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A Simplified Methodology for Estimating the Pressure Buildup and Hydrogen Concentration Within a 2R/6M Container

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ABSTRACT

A simplified and bounding methodology for analyzing the pressure buildup and hydrogen concentration within an unvented 2R container was developed (the 2R is a sealed container within a 6M package). The specific case studied was the gas buildup due to alpha radiolysis of water moisture sorbed on small quantities (less than 20 Ci per package) of plutonium oxide. Analytical solutions for gas pressure buildup and hydrogen concentration within the unvented 2R container were developed. Key results indicated that internal pressure buildup would not be significant for a wide range of conditions. Hydrogen concentrations should also be minimal but are difficult to quantify due to a large variation/uncertainty in model parameters. Additional assurance of non-flammability can be obtained by the use of an inert backfill gas in the 2R container.

Acknowledgements

The authors wish to express their appreciation to members of the Nonactinide Isotope and Sealed Source Management Group (NISSMG), especially Jim Low (DOE/AL), Gary Robertson (DOE/AL) and Dave Parks (INEEL), who cooperated by providing insight and general support of this effort. Thanks go to the Mound Plant personnel, Ray Finney, Steve Brown and especially Gayle Shockey, who provided information on their needs, capabilities, facilities and their materials. Particular thanks are extended to Dr. Martin Sherman (SNL, Org 6422) for his guidance in chemical kinetics and supplying radiolysis models he had previously developed for DOE. Thanks go to Jim Pierce of the SNL Transportation Safety & Security Analysis Department (6141) who provided transportation guidance on the regulations and the 6M packaging and a path forward for accomplishing this task.

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GLOSSARY, ACRONYMS, AND ABBREVIATIONS

2R	Inner container within a 6M package
6M	Type B transport package per DOT regulations
AMU	Atomic Mass Unit
CFR	Code of Federal Regulations
DOT	Department of Transportation
G-value	A (constant) value assigned to a material which generated gases due to radiolysis and is defined as the number of gas molecules produced for each 100 eV of energy absorbed by the material.
SNL	Sandia National Laboratories

NOTATION

Unless otherwise stated, variable units are given within parentheses following the descriptions and numbers in brackets refer to equations in which symbols are first used or thoroughly defined.

$ATWT(H_2O)$ = atomic weight of water (= 18.0153 AMU), [5.1-1]

$ATWT(PuO_2)$ = atomic weight of plutonium (mixture) oxide (= 271.15 AMU, see Appendix B), [5.1-1]

C = curies of alpha activity (Ci), [4.1-1]

$\langle E \rangle$ = average energy of alpha particle emitted from radionuclide (MeV), [A-2]

$\dot{g}$ = gas generation rate (moles/yr), [4.1-1]

$\dot{g}(H_2)$ = hydrogen gas generation rate (moles/yr), [4.1-1]

$\dot{g}(total)$ = total gas generation rate (moles/yr), [5.1-1]

G = number of gas molecules produced for each 100 eV of energy absorbed by the material (molecules/100 eV), [4.1-1]

$G(H_2)$ = G-value for hydrogen gas generation (molecules of H_2/100 eV), [5.1-1]

$G(total)$ = G-value for total gas generation (molecules/100 eV), [4.1-1]

H/X = moderator-to-fissile atom ratio (fraction), [5.1-1]

$\Delta H_2^{\max}$ = maximum number of moles of hydrogen gas generated (moles), [5.1-5]

$[H_2]$ = hydrogen concentration (molar fraction), [5.1-4]

$[H_2]^{max}$ = maximum hydrogen concentration (molar fraction), [D-3]

$[H_2O]^{w\%}$ = moisture (water) weight percent in plutonium oxide (%), [5.1-1]

N_a = Avogrado's number (6.0221367E+23 molecules/mole, Ref. Parrington 1996), [A-1]

N_{gas} = number of moles of gas within 2R (moles), [5.1-2]

ΔN_{H_2} = number of moles of H_2 gas generated within 2R (moles), [5.1-5]

P = gas pressure in void regions of 2R (atm), [5.1-2]

ΔP^{max}	=	total gas pressure (psig), [D-5]
$\widetilde{R}$	=	universal gas constant (8.2057E-05 m^3-atm/mole-K), [5.1-2]
t	=	time (yr), [5.1-2]
t_{max}	=	maximum time available for gas generation – limited by moisture content (yr), [5.1-6]
$t(5\%\ H_2)$	=	time to reach 5% H_2 gas concentration in void region of 2R (yr), [5.1-4]
$t(212.5\ psig)$	=	time to reach 212.5 psig in void region of 2R (yr), [5.1-3]
T_{2R}	=	temperature within 2R (deg. K), [5.1-2]
V_{IC}	=	total volume of inner container (m^3), [5.1-2]
V_{2R}	=	total inner volume of 2R (m^3), [5.1-2]
ε_{IC}	=	void fraction of inner most container (volume fraction), [5.1-2]
ε_{2R}	=	void fraction of 2R container, not including inner container (volume fraction), [5.1-2]
ε'_{2R}	=	average void fraction of 2R, including inner container (volume fraction), [5.1-2]
λ	=	decay constant for radionuclide (sec^{-1}), [A-1]
$\tau_{1/2}$	=	half-life of radionuclide (yr), [A-1]

1. EXECUTIVE SUMMARY

A methodology was developed to analyze the pressure buildup and hydrogen concentration within an unvented container and its contents. The specific case modeled in this study is that of a 2R container (inner container within a 6M package) that is used to transport small quantities (less than 20 Ci) of plutonium oxide. The plutonium oxide material is from the Mound Laboratory (Ottinger 2000) and had previously been thermally treated. In total, there are nine small quantity sources of plutonium oxide (i.e., maximum of 20 curies of activity with total plutonium masses less than 100 grams in a single container). The only source of gas generation is due to alpha radiolysis of water (moisture) sorbed on the plutonium oxide. The radiolysis phenomena breaks-up the chemical bonds between the hydrogen and oxygen atoms in the water molecules. This will result in the release of hydrogen gas, while the oxygen atoms combine with plutonium oxides to generate "super oxides." Since the quantities of plutonium oxides and water molecules are very small, the consequences of gas generation are minimal. However, the history and condition of the plutonium oxides is not known to ultimate precision and the moisture content since packaging has not been measured or recorded. Process knowledge is sufficient to determine that the plutonium oxide has no measurable impurities. To demonstrate that these materials meet the requirements for safe transport in the 2R container, bounding (extremely conservative) models for gas generation rates and resulting consequences were used.

The modeling of the 2R container included the influence of small sealed inner containers within the void region of the 2R container. The following analyses were performed:

- Evaluation of transient pressure buildup within an unvented 2R container at rest via a one-region model (credit was not taken for flow resistance through the inner container lid).
- Evaluation of transient hydrogen concentration levels within an unvented 2R at rest via a one-region model. The one region model combined with the other simplifying assumptions results in a conservative, bounding model for the gas generation within the 2R containers

The analysis of an unvented 2R container without the use of hydrogen mitigating processes such as hydrogen getter or recombiner catalysts indicated that:

(1) The time to reach appreciable hydrogen concentration levels is always less than that to reach a maximum pressure differential of 212.5 psig. The maximum container pressure has been determined to be 850 psig (Radloff 1998), corresponding to a safety factor of four.

(2) The time required to reach 212.5 psig was calculated to be greater than 20 years for payloads of 20 curies of activity even when combined with high gas generation rate constants (i.e., G(total) = 0.05) and small voided regions.

(3) The time required to reach hydrogen concentration levels of 5% was calculated to be within one year for the same conditions as above.

The analyses for pressure and hydrogen buildup values were performed at several levels of conservatism (i.e., without credit given for: (a) depletion of sorbed water moisture in the plutonium oxide, (b) reverse chemical reaction rates, and (c) best estimates for gas generation rates). All the results indicated that gas pressure buildup is insignificant in comparison to the structural integrity of the 2R container, and no pressure mitigation measures were needed. Calculations for hydrogen concentration values were strongly dependent upon the level of conservatism in the model used along with assumed input variables. As a precaution, it is recommended that the 2R containers be back-filled with an inert gas such as argon. This simple loading process will not mitigate the hydrogen gas generation process, but it will serve as an assurance that flammable gas mixtures will not be generated. This process should be considered a safety assurance. Backfilling of canisters for shipping is considered a good engineering practice because the process is simple, straight forward, allows working with a known gas composition, and adds to the safety of the container.

2. INTRODUCTION

Approximately 217 grams of plutonium (Pu) in several containers are currently held at Mound (BWXTO). Material disposition maps developed by the Nuclear Material Integration Project show the baseline for the disposition of the Pu-239 from Mound to be the Savannah River Site. While the materials have been stored with no indications of leakage or contamination for more than 20 years, the regulations governing the transport of the material requires that several characteristics be met. The most difficult characteristic to analyze is the gas generation. This study outlines the approach taken to bound the potential gas generation of the materials for shipping.

Gas generation, specifically of hydrogen, was studied for the 2R inner container for the 6M package. The 2R inner container, shown in Figure 2-1, is analyzed for potential gas generation for the most conservative case of the 9 containers of materials as described Appendix D (taken from Ottinger 2000).

Applicable regulations concerning transportation in the DOT Specification 6M packaging and a discussion of the Mound material compliance is provided in Ottinger 2000. It is assumed that this material originated at Hanford and is relatively pure. It was modified and subsequently heat treated at Mound at 100 ^{0}C for 24 hours and used for an assay system (Ottinger 2000).

To simplify the models and analyze the conditions where the information is not as precise as it needs to be, the following simplifications and assumptions were made:

- The geometry was assumed to be a single control volume (one region). The implications of this simplification are that all gas in the innermost container is assumed to uniformly occupy the available space.
- The only viable source of gas generation is due to alpha radiolysis of water moisture sorbed on the plutonium oxide.
- The 2R container is unvented.
- A maximum allowable pressure of 212.5 psig was used in the analyses, which corresponds to a safety factor of 4 from the determined pressure limit of 850 psig for the 2R container (Radloff 1998).

This report provides the analysis of the potential pressures and hydrogen concentrations within the 2R inner container. The analyses considered the following effects:

1. An assessment of the alpha radiolysis G-values (number of gas molecules produced for each 100 eV of absorbed energy) for plutonium oxide.
2. Gas generation rates due to alpha radiolysis expected for the plutonium oxide from Mound Laboratory.
3. The maximum pressure buildup that can be expected within the unvented 2R container.
4. The corresponding hydrogen gas concentrations.
5. Sensitivity studies for the key parameters.

Section 3 states the specific problem analyzed and describes the approach taken, while Section 4 describes the gas generation sources and rates considered for pressurization. Sections 5 and 6 presents the results, conclusion and recommendations.

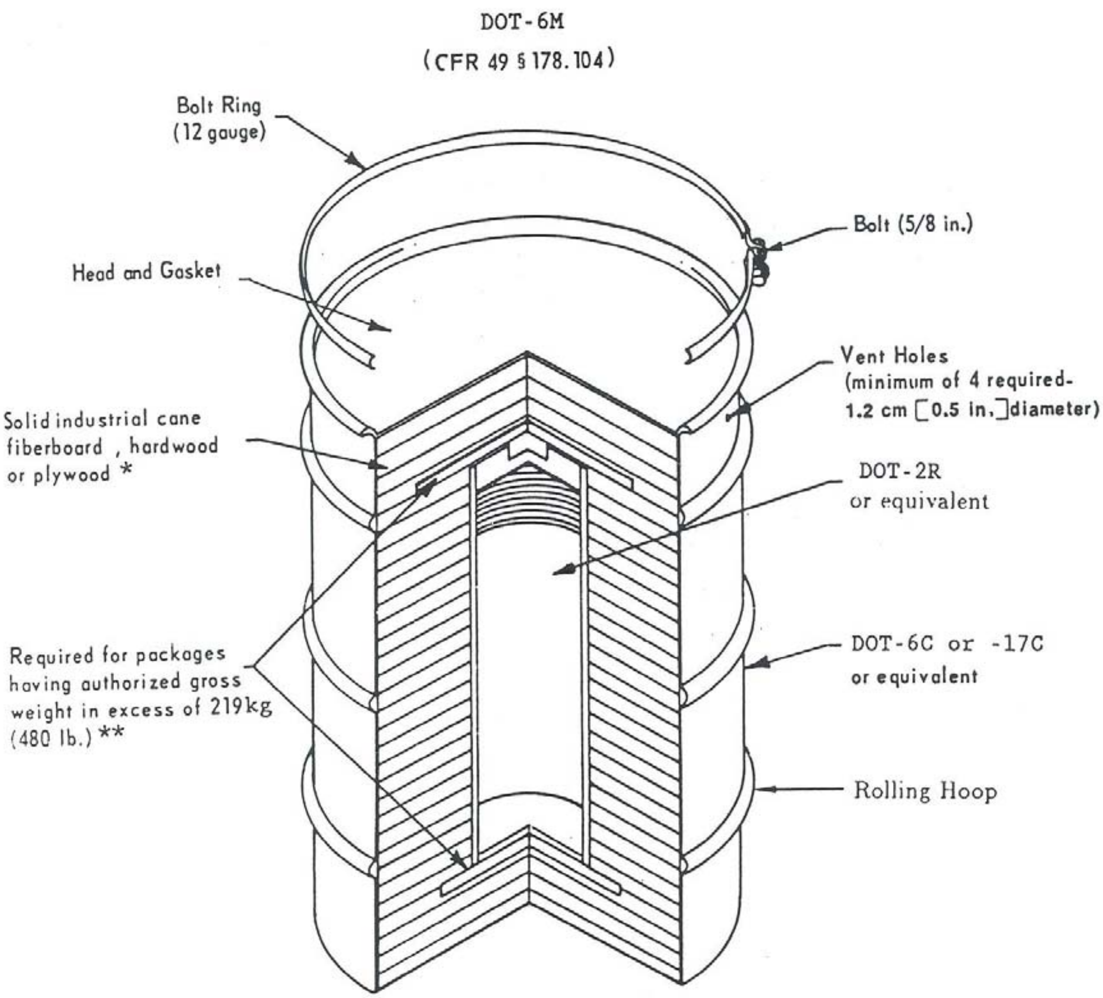

Figure 2-1. Geometry of 6M containers (taken from Edling 1975)

* Current design uses Celotex® material (high density).

** Steel-bearing plates.

3. STATEMENT OF THE PROBLEM AND DESCRIPTION OF APPROACH

PROBLEM STATEMENT:
This report provides an analytical description of the gas pressure and hydrogen concentration within an unvented 2R container with a payload of plutonium oxide. The plutonium oxide had previously been thermally treated and is limited to small quantities of less than 20 curies of activity with a total plutonium mass less than 100 grams.

The goal of this study was to perform the following analyses:

1. Evaluate the transient pressure buildup within an unvented 2R.
2. Evaluate the transient hydrogen concentration levels within an unvented 2R.

PROBLEM APPROACH:
The 2R container was modeled using a one-region geometry during all of the analyses. The void region was defined as the volume inside the 2R container less the volume of the inner most container. The problem was approached using multiple levels of conservatism followed by the appropriate sensitivity studies as follows:

1. **Determine the gas generation rates expected in the plutonium oxide material**.
2. **Perform the extremely conservative analysis:** Evaluate the time necessary to reach the maximum allowable hydrogen concentration and pressure levels. This level of analysis does not take into consideration limited absorbed water sources or radionuclide decay.
3. **Analyze the sensitivity of the radiolytic hydrogen generation rates:** The analysis used a wide range of experimentally determined radiolytic hydrogen generation rates.
4. **Perform the moderately conservative analysis:** Evaluate the maximum time for gas generation production due to limited quantities of absorbed water in the plutonium oxide using the upper bounds of probable moisture content. The corresponding maximum hydrogen concentration and gas pressure were also evaluated at the maximum time.
5. **Analyze the sensitivity of the moisture content:** Concern existed regarding the amount of moisture absorbed by the material.
6. **Perform the "best estimate" analysis:** Best estimate values for the absorbed moisture content and the G-value for the plutonium materials were used.
7. **Asertain conservatism:** The results of the best estimate analysis were compared to the other analyses to understand the level of conservatism introduced into the earlier analyses.

A summary of the conservatism included into the problem is shown in Table 3-1.

As identified above, the analyses for pressure and hydrogen buildup values are to be performed at several levels of conservatism (i.e., with and without credit given for: (a) depletion of sorbed water moisture in the plutonium oxide, and (b) best estimates for gas generation rates). Table 3-1 gives a synopsis of the conservatism in the models.

Table 3-1. Levels of Conservatism in Computations

Conservative Level	Description
Extremely Conservative	No credit is taken for: (1) depletion of moisture in host material, (2) "best estimate" value of G-value, and (3) "best estimate" value for moisture.
Moderately Conservative	No credit is taken for: (1) "best estimate" value of G-value and (2) "best estimate" value for moisture in host material.
Best Estimate	Analysis performs using (1) depletion of moisture in host material, (2) "best estimate" value of G-value, and (3) "best estimate" value for moisture.

4. GAS GENERATION RATES

This section identifies the potential sources of hydrogen gas generation and provides a survey of reported gas generation rates for a range of plutonium oxide samples. The gas generation rate values presented here are not all-inclusive, but rather, are presented to provide a measure of the order of magnitude of gas generation rates for plutonium oxides to be transported in an unvented 2R container.

4.1. Gas Generation Sources

In general, the gas generation in plutonium oxides and other transuranic (TRU) materials can be attributed to five mechanisms:

(1) Radiolysis
(2) Bacterial decomposition
(3) Thermal degradation
(4) Chemical corrosion
(5) Vapor pressure of the plutonium oxide

4.1.1 Radiolysis

Radiolysis is the process where ionizing radiation collides with matter resulting in broken atom/molecule bonds. Consequently, molecules can be released as gases. This process can occur with all types of ionizing radiation (alpha, betas, gammas, neutrons, photons, etc.,). Alphas have the largest potential for radiolysis due to the large Linear Energy Transfer (LET) values associated with them. Since the material under study here is plutonium oxide, only alpha-radiolysis is of importance (from data in Parrington 1996 it can be identified that high energy alphas are emitted from plutonium isotopes, see Appendix A for radioactivity properties of key plutonium isotopes). In addition, the dissociation of the sorbed water in the plutonium oxide molecules caused by alpha particle collisions yields hydrogen (the oxygen molecules combines with the plutonium to form "super" oxides). A measure of the rate of gas generation in radiolytic processes is expressed by the G-value. The G-value is the number of gas molecules produced for each 100 eV of energy absorbed by the plutonium oxide/moisture mixture. G-values are a function of the material type and the dose rate. (Dose rate is defined as the rate at which energy is absorbed per gram of material.) Assuming that all the alpha energy is deposited in the material, the upper limit for the total gas generation rate, $\dot{g}$ (in moles of gas per 2R per year), may be calculated from the total gas G-value of the material. This is given by the expression (for plutonium oxide materials, see Appendix C):

$$\dot{g}(total) = 0.10\, G(total)\, C \qquad (moles/yr) \qquad (Eq.\ 4.1-1)$$

where,

$\dot{g}(total)$ = total gas generation rate (moles/yr)
$G(total)$ = G-value for total gas generation (molecules/100eV)
C = Curies of plutonium oxide in container (Ci)

The data used to derive the relationship in Equation 4.1-1 can be found in Appendices B and C (Appendix B contains information for the isotopic distribution in plutonium oxide and Appendix C contains the evaluation of the "0.10" conversion factor within Equation 4.1-1).

Applying Equation 4.1-1 to gas generation analyses requires the existence of experimental data for the G-value. Data for plutonium oxide was identified in Sherman 1999 (a copy of this reference can be found in Appendix E). This particular experimental data was for $\dot{g}(total)$; the total gas generation rate measured for different radioactivity intensities. Using Equation 4.1-1 in reverse form, the G-values for five plutonium oxide cases were determined from data in Sherman 1999. The results are presented in Table C-2, which indicates that possible G-values range from 0.0010 up to 0.15. The lower value is expected to be the "best estimate" (most reasonable estimate) for G since it was derived from a more controlled experiment than the others were. In order to avoid the need to gather more data to collaborate the lower value, the analysis results will study the entire range of possible G-values. The outcome depends on moderately conservative results (see Sherman 1999 and Appendix C for more information).

After the G-values were determined for plutonium oxides, the G-values were used to estimate gas generation rates for plutonium oxides from the Mound Laboratory. There are nine plutonium oxide containers studied (see Table D-1 and Ottinger 2000 for mass quantities). These small quantity sources have masses ranging from 2.26 up to 82.24 grams of plutonium with corresponding radioactivity inventories of 0.45 up to 17.55 Ci.

4.1.2 Bacteriological Decomposition

If organic materials were available in the material and bacteria and/or fungi were present in sufficient quantities, then significant microbial growth and biological degradation of the organic matter under ideal conditions may lead to gas generation. Bacterial degradation of organic mater yields essentially only carbon dioxide in an aerobic or anaerobic atmosphere. Since the plutonium oxide in this study has undergone a thermal treatment and shows no indications of co-mingling with oil or other non-metal materials, there will be no bacteriological decomposition.

4.1.3 Thermal Degradation

A third possible source of gas generation is thermal degradation. Gas production in the absence of radiation has been observed for several organic materials. Since the material under consideration here is plutonium oxide, thermal degradation is not expected since the plutonium oxide is not organic and does not undergo thermal degradation.

4.1.4 Chemical Corrosion

The generation of hydrogen gas from chemical (low pH) corrosion of the steel alloy used for the 2R container is only significant for long-timeframes when available high moisture air or free liquids are available. Since: (1) there are no free liquids/water internal for the containers, (2) the containers exhibit no visible bulging, and (3) the outside of the containers do not exhibit corrosion, this gas generation mechanism is not expected.

4.1.5 Vapor Pressure

Data for the vapor pressure of plutonium oxide was identified in the Plutonium Handbook (Wick 1980). This data, in inverse temperature form, is shown in Figure 4-1 and clearly indicates that the vapor pressure of plutonium oxide is not importance for this study (eg., vapor pressure is significantly less than the 212.5 psig level).

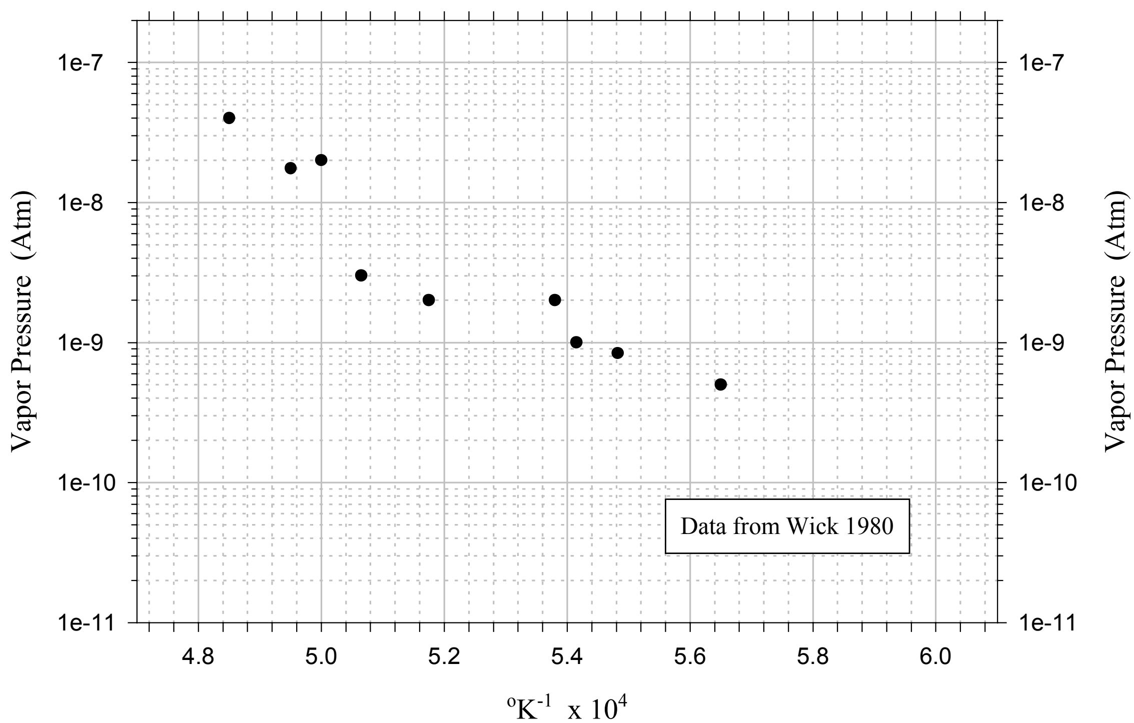

Figure 4-1. Vapor pressure for plutonium oxide in oxygen (after Wick 1980).

5. RESULTS

The results from this study are presented for the different levels of conservatism. Key results from this study are:

(1) The hydrogen-to-fissile atom ratio (H/X), which is of concern for criticality control, was identified to be below the H/X limit of 3 for water moisture weight percentages less than 9 ^{w}% (much greater than any expected values even when moderately conservative).
(2) The time to reach appreciable hydrogen concentration levels is always less than the time to reach the maximum allowable pressure differential of 212.5 psig (since the structural integrity of the container has been determined to be 850 psig, this corresponds to a safety factor of four).
(3) The time required to reach 212.5 psig may be on the order of 20 to hundreds of years for payloads of 20 curies of activity or less even when combined with high gas generation rate constants (i.e., G(total) = 0.05) and small voided regions).
(4) The time required to reach hydrogen concentration levels of 5% (a flammability level achievable only in the presence of oxygen) may be less than one year.

5.1 Results for H/X (Moderator-to-Fissile Atom Ratio)

The moderator-to-fissile atom ratio is of major concern for criticality safety. Detailed studies on plutonium assemblies (Wick 1980) have identified that a critical assembly of Pu-239 could be generated for plutonium mass of approximately 0.65 kg only if special conditions are meet (e.g., spherical geometry, reflected boundary conditions, slurry mixture of plutonium in water, moderate temperatures, etc.). A key feature of criticality of plutonium/water assemblies is that very large values for the moderator-to-fissile atom ratio (H/X values of approximately 900, see pg. 878 Wick 1980) are needed for optimal criticality conditions. Only under those extreme conditions can a critical assembly be generated with fissile masses under 1 kg. For dry systems of plutonium metal and plutonium oxide, the amount of mass to generate a critical assembly is greatly increased (i.e., dry fissile masses on the order of 10 kg are then needed). To insure criticality safety, an activity limit of 20 curies and a H/X ratio limit of three (essentially a dry system) are applied for the payload of the 2R container.

The H/X ratio (moderator-to-fissile atom ratio) can be determined from Equation 5.1-1, and important results are presented in Table 5-1 and shown in Figure 5-1.

$$H / X = STOC(H_2) \frac{[H_2O]^{w}\%}{100\% - [H_2O]^{w}\%} \frac{ATWT(PuO_2)}{ATWT(H_2O)} \qquad [Eq.\ 5.1-1]$$

where,

$ATWT(H_2O)$ = atomic weight of water = 18.0153 AMU
$ATWT(PuO_2)$ = atomic weight of plutonium oxide = 271.15 AMU (this value was determined in Table B-2 and corresponds to a plutonium mixture having an isotopic distribution given by Table B-1, see Appendix B for values)
$[H_2O]^{w}\%$ = Water moisture weight percent in plutonium oxide
$STOC(H_2)$ = 2 = stoichiometric coefficient for hydrogen gas

Table 5-1. H/X Ratio Values for Various Water Moisture Contents for Plutonium Oxide

Moisture (^{w}%)	H/X Ratio [a] (- -)	Moisture (^{w}%)	H/X Ratio [a] (- -)	Moisture (^{w}%)	H/X Ratio [a] (- -)
0.25	0.0754	1.25	0.3810	3.00	0.9310
0.50	0.1513	1.50	0.4584	5.00	1.5843
0.75	0.2275	1.75	0.5362	7.50	2.4407
1.00	0.3041	2.00	0.6143	9.06	2.9990

(a) Values calculated using Equation 5.1-1.

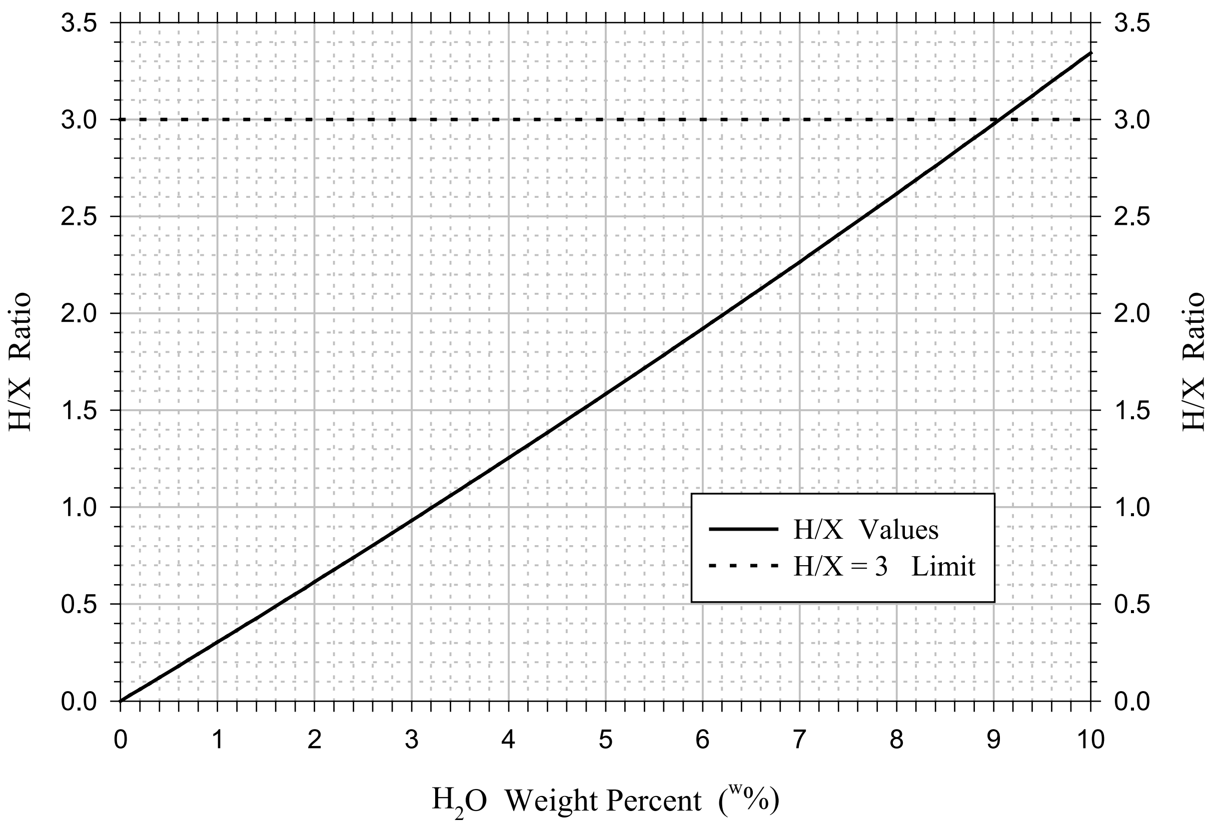

Figure 5-1. H/X ratio as a function of water moisture (weight percent) sorbed in plutonium oxide (data from Table 5-1).

