

Evaluation of Hydrogen Generation and Maximum Normal Operating Pressure for Waste Transportation Packages

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ABSTRACT

The U.S. Nuclear Regulatory Commission certifies several types of radioactive waste packages and verifies that the package designers have shown that there will be no significant chemical, galvanic, or other reactions among the package components and contents, in accordance with Title 10 of the *Code of Federal Regulations* (10 CFR) 71.43(d). For a transportation package containing substances that could generate hydrogen gas, the package designer should calculate the gas generation rate and ensure that it is limited to a molar quantity of no more than 5 percent by volume in the package over a 60-day shipping period under standard temperature and pressure conditions. In addition, the maximum normal operating pressure (MNOP) of the containment vessel should be designed below the design pressure. Therefore, the MNOP calculations should include the hydrogen gas generated in the payload and released into the inner cavity. Package designers have used various approaches to estimate hydrogen gas generation and demonstrate compliance with the regulatory limits. Because it may be difficult to directly measure the hydrogen gas concentrations during transportation operations, it is important that designers use consistent and reliable methods to evaluate hydrogen gas generation. This paper presents a generic evaluation approach for estimating hydrogen generation from radiolysis and thermal decomposition in generic transportation packages. It also presents the calculation of associated MNOP induced by the potential combined effects of radiolysis, thermal decomposition, thermal expansion, and water vapor. In addition, this paper discusses a generic inerting process commonly used to control combustible gases during the normal conditions of transport. A fictitious data set is used to illustrate the evaluation approach.

Keywords:

hydrogen generation, decay heat, radiolysis, thermal expansion, thermal decomposition, maximum normal operating pressure (MNOP), and inerting.

INTRODUCTION

Hydrogen gas and water precipitate generated during transportation may adversely impact the structural and overall integrity of the package or its contents. Among other factors, package designers should consider (1) the generation of explosive quantities of hydrogen or other combustible gases, (2) increased neutron multiplication in the fuel in a package because of boron precipitation from a chemical reaction among the borated water and package materials, (3) changes in package and fuel cladding thermal properties, such as emissivity, (4) the binding of mechanical surfaces, especially fuel-to-basket clearances, and (5) the degradation of any safety components, either because of the direct effects of the reactions or because of the combined effects of the reactions and the exposure of the materials to neutron and gamma radiation, high temperatures, and other possible conditions.

The potential mechanisms of gas generation include radiolysis, chemical reaction, thermal degradation, and biological activity. Restricting the contents of the transportation package to solid inorganic materials and prohibiting explosives, pyrophorics, and corrosives (pH less than 2 or greater than 12.5) will preclude the potential for gas generation from biological activity. The imposition of material compatibility requirements further reduces the possibility of chemical reactions that might produce gases in the package.

The remaining mechanisms for gas generation are radiolysis and thermal degradation. Based on the experiments, solid inorganic materials have a G value of zero (i.e., solid inorganic materials do not generate hydrogen or other gases through radiolysis). However, solidified or dewatered material may contain some water molecules in the composition, and a small amount of water may remain in the cavity after the vacuum draining. The gases generated from the residual water through radiolysis include hydrogen and oxygen.

Radiolysis is the decomposition of a material as a result of radiation exposure. The radiation source may include alpha, beta, or gamma radiation, or a combination of these. Of all the radiation-chemical reactions that have been studied, the most important one is the decomposition of water. This decomposition is induced mainly by the alpha particles that can be entirely absorbed by very thin layers of water. Recently, some nontraditional methods for the generation of hydrogen have prompted reconsideration of the radiolytic splitting of water, where the interaction of various types of ionizing radiation (alpha, beta, and gamma) with water produces molecular hydrogen. When a package contains water or organic substances that could potentially generate hydrogen gas, evaluation must be made through tests and analyses to demonstrate compliance with the criteria in Title 10 of the *Code of Federal Regulations* (10 CFR) 71.43(d) over a period of 60 days (i.e., twice the expected shipment period and a delay of 30 days). Thus, the maximum shipping period used in the analysis of gas generation in a sealed package is 60 days.

In 10 CFR 71.43(d), the U.S. Nuclear Regulatory Commission requires that the materials and construction of a package must ensure that no significant chemical, galvanic, or other reaction will occur among the packaging components, among package contents, or between the package components and the package contents, including a possible reaction from in-leakage of water, to the maximum credible extent. The hydrogen generated must be limited to a molar quantity that would be no more than 5% by volume of the innermost layer of containment if present at a standard temperature of 0 degrees Celsius (C) (32 degrees Fahrenheit (F)) and a pressure of 14.7 pounds-force per square inch absolute (psia) (STP). The gases generated in the payload and released into the cavity shall be controlled to maintain the pressure within the containment vessel below the acceptable design pressure, in accordance with NUREG-1609, "Standard Review Plan for Transportation Packages for Radioactive Material," issued May 1999 [4].

The hydrogen generation in a shipping package shall be evaluated by the following parameters:

- chemical composition of the waste (waste type),
- gas generation potential of the waste material type (quantified by the G value) for hydrogen, which is the number of molecules of hydrogen generated per 100 electron volts (eV) of energy absorbed,
- gas release resistance (type of payload container and type and maximum number of confinement layers used), and
- shipping period (in general, a 60-day shipping period for noncontrolled shipment).

This paper focuses on the methodology applicable to predict the hydrogen generation and the resulting maximum normal operating pressure (MNOP) in a shipping package. The MNOP refers to the maximum pressure that will develop in the containment system in a period of 1 year under the heat condition of an ambient temperature of 38 degrees C (100 degrees F), still air, and insolation, and in the absence of venting, external cooling by an ancillary system, or operational controls during transport. This paper provides a basic evaluation of compliance with the regulatory requirements related to hydrogen gas generation and the corresponding MNOP.

