DETERMINATION OF HYDROGEN GAS GENERATION RATES AND EFFECTIVE G-VALUES FROM REMOTE-HANDLED TRU (RH-TRU) WASTE

by
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ABSTRACT

Seventeen remote-handled (RH) transuranic (TRU) waste canisters currently are stored in vertical, underground shafts at Technical Area (TA)-54, Area G, at Los Alamos National Laboratory (LANL). These 17 RH TRU waste canisters are destined to be shipped to the Waste Isolation Pilot Plant (WIPP) for permanent disposal in the geologic repository. Currently, these canisters represent the only RH-TRU waste packaged in shielded canisters according to the WIPP-WAC (Rev. 3.). As the RH TRU canister is likely to be the final payload container prior to placement into the 72-B cask and shipment to the WIPP, these waste canisters provide a unique opportunity to establish the hydrogen generation rate and flammable gas concentrations in packaged RH-TRU waste. The hydrogen gas generation rate and flammable gas concentrations must be measured before these canisters can be sent to WIPP.

Hydrogen gas generation rates from the RH-TRU canisters have for the most part been very small for the particular waste geometries and components in the Los Alamos investigation. These measurements have been made by sealing the headspace volume by addition of large non-permeable sampling bags and measuring the H_2 and other gas constituents in the headspace of the canister over a long period of time. Although the hydrogen and oxygen levels in the "sealed" canisters are low, other secondary gas phase chemistry observations proved to be of interest in explaining the gas phase interactions in the RH-TRU waste headspace volume. For example, several RH-TRU canisters were found to be significantly depleted of oxygen. Also, the actual measurement of the gas generation rates proved to be technically challenging because of the constant atmospheric breathing of the RH-TRU canisters when allowed to be in contact with the atmosphere.

BACKGROUND

Seventeen RH TRU waste canisters (hereinafter referred to as waste canisters) currently are stored in vertical, underground shafts at Technical Area (TA) 54, Area G, at Los Alamos National Laboratory (LANL). These 17 RH TRU waste canisters are destined to be shipped to the Waste Isolation Pilot Plant (WIPP) for permanent disposal in the geologic repository. Currently, these canisters represent the only RH TRU waste packaged in canisters. As the RH TRU canister is likely to be the final payload container prior to placement into the 72-B cask and shipment to the WIPP, these waste canisters provide a unique opportunity to ascertain representative flammable gas concentrations in packaged RH-TRU waste.

Hydrogen, which is produced by the radiolytic decomposition of hydrogenous constituents in the waste matrix including moisture, is the primary flammable gas of concern with RH TRU waste. Title 10 Code of Federal Regulations Part 71, "Packaging and Transportation of Radioactive Material," (1) and the Safety Analysis Report for the RH TRU 72-B SARP (2) limit the hydrogen

concentration in any layer of confinement in a shipping package or payload, during a 60-day shipping period, to less than or equal to five percent by volume. The SARP allows waste generators two options for demonstrating compliance with the hydrogen concentration limits: 1) show compliance with the maximum allowable gas generation rate; and 2) show compliance with the maximum allowable wattage (i.e., decay heat) limits.

The primary objectives of this work, which is supported by the U.S. Department of Energy (DOE) Mixed Waste Focus Area, are to sample and analyze the waste canister headspace gases of 10 of the 17 waste canisters to evaluate the potential for flammable gas generation and to evaluate compliance with the transportation requirements specified in the 72-B SARP (2). Based on the results of the sampling, the hydrogen gas generation rate will be calculated for comparison to the applicable maximum allowable hydrogen generation rate (mole/sec) limits specified in the SARP. The key data to be produced in this experiment are the hydrogen concentration, hydrogen gas generation rate, and effective hydrogen G-value. The effective G-value provides a measure of the number of molecules of hydrogen formed per 100 electron volts (eV) of emitted ionizing radiation. A secondary objective of the experiment is to determine the headspace gas concentrations of other gases (e.g., oxygen, nitrogen, carbon dioxide, carbon monoxide, and volatile organic compounds [VOCs]) that are produced by radiolysis or present when the waste was packaged. Additionally, the temperature, pressure, and the exhale/inhale flow rate due to atmospheric pressure and temperature changes of the headspace gas will be measured.