5.2 Results for Gas Pressure and Hydrogen Concentration

The model for the gas pressure and hydrogen concentrations within the 2R container was generated using a mole balance and the ideal gas law. For a sealed 2R container, the number of moles of gas is given by:

$$N_{gas} = \frac{P(t=0)\,\varepsilon^{/}_{2R}\,V_{2R}}{\widetilde{R}T_{2R}(t=0)} + \dot{g}_{total}\,t \qquad [Eq.\ 5.1-2]$$

where,

N_{gas} = total number of moles of gas within 2R
$P(t=0)$ = initial pressure of air in 2R
$\varepsilon^{/}_{2R}$ = average void fraction of 2R, including inner container
= $\varepsilon_{2R} + \varepsilon_{IC} \times V_{IC}/V_{2R}$
ε_{2R} = void fraction of 2R, not including inner container
ε_{IC} = void fraction of inner container
V_{2R} = total volume of 2R
V_{IC} = total volume of inner container
$T_{2R}(t=0)$ = temperature within 2R at time = 0
$\dot{g}(total)$ = total gas generation rate (assumed to be isothermal)
t = time
$\widetilde{R}$ = universal gas constant = 8.2057E-05 m^3-atm/mole-K

Using Equation 5.1-2, the time to reach the 5% H_2 concentration and the pressure limit (212.5 psig, which includes a safety factor of four) are given by Equations 5.1-3 and 5.1-4, respectively (note – these solutions are extremely conservative).

$$t(212.5\,psig) = \frac{\Delta P}{\left(0.10\,G(total)\,C\right)\left(\dfrac{\widetilde{R}T_{2R}(t=0)}{\varepsilon^{/}_{2R}V_{2R}}\right)} \qquad [Eq.\ 5.1-3]$$

$$t(5\%\,H_2) = \frac{(0.05 - [H_2(t=0)])\,\dfrac{P(t=0)\,\varepsilon^{/}_{2R}V_{2R}}{\widetilde{R}T_{2R}(t=0)}}{0.10\,C\left(G(H_2) - 0.05\,G(total)\right)} \qquad [Eq.\ 5.1-4]$$

Using Equations 5.1-3 and 5.1-4, a sensitivity analysis was performed for a wide range of curie payloads (0 $\rightarrow$ 20 Ci), G(total) values (0.05 $\rightarrow$ 0.25, moderately conservative), and $G(H_2)/G$(total) ratios (0.2 $\rightarrow$ 1.0). The results are presented in Figures 5-2 and 5-3. These figures are formatted as dual 2D-plots. The bottom figure uses the y-axis for the independent variable (curie loading). The x-axis of this plot is then used for the dependent results (total gas generation), and the several curves identify the response expected for various values of G(total). After the total gas generation has been determined, then the upper figure can be used in the classical form to identify the net result (time to reach a predetermined pressure or hydrogen concentration) for various ratios of $G(H_2)/G$(total). As an example, from Figure 5-2 it can be identified that a curie loading of 10.0 Ci in a single package would result in a total gas generation rate of 0.20 moles/yr if G(total) equals 0.20 (see lower portion of Figure 5-2). Applying this total gas generation rate along with a temperature of 121.1^{0}C would result in a t(212.5 psig) value of approximately 14 years.

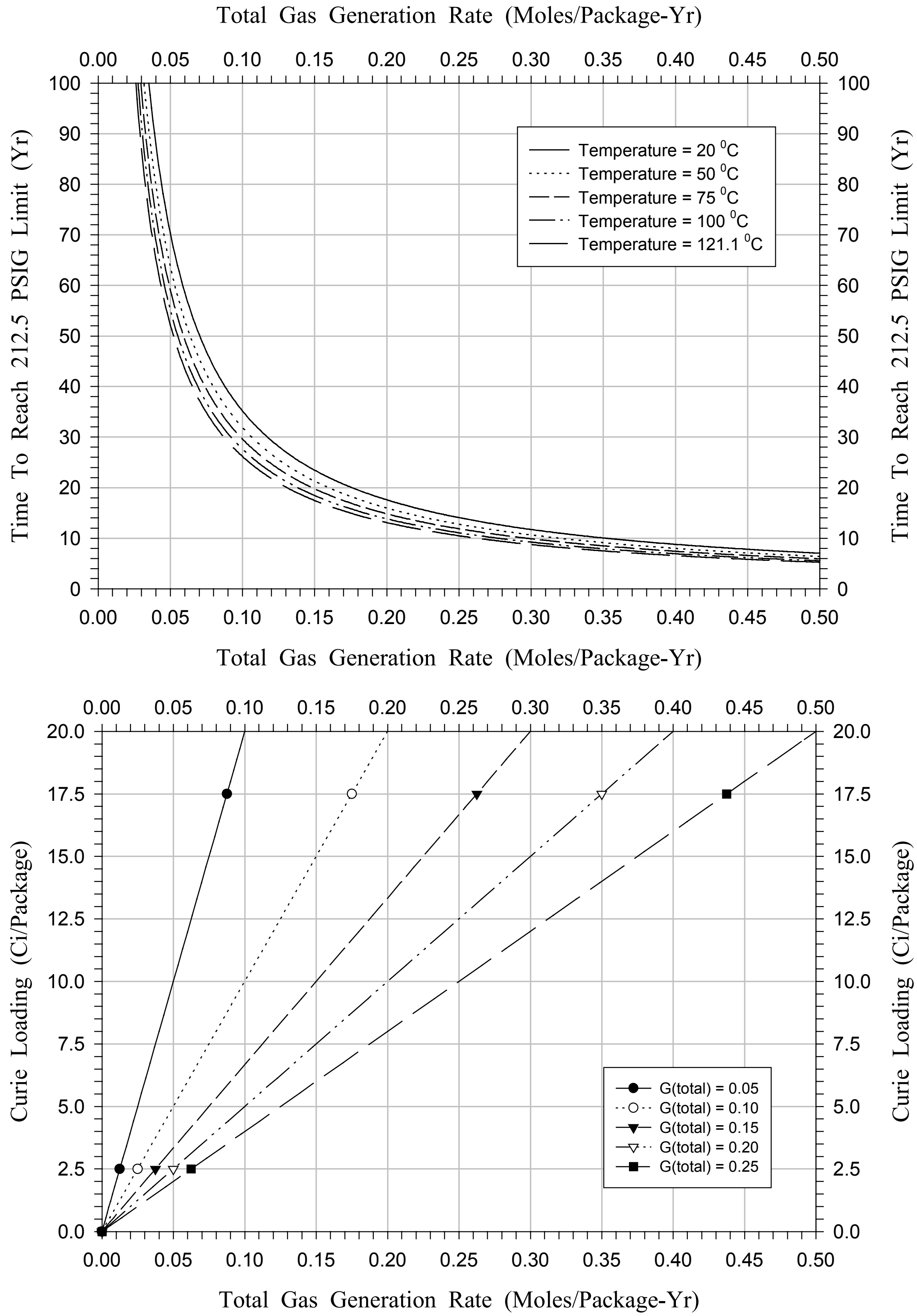

Figure 5-2. Time to reach gas pressure limit (212.5 psig) within an unvented 2R. (This is extremely conservative; does not account for moisture depletion.)

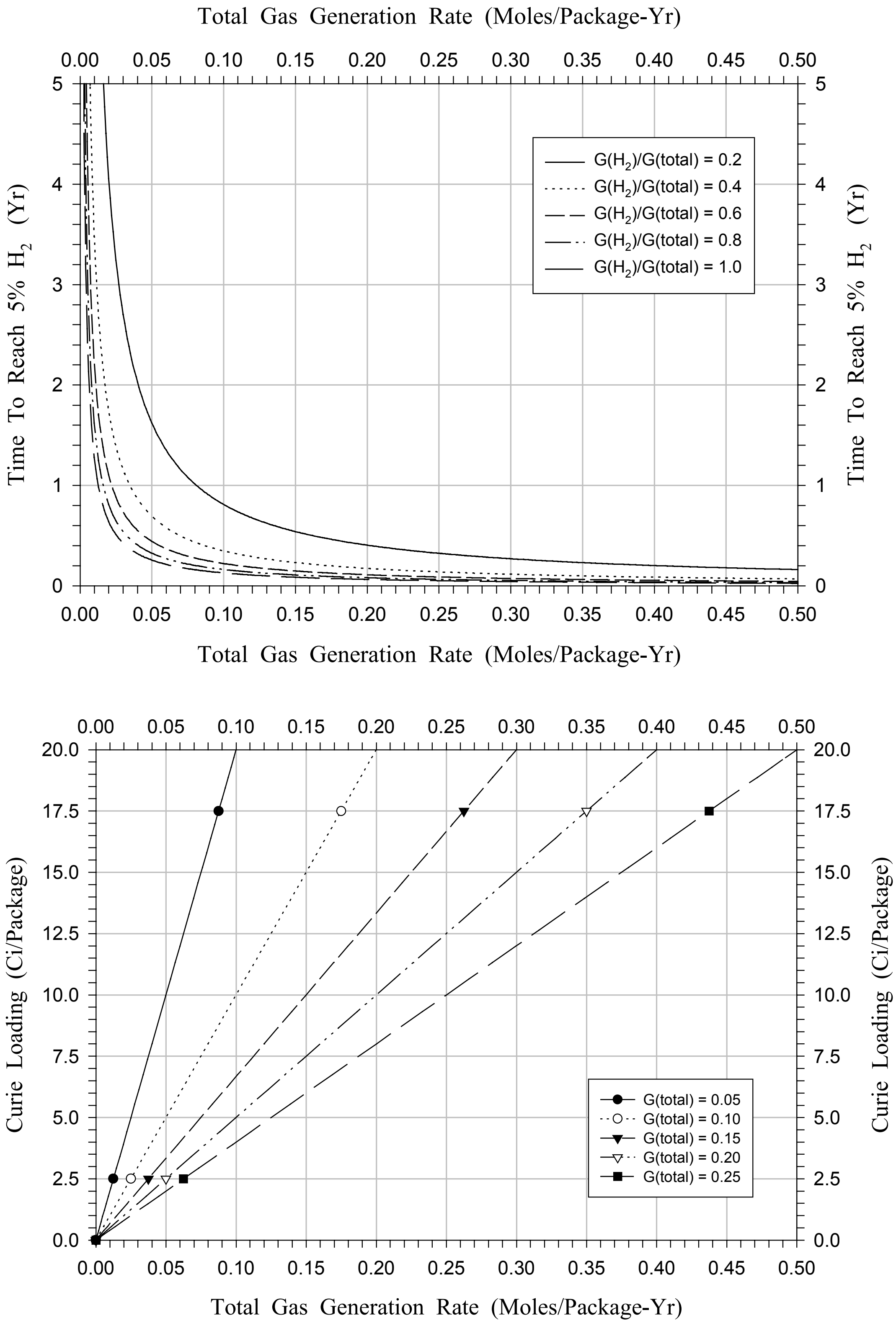

Figure 5-3. Time to reach hydrogen gas concentration of 5% by volume within an unvented 2R (ε'_{2R} = 0.758, initial hydrogen concentration of 0%). (This is extremely conservative; does not account for moisture depletion.)

The overall findings that can be identified in Figures 5-2 and 5-3 are:

(1) The time reach a 5% hydrogen concentration is always less than the time that it takes to reach 212.5 psig (the maximum normal operating pressure goal).
(2) The times needed to reach the pressure limit (212.5 psig) are in excess of 20 years (even for extremely conservative gas generation rates) and no concerns on pressure buildup are evident.
(3) The time to reach the 5% hydrogen concentration is very sensitive to the G-values used. The range of G-values used for the sensitivity analysis is very wide and uses values that are expected to be larger than nominal values. However, not enough quantified information is available to guarantee that credit can be given for lower G-values.

The above equations and figures correspond to an extremely conservative scenario where an infinite supply of moisture is assumed. If credit is given for knowledge of the initial moisture content of the plutonium oxide (moderately conservative), then the gas generation model can take into account the depletion of water as a function of time. Equation 5.1-5 identifies the relationship between the gas generation rate to the material G-value and the curie payload. Solving this equation for the maximum time that gas generation can exist, yields Equation 5.1-6. From Equation 5.1-6, the general solutions for hydrogen concentration and total gas pressure can be obtained and are presented in Equations 5.1-7 and 5.1-8. Numerical solutions for the maximum times for gas buildup and maximum hydrogen concentration can be found in Appendix D.

$$\Delta N_{H_2}(t) = \dot{g}(H_2)\,t = 0.10\,G(H_2)\,C\,t \qquad [Eq.\ 5.1-5]$$

where,

ΔN_{H_2} = number of moles of hydrogen gas generated

$$t_{\max} = \frac{\Delta N_{H_2}^{\max}}{0.10\,G(H_2)\,C} \qquad [Eq.\ 5.1-6]$$

where,

t_{max} = maximum time available for gas generation (limited by moisture content)

$$[H_2] = \left\{ \begin{array}{ll} \dfrac{0.10G(H_2)Ct}{\dfrac{P(t=0)\varepsilon_{2R}^{/}V_{2R}}{\widetilde{R}T_{2R}(t=0)} + 0.10G(total)Ct} & for\ t < t_{\max} \\ \dfrac{0.10G(H_2)Ct_{\max}}{\dfrac{P(t=0)\varepsilon_{2R}^{/}V_{2R}}{\widetilde{R}T_{2R}(t=0)} + 0.10G(total)Ct_{\max}} & for\ t \ge t_{\max} \end{array} \right\} \qquad [Eq.\ 5.1-7]$$

$$\Delta P(t) = \begin{cases} \dfrac{\tilde{R}T_{2R}(t)}{\varepsilon_{2R}^{/}V_{2R}}\left(0.10G(total)Ct\right) & for\ t < t_{\max} \\ \dfrac{\tilde{R}T_{2R}(final)}{\varepsilon_{2R}^{/}V_{2R}}\left(0.10G(total)Ct_{\max}\right) & for\ t \geq t_{\max} \end{cases} \qquad [Eq.5.1-8]$$

Using Equations 5.1-7 and 5.1-8, Figures 5-4 through 5-9 were generated. These figures were generated in triple sets for varying values of moisture content. The moistures investigated were: $5.0^{w}\%$, $2.8^{w}\%$, and $0.752^{w}\%$. The $5.0^{w}\%$ value corresponds to a conservative bounding quantity which is never expected to be exceeded. The $2.8^{w}\%$ value corresponds to the highest moisture content assayed in LANL 1999. The $0.752^{w}\%$ values corresponds to the lowest moisture content for untreated plutonium oxides (LANL 1999). Even the lowest of these three values is conservative since the plutonium oxides from Mound had initially been heat treated. A first order estimate would be that the Mound plutonium oxides could have a moisture content that is an order of magnitude lower than the lowest value considered in this study. These figures indicate that the pressure buildup and hydrogen concentration linearly increases until depletion of the sorbed moisture in the plutonium oxide has occurred. After that period of time, the values remain constant due to depletion of moisture. A significant finding from the figures was that the gas pressure buildup and hydrogen concentrations are severely limited by the moisture content. If confirmatory information were available to identify that the Mound materials do indeed have moisture contents that are an order of magnitude less than those investigated in Figure 5-4 through 5-9, then insignificant pressure buildup and hydrogen concentration values could be presented as final results.

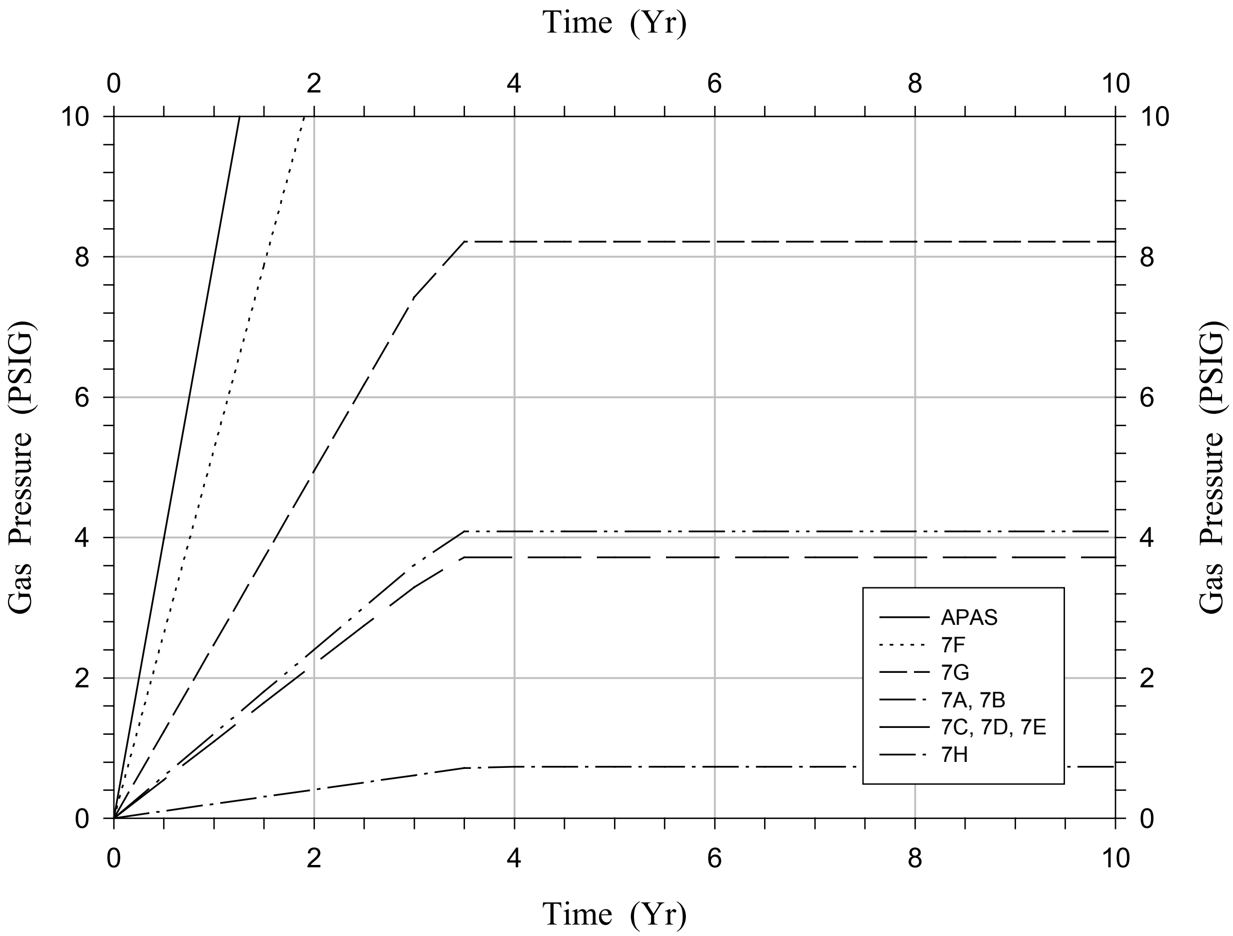

Figure 5-4. Gas pressure as a function of time within an unvented 2R with initial absorbed moisture content of 5^{w}% (ε'_T = 0.758, $G(H_2) = G(total)$ = 4.38E-02, $T_{2R}(time{=}0)$ = 293.15K; see Table D-2 for t_{max} and curie values and Table D-3 for max hydrogen concentration).

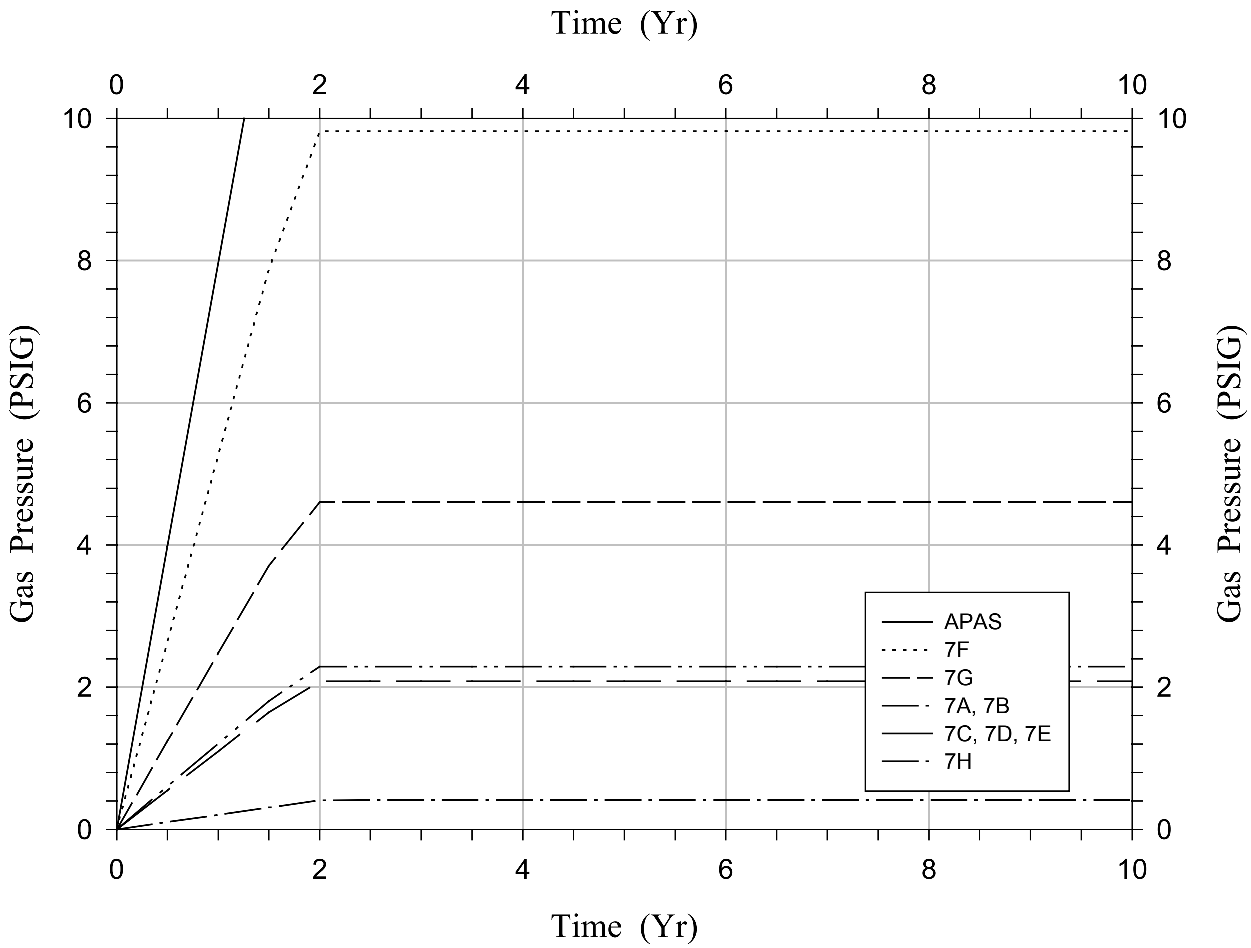

Figure 5-5. Gas pressure as a function of time within an unvented 2R with initial absorbed moisture content of 2.8^{w}% (ε'_T = 0.758, *G(H$_2$)* = *G(total)* = 4.38E-02, $T_{2R}(time=0)$ = 293.15K; see Table D-2 for t_{max} and curie values and Table D-3 for max hydrogen concentration).

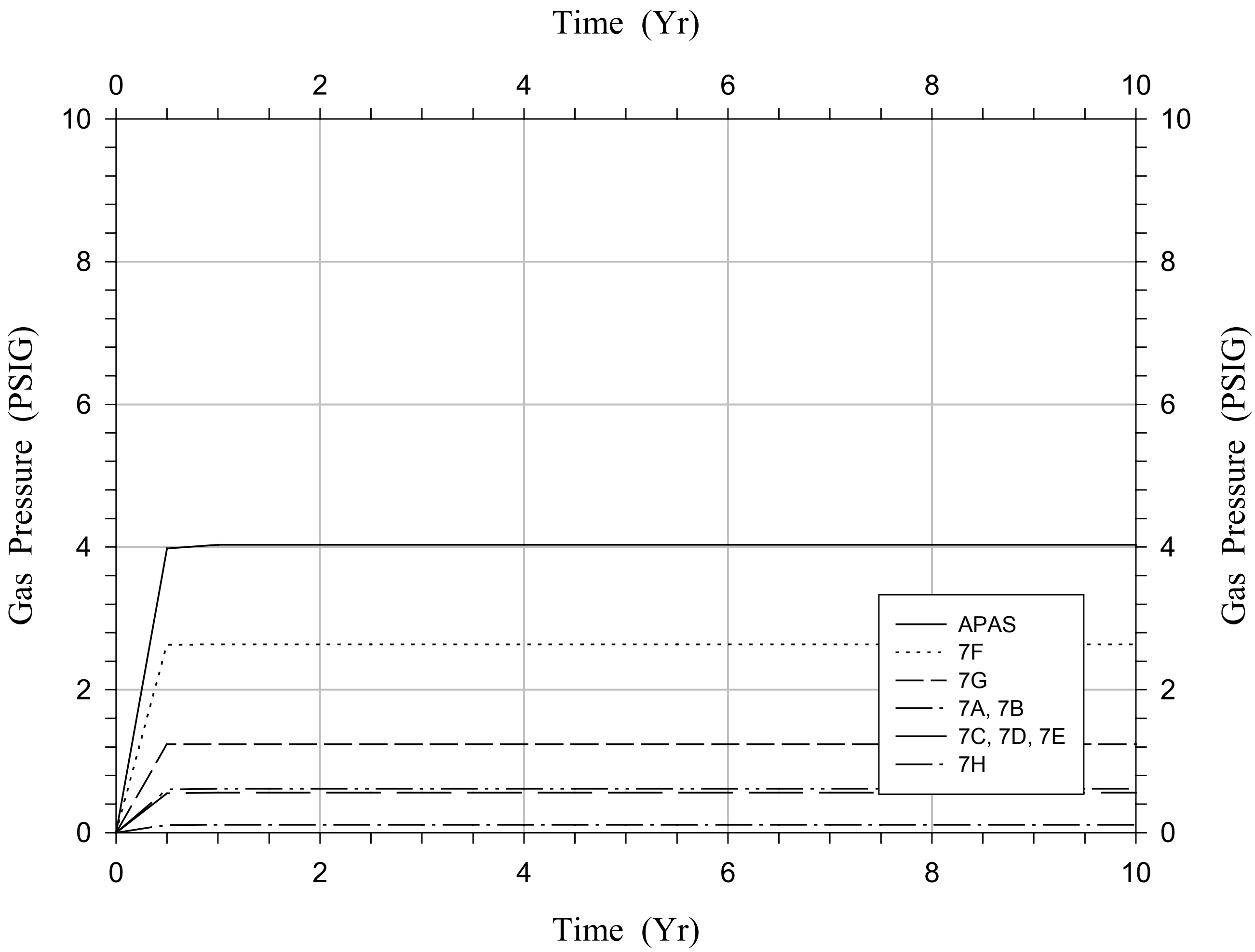

Figure 5-6. Gas pressure as a function of time within an unvented 2R with initial absorbed moisture content of 0.752^{w}% (ε'_T = 0.758, $G(H_2)$ = $G(total)$ = 4.38E-02, $T_{2R}(time{=}0)$ = 293.15K; see Table D-2 for t_{max} and curie values and Table D-3 for max hydrogen concentration).

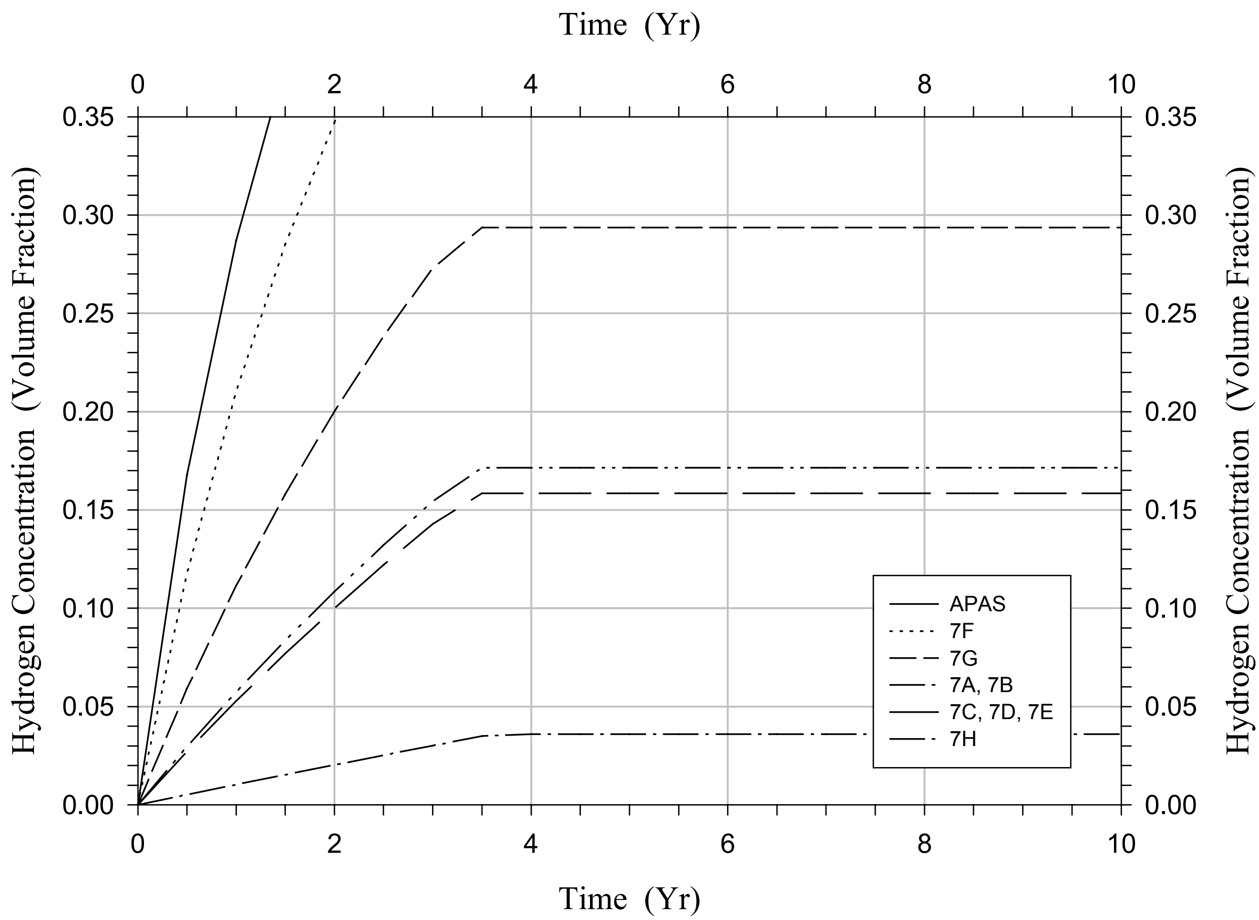

Figure 5-7. Hydrogen gas concentration as a function of time within an unvented 2R with initial absorbed moisture content of 5^{w}% (ε'_T = 0.758, $G(H_2)$ = $G(total)$ = 4.38E-02, $T_{2R}(time{=}0)$ = 293.15K; see Table D-2 for t_{max} and curie values and Table D-3 for max hydrogen concentration).

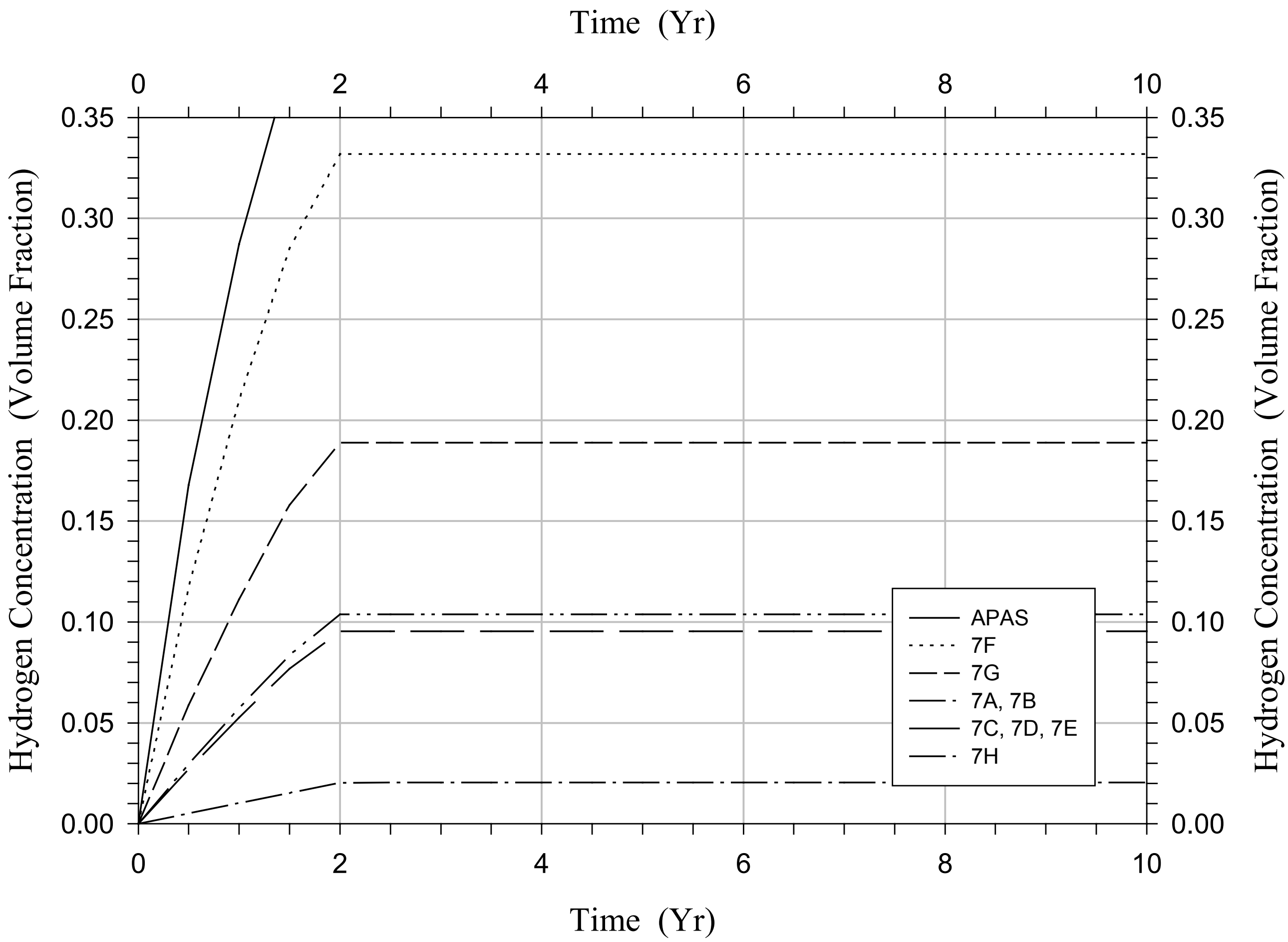

Figure 5-8. Hydrogen gas concentration as a function of time within an unvented 2R with initial absorbed moisture content of 2.8^{w}% ε'_T = 0.758, $G(H_2)$ = $G(total)$ = 4.38E-02, $T_{2R}(time=0)$ = 293.15K; see Table D-2 for t_{max} and curie values and Table D-3 for max hydrogen concentration).