MATHEMATICAL MODEL AND APPROACH

Hydrogen Generation

The 5% (by volume) limit on hydrogen concentration can be converted into a decay heat limit per package because radiolysis of the waste materials is the primary mechanism for hydrogen generation in transuranic (TRU) waste. The hydrogen generation rate of the transportation package is determined by a methodology developed by the U.S. Department of Energy for TRU wastes [1].

The hydrogen generation rate, N_G (moles/second (s)), is determined by

$$N_G = W \times [\sum_i(F_i \times G_i) \times F_p] \times C \quad (\text{Eq. 1})$$

where W is the total decay heat (watts), F_i is the fraction of energy emitted of type i and absorbed by the material, G_i is the number of gas molecules generated per 100 eV of energy absorbed by the contents, and C ($C = 1.04 \times 10^{-5}$ (g-mole)(eV) / (molecule)(watt-s)) is the conversion factor based on the units used in the measurement.

The effective G value, G_{EFF} , is determined from Eq. (2) [2, 3],

$$G_{\text{EFF}} = \sum_i(F_i \times G_i) \times F_p \quad (\text{Eq. 2})$$

where F_p is the fraction of energy emitted by the radioactive materials absorbed by the waste. It is conservatively assumed that all the decay energy is absorbed by the waste ($F_p = 1.0$). As discussed, the effective G value can be substituted into Eq. (1), resulting in:

$$N_G = W \times G_{\text{EFF}} \times C \quad (\text{Eq. 3})$$

G_{EFF} is the effective G value for the contents, in number of gas molecules generated per 100 eV of ionizing radiation absorbed by the contents (potential gas-producing material). The hydrogen concentration, C_H , in liters of hydrogen per liters of void, at the end of the shipping period is determined by Eq. (4):

$$C_H = N_G \times t \times C_F \times \text{Void}^{-1} \quad (\text{Eq. 4})$$

where t ($t = 60$ days = 5.184×10^6 seconds) is the time since the package was sealed, which equals the shipping period, in seconds; C_F is the conversion factor ($= 22.4$ liter/mole = 1366.9 in³/mole) at STP; and Void is the void volume in which gas can accumulate, in liters.

Combining Eqs. (3) and (4) gives:

$$C_H = W \times [\sum_i(F_i \times G_i) \times F_p] \times C \times t \times C_F / \text{Void}^{-1} \quad (\text{Eq. 5})$$

Rearranging Eq. (5) gives:

$$W = C_H \times \text{Void} / \{[\sum_i(F_i \times G_i) \times F_p] \times C \times t \times C_F\} \quad (\text{Eq. 6})$$

where C_H is hydrogen concentration by volume and the subscript i represents the water. The package contents are limited to TRU wastes, typically metal, that are usually loaded underwater. The methodology assumes that draining the package and dewatering the contents (as applicable) will leave some water in the void space, and hydrogen can be generated by radiolysis from this residual water.

The bounding G value of water (G_w) is conservatively assumed to be 1.6 molecules per 100 eV, which is independent of radiation type [1]. The void volume (Void) can be derived from the void fraction (F_v), which is defined as the smallest void volume in which the hydrogen could be accumulated.

To evaluate the decay heat wattage limit for maximum hydrogen content, Eq. (6) uses a 5% hydrogen concentration for C_H . The methodology also conservatively assumes that the contents completely absorb the total decay energy (all gamma or beta decay energy). Applying these values, Eq. (6) gives:

$$W = 0.05 F_v V_{CAVITY} / (F_w \times 1.6 \times 10^{-2} \times 1 \times 1.04 \times 10^{-5} \times 5.184 \times 10^6 \times 1366.9) \quad (\text{Eq. 7})$$

Thus,

$$W = 2.59 \times 10^{-3} \text{ Void} / F_w \quad (\text{Eq. 8})$$

Here, F_w is the weight fraction of the water in the contents and the Void is a void volume occupied by hydrogen. Based on Eq. (8), the decay heat limit depends on two variables: (1) the mass fraction of the water in the payload contents (F_w) and (2) the size of the void volume (Void or $F_v \times V_{CAVITY}$) in which the accumulated hydrogen occupies.

This gas generation methodology is not specific to a particular material type, since all the decay heat is conservatively assumed to be absorbed and the radiation invariant bounding G value is used for the evaluation. Therefore, the gas generation equation is unchanged for all the allowed content forms (e.g., hardware, powder, resin, and even solidified liquid) in TRU waste. To the limited decay heat (W) for the limited hydrogen concentration of less than 5 in the package cavity, the void fraction in the package cavity (F_v) and the weight fraction of the water in the contents (F_w) can be calculated by the void-fraction approach when there is a liner in the package:

$$M_{PW} = M_{CC} - M_L \quad (\text{Eq. 9})$$

$$V_{PW} = M_{PW} / \rho_{PW} \quad (\text{Eq. 10})$$

Here, M_{PW} is the mass of the payload waste, M_{CC} is the mass of the package content, and M_L is the mass of the liner. If the ratio of the volume of the water to the volume of the package waste ($w\%$) is given, the mass of the water (M_w) is calculated as

$$V_w = w\% \times V_{PW} \quad (\text{Eq. 11})$$

$$M_w = \rho_w \times V_w \quad (\text{Eq. 12})$$

If the mass of the water (M_w) is given directly, the weight fraction of the water (F_w) is calculated as

$$F_w = M_w / (M_L + M_{PW}) \quad (\text{Eq. 13})$$

$$\text{Void} = V_{CAVITY} - V_{PW} \quad (\text{Eq. 14})$$

$$F_v = V_{VOID} / V_{CAVITY} \quad (\text{Eq. 15})$$

Then, substitute the calculated Void from Eq. (14) and F_w from Eq. (13) into Eq. (8) to solve the allowable decay heat limit for the maximum hydrogen concentration of 5%.