A detailed analysis of the waste canister characterization data was performed to prioritize canisters for gas sampling. Appendix A of the program test plan (3) describes the multicriteria decision-making technique that was used to select the 10 waste canisters for sampling.

WASTE CHARACTERISTICS

The RH-TRU waste inventory at the LANL consists of one waste form, solid inorganic and organic waste. The solid inorganic and organic waste form consists of process waste from the examination of fuel pins irradiated in a nuclear reactor consisting mainly of cladding and hardware from the fuel pins. Included in this waste are fuel remnants from the preparation and examination of the fuel pins. The remaining waste is from the decommissioning of the hot cell facility, and includes experiment components, in-cell equipment, and decontamination residue.
The LANL waste was generated in Wing 9, SM-29 of the Chemical Materials Research (CMR) building, with interim storage at LANL TA-54 (Area G). Explosives and compressed gases are not used in the examination of irradiated fuel pins or in the decommissioning of the hot cell facility. Verification of compliance with the restrictions on prohibited items (i.e. free liquids, sealed containers, pyrophorics, explosives, corrosives, and compressed gases) was performed through site-specific procedures governing packaging and compliance operations. Pyrophorics were reacted before packaging. Reaction and solidification of resulting liquid is verified by visual inspection. Corrosives were neutralized by reaction with appropriate neutralizers before packaging.

The waste was packaged in optional one-gallon galvanized metal paint cans placed inside an alpha transfer can with a lid that has been shown to leak gas freely. The alpha transfer cans are comprised of a polycarbonate lid and polypropylene body. The alpha transfer can was then placed into a welded RH steel can (0.25 inch thick wall), which contains a sintered bronze filter. A minimum of 10 RH cans were placed into a vented (filtered) 55-gallon, DOT 17C steel drum. A combination of loose waste and the welded metal RH cans were also placed in the drum. Three drums were then overpacked in the RH-TRU waste canister, which is filtered.

The isotopic data including mean activity and standard deviation or error of the activity are presented for each canister in Table 1 based on data from Field and Del Mar (4) and waste canister data sheets at the time of packaging. The canisters were packaged eight and a half to ten years ago. Based on statistical conventions the standard deviation of the activity estimate is assumed to be equal to the error of the activity. In all the canisters where measurement errors are available, the standard deviation of the activity estimate is 50% of the activity value.

In calculating the decay heat of a canister the individual radionuclide activity plus error was multiplied by the decay heat per activity value (i.e., watt/Ci) and the resulting individual radionuclide decay heat contributions were summed to arrive at the canister decay heat for comparison to the SARP limits. Calculated decay heats for the canisters are presented in Table 2. The RADCALC code was used to simulate the decay and ingrowth of the original isotopic activities from the time of waste packaging to the midpoint date of canister sampling (i.e., July 12, 1999). The code calculates the radiolytic generation of hydrogen gas in packages and the decay heat. The code contains a decay algorithm originally developed for the Fast Flux Test Facility for calculating time-dependent activity in parents and daughters. The radionuclide database is taken from ENDF/B-VI, which includes over 280 radionuclides. G-values for α, β or γ are tabulated from published data for a wide variety of materials or the user can input G-values. The user can enter weight values for materials and RADCALC will calculate weighted-average G-values. The code contains curve fits for gamma absorption factors calculated with the MCNP code for 14 different common packages. Beta and alpha energy is assumed to be 100% absorbed. The current version 2.01 calculates the hydrogen gas generation rate from an input G-value.

The duration of decay calculations and the time corrected decay heat value for each canister are also listed in Table 2. Additional transportation parameters of interest including canister net weight, dose rate or exposure, and fissile gram equivalents (FGEs) are also listed in Table 2. The FGE values are based on the sum of the average activity and standard deviation of the activity for Pu-239 and U-235.