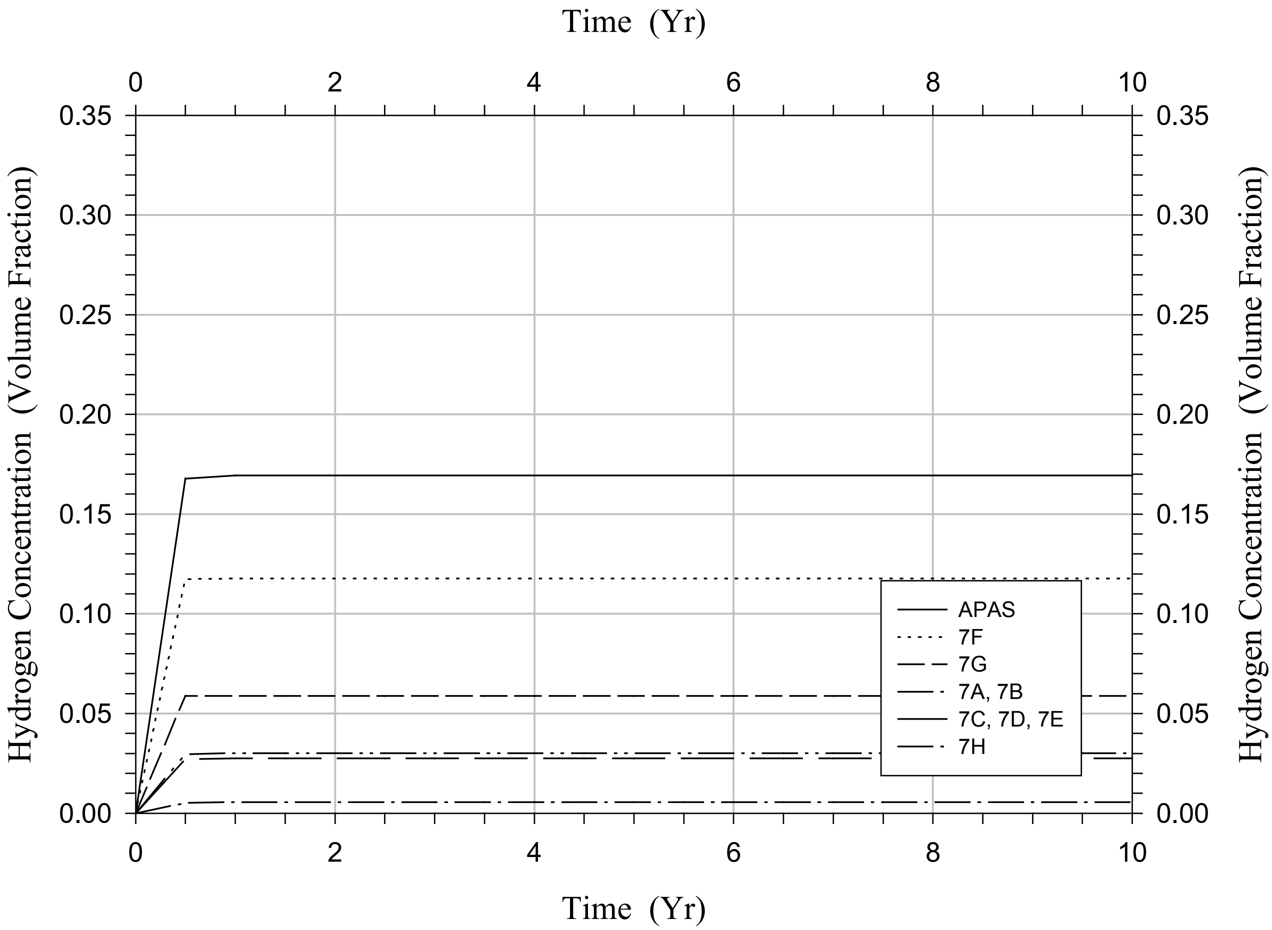

Figure 5-9. Hydrogen gas concentration as a function of time within an unvented 2R with initial absorbed moisture content of 0.752^{w}% (ε'_T = 0.758, *G(H$_2$)* = *G(total)* = 4.38E-03, $T_{2R}(time=0)$ = 293.15K; see Table D-2 for t_{max} and curie values and Table D-3 for max hydrogen concentration).

6. CONCLUSIONS AND RECOMMENDATIONS

The results obtained in this study indicated that gas pressure buildup is insignificant in comparison to the structural integrity of the 2R container, and no pressure mitigation requirements are needed. Calculations for hydrogen concentration values were strongly dependent upon the level of conservatism in the model used. Without additional information or test data it would be difficult to receive credit for many of the model features which lower the conservatism in the concentration calculations; it is thus proposed that the 2R containers be back-filled prior to shipment with an inert gas (such as argon). This simple loading process will not mitigate the hydrogen gas generation, but it will serve as an assurance that flammable gas mixtures will not be generated. This process should be considered a safety assurance and not an operational requirement.

7. EPILOGUE

This report in draft form was distributed electronically to personnel at the Mound and Savannah River Sites. It and other materials issues were discussed in a series of conference calls between Sandia National Laboratories, Mound Plant and Savannah River Site personnel. The initial information from Mound on this plutonium had been received by the Sandia Nonactinide Isotopes and Sealed Sources Management Group (NISSMG) technical team in late July, 2000.

On Monday, October 9, 2000 Mound personnel loaded the 6M containers into a truck for shipment. The inner containers with the plutonium oxide had been loaded into the 2Rs (in the 6Ms) and then inerted with argon. The shipment was received at the Savannah River Site the next day.

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9. APPENDICES

9.1. Appendix A -- Generic Properties for Key Transuranic Radionuclides

This appendix contains an abbreviated description of the radioactivity and radiolysis properties of key transuranic radionuclides. These properties are used for analyses in the other appendices.

Table A-1 identifies the radioactive properties of dominant plutonium isotopes and Am-241. This table was developed to identify the specific activity and the specific power for these radionuclides. Significant findings from this table were that Pu-241 has a large specific activity (activity per unit mass) and specific power values. Equations A-1 and A-2 were used to determine the specific activity and power values.

$$Specific\ Activity = \lambda N = \frac{\ln(2)}{\tau_{1/2}} \frac{N_a}{ATWT} \qquad [Eq.\ A-1]$$

where,

λ = decay constant
N = number of molecules per unit mass
$\tau_{1/2}$ = radionuclide half-life (see Table A-1)
N_a = Avogadro's number = 6.0221367E+23 molecules/mole
$ATWT$ = atomic weight (AMU)

$$Power = <E> \lambda N = <E> \frac{\ln(2)}{\tau_{1/2}} \frac{N_a}{ATWT} \qquad [Eq.\ A-2]$$

where,

$<E>$ = average energy of emitted (ionizing) particle

Table A-2 identifies the expected expression for gas generation due to alpha radiolysis of plutonium oxide material. The expression in the last column presented in Table A-2 identifies the gas generation rate for each radionuclide (not for the plutonium mixture). This is not dependent upon the type of material in question. That dependence is included in the G-value, which is an empirically determined constant. This dependence is reflected in the definition of the G-value which is: "A value assigned to a material which generated gases due to radiolysis and is defined as the number of gas molecules produced for each 100 eV of energy absorbed by the material or waste matrix". Thus all the dependence of the gas generation upon the host material (plutonium oxide in this study) is incorporated in the G-value. Equations A-3 and A-4 were used to generate Table A-2.

$$G = G - value = \frac{\#\ gas\ molecules}{100\, eV\ deposited} \qquad [Eq.\ A-3]$$

$$\dot{g} = <E>\, G\, C = 0.01939 <E>\, G\, C\ (moles / yr) \qquad [Eq.\ A-4]$$

where,

$\dot{g}$ = gas generation rate (moles/yr)
C = curies of alpha activity (Ci

Table A-1. Specific Activity and Specific Power for Key Transuranic Radionuclides

Nuclide ID	Half-Life $\tau_{1/2}$ (a) (yr)	Atomic Weight *ATWT* (a)	α–Energy <*E*> (b) (MeV)	Specific Activity A' (c) (Ci/gm)	Specific Power P' (d) (watts/gm)
Pu 238	8.77 E +01	238.050	5.49921	17.12429	0.55825
Pu 239	2.41 E +04	239.052	5.15540	0.06205	0.00190
Pu 240	6.56 E +03	240.054	5.16830	0.22702	0.00031
Pu 241	1.44 E +01	241.057	0.0208 (e)	102.99061	0.01270
Pu 242	3.75 E +05	242.059	4.90090	0.00394	0.00011
Am 241	4.33 E +02	241.057	5.48574	3.42747	0.11146

(a) Data taken from Parrington 1996.
(b) Data taken from Lederer 1978.
(c) Values calculated using Equation A-1.
(d) Values calculated using Equation A-2.
(e) Pu-241 is primarily a low energy beta emitter, the energy-value presented is for β–decays (note, the relative few alphas emitted by Pu-241 are insignificant contributors to the specific power.

Table A-2. Computed Values for Gas Generation Rates for Key Transuranic Radionuclides

Nuclide ID	α–Energy <*E*> (a) (MeV)	Gas Generation Rate $\dot{g}(total)$ (b) (mole/yr)
Pu 238	5.49921	0.10662 x *G* x *C*
Pu 239	5.15540	0.09996 x *G* x *C*
Pu 240	5.16830	0.10021 x *G* x *C*
Pu 241	NA (c)	NA
Pu 242	4.90090	0.09502 x *G* x *C*
Am 241	5.48574	0.10636 x *G* x *C*

(a) Data taken from Lederer 1978.
(b) Gas generation rate presented in following expression with corresponding units of (moles/yr) only when: *G* = *G*-value (# molecules / 100 eV absorbed) and *C* = the radioactivity (α-Curies). Values calculated using Equation A-4.
(c) Pu-241 is primarily a beta emitter that has insignificant contribution to the overall radiolysis from the plutonium mixture.

9.2. Appendix B -- Properties for Transuranic Radionuclides in Isotopic Distribution from Sherman 1999

This appendix contains calculated results for the estimated gas generation rate constants for radionuclide isotope distributions identified in Sherman 1999. These gas generation values are used in Appendix C to estimate hydrogen concentration and gas pressure values.

Table B-1 identifies the radionuclide isotopic distribution for plutonium oxides investigated in Sherman 1999. Conversion of radioactivity value to mass values was performed using data from Appendix A. Further calculations in Table B-2 are used to determine specific activities specifically for the isotopic distribution identified in Sherman 1999.

Table B-1. Transuranic Isotopic Distribution from Sherman 1999

Nuclide	Total Curies			Mass	Wt %
ID	(Ci) (a)	(%)	(Ci/gm) (b)	(gm)	
Pu 238	4.33 E –01	0.77325	17.124	2.53 E –02	0.050
Pu 239	2.90 E +00	5.17881	0.062	4.67 E +01	91.680
Pu 240	7.62 E –01	1.36078	0.227	3.36 E +00	6.585
Pu 241	5.10 E +01 (c)	91.07566	102.991	4.95 E –01	0.971
Pu 242	3.98 E –04	0.00071	0.004	1.01 E –01	0.198
Am 241	9.02 E –01	1.61079	3.427	2.63 E –01	0.516
Sum =	55.99740 (d)	100.00		50.975	100.00

(a) Curie isotopic distribution from Sherman 1999.
(b) Specific activities take from Table A-1.
(c) This value is for beta activity (the branching fraction for alphas from Pu-241 is very small).
(d) The value of 55.9970 Ci corresponds to total activity, the activity due to alphas is only 4.9974 α–Ci.

Table B-2. Radionuclide Information for Transuranic Nuclides for Isotopic Distribution from Sherman 1999

Nuclide ID	Wt % (Ci)	Atomic Weight *ATWT* (AMU)	Wt % / ATWT (AMU)
Pu 238	4.9604 E –02	238.04955	2.0838 E –04
Pu 239	9.1680 E +01	239.05216	3.8351 E –01
Pu 240	6.5847 E +00	240.05381	2.7430 E –02
Pu 241	9.7144 E –01	241.05684	4.0299 E –03
Pu 242	1.9824 E –01	242.05874	8.1899 E –04
Am 241	5.1627 E –01	241.05682	2.1417 E –03
		Sum =	0.41814

(a) Date for isotopic distribution taken from Sherman 1999.

(b) The atomic weight of the plutonium isotopic mixture can be determined using Equation 2.57 from Lamarsh 1983 (pg. 36) and the sum of Wt% / ATWT. The results of this calculation, along with other isotopic calculations, yield:

Pu-mixture (Sherman-1999 isotopics) ATWT = 239.15 (AMU)
PuO_2-mixture (Sherman-1999) isotopics) ATWT = 271.15 (AMU)
PuO_2-mixture / Pu Weight Ratio = 1.1338

PuO_2 Isotopic Curies = 55.997 (Ci) = 51.0 (β-Ci) + 4.997 (α-Ci)
Pu Isotopic Mass = 50.975 (gm)
PuO_2 Mixture Mass = 57.795 (gm)
PuO_2 Isotopic Ci/Mass Ratio = 0.96889 (Ci/gm)
PuO_2 Isotopic α-Ci/Mass Ratio = 0.08647 (α-Ci/gm)

9.3. Appendix C -- Gas Generation Rates for Transuranic Radionuclides in Isotopic Distribution from Sherman 1999

This appendix contains calculated results for the estimated hydrogen gas concentration and pressure for radionuclide isotope distributions identified in Sherman 1999.

Table C-1 is used to determine the overall gas generation rates for the Sherman 1999 isotopics.

Table C-1. Gas Generation Rates Information for Transuranic Isotopic Distribution from Sherman 1999

Nuclide ID	Gas Generation [a] Rate Constant	Sherman Isotopics [b] (α-Ci)	(α-Ci %)	Curie Fraction x Gas Gen. Rate Const. [c]
Pu 238	1.0662 E –01	4.33 E -01	8.6645	9.2381 E –03
Pu 239	9.9956 E –02	2.90 E +00	58.0302	5.8005 E –02
Pu 240	1.0021 E –01	7.62 E -01	15.2479	1.5280 E –02
Pu 241	NA	NA	NA	NA
Pu 242	9.5021 E –02	3.98 E -04	0.0080	7.5676 E –06
Am 241	1.0636 E –01	9.02 E -01	18.0494	1.9197 E –02
			Sum =	0.10173 [d]

(a) Data from Table A-2.
(b) Data taken from Sherman 1999.
(c) Calculated using Equation A-3 and A-4 and <*E*> values for Table A-1.
(d) In this study this number is simply rounded to a value of 0.1 .

Table C-2. Computed G-Value Rates Information for Transuranic Isotopic Distribution from Sherman 1999

Case ID	Gas Generation Rate / mass [a] $\dot{g}(total)$ (mole/s-gm)	(mole/yr-gm)	Calculated [b,c] *G–value*
SHERMAN-1999	2.89722 E –13	9.14294 E –06	1.0574 E –03
SRS Case 1	1.20000 E –11	3.78691 E –04	4.3794 E –02
SRS Case 2	4.04000 E –11	1.27493 E –03	1.4744 E –01
SRS Case 3	8.62000 E –13	2.72027 E –05	3.1459 E –03
SRS Case 5	1.54000 E –11	4.85987 E –04	5.6203 E –02

(a) Gas generation values presented are initial values only. The gas generation rates will decrease with time since radioactivity is decreasing with time (Sherman 1999).
(b) Calculated using Equation A-4, with a gas generation rate constant of 0.1 (see footnote (d) of Table C-1) and a α-curie density of 0.08647 (α-Ci/gm) (see footnote from Table B-2).
(c) It is assumed that the SRS cases have the same isotopic mixture as Sherman 1999. If their isotopic mixture is lower in the Pu-241 percentage then the G-values will be lower in the PU-241 percentage then the G-values will be lower.

9.4. Appendix D -- Computed Water Moisture Content of Plutonium Oxides from Mound Laboratory, Maximum Duration Times for Alpha Radiolysis, and Maximum Hydrogen Gas Concentrations and Pressure in an Unvented 2R Container

This appendix contains calculated results for estimated water mass and mole content for plutonium oxides from the Mound Laboratory. Also presented is the maximum duration of time that the water could undergo alpha radiolysis along with the hydrogen concentration and gas pressures at these maximum times.

Equations D-1 and D-2 identify the number of moles produced by radiolysis and the maximum amount of elapsed time ($t_{\max}$) that gas generation can be maintained for a given initial maximum number of hydrogen moles (within sorbed water moisture). Equation D-3 is the solution for the maximum hydrogen concentration that would occur at $t_{\max}$. For cases such as the radiolysis of sorbed water moisture on plutonium oxide, the gas generated is pure hydrogen (oxygen release by radiolysis is further sorbed to generate super oxides) and Equation D-3 can be simplified to give Equation D-4. Likewise Equations D-5 and D-6 identify the maximum pressure buildup due to radiolysis.

Table D-1 identifies the moisture composition of the plutonium oxides. Table D-2 uses the hydrogen content (mole inventory) values from Table D-1 and determines the maximum amount of time for which alpha radiolysis can occur. These times are then used to make Table D-3, which presents the maximum hydrogen concentrations and pressures.

$$\Delta N_{H_2} = \dot{g}(H_2)\, t = 0.10\, G(H_2)\, C\, t \qquad [Eq.\ D-1]$$

where,

ΔN_{H2} = number of moles of hydrogen gas generated (moles)
$\dot{g}(H_2)$ = hydrogen gas generation rate (moles/yr)
t = time (yr)
$G(H_2)$ = G-value for hydrogen gas generation (molecules/100eV)
C = α-Curies of plutonium oxide in container (Ci)

$$t_{\max} = \frac{\Delta N_{H_2}^{\max}}{0.10\, G(H_2)\, C} \qquad [Eq.\ D-2]$$

where,

N_{gas} = total number of moles of gas within 2R
t_{max} = maximum time available for gas generation (limited by moisture content)

$$[H_2]^{\max} = \frac{\Delta N_{H_2}^{\max}}{\dfrac{P(t=0)\,\varepsilon_{2R}^{/}\,V_{2R}}{\widetilde{R}T_{2R}(t=0)} + \dfrac{G(total)}{G(H_2)}\;\Delta N_{H_2}^{\max}} \qquad [Eq.\ D-3]$$

where,

$P(t=0)$ = initial pressure of air in 2R
$G(total)$ = G-value for total gas generation (molecules/100eV)
$\varepsilon^{/}_{2R}$ = average void fraction of 2R, not including inner container
= $\varepsilon_{2R} + \varepsilon_{IC} \times V_{IC}/V_{2R}$ (= 0.758 using assumptions below)
ε_{2R} = void fraction of 2R, not including inner container (= 0.75)
ε_{IC} = void fraction on inner container (assumed = 0.50)
V_{2R} = total volume of 2R (assumed = 5853. cm^3)
V_{IC} = total volume of inner container (assumed = 400. cm^3)
$T_{2R}(t=0)$ = temperature within 2R at time = 0
t = time
$\widetilde{R}$ = universal gas constant = 8.2057E-05 (m^3-atm/mole-K)

When $G(H_2) = G(total)$, then Equation D-3 can be reduced to:

$$[H_2]^{\max} = \frac{1}{\left(\dfrac{P(t=0)\,\varepsilon_{2R}^{/}\,V_{2R}}{\widetilde{R}\,T_{2R}(t=0)\,\Delta N_{H_2}^{\max}} + 1\right)} \qquad [Eq.\ D-4]$$

$$\Delta P^{\max} = \frac{\widetilde{R}\,T_{2R}(final)}{\varepsilon_{2R}^{/}\,V_{2R}}\;\Delta N_{H_2}^{\max}\;\frac{G(total)}{G(H_2)} \qquad [Eq.\ D-5]$$

When $G(H_2) = G(total)$, then Equation D-5 can be reduced to:

$$\Delta P^{\max} = \frac{\widetilde{R}\,T_{2R}(final)}{\varepsilon_{2R}^{/}\,V_{2R}}\;\Delta N_{H_2}^{\max} \qquad [Eq.\ D-6]$$

Table D-1. Computed Hydrogen Content for Plutonium Oxide from Mound Laboratory (Extremely Conservative)

Container [a] ID	Mass [b] Total Pu (gm)	Total PuO_2 [c] (gm)	H_2O (gm)	H_2 (gm)	H_2 (moles)
Moisture Content = 5.0^{w}%					
7A	12.54	14.2179	0.71089	0.07955	0.03946
7B	12.54	14.2179	0.71089	0.07955	0.03946
7C	11.41	12.9367	0.64683	0.07238	0.03590
7D	11.41	12.9367	0.64683	0.07238	0.03590
7E	11.41	12.9367	0.64683	0.07238	0.03590
7F	53.78	60.9758	3.04679	0.34115	0.16923
7G	25.20	28.5718	1.42859	0.15986	0.07930
7H	2.26	2.5851	0.12925	0.01434	0.00711
APAS	82.24	93.2437	4.66219	0.52169	0.25879
Moisture Content = 2.8^{w}%					
7A	12.54	14.2179	0.39810	0.04455	0.02210
7B	12.54	14.2179	0.39810	0.04455	0.02210
7C	11.41	12.9366	0.36223	0.04053	0.02011
7D	11.41	12.9366	0.36223	0.04053	0.02011
7E	11.41	12.9366	0.36223	0.04053	0.02011
7F	53.78	60.9758	1.070732	0.19105	0.09477
7G	25.20	28.5718	0.80001	0.08952	0.04441
7H	2.26	2.5624	0.07175	0.00803	0.00398
APAS	82.24	93.2437	2.61082	0.29215	0.14492
Mositure Content = 0.752 ^{w}%					
7A	12.54	14.2179	0.10692	0.01196	0.00593
7B	12.54	14.2179	0.10692	0.01196	0.00593
7C	11.41	12.9367	0.09728	0.01089	0.00540
7D	11.41	12.9367	0.09728	0.01089	0.00540
7E	11.41	12.9367	0.09728	0.01089	0.00540
7F	53.78	60.9758	0.45854	0.05131	0.02545
7G	25.20	28.5718	0.21486	0.02404	0.01193
7H	2.26	2.5624	0.01927	0.00216	0.00107
APAS	82.24	93.2437	0.70119	0.07846	0.03892

(a) Containers used at Mound Laboratory for small quantity (less than 20 Ci) plutonium oxide sources.
(b) Plutonium mass values obtained from Ottinger 2000.
(c) Conversion factor = 1.1338 used, value from Table B-2.

Table D-2. Computed Maximum Duration for Alpha Radiolysis for Plutonium Oxide from Mound Laboratory (Extremely Conservative)

Container ID (moles)	H_2 (moles)	Total Curies (α-Ci)	T_{max} (yr) [(a)] For Following G-Values 1.06E-03	4.38E-02	1.47E-01	3.15E-03	5.62E-02
Moisture Content = 5.0^w%							
7A	0.03946	2.65	140.82	3.40	1.01	47.33	2.65
7B	0.03946	2.65	140.82	3.40	1.01	47.33	2.65
7C	0.03590	2.42	140.31	3.39	1.01	47.16	2.64
7D	0.03590	2.42	140.31	3.39	1.01	47.16	2.64
7E	0.03590	2.42	140.31	3.39	1.01	47.16	2.64
7F	0.16923	11.58	138.21	3.34	0.99	46.46	2.60
7G	0.07930	5.45	137.60	3.32	0.99	46.25	2.59
7H	0.00711	0.45	149.46	3.61	1.07	50.24	2.81
APAS	0.25879	17.55	139.45	3.37	1.00	46.87	2.62
Moisture Content = 2.8^w%							
7A	0.02210	2.65	78.86	1.90	0.57	26.51	1.48
7B	0.02210	2.65	78.86	1.90	0.57	26.51	1.48
7C	0.02011	2.42	78.58	1.90	0.56	26.41	1.48
7D	0.02011	2.42	78.58	1.90	0.56	26.41	1.48
7E	0.02011	2.42	78.58	1.90	0.56	26.41	1.48
7F	0.09477	11.58	77.40	1.87	0.56	26.01	1.46
7G	0.04441	5.45	77.06	1.87	0.55	25.90	1.45
7H	0.00398	0.45	83.70	2.02	0.60	28.13	1.57
APAS	0.14492	17.55	78.09	1.89	0.56	26.25	1.47
Moisture Content = 0.752^w%							
7A	00593	2.65	21.18	0.51	0.15	7.12	0.40
7B	0.00593	2.65	21.18	0.51	0.15	7.12	0.40
7C	0.00540	2.42	21.10	0.51	0.15	7.09	0.40
7D	0.00540	2.42	21.10	0.51	0.15	7.09	0.40
7E	0.00540	2.42	21.10	0.51	0.15	7.09	0.40
7F	0.02545	11.58	20.79	0.50	0.15	6.99	0.40
7G	0.01193	5.45	20.70	0.50	0.15	6.96	0.39
7H	0.00107	0.45	22.48	0.54	0.16	7.56	0.42
APAS	0.03892	17.55	20.97	0.51	0.15	7.05	0.39

(a) Mole values form Table D-1 and α-Curie values obtained from Ottinger 2000. Max time values calculated using Equation D-2. (Note, this table assumes that activity is 100% α-curies.)

Table D-3. Computed Maximum Hydrogen Concentrations and Maximum Normal Operating Pressures for Alpha Radiolysis for Plutonium Oxide from Mound Laboratory (Extremely Conservative)

Container ID	H_2 Moles ΔN_{H2}^{max} (moles)	$[H_2]^{max}$ $G(H_2) = G(total)$	ΔP^{max} (a) $G(H_2) = G(total)$, (Atm)	T_{final} = 394.25 K (PSIG)
Moisture Content = 5.0^w%				
7A	0.03946	0.17140	0.27820	4.08953
7B	0.03946	0.17140	0.27820	4.08953
7C	0.03590	0.15840	0.25313	3.72101
7D	0.03590	0.15840	0.25313	3.72101
7E	0.03590	0.15840	0.25313	3.72101
7F	0.34115	0.47010	1.19311	17.53866
7G	0.15986	0.29363	0.55906	8.21819
7H	0.01434	0.03594	0.05014	0.73703
APAS	0.52169	0.57566	1.82449	26.81999
Moisture Content = 2.8^w%				
7A	0.02210	0.10381	0.15579	2.29014
7B	0.02210	0.10381	0.15579	2.29104
7C	0.02011	0.09535	0.14175	2.08377
7D	0.02011	0.09535	0.14175	2.08377
7E	0.02011	0.09535	0.14175	2.08377
7F	0.09477	0.33191	0.66814	9.82165
7G	0.04441	0.18883	0.31307	4.60219
7H	0.00398	0.02045	0.02808	0.41274
APAS	0.14492	0.43172	1.02171	15.01919
Moisture Content = 0.752^w%				
7A	0.00593	0.03017	0.04184	0.61506
7B	0.00593	0.03017	0.04184	0.61506
7C	0.00540	0.02753	0.03807	0.55965
7D	0.00540	0.02753	0.03807	0.55964
7E	0.00540	0.02753	0.03807	0.55964
7F	0.02545	0.11772	0.17944	2.63781
7G	0.01193	0.05884	0.08408	1.23602
7H	0.00107	0.00558	0.00754	0.11085
APAS	0.03892	0.16946	0.27440	4.03373

(a) Mole values from Table D-1. Max hydrogen concentration and pressure values calculated using Equations D-4 and D-6.

9.5. Appendix E -- Copy of Sherman 1999 Memo

This appendix contains a reprint of a technical memorandum produced by Martin Sherman (Sandia National Laboratories) for the radiolysis rates from plutonium oxides. These oxides have an inherent radiolysis rate due to the sorbed water moisture on their surface. This memo was generated as part of a more indepth technical project which generated a model that could be used to estimated gas generation rates due to alpha radiolysis of plutonium oxides.

**Note: Signed version of attached memo kept on file.
Enclosed copy reformatted to fit within required borders for this report.**

Date: October 27, 1999

From: M. P. Sherman

To: G. Lanthrum, J. McFadden, A. Savino, W. Josephson, J. Haschke, T. Luera

Subject: Gas generation model for Pu Oxides

I. The "Players"

This memorandum presents results describes the model being developed to estimate the gas generation inside plutonium waste containers, and contains preliminary results for "pure" PuO_2 waste. Later memoranda will have improvements and corrections, and extensions to other waste forms. My thanks to Gary Lanthrum of DOE/AL for helping us obtain funding for this work.

Our consultant, John Haschke, is supplying estimates of the relevant chemical reactions and the corresponding reaction rates. He has been evaluating experimental work done at LANL and SRS. The reactions and their rates used in the model are largely his work. In response to my request, he submitted a short note on the reaction rates, and then a revised note. A copy of his original and revised note appears in the Appendix A.

Janet McFadden, Anthony Savino, and Walt Josephson at Waste Management Technical Services are fully cooperating in our effort. They , supplied me with information on the radiolysis rate. Our model is being input into the RADCALC program. RADCALC has a sophisticated radiolysis model, but is only now including "back reactions."

Elizabeth Conrad at Rocky Flats has expressed interest in being involved in our model development. She suggested we include Jerry Stakebake, who has written several papers on Plutonium chemistry. There is considerable experimental effort on gas generation at Westinghouse Savannah River. They may wish to get involved in the modeling effort.

Meanwhile, at LANL, John Lyman is developing a model with similar objectives. He is using Robert Penneman as his chemical kinetics consultant. Having a second independent model should help show if certain conclusions are "robust." By "robust," I mean the conclusions from the model are insensitive to variations of the model assumptions. In particular, we will look to see if the models eliminate the possibility of large pressure generation and of detonable atmospheres.

II. The Model

The three most important results expected of the model are time histories of:

- pressure,
- oxygen concentration
- hydrogen concentration,

Initially, the model will assume a "reasonable" constant temperature. Later improvements may include time-varying temperature and perhaps temperatures determined by transient heat transfer models. For long-term storage, times of up to 50 years are of interest. For transportation of the wastes, knowledge of the behavior during much shorter time periods is adequate.
The model consists of a set of first-order ordinary differential equations. The initial conditions for the calculation are::

- PuO_2 mass (g)
- Specific area of PuO2, m^2/g
- Specific radiolysis rate (moles of H_2/g-h)
- Volume of the container (m^3)
- Temperature (K)
- Initial oxygen concentration (mol)
- Initial water concentration, absorbed and in gas phase (mol)
- Other gas initial concentrations (O_2, N_2, A, He, etc.)

III. Important chemical and radiochemical reactions

Although all would agree that there are chemical reactions in the gas volume, there seems to be a consensus that gas phase chemical reactions are overshadowed by surface catalyzed chemical reactions. Likewise, the important radiolysis reaction appears to be water on (or in) the surface of the PuO_2, and not radiolysis of water vapor. Haschke postulates that for the pure oxide, the following three reactions are sufficient to model the behavior of the system.

1) Radiolysis of water by alpha particles $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

2) Surface catalyzed H_2-O_2 recombination

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(ads)$

3) Oxygen absorption-hydrogen generation on PuO_2

a) $PuO_2(s) + \frac{x}{2}O_2 + H_2O(ads) \rightarrow PuO_{2+x}(s) + H_2O(ads)$ (if O_2 is present)

b) $PuO_2(s) + xH_2O(ads) \rightarrow PuO_{2+x}(s) + xH_2$ (if O_2 is not present)

In the initial steps of reactions 3a and 3b surface water is broken up and oxygen absorbed by the PuO_2 solid. The remaining hydrogen-containing radicals on the surface preferentially form water with gaseous oxygen, or if gaseous oxygen is not present, form H_2 molecules, which are released into the gas. The rate for reactions 3a and 3b, is identical, implying that the common first part of the reaction is rate limiting. Notice in reaction 3a, water is a catalyst, and gaseous oxygen is consumed. In reaction 3b water is the reactant, and gaseous hydrogen is produced.