Maximum Normal Operating Pressure

NUREG-1609 [4] provides the guidance to determine the MNOP and to ensure that the MNOP calculation has considered all possible sources of gases, such as the following:

- hydrogen or other gases resulting from the radiolysis of water
- gases initially present in the package
- saturated vapor, including water vapor from the contents or the packaging
- hydrogen or other gases from the thermal decomposition of materials

Pressure Induced by the Radiolysis of Water and the Subsequent Thermal Expansion

The maximum pressure within the transportation package under normal conditions of transport should be calculated based on the bounding values. With radiolysis as the primary mechanism for hydrogen gas generation, the major factors affecting the internal pressure are the radiolytic gas generation (P_G), the thermal expansion of gases (P_T), and the vapor pressure (P_V) of water within the containment vessel. The temperatures required to calculate the pressure increases include the bulk average payload temperature (T_P), the bulk average void volume (gas) temperature (T_{VV}), and the minimum package inner wall temperature (T_{IW}). The T_P is used to correct the effective G value, the T_{VV} is used to correct the thermal expansion (i.e., heatup) of gases, and the T_{IW} is used to calculate the water vapor pressure contribution based on the temperature of the coolest or condensing surface on the inner wall of the package.

With radiolysis as the primary mechanism for hydrogen gas generation, the calculation of maximum pressure in the containment vessel should (1) consider the immediate release of gases from any inner container/confinement layers to the containment vessel, (2) assume that sufficient moisture is present for saturated water vapor at any temperature, and (3) evaluate the gas generation for a maximum 60-day shipping period.

The temperature-corrected effective G value, G_{EFF} , is based on the bulk average payload temperature and is calculated using the Arrhenius equation [2, 3] (Eq. 16):

$$G_{EFF}(T_P) = G_{EFF}(T_{REF}) \exp \left[\frac{E_A}{R} \left(\frac{T_P - T_{REF}}{T_P \times T_{REF}} \right) \right] \quad (\text{Eq. 16})$$

Here, $G_{eff}(T_P)$ is the effective G value based on bulk average payload temperature (T_P), $G_{EFF}(T_{REF})$ is the effective G value based on the room temperature (T_{REF}), R is the gas constant, and E_A is the activation energy. The activation energy (E_A) is the energy necessary to initiate the reaction, and the activation energy for the radiolytic gas generation in most materials appears to be less than or equal to 3 kilocalories (kcal)/mole, which results in a weak temperature dependence. The radiolysis of the water has been found to be temperature independent and therefore has an apparent activation energy of 0.0 kcal/mole [1].

Next, the $G_{EFF}(T_P)$ is substituted into Eq. (1) to determine the radiolytic gas generation (N_G). The total amount of the radiolytic gases (V_{RG}) generated at STP at the end of 60 days is calculated as

$$V_{RG}(\text{STP}) = N_G \times (60 \text{ days}) \times (86,400 \text{ seconds/day}) \times C_F \quad (\text{Eq. 17})$$

Then, when the radiolytic gases are heated to the bulk average void volume gas temperature (T_{VV}), the corresponding volume is derived based on the thermal-volume expansion:

$$V_{RG}(T_{VV}) = V_{RG}(STP) \frac{T_{VV}}{T_{STP}} \quad (\text{Eq. 18})$$

The final pressure (P_G) generated by the radiolytic gas generation is

$$P_G = 14.7 \frac{V_{RG}(T_{VV})}{\text{Void}} \quad (\text{Eq. 19})$$

Pressure Increased by the Initial Gas and the Subsequent Thermal Expansion

The initial pressure of gas present inside the package cavity at a room temperature of T_{STP} (298 kelvin (K) or 25 degrees C) is 14.7 psia. When the gas is heated up to the bulk average void volume gas temperature (T_{VV}), the increased pressure associated with this increase in temperature as a result of the thermal expansion of gas is calculated as

$$P_{IT} = 14.7 \frac{T_{VV}}{T_{STP}} \quad (\text{Eq. 20})$$

Pressure by Water Vapor

To be conservative in the evaluation of the MNOP, the package is assumed to contain sufficient moisture for saturated water vapor at any temperature. The pressure increase, as a result of the water vapor, is given by using the Bolton equations [5] for the saturation vapor pressure of the water vapor as a function of the temperature. In general, Eqs. (21) and (22) are accepted with minimum differences:

$$P_{WV} = 0.0886 \times 10^{(7.5 T_{MIN}) / (T_{MIN} + 237.3)} \quad (\text{Eq. 21})$$

or

$$P_{WV} = 0.0886 \exp[(17.67 T_{MIN}) / (T_{MIN} + 243.5)] \quad (\text{Eq. 22})$$

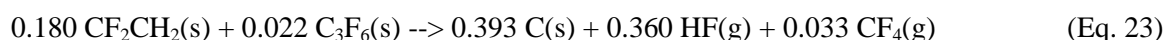
Here, T_{MIN} is the temperature (in degrees C) of the coolest or condensing surfaces at the inner wall of the containment vessel, and P_{WV} is the pressure (psia) from the water vapor. Table I compares water vapor pressures, ranging from 0 degrees C to 100 degrees C, calculated using Eqs. (21) and (22).

