catalyst beds composed of 80% Engelhard Deoxo D and 20% silicone-coated AECL catalysts or a test-proven equivalent. (This catalyst mix is wet resistant and recovers rapidly after being submerged in water.)
- The amount of exposed catalyst required is proportional to the gas generation rate. The recommended ratio of the bulk volume of the mixed catalyst to the gas generation rate, in mL of catalyst per mL of $H_2 + O_2$ gas produced per hour, is 1.0. Thus, a generation rate of 50 mL/h requires a 50-mL bed of the mixed catalyst. Where multiple beds are needed to preclude submersion, each bed should contain this volume of the mixed catalyst.
- The recommended ratio of bed volume in mL to exposed (screened) area in cm^2 is 1.0. This results in a 1-cm-thick bed of the mixed catalyst when screened on one side.

The catalytic recombiners designed for the TMI-2 core debris canisters are consistent with this criteria. These mixed-bed recombiners are projected to maintain the oxygen concentration below ~0.5%, or the hydrogen concentration below ~1.0%, even under the very wet conditions in a maximum-loaded TMI-2 canister. Further, the testing was performed using hydrogen and oxygen generation rates which were a factor of 3 higher than those used to size the beds. Tests conducted at temperatures below freezing showed that the catalyst beds, as designed, would remove hydrogen and oxygen gases at the design rate for at least a few weeks under these temperature extremes.

8.0 SAFETY

The hazards of handling hydrogen gas have been evaluated over many decades, and literature provides tables for specific mixtures with air, oxygen, etc. (Perry 1950; Wheast 1967). Hydrogen gas has the following characteristics:

- o Extreme flammability in concentrations of 4.1 to 74.2 vol% in air
- o Requires an oxidizing agent in minimum quantity (usually oxygen, minimum 5.0%) to be flammable
- o Easily ignited and burns with a hot, nearly invisible flame.

These characteristics lead to a single conclusion: avoid any conditions that can produce combustion within a container. This precaution also extends to gases leaking or being vented from a container, and to potential accumulation in buildings or other enclosures in which canisters of waste may be stored.

8.1 HYDROGEN REACTIONS WITH VARIOUS OXIDANTS

The Bureau of Mines (Zabetakis 1965) provides considerable information on this subject, including the following limits of flammability of hydrogen in various oxidants at 25° C and atmospheric pressure shown in table 8-1.

Table 8-1. Flammability Limits
of Hydrogen in Various Oxidants at 25 °C and Atmospheric Pressure.

Oxidant	Lower limit	Upper limit
Oxygen	4.0	95
Air	4.0	75
Chlorine	4.1	89
N ₂ O	3.0	84
NO	6.6	66

Detonations can occur at higher concentrations (>~17% hydrogen in air).

There are also flammability limits for the oxidants. For instance, the lower flammability limit of oxygen in hydrogen is 5%. Oxygen is more likely than hydrogen to be consumed (scavenged) by chemical reactions with other materials in a waste canister. Also, the oxygen gas generation rate is only half that of hydrogen in the water radiolysis process. These factors often make the control of oxygen more advantageous than the control of hydrogen. Under this control condition, the initial atmosphere must be inerted and air inleakage excluded, usually by maintaining the canister internal pressure above atmospheric pressure. In addition, assurance must be obtained that no oxygen producing reactions will occur, such as those which would convert nitrates to nitrites, or that other oxidizers such as NO or N₂O will be produced.

8.2 CATALYSTS

Catalysts introduced suddenly into an atmosphere of a flammable hydrogen-oxygen mixture can become an ignition source. Therefore, in retrofit situations, containers should be vented and purged prior to the initial introduction of a catalyst bed to prevent the possibility of ignition. Where gas concentrations (H₂ and O₂) are under the flammability limits, the recombination reaction proceeds slowly and rapid heating or burning does not occur.