Haschke has been a chief proponent of the existence of super-stoichiometric PuO_{2+x}. Some people still have reservations about the existence of PuO_{2+x}. The evidence for the existence of super-stoichiometric PuO_{2+x}. appears to be winning over people working in the area. However, for our model, the important point is that oxygen disappears without the loss of hydrogen, or after the oxygen is gone, water disappears, and hydrogen appears without oxygen. The exact nature of how PuO_2 holds the additional oxygen is not critical. It may be necessary to know what is the capacity of the oxide for holding oxygen. Evidence shows that “x” is at least 0.3.

IIIa Radiolysis

Because the bulk of the radiolysis is due to alpha radiation, and alpha particles have small penetration distances, only a fraction of the alpha particles reach the surface of the oxide. Clearly this is a more complex problem than radiolysis by gamma radiation which is moderately well understood. The radiolysis rate for PuO_2 is not well known. I received two sets of data on the radiolysis rate from McFadden and Savino. They differ by orders of magnitude.

The first set of data was for a case in which 1450 grams of PuO2 was considered. The isotopic mixture was expressed in terms of Curies of activity for each isotope.

isotope	curies
Pu-238	4.33E-001
Pu-239	2.90E+000
Pu-240	7.62E-001
Pu-241	5.10E+001
Pu-242	3.98E-004
Am-241	9.02E-001

The rate of radiolysis for the sample is given in Table 1. Note that the radiolysis rate increases with time due to the formation of more active species. Eventually, the activity must decrease, but not in the first 40 years. The G factors used were 0.026 for the alpha particles, 0.0088 for the beta particles, and 0.0074 for the gamma radiation. For further details of the computation contact McFadden or Savino.

Table 1
Radiolysis rate (dH2/dt) of 1450 g PuO_2 sample

time	cm^3/h
0 days	0.037
10 days	0.037
100 days	0.0372
1 year	0.0376
2 yr	0.0381
4 yr	0.0391
6 yr	0.040
8 yr	0.0408
10 yr	0.0416
15 yr	0.043
20 yr	0.0442
30 yr	0.0456
40 yr	0.0463

Using one atmosphere pressure, 25 °C (298 K) temperature, and the gas constant $\Re$= 8.31451 J/mol-K, 1 cc = 4.088×10^{-5} mol. The initial radiolysis rate is 1.513×10^{-6} mol/h. dividing by the mass of the sample, we get **1.043×10^{-9} mol/g-h**. **This is the value we will use in all our computations**.

The data in Table 2 are from Savannah River experimental results sent to me by McFadden. Contact McFadden and/or Savannah River for more details. Haschke has analyzed the data and believes these data are a result not primarily radiolysis but are dominated by reaction 3a. If we consider cases 1, 2, or 5, and multiply the last column by our conversion factor, we get ~ 4×10^{-8} to 10^{-7} mol/g-h. These are much higher than the previous results. However, Case 3 gives much lower results.

Table 2
Radiolysis

SRS Model Results

	umoles/day	fissile g	umoles/day/g	moles/s/g	20C, 1 atm cc/hr/g
Case 1	52.98	51	1.04	1.2E-11	1.04E-03
Case 2	23.28	6.67	3.49	4.04E-11	3.50E-03
Case 3	0.63	8.46	0.074	8.62E-13	7.46E-05
Case 5	10.03	7.53	1.33	1.54E-11	1.34E-03

SRS Model Results

IIIb. The H_2-O_2 recombination reaction

It is been known for some time that combustion experiments on the flammability and detonability of H_2-O_2-diluent gas mixtures must be conducted quickly (minutes to seconds) at moderately elevated temperatures (200 – 400 °C), before significant amounts of the gases have had time to recombine. These temperatures are below the autoignition (explosion limit) temperatures. The overwhelming fraction of the recombination takes place at catalytic surfaces, and not in the gas volume. It is interesting to note that many of these experiments were conducted in stainless steel containers, which we now know to be catalytic for the recombination. The elementary reactions that result in the gas phase oxidation of hydrogen are reasonably well known, with fair estimates of the individual reaction rates. However, data on surface catalyzed recombination is less well known. From chemical kinetic considerations, we expect the rate to be a function of surface area, surface material and surface condition, temperature, and possibly hydrogen and oxygen concentration.

Haschke has examined the literature that contains information on the recombination rate of hydrogen and oxygen on PuO_2.[1-5] See Appendix B for details. Quigley [6] carried out a series of tests using H_2-O_2-diluent gas mixtures in stainless steel containers with various potentially catalytic surfaces inside. He used CeO_2 surfaces as a simulant to PuO_2, but without radioactivity. Both Haschke and I have gone over Quigley's report [6], which is not well written. We were not able to get any quantitative results. However, three qualitative results are intriguing. Quigley found that stainless steel was a good catalyst for recombination, that CeO_2 was a far better catalyst than the stainless steel, and that the recombination rate increases with increased temperature.

Haschke has been examining the other data on recombination. One important result he detected is that the presence of water on the PuO_2

surface greatly reduces the recombination rate. [H2O} is the surface concentration of water. Haschke says in the Appendix B,

> "At each temperature, the initial ($[H_2O]=0$) rate of H_2O formation by $H_2 + O_2$ combination greatly exceeds the rate of water-catalyzed reaction that apparently initiates as soon as water appears in the system. The combination rate progressively decreases as the H_2O accumulates on the oxide surface, but the PuO_2 + O2 rate remains constant or increases slightly. …Ultimately, the rate of oxygen consumption by H2 + O_2 combination falls below the rate of O_2 consumption by the water-catalyzed PuO2 + O_2 reaction and makes an increasingly smaller contribution to the loss of oxygen over time."

The following are Haschke's recommendations for reaction rates. The units of the left side term are in mol/m^2-h, and the units of [H2O] are in μmol/m_2 on the oxide surface.

At 25°C $\ln(dH_2O/dt) = -20.3 - 2.30[H_2O]$
At 50°C, $\ln(dH_2O/dt) = -12.20 - 0.18[H_2O]$
At 100°C, $\ln(dH_2O/dt) = -11.1 - 0.18[H_2O]$
At 200°C, $\ln(dH_2O/dt) = -9.55 - 0.17[H_2O]$

Note that there is no dependence on the gaseous concentration of hydrogen or oxygen in the above equations. Haschke has stated that there is not enough experimental information to include these effects yet. Notice the 25°C rate seems lower than expected compared to the other rates. Haschke stated that the form of the PuO_2 powder was different for this case than that used for all the higher temperatures.

IIIc. Oxygen removal-hydrogen production chemical reaction

Because of the work described in Morales, Haschke, and Allen [1] we have reaction rates as a function of PuO_2 surface area and temperature. The fit to their data is given by [1]

(5) $$\ln(R) = -6.441 - 4706/T$$

The units of R are mol O/m^2-h. The activation energy for the reaction is given as 9.4±0.6 kcal/mole. Since the gas constant, $\Re$= 1.987 kcal/mol-K,
$9400/\Re = 4731$ K ≅ 4706 K, as shown above. The work does not fix the dependence on the oxygen or hydrogen concentration, nor on the saturation of the PuO_{2+x}. "x" is probably no less than 0.3. 0.3 is cited in the DOE proposed standard .[7]

IV. The mathematical formulation – equations and initial conditions

The chemical Reaction equations are of the form of a system of first order differential equations with initial conditions.

(1)) $$\frac{dy_i}{dt} = f_i\left(y_1, y_2, \ldots y_n\right) \qquad y_i(0) = y_{i0} \qquad i = 1, 2, \ldots, n$$

We can write the system using two or three equations. Let O_2, be the number of moles of gaseous O_2, H_2, be the number of moles of gaseous H_2, and H_2O be the number of moles of water on the oxide. We will neglect the presence of water vapor. Let $Rate_1$, $Rate_2$, $Rate_{3a}$, and $Rate_{3b}$, be the rates of the radiolysis, recombination, and the oxygen removal and hydrogen production reactions. The stoichiometry gives the following equations

(2) $$\frac{dO_2}{dt} = \tfrac{1}{2} \cdot \left[\text{Rate}_1 - \text{Rate}_2 - \text{Rate}_{3a}\right]$$

(3) $$\frac{dH_2}{dt} = \text{Rate}_1 - \text{Rate}_2 + \text{Rate}_{3b}$$

(4) $$\frac{dH_2O}{dt} = -\text{Rate}_1 + \text{Rate}_2 - \text{Rate}_{3b} = -\frac{dH_2}{dt}$$

$Rate_1$ is given by

(5) $$\text{Rate}_1 \Big/ A = \begin{cases} 1.45 \times 10^{-7}\ \text{mol/m}^2 - \text{h} & \text{if surface water is present} \\ 0 & \text{if there is no surface water} \end{cases}$$

where A is the effective surface area of the PuO_2. Note that $Rate_1$ is piecewise constant. For reactions 3a and 3b,

(6) $$\frac{\text{Rate}_{3a}}{A} = \begin{cases} \exp\{-6.441 - 2407/T\} & \text{if } O_2 > 0 \\ 0 & \text{if } O_2 \le 0 \text{ or } x \ge 0.3 \end{cases}$$

(7) $$\frac{\text{Rate}_{3b}}{A} = \begin{cases} \exp\{-6.441 - 2407/T\} & \text{if } H_2O > 0 \text{ and } O_2 \le 0 \\ 0 & \text{if } H_2O \le 0 \text{ or } O_2 > 0 \text{ or } x \ge 0.3 \end{cases}$$

Since the temperature, T, is assumed constant, these rates are also piecewise constant. The only rate that is not piecewise constant is the second reaction.

(8) $\mathrm{Rate}_2/A = \exp\{-20.3 - 2.30[H_2O]\} = \exp\{-20.3 - 2.30 \cdot y_3/A\}$

The pressure is obtained from the perfect gas law,

(8) $$p = N\Re T/V.$$

where N is the total number of gaseous moles, $\Re$ = 8.31451 J/mol-K, the universal gas constant, and V the volume. The number of moles would be the sum of that of oxygen, hydrogen, and other gases. By assumption, the number of moles of other gases such as nitrogen is constant. For combustion considerations such as the flammability and detonability of the mixture, we need the mole fractions of the hydrogen and oxygen. These are simply,

(9) $$X_{O_2} = \frac{O_2}{N}; \quad X_{H_2} = \frac{H_2}{N}$$

Finally, the "x" in $PuO_{2+}x$ is given by

(10) $$x = \frac{2\Delta O_2}{PuO_2}$$

where ΔO_2 is the number of moles of O_2 taken up by the PuO_2.

V. Difficulties solving the equations

Solving an initial value problem for a set of ODEs, Eqs. 1, is usually straightforward unless we have one of the following difficulties:

- derivatives have singularities,
- derivative have discontinuities (or fast changes)
- system is "stiff."

For our system of equations there are no singularities and the system is not stiff. However, the derivatives do have discontinuities. The first change seem in the solutions to be given in the next sections is the near linear disappearance of oxygen. The solution advances without trouble until the oxygen disappears. Consider the values of the rates in the sample cases,

(11) $$\frac{dO_2}{dt} = 0.5 * [\mathrm{Rate}_1 - \mathrm{Rate}_2 - \mathrm{Rate}_{3a}] = \begin{cases} 0.5 \cdot [0.522 \cdot 10^{-5} - 0.361 \cdot 10^{-5} - 0.249 \cdot 10^{-1}] & O_2 > 0 \\ 0.5 \cdot [0.522 \cdot 10^{-5}] & O_2 \le 0 \end{cases}$$

I include a negative concentration of oxygen, because the ODE solver will tend to drop below zero. Schematics of the solution near the time the oxygen disappears is shown in the following figure.

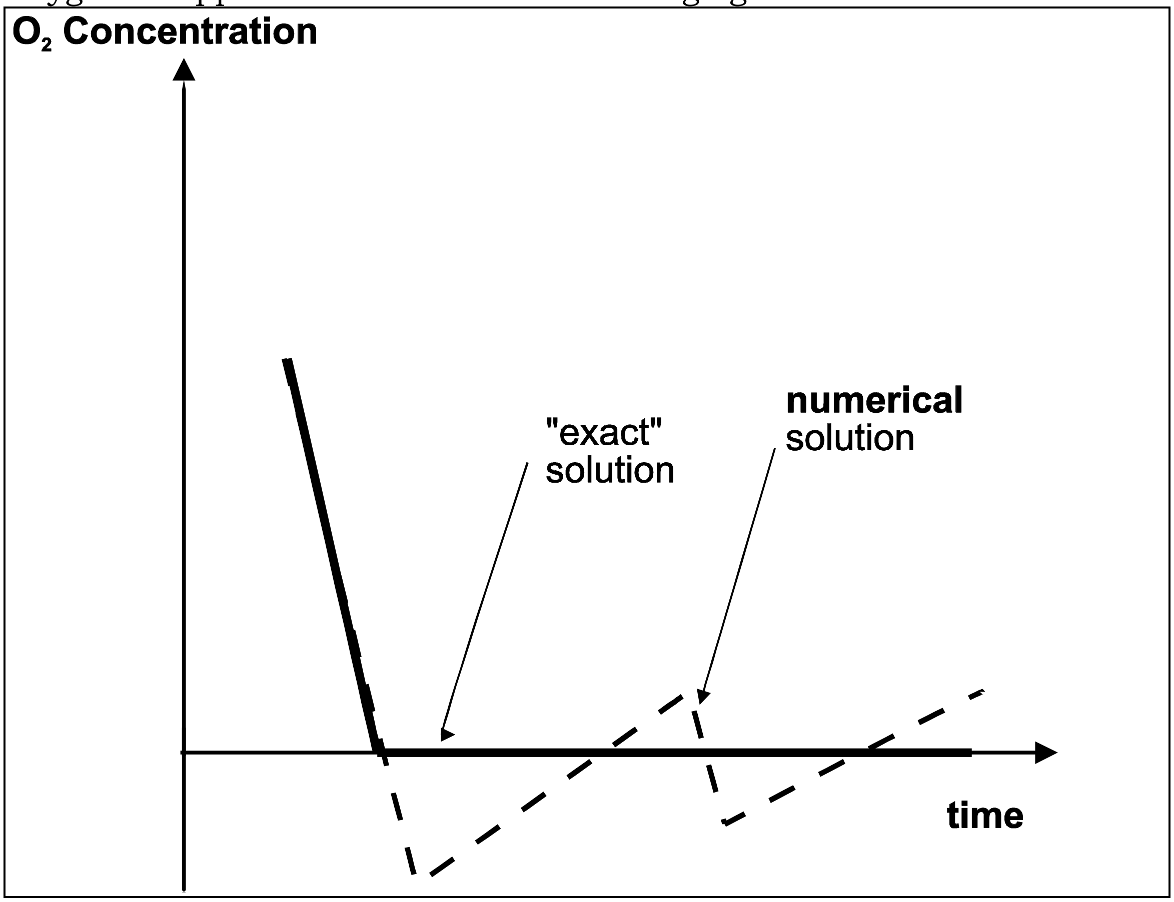


Figure 1. Schematic of what happens when O_2 concentration goes to zero

As the oxygen concentration approaches zero, the slope is steeply negative. An integration step ends at a slightly negative value. For the next step, the slope is positive. In one or more steps, the concentration ends at a positive value. The slope is again steeply negative. The cycle keeps repeating. The adaptive step control will cause the step size to be small because of the “zig-zags.” Now consider what happens if we force the step size to be smaller and smaller. The “zig-zags will get lower in amplitude and higher in frequency. The limit will be the “exact” solution shown in Fig. 1. In reality, reactions do not suddenly stop as the reactant concentrations go to zero, but must diminish. The “real” solution would then not have the discontinuous slope, but the corner would be rounded. However, for our model, the “exact” solution is the correct one.

How do we handle this difficulty? There are two approaches. If we keep the step size painfully small, we can muddle through with only slight errors and very long computer run times. This is the approach used (unconsciously) to generate the results used at the Quarterly PSC meeting in Washington because of an error which kept the step size very small. The second approach is to set the oxygen to zero and drop the oxygen equation. This will permit continued rapid integration up to the disappearance of the water, where the solution stops changing. The main program or subroutine ODEINT has to switch between different equation sets. This is clumsy, but I do not see an elegant solution to the problem. ODE solvers do not like equations with discontinuous derivatives.

V. Numerical solution – Case 1

For volume, we will use that of the inner can of the 3013 waste container. Its free volume is approximately 2.4 liters = 2.4×10^{-3} m^3. We will assume 5.0 kg of oxide, the limit in the DOE standard. Assume a specific surface area of 4.8 m^2/g, a value for the oxide used in Ref. 7. The initial amount of water is assumed to be 0.05% of that of the oxide, 2.5 g = 0.14 mol, one-tenth the DOE standard. The initial atmosphere is assumed dry air at one atmosphere pressure and 50 °C (348 K), and a trace of hydrogen. To avoid numerical difficulties, an initial mole fraction of hydrogen of 0.001 was used.

The calculations were done using painfully small step sizes. shown in Fig. 1 ~ 3 hours on a 200 MHz Pentium II personal computer using a Lahey Fortran 95 compiler, and fourth order Runge-Kutta routines from Numerical Recipes. In view of the simplicity of the results, the calculation time is excessive. In all likelihood we need to use a stiff solver. See Appendix B.

The results are quite simple. First oxygen is removed nearly linearly in approximately 0.4 of an hour. After the oxygen is gone, then the water is removed nearly linearly and is replaced by gaseous hydrogen. After just under six hours all the water is gone, and hydrogen production stops. In our simple model, no further changes take place.

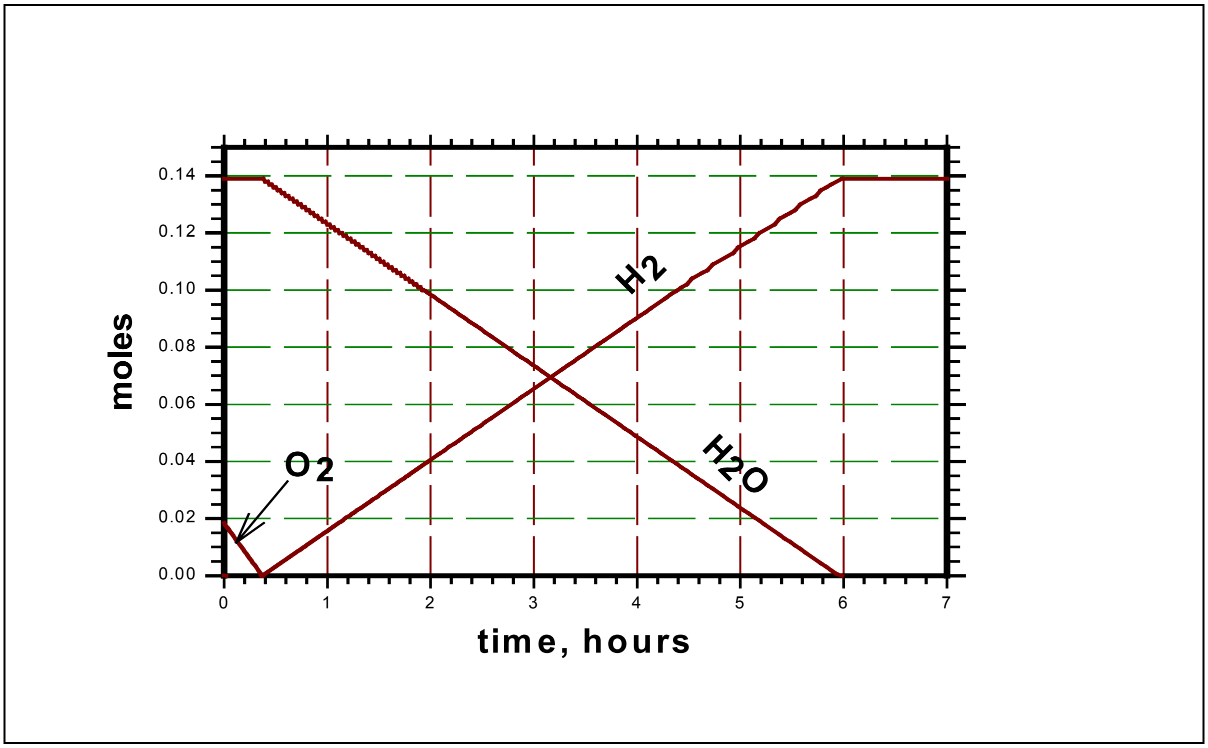


Figure 1. Case 1. Initial gas composition dry air. PuO_2 mass = 5.0 kg. Pressure = 1 atmosphere. Temperature = 50 °C, Volume = 2.4 x 10^{-3} m^3.H_2O is assumed all surface absorbed.

Because the temperature and volume are assumed constant, the pressure is linearly proportional to the number of gas moles. Initially, there are 0.08804 moles of gas, of which 0.0184 are oxygen, and 0.13889 moles of absorbed water. **Hence the minimum pressure when the oxygen is gone is 0.79 bar, and the peak pressure when all the hydrogen has been generated is 2.37 bar.**

Case 2

In Case 2, the water content is assumed 0.5% of the oxide mass, the DOE standard. All other initial conditions are the same as in Case 1. The results are shown in Figs. 2 and 3. The oxygen concentration falls nearly linearly in the same time as in Case 1. After the oxygen is gone, the water decreases linearly and the hydrogen increases linearly. Since there is ten times more water present, it takes ten times as long to disappear. Likewise, there is ten times more hydrogen generated. The final pressure is 16.573 bar (16.360 atm, 240.4 psia). This is a substantial pressure, but does not threaten the 3013 as long as there is no combustion.

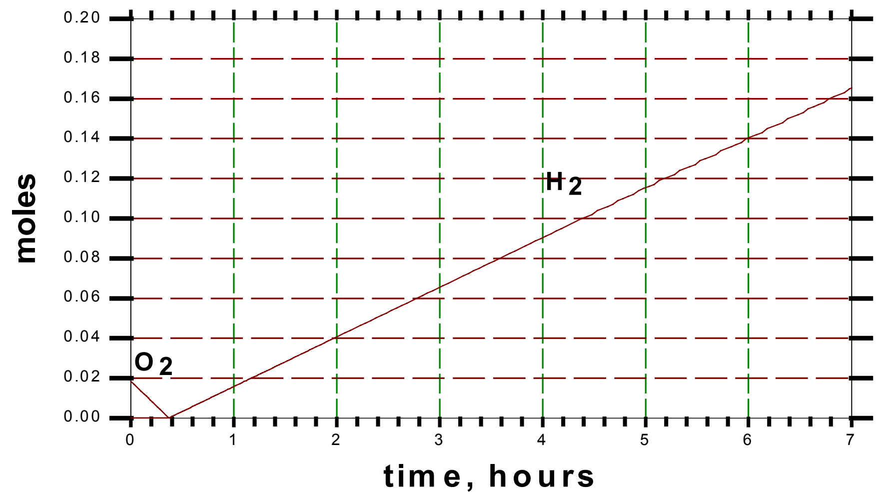


Figure 2. Case 2 O_2 and H_2 for first seven hours. H_2O is off-scale.

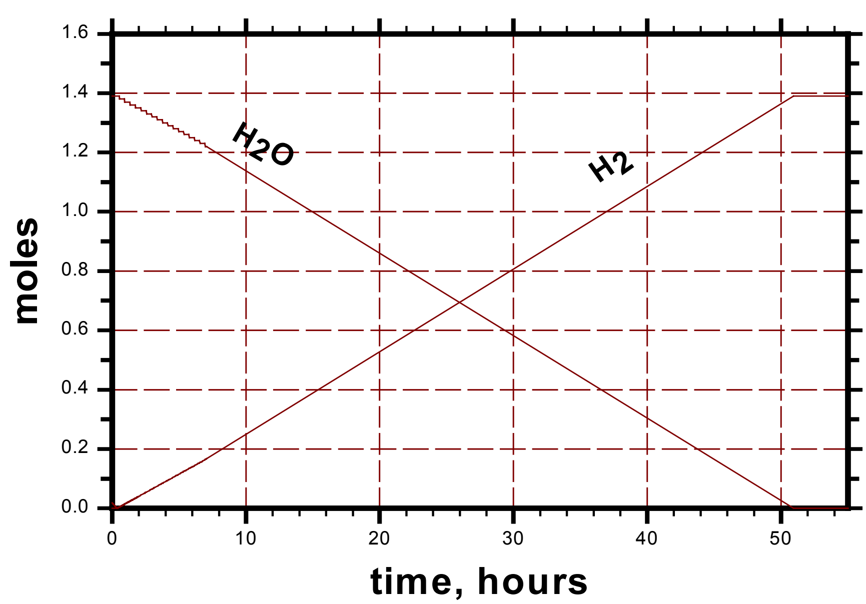


Figure 3. Case 2. H_2 and H_2O out to 55 hours. O2 is too small to be seen.

Appendix A [of Sherman 1999 memo]
Copies of Haschke e-mail memoranda

First Memorandum

IMPORTANT CHEMICAL REACTIONS

Before defining reactions, I need to define the chemical system. Three possibilities for pure oxide come to mind.

1. PuO_2 and H_2O
2. PuO_2,O_2 and H_2O
3. PuO_2, O_2, H_2O and organic residues.

I will limit the consideration to cases 1 and 2.

<u>Case 1 Reactions</u>:
<u>Rate @ 25^oC</u>

<u>chemical reaction</u> – $PuO_2(s) + \chi H_2O$ (g,ads) $\rightarrow PuO_2 + \chi\ H_2(g)$:

$$\frac{dH_2}{dt} = 1.3x10^{-10}\, mol/m^2 - h$$

<u>radiolysis</u> – H_2O (α-particles) $\rightarrow H_2(g) + O_2(g)$
(this is not my area, but I gather from the meeting that G = 1.0.)

chemical recombination – $H_2(g) + O_2(g)$ (ads, g):

on clean PuO_2 <u>$dH_2O/dt = 8.3 \times 10^{-9}$ mol/m^2-h</u>
: after H_2O product absorbs on surface <u>$dH_2O/dt = 3 \times 10^{-10}$ mol/m^2-h</u>

The recombination rate decreases as H_2O is formed, implying that the product is autotoxic. The rate depends on the cleanliness of the oxide surface; i.e. dH_2O/dt is a function of the concentration of H_2O absorbed on the oxide surface. (Evaluation of data for PuO_2 and stainless steel is needed.)

<u>Case 1</u> generates (or appears to generate) O_2 from the radiolysis reaction and H_2 from both The chemical and radiolysis processes. However, there is another path for removal of O_2 in addition to recombination. That reaction is the water-catalyzed reaction of PuO_2 with O_2 (The catalytic cycle is described in my presentation at SRS – but I just remembered that I did not send you a copy as I intended.) If O_2 is present from radiolysis (or as a constituent of the atmosphere) it reacts at the rate of

the chemical (Pu)$_2$ + H_2 O) reaction after adjustment for the difference of 2 in stoichiometry.

Rate @ 25^{o}C

$PuO_2 + \chi/2\ O_2\ (g) \rightarrow PuO_{2+x}(s)$ $\quad -\frac{dO_2}{dt} = 6x10^{-11} mol/m^2 - h$

(1/2 the value of the dH_2/dt)

Experimental data show the O_2 reacts via the H_2O-catalyzed reaction first. The H_2O is Formed by radiolysis it reacts by this same path as it forms. (There are 2 pathways for Removing radiolytic O_2 – I am not certain which is the faster process.)

Case 2. Atmospheric O_2 is consumed first by the above H_2O catalyzed reaction. After all O_2 is removed, the PuO_2 + H_2O reaction generates H_2. Radiolysis produces O_2 from H_2O and extends the water-catalyzed process at the expense of the PuO_2 + H_2O reaction. (Therefore, it is important to include the water-catalyzed Pu + O_2 reaction in Case 1 as well as in Case 2.) Note: H_2O-catalyzed Pu + O_2 goes first, even though its theoretical rate is ½ that of the PuO_2 + H_2O reaction.

Reversibility and Extent

At room temperature x values approaching 0.3 are observed. Therefore, the oxide is capable of accommodating a lot of O from O_2 and H_2O. The measurement by Morales (LA-13597-MS) indicate that the rate of PuO_2 + H_2O is independent of x for values of χ up to 0.17 and earlier work shows that is true at 25^{o}C for x up to 0.27.

Reversible reaction is not observed at room temperature. $PuO_{2+\chi}$ can be kept in high vacuum (10^{-10} torr) for weeks without indication of O_2 loss (χ~ 0.17). Morales tells me that O_2 appears only when $PuO_{2+\chi}$ is heated above 300^{o}C in dynamic vacuum.

The most important issue regarding the Pu + H_2O reaction is the equilibrium point determined by the equilibrium H_2 pressure: K_T for the PuH_2O rxn is

$K_T = \frac{PH_2}{PH_2O}$ (where PH_2O is limited by the equilibrium vapor pressure of H_2O at T)

Equilibrium pressure for $PuO_{2+\chi}$ have not been measured and are expected to vary with χ, as well as with T. At 25°C, PH_2 exceeds 1.5 atm for χ = 0.26.

Attainment of the equilibrium H_2 pressure will stop the PuO_2+H_2O reaction, but should not prevent the H_2O-catalyzed PuO_2+O_2 reaction from occurring because it is independent of H_2 pressure. (The model needs to include an equilibrium PH_2 limit on the PuO_2 + H_2O reaction.)

As I consider the formulation of a model, there will need to be an O_2 concentration at which the PuO_2 + H_2O reaction starts, even though there are traces of residual O_2. I have been working on the Pu + H_2O and water-catalyzed Pu + O_2 reactions for the past couple of weeks and see that the reaction of H_2O has occurred for moist air with residual O_2 mole fractions of 0.00005 to 0.0001 present.

Case 3 is down the road and I don't know if such a system needs to be considered.

Second memorandum

IMPORTANT CHEMICAL REACTIONS

Three possible systems are readily identified for pure oxide.

4. PuO_2 and H_2O
5. PuO_2,O_2 and H_2O
6. PuO_2, O_2, H_2O and organic residues.

Consideration is limited to Cases 1 and 2 at 25°C.

<u>Dependence of Case 1 Reactions on Temperature and Water Concentration</u>:

Chemical reaction
$PuO_2(s) + x\,H_2O\,(g,ads) \rightarrow PuO_{2+x}\,(s) + x\,H_2(g)$.

The temperature dependence of dH_2/dt for this reaction at PH^2O = 24 torr is described by the Arrhenius equation reported for the 25-350°C range [1]:

$\mathrm{In}(dH^2/dt) = 6.441 - (4706/T)$.

The rate is independent of PH_2O at 25°C, but the dependence on water pressure is uncertain at higher temperatures. Based on the dependence observed for the same process during the reaction of plutonium metal, the dependence (if it exists) is $(PH_2O)^{1,2}$ [2]. This equation also defines the temperature dependence of $-dO_2/dt$ for the water-catalyzed PuO_2+O_2 reaction.

Radiolysis:

H_2O (ads,g) (α-particles) $\rightarrow$ H_2(g) + O_2(g)

This information from SRS via Janet McFadden does not help with interpretation of the reaction kinetics. A detailed description of the conditions and analytical results that lead to the reported observations is needed in order to make an assessment. (They may have been summarized at the SRS meeting, but I did not understand. In part, they seemed to directly contradict reproducible observations at LANL showing that measurable amounts of O_2 do not form when PuO_2 is exposed to H_2O [1,3] and that water is formed when PuO_2 is exposed to mixture containing H_2+O_2 [3,4].)

Chemical recombination:

H_2 (g) + O_2 (g) $\rightarrow$ H_2O (ads, g).

The dependence on dH_2O/dt on temperature and on the concentration of water on the surface of pure oxide has been determined by evaluating data for 25°C [1] and for 50, 100, 200 and 300°C [3,4]. These results show that the combination reaction is a surface-catalyzed process occurring on the oxide. The combination rate depends on the surface concentration of water, $[H_2O]$, adsorbed on the oxide. Water-free oxide surfaces are most active. As the combination reaction proceeds, dH_2O/dt decreases because of the H_2O product adsorbs on the oxide and progressively poisons the catalytic activity by blocking active surface sites.

The combination rate is a complex function of $[H_2O]$ and T. At 25°C, H_2O interacts with the oxide surface by chemisorption as hydroxide (OH) and physisorption as molecular water [5]. At high temperature, $[H_2O]$ is reduced by thermal instability of adsorbed species. More active sites are created, but the concentrations of adsorbed H_2 and O_2 are reduced. The situation is further complicated by the likelihood that oxide activity depends on the preparative history of the oxide. Evaluation of PVT data measured at 25°C [3] and elevated temperatures [4] shows: (1) that the initial combination rate reaches a maximum at 200°C and decrease at higher temperatures and (2) that $\ln(dH_2O/dt)$ for the combination reaction is proportional to $[H_2O]$. The results are:

At 25^{o}C, $\ln(dH_2O/dt) = -20.3 - 2.30\ [H_2O]$. Measurements were made with oxide prepared from weapons-grade gallium alloy.