Table I. Comparison of Water Vapor Pressures Calculated Using Eqs. (21) and (22)

T _{MIN} (°C)	10	20	40	60	80	100 °C
P _{WV} from Eq. (21) (psia)	0.18	0.34	1.07	2.89	6.89	14.82
P _{WV} from Eq. (22) (psia)	0.18	0.34	1.07	2.91	7.00	15.19

Pressure Induced by the Thermal Decomposition of Materials

Although the gases released from the thermal decomposition or the thermal degradation of materials (e.g., O-ring) are not expected to generate significant hydrogen or other hydrogen gases, the analysis of the pressure in the containment vessel should consider them. However, the thermal decomposition is evaluated using a reaction scheme that generates the maximum number of gaseous reaction products and the maximum pressure rise. The reaction products resulting from the pyrolysis of the elastomeric O-rings in air can be HF and CF₄. The calculation described in this paper is a sample calculation and is mainly used to show the methodology to calculate the pressure rise resulting from the thermal decomposition caused by the material (e.g., O-ring) degradation. Based on the literature [6, 7] and on the reasoning that the formation of HF will completely account for the hydrogen present in the degraded materials, the decomposition reaction equation is formulated as



The mass for fluorine (F), hydrogen (H), and carbon (C) can be derived by using the mass of reactants $m(\text{CF}_2\text{CH}_2)$ and $m(\text{C}_3\text{F}_6)$, as well as the molecular mass of $M(\text{F})$, $M(\text{H})$, $M(\text{C})$, $M(\text{CF}_2\text{CH}_2)$, and $M(\text{C}_3\text{F}_6)$ in Eqs. (24a–e):

$$m(\text{F}) = m(\text{CF}_2\text{CH}_2) \frac{M(\text{F})}{M(\text{CF}_2\text{CH}_2)} \quad (\text{Eq. 24a})$$

$$m(\text{H}) = m(\text{CF}_2\text{CH}_2) \frac{M(\text{H})}{M(\text{CF}_2\text{CH}_2)} \quad (\text{Eq. 24b})$$

$$m(\text{C}) = m(\text{CF}_2\text{CH}_2) \frac{M(\text{C})}{M(\text{CF}_2\text{CH}_2)} \quad (\text{Eq. 24c})$$

$$m(\text{F}) = m(\text{C}_3\text{F}_6) \frac{M(\text{F})}{M(\text{C}_3\text{F}_6)} \quad (\text{Eq. 24d})$$

$$m(\text{C}) = m(\text{C}_3\text{F}_6) \frac{M(\text{C})}{M(\text{C}_3\text{F}_6)} \quad (\text{Eq. 24e})$$

By adding the mass of fluorine (F), hydrogen (H), and carbon (C), and assuming the complete liberation and formation of HF(g) and CF₄(g), the following are required for gas pressure generation in thermal decomposition:

- the volume and the mass of the thermally degraded materials (e.g., elastomeric O-rings)

- the total mole or mass of the hydrogen in the reactants of Eq. (23)
- the mole or mass of gases available for reaction products, such as HF(g) and CF₄(g) in Eq. (23), if it is conservatively assumed that all the hydrogen is liberated to form the maximum gaseous products
- the pressure increase as a result of thermal decomposition of the materials, based on the ideal gas equation

$$P_{TD} = \frac{n_{GAS} R_U T_{VV}}{V_{oid}} \quad (\text{Eq. 25})$$

Here, P_{TD} is the pressure of the gases released from the thermal decomposition of the materials, n_{GAS} is the total mole number of the gases in the reaction products, and R_U is the universal gas constant ($R_U = 82.056 \text{ atm-cm}^3/(\text{mole-K})$), which has the same value for all gases. Therefore, the maximum pressure inside the package at the end of 60 days is

$$P_{MAX} = P_G + P_{TD} + P_{IT} + P_{WV} \quad (\text{Eq. 26})$$

CONTROL OF HYDROGEN GAS GENERATION BY INERTING

Inerting process is used to dewater the container if the hydrogen generated is predicted or expected to be greater than 5% in any portion of the package up to a 60-day shipping period. Inerting is intended to limit the oxygen concentration to less than 5% (by volume) over the same period considered for hydrogen generation. If a leak path can be established between the container and the package cavity, the package cavity will also be inerted. The bulk of the free water is removed from the container by displacing the water with helium or nitrogen gas. In general, the inerting operation is done right before the package is loaded. The following steps provide a general procedure for the inerting of the secondary container, the package cavity, or both to achieve an oxygen concentration of less than 5%:

- (1) Connect a nitrogen supply.
- (2) Pressurize with nitrogen to the required pressure (greater than 14.7 psia) for the required time (e.g., 15 minutes).
- (3) Depressurize to approximately 0 pounds per square inch gauge (psig) (14.7 psia).
- (4) Repeat steps 2 and 3 at least two more times until the system is pressurized by the inert gas to the predetermined pressure.

It is difficult to rely on inerting as a safety basis for mitigating the effects of hydrogen generation because of the difficulty of demonstrating that the inert gas effectively occupies the containment vessel where the combustible gases are generated. In addition, it is difficult to quantitatively analyze the concentrations of combustible gases with the presence of inert gas in a complex containment vessel geometry. For example, the inerting operation may be inappropriate for the following packaging conditions: (1) adjacent vent and drain ports located at the same end of the package, (2) small packaging diameter-to-length ratio, (3) absence of an internal injection path, and (4) port orientation incompatible with tracer gas characteristics (specific gravity). It may not be clear whether the inerting operation has produced a distributive concentration of the inert gas or a uniform concentration throughout the packaging cavity. Therefore, it is difficult to generically identify an appropriate inert gas for all transportation package designs and contents.

The inerting process can be conditionally acceptable if the physical and chemical properties of the inert gas can be well characterized and the intended inerting effects can be well demonstrated with applicable test data for a specific packaging configuration. An inerting operation application to suppress the generation of hydrogen gas depends on further development of regulatory guidance, technical capabilities, and quality assurance programs.

