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Subject: ESTIMATION OF HYDROGEN GENERATION RATES FROM RADIOLYSIS IN WIPP PANELS

Dear Mr. Mercer:

Based on my experience in analyzing hydrogen gas generation from radiolysis in transuranic (TRU) waste transportation, Mr. Roger Nelson of DOE-CBFO requested my estimation of radiolytic hydrogen gas generation rates in WIPP repository panels. This letter provides a hydrogen gas generation rate estimate for a representative WIPP panel, discusses the methodology used to obtain that estimate, and discusses potential impacts of flammability from this radiolytic generation of hydrogen.

Summary

Based on an analysis of the Panel 3 inventory, the hydrogen gas generated due to radiolysis from a WIPP panel filled with emplaced contact-handled (CH)-TRU waste can be conservatively estimated to be **4.497E-05** moles per second. An average concentration of 5% (by volume) hydrogen in a filled WIPP panel is reached only after approximately 20 years. While 5% is the lower flammability limit for hydrogen, much higher concentrations, and therefore much longer time periods, are associated with any significant impacts of a potential deflagration event due to the radiolytic generation of hydrogen.

Purpose and Scope

TRU waste disposed of in the WIPP panels has the potential to generate hydrogen from radiolysis. The purpose of this letter is to provide an estimate of the hydrogen gas generation rate in a representative WIPP panel from radiolysis. The Panel 3 inventory (Reference 1) is used as the basis for the gas generation profile from a panel.

Methodology for Estimation of Hydrogen Gas Generation Rate in a WIPP Panel

At the present time, Panels 1 and 2 have been filled with waste and closed, with Panel 3 partially full and continuing to receive waste. For the purpose of this study, it is assumed that Panel 3 is representative of a typical panel at the WIPP site. This is a reasonable assumption given that the current inventory profile with Idaho National Laboratory (INL) being the dominant inventory contributor is likely to be representative of future panels (with INL having the largest remaining fraction of the waste inventory slated for disposal at WIPP). Panels 1 and 2 represent early waste disposal operations and the clean up of the Rocky Flats Environmental Technology Site. Data for the Panel 3 inventory were obtained from the WIPP Waste Information System (WWIS) (Reference 1).

The parameters of interest in estimating the radiolytic hydrogen gas generation rate per WIPP panel are as follows:

- Number of containers by waste material type: The waste material type is a classification used by the WIPP transportation system based on the gas generation potential of the waste (Reference 2). Examples of waste material types are Waste Material Type I.1, Solidified Inorganics (where the potential for hydrogen generation is from the radiolysis of water), and Waste Material Type III.1, Solid Organics (where the potential for hydrogen generation is from radiolysis of the plastic and other organic materials). The radiolytic potential for hydrogen generation is quantified by a “G value” for each waste material type (Reference 3). The hydrogen G value is defined as the number of molecules of hydrogen generated per 100 electron volts (eV) of energy absorbed.

- Decay heat values of the containers: The decay heat values are reported per container and include the error associated with the method used to determine the decay heat value. This parameter, along with the G value, can be used to estimate the hydrogen gas generation rate from the panel.

- Hydrogen gas generation rates of the containers: Hydrogen gas concentrations in the headspace of the containers are available for those containers that were shipped using the headspace hydrogen measurement data. These containers are a subset of the entire Panel 3 inventory (measurement is an option if transportation decay heat limits based on theoretical bounding G values are exceeded). While G values for the different waste materials types exist from the literature based on bounding materials (Reference 3), the headspace measurement data provides a more realistic estimate of the potential hydrogen gas generation from a container. Measured headspace hydrogen data and corresponding hydrogen generation rates and their decay heat values can be used to determine “effective G values” for the different waste material types, which, in turn, can be used to estimate a more realistic hydrogen gas generation rate from the panel.

The governing equation for determining the radiolytic gas generation rate in moles/second (Cg) is as follows (Reference 3):

Equation 1

$$Cg = W \times G \times C$$

where,

W	=	Total decay heat (watts)
G	=	Number of molecules of hydrogen gas produced per 100 eV of energy absorbed
C	=	Conversion constant
	=	(1 joule/W-sec) x (1E7 erg/joule) x (1 eV/1.6E-12 erg) x (1 g-mole/6.02E23 molecules)
	=	1.04E-5 (g-mole)(eV)/(molecule)(W-sec)
	=	1.04E-7 (g-mole)(100 eV)/(molecule)(W-sec).

For waste material types with containers with measurement data, the decay heat values of the containers were summed along with the hydrogen generation rates, and Equation 1 was used to determine the effective G values. For waste materials types without any containers with measurement data, mean G values from the governing WIPP transportation documents were used (Reference 2). The effective G values were then applied by waste material type to the entire Panel 3 inventory to estimate the hydrogen generation rate from the Panel.