Table 1. Canister Radionuclide Activity Characteristics

Canister	Pu-239 Activity (Standard Deviation or Error) (Ci)	U-235 Activity (Standard Deviation or Error) (Ci)	Cs-137 Activity (Standard Deviation or Error) (Ci)	Sr-90 Activity (Standard Deviation or Error) (Ci)	Y-90 Activity (Standard Deviation or Error) (Ci)	Ru-106 Activity (Standard Deviation or Error) (Ci)	Rh-106 Activity (Standard Deviation or Error) (Ci)	Pm-147 Activity (Standard Deviation or Error) (Ci)	Sb-125 Activity (Standard Deviation or Error) (Ci)	Te-125m Activity (Standard Deviation or Error) (Ci)	Eu-155 Activity (Standard Deviation or Error) (Ci)	Ba-137m Activity (Standard Deviation or Error) (Ci)
LA03	.47(0.23)	6.9E-5(3.56E-5)	10(5)	9.2(4.6)	9(4.5)	.074(.037)	.074(.037)	.58(.29)	.41(.2)	.17(.08)	.19(.09)	9.5(4.7)
LA04	2.31E-02	3.40E-06	5.00E-01	4.57E-01	4.57E-01	3.67E-03	3.67E-03	2.86E-02	2.04E-02	8.45E-03	9.35E-03	4.69E-01
LA05	.042(.021)	6.16E-6(3.08E-6)	.906(.453)	.828(.414)	.828(.414)	.00664(.00332)	.00664(.00332)	.0517(.0259)	.0369(0.0184)	.0153(.00766)	.0169(0.00847)	.85(.425)
LA06	.15(.0752)	2.21E-5(1.1E-5)	3.25(1.63)	2.97(1.49)	2.97(1.49)	.0238(.0119)	.0238(.0119)	.186(.0928)	.132(0.0661)	.0544(0.0275)	.0608(.0304)	3.05(1.52)
LA07	16.9(8.45)	1.49E-6(7.44E-7)	365(183)	334(167)	334(167)	2.68(1.34)	2.68(1.34)	20.8(10.4)	14.9(7.43)	6.17(3.09)	6.83(3.41)	342(171)
LA08	16.8(8.41)	1.49E-6(7.44E-7)	363(182)	332(166)	332(166)	2.66(1.33)	2.66(1.33)	20.7(10.4)	14.8(7.39)	6.14(3.07)	6.79(3.4)	341(170)
LA09	16.6(8.3)	1.49E-6(7.44E-7)	359(179)	328(164)	328(164)	2.63(1.31)	2.63(1.31)	20.5(10.2)	14.6(7.3)	6.06(3.03)	6.7(3.35)	336(168)
LA10	14.5(7.26)	1.49E-6(7.44E-7)	314(157)	287(143)	287(143)	2.3(1.15)	2.3(1.15)	17.9(8.96)	12.8(6.38)	5.3(2.65)	5.87(2.93)	294(147)
LA11	15.4(7.69)	1.49E-6(7.44E-7)	332(166)	304(152)	304(152)	2.44(1.22)	2.44(1.22)	19(9.49)	13.5(6.76)	5.62(2.81)	6.21(3.11)	312(156)
LA12	14.8(7.39)	1.49E-6(7.44E-7)	319(160)	292(146)	292(146)	2.34(1.17)	2.34(1.17)	18.2(9.12)	13(6.5)	5.4(2.7)	5.97(2.99)	300(150)
LA13	14.8(7.39)	1.49E-6(7.44E-7)	319(160)	292(146)	292(146)	2.34(1.17)	2.34(1.17)	18.2(9.11)	13(6.49)	5.39(2.7)	5.97(2.98)	299(150)
LA14	13.3(6.65)	1.49E-6(7.44E-7)	287(144)	263(131)	263(131)	2.11(1.05)	2.11(1.05)	16.4(8.2)	11.7(5.85)	4.86(2.43)	5.37(2.69)	270(135)
LA15	9.9(4.95)	1.49E-6(7.44E-7)	214(107)	195(97.7)	195(97.7)	1.57(.783)	1.57(.783)	12.2(6.1)	8.7(4.35)	3.61(1.81)	4(2)	201(100)
LA16	1.39(.694)	2.04E-4(1.02E-4)	30(15)	27.4(13.7)	27.4(13.7)	.22(.11)	.22(.11)	1.71(.857)	1.22(.611)	.507(1.254)	.561(.281)	28.1(14.1)
LA17	1.81(.904)	2.66E-4(1.33E-4)	39.1(19.5)	35.7(17.9)	35.7(17.9)	.286(.143)	.286(.143)	2.23(1.12)	1.59(.795)	.66(.33)	.73(.365)	36.6(18.3)
LA18	.729(.365)	1.07E-4(5.35E-5)	15.8(7.88)	14.4(7.2)	14.4(7.2)	.115(.0577)	.115(.0577)	.899(.45)	.641(.321)	.266(.133)	.295(.147)	14.8(7.39)
LA19	1.50E+00	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR

NR = Not Reported

Table 2. Canister Transportation Parameters

Canister	Rank for Headspace Gas Sampling	Net Weight (lb)	Exposure at 1 meter (R/hr)	Decay Heat Initial (W)	Average Age of Waste as of 7/12/99 (yr)	Decay Heat as of 7/12/99 (W)	Fissile Gram Equivalent (FGE) (g)
LA03	16	2,600	3	0.172	9.24	0.155	78
LA04	11	2,730	NR	0.009	8.87	0.008	2
LA05	13	3,010	0	0.016	8.76	0.014	7
LA06	14	2,650	1	0.056	8.44	0.051	25
LA07	3	3,240	117	6.276	9.86	5.546	539
LA08	5	3,150	116	6.240	9.49	5.559	536
LA09	2	3,140	115	6.162	9.44	5.498	529
LA10	4	3,170	100	5.389	9.54	4.806	463
LA11	6	3,030	106	5.709	9.51	5.080	491
LA12	7	2,890	102	5.487	9.65	4.884	472
LA13	8	3,020	102	5.487	9.42	4.884	472
LA14	9	3,000	1.0E+05[a]	4.936	9.28	4.394	424
LA15	1	3,040	1.2E+05[a]	3.671	9.18	3.295	316
LA16	10	2,190	10	0.515	9.34	0.460	230
LA17	12	2,020	13	0.671	9.26	0.599	300
LA18	15	2,240	5	0.271	9.11	0.241	121
LA19	17	2,880	NR	0.070	NA	0.070	24

a = at contact

EXPERIMENTAL CONFIGURATION

Straightforward techniques and off-the-shelf, commercially available equipment was used to sample the headspace gas of the waste canisters. The canisters were sampled in place and all analyses were conducted at LANL using standard laboratory equipment calibrated with known gas standards. The details of the experimental design, equipment, and sampling methodology are provided in the program test plan (3). The test plan also outlines the methodology for analyzing the data to arrive at hydrogen gas generation rates and effective G-values. This section provides a summary of the experimental configuration.

Figure 1 provides a process flow diagram of the experimental configuration. Sampling lines that communicate with the headspace of the waste canisters were installed by attaching a sampling probe to the top of each canister. The top of each canister contains a HEPA filter for filtering gas that is exhaled/inhaled due to atmospheric pressure and temperature changes. Samples of the headspace gas were withdrawn periodically depending on the outside atmospheric temperature and pressure conditions and analyzed with either an MTI 200 Micro-gas chromatograph (GC) or mass spectrometer (MS). The headspace gas of the selected waste canisters was sampled and analyzed to determine the concentrations of hydrogen, oxygen, and nitrogen. The temperature was measured each time a waste canister was sampled using a digital thermometer or a temperature thermocouple attached to the top of the waste canister.

Level I data quality objectives (DQOs) were established for the analysis of hydrogen as described in the test plan (3) because these data are mandatory for the success of this

experiment. The quality assurance objectives (QAOs) established by the Transuranic Waste Characterization Quality Assurance Program Plan (5) (QAPP) were instituted as Level I DQOs for the hydrogen analysis.