DISCUSSION AND RESULTS

In addition to 10 CFR 71.43(d), NUREG-1609 [4] also specifies the regulatory requirements for gas generation to (1) ensure that the application demonstrates that hydrogen gas comprises less than 5% by volume of the total gas inventory within any confined volume (Thermal Review 3.5.4.2) and (2) confirm that the application demonstrates that any combustible gases generated in the package during a period of 1 year do not exceed 5 percent of the free gas volume in any confined region of the package (Containment Review 4.5.2.3). The challenges relate to (1) how to comply with the hydrogen gas generation requirements to have hydrogen at levels less than 5 percent by volume and (2) how to ensure that the MNOP includes all pressure sources and complies with the design limit.

The thermal and containment evaluations, in the cases with hydrogen generation, are focused on the following conditions:

- The determination of the maximum internal pressure expected during normal conditions of transport includes all worst case effects of gas generation, but the determination of the MNOP, defined in 10 CFR 71.4, “Definitions,” does not consider flammability. Therefore, the MNOP must be less than the design pressure from the containment vessel at the temperature given in 10 CFR 71.71(c)(1).
- The maximum internal pressure expected during hypothetical accident conditions (defined in 10 CFR 71.73, “Hypothetical Accident Conditions”), with the MNOP as the initial internal pressure, does not consider flammability.
- The pressures attributed to radiolysis, thermal expansion, thermal decomposition and water vapor must be summed if all happen under normal conditions of transport, and the resulting maximum pressure should be less than the containment vessel design pressure at the temperature given in 10 CFR 71.71(c)(1).

The calculation of hydrogen generation for typical payload forms loaded underwater depends on the amount of water in the package cavity after the package is drained. Figure 1 shows the allowable decay heat limit vs. the percentage of the water mass within the package content mass (4,500, 5,000, and 5,500 lb, given the density of the content (0.080 lb/cubic inch (in³)), the volume of the package cavity (70,000 in³), and the effective G value of water (1.6 molecules/100eV), to limit the hydrogen generation to less than 5% in volume for a 60-day package shipment. Figure 1 shows that the allowable decay heat limit decreases as the water percentage increases, for any mass of the contents, and the allowable decay heat limit increases as the mass of payload contents increases for the hydrogen generation less than 5% in volume.

Figure 2 depicts the allowable decay heat limit vs. the percentage of the water mass within the package contents under content densities of 0.075, 0.080, and 0.085 lb/in³, given the mass of the contents (5,000 lb), the volume of the package cavity (70,000 in³) and the effective G value of water (1.6 molecules/100eV), to limit hydrogen generation to less than 5% in volume for a 60-day package shipment. For all content densities, the allowable decay heat limit decreases as the water percentage increases. The allowable decay heat limit increases as the content density increases for the hydrogen

generation less than 5% in volume, but it has a larger gradient under a lower water percentage, as shown in Figure 2.

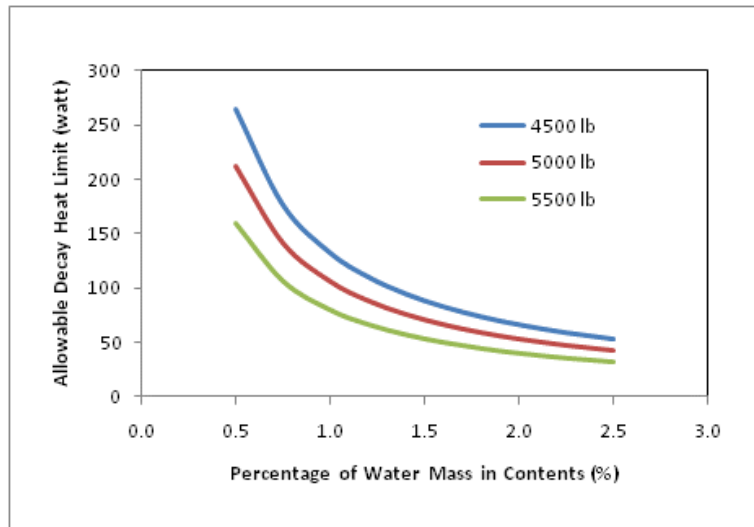


Fig. 1. Decay heat limit vs. percentage of water mass in contents to limit hydrogen generation to less than 5% in volume ($\rho_{CC} = 0.080 \text{ lb/in}^3$, $V_{CAVITY} = 70,000 \text{ in}^3$, and $G_w = 1.6 \text{ molecules/100eV}$).

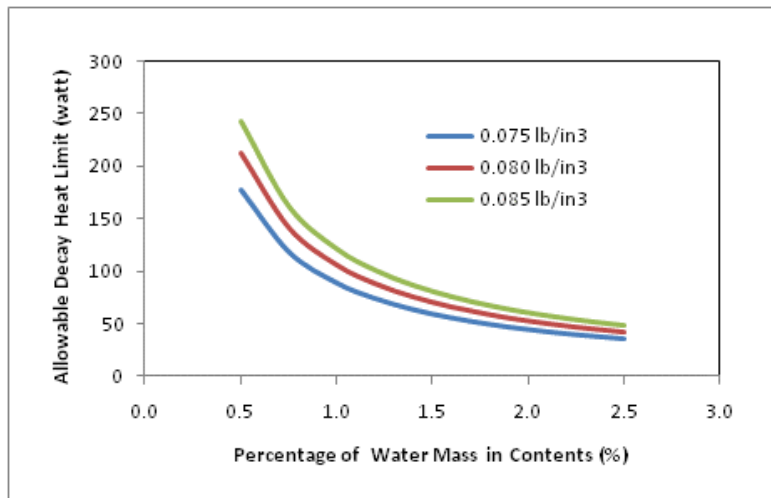


Fig. 2. Decay heat limit vs. percentage of water mass in contents to limit hydrogen generation to less than 5% in volume ($M_{CC} = 5,000 \text{ lb}$, $V_{CAVITY} = 70,000 \text{ in}^3$, and $G_w = 1.6 \text{ molecules/100eV}$).