At 50^{o}C, $\ln(dH_2O/dt) = -12.20 - 0.18\ [H_2O]$.
At 100^{o}C, $\ln(dH_2O/dt) = -11.0 - 0.18\ [H_2O]$.
At 200^{c}C, $\ln(dH_2O/dt) = -9.55 - 0.17\ [H_2O]$.
These measurements were made with oxide obtained by oxidation of high-purity (electrofined) metal.

In each of the above equations, $\ln(dH_2O/dt)$ is in units of mol H_2O/m^2 h and $[H_2O]$ is in units of □mol H_2O/m^2 of oxide surface. The initial maximum rate at each temperature is defined by the intercept ($[H_2O]$ = 0).

Oxygen is simultaneously consumed by both the H_2+O_2 and the water-catalyzed PuO_2+O_2 reactions. At each temperature, the initial($[H_2O]$ = 0) rate of H_2O formation by H_2+O_2 combination greatly exceeds the rate of the water-catalyzed reaction that apparently initiates as soon as water appears in the system. The combination rate progressively decreases as H_2O accumulates on the oxide surface, but he PuO_2+O_2 rate remains constant or increases slightly as additional water is formed (if there is PH_2O dependence). Ultimately, the rate of oxygen consumption by H_2+O_2 combination falls below the rate of the rate of O_2 consumption by the water-catalyzed PuO_2+O_2 reaction and makes an increasingly smaller contribution to the loss of oxygen over time. However, the water-catalyzed reaction continues to consume oxygen at a constant rate until it is depleted.

Net water-catalyzed chemical reaction:

$$PuO_2\ (s) + \chi/2\ O_2\ (g) \rightarrow PuO_{2+x}{}^{(s)}$$

As noted above, the temperature dependence if this reaction is given by the Arrhenius equation for the Pu+H_2O reaction.

References:

1. L. A. Morales, J. M. Haschke, and T. H. Allen, "Kinetics of Reaction Between Plutonium Dioxide and Water at 25^{o}C to 350^{o}C: Formation and Properties of the PuO_{2+x} Phase," Report LA-13597-MS, Los Alamos National Laboratory, Los Alamos, NM, May 1999.
2. J. M. Haschke, T. H. Allen, and J. L. Stakebake, J. Alloys Comp., **243** (1996) 23.

3. J. M. Haschke and T. H. Allen, “Interactions of Plutonium Dioxide with Water and Oxygen-Hydrogen Mixtures,” Report LA-13537-MS, Los Alamos National Laboratory, Los Alamos, NM, January 1999.
4. L. A. Morales, “Preliminary Report on the Recombination Rates of Hydrogen and Oxygen over Pure and Impure Plutonium Oxides,” Report LA-UR-98-5200, Los Alamos National Laboratory, Los Alamos, NM, 1998.
5. J. M. Haschke and T. E. Ricketts, J. Alloys Comp., **252** (1997)

Appendix B *[of Sherman 1999 memo]*
Numerical analysis aspects

Chemical reaction equations can be expressed as a coupled system of first-order differential equations.

$$(1) \qquad \frac{dy_i}{dt} = f_i(y_1, y_2, \ldots y_n) \qquad y_i(0) = y_{i0} \qquad i = 1, 2, \ldots, n$$

This is the classic initial value problem for which a great deal of information is known, and can be found in many books, e.g. "Numerical Recipes."[2]. Obtaining a solution is easy unless there are the complications:

a) singularities or discontinuities in one or more of the f_i, or,
b) the system of equations is "stiff."

Our equations do not have I do not have any singularities, but the rate expressions do have discontinuities. As presently formulated, the reaction rates go abruptly to zero when the reactant concentrations go to zero. Stiff systems are very common when solving the differential equations of chemical reaction systems. **A differential equation system is stiff if the required step size for stability (using ordinary differential equation solvers) is much less than that required for accuracy**.

A single differential equation can be stiff, but it is more common to have stiffness when there are a system of coupled equations. In a chemical system simulation, the system will be stiff when we have reactions with very different characteristic times. Ordinary differential equation solvers can not take time steps much larger than the characteristic time of the fastest reaction, or they go unstable – truncation errors grow exponentially. However, the integration time of interest is usually of the order of the characteristic time of the slowest reaction.

I find the following approach clarifies the stiffness problem. We linearize the equation around a time t_0,up to which the solution is known. As long as there are no singularities or discontinuities of the right-hand sides, and we do not go far from t_0, this is a good approximation.

$$(2) \qquad \frac{dy_i}{dt} = f_i(y_1, y_2, \ldots, y_n) \cong f_i(y_{10}, y_{20}, \ldots, y_{n0}) + \sum_{j=1}^{n} \left(\frac{\partial f_i}{\partial y_j} \right) (y_j - y_{j0})$$

Expressed in matrix notation

(3) $$\frac{d}{dt}\mathbf{Y} = \mathbf{F_0} + \mathbf{J} \bullet (\mathbf{Y} - \mathbf{Y_0})$$

Where **J** is the Jacobian, a square matrix of the partial derivatives $\partial f_i / \partial y_j$, **Y** the vector of n elements which are the unknowns yi, Y_0 the corresponding vector of initial values, and $\mathbf{F_0}$ the vector whose elements are the f_i. For clarity, we will discuss only the simplest case, where all the eigenvalues of J, λ_1, λ_2, …,λ_n, are real and distinct (and probably negative). The argument can be extended if needed to more complex cases where the eigenvalues are complex and/or we have identical eigenvalues. The solutions will consist of exponential terms of the form constant•·exp(λ_jt).. The eigenvalues are the reciprocal of the characteristic times of the problem. Consider the eigenvalues ordered in decreasing absolute value, λ_1, λ_2, …λ_n. We usually want to integrate the equation for a time period of the order of $\Delta t \approx |1/\lambda_n|$. At the start of the calculation, where changes can be rapid, the time step should be much shorter to maintain accuracy, $\Delta t \approx |1/\lambda_1|$ For most methods of solving the equations, Runge Kutta, Predictor-Corrector, etc., the solution becomes unstable if much larger step sizes than $\Delta t \approx |1/\lambda_1|$ are used. However, the term involving λ_1 soon becomes small, and there are no fast changes in the solution. We would like to then use larger time steps, but are held back by stability limits. **An excessive number of integration steps (e. g. 10^6 or more) is required if $|\lambda_1| >>> |\lambda_n|$, i.e., the system is stiff**. A single equation can be stiff if the characteristic time $|1/\lambda|$ is much less than the time period to be integrated. In our case where we want to follow the solution for a period of 50 years, we can get stiffness in any of the eigenvalues has a characteristic time much less than 50 years.

The way around the stiffness problem is to use an integration method that is unconditionally stable. Such methods exist (e.g., the Gear method). Present day packages of numerical routines that solve differential equations usually contain one "stiff" solver. The stiff solver is usually inferior in accuracy (or slower) than ordinary solvers if the system is not stiff, or there are rapid changes in the solution. Typically, they will be more difficult to use than Runge Kutta and other methods. Hence, stiff solvers should be used only when the system is stiff. The indication the solver is finding the system stiff, is the use of small step sizes by routines with automatic step size control when the solution is changing slowly.

Packages of differential equation solvers include several different types of solvers. Each solver has a range of problems in which it is the best one. All packages contain one or more Runge Kutta routines. Invariably these are the easiest to use, and are the most trouble free. Modern Runge-Kutta routines have automatic step size control to maintain a solution of a specified accuracy. They are a natural first choice when starting a new problem. The disadvantage of Runge Kutta methods is they may be slower than competing approaches. Most packages contain a solver of the predictor-corrector type (e.g., Adams-Bashforth-Moulton method). They may contain a solver using Richardson extrapolation (e.g., Bulirsch-Stoer method). These methods usually also have automatic step size control. If computation time is important, it may be worth while to examine their use in place of Runge Kutta. However, if the system is stiff, all the previous mentioned methods will be slow. A stiff solver is needed. As previously mentioned, one is usually included in all packages.

Appendix C *[of Sherman 1999 memo]*
Analytical Solutions

For comments on the general solution of the system of equations, Eq. 1, see Appendix B. We will require a numerical approach when we obtain more exact (and complex) expressions for the rate constants. Even with the present comparatively simple system, a numerical solution is useful. However, we can solve part of the system analytically, although the solution is complex and of questionable usefulness.

The equation for water is uncoupled from the other two equations and can be solved analytically. The rate of change of hydrogen, and hence the change in hydrogen, is opposite to that of the water. The solution is complex and hence difficult to see how it could be input into the solution of the oxygen equation. Furthermore, because we have piecewise constant rate expressions, care must be given that we switch the form of the solutions at the break points.

Consider Eq. 4. We can write it

(1) $$\frac{dy}{dt} = -R + C\exp(-y/A)$$

where R, C and A are constants. Let u = exp(-y/A). Hence du = -(u/A)dy. Our equation becomes

(2) $$-\frac{A}{u}\frac{du}{dt} = -R + Cu$$

Separating variables and using partial fractions

(3) $$-\frac{dt}{A} = \frac{du}{u(-R+Cu)} = -\frac{du}{Ru} + \frac{Cdu}{R(-R+Cu)}$$

Integrating,

(4) $$\frac{t}{A} = \frac{1}{R}\ln\left[\frac{u}{u_0}\right] - \frac{C}{R}\ln\left[\frac{Cu-R}{Cu_0-R}\right]$$

After some algebra,

(1) $$\exp\left\{-\frac{Rt}{A}\right\} = \left[\frac{Cu-R}{Cu_0-R}\right]^C \left[\frac{u_0}{u}\right]$$

References

1. L. A. Morales, J. M. Haschke, and T. H. Allen, "Kinetics of Reaction Between Plutonium Dioxide and Water at 25°C to 350°C: Formation and Properties of the PuO_{2+x} Phase," Report LA-13597-MS, Los Alamos National Laboratory, Los Alamos, NM, May 1999.
2. J. M. Haschke, T. H. Allen, and J. L. Stakebake, J. Alloys Comp., **243** (1996) 23.
3. J. M. Haschke and T. H. Allen, "Interactions of Plutonium Dioxide with Water and Oxygen-Hydrogen Mixtures," Report LA-13537-MS, Los Alamos National Laboratory, Los Alamos, NM, January 1999.
4. L. A. Morales, "Preliminary Report on the Recombination Rates of Hydrogen and Oxygen over Pure and Impure Plutonium Oxides," Report LA-UR-98-5200, Los Alamos National Laboratory, Los Alamos, NM, 1998.
5. J. M. Haschke and T. E. Ricketts, J. Alloys Comp., **252** (1997
6. Quigley, G. P., "Hydrogen/Oxygen Recombination Rates in 3013-Type Environments: A Report on the Rate of Loss of Hydrogen and Oxygen from Cells Containing Non-Radiolytic Samples," LA-UR-98-4864, 1998.
7. Press, W. H., et al. Numerical Recipes, Cambridge Univ. Press, 1986.

9.6. Appendix F – Copy of Ottinger 2000 Memo

This appendix contains a reprint of a project memo that give an overview of the assistance provided by the Nonactinide Isotopes and Sealed Sources Management Group NISSMG Team for the disposition of orphan nuclear materials at the Mound facility. Also discussed is the technical analysis necessary to meet DOT and DOE shipping requirements, in particular the issue of the generation of hydrogen gas from plutonium oxide.

Note: Signed version of attached memo kept on file. Enclosed copy reformatted to fit within required borders for this report.

Sandia National Laboratories

Albuquerque, New Mexico 87185-0748

date: September 19, 2000

to: Distribution

from: Cathy A. Ottinger, 6413, MS-0748; Lawrence C. Sanchez, 6849, MS-0779

Original signed by Cathy A. Ottinger and Lawrence C. Sanchez

subject: Mound Pu-239 Gas Generation

Summary

BWXTO (Mound) has approximately 217 grams of Pu-239, in the form of PuO_2, that must be removed from the site to achieve closure milestones. The site baseline, according to the Material Disposition Maps developed as part of the Nuclear Material Integration Project, is to ship this material to Savannah River Site (SRS). As part of the Non-actinide Isotopes and Sealed Sources Management Group (NISSMG) activity, we are assisting Mound in determining the suitability of this material for shipment off-site in the DOT Specification 6M packaging, which is a Type B packaging. This study has focused on the potential for hydrogen gas generation from the Pu-239 material and compliance with relevant regulations.

To assist in demonstrating the suitability of this material for shipment in the 6M packaging, characteristics and historical process information was collected. The information about this material was obtained from Mound personnel and is included as an attachment to this memo. As a part of this study, we contacted various subject matter experts in the areas of the characteristics of Pu oxides in storage, gas generation, and nuclear materials transportation. As the materials characteristics were based on process knowledge, a bounding study on the potential gas generation rates was performed. These studies showed the Mound materials to be compliant with all relevant regulations concerning gas generation for transportation in the DOT Specification 6M packaging. The results are documented in this memo and in the attachment paper, by Lawrence Sanchez, documenting his systems calculations. Recommendations covering the shipment preparation are included at the end of this memo.

Material Characterization and Configuration

Information has been received from Mound personnel in the form of faxes, email text descriptions, photos, and copies of x-rays. The information provided is shown in Attachment 1, with a summary provided here.

Mound has nine containers in three different packaging configurations. Table 1, provided by Mound personnel, shows the quantity of material in each package.

Table 1. APAS Samples Pu Mass

CONTAINER ID	Pu Element (grams)	Pu-239 Isotope (grams)
7A	12	11
7B	12	11
7C	11	10
7D	11	10
7E	11	10
7F	53	47
7G	25	22
7H	2	2
SPECIAL APAS *	80	72
TOTAL	217	195

*SPECIAL APAS contains material from original containers: CP1131, CP1132, CP1133, CP1134, CP1135, CP1136, and CAN X

Historical data describes the material as $^{239}PuO_2$ spiked with 0.8% Pu-238 and containing approximately 12% Pu-240. It is referred to as "APAS material" as it was developed for an Automated Plutonium Assay System. These containers were packaged in May 1978. The material was dried at 110°C for 24 hours and then handled in an inert glove box with a moisture content of < 1 ppm. It is assumed that this material originated from Hanford and is relatively pure, since it was used for an assay system.

Values for mass, curies and wattage for each container and for each isotope were calculated from this information and are shown in Table 2.

Table 2. Calculated Values of Pu isotopes in Mound mixture.

Cont. ID	Pu (grams)	Pu-239 (grams)	Pu-239 (Curies)	Pu-239 (watts)	0.8% Pu-238 (grams)	0.8% Pu-238 (Curies)	0.8% Pu-238 (watts)	12% Pu-240 (grams)	12% Pu-240 (Curies)	12% Pu-240 (watts)
7A	12	11	0.68	0.02	0.10	1.63	0.05	1.44	0.33	0.00
7B	12	11	0.68	0.02	0.10	1.63	0.05	1.44	0.33	0.00
7C	11	10	0.62	0.02	0.09	1.50	0.05	1.32	0.30	0.00
7D	11	10	0.62	0.02	0.09	1.50	0.05	1.32	0.30	0.00
7E	11	10	0.62	0.02	0.09	1.50	0.05	1.32	0.30	0.00
7F	53	47	2.91	0.09	0.42	7.21	0.24	6.36	1.46	0.00
7G	25	22	1.36	0.04	0.20	3.40	0.11	3.00	0.69	0.00
7H	2	2	0.12	0.00	0.02	0.27	0.01	0.24	0.06	0.00
APAS	80	72	4.46	0.14	0.64	10.88	0.36	9.60	2.21	0.00
totals	217	195	12.09	0.37	1.74	29.51	0.97	26.04	5.99	0.01

Cont. ID	Pu (grams)	Total per container (grams)	Total per container (Curies)	Total per container (watts)
7A	12	12.54	2.65	0.07
7B	12	12.54	2.65	0.07
7C	11	11.41	2.42	0.07
7D	11	11.41	2.42	0.07
7E	11	11.41	2.42	0.07
7F	53	53.78	11.58	0.33
7G	25	25.20	5.45	0.15
7H	2	2.26	0.45	0.01
APAS	80	82.24	17.55	0.50
totals	217	222.78	47.59	1.35

Data used to calculate data in table 2 above taken from:

Isotope	Specific Activity (taken from 49 CFR 173.435) Pu-238	Pu-239	Pu-240
Ci/g	1.70 E + 01	6.20 E - 02	2.30 E - 01
Ci/g	17.00	0.062	0.230

	Thermal Power (from attached L. Sanchez memo)		
Isotope	Pu-238	Pu-239	Pu-240
W/g	0.55825	0.00190	0.00031

Seven of the containers consist of a "center post" inner can with different sizes of two crimp sealed food pack cans outside. The largest single quantity is contained in a thin walled container inside a 2R container. The smallest quantity is contained in a small can inside multiple food pack cans, inside a #12 cal can. Photos of these were provided by Mound and are shown in Attachment 1.

The details of the nested cans for each configuration and the supplied or calculated volumes are provided in Attachment 2.

Analysis

The characteristics of the Mound material and predicted gas generation rates were compared to the relevant regulations for shipment in the DOT Specification 6M packaging. Specifically, 49 CFR 173.416, 49 CFR 173.417 and DOE Order 460.1A were examined in detail for compliance issues.

The DOT Specification 6M packaging is covered by 49 CFR 173.416, which limits contents to those that will not undergo pressure-generating decomposition at temperatures up to 121ºC and has a 10 watt decay heat limit. Based upon the material composition supplied by Mound, this material is well below the 10 watt limit. The bounding calculations show, for an infinite supply of water in the container, the time for potential gas generation from the radiolysis of water at 121ºC to cause pressures in the 6M 2R to reach 212.5 psig is on the order of several tens of years, so this appears to be acceptable also. With more realistic moisture contents and depletion of moisture by radiolysis, for most of the containers, pressures will be substantially lower.

The requirement that the material must be sealed in metal cans within the 2R and a limit of H/X (hydrogen/fissile atoms) of 3 is covered in 49 CFR 173.417. The material is within multiple metal cans, including in the various containers, food packs, center post can and a 2R and Mound reports that no external contamination has been found on any of the cans. Although the moisture content was low when the cans were initially sealed in an inert glovebox, changes with time are not available for this material. So, based on the parametric calculations for H/X looking at various moisture percentages, the H/X for this material will be acceptable if the moisture content is 9% or less (see Attachment 3). The highest as-received weight percent moisture for plutonium oxides in storage measured by supercritical fluid extraction as reported in LA-UR-99-3053 for the MIS project was 2.8%, for material that had no stabilization. So, the Mound material, stabilized as previously described, should also be acceptable for the H/X ratio limit.

DOE Order 460.1A requires a DOT Specification Container and a limit of 20 Curies or less for this type of shipment. Mound is planning on shipping all but one of these containers in the DOT Specification 6M and will use multiple 6M packages to ship the eight containers, so they can stay below the 20 curie limit.

Conversations with Subject Matter Experts

Meetings with Jim Pierce

Jim Pierce of Sandia National Laboratories Transportation Safety & Security Analysis Department, who was the 6M Project Subgroup Task Team Leader, served as our subject matter expert regarding 6M transportation, specifically including pressure and structural capabilities of the 2R. We obtained the 6M Project Completion Report, dated June 1, 1998 from him. He covered the areas of this report that we would find useful, although this report was directed toward containers with greater than 20 curies, while all of the 6M's that Mound will be shipping with this material will be less than 20 curies. He specifically pointed out the section with the pressure calculation and the reference to the structural analysis of the 2R. He also provided direction and guidance on requirements and a path forward.

Discussion with Rich Szempruch

Rich Szempruch of BWHC served as our subject matter expert in historical Pu moisture characterization. In a phone conversation with Rich Szempruch concerning moisture characteristics of PuO_2 and the Mound material, he stated that historically, for plutonium production runs of 3 months, at one of the Hanford plants, with treatment at 450ºC that the average was 0.57% LOI. For cans of material that were stabilized at 600ºC for a few hours (within one shift) most (~98%) met <1% LOI; the remaining required a second heat stabilization for a similar time. It is very likely that the Mound material originated at Hanford and had these characteristics; however, it was modified and subsequently heat treated at Mound at 110ºC for 24 hours.

Requirements Related to Gas Generation

49 CFR 173.416 Authorized Type B packages

"Each of the following packages is authorized for shipment of quantities exceeding A_1 or A_2, as appropriate: (c) DOT Specification 6M metal packaging, only for solid or gaseous Class 7 (radioactive) materials that will not undergo pressure-generating decomposition at temperatures up to 121ºC (250ºF) and that do not generate more than 10 watts of radioactive decay heat."

From Mound's historical information, the material was heated to a temperature of 110ºC for 24 hours and then handled in an inert glove box. Based on the bounding (extremely conservative) calculations in the L. Sanchez memo (Attachment 3), for an infinite supply of water in the container, the time for potential gas generation from the radiolysis of water at 121ºC to cause pressures in the 6M 2R to reach 212.5 psig, is on the order of several tens of years. Based on the amount of water available with 5 weight % moisture and the depletion of that water, the maximum pressure in the 6M 2R is less than 30 psig at a temperature of 121ºC.

From Attachment B of the 6M Project Completion Report dated June 1, 1998, a detailed finite element structural analysis of the DOT 6M 2R was conducted at Sandia National Laboratories (Ref. Letter Report, dated April 22, 1998, Hal D. Radloff, Dept. 6342). It was determined that no yielding of vessel material occurred up to internal pressures of 850 psig. Thus, for a pressure of 212.5 psig there would be a factor of safety of 4.0.

Based on the calculations for the material quantities, shown in Table 2, the maximum decay heat for any single container is 0.50 watts, well below 10 watts. The total for all nine containers is 1.35 watts.

49 CFR 173.417 Authorized fissile materials packages

"(b) Fissile Class 7 (radioactive) materials with radioactive content exceeding A_1 or A_2 must be packaged in one of the following packagings: (2) DOT Specification 6M metal packaging. These packages must contain only solid Class 7 (radioactive) materials that will not decompose at temperatures up to 121ºC (250ºF). Radioactive decay heat output may not exceed 10 watts. Class 7 (radioactive) materials in other than special form must be packaged in one or more tightly sealed metal cans or polyethylene bottles within a DOT Specification 2R containment vessel."

For containers 7A-G, the PUO_2 is within a "center post" can with metal seals within the metal food pack cans. For container 7H, the PUO_2 is within a small screw top can within multiple food pack cans and a metal cal can. For the Special APAS container, the PUO_2 is within a metal can within a 2R vessel. Based on a phone conversation with Gayle Shockey of Mound, no external contamination was measured on any of the containers. The Mound containers (except 7H) will be placed within the 6M 2R for shipment.

"(I) For fissile material with a criticality TI equal to 0.0, packages are limited to the following amounts of fissile Class 7 (radioactive) materials: …0.9 kilograms of plutonium (except that due to the 10-watt thermal decay heat limitation, the limit for plutonium-238 is 0.02 kilograms)…. The maximum ratio of hydrogen to fissile material may not exceed three, including all the sources of hydrogen within the DOT Specification 2R containment vessel. (ii) Maximum quantities of fissile material and other restrictions for materials with a criticality TI of greater than 0.0 are given in table 5. … Where a maximum ratio of hydrogen to fissile material is specified in table 5, only the hydrogen interspersed with the fissile material must be considered."

Applicable excerpt from *table 5 - Authorized Contents for Specification 6M packages (quantity in kilograms):*

Plutonium [2,3] *Compounds*		*Minimum Transportation Index*	*Maximum no. pkgs transported as a fissile material control shipment*
H/X = 0 [8]	*H/X <=3*		
0.9	*0.9*	*0*	*N/A*
4.1	*3.4*	*0.1*	*1,250*
4.5	*4.1*	*0.2*	*625*
	4.5	*0.5*	*250*

2 Minimum percentage of plutonium-240 is 5 weight percent.
3 4.5 kilogram limitation of plutonium due to watt decay heat limitation.
8 H/X is the ratio of hydrogen to fissile atoms in the inner containment.

The lowest quantity of the Pu-239 limits is 0.9 kilograms (900 grams), while the total quantity of the material in the nine cans of Mound material is less than 225 grams.

From Mound's historical information, the material was packaged in May 1978 and the material was heated to a temperature of 110ºC for 24 hours and then handled in an inert glove box with a moisture content of < 1 ppm. However, the moisture content of the material cannot be measured today at Mound. Based on conversations with Jim Pierce, food pack cans can "breathe" over time and moisture may then get into crimp sealed food pack cans. So, a reverse engineering process was used to look at how much moisture would have to be absorbed onto the PUO_2 for this material to exceed the H/X limit of 3. Based on the bounding calculations in the L. Sanchez memo (Attachment 3) a moisture content exceeding 9% would be necessary to reach the H/X limit of 3.

The Material Identification and Surveillance (MIS) project has analyzed Hanford and Rocky Flats Environmental Technology Site (RFETS) items representing a portion of oxides to be packaged for long term storage (LA-UR-99-3053). The Hanford and RFETS items were shipped to LANL using double- or triple-containment food-pack canisters. Each container was filled and sealed in air. Two of the items received from RFETS were described as pyrochemical cell cleanout material. This material had not been previously stabilized; that is, there was no calcination at RFETS. Whereas, the Mound material was heated to 110ºC for 24 hours and then handled in an inert glove box with a moisture content of < 1 ppm. The as-received wt % moisture on these two RFETS items was 2.802% and 0.752% as determined by the supercritical fluid extraction analysis. Three other items received from RFETS were identified as dissolution residuals. One item was calcined at 200-250ºC, and the other two were calcined at 250-300ºC. The as-received wt % moisture was 0.000%, 0.148%, and 0.460% as determined by the supercritical fluid extraction analysis. For the 34 MIS items, the highest as-received weight percent moisture was reported to be 2.8 wt% (for the item previously described), based on the supercritical fluid extraction analysis for moisture.

DOE O 460.1A PACKAGING AND TRANSPORTATION SAFETY

"4. REQUIREMENTS.

Offsite Hazardous Materials Packaging and Transportation Safety.

(1) Packaging and Transportation Safety.

(a) Each package and shipment of hazardous materials shall be prepared in compliance with Hazardous Materials Regulations of the Department of Transportation (DOT) [Title 49 Code of Federal Regulations (CFR) Parts 106-199] and applicable tribal, State, and local regulations not otherwise preempted by DOT.

(4) Special Requirements for Radioactive Material Packagings.
(b) Type B or Fissile Radioactive Material Packagings. In addition to packagings authorized by the Hazardous Materials Regulations, each person who offers for transportation a Type B and/or fissile quantity of radioactive materials also may use a packaging certified by Headquarters Certifying Official or NRC. NRC-certified Type B and fissile packagings that have a current Certificate of Compliance may be used by DOE and DOE contractors only under the conditions specified in the Certificate, and only after DOE is registered with NRC as a user. Packagings that have a current DOE Certificate of Compliance issued by the Headquarters Certifying Official may be used by DOE and DOE contractors only under the conditions specified in the Certificate.

(c) Plutonium Packagings.

1. Each person who offers plutonium for transportation in excess of 20 Curies per package shall use a packaging approved by the Headquarters Certifying Official or the NRC.

DOE G 460.1-1, IMPLEMENTATION GUIDE for Use with DOE O 460.1A, PACKAGING AND TRANSPORTATION SAFETY

4. SPECIAL PACKAGING FOR RADIOACTIVE MATERIALS
4.4 USE OF OTHER APPROVED OR CERTIFIED PACKAGINGS

DOE contractors may use any of the following in addition to the DOE approved packagings, as long as all regulatory requirements and any special provisions for the packagings are met.

4.4.2 Department of Transportation Specification Containers. Packaging designs which have been published in the Hazardous Materials Regulations as specification packagings may be used provided that all provisions of the DOT specification and applicable quality assurance requirements are met and provided that use of the packaging is not prohibited by DOE O 460.1A [i.e., the restriction on plutonium packagings at DOE O 460.1A, 4.a.(4)(c)]."

The 6M packaging is a DOT specification container covered in 49 CFR 178.354 of the Hazardous Materials Regulations. The largest single container (Special APAS) has less than 18 curies of plutonium, so each will have less than 20 curies in each 6M 2R packaging.

NRC Information Notice

The Mound material shipment is not proposed for a NRC certified packaging under NRC regulations, but it may prove useful to look at one of the NRC Information Notices for relevant, if not, required guidance.

NRC "IE Information Notice No. 84-72: *Clarification of Conditions for Waste Shipments Subject to Hydrogen Gas Generation" states: (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/ft-3 at 14.7 psia and 70<deg>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%.*

Depending upon the gas generation rate, the time to reach 5% H_2 concentration can be on the order of part of a year (see L. Sanchez paper, Attachment 3). While the shipping time in the 6M will be relatively short, the time that the inner containers have already been sealed is more than 20 years. So, as an added level of conservatism it would be prudent to consider inerting each 2R prior to closing it for shipment.

Recommendations

In order to meet the requirements of DOE Order 460.1A, each 6M must have 20 curies or less. The Special APAS unit is approximately 17.55 curies, closest to the 20 curie limit of DOE Order 460.1A, so it is recommended to ship it by itself in a 6M 2R. Mound has multiple options for arranging the other containers in the 6M 2R's, so long as the total curie content is 20 curies or less, in each. As an added level of conservatism, as a "good practice," we recommend inerting the 2R's prior to closing for shipment.

Distribution (with attachments):

Ray Finney, BWXTO (Mound)
Steve Brown, BWXTO (Mound)
Gayle Shockey, BWXTO (Mound)
Jim Low, DOE/AL
G. D. Roberson, DOE/AL
Dave Parks, INEEL
MS-0727 Gary Polansky, SNL, 6406
MS-0779 Larry Sanchez, SNL, 6849
MS-0717 Jim Pierce, SNL, 6141
MS-1146 Martin Sherman, SNL, 6422
MS-0748 Cathy Ottinger, SNL, 6413
MS-0748 6413 Day File

Attachment 1

Information Supplied by Mound

7-26-00
Revised

Pu-239 Shipment

It is necessary to demonstrate that there is no gas generation hazard involved in an upcoming Pu-239 shipment. Approximately 217 grams of plutonium is to be shipped from BWXTO (Mound) to Savannah River. Apparently Ray Finney and Steve Brown (Mound) have discussed this with you and have asked me to compile the information you need to calculate H/X ratios for this material.

We have nine containers with three different packaging configurations to be considered. I am providing photos and X-Ray images of the packages, approximate dimensions, and packaging material descriptions as well as the amount of material in each package. Table 1 lists the packages by IDs, the total grams of Pu in each, and grams of Pu-239 in each.

Historical data describes the material as $^{239}PuO_2$ spiked with 0.8% Pu-238 and containing approximately 12% Pu-240. It is referred to as "APAS material" as it was developed for an Automated Plutonium Assay System. These containers were packaged in May, 1978. The material was dried at 110^{o}C for 24 hours and then handled in an inert glove box with a moisture content of < 1 ppm.

Packaging configuration #1 consists of a heavy walled stainless "center post" container crimp sealed in a #300 food pack can. This was overpacked into a 401 X 411 crimp sealed food pack can with a small amount of stainless steel wool. There are seven items (7A, 7B, 7C, 7D, 7E, 7F, & 7G) packaged in this manner (see photos #1-4) *[Figures 1-5]*. I am including a H/X calculation attempt made by one of my coworkers for packaging configuration #1 (see H:X Calculation). Please see "Initial Volume" for measurements we made with a center post container and a #300 can.

There is a slight variation of the above packaging for 7A. This is in a center post container and a #300 can like 7B-7G however, unlike the others, the #300 can is bagged and taped and overpacked in a 404 X 700 food pack can with two stainless steel wool pads (see photos #4 & 5) *[Figures 5-6]*. Please see the photos for approximate dimensions.

The outer can in packaging configuration #2 is in what we call a #12 cal can. This is aluminum (photo #6) *[Figure 7]* and contains the sample named 7H. The X-Ray (photo#7) *[Figure 8]* shows several layers of containment within. Please see photo #7 for approximate dimensions and materials involved. We are investigating the possibility of opening the outer three levels of containment (#12 cal can, #10 food pack can, and the open quart can) and bagging and overpacking the remainder in a 404 X 700 food pack can. This is the desired configuration, but we're not sure we can obtain authorization to do so here at Mound. Could you calculate the H/X for both the as-is configuration and the desired one?

Packaging configuration #3 consists of two levels of containment. The outer container (photo #8 & 8b) *[Figures 9-10]* is a heavy-walled steel 2R and is called “special APAS.” This contains the material originally in units listed in Table 1 as CP1131, CP1132, CP1133, CP1134, CP1135, CP1136, and CAN X. The X-Ray (photo #9) *[Figure 11]* shows one container inside (not seven). The inner container has a welded thin-walled stainless body with two heavy stainless “lids.” This container (called an APAS unit) contains 80 grams of Pu (72 g. Pu239) with the internal volume being “void” except for the volume taken up by the PuO_2. We cannot tell how thick the outer container is and will have to assume it is nearly solid except for the volume taken up by the internal APAS unit. The APAS unit does not shift when the outer container is inverted.