Pure gases were used for laboratory control standards (LCSs) in the calibration the GC and MS instruments and to determine their accuracy. Standards that contain mixtures of gases were obtained from reputable vendors. The GC and MS instruments were calibrated, as directed and at the frequencies specified by approved procedures using National Institute of Standards and Technology (NIST)-traceable sources, to ensure that the observed hydrogen concentrations fall within their calibration range. The GC and MS instruments were also calibrated if they failed quality assurance tests and before being placed in service after being repaired. The GC and MS instruments met the DQOs for precision and accuracy specified in Section 5.0 of the test plan (3). At least one LCS was included with each batch of samples where 20 or less samples comprise one batch. Each batch also included at least one duplicate LCS or sample to determine the precision of the experiment. Additionally, each batch included at least one field blank to determine the background levels of the analytes and one equipment blank to verify that the analysis system was not contaminated. All data were recorded and documented following standard LANL laboratory policy. All sampling and analysis were conducted as directed by approved procedures. Completed chain-of-custody (COC) forms were used when samples were transferred to an analytical laboratory apart from the samplers.

Volume calibrated 5-cc No-Con syringes were initially used to obtain and transfer headspace gas samples for laboratory analysis. A digital flow meter and totalizer were used to measure total gas flow through the sample tube. The first sampling was performed using an open system. Subsequent sampling cycles involved gas sampling from a closed system with a non-permeable Cali-5 Bond 15-liter bag attached to the exhaust of the sampling line. Starting on July 16, 1999, a 50-cc No-Con syringe was used to withdraw samples.