Figure 3 shows the allowable decay heat limit vs. the percentage of the water mass within the package contents for cavity volumes of 65,000, 70,000, and 75,000 in^3 , given the mass of the contents (5,000 lb), the density of the waste (0.080 lb/in^3), and the effective G value of water (1.6 molecules/100eV), to limit hydrogen generation to less than 5% in volume for a 60-day package shipment. As shown in Figure 3, the allowable decay heat limit increases as the package cavity volume increases, and decreases with the increased water percentage.

Figure 4 indicates the allowable decay heat limit vs. the percentage of the water mass within the package contents for effective G values of the various content types ($G_w = 1.6, 0.5, 2.1, \text{ and } 4.1 \text{ per } 100 \text{ eV}$ of

energy absorbed by the contents for TRU inorganic absorbed waste, particulate waste, concreted waste and organic waste, respectively). Given the content mass of 5,000 lb, the waste density of 0.080 lb/in³, and the package cavity volume of 70,000 in³, to limit hydrogen generation to less than 5% in volume for a 60-day package shipment, it implies that the effective G values for the various payload content types play an important role in determining the allowable decay heat limit, from the perspective of hydrogen generation. The decay heat limit decreases when the effective G value increases, as shown in Figure 4.

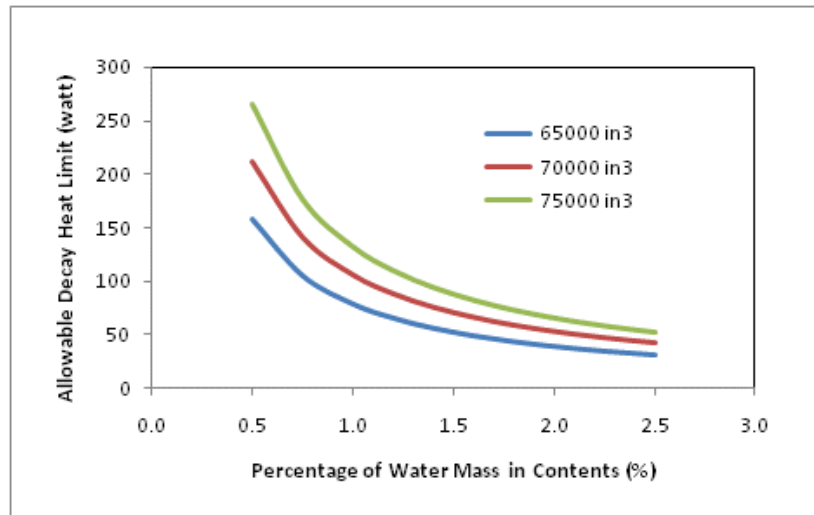


Fig. 3. Decay heat limit vs. percentage of water mass in contents to limit hydrogen generation to less than 5% in volume ($M_{CC} = 5,000$ lb, $\rho_{CC} = 0.080$ lb/in³, and $G_w = 1.6$ molecules/100eV).

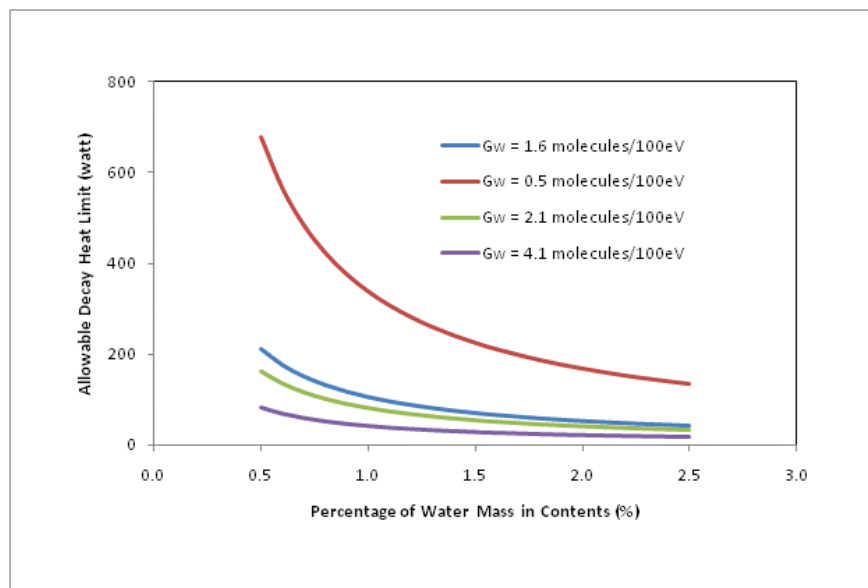


Fig. 4. Decay heat limit vs. percentage of water mass in contents to limit hydrogen generation to less than 5% in volume ($M_{CC} = 5,000$ lb, $\rho_{CC} = 0.080$ lb/in³, and $V_{CAVITY} = 70,000$ in³).

Figure 5 shows that the MNOP varies under content masses of 4,500, 5,000, and 5,500 lb, given the density of the content (0.080 lb/in³), the volume of the cavity (70,000 in³), and the effective G value of the water (1.6 molecules/100eV) to limit hydrogen generation to less than 5% in volume for a 60-day

package shipment. Figure 5 indicates that the MNOP decreases as the mass of water increases because the allowable decay heat is reduced (see Fig. 4) and therefore, the package cavity temperatures are reduced and the internal pressures generated from the water vapor, the thermal decomposition, and the thermal expansion of initial gas are reduced too. The MNOP increases as the mass of the payload contents increase. Correspondingly, the content volume is increased and the void volume decreases when the overall volume of package cavity is unchanged. Therefore, the corresponding pressure increases with a reduced void volume due to ideal-gas law.