8.3 OVERPRESSURE VERSUS FLAMMABILITY

As either of the key problems of flammability or overpressure is addressed, the investigator should ensure that conditions are not introduced that produce a potential hazard from the other. Each corrective action has the potential for affecting both, and complete evaluations and projections should be made prior to taking the corrective action.

Also, shipping and long-term storage provide significant differences in basic parameters, especially the time factor. Evaluations should be made for both overpressureization and flammability under all projected canister handling and storage conditions.

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APPENDIX A

U.S. NUCLEAR REGULATORY COMMISSION REQUIREMENTS FOR WASTE SHIPMENTS SUBJECT TO HYDROGEN GAS GENERATION

SSINS No.: 6835
IN 84-72

UNITED STATES
NUCLEAR REGULATORY COMMISSION
OFFICE OF INSPECTION AND ENFORCEMENT
WASHINGTON, D. C. 20555

September 10, 1984

IE INFORMATION NOTICE NO. 84-72: CLARIFICATION OF CONDITIONS FOR WASTE SHIPMENTS SUBJECT TO HYDROGEN GAS GENERATION

Addressees:

All nuclear power reactor facilities holding an operating license (OL) or construction permit (CP) and certain registered users of NRC Certificates of Compliance for transport packages.

Purpose:

The NRC's Office of Nuclear Materials Safety and Safeguards (NMSS) has identified a need to clarify conditions relating to the use of NRC-certified packages for shipment of wastes.

Discussion:

A potential exists for the generation of combustible quantities of hydrogen for certain waste forms containing radioactive material. This is pertinent to shipments of resins, binders, waste sludge, and wet filters. It is not pertinent to dry compacted or uncompacted waste and irradiated hardware.

In general, applications for waste package certificates of compliance have not addressed the potential for generation of combustible gas mixtures. Generic requirements have recently been included in certain NRC Certificates of Compliance to preclude the possibility of significantly reducing packaging effectiveness in use. These conditions are typically stated as follows:

- (1) For any package containing water and/or organic substances that could radiolytically generate combustible gases, it must be determined by tests and measurements of a representative package whether or not 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 (i.e., 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%.

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Page 2 of 2

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.

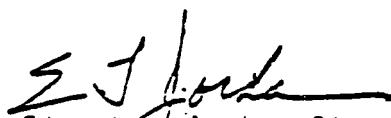
- (2) For any package containing materials with radioactivity concentration not exceeding that for low specific activity (LSA) material, and shipped within 10 days of preparation, or within 10 days after venting of drums or other secondary containers, the determination in (1) above need not be made,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

The generation of combustible gases is dependent on the waste form, radioactive concentration and isotope, free volume, total mass and accumulated dose in the waste. In addition, packaging limitations such as effective shielding provided may preclude the radioactive concentrations and hence the generation of combustible gases.

It is believed, in most cases, that the above combustible gas criteria for waste not exceeding LSA concentrations will be met by ensuring that waste packages are shipped within 10 days of preparation. However, in those cases where this is not feasible, licensees may request a specific approval for their proposed shipment. The application should address those factors that would preclude the generation of combustible gases over at least twice the expected shipment time. Such applications should be directed to NMSS.

In all other cases, a determination must be made in accordance with the provisions of the certificate that the requirements of (1) above are met. Any tests and measurements that are representative of the waste to be shipped and address the factors that affect gas generation may be used. The determination should be documented and retained as part of the records for the shipment.

Recipients of this notice should review the information discussed for possible applicability to their waste shipments. No written response to this information notice is required. If you have any questions regarding this matter, please contact NMSS.



Edward J. Jordan, Director
Division of Emergency Preparedness
and Engineering Response
Office of Inspection and Enforcement

Technical Contact: C. E. MacDonald, NMSS
301-427-4122

Attachment:
List of Recently Issued IE Information Notices



UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20585

Transportation Certification Branch
Approval Record
Combustible Gas Mixtures

Conditions were imposed on packages containing water and/or organic substances to limit the accumulation of radiolytically generated gases over the shipping period to preclude the possibility of significantly reducing the packaging effectiveness due to explosion.