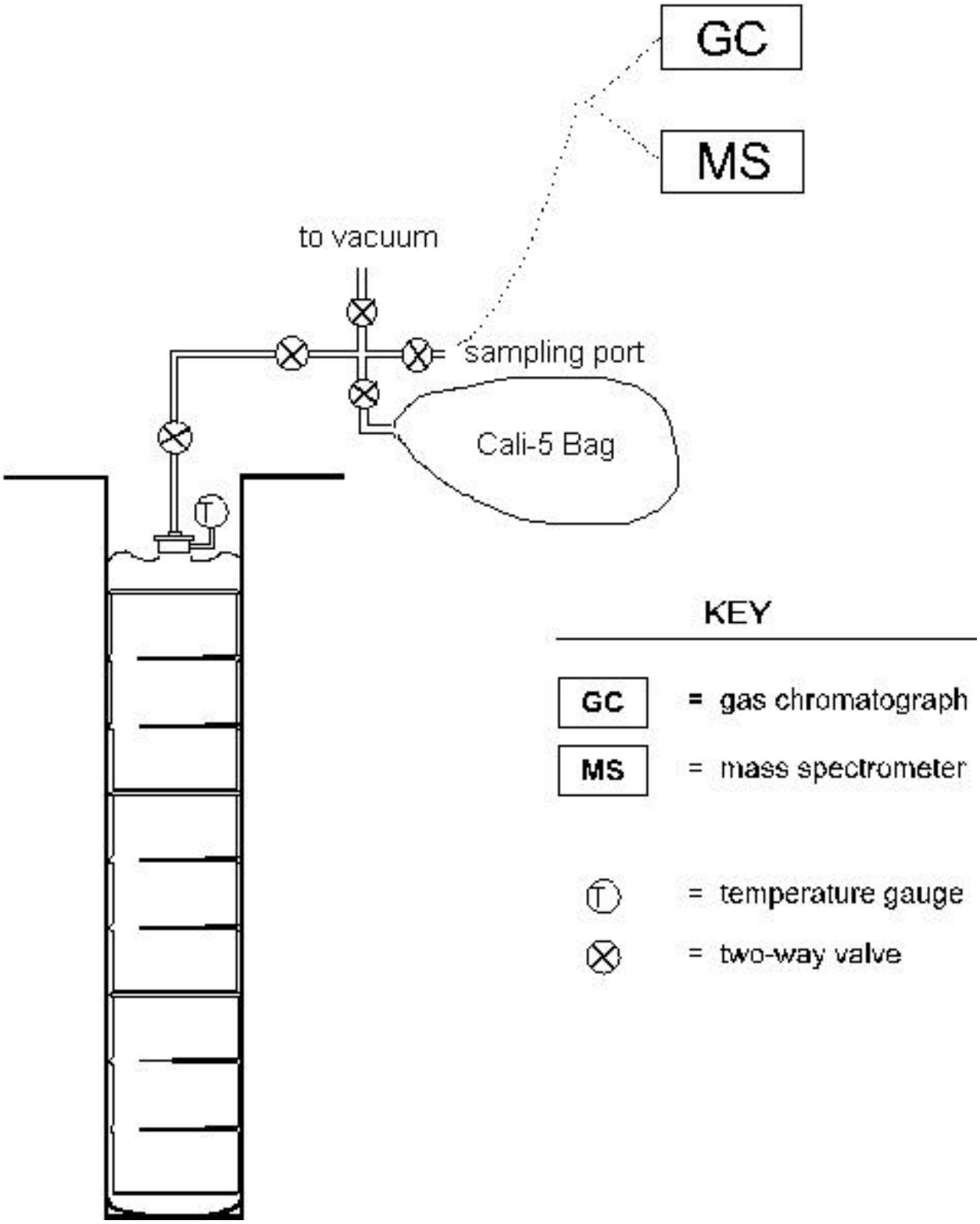
RESULTS

The headspace gas of each of the 10 selected waste canisters was sampled at least 5 times over a period of 11 weeks at TA-54, Area G between June and August 1999. The canisters were sampled during the summer months because sampling during the remaining months is not feasible in the out-of-doors canister storage area.

Hydrogen was measured in all the canisters and is most probably generated from the radiolysis of the hydrogenous materials including free and combined moisture present in the waste. The hydrogen concentration ranges from 0.1 volume percent in LA16 to 1.7 volume percent in LA10. The oxygen concentration in all canisters is below the normal concentration of oxygen in air indicating that oxygen is being consumed in all the canisters. The oxygen concentration ranges from four volume percent in LA09 to 18 volume percent in LA16. The nitrogen concentration ranges from 70 volume percent in LA16 to 90 volume percent in LA10. It is believed that the majority of the remaining gas in the canisters is carbon dioxide and carbon monoxide. Helium was detected in canisters LA07, LA10, and LA11 but was not quantified. The helium concentration in LA10 is very low and approaches the instrument lower detection limit.

Table 3 lists the rank of each canister for sampling and the decay heat in each canister as of July 12, 1999. The average concentration for each gas and the standard deviation were calculated for each canister with the results of the statistical analyses summarized in Table 3.

Figure 1. Experimental Configuration



For each sampling cycle, the measured gas flow rate in units of cm^3/min was converted into units of mole/sec using the ideal gas law and the appropriate temperature. The average gas flow rate was calculated for each canister using only the positive measured gas flow rates i.e., when the atmospheric pressure conditions result in an exhaust of headspace gas. The average flow rates and standard deviations for the canisters are listed in Table 3. The last two columns of Table 3 list the corresponding percentage of hydrogenous materials and the percentage of solidified cans in each waste canister. Based on the results of the sampling, four of the ten canisters were selected for more detailed gas generation data analyses during FY 2000. The four canisters that were selected are LA07, LA08, LA10, and LA15. The rationale for selecting these four canisters is provided below.

LA07 was ranked number three for sampling. The canister has a low oxygen content, the second highest decay heat, the lowest hydrogenous content, no solidified cans, and relatively high hydrogen concentration.

LA08 was ranked number five for sampling. The canister has the highest decay heat, the second highest oxygen content, 15.9 percent hydrogenous materials, no solidified cans, and relatively low hydrogen concentration.