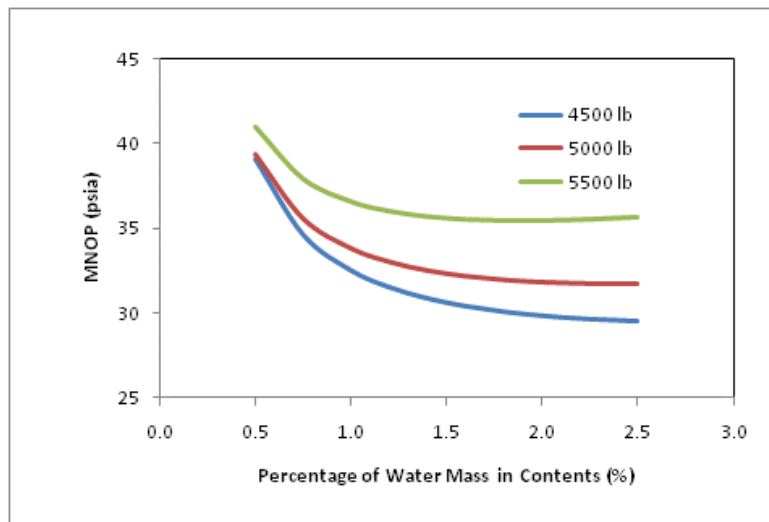


Fig. 5. MNOP vs. percentage of water mass in contents to limit hydrogen generation to less than 5% in volume ($\rho_{CC} = 0.080 \text{ lb/in}^3$, $V_{CAVITY} = 70,000 \text{ in}^3$, and $G_w = 1.6 \text{ molecules/100eV}$).

Figure 6 shows that the MNOP changes under content densities of 0.075, 0.080, and 0.085 lb/in^3 , given the mass of the contents (5,000 lb), the volume of the cavity (70,000 in^3), and the effective G value of the water (1.6 molecules/100eV) to limit hydrogen generation to less than 5% in volume for a 60-day package shipment. For all content densities, the MNOP decreases with the increased mass of water because the allowable decay heat is further reduced (see Figures 1-4) to reduce both package cavity temperatures and internal pressures generated from the water vapor, the thermal decomposition, and the thermal expansion of initial gas. The MNOP also decreases with the increased density of the contents because the volume of the package contents is decreased with an increased content density when both mass of the contents and volume of the package cavity are maintained constant. Under this premise, the void volume increases and the corresponding pressure decreases due to ideal-gas law.

Figure 7 shows that the MNOP varies under package cavity volumes of 65,000, 70,000, and 75,000 in^3 , given the mass of the contents (5,000 lb), the density of the waste (0.080 lb/in^3), and the effective G value of the water (1.6 molecules/100eV) to limit hydrogen generation to less than 5% in volume for a 60-day package shipment. As shown in Figure 7, the MNOP decreases with the increased mass of water. The MNOP also decreases as the volume of the package cavity increases. This indicates that the void volume within the package will increase and the resulting MNOP will decrease when both mass and density of the payload contents are fixed.

It is noted per 10 CFR 71.85 when the MNOP exceeds 35 kilopascals (5 psig), the licensee shall test the containment system at an internal pressure at least 50% higher than the MNOP to verify the capability of the package to maintain the structural integrity at that test pressure.

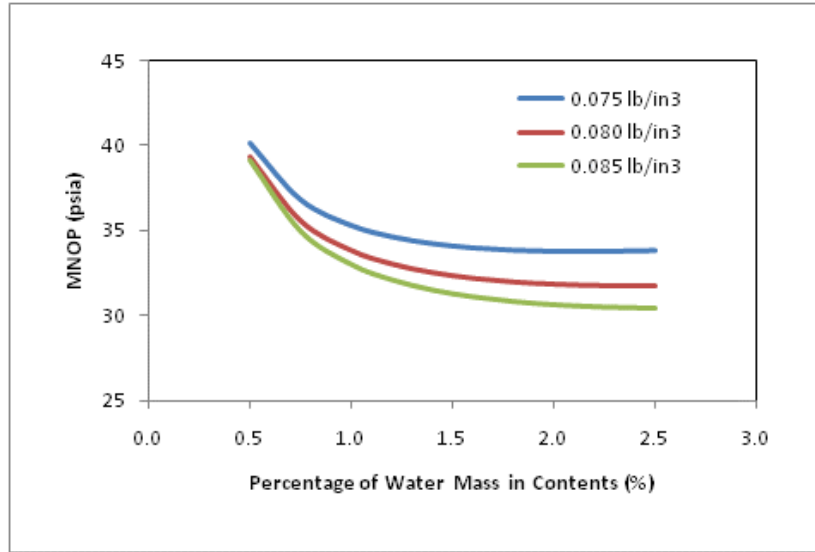


Fig. 6. MNOP vs. water percentage to limit hydrogen generation to less than 5% in volume ($M_{CC} = 5,000$ lb, $V_{CAVITY} = 70,000$ in³, $G_w = 1.6$ molecules/100eV).