These effective G values are more representative of hydrogen generation from CH-TRU waste, as they are based on actual measurements. The theoretical G values of pure materials (like polyethylene) are not representative of the hydrogen gas generated in CH-TRU waste containers, as the waste is a mixture of different materials and a portion of the energy is likely deposited in materials with less gas generation potential (some energy may be deposited in inorganic materials that do not generate any hydrogen). As discussed later, effective G values also are not constant in time and most likely decrease asymptotically as the matrix is depleted.

Panel 3 has 319 containers of Waste Type IV (Solidified Organic material) that do not have a bounding G value and were individually tested to determine the hydrogen generation rate (Reference 2). These hydrogen generation rates are determined at a temperature of 135°F to simulate worst-case transportation conditions (Reference 2). Evidence from previous room temperature testing at the sites shows that hydrogen generation rates are much smaller at lower temperatures (Reference 4). Because the expected temperature in the repository is well below the temperature at which the hydrogen generation rates were determined for these containers, the tested rates were reduced by a factor of two to estimate the hydrogen generation rates from these Waste Type IV containers in the panels.

Finally, the total hydrogen generation rate determined for the containers currently in Panel 3 was scaled up to estimate the rate when the panel is filled with a similar distribution of containers. The scaling factor was based on the percent fill level for the panel in terms of the number of stacks filled (as of June 19, 2006, the time of the data analysis) and the remaining number of stacks available (~63% of the panel was filled at the time of data analysis) (Reference 5).

Results and Discussion

The results of this analysis for the hydrogen gas generation rate for Panel 3 are provided in Table 1. As shown, the scaled hydrogen gas generation rate for the entire panel is **4.497E-05** moles per second. Assuming a full panel inventory of 80,000 55-gallon drum equivalents of waste, this translates to a rate of 0.397 liters of hydrogen per drum per year.

Table 1. Estimate of Hydrogen Gas Generation Rate for a Representative WIPP Panel

Waste Material Type	No. Containers	Inventory (watts)	G Value[a]	Constant	Hydrogen Gas Generation Rate (moles/second)
I.1	3,942	216.522	0.307	1.04E-07	6.913E-06
I.2	4,333	414.408	0.122	1.04E-07	5.258E-06
I.3	0	0.000	0.4	1.04E-07	0.000E+00
II.1	412	59.043	0.055	1.04E-07	3.377E-07
II.2	228	139.822	0	1.04E-07	0.000E+00
II.3	0	0.000	0.08	1.04E-07	0.000E+00
III.1[b]	17,231	1921.012	0.066	1.04E-07	1.319E-05
III.2	107	66.375	0.044	1.04E-07	3.037E-07
III.3	3	4.622	0.044	1.04E-07	2.115E-08
IV.1	319				2.440E-06
				Total	2.846E-05
				Gas generation rate scaled to fill panel	**4.497E-05**

[a] Measurement data used to estimate G values for Waste Material Types I.1, I.2, II.1, III.1, and III.3. Mean values from transportation analysis (Reference 2) used to derive G values for Waste Material Types I.3, II.2, II.3, and III.2.
[b] G value calculated using data for containers that met dose criteria of >0.012 watt*year (Reference 2). A large data set was available and this data is representative of the larger time frames expected in the repository.

To determine the hydrogen concentration in a typical panel as a function of time, an estimate of the overall void volume in a panel is needed. This void volume consists of the following components:

- Void volume in waste containers: Characterization data indicate that CH-TRU waste containers have large void volumes. A typical combustible debris waste 55-gallon drum has been estimated to have a void volume of 155.4 liters or ~75% (Reference 6). For this analysis, conservatively assuming an average of 50% void volume in the containers, the available void volume of 80,000 55-gallon drums = 8.32E+06 liters.

- Available void volume in MgO sacks: In a panel, each stack comprised of three layers of seven-packs is covered with an approximately 24-inch high sack of MgO with a diameter of approximately 72 inches. Assuming 3,630 stacks per panel (Reference 5), the volume occupied by the MgO is roughly 5.81E+06 liters. Conservatively assuming a porosity of 0.3 for the MgO, 0.3 x 5.81E+06 or 1.74E+06 liters of void space is available for hydrogen accumulation.

- Available void volume in the space above the MgO sacks: After the MgO sacks are emplaced on top of the stacks, there is approximately 18 inches of open space above the MgO sacks, which provides an additional void volume in the 33-foot-wide by

300-foot-long rooms. This volume can be calculated as 33' x 300' x 1.5' = 14,850 ft^3 or 4.21E+05 liters per room or 2.94E+06 liters per panel (seven rooms per panel).

Therefore, the total available void volume for gas accumulation is 8.32E+06 + 1.74E+06 + 2.94E+06 = 1.30E+07 liters. Five percent of this volume = 6.5E+05 liters. At a generation rate of 0.397 liters/drum/year, 3.18E+04 liters of hydrogen are generated from the 80,000 drums in a panel in one year. Therefore, 6.5E+05/3.18E+04 or more than 20 years will be needed to reach an average concentration of 5% hydrogen in a panel.