LA10 was ranked number four for sampling. The canister has a relatively midrange decay heat, a midrange hydrogen concentration, a relatively low oxygen concentration, the second lowest hydrogenous materials content, and the lowest percentage of solidified cans for canisters containing these cans.

LA15 was ranked number one for sampling. The canister has the second to the lowest decay heat, the highest percentage of hydrogenous materials, the highest percentage of solidified cans, a relatively high oxygen concentration, and a relatively low hydrogen concentration.

Table 3. Statistical Summary of Sampling Data

Canister	Rank for Headspace Gas Sampling	Decay Heat (W) as of 7/12/99	Average (Standard Deviation) Hydrogen Concentration (Vol%)	Average (Standard Deviation) Oxygen Concentration (Vol%)	Average (Standard Deviation) Nitrogen Concentration (Vol%)	Average Gas Flow Rate (mol/s)	Standard Deviation of Gas Flow Rate (mol/s)	Percentage Hydrogenous Materials	Percentage Solidified Waste Cans
LA07	3	5.546	1.10(0.31)	6.91(3.73)	78.07(2.27)	1.9E-06	9.2E-07	2.7	0.0
LA08	5	5.559	0.74(0.26)	13.82(2.69)	75.52(3.73)	2.2E-06	6.1E-07	15.9	0.0
LA09	2	5.498	1.32(0.14)	5.80(2.13)	83.32(3.72)	1.2E-06	2.6E-07	31.5	5.6
LA10	4	4.806	1.55(0.14)	6.16(1.47)	83.55(3.72)	1.5E-06	1.0E-06	39.8	11.1
LA11	6	5.080	1.21(0.10)	5.47(1.29)	83.55(3.99)	1.7E-06	7.3E-07	18.3	8.3
LA12	7	4.884	0.98(0.02)	5.91(1.14)	84.25(2.86)	2.9E-06	6.5E-07	39.9	8.3
LA13	8	4.884	0.45(0.03)	11.52(0.84)	83.98(3.51)	2.0E-06	1.3E-06	33.3	13.9
LA14	9	4.394	0.38(0.11)	12.15(1.23)	80.44(3.66)	2.0E-06	3.2E-07	31.8	22.2
LA15	1	3.295	0.62(0.13)	12.44(3.17)	78.87(2.91)	2.5E-06	2.2E-07	50.0	50.0
LA16	10	0.460	0.11(0.02)	17.30(0.50)	79.81(4.12)	2.8E-06	5.3E-07	9.3	0.0

Based on the results of the sampling to date, the hydrogen gas generation rate was calculated for these four canisters through four separate models or methodologies:

- Hydrogen gas generation rate based on the measured gas flow rate and hydrogen concentration.
- Hydrogen gas generation rate based on the product of the canister filter diffusivity characteristic and the measured hydrogen concentration.
- Hydrogen gas generation rate based on the product of the highest credible G-value and canister decay heat. The G value of 1.09 molecules/100 eV is based on wet cellulosics as determined through the DOE Matrix Depletion Program (MDP) testing (6).
- Hydrogen gas generation rate based on the product of the highest credible G-value, canister decay heat, and percentage hydrogenous material in canister.

The results are presented in Table 4.

Table 4. Calculated Hydrogen Gas Generation Rates

Canister	Decay Heat (W)	Average Apparent Hydrogen Generation Rate Based On Positive Gas Flow Rate (mol/s)	Average Apparent Hydrogen Generation Rate Based on Canister Diffusivity Characteristic (mol/s)	Hydrogen Gas Generation Rate Based on G Value of 1.09 (mol/s)	% Hydrogenous Materials	Hydrogen Gas Generation Rate Based on G Value of 1.09 x % Hydrogenous Materials (mol/s)
LA07	5.546	2.4E-08	7.3E-07	6.3E-07	2.7	1.7E-08
LA08	5.559	2.1E-08	4.9E-07	6.3E-07	15.9	1.0E-07
LA10	4.806	2.2E-08	1.0E-06	5.4E-07	39.8	2.2E-07
LA15	3.295	1.7E-08	4.2E-07	3.7E-07	50.0	1.9E-07

The lowest hydrogen gas generation rates are given by the gas flow rate model. The hydrogen gas generation rates based on the canister diffusivity characteristic model and the dose-dependent (i.e. MDP) G-value model are in good agreement.