Part of the conditions included "...it must be determined by tests and measurements of a representative package whether or not...."

There is no reason to believe that calculational methods could not be used as means of determining gas generation. So as not to preclude a valid analysis, part of the condition to limit the accumulation of radiolytically generated gases is revised to read "...it must be determined by tests and measurements or by analysis of a representative package whether or not...."

The analytic approach involves determining the hydrogen generated in the waste by radiolysis based on the absorbed dose of the waste over a given period of time. To satisfy the condition to preclude a combustible mixture, the period since closure and twice the shipping time must be considered. The calculation requires that the properties of the waste are known. These properties may be determined from test and measurement of representative waste forms or from data that is applicable to the waste form. The determination should be documented and retained as part of the records for the shipment.


Charles E. MacDonald, Chief
Transportation Certification Branch
Division of Fuel Cycle and
Material Safety, NMSS

Date: MAY 22 1985

APPENDIX B

DETERMINING VOID VOLUME BY GAS/PRESSURE LOSS

A container may be loaded with materials of unknown density and volume, making determination of the void volume by weight measurements alone impossible. If the container is valved, a gas sample bomb of adequate size may be attached and used along with pressure measurements to determine void volume.

The pressure of the container gas is governed approximately by the ideal gas law, $PV = nRT$. If we operate at known or constant temperature, the fixed volume, V , can be measured effectively by changing the volume of gas, n , by a known quantity and observing the change in pressure, P .

Initial conditions in container:

$$P_0V_0 = n_0RT_0 \quad (1)$$

Final conditions in container after adding a known volume of gas from the attached gas sampler bomb:

$$P_1V_1 = n_1RT_1 \quad (2)$$

where

n_0 and n_1 = moles of gas, initial and final, respectively,
 n = the gas added, expressed in moles,
 $V_1 = V_0$ = the void volume of the container,
 R = gas constant,
 $T_1 = T_0$ (or both T_1 and T_0 are known) temperature of the container,
 P_0 and P_1 = pressure, initial and final, respectively,

$$n = n_1 - n_0 = \frac{P_1V_1}{RT_0} - \frac{P_0V_0}{RT_0} \quad (3)$$

By allowing the container to equilibrate after adding the gas, and taking all measurements at near ambient temperatures ($T_0 = T_1$), we can:

let

$$RT_0 = RT_1 = RT \quad (4)$$

then

$$n = V_0 \frac{(P_0 - P_1)}{RT} \quad (5)$$

and

$$V_0 = RT \frac{(n)}{(P_0 - P_1)} \quad (6)$$

If you start by measuring the initial pressure of both the vessel and the gas sampler, and you know the volume of the gas sampler bomb (sampler size should approximate the best estimate of the void volume for optimum results), then the change in the sampler conditions will be comparable to that in the vessel void volume as follows:

$$V_2 = RT \frac{(n)}{(P_2 - P_1)} \quad (7)$$

where

V_2 = volume of sampler bomb,

P_2 = initial pressure of sample bomb,

n = moles of gas lost (or gained) from sampler to the void volume of the container.

Since n in both equations 6 and 7 is the same, then:

$$n = \frac{V_0(P_0 - P_1)}{RT} = \frac{V_2(P_2 - P_1)}{RT} \quad (8)$$

and, therefore

$$V_0 = V_2 \frac{(P_2 - P_1)}{(P_0 - P_1)} \quad (9)$$

By a series of pressurizations and/or purgings of the sampler bomb, (with a judicious period for temperature stabilization between each step) the void volume of the container can be closely measured.

Container and test assembly integrity should be verified to avoid errors due to leaks. Section 5.2.3.3 discusses some methods to check and compensate for leakage effects.

Leaks may also be checked by conducting careful pressure bomb tests in both a pressure-increase and pressure-decrease mode. Discrepancies between the two volume estimates will indicate the magnitude of any leakage.