In terms of the potential impacts of flammability from this radiolytic generation of hydrogen, several factors need to be considered:

- The G values used for this analysis, while based on measurement data, are still conservative, as the hydrogen generation rates are assumed to be constant over long time periods in the repository. In reality, as the matrix is depleted, the G values and hydrogen generation rates are expected to decrease asymptotically to very low values. Figure 1 (Reference 7) presents this concept based on theoretical analysis that supports the conclusion that gas generation decreases with increasing dose.

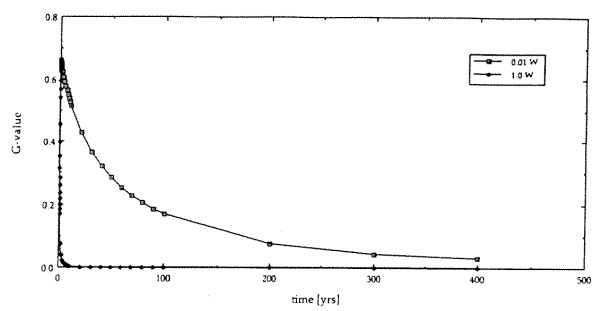

Figure 6-10. Comparison of hypothetical 0.01 W and 1.0 W G-values vs. time.

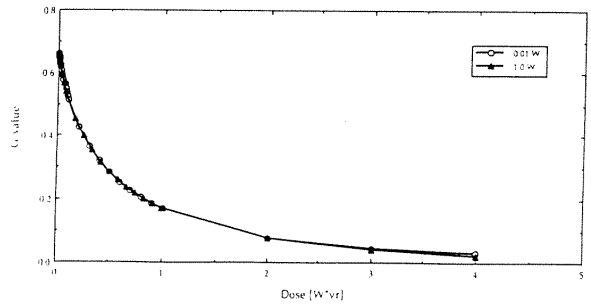

Figure 6-11. Comparison of hypothetical 0.01 W and 1.0 W G-values vs. dose.

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Figure 1. Theoretical analysis of gas generation as a function of time and dose.

- While 5% is the lower flammability limit for hydrogen, testing at the Savannah River Site (Reference 8) indicates that greater than 15% hydrogen is necessary even for lid ejection from a 55-gallon drum, with no catastrophic failure of the drums observed. These tests were also performed with empty drums. In actual waste drums, the presence of waste tends to reduce the pressure and consequence of a hydrogen deflagration. Given the timeframe to reach 5% hydrogen (20+ years), much longer timeframes will be needed for the radiolytic hydrogen to reach higher concentrations and cause a potentially significant deflagration event in the underground WIPP panels.

- Characterization data (Reference 9) indicate that hydrogen generation in typical combustible debris is often accompanied by the consumption of oxygen. Even if an ignition source is assumed to be present, it is unlikely that the hydrogen and oxygen concentrations in the WIPP panels will lead to ideal conditions with respect to the impacts of a deflagration event.

Conclusions

Hydrogen generation due to radiolysis in the WIPP panels is expected to be a slow process, with an average concentration of 5% hydrogen in the panel reached only after more than 20 years. The hydrogen generation rates used in this analysis are conservative and are expected to decrease over time during the disposal period. Experimental data indicates that hydrogen concentrations well above 5% and, therefore, much longer time periods are needed for a potential deflagration event of any significant impact in a WIPP panel.

References

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9. Clements, T. L., Jr., and D. E. Kudera, 1985, “TRU Waste Sampling Program,” Vol. 1, EGG-WM-6503, EG&G Idaho, Inc., Idaho Falls, Idaho.

If you have any questions or comments, please feel free to contact me at (505) 878-1344.

Sincerely,

(Original signature on file)

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cc: R. Nelson, CBFO ED

Selected Credentials of Author

- Bachelor of Technology, Chemical Engineering, Indian Institute of Technology, Madras, India; 1984
- Ph.D., Environmental Engineering (Department of Civil Engineering), University of Notre Dame, Notre Dame, Indiana; 1988
- 18 years of experience in radioactive waste management, safety analysis, and gas generation analysis in radioactive waste transport
- Committee Member, ANSI 14.32, Gas Generation in Packages Used for Storage or Transportation of Radioactive Materials (currently inactive)
- Subject Matter Expert, Pu-238 Decision Analysis, Sandia National Laboratories (1998)
- Panel Member and Invited Speaker, Packaging and Transportation Symposium 2000, Los Alamos National Laboratory, Santa Fe, New Mexico (November 2000)
- Program Advisory Committee, Waste Management Symposium (2001 – present)
- Expert witness, U.S. Department of Energy, State of New Mexico (2002)
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