The fact that the gas flow rates for a single canister fluctuate from positive, to no flow, to negative flow indicates that this is probably due to daily pressure and temperature variations. A sensitivity analysis was performed on temperature and pressure. The analysis indicates that daily fluctuations in temperature and pressure can produce the apparent flow rates that have been measured. A correlation analysis was performed of canister decay heats and measured gas flow rates. The correlation coefficient based on data for all ten canisters is –0.58 indicating that the gas flow rate is not correlated to hydrogen generation by radiolysis. A correlation analysis of decay heats and measured hydrogen concentrations provided a correlation coefficient of 0.66 based on data for all ten canisters. Based on the materials present in the canisters, the plausible mechanisms of gas generation, the consumption of oxygen, the good agreement between hydrogen rates derived from the diffusivity characteristic model and the

dose-dependent G-value model it is concluded that radiolysis is the dominant mechanism of hydrogen generation.

CONCLUSIONS

Waste generators have two options for demonstrating compliance with the hydrogen concentration limits: 1) show compliance with the maximum allowable gas generation rate; and 2) show compliance with the maximum allowable wattage (i.e., decay heat) limits. Based on current decay heats, nine of the ten sampled canisters exceed the SARP decay heat limit of 0.6903 watt/canister. Therefore, compliance of these nine canisters must be demonstrated through option one i.e., determination of the hydrogen gas generation rate and comparison to the limit.

The Mixed Waste Focus Area is currently evaluating the feasibility of deploying a variety of hydrogen getter or recombiner materials to facilitate TRU waste shipments. If hydrogen getters or recombiners are used, the decay heat limit could be increased to 0.9969 watt/canister if the getter/recombiner material is placed inside the 72-B Inner Containment Vessel (ICV). The dose-dependent G-value of 1.09 molecules/100 eV based on the results of the MDP would increase the allowable decay heat limit to 3.090 watt/canister. A combination of hydrogen getter/recombiner deployment and dose-dependent G-value would increase the allowable decay heat limit to 4.462 watt/canister. Even with this revised limit, seven of the ten canisters will exceed the decay heat limit. In order to transport these canisters, compliance with the allowable hydrogen gas generation rates must be demonstrated for these seven canisters. The current hydrogen gas generation rate limit per canister is 1.934×10^{-7} mole/sec. Through deployment of hydrogen getter/recombiner in the ICV, this limit may be increased to 2.793×10^{-7} mole/sec.

Hydrogen was detected in all ten of the sampled canisters with concentrations ranging from 0.10 volume percent to as high as 1.7 volume percent. The oxygen concentration ranges from 4 volume percent in LA09 to 18 volume percent in LA16. The oxygen concentrations are thus below those in air and indicate that oxygen is being consumed, which is expected to occur through radiolysis of the hydrogenous materials present in the waste and recombination with hydrogen in a radioactive environment. This is substantiated by the fact that the correlation coefficient for oxygen concentration and decay heat is –0.7. The ratio of beta and gamma activity to that of alpha activity is a constant for all the canisters and equal to 7.77.

Daily variations in the temperature and pressure can produce the apparent flow rates that have been measured. There is good agreement between hydrogen gas generation rates derived from the diffusivity characteristic model and the dose-dependent G-value model. However, there is insufficient data at this time to establish a definitive hydrogen gas generation rate for each canister.

All of the canisters meet the canister gross weight requirements. Eight of the canisters exceed the 325 gram FGE limit. Shielding analysis or measurements on a loaded cask would need to be performed to evaluate compliance with the external dose rate requirements of 200 mrem/hr at the surface of the cask and 10 mrem/hr at two meters distance from the cask. VOC concentration data are not available to ascertain compliance with the 500 ppmv limit on flammable VOCs, but will be obtained in FY 2000.

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