I hope this is all the information you need to settle the gas generation issue for this shipment. Feel free to call me with any questions you may have.

Thank you for your help!

Gayle C. Shockey
937-865-4209
shocgc@doe-md.gov

Figure 1. Inner Container Components (7A, B, C,D,E, F, G)

Figure 2. Series of Nested Containers (7B, C, D, E, F, G)

Figure 3. Nested Containers with Stainless Steel Wool (7B, C, D, E, F, G)

Figure 4. Nested Containers (Top View)


2R
Container
Special APAS
PU-239
404 x 700
Can
401 x 411 Cans
7A
7G
7B
7C
7D
7F
7E

Figure 5. Outer Containers (Actual Containers)

Figure 6. Outer Container (7A)

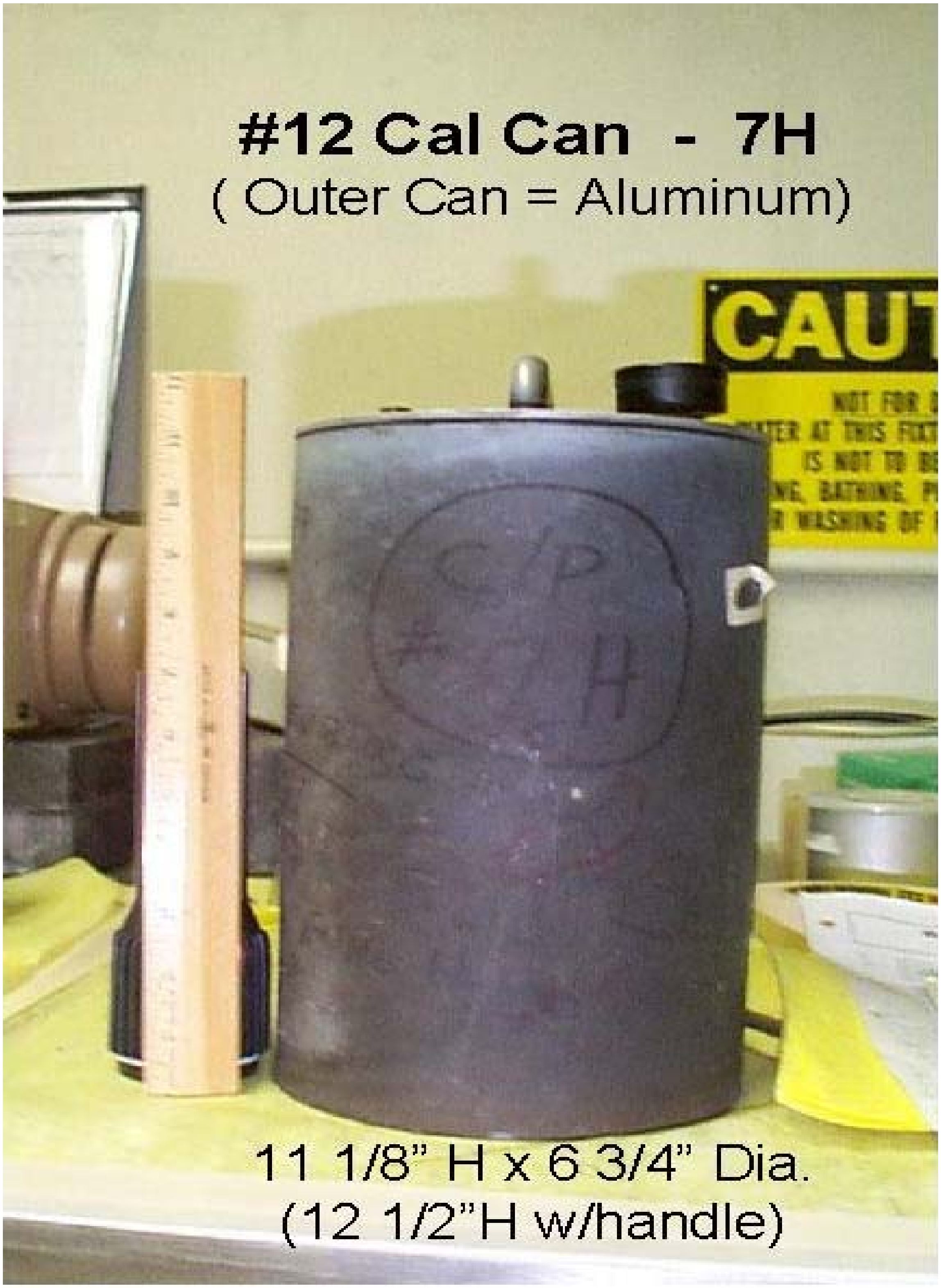
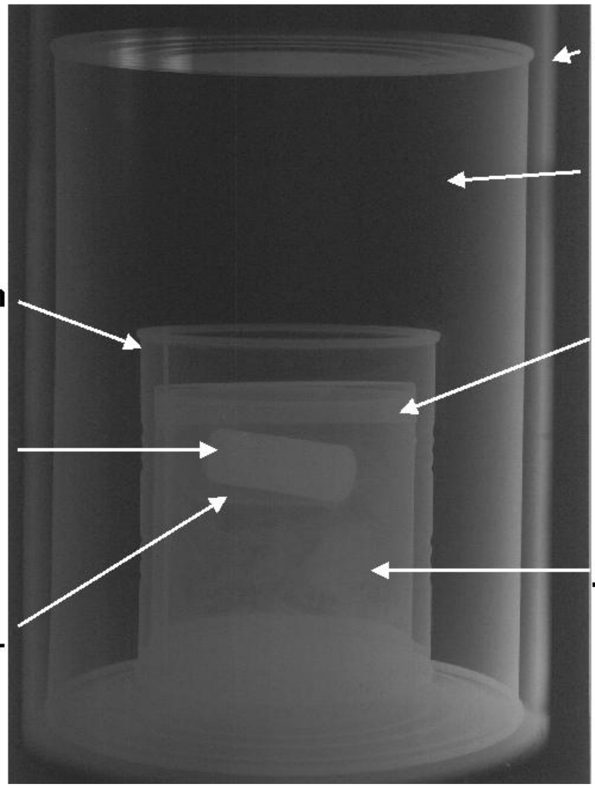


Figure 7. Outer Container (7H)



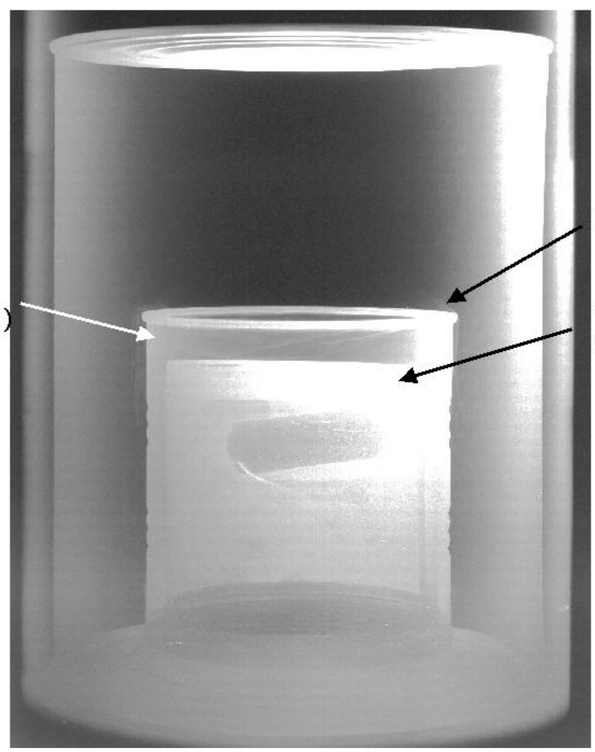


Figure 8. X-rays of Container 7H

Carbon Steel
2R Container
8003.2g
(11 3/4" H x 4 3/4" Dia.)

Figure 9. Special APAS Container

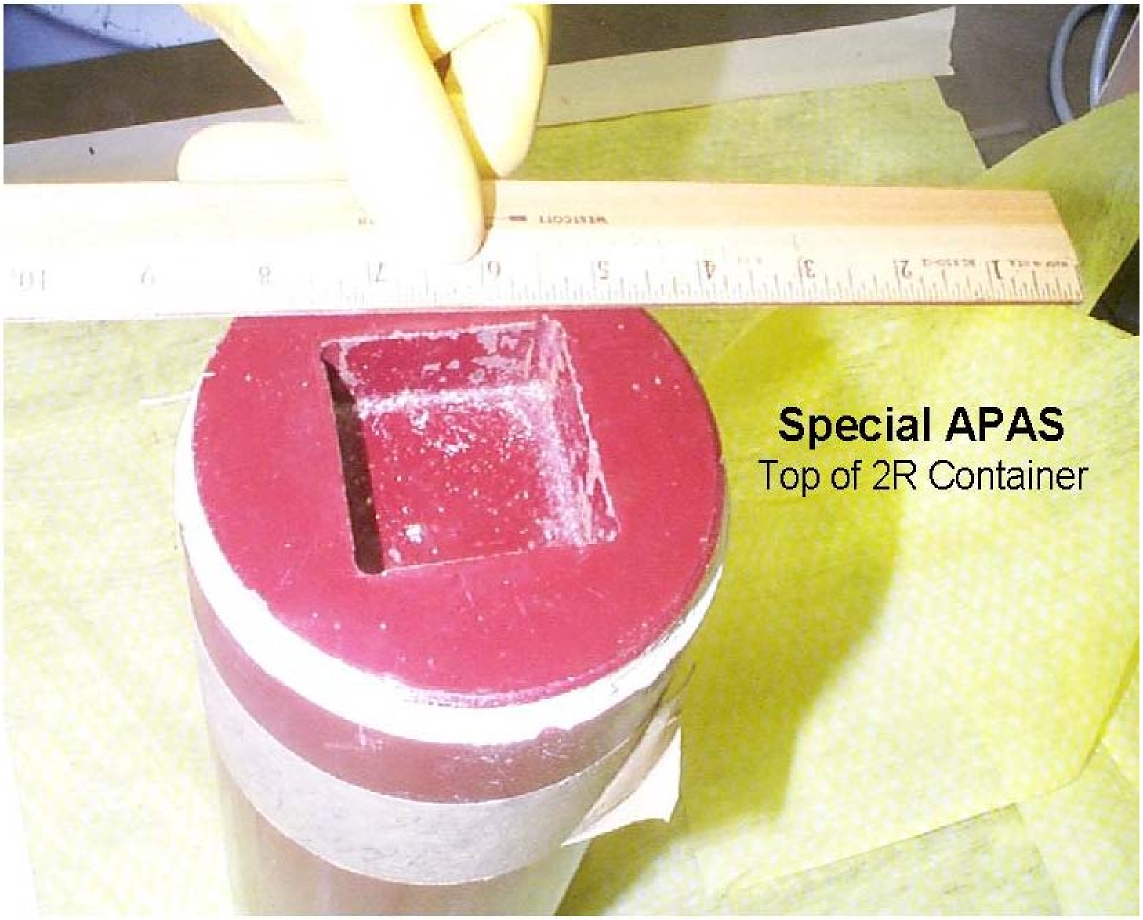


Figure 10. Top of Special APAS Container

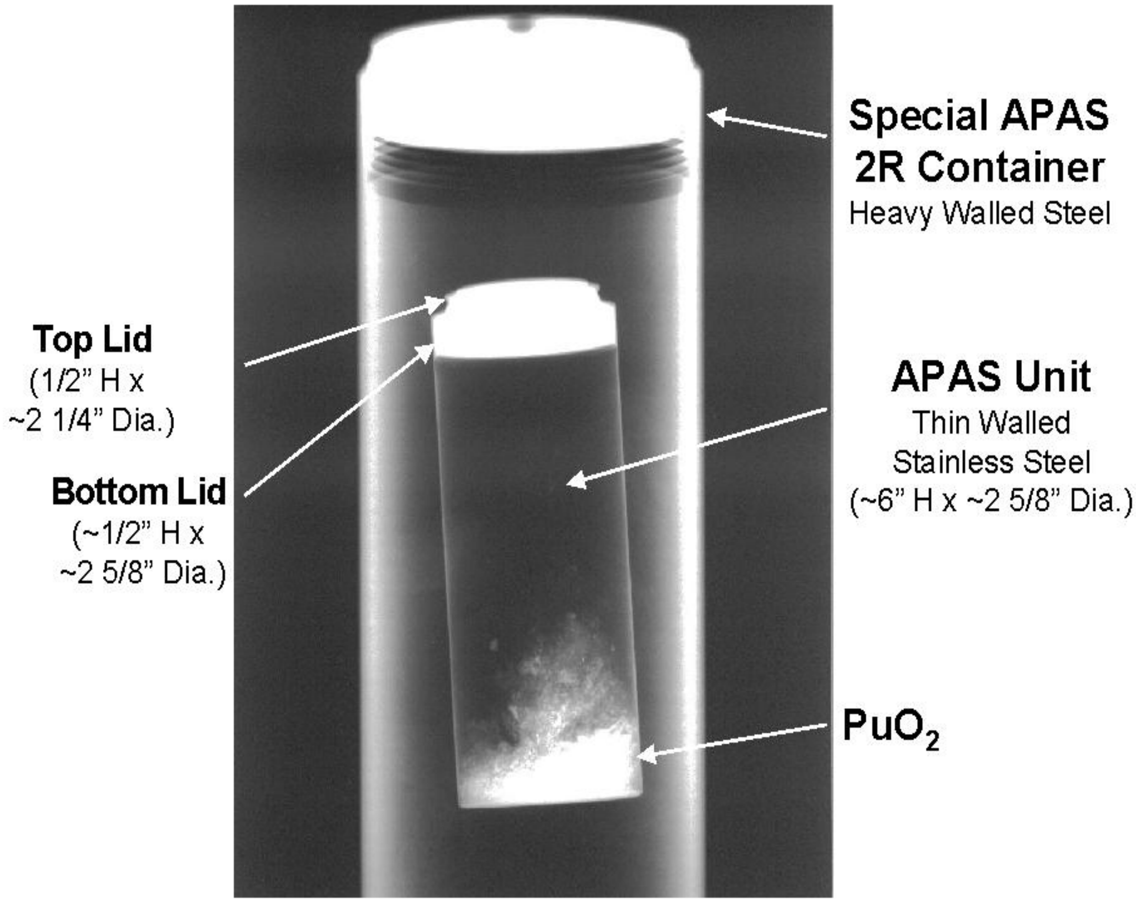


Figure 11. X-ray of Special APAS Container

Attachment 2

Nested Container Details and Volumes

The details of the nested cans for each configuration and the supplied or calculated volumes are provided here.

		Diameter (in)	Height (in)	Volume (in^3)	Volume (cm^3)	Volume (m^3)	Void Fraction
7B - (12.54 g / 2.65 Ci)							
Inside	Pu volume				2.79	2.79E-06	
	Center Post (CP)				90	9.00E-05	
	void fraction (1 - Pu / center post vol.)						0.969
	volume of center post (521-121=400cm^3)						
	void volume				121	1.21E-04	
	#300 food pack can	3"	4 1/2"	31.81	521	5.21E-04	
	void volume						
	401 x 411 food pack can	4 1/16"	4 11/16"	60.76	996	9.96E-04	
	void volume						
Outside	2R (6M)	5.25" ID	16.5" inside	357.18	5853	5.85E-03	
	void fraction (1 - Pu / 2R vol.)						1.000
	void fraction (1 - Pu+CP / 2R vol.)						0.931
7C, 7D, 7E - (11.41 g / 2.42 Ci)							
Inside	Pu volume				2.54	2.54E-06	
	Center Post				90	9.00E-05	
	void fraction (1 - Pu / center post vol.)						0.972
	volume of center post (521-121=400cm^3)						
	void volume				121	1.21E-04	
	#300 food pack can	3"	4 1/2"	31.81	521	5.21E-04	
	void volume						
	401 x 411 food pack can	4 1/16"	4 11/16"	60.76	996	9.96E-04	
	void volume						
Outside	2R (6M)	5.25" ID	16.5" inside	357.18	5853	5.85E-03	
	void fraction (1 - Pu / 2R vol.)						1.000
	void fraction (1 - Pu+CP / 2R vol.)						0.931

		Diameter (in)	Height (in)	Volume (in3)	Volume (cm3)	Volume (m3)	Void Fraction
7F - (53.78 g / 11.58 Ci)							
Inside	Pu volume				11.95	1.20E-05	
	Center Post				90	9.00E-05	
	void fraction (1 - Pu / center post vol.)						0.867
	volume of center post (521-121=400cm^3)						
	void volume				121	1.21E-04	
	#300 food pack can	3"	4 1/2"	31.81	521	5.21E-04	
	void volume						
	401 x 411 food pack can	4 1/16"	4 11/16"	60.76	996	9.96E-04	
	void volume						
Outside	2R (6M)	5.25" ID	16.5" inside	357.18	5853	5.85E-03	
	void fraction (1 - Pu / 2R vol.)						0.998
	void fraction (1 - Pu+CP / 2R vol.)						0.930
7G - (25.20 g / 5.45 Ci)							
Inside	Pu volume				5.60	5.60E-06	
	Center Post				90	9.00E-05	
	void fraction (1 - Pu / center post vol.)						0.938
	volume of center post (521-121=400cm^3)						
	void volume				121	1.21E-04	
	#300 food pack can	3"	4 1/2"	31.81	521	5.21E-04	
	void volume						
	401 x 411 food pack can	4 1/16"	4 11/16"	60.76	996	9.96E-04	
	void volume						
Outside	2R (6M)	5.25" ID	16.5"inside	357.18	5853	5.85E-03	
	void fraction (1 - Pu / 2R vol.)						0.999
	void fraction (1 - Pu+CP / 2R vol.)						0.931
7A - (12.54 g / 2.65 Ci)							
Inside	Pu volume				2.79	2.79E-06	
	Center Post				90	9.00E-05	
	void fraction (1 - Pu / center post vol.)						0.969
	void volume				121	1.21E-04	
	#300 food pack can (bagged & taped)	3"	4 1/2"	31.81	521	5.21E-04	
	void volume						
	404 x 700 food pack can	4 1/4"	7"	99.30	1627	1.63E-03	
	void volume						
Outside	2R (6M)	5.25" ID	16.5"inside	357.18	5853	5.85E-03	
	void fraction (1 - Pu / 2R vol.)						1.000
	void fraction (1 - Pu+CP / 2R vol.)						0.931

		Diameter (in)	Height (in)	Volume (in3)	Volume (cm3)	Volume (m3)	Void Fraction
7H - (2.26 g / 0.45 Ci)							
Inside	Pu volume				0.50	5.01E-07	
	small screw top cal can	3/4"	2"	0.88	14.5	1.45E-05	
	void fraction (1 - Pu / small cal can vol.)						0.965
	glass ~ 50 cc beaker						
	plastic bag or "chemwipes"						
	void volume						
	#4 press fit can	~ 3 5/8"	~ 4"	41.28	676	6.76E-04	
	open quart food pack can	~ 4 1/2"	~ 5"	79.52	1303	1.30E-03	
	plastic bag						
	void volume						
	#10 food pack can	5 7/8"	~ 10"	271.08	4442	4.44E-03	
	void volume						
Outside	#12 cal can	6 3/4"	11 1/8"	398.10	6524	6.52E-03	
	#12 cal can w/handle		12 1/8"				
	overpack - TBD						
Special APAS - (82.24 g / 17.55 Ci)							
Inside	Pu volume				18.28	1.83E-05	
	welded thin-walled stainless can	~ 2 5/8"	~6"	32.47	532	5.32E-04	
	void fraction (1 - Pu / SS can vol.)						0.966
	void volume						
Outside	$2R_i$	4 3/4"	11 3/4"	208.22	3412	3.41E-03	
	void volume						
	2R (6M)	5.25" ID	16.5" inside	357.18	5853	5.85E-03	
	void fraction (1 - Pu / 2R vol.)						0.997
	void fraction (1 - Pu+$2R_i$+SS / 2R vol.)						
Food pack cans are crimp sealed.							
Grams and curies are slightly higher than the numbers from the Mound accountability data due to rounding.							

Attachment 3

A Simplified Methodology for Estimating the Hydrogen Concentration and Pressure Buildup Within a 2R Container

Lawrence C. Sanchez
Cathy A. Ottinger
Gary F. Polansky

Note: This attachment of the original memo became the main portion of this SAND report and is not printed here.

9.7. Appendix G -- Computer Code Used in MNOP Calculations

This appendix contains an ANSI standard FORTRAN77 computer code written to analyze the pressure buildup within a seal container due to radiolysis of plutonium oxides.