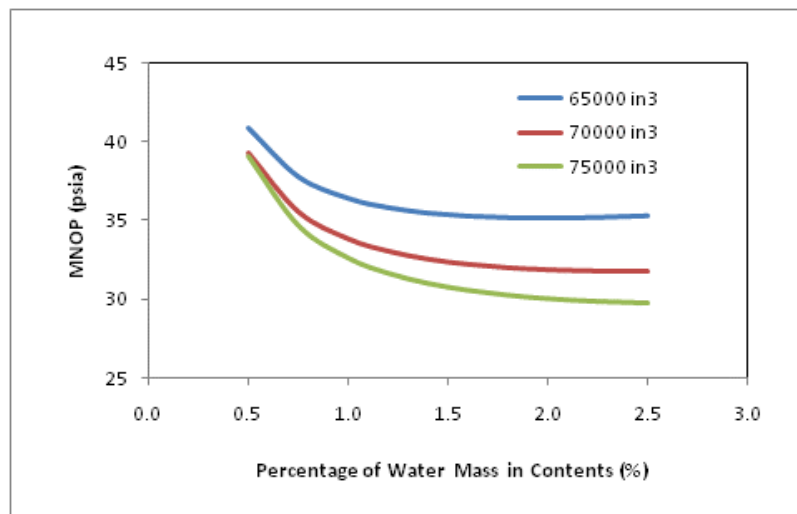


Fig. 7. MNOP vs. water percentage to limit hydrogen generation to less than 5% in volume ($M_{CC} = 5,000$ lb, $\rho_{CC} = 0.080$ lb/in³, $G_w = 1.6$ molecules/100eV).

CONCLUSIONS

The methodology described in this paper describes an alternative approach to demonstrate compliance with the gas generation requirements and the corresponding MNOP for a radioactive waste transportation package. The gas generation model, the gas generation compliance method, and the calculation of MNOP must all meet the requirements of 10 CFR Part 71, “Packaging and Transportation of Radioactive Material.” To do this, all analyses and testing under normal conditions of transport and hypothetical accident conditions must consider hydrogen generation and the calculation of the hydrogen-induced MNOP. The most cost-effective approach to evaluating hydrogen generation is to quantify the allowable package decay heat based on the allowable hydrogen limit specified in NUREG-1609 [4].

Package designers should assess the potential for the generation and ignition of hydrogen gas during all phases of package operations and implement compensatory actions to minimize the potential for the generation and ignition of explosive gases.

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NOMENCLATURE

C	conversion constant for the units used ($C = 1.04 \times 10^{-5}$ (moles)(eV)/[(molecule)(watt-second)])
C_F	conversion factor ($C_F = 22.4$ liters/mole = 1366.9 in ³ /mole)
C_H	hydrogen concentration in liters of hydrogen per liters of void
E_A	activation energy ($E_A = 0.0$ kcal/mole for water)
F_i	fraction of energy emitted of type i and absorbed by the material
F_P	fraction of energy emitted by the radioactive materials absorbed by the waste
F_V	void fraction
F_W	weight fraction of the water
G_{EFF}	effective G value (molecule/(100eV))
G_i	number of gas molecules generated per 100 eV of energy absorbed by the contents
G_W	bounding G value for water (1.6 molecules/(100 eV))
M_L	mass of the liner (lb)
M_{CC}	mass of the package contents (lb)
M_{PW}	mass of payload waste (lb)
M_W	mass of the water (lb or gram)
N_G	gas generation rate (moles/second)
n_{GAS}	mole number of the gases in reaction products of thermal decomposition (mole)
P_{atm}	atmospheric pressure ($P_{atm} = 14.7$ psia)
P_G	pressure by the radiolysis and the subsequent thermal expansion (psia)
P_{IT}	pressure by the initial gas and the subsequent thermal expansion (psia)
P_{TD}	pressure by the thermal decomposition of contents and packaging (psia)
P_{WV}	pressure by water vapor within the containment vessel (psia)
P_{MAX}	maximum pressure inside the package at the end of 60 days (psia)
R	gas constant ($R = 1.99 \times 10^{-3}$ kcal/(mole-K))
R_U	universal gas constant ($R_U = 82.056$ atm-cm ³ /(mole-K))
T_{MIN}	temperature of the coolest surface on the inner wall of the containment vessel (degrees C)
T_P	payload temperature (K)
T_{STP}	standard room temperature at 1 atmosphere ($T_{STP} = 25$ degrees C or 298 K)
T_{VV}	bulk average void volume gas temperature (K)
t	shipping period (second)
V_{CAVITY}	volume of the package cavity (in ³)
V_{PW}	volume of the payload waste (cubic centimeters (in ³))
V_{RG}	volume of the radiolysis gas (in ³)
V_{SW}	volume of the solidified waste (in ³)
Void	void volume in the liner (in ³)

V_w volume of the water after dewatering (in³)
 W limit of the decay heat (watt)

Greek Symbols

ρ_{CC} density of the package contents (lb/in³)
 ρ_{PW} density of the payload waste (lb/in³)
 ρ_w density of the water (lb/in³)

REFERENCES

1. B.L. ANDERSON, M.K. SHEAFFER, and L.E. FISCHER, “Hydrogen Generation in TRU Waste Transportation Packages,” NUREG/CR-6673, Lawrence Livermore National Laboratory, prepared for U.S. Nuclear Regulatory Commission (2000).
2. “CH-TRU Payload Appendices,” Revision 2, U.S. Department of Energy (2007).
3. “RH-TRU Payload Appendices,” Revision 0, U.S. Department of Energy (2006).
4. “Standard Review Plan for Transportation Packages for Radioactive Material,” NUREG-1609, U.S. Nuclear Regulatory Commission (1999).
5. D. BOLTON, “The Computation of Equivalent Potential Temperature,” Monthly Weather Review, Vol. 108, pp. 1046-1053 (1980).
6. J.B. RUBIN, “Thermal Decomposition of Viton O-Rings for the PAT-1 Packaging Accident Scenario,” LA-UR-09-05112, Los Alamos National Laboratory (2006).
7. A.K. BUMHAM and A.K. WEESE, “Kinetics of Thermal Degradation of Explosive Binders Viton A, Estane, and Kel-F,” Thermochemica Acta 426, pp. 85-92 (2005).