Table G-1. Listing of Computer Code GASGEN (Version 1.05). (Selected Results From This Code Are Presented in Appendix H)

```
C23456789012345678901234567890123456789012345678901234567890123456789012NISS0001
C        1         2         3         4         5         6         7  NISS0002
C                                                                       NISS0003
C     GGGGGG       AAAA       SSSSSS     GGGGGG     EEEEE    NN    NN   NISS0004
C    GG    GG     AA  AA     SS    SS   GG    GG    EE       NN    NN   NISS0005
C   GG           AA    AA    SSS       GG           EE       NNN   NN   NISS0006
C   GG   GGGG    AAAAAAAA     SSSS     GG   GGGG    EEEEE    NN N  NN   NISS0007
C   GG     GG    AA    AA         SS   GG     GG    EE       NN  N NN   NISS0008
C    GG    GG    AA    AA   SS   SSS    GG    GG    EE       NN   NNN   NISS0009
C     GGGGGG     AA    AA    SSSSSS      GGGGGG     EEEEE    NN    NN   NISS0010
C                                                                       NISS0011
C   A GAS GENERATION/MOLE BALANCE SET OF CALCULATIONS  FOR DETERMINING  NISS0012
C   THE "MAXIMUM NORMAL OPERATING PRESSURE" (MNOP) VALUES FOR UNVENTED  NISS0013
C   SHIPPING CASKS/CONTAINERS.  GAS PRESSURE  BUILDUP IS  DUE TO ALPHA  NISS0014
C   RADIOLYSIS OF PLUTONIUM-OXIDE (WASTE MATRIX MATERIAL).              NISS0015
C                                                                       NISS0016
C      _/_/_/  _/    _/  _/                                      _/_/_/ NISS0017
C    _/       _/_/  _/  _/   SANDIA NATIONAL LABORATORIES        _/_/   NISS0018
C   _/_/_/   _/ _/ _/  _/   NUCLEAR WASTE MANAGEMENT CENTER _/_/_/_/_/_/NISS0019
C        /  _/  _/_/  _/                                   _/  _/_/  _/ NISS0020
C _/_/_/   _/    _/  _/_/_/_/                             _/  _/_/  _/  NISS0021
C                                                           _/_/_/      NISS0022
C                  *************************                           NISS0023
C                  *       ISSUED BY       *                           NISS0024
C                  *  SANDIA LABORATORIES, *                           NISS0025
C                  *   A PRIME CONTRACTOR  *                           NISS0026
C                  ********     TO THE     *                           NISS0027
C                         *  UNITED STATES *                           NISS0028
C                         *   DEPARTMENT   *                           NISS0029
C                         *       OF       *                           NISS0030
C                         *     ENERGY     *                           NISS0031
C      *********************  ---NOTICE---  *********************       NISS0032
C      *THIS REPORT WAS PREPARED AS AN ACCOUNT OF WORK SPONSORED*       NISS0033
C      *  BY THE UNITED STATES GOVERNMENT.  NEITHER THE UNITED  *       NISS0034
C      *   STATES NOR THE UNITED STATES DEPARTMENT OF ENERGY,   *       NISS0035
C      *               NOR ANY OF THEIR EMPLOYEES,              *       NISS0036
C      * NOR ANY OF THEIR CONTRACTORS, SUBCONTRACTORS, OR THEIR *       NISS0037
C      * EMPLOYEES, MAKES ANY WARRANTY, EXPRESS OR IMPLIED, OR  *       NISS0038
C      * ASSUMES ANY LEGAL LIABILITY OR RESPONSIBILITY FOR THE  *       NISS0039
C      *          **********    ACCURACY,   **********          *       NISS0040
C      *          *        *  COMPLETENESS  *        *          *       NISS0041
C      *          *        *  OR USEFULNESS *        *          *       NISS0042
C      *          *        *     OF ANY     *        *          *       NISS0043
C      *          *        *  INFORMATION,  *        *          *       NISS0044
C      *          *        *   APPARATUS,   *        *          *       NISS0045
C      *       ****        *     PRODUCT    *        ****       *       NISS0046
C      *       *           *   OR PROCESS   *           *       *       NISS0047
C      *       *           *   DISCLOSED,   *           *       *       NISS0048
C      *       *           *  OR REPRESENTS *           *       *       NISS0049
C      *       *          **    THAT ITS    **          *       *       NISS0050
C      *       *          **  USE WOULD NOT **          *       *       NISS0051
C      *********          **    INFRINGE    **          *********       NISS0052
C                         **    PRIVATELY   **                          NISS0053
C                         **      OWNED     **                          NISS0054
C                         **     RIGHTS.    **                          NISS0055
C                         **                **                          NISS0056
C                         **                **                          NISS0057
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C                         **                 **
C                         *******************
C
C
C
C2345678901234567890123456789012345678901234567890123456789012345678901
C        1         2         3         4         5         6         7
C
C
C ********************************************************************
C ********************************************************************
C ******************* M O D U L E   G A S G E N *********************
C ********************************************************************
C ********************************************************************
C
C2345678901234567890123456789012345678901234567890123456789012345678901
C        1         2         3         4         5         6         7
C
C   PROGRAM : GASGEN.FOR     VERSION : 1.05        TYPE  : F77
C   SYSTEM  : Independent    DATE    : SEPT, 2000   CLASS : UNCLASSIFIED
C   PROGRAMMER : L.C.SANCHEZ (SNL Org-6849)
C
C   +-----------------------------------------------------------------+
C   |                                                                 |
C   |              C O D E  -  G A S G E N . F O R                    |
C   |                                                                 |
C   |                  LAWRENCE C. SANCHEZ                            |
C   |                                                                 |
C   |                                                                 |
C   |                    D I S C L A I M E R                          |
C   |                    - - - - - - - - - -                          |
C   |                                                                 |
C   |   THIS COMPUTER  PROGRAM WAS  PREPARED AS AN  ACCOUNT OF  WORK   |
C   |   SPONSORED  BY AN  AGENCY OF THE  UNITED  STATES  GOVERNMENT.   |
C   |   NEITHER THE UNITED STATES GOVERNMENT NOR ANY AGENCY THEREOF,   |
C   |   NOR ANY  OF THEIR EMPLOYEES,  NOR ANY OF THEIR  CONTRACTORS,   |
C   |   SUBCONTRACTORS,  OR  THEIR  EMPLOYEES,  MAKES ANY  WARRANTY,   |
C   |   EXPRESS  OR  IMPLIED,  OR  ASSUMES ANY  LEGAL  LIABILITY  OR   |
C   |   RESPONSIBILITY   FOR   THE   ACCURACY,   COMPLETENESS,   OR    |
C   |   USEFULNESS  OF  ANY  INFORMATION,   APPARATUS,  PRODUCT,  OR   |
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C   |   NAME,  TRADEMARK,  MANUFACTURER,   OR  OTHERWISE,  DOES  NOT   |
C   |   NECESSARILY   CONSTITUTE   OR   IMPLY   ITS   ENDORSEMENT,     |
C   |   RECOMMENDATION,  FAVORING BY  THE  UNITED STATES GOVERNMENT,   |
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C   |   GOVERNMENT,  ANY  AGENCY THEREOF OR ANY OF THEIR CONTRACTORS   |
C   |   OR SUBCONTRACTORS.                                            |
C   |                                                                 |
C   |                                                                 |
C   |   GASGEN.FOR  IS A  F77 COMPUTER PROGRAM  FOR DETERMINING  THE   |
C   |   GAS PRESSURE BUILDUP  WITHIN AN  UNVENTED CASK/CONTAINER DUE   |
C   |   TO  ALPHA RADIOLYSIS OF HOST MATRIX MATERIAL. THIS CODE USES   |
C   |   THE  GAS MOLE BALANCE METHOD  TO PERFORM THE "MNOP" CALCULA-   |
C   |   TIONS.  THIS CODE IS CURRENTLY  CONFIGURED FOR  ALPHA RADIO-   |
C   |   LYSIS OF  WATER/MOISTURE SORBED ON THE  SURFACE OF PLUTONIUM   |
C   |   OXIDE.  (THE  CODE CAN BE  USED FOR  OTHER HOST  MATRICES BY   |
C   |   SIMPLY CHANGING THE G-VALUES TO NEW VALUES FOR THE NEXT MAT-   |
C   |   ERIAL  UNDER CONSIDERATION).  THE CODE IS  SETUP TO  PERFORM   |
C   |   THESE CALCULATIONS FOR  A WIDE VARIATION  IN GAS  GENERATION   |
C   |   RATES AND TEMPERATURES. THE VALUES  OF THE  ABOVE PARAMETERS   |
C   |   ARE  HARD CODED BELOW  WITHIN THE CODE. THE  OUTPUT FROM THE   |
C   |   CODE ARE PRESENTED IN FOLLOWING FILES:                        |
C   |                                                                 |
C   |   OUTPUT DATA FILES  : CONTENTS                                 |
C   |   ----------------------------------------------------------    |
C   |   1)  Table1.dat  :  SPECIFIC THERMAL POWER FOR RADIONUCIDES    |
C   |   2)  Table2.dat  :  ALPHA RADIOLYSIS GAS GENERATION RATE       |
```

```
C   |   3)  Table3.dat  :  Sherman-1999 ISOTOPIC PROPERTIES             |
C   |   4)  Table4.dat  :  Sherman-1999 PuO2 (Mixture) PROPERTIES       |
C   |   5)  Table5.dat  :  Sherman-1999 PuO2 GAS GENERATION RATES       |
C   |   6)  Table6.dat  :  Sherman-1999 PuO2 G-VALUES                   |
C   |   7)  Table7.dat  :  TIME TO REACH 5% H2 CONCENTRATION AND TIME   |
C   |                   :  TO REACH MNOP LIMIT (212.5 PSIG)             |
C   |   8)  Table8.dat  :  TIME TO REACH 5% H2 CONCENTRATION vs. GAS    |
C   |                   :  GENERATION RATE                              |
C   |   9)  Table9.dat  :  TIME TO REACH MNOP LIMIT (212.5 PSIG)  vs.   |
C   |                   :  GAS GENERATION RATE                          |
C   |   10) HXratio.dat :  MODERATOR-TO-FISSILE ATOM RATIO AS A         |
C   |                   :  FUNCTION OF W% MOISTURE                      |
C   |   11) Fig1.dat    :  H2 CONCENTRATION vs. TIME (5wt% MOISTURE)    |
C   |   12) Fig2.dat    :  PRESSURE (MNOP) vs. TIME (5wt% MOISTURE)     |
C   |   13) Fig3.dat    :  H2 CONCENT vs. TIME (2.8wt% MOISTURE)        |
C   |   14) Fig4.dat    :  PRESSURE (MNOP) vs. TIME (2.8wt% MOISTURE)   |
C   |   15) Fig5.dat    :  H2 CONCENT vs. TIME (0.752wt% MOISTURE)      |
C   |   16) Fig6.dat    :  PRESSURE (MNOP) vs. TIME (0.752wt% MOISTURE) |
C   |                                                                   |
C   +-------------------------------------------------------------------+
C
C23456789012345678901234567890123456789012345678901234567890123456789012
C       1         2         3         4         5         6         7
C
C
C-----M A I N----P R O G R A M-----------------------------------------+
C
      PROGRAM MAIN       ! ALL ANALYSES IS PERFORMED AT SUBROUTINE LEVEL
C
      CALL DRIVER
C
      STOP
      END
C---------------------------------------------------------------------+
C
C**********************************************************************
C
C                                                            **********
C                                                            * DRIVER *
C                                                            **********
      SUBROUTINE DRIVER
      implicit double precision (a-h,o-z)
      common/blk000/Version
      Version = 1.05
C
      Call Table1    ! Generate Table  #1 data     (in File: Table1.dat)
      Call Table2    ! Generate Table  #2 data     (in File: Table2.dat)
      Call Table3    ! Generate Table  #3 data     (in File: Table3.dat)
      Call Table4    ! Generate Table  #4 data     (in File: Table4.dat)
      Call Table5    ! Generate Table  #5 data     (in File: Table5.dat)
      Call Table6    ! Generate Table  #6 data     (in File: Table6.dat)
      Call Table789  ! Generate Tables #7,8,9      (in File: Table7.dat)
C              |                            (Table8.dat, Table9.dat)
      Call Fig5678   ! Generate Figs #5,6,7,8 data  (in Files: Fig5.dat)
C              !                      (Fig6.dat, Fig7.dat, Fig8.dat)
      Call HXratio   ! Generate H/X Ratio values   (in File:HXratio.dat)
C
      STOP
      END
C                                                         *************
C                                                         * Table 789 *
C                                                         *************
      SUBROUTINE TABLE789
      implicit double precision (a-h,o-z)
      dimension  time_5h(5) , time_212_press(5)
      common/blk000/Version
      common/blk010/V2r,eps_ave,R_const              ! Var Common Block
c
      iflagd = 0
c
c
```

```
      T0        =  20.0d+00 + 273.15d+00
c                         ! Initial temperature of containers    [K]
      P0        = 1.0d+00     ! Initial pressure in containers     [atm]
      h2conc_t0 = 0.00d+00    ! Initial H2 concentration in containers
      V2r       = 5853.0d+00  ! Internal volume of 2R container   [cm^3]
      V2r       = V2r/1.0d+06 !                                    [m^3]
      Vic       = 400.0d+00   ! Internal volume of inner container[cm^3]
      Vic       = Vic/1.0d+06 !                                    [m^3]
      eps2r     = 0.75d+00    ! Void fraction of 2r container [no dimen]
      epsic     = 0.50d+00    ! Void fraction of inner container   [ " ]
      eps_ave   = eps2r+epsic*(Vic/V2r)  ! Average void fraction   [ " ]
      R_const   = 82.057D-06  ! Universal gas constant  [m^3-atm/mole-K]
c
      write(6,'(//,''  Code: GasGen    Version:'',f5.2)')  Version
      write(6,9111)
 9111 format(///,t3,65('-'))
      write(6,9112) T0,P0,h2conc_t0V2r,V2r*1.0d6,Vic,Vic*1.0d6,
     +  eps2r,epsic,eps_ave,R_const
 9112 format(
     +  t3,'INITIAL  INPUT  PARAMETERS   (Benchmark Calculations',
     +/,t5,'T0       = ',f6.1,' Initial temperature of containers  [K]',
     +/,t5,'P0       = ',f6.1,' Initial pressure in containers   [atm]',
     +/,t5,'H2conc_t0= ',f6.4,' Initial H2 conc in containers    [atm]',
     +/,t5,'V2r      = ',f6.5,' Internal volume of 2R container  [m^3]',
     +/,t5,'V2r      = ',f6.1,'                                 [cm^3]',
     +/,t5,'Vic      = ',f6.5,' Internal volume of inner containr[m^3]',
     +/,t5,'Vic      = ',f6.2,'                                 [cm^3]',
     +/,t5,'eps2r    = ',f6.3,' Void fraction of 2r container [no dim]',
     +/,t5,'epsic    = ',f6.3,' Void fraction of inner container [ " ]',
     +/,t5,'eps_ave  = ',f6.3,' Average void fraction            [ " ]',
     +/,t5,'R_const  = ',1p1d10.3,
     +                    ' Universal gas constant    [m^3-atm/mole-K]')
      write(6,9113)
 9113 format(t3,65('-'),//)
c
c     SOLVE PROBLEM IN MKS units!!!
c
      Gtot = 0.25d+00 ! G-value gas constant [molecules/100eV deposited]
      Gh2  = Gtot/2.0d+00   ! G-value for H2 [molecules/100eV deposited]
      Ci   = 1.00d+00       ! Total alpha alpha activity  [Ci]
      h2conc_t0 = 0.00d+00  ! Initial H2 concentration in containers
c
      write(6,9211)
 9211 format(///,t3,65('-'))
      write(6,9212) Gtot,Gh2,Ci,h2conc_t0
 9212 format(
     +   t3,'VARYING  INPUT  PARAMETERS',
     + /,t5,'Gtot  = ',f5.3,' G-value gas constant ',
     +                                  '[molecules/100eV deposited]',
     + /,t5,'Gh2   = ',f5.3,' G-value for H2 ',
     +                                  '[molecules/100eV deposited]',
     + /,t5,'Ci    = ',f5.2,' Total alpha alpha activity ',
     +                                  ' [Ci]',
     + /,t5,'h2conc_t0 = ',f5.3,' Initial H2 concentration in ',
     +                                  ' containers')
      write(6,9213)
 9213 format(t3,65('-'),//)
c
c
      do 1000 time = 0.0d0 , 100.0d0 , 1.0d0             ! Time  [days]
          g_total = 0.099d+00*Gtot*Ci  ! Total gas generation [moles/yr]
          time_yr = time / 365.25d+00
          xn_gas  = (P0 * eps_ave * V2r)/(R_const*T0) + g_total*time_yr
          TEMP    = T0
          PRESS   = xn_gas*R_const*TEMP/(eps_ave*V2r)
          write(6,9000) time,xn_gas,PRESS
 9000     format(t5,'Time =',1p1d10.3,' [days]',t30,'N_gas =',1p1d10.3,
     +    ' [moles]',t58,'Pres ='1p1d10.3,' [atm]')
 1000 continue

c
```

```fortran
c
      Gh2 = Gtot/2.0d+00    ! G-value for H2 [molecules/100eV deposited]
      time_5per = ( (0.05d+00 - h2conc_t0)*((P0*eps_ave*
     +            V2r)/(R_const*T0))) /(0.10d+00*Ci*
     +            (Gh2 - 0.05d+00*Gtot) )
      write(6,9100) time_5per,(time_5per*365.25d+00)
 9100 format(//,t5,'Time to reach 5% H2 concentration =',1p1d10.3,
     +' [yr]  = ',1p1d10.3,'[days]')
c
      T_final   = 121.1d+00 + 273.15d+00
      time_212p = (212.5d+00/(14.7d+00*P0)) /
     +            (0.10d+00*Gtot*Ci *
     *            (R_const*T_final)/(voidfr*V2r))
      write(6,9101) time_212p,(time_5per*365.25d+00)
 9101 format(//,t5,'Time to reach 212.1 PSIG =',1p1d10.3,
     +' [yr]  = ',1p1d10.3,'[days]')
c
c
c
      T_final = 121.1d+00 + 273.15d+00
c
      open(17,file='Table7.dat',status='unknown')
      write(17,'(//,''  Code: GasGen    Version:'',f5.2)')  Version
      write(17,9102)
 9102 format(
     + //,1x,'TABLE #7',
     +  /,t3,65('-'))
      write(17,9103) T0,T_final,P0,h2conc_t0,V2r,V2r*1.0d6,Vic,
     +  Vic*1.0d6,eps2r,epsic,eps_ave,R_const
 9103 format(
     +  t3,'INITIAL  INPUT  PARAMETERS',
     +/,t5,'T0       = ',f6.1,' Initial temperature of containers  [K]',
     +/,t5,'T_Final  = ',f6.1,' Initial temperature of containers  [K]',
     +/,t5,'P0       = ',f6.1,' Initial pressure in containers   [atm]',
     +/,t5,'H2conc_t0= ',f6.4,' Initial H2 conc in containers    [atm]',
     +/,t5,'V2r      = ',f6.5,' Internal volume of 2R container  [m^3]',
     +/,t5,'V2r      = ',f6.1,'                                 [cm^3]',
     +/,t5,'Vic      = ',f6.5,' Internal volume of inner containr[m^3]',
     +/,t5,'Vic      = ',f6.2,'                                 [cm^3]',
     +/,t5,'eps2r    = ',f6.3,' Void fraction of 2r containr[no dimen]',
     +/,t5,'epsic    = ',f6.3,' Void fraction of inner container [ " ]',
     +/,t5,'eps_ave  = ',f6.3,' Average void fraction            [ " ]',
     +/,t5,'R_const  = ',1p1d10.3,
     +' Universal gas constant    [m^3-atm/mole-K]')
      write(17,9104)
 9104 format(t3,65('-'),//)
c
      write(17,9650)
 9650 format(
     + //,1x,71('-'),
     +  /,t2,'Activity',t12,'Void',t19,'G(H2)',t29,'G(total)',
     +   t39,'g_total',t51,'t(5%)',t60,'t(212.5 psig)',
     +  /,           t12,'Fraction', t51,t62,'at 121 C'
     +  /,t2,'(Ci/pack)',
     +   t39,'(mole/yr)',t51,'(yrs)',t62,'(yrs)',
     +  /,1x,71('-') )
      do 5000 curies = 2.5d0 , 20.00001d0 , 2.5d0
          do 4000 voidfr = 0.50d0 , 0.90001d0 , 0.10d0
              do 3000 iGtot = 1 , 5 , 1
                  if(iGtot.eq.1)  Gtot = 1.0d-05
                  if(iGtot.eq.2)  Gtot = 1.0d-04
                  if(iGtot.eq.3)  Gtot = 1.0d-03
                  if(iGtot.eq.4)  Gtot = 1.0d-02
                  if(iGtot.eq.5)  Gtot = 1.0d-01
                  do 2000 igh2 = 1 , 2 , 1
                      if(igh2.eq.1)  Gh2 = Gtot/2.0d0
                      if(igh2.eq.2)  Gh2 = Gtot
                      gas_gener = 0.099d0 * Gtot * curies
                      time_5per = ( (0.05d+00 - h2conc_t0)*((P0*voidfr*
     +                            V2r)/(R_const*T0))) /(0.10d+00*curies*
     +                            (Gh2 - 0.05d+00*Gtot) )
```

```
          if(iflagd.ge.1)  then          ! Diagnostics Write Statement
                      term1 = ( (0.05d+00 - h2conc_t0)*((P0*voidfr*
     +                            V2r)/(R_const*T0)))
                      term2 = (0.10d+00*curies*
     +                            (Gh2 - 0.05d+00*Gtot) )
                      write(17,9301)  h2conc_t0,t0,P0,voidfr,V2r,
     +                                  R_const,curies,Gh2,Gtot,term1,term2
 9301                 format(
     +                /,t7,'h2conc_t0      = ',1p1e14.7 ,
     +                /,t7,'t0             = ',1p1e14.7 ,
     +                /,t7,'P0             = ',1p1e14.7 ,
     +                /,t7,'voidfr         = ',1p1e14.7 ,
     +                /,t7,'V2r            = ',1p1e14.7 ,
     +                /,t7,'R_const        = ',1p1e14.7 ,
     +                /,t7,'curies         = ',1p1e14.7 ,
     +                /,t7,'Gh2            = ',1p1e14.7 ,
     +                /,t7,'Gtot           = ',1p1e14.7 ,
     +                /,t7,'term #1        = ',1p1e14.7 ,
     +                /,t7,'term #2        = ',1p1e14.7 )
          endif
                      time_212p = (212.5d+00/14.7d+00) /
     +                            ( 0.10d+00*Gtot*curies *
     +                                  (R_const*T_final)/(voidfr*V2r) )
                      if(igh2.eq.1.and.iGtot.eq.1)  then
                        write(17,9660) curies , voidfr , Gh2 , Gtot ,
     +                              gas_gener , time_5per , time_212p
 9660                   format(t4,0p1f4.1,t12,0p1f4.2,t19,1p1e8.2,t29,
     +                         1p1e8.2,t39,1p1e8.2,t51,1p1e8.2,t62,
     +                         1p1e8.2)
                       else
                        write(17,9665)                   Gh2 , Gtot ,
     +                              gas_gener , time_5per , time_212p
 9665                   format(            t19,1p1e8.2,t29,1p1e8.2,
     +                         t39,1p1e8.2,t51,1p1e8.2,t62,1p1e8.2)
                      endif
 2000             continue
 3000         continue
 4000     continue
 5000 continue
      write(17,9670)
 9670 format(1x,71('-') )
      close(17)
c
c
      open(18,file='Table8.dat',status='unknown')
c
      do 7000 gas_gen_rate = 0.0d0 , 0.500010d0 , 0.0010d0
          do 6000 j_gh_gtot_ratio = 1 , 5 , 1
            if(gas_gen_rate.eq.0.0d0)  then
              gh_gtot_ratio = dfloat(j_gh_gtot_ratio) / 5.0d0
              time_5h(j_gh_gtot_ratio) =
     +        ( (0.05d+00 - h2conc_t0)*((P0*voidfr*V2r)/(R_const*T0))) /
     +                      ( (gh_gtot_ratio - 0.05d+00)*0.00010d0 )
             else
              gh_gtot_ratio = dfloat(j_gh_gtot_ratio) / 5.0d0
              time_5h(j_gh_gtot_ratio) =
     +        ( (0.05d+00 - h2conc_t0)*((P0*voidfr*V2r)/(R_const*T0))) /
     +                      ( (gh_gtot_ratio - 0.05d+00)*gas_gen_rate )
            endif
 6000     continue
          if(gas_gen_rate.eq.0.0d0)  then
              write(18,9801)  0.00010d0 , (time_5h(i),i=1,5)
 9801         format(6(3x,1p1e10.3))
            else
              write(18,9801)  gas_gen_rate , (time_5h(i),i=1,5)
          endif
 7000 continue
      close(18)
c
c
      open(19,file='Table9.dat',status='unknown')
```

```
c
      do 8500 gas_gen_rate = 0.0d0 , 0.500010d0 , 0.0010d0
          do 8000 j_temp_final = 1 , 5 , 1
            if(j_temp_final.eq.1)  temp_c =  20.0d+00
            if(j_temp_final.eq.2)  temp_c =  50.0d+00
            if(j_temp_final.eq.3)  temp_c =  75.0d+00
            if(j_temp_final.eq.4)  temp_c = 100.0d+00
            if(j_temp_final.eq.5)  temp_c = 121.1d+00
            T_final = temp_c + 273.15d+00     ! Temperature in [deg K]
            if(gas_gen_rate.eq.0.0d0)  then
                time_212_press(j_temp_final) = (212.5d+00/14.7d+00) /
     +                    ( 0.00010d0 * (R_const*T_final)/(voidfr*V2r) )
             else
                time_212_press(j_temp_final) = (212.5d+00/14.7d+00) /
     +                 ( gas_gen_rate * (R_const*T_final)/(voidfr*V2r) )
            endif
 8000     continue
          if(iflagd.ge.1)  then          ! Diagnostics Write Statement
                      write(19,9302)  voidfr,V2r,
     +                               R_const,T_final,gas_gen_rate
 9302                 format(
     +                /,t7,'voidfr         = ',1p1e14.7 ,
     +                /,t7,'V2r            = ',1p1e14.7 ,
     +                /,t7,'R_const        = ',1p1e14.7 ,
     +                /,t7,'T_final        = ',1p1e14.7 ,
     +                /,t7,'gas_gen_rate   = ',1p1e14.7 )
          endif
          if(gas_gen_rate.eq.0.0d0)  then
              write(19,9801)  0.00010d0    , (time_212_press(i),i=1,5)
            else
              write(19,9801)  gas_gen_rate , (time_212_press(i),i=1,5)
          endif
 8500 continue
      close(19)
c
c
 9999 return
      end
c                                                          ***********
c                                                          * HXRATIO *
c                                                          ***********
      subroutine hxratio
c     This  subroutine is used to  generate data for  a figure that will
c     present the  H/X (moderator-to-fissile atom ratio)  as a function
c     of the  weight percent of  absorbed  water within plutonium  oxide
c     (i.e., PuO2-xH2O).  This subroutine will  write-out the  data into
c     an ASCII text file named: "HXratio.dat".
c
      implicit double precision (a-h,o-z)
      common/blk000/Version
c
      open(11,file='HXratio.dat',status='unknown')    ! Open output file
c
      atwt_h2o = 2.0d0*(1.00794d0) + 15.9994d0        ! Atomic wt of H2O
      atwt_puo2 = 239.052156d0 + 2.0d0*(15.9994d0)    ! Atomc wt if PuO2
      const1 = 2.0d0 * atwt_puo2 / atwt_h2o           ! Constant #1
c
      write(11,'(//,''  Code: GasGen    Version:'',f5.2)')  Version
      write(11,9000)
 9000 format('H/X  Ratio as a Function of w% Moisture',t56,'Title',
     +     /,'Wt% Moisture',t56,'X-title',
     +     /,'H/X  Ration',t56,'Y-title',
     +     /,' 0 0 0',t56,'Plot code')
      do 1000 h2o_wtper = 0.0d0 , 10.00001d0 , 0.1d0  ! Wt% H2o in PuO2
          hx_ratio = const1 * h2o_wtper / (100.0d0 - h2o_wtper)  ! Ratio
          write(11,9100) h2o_wtper , hx_ratio         ! Write output
 9100     format(2(4x,1p1e14.7))
 1000 continue
c
c
      close(11)                                      ! Close output file
```

```
c                                                                       NISS0484
c                                                                       NISS0485
 9999 return                                                            NISS0486
      end                                                               NISS0487
c                                                            ***********NISS0488
c                                                            * Table 1 *NISS0489
c                                                            ***********NISS0490
      subroutine table1                                                 NISS0491
c     This subroutine is used to generate data for Table #1.  This tableNISS0492
c     identifies the  specific activity  and  specific thermal power forNISS0493
c     several  key radionuclides.  This  subroutine  will  write-out theNISS0494
c     data into an ASCII text file named: "Table1.dat".                 NISS0495
c                                                                       NISS0496
      parameter (idim=6)                              ! Default dimensionNISS0497
      implicit double precision (a-h,o-z)                               NISS0498
      character*5  cnucli(idim)                                         NISS0499
      dimension  tauhaf(idim)     , atwt(idim)      , energy(idim) ,    NISS0500
     +           spec_activi(idim), spec_power(idim)                    NISS0501
c                                                                       NISS0502
      common/blk000/Version                                             NISS0503
      common/blk001/cnucli                        ! Character Common BlockNISS0504
      common/blk002/atwt,energy                     ! Array Common BlockNISS0505
      common/blk003/xna,conver1,conver2,conver3,conver4!Var Common BlockNISS0506
      common/blk004/spec_activi,spec_power          ! Array Common BlockNISS0507
c                                                                       NISS0508
c                                                                       NISS0509
      cnucli(1) = 'Pu238'                             ! Nuclide: Pu-238 NISS0510
      cnucli(2) = 'Pu239'                             ! Nuclide: Pu-239 NISS0511
      cnucli(3) = 'Pu240'                             ! Nuclide: Pu-240 NISS0512
      cnucli(4) = 'Pu241'                             ! Nuclide: Pu-241 NISS0513
      cnucli(5) = 'Pu242'                             ! Nuclide: Pu-242 NISS0514
      cnucli(6) = 'Am241'                             ! Nuclide: Am-241 NISS0515
c                                                                       NISS0516
      tauhaf(1) = 87.7d+00                            ! Halflife: Pu-238NISS0517
      tauhaf(2) = 2.410d+04                           ! Halflife: Pu-239NISS0518
      tauhaf(3) = 6.56d+03                            ! Halflife: Pu-240NISS0519
      tauhaf(4) = 14.4d+00                            ! Halflife: Pu-241NISS0520
      tauhaf(5) = 3.75d+05                            ! Halflife: Pu-242NISS0521
      tauhaf(6) = 432.7d+00                           ! Halflife: Am-241NISS0522
c                                                                       NISS0523
      atwt(1) = 238.049553d+00                   ! Atomic Weight: Pu-238NISS0524
      atwt(2) = 239.052156d+00                   ! Atomic Weight: Pu-239NISS0525
      atwt(3) = 240.053808d+00                   ! Atomic Weight: Pu-240NISS0526
      atwt(4) = 241.05684d+00    ! (Using E.021)   Atomic Weight: Pu-241NISS0527
      atwt(5) = 242.058737d+00                   ! Atomic Weight: Pu-242NISS0528
      atwt(6) = 241.056822d+00                   ! Atomic Weight: Am-241NISS0529
c                                                                       NISS0530
      energy(1) = 5.49921d+00              ! Alpha energy (MeV): Pu-238NISS0531
      energy(2) = 5.1554d+00               ! Alpha energy (MeV): Pu-239NISS0532
      energy(3) = 5.16830d+00              ! Alpha energy (MeV): Pu-240NISS0533
      energy(4) = 5.055d+00                ! Alpha energy (MeV): Pu-241NISS0534
      energy(5) = 4.9009d+00               ! Alpha energy (MeV): Pu-242NISS0535
      energy(6) = 5.48574d+00              ! Alpha energy (MeV): Am-241NISS0536
c                                                                       NISS0537
      xna = 6.0221367d+23         ! Avogadro's Number  (molecules/mole)NISS0538
      conver1 = 3.155693d+07      ! Conversion Factor  (yr -> sec)     NISS0539
      conver2 = 3.7d+10           ! Conversion Factor  (Ci -> bq)      NISS0540
      conver3 = 1.602177d-19      ! Conversion Factor  (eV -> J)       NISS0541
      conver4 = 1.0d+06           ! Conversion Factor  (eV -> MeV)     NISS0542
c                                                                       NISS0543
c                                                                       NISS0544
      open(11,file='Table1.dat',status='unknown')                       NISS0545
      write(11,'(//,''  Code: GasGen    Version:'',f5.2)')  Version     NISS0546
      write(11,9000)                                                    NISS0547
 9000 format(                                                           NISS0548
     + /,'    TABLE #1     Generic Radionuclide Information',           NISS0549
     + /,' +---------------------------------------------------------+',NISS0550
     + /,' | Nucl  | Tau 1/2  |  ATWT   | <E>  | Spec Act  |SpecPower|',NISS0551
     + /,' |  ID   | (yr)     |         | (MeV | (Ci/gm)   |(w/gm)   |',NISS0552
     + /,' +-------+----------+---------+------+-----------+---------+')NISS0553
cdata+ /,' | Pu238 | 1.23e+12 | 239.123 | 5.11 | 102.99123 | 3.08625 |  NISS0554
```

```
      do 1000 i = 1, idim          ! Number of Isotopies
          spec_activi(i) = (dlog(2.0d+00) * xna) / (tauhaf(i) * atwt(i)
     +                    * conver1 * conver2)
          spec_power(i) = spec_activi(i) * conver2 * energy(i) * conver3
     +                    * conver 4
          write(11,9100)  cnucli(i),tauhaf(i),atwt(i),energy(i),
     +                                     spec_activi(i),spec_power(i)
 9100     format(' | ',a5,' |',1p1e9.2,' |',0p1f8.3,' |',0p1f5.2,' |',
     +           0p1f10.5, ' |',0p1f8.5,' |')
 1000 continue
      write(11,9200)
 9200 format(
     +   ' +-------+---------+---------+------+----------+---------+')
c
c
      close(11)                                      ! Close output file
c
c
 9999 return
      end
c                                                          ***********
c                                                          * Table 2 *
c                                                          ***********
      subroutine table2
c     This subroutine is used to generate data for Table #2.  This table
c     identifies  the gas generation rate  due to alpha-radiolysis. This
c     subroutine will  write-out the data into an ASCII text file named:
c     "Table2.dat".
c
      parameter (idim=6)                             ! Default dimension
      implicit double precision (a-h,o-z)
      character*5  cnucli(idim)
      dimension  energy(idim),gas_gen(idim)
      dimension  atwt(idim)
c
      common/blk000/Version
      common/blk001/cnucli                      ! Character Common Block
      common/blk002/atwt,energy                     ! Array Common Block
      common/blk003/xna,conver1,conver2,conver3,conver4!Var Common Block
      common/blk007/gas_gen                         ! Array Common Block
c
c
      open(12,file='Table2.dat',status='unknown')
      write(12,'(//,''  Code: GasGen    Version:'',f5.2)')  Version
      write(12,9000)
 9000 format(
     + /,'    TABLE #2     Alpha Radiolysis Gas Generation Rate',
     + /,' +----------------------------------------------+',
     + /,' | Nucl  |  <E>     |  Gas Generation Rate       |',
     + /,' |  ID   | (MeV)    |   (mole/yr)                |',
     + /,' +-------+----------+---------------------------+')
cdata+ /,' | Pu238 | 5.49921  |  0.10662   x G x C         |
c
      conver5 = (1.0d0/100.0d0) * conver4 * conver2 * conver1 / xna
      do 1000 i = 1, idim          ! Number of Isotopies
          gas_gen(i) = conver5 * energy(i)
          write(12,9100)  cnucli(i),energy(i),gas_gen(i)
 9100     format(' | ',a5,' |',0p1f8.5,'  | ',0p1f8.5,'   x G x C     ',
     +           '    |')
 1000 continue
      write(12,9200)
 9200 format(
     +   ' +-------+----------+---------------------------+',
     + /,'    G is the G-value [#molecules/100 eV absorbed]',
     + /,'    C is the radioactivity  [Curies]'  )
c
c
      close(12)                                      ! Close output file
c
c
 9999 return
```

```fortran
      end
c                                                         ***********
c                                                         * Table 3 *
c                                                         ***********
      subroutine table3
c     This subroutine is used to generate data for Table #3.  This table
c     identifies  the weight fractions  for  isotopics given in the ref-
c     erence: Sherman 1999.
c
      parameter (idim=6)                           ! Default dimension
      implicit double precision (a-h,o-z)
      character*5  cnucli(idim)
      dimension sh_curie(idim) , sh_mass(idim)  , sh_wtper(idim) ,
     +          spec_activi(idim), spec_power(idim), sh_cuper(idim)
      dimension  atwt(idim)      , energy(idim)
c
      common/blk000/Version
      common/blk001/cnucli                     ! Character Common Block
      common/blk002/atwt,energy                    ! Array Common Block
      common/blk003/xna,conver1,conver2,conver3,conver4!Var Common Block
      common/blk004/spec_activi,spec_power         ! Array Common Block
      common/blk005/sh_wtper                       ! Array Common Block
      common/blk006/sh_curie_tot,sh_mass_tot         ! Var Common Block
      common/blk008/sh_curie,sh_cuper,sh_mass      ! Array Common Block
c
c
      open(13,file='Table3.dat',status='unknown')
      write(13,'(//,''  Code: GasGen    Version:'',f5.2)')  Version
      write(13,9000)
 9000 format(
     + /,'    TABLE #3     Data for Sherman-1999 Isotopics',
     + /,' +-------------------------------------------------------+',
     + /,' | Nucl  |         Curies          |   Mass   |   WT %   |',
     + /,' |  ID   |   (Ci)     (%)   (Ci/gm) |   (gm)   |          |',
     + /,' +-------+-------------------------+----------+----------+')
cdata+ /,' | Pu238 | 4.33E-01  90.12  17.124 | 2.53E-02 |  90.123  |',
c
      sh_curie(1) = 4.33d-01                          ! Nuclide: Pu-238
      sh_curie(2) = 2.90d+00                          ! Nuclide: Pu-239
      sh_curie(3) = 7.62d-01                          ! Nuclide: Pu-240
      sh_curie(4) = 5.10d+01                          ! Nuclide: Pu-241
      sh_curie(5) = 3.98d-04                          ! Nuclide: Pu-242
      sh_curie(6) = 9.02d-01                          ! Nuclide: Am-241
c
      sh_curie_tot = 0.0d+00
      sh_mass_tot  = 0.0d+00
      sh_cuper_tot = 0.0d+00
      do 1000 i = 1, idim
          sh_mass(i)   = sh_curie(i)  / spec_activi(i)
          sh_curie_tot = sh_curie_tot + sh_curie(i)
          sh_mass_tot  = sh_mass_tot  + sh_mass(i)
 1000 continue
c
      sh_wtper_tot = 0.0d+00
      do 2000 i = 1, idim
          sh_cuper(i) = 100.0d+00 * sh_curie(i) / sh_curie_tot
          sh_cuper_tot = sh_cuper_tot + sh_cuper(i)
          sh_wtper(i) = 100.0d+00 * sh_mass(i) / sh_mass_tot
          sh_wtper_tot = sh_wtper_tot + sh_wtper(i)
 2000 continue
c
      do 3000 i = 1, idim          ! Number of Isotopies
          write(13,9100)  cnucli(i) , sh_curie(i) , sh_cuper(i),
     +                    spec_activi(i), sh_mass(i) , sh_wtper(i)
 9100     format(' | ',a5,' |',1p1e9.2,0p1f7.2,0p1f8.3,' |',1p1e9.2,
     +           ' |',0p1f8.3,'  |')
 3000 continue
      write(13,9200)
 9200 format(
     +   ' +-------+-------------------------+----------+----------+',
     + /,'   Isotopic distribution from Sherman-1999' )
```

```
      write(13,9300)  sh_curie_tot , sh_mass_tot , sh_wtper_tot
 9300 format(t6,'Sum=',0p1f9.5,t31,'SUM=',1p1e11.4,3x,0p1f6.2)
c
c
      close(13)                                      ! Close output file
c
c
 9999 return
      end
c                                                            ***********
c                                                            * Table 4 *
c                                                            ***********
      subroutine table4
c     This subroutine is used to generate data for Table #4.  This table
c     identifies  the isotpoic  average  atomic mass  for the PU mixture
c     based on data from Reference: Sherman 1999.
c
      parameter (idim=6)                             ! Default dimension
      implicit double precision (a-h,o-z)
      character*5  cnucli(idim)
      dimension sh_curie(idim) , sh_mass(idim)  , sh_wtper(idim) ,
     +           spec_activi(idim), spec_power(idim)
      dimension  atwt(idim)      , energy(idim)
c
      common/blk000/Version
      common/blk001/cnucli                      ! Character Common Block
      common/blk002/atwt,energy                     ! Array Common Block
      common/blk003/xna,conver1,conver2,conver3,conver4!Var Common Block
      common/blk004/spec_activi,spec_power          ! Array Common Block
      common/blk005/sh_wtper                        ! Array Common Block
      common/blk006/sh_curie_tot,sh_mass_tot          ! Var Common Block
      common/blk009/sh_gas_gen_tot,sh_wt_ratio        ! Var Common Block
c
c
      open(14,file='Table4.dat',status='unknown')
      write(14,'(//,''  Code: GasGen    Version:'',f5.2)')  Version
      write(14,9000)
 9000 format(
     + /,'    TABLE #4     Data for Sherman-1999 Isotopics',
     + /,' +----------------------------------------------------+',
     + /,' |  Nucl   |     WT %     |   ATWT      | WT % / ATWT  |',
     + /,' |   ID    |     (Ci)     |             |              |',
     + /,' +---------+--------------+-------------+--------------+')
cdata+ /,' |  Pu238  |  4.96013E-02 |  238.05000  |  2.0800E-04  |',
c
      sh_wtatwt_tot = 0.0d+00
      do 1000 i = 1, idim
          sh_wtatwt_tot  = sh_wtatwt_tot  + sh_wtper(i)/atwt(i)
 1000 continue
c
      do 3000 i = 1, idim          ! Number of Isotopies
          write(14,9100)  cnucli(i) , sh_wtper(i) , atwt(i),
     +                    sh_wtper(i)/atwt(i)
 9100     format(' |  ',a5, '  | ',1p1e11.4,'  |  ',0p1f9.5,'  | ',
     +           1p1e11.4,'  |')
 3000 continue
      write(14,9200)
 9200 format(
     +   ' +---------+--------------+-------------+--------------+')
      write(14,9300)  sh_wtatwt_tot
 9300 format(t38,'SUM =',1p1e11.4,
     + /,'   Isotopic distribution from Sherman-1999',/ )
      write(14,9400) 100.0d+00 / sh_wtatwt_tot
 9400 format(t10,'Pu-mixture (SHERMAN-1999 isotopics)  ATWT =',1p1e11.4)
      write(14,9500) 100.0d+00 / sh_wtatwt_tot + 2.0d+00*15.9994d+00
 9500 format(t8,'PuO2-mixture (SHERMAN-1999 isotopics)  ATWT =',
     +       1p1e11.4)
      sh_wt_ratio = (100.0d+00 / sh_wtatwt_tot + 2.0d+00*15.9994d+00)
     +           / (100.0d+00 / sh_wtatwt_tot)
      write(14,9600)  sh_wt_ratio
 9600 format(t16,'PuO2-mixture/Pu  WT Ratio =',1p1e11.4)
```

```
      write(14,9700)  sh_curie_tot
 9700 format(/,t21,'PuO2 Isotopic Curies =',1p1e11.4)
      write(14,9800)  sh_mass_tot
 9800 format(t25,'Pu Isotopic Mass =',1p1e11.4)
      write(14,9850)  sh_mass_tot * sh_wt_ratio
 9850 format(t24,'PuO2 Mixture Mass =',1p1e11.4)
      write(14,9900)  sh_curie_tot / (sh_mass_tot * sh_wt_ratio)
 9900 format(t14,'PuO2 Isotopic Ci/Mass Ratio =',1p1e11.4)
c
c
      close(14)                                        ! Close output file
c
c
 9999 return
      end
c                                                                ***********
c                                                                * Table 5 *
c                                                                ***********
      subroutine table5
c     This subroutine is used to generate data for Table #5.  This table
c     identifies  the weight fractions  for  isotopics given in the ref-
c     erence: Sherman 1999.
c
      parameter (idim=6)                               ! Default dimension
      implicit double precision (a-h,o-z)
      character*5  cnucli(idim)
      dimension sh_curie(idim) , sh_mass(idim)  , sh_wtper(idim) ,
     +           spec_activi(idim), spec_power(idim), sh_cuper(idim)
      dimension  atwt(idim)      , energy(idim)
      dimension  gas_gen(idim)
c
      common/blk000/Version
      common/blk001/cnucli                         ! Character Common Block
      common/blk002/atwt,energy                        ! Array Common Block
      common/blk003/xna,conver1,conver2,conver3,conver4!Var Common Block
      common/blk004/spec_activi,spec_power             ! Array Common Block
      common/blk005/sh_wtper                           ! Array Common Block
      common/blk006/sh_curie_tot,sh_mass_tot             ! Var Common Block
      common/blk007/gas_gen                            ! Array Common Block
      common/blk008/sh_curie,sh_cuper,sh_mass          ! Array Common Block
      common/blk009/sh_gas_gen_tot,sh_wt_ratio           ! Var Common Block
c
c
      open(15,file='Table5.dat',status='unknown')
      write(15,'(//,''  Code: GasGen    Version:'',f5.2)')  Version
      write(15,9000)
 9000 format(
     + /,'    TABLE #5     Data for Sherman-1999 Isotopics',
     + /,' +-----------------------------------------------------------+',
     + /,' | Nucl  | Gas Gener  |  SHERMAN  Isotopics | Ci Frac * Gas|',
     + /,' |  ID   | Rate Const |   (Ci)       (Ci%)  |Gen Rate Const|',
     + /,' +-------+------------+--------------------+--------------+')
cdata+ /,' | Pu238 | 1.2345E-11 | 4.33E-01    90.123  | 4.96013E-02  |',
c
c
      sh_gas_gen_tot = 0.0d+00
      do 3000 i = 1, idim          ! Number of Isotopies
          sh_gas_gen_tot = sh_gas_gen_tot +
     +                                sh_cuper(i) * gas_gen(i)/100.0d+00
          write(15,9100)  cnucli(i) , gas_gen(i) , sh_curie(i) ,
     +                    sh_cuper(i) , sh_cuper(i) * gas_gen(i)/100.0d0
 9100    format(' | ',a5,' |',1p1e11.4,' |',1p1e9.2,'  ',0p1f9.5,' | ',
     +          1p1e11.4,'  |')
 3000 continue
      write(15,9200)
 9200 format(
     +   ' +-------+------------+--------------------+--------------+')
      write(15,9300)  sh_gas_gen_tot
 9300 format(t43,'SUM=',1p1e11.4,
     + /,'    Data for Sherman-1999 isotopics')
c
```

```
c                                                                       NISS0839
      close(15)                                     ! Close output fileNISS0840
c                                                                       NISS0841
c                                                                       NISS0842
 9999 return                                                            NISS0843
      end                                                               NISS0844
c                                                          ***********NISS0845
c                                                          * Table 6 *NISS0846
c                                                          ***********NISS0847
      subroutine table6                                                 NISS0848
c     This subroutine is used to generate data for Table #6.  This tableNISS0849
c     identifies  the weight fractions  for  isotopics given in the ref-NISS0850
c     erence: Sherman 1999.                                             NISS0851
c                                                                       NISS0852
      parameter (idim=6)                            ! Default dimensionNISS0853
      implicit double precision (a-h,o-z)                               NISS0854
      character*5  cnucli(idim)                                         NISS0855
      character*12  cname                                               NISS0856
      dimension sh_curie(idim) , sh_mass(idim)  , sh_wtper(idim) ,      NISS0857
     +           spec_activi(idim), spec_power(idim), sh_cuper(idim)    NISS0858
      dimension  atwt(idim)      , energy(idim)                         NISS0859
      dimension  gas_gen(idim)                                          NISS0860
c                                                                       NISS0861
      common/blk000/Version                                             NISS0862
      common/blk001/cnucli                      ! Character Common BlockNISS0863
      common/blk002/atwt,energy                     ! Array Common BlockNISS0864
      common/blk003/xna,conver1,conver2,conver3,conver4!Var Common BlockNISS0865
      common/blk004/spec_activi,spec_power          ! Array Common BlockNISS0866
      common/blk005/sh_wtper                        ! Array Common BlockNISS0867
      common/blk006/sh_curie_tot,sh_mass_tot          ! Var Common BlockNISS0868
      common/blk007/gas_gen                         ! Array Common BlockNISS0869
      common/blk008/sh_curie,sh_cuper,sh_mass       ! Array Common BlockNISS0870
      common/blk009/sh_gas_gen_tot,sh_wt_ratio        ! Var Common BlockNISS0871
      iflagd = 0                                                        NISS0872
c                                                                       NISS0873
c                                                                       NISS0874
      open(16,file='Table6.dat',status='unknown')                       NISS0875
      write(16,'(//,''  Code: GasGen    Version:'',f5.2)')  Version     NISS0876
      write(16,9000)                                                    NISS0877
 9000 format(                                                           NISS0878
     + /,'    TABLE #6     Data for Sherman-1999 Isotopics',            NISS0879
     + /,' +------------------------------------------------------+',NISS0880
     + /,' |    Case      | Gas Generation Rate/mass |  Calculated   |',NISS0881
     + /,' |     ID       | (mole/s-gm) (mole/yr-gm) |  G-value      |',NISS0882
     + /,' +--------------+--------------------------+---------------+')NISS0883
cdata+ /,' | SHERMAN-1999 | 1.12345e-12  1.12345e-12 |  1.12345e-12  |',NISS0884
c                                                                       NISS0885
c                                                                       NISS0886
      do 3000 i = 1, 5             ! Number of Cases                    NISS0887
          if(i.eq.1)  cname = 'SHERMAN-1999'                            NISS0888
          if(i.eq.2)  cname = 'SRS Case 1  '                            NISS0889
          if(i.eq.3)  cname = 'SRS Case 2  '                            NISS0890
          if(i.eq.4)  cname = 'SRS Case 3  '                            NISS0891
          if(i.eq.5)  cname = 'SRS Case 5  '                            NISS0892
          if(i.eq.1)  gas_rate = 1.043d-09 / 3600.0d+00                 NISS0893
          if(i.eq.2)  gas_rate = 1.2d-11                                NISS0894
          if(i.eq.3)  gas_rate = 4.04d-11                               NISS0895
          if(i.eq.4)  gas_rate = 8.62d-13                               NISS0896
          if(i.eq.5)  gas_rate = 1.54d-11                               NISS0897
          G_value = gas_rate / (  sh_gas_gen_tot *                      NISS0898
     +               (sh_curie_tot / (sh_mass_tot * sh_wt_ratio))  )NISS0899
          G_value = G_value * 365.25d+00 * 24.0d+00 * 60.0d+00 * 60.0d+0NISS0900
          if(iflagd.ge.1)  then         ! Diagnostics Write Statement  NISS0901
              write(16,9101)  gas_rate , sh_gas_gen_tot ,               NISS0902
     +                        sh_curie_tot , sh_mass_tot ,              NISS0903
     +                        sh_wt_ratio                               NISS0904
 9101         format(                                                   NISS0905
     +        /,t7,'gas_rate       = ',1p1e14.7 ,                       NISS0906
     +        /,t7,'sh_gas_gen_tot = ',1p1e14.7 ,                       NISS0907
     +        /,t7,'sh_curie_tot   = ',1p1e14.7 ,                       NISS0908
     +        /,t7,'sh_mass_tot    = ',1p1e14.7 ,                       NISS0909
```

```
     +        /,t7,'sh_wt_ratio    = ',1p1e14.7 )
          endif
          write(16,9100)  cname , gas_rate ,
     +                    gas_rate*60.0d0*60.0d0*24.0d0*365.25d0,G_value
 9100     format(' | ',a12,' |',1p1e12.5,1x,1p1e12.5,' | ',1p1e12.5,
     +           '  |')
 3000 continue
      write(16,9200)
 9200 format(
     +   ' +-------------+-----------------------+--------------+',
     + /,'    NOTE:  Gas generation rates will decrease with time',
     + /,'           since activity decreases with time.',
     +//,'    G-value s in units of [#molecules/100 eV absorbed]')
c
c
      close(16)                                     ! Close output file
c
c
 9999 return
      end
c                                                       ************
c                                                       * Fig 5678 *
c                                                       ************
      subroutine fig5678
c     This subroutine is used to generate data for  Figures 5-4 and 5-5.
c     This table identifies  time dependence of the  hydrogen concentra-
c     tion and  total gas pressure buildup in an  unvented 2R container.
c
      parameter (idim=6)                            ! Default dimension
      implicit double precision (a-h,o-z)
      character*5  cnucli(idim)
      character*12  cname
      dimension sh_curie(idim) , sh_mass(idim)  , sh_wtper(idim) ,
     +          spec_activi(idim), spec_power(idim), sh_cuper(idim)
      dimension  atwt(idim)      , energy(idim)
      dimension  gas_gen(idim) , xMax_Moles_H2(idim) , Tot_Curies(idim)
      dimension  H2_Conc(idim) , xMNOP(idim) , tMax(idim)
c
      common/blk000/Version
      common/blk001/cnucli                      ! Character Common Block
      common/blk002/atwt,energy                     ! Array Common Block
      common/blk003/xna,conver1,conver2,conver3,conver4!Var Common Block
      common/blk004/spec_activi,spec_power          ! Array Common Block
      common/blk005/sh_wtper                        ! Array Common Block
      common/blk006/sh_curie_tot,sh_mass_tot          ! Var Common Block
      common/blk007/gas_gen                         ! Array Common Block
      common/blk008/sh_curie,sh_cuper,sh_mass       ! Array Common Block
      common/blk009/sh_gas_gen_tot,sh_wt_ratio        ! Var Common Block
      common/blk010/V2r,eps_ave,R_const               ! Var Common Block
      voidfr = eps_ave
      iflagd = 0
c
c
      open(21,file='Fig1.dat',status='unknown')
      open(22,file='Fig2.dat',status='unknown')
      open(23,file='Fig3.dat',status='unknown')
      open(24,file='Fig4.dat',status='unknown')
      open(25,file='Fig5.dat',status='unknown')
      open(26,file='Fig6.dat',status='unknown')
      write(21,'(//,''  Code: GasGen    Version:'',f5.2)')  Version
      write(21,9001)
 9001 format(
     + /,'    FIG #1     Data for Hydrogen Concentration vs. Time',
     + /,' +-------------------------------------------------------+',
     + /,' | Time|      Hydrogen Gas Concentration   (5wt% Moisture) |',
     + /,' | (yr)| (7A/7B)  (7C/7D/7E)  (7F)      (7G)     (7H)   APAS',
     + /,' +-----|---------|---------|---------|--------|--------|----')
cdata+ /,' 100.00 1.123e-12 1.123e-12 1.123e-12 1.23e-12 1.23e-12 1.23',
      write(22,'(//,''  Code: GasGen    Version:'',f5.2)')  Version
      write(22,9002)
 9002 format(
```

```
     + /,'    FIG #2     Data for Pressure (MNOP) vs. Time',            NISS0981
     + /,' +---------------------------------------------------------+',NISS0982
     + /,' | Time|        Pressure  (MNOP, <PSIG>)   (5wt% Moisture) |',NISS0983
     + /,' | (yr)| (7A/7B)  (7C/7D/7E)  (7F)      (7G)      (7H)   APAS',NISS0984
     + /,' +-----|---------|---------|---------|--------|--------|----')NISS0985
      write(23,'(//,''  Code: GasGen    Version:'',f5.2)')  Version     NISS0986
      write(23,9003)                                                    NISS0987
 9003 format(                                                           NISS0988
     + /,'    FIG #3     Data for Hydrogen Concentration vs. Time',     NISS0989
     + /,' +---------------------------------------------------------+',NISS0990
     + /,' | Time|      Hydrogen Gas Concentration (2.8wt% Moisture) |',NISS0991
     + /,' | (yr)| (7A/7B)  (7C/7D/7E)  (7F)      (7G)      (7H)   APAS',NISS0992
     + /,' +-----|---------|---------|---------|--------|--------|----')NISS0993
cdata+ /,' 100.00 1.123e-12 1.123e-12 1.123e-12 1.23e-12 1.23e-12 1.23',NISS0994
      write(24,'(//,''  Code: GasGen    Version:'',f5.2)')  Version     NISS0995
      write(24,9004)                                                    NISS0996
 9004 format(                                                           NISS0997
     + /,'    FIG #4     Data for Pressure (MNOP) vs. Time',            NISS0998
     + /,' +---------------------------------------------------------+',NISS0999
     + /,' | Time|        Pressure  (MNOP, <PSIG>) (2.8wt% Moisture) |',NISS1000
     + /,' | (yr)| (7A/7B)  (7C/7D/7E)  (7F)      (7G)      (7H)   APAS',NISS1001
     + /,' +-----|---------|---------|---------|--------|--------|----')NISS1002
      write(25,'(//,''  Code: GasGen    Version:'',f5.2)')  Version     NISS1003
      write(25,9003)                                                    NISS1004
 9005 format(                                                           NISS1005
     + /,'    FIG #5     Data for Hydrogen Concentration vs. Time',     NISS1006
     + /,' +---------------------------------------------------------+',NISS1007
     + /,' | Time|    Hydrogen Gas Concentration (0.752wt% Moisture) |',NISS1008
     + /,' | (yr)| (7A/7B)  (7C/7D/7E)  (7F)      (7G)      (7H)   APAS',NISS1009
     + /,' +-----|---------|---------|---------|--------|--------|----')NISS1010
cdata+ /,' 100.00 1.123e-12 1.123e-12 1.123e-12 1.23e-12 1.23e-12 1.23',NISS1011
      write(26,'(//,''  Code: GasGen    Version:'',f5.2)')  Version     NISS1012
      write(26,9006)                                                    NISS1013
 9006 format(                                                           NISS1014
     + /,'    FIG #6     Data for Pressure (MNOP) vs. Time',            NISS1015
     + /,' +---------------------------------------------------------+',NISS1016
     + /,' | Time|      Pressure  (MNOP, <PSIG>) (0.752wt% Moisture) |',NISS1017
     + /,' | (yr)| (7A/7B)  (7C/7D/7E)  (7F)      (7G)      (7H)   APAS',NISS1018
     + /,' +-----|---------|---------|---------|--------|--------|----')NISS1019
c                                                                       NISS1020
c                                                                       NISS1021
      do 6000 icase = 1, 3    ! Case = 1 for 5wt%, 2 for 2.8wt% MoistureNISS1022
c                             !                  3 for 0.752wt% MoistureNISS1023
          xMax_Moles_H2(1) = 0.03946d+00   ! 7A/7B                      NISS1024
          xMax_Moles_H2(2) = 0.03590d+00   ! 7C/7D/7E                   NISS1025
          xMax_Moles_H2(3) = 0.16923d+00   ! 7F                         NISS1026
          xMax_Moles_H2(4) = 0.07930d+00   ! 7G                         NISS1027
          xMax_Moles_H2(5) = 0.00711d+00   ! 7H                         NISS1028
          xMax_Moles_H2(6) = 0.25879d+00   ! APAS                       NISS1029
        if(icase.eq.2)  then                                            NISS1030
          do 500 i=1,6                                                  NISS1031
              xMax_Moles_H2(i) = xMax_Moles_H2(i)*2.8d+00/5.0d+00       NISS1032
  500     continue                                                      NISS1033
        endif                                                           NISS1034
        if(icase.eq.3)  then                                            NISS1035
          do 750 i=1,6                                                  NISS1036
              xMax_Moles_H2(i) = xMax_Moles_H2(i)*0.752d+00/5.0d+00     NISS1037
  750     continue                                                      NISS1038
        endif                                                           NISS1039
      Tot_Curies(1) =  2.65d+00   ! 7A/7B                               NISS1040
      Tot_Curies(2) =  2.42d+00   ! 7C/7D/7E                            NISS1041
      Tot_Curies(3) = 11.58d+00   ! 7F                                  NISS1042
      Tot_Curies(4) =  5.45d+00   ! 7G                                  NISS1043
      Tot_Curies(5) =  0.45d+00   ! 7H                                  NISS1044
      Tot_Curies(6) = 17.55d+00   ! APAS                                NISS1045
c     G_Total = 3.97d-03   ! G(total)-value for all cases  OLD VALUE    NISS1046
      G_Total = 4.38d-02   ! G(total)-value for all cases               NISS1047
      G_H2    = G_Total    ! G(H2)-value for all cases                  NISS1048
      T_Initial = 20.0d+00 + 273.15d+00                                 NISS1049
      T_Final = 121.1d+00 + 273.15d+00                                  NISS1050
      P0      = 1.0d+00    ! Initial Pressure (Atm)                     NISS1051
```

```
      do 3000 i = 1, 6             ! Number of Cases
          tMax(i) = xMax_Moles_H2(i) / (0.10 * G_H2 * Tot_Curies(i))
 3000 continue
      if(icase.eq.1)  then
        write(21,9101)  (i,tMax(i), i=1,6)
        write(22,9101)  (i,tMax(i), i=1,6)
      endif
      if(icase.eq.2)  then
        write(23,9101)  (i,tMax(i), i=1,6)
        write(24,9101)  (i,tMax(i), i=1,6)
      endif
      if(icase.eq.3)  then
        write(25,9101)  (i,tMax(i), i=1,6)
        write(26,9101)  (i,tMax(i), i=1,6)
      endif
 9101 format(t7,'tMax(',i2,')= ',1p1e14.7)
      do 5000 time = 0.0d+00 , 100.0d+00 , 0.50d+00   ! Time (yr)
          do 4000 i = 1, 6         ! Number of Cases
              if(time.lt.tMax(i))  then
                  H2_Conc(i) = (0.10d0 * G_H2 * Tot_Curies(i) * time) /
     +                         ((P0*voidfr*V2r)/(R_const*T_Initial) +
     +                         0.10d+00*G_total*Tot_Curies(i)*time)
                  xMNOP(i) = ((R_const*T_Final)/(voidfr*V2r)) *
     +                        (0.10d0 * G_total * Tot_Curies(i) * time)
                else
                  H2_Conc(i) = (0.10d0*G_H2 * Tot_Curies(i) * tMax(i)) /
     +                         ((P0*voidfr*V2r)/(R_const*T_Initial) +
     +                         0.10d+00*G_total*Tot_Curies(i)*tMax(i))
                  xMNOP(i) = ((R_const*T_Final)/(voidfr*V2r)) *
     +                        (0.10d0*G_total * Tot_Curies(i) * tMax(i))
              endif
 4000     continue
          iunita = 19 + 2*icase
          iunitb = iunita + 1
            write(iunita,9100) time, H2_Conc(6), H2_Conc(3), H2_Conc(4),
     +                               H2_Conc(1), H2_Conc(2), H2_Conc(5)
            write(iunitb,9100) time, xMNOP(6)*14.70d0, xMNOP(3)*14.70d0,
     +                               xMNOP(4)*14.70d0, xMNOP(1)*14.70d0,
     +                               xMNOP(2)*14.70d0, xMNOP(5)*14.70d0
 9100     format(1x,f7.2,6(2x,1p1e10.3))
 5000 continue
 6000 continue
c
c
      close(21)                                  ! Close output file
      close(22)
      close(23)
      close(24)
      close(25)
      close(26)
c
c
 9999 return
      end
```

9.8. Appendix H -- Standard Output From Computer Code

This appendix contains the standard output (screen copy) from the code GASGEN used to compute the Maximum Normal Operating Pressure (MNOP) values for plutonium oxides within a sealed 6M container (utilizing an inner 2R sealed container).

Table H-1. Computational Results from GASGEN Code (Version 1.05) for Maximum Normal Operating Pressures

```
-----------------------------------------------------------------
INITIAL  INPUT  PARAMETERS
  T0    =  293.0 Initial temperature of containers  [K]
  P0    =    1.0 Initial pressure in containers   [atm]
  V2r   = .00585 Internal volume of 2R container  [m^3]
  V2r   = 5853.0                                 [cm^3]
  Vic   = .00040 Internal volume of inner container [m^3]
  Vic   = 400.00                                   [cm^3]
  eps2r =  0.200 Void fraction of 2r container [no dimen]
  epsic =  0.225 Void fraction of inner container   [ " ]
  eps_ave = 0.215 Average void fraction             [ " ]
  R_const = 8.206D-05 Universal gas constant    [m^3-atm/mole-K]
-----------------------------------------------------------------
```

```
-----------------------------------------------------------------
VARYING  INPUT  PARAMETERS
  Gtot  = 0.250 G-value gas constant [molecules/100eV deposited]
  Gh2   = 0.125 G-value for H2 [molecules/100eV deposited]
  Ci    =  1.00 Total alpha alpha activity  [Ci]
  h2conc_t0 = 0.010 Initial H2 concentration in  containers
-----------------------------------------------------------------

  Time = 0.000D+00 [days]  N_gas = 5.243D-02 [moles]   Pres = 1.000D+00 [atm]
  Time = 1.000D+00 [days]  N_gas = 5.250D-02 [moles]   Pres = 1.001D+00 [atm]
  Time = 2.000D+00 [days]  N_gas = 5.257D-02 [moles]   Pres = 1.003D+00 [atm]
  Time = 3.000D+00 [days]  N_gas = 5.263D-02 [moles]   Pres = 1.004D+00 [atm]
  Time = 4.000D+00 [days]  N_gas = 5.270D-02 [moles]   Pres = 1.005D+00 [atm]
  Time = 5.000D+00 [days]  N_gas = 5.277D-02 [moles]   Pres = 1.006D+00 [atm]
  Time = 6.000D+00 [days]  N_gas = 5.284D-02 [moles]   Pres = 1.008D+00 [atm]
  Time = 7.000D+00 [days]  N_gas = 5.291D-02 [moles]   Pres = 1.009D+00 [atm]
  Time = 8.000D+00 [days]  N_gas = 5.297D-02 [moles]   Pres = 1.010D+00 [atm]
  Time = 9.000D+00 [days]  N_gas = 5.304D-02 [moles]   Pres = 1.012D+00 [atm]
  Time = 1.000D+01 [days]  N_gas = 5.311D-02 [moles]   Pres = 1.013D+00 [atm]
  Time = 1.100D+01 [days]  N_gas = 5.318D-02 [moles]   Pres = 1.014D+00 [atm]
  Time = 1.200D+01 [days]  N_gas = 5.324D-02 [moles]   Pres = 1.016D+00 [atm]
  Time = 1.300D+01 [days]  N_gas = 5.331D-02 [moles]   Pres = 1.017D+00 [atm]
  Time = 1.400D+01 [days]  N_gas = 5.338D-02 [moles]   Pres = 1.018D+00 [atm]
  Time = 1.500D+01 [days]  N_gas = 5.345D-02 [moles]   Pres = 1.019D+00 [atm]
  Time = 1.600D+01 [days]  N_gas = 5.352D-02 [moles]   Pres = 1.021D+00 [atm]
  Time = 1.700D+01 [days]  N_gas = 5.358D-02 [moles]   Pres = 1.022D+00 [atm]
  Time = 1.800D+01 [days]  N_gas = 5.365D-02 [moles]   Pres = 1.023D+00 [atm]
  Time = 1.900D+01 [days]  N_gas = 5.372D-02 [moles]   Pres = 1.025D+00 [atm]
```

```
Time = 2.000D+01 [days]  N_gas = 5.379D-02 [moles]   Pres = 1.026D+00 [atm]
Time = 2.100D+01 [days]  N_gas = 5.385D-02 [moles]   Pres = 1.027D+00 [atm]
Time = 2.200D+01 [days]  N_gas = 5.392D-02 [moles]   Pres = 1.028D+00 [atm]
Time = 2.300D+01 [days]  N_gas = 5.399D-02 [moles]   Pres = 1.030D+00 [atm]
Time = 2.400D+01 [days]  N_gas = 5.406D-02 [moles]   Pres = 1.031D+00 [atm]
Time = 2.500D+01 [days]  N_gas = 5.413D-02 [moles]   Pres = 1.032D+00 [atm]
Time = 2.600D+01 [days]  N_gas = 5.419D-02 [moles]   Pres = 1.034D+00 [atm]
Time = 2.700D+01 [days]  N_gas = 5.426D-02 [moles]   Pres = 1.035D+00 [atm]
Time = 2.800D+01 [days]  N_gas = 5.433D-02 [moles]   Pres = 1.036D+00 [atm]
Time = 2.900D+01 [days]  N_gas = 5.440D-02 [moles]   Pres = 1.037D+00 [atm]
Time = 3.000D+01 [days]  N_gas = 5.446D-02 [moles]   Pres = 1.039D+00 [atm]
Time = 3.100D+01 [days]  N_gas = 5.453D-02 [moles]   Pres = 1.040D+00 [atm]
Time = 3.200D+01 [days]  N_gas = 5.460D-02 [moles]   Pres = 1.041D+00 [atm]
Time = 3.300D+01 [days]  N_gas = 5.467D-02 [moles]   Pres = 1.043D+00 [atm]
Time = 3.400D+01 [days]  N_gas = 5.474D-02 [moles]   Pres = 1.044D+00 [atm]
Time = 3.500D+01 [days]  N_gas = 5.480D-02 [moles]   Pres = 1.045D+00 [atm]
Time = 3.600D+01 [days]  N_gas = 5.487D-02 [moles]   Pres = 1.047D+00 [atm]
Time = 3.700D+01 [days]  N_gas = 5.494D-02 [moles]   Pres = 1.048D+00 [atm]
Time = 3.800D+01 [days]  N_gas = 5.501D-02 [moles]   Pres = 1.049D+00 [atm]
Time = 3.900D+01 [days]  N_gas = 5.507D-02 [moles]   Pres = 1.050D+00 [atm]
Time = 4.000D+01 [days]  N_gas = 5.514D-02 [moles]   Pres = 1.052D+00 [atm]
Time = 4.100D+01 [days]  N_gas = 5.521D-02 [moles]   Pres = 1.053D+00 [atm]
Time = 4.200D+01 [days]  N_gas = 5.528D-02 [moles]   Pres = 1.054D+00 [atm]
Time = 4.300D+01 [days]  N_gas = 5.535D-02 [moles]   Pres = 1.056D+00 [atm]
Time = 4.400D+01 [days]  N_gas = 5.541D-02 [moles]   Pres = 1.057D+00 [atm]
Time = 4.500D+01 [days]  N_gas = 5.548D-02 [moles]   Pres = 1.058D+00 [atm]
Time = 4.600D+01 [days]  N_gas = 5.555D-02 [moles]   Pres = 1.059D+00 [atm]
Time = 4.700D+01 [days]  N_gas = 5.562D-02 [moles]   Pres = 1.061D+00 [atm]
Time = 4.800D+01 [days]  N_gas = 5.568D-02 [moles]   Pres = 1.062D+00 [atm]
Time = 4.900D+01 [days]  N_gas = 5.575D-02 [moles]   Pres = 1.063D+00 [atm]
Time = 5.000D+01 [days]  N_gas = 5.582D-02 [moles]   Pres = 1.065D+00 [atm]
Time = 5.100D+01 [days]  N_gas = 5.589D-02 [moles]   Pres = 1.066D+00 [atm]
Time = 5.200D+01 [days]  N_gas = 5.596D-02 [moles]   Pres = 1.067D+00 [atm]
Time = 5.300D+01 [days]  N_gas = 5.602D-02 [moles]   Pres = 1.068D+00 [atm]
Time = 5.400D+01 [days]  N_gas = 5.609D-02 [moles]   Pres = 1.070D+00 [atm]
Time = 5.500D+01 [days]  N_gas = 5.616D-02 [moles]   Pres = 1.071D+00 [atm]
Time = 5.600D+01 [days]  N_gas = 5.623D-02 [moles]   Pres = 1.072D+00 [atm]
Time = 5.700D+01 [days]  N_gas = 5.629D-02 [moles]   Pres = 1.074D+00 [atm]
Time = 5.800D+01 [days]  N_gas = 5.636D-02 [moles]   Pres = 1.075D+00 [atm]
Time = 5.900D+01 [days]  N_gas = 5.643D-02 [moles]   Pres = 1.076D+00 [atm]
Time = 6.000D+01 [days]  N_gas = 5.650D-02 [moles]   Pres = 1.078D+00 [atm]
Time = 6.100D+01 [days]  N_gas = 5.657D-02 [moles]   Pres = 1.079D+00 [atm]
Time = 6.200D+01 [days]  N_gas = 5.663D-02 [moles]   Pres = 1.080D+00 [atm]
Time = 6.300D+01 [days]  N_gas = 5.670D-02 [moles]   Pres = 1.081D+00 [atm]
Time = 6.400D+01 [days]  N_gas = 5.677D-02 [moles]   Pres = 1.083D+00 [atm]
Time = 6.500D+01 [days]  N_gas = 5.684D-02 [moles]   Pres = 1.084D+00 [atm]
Time = 6.600D+01 [days]  N_gas = 5.690D-02 [moles]   Pres = 1.085D+00 [atm]
Time = 6.700D+01 [days]  N_gas = 5.697D-02 [moles]   Pres = 1.087D+00 [atm]
Time = 6.800D+01 [days]  N_gas = 5.704D-02 [moles]   Pres = 1.088D+00 [atm]
Time = 6.900D+01 [days]  N_gas = 5.711D-02 [moles]   Pres = 1.089D+00 [atm]
Time = 7.000D+01 [days]  N_gas = 5.718D-02 [moles]   Pres = 1.090D+00 [atm]
Time = 7.100D+01 [days]  N_gas = 5.724D-02 [moles]   Pres = 1.092D+00 [atm]
Time = 7.200D+01 [days]  N_gas = 5.731D-02 [moles]   Pres = 1.093D+00 [atm]
Time = 7.300D+01 [days]  N_gas = 5.738D-02 [moles]   Pres = 1.094D+00 [atm]
Time = 7.400D+01 [days]  N_gas = 5.745D-02 [moles]   Pres = 1.096D+00 [atm]
Time = 7.500D+01 [days]  N_gas = 5.751D-02 [moles]   Pres = 1.097D+00 [atm]
Time = 7.600D+01 [days]  N_gas = 5.758D-02 [moles]   Pres = 1.098D+00 [atm]
Time = 7.700D+01 [days]  N_gas = 5.765D-02 [moles]   Pres = 1.100D+00 [atm]
Time = 7.800D+01 [days]  N_gas = 5.772D-02 [moles]   Pres = 1.101D+00 [atm]
Time = 7.900D+01 [days]  N_gas = 5.778D-02 [moles]   Pres = 1.102D+00 [atm]
Time = 8.000D+01 [days]  N_gas = 5.785D-02 [moles]   Pres = 1.103D+00 [atm]
Time = 8.100D+01 [days]  N_gas = 5.792D-02 [moles]   Pres = 1.105D+00 [atm]
Time = 8.200D+01 [days]  N_gas = 5.799D-02 [moles]   Pres = 1.106D+00 [atm]
Time = 8.300D+01 [days]  N_gas = 5.806D-02 [moles]   Pres = 1.107D+00 [atm]
Time = 8.400D+01 [days]  N_gas = 5.812D-02 [moles]   Pres = 1.109D+00 [atm]
Time = 8.500D+01 [days]  N_gas = 5.819D-02 [moles]   Pres = 1.110D+00 [atm]
Time = 8.600D+01 [days]  N_gas = 5.826D-02 [moles]   Pres = 1.111D+00 [atm]
Time = 8.700D+01 [days]  N_gas = 5.833D-02 [moles]   Pres = 1.112D+00 [atm]
Time = 8.800D+01 [days]  N_gas = 5.839D-02 [moles]   Pres = 1.114D+00 [atm]
Time = 8.900D+01 [days]  N_gas = 5.846D-02 [moles]   Pres = 1.115D+00 [atm]
Time = 9.000D+01 [days]  N_gas = 5.853D-02 [moles]   Pres = 1.116D+00 [atm]
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Time = 9.100D+01 [days]  N_gas = 5.860D-02 [moles]   Pres = 1.118D+00 [atm]
Time = 9.200D+01 [days]  N_gas = 5.867D-02 [moles]   Pres = 1.119D+00 [atm]
Time = 9.300D+01 [days]  N_gas = 5.873D-02 [moles]   Pres = 1.120D+00 [atm]
Time = 9.400D+01 [days]  N_gas = 5.880D-02 [moles]   Pres = 1.121D+00 [atm]
Time = 9.500D+01 [days]  N_gas = 5.887D-02 [moles]   Pres = 1.123D+00 [atm]
Time = 9.600D+01 [days]  N_gas = 5.894D-02 [moles]   Pres = 1.124D+00 [atm]
Time = 9.700D+01 [days]  N_gas = 5.900D-02 [moles]   Pres = 1.125D+00 [atm]
Time = 9.800D+01 [days]  N_gas = 5.907D-02 [moles]   Pres = 1.127D+00 [atm]
Time = 9.900D+01 [days]  N_gas = 5.914D-02 [moles]   Pres = 1.128D+00 [atm]
Time = 1.000D+02 [days]  N_gas = 5.921D-02 [moles]   Pres = 1.129D+00 [atm]


Time to reach 5% H2 concentration = 1.585D+02 [yr]  =  5.788D+04[days]
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