THE DETERMINATION OF THE RATE OF HYDROGEN GENERATION FROM TRANSURANIC 003 TYPE ORGANIC SLUDGE

by

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The Determination of the Rate of Hydrogen Generation from Transuranic 003 Type Organic Sludge.

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Abstract
Experiments were performed to estimate a waste stream encompassing, effective G-value for hydrogen generation within the transuranic waste stream IDC 003 Organic Setup sludge. This waste stream is a combination of machine cutting oils and degreasing solvents with plutonium fines sorbed into an inert gypsum or calcium silicate matrix. Four 50-g sludge samples were sealed in separate canisters. Each canister was fitted with a sampling port and pressure monitor. During the experiment one of the canister seals failed and that sample was lost from the experiment. The three remaining samples were taken through four separate test periods in which duration between beginning and ending atmosphere sampling varied from a maximum of 61 days for the first experiment to a minimum of 9 days for the fourth set of experiments. The temperature was varied during the experiment with three of the tests being conducted at 135 °F and one experiment at 68 °F. The G-values determined from a single sample after a time interval of 60 days at 135°F were 2.4-, 4.8- and 13-molecules H_2/100 eV for three separate sludge samples. A second test was performed at room temperature immediately after the initial 60-day test using the same test specimens. Gas samples were collected after a 25-day interval and the G-values were determined to be 1.2-, 2.8- and 2.3-molecules H_2/100 eV. Then a 13-day test at 135 °F was performed; the G-values were 3.1-, 3.3- and 5.4-molecules H_2/100 eV. In a final 9-day test at 135 °F the G-values for the group were 1.7-, 6.4- and 8.1-molecules H_2/100 eV. Hydrogen gas generation rates within the sample group did not correlate well with ionizing energy deposition in these experiments thereby precluding determination of a G-value for the IDC 003 sludge. Indications of hydrogen storage and complex radiochemistry were seen. The design and construction of the test canisters and an appropriate sampling manifold to measure trace hydrogen at parts per million (ppm) levels is described.

Introduction
The INEEL has several thousand drums of waste sludge classified as Item Description Code (IDC) 003: Organic Setups. The Organic Setups are one of several types comprising the TRUPACT-II grouping Waste Type IV, Solidified Organics. The relation between the rate of radiolytic gas generation to ionizing energy deposition in the setup sludge, as with most Type IV wastes, is not understood.

Wastes with known relationships between gas generation and ionizing energy deposition comprise the TRUPACT-II Analytical Category of wastes. Wastes lacking known relations, such as Type IV Organics, are Test Category wastes. Analytical Category wastes may be qualified for TRUPACT-II payload inclusion by calculation. TRUPACT-II payload inclusion decisions for Test Category wastes are, on the other hand, made only on a drum-by-drum basis through drum-scale testing. As an alternative, Test Category wastes remain candidates for study to establish an accurate and representative G-value to qualify the waste into the Analytical Category.

The TRUPACT-II SAR has reported G-values for IDC 003 sludge of 15- and 22-molecules H_2/100 eV based on Drum Scale experiments (1). The authors were unable to explain this phenomena and eluded to the possible corrosion of the drums that contained the sludge. These values were too large for Analytical Category inclusion.

This study was conducted with the goal of establishing a waste stream encompassing relation between the ionizing energy absorbed in the sample to radiolytic gas generation, i.e., a "G-value" for the INEEL's IDC 003 inventory. A set of experiments were designed to determine the effective G-value for IDC 003 waste. The goal was to measure hydrogen and methane gases that were generated over a 60-day interval for samples maintained at 135 °F. These conditions correspond to specifications for Test Category measurements as specified in the TRUPACT-II SAR. The effective G-value will be defined as the quotient of the gas generation rate to the ionizing energy deposition rate. The G-value is commonly discussed in units of molecules of hydrogen per 100 eV of ionizing energy deposited (i.e. molecules H_2/ 100 eV).

Experimental

Four samples of IDC 003 sludge were obtained, each with a mass of approximately 50 g. The samples were separately contained in four 250-ml glass sampling jars (I-chem). These sludge samples were remnants from a previous sampling and characterization campaign in which the actinide contents had been determined by radiochemistry performed at the Idaho Nuclear Technology Center (INTEC). This group of samples was chosen from a larger inventory of about forty potential samples based on having the highest alpha activity concentrations and therefore having the highest expected gas generation rates presuming generation would be a function of radiolytic energy deposition. The specific activities and masses of the four samples are provided in Table I.

Table I. IDC 003 Sludge Sample Mass, Actinide Activity Concentrations, and Sludge Mass-Normalized Ionizing Energy Deposition Rates.
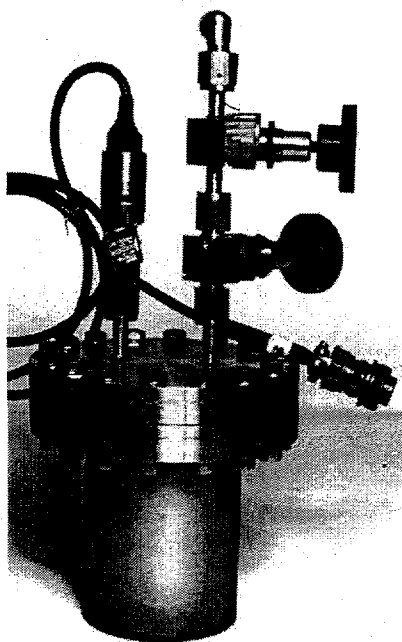
Test Canister # (Sample ID #)	Sludge Mass (g)	Actinide Activity Concentration			Energy Deposition Rate (eV/day/g_{sludge})
		Pu-239 (pCi/g)	Am-241 (pCi/g)	Pu-238 (pCi/g)	
1 (ID00173810CM1)	60.31	1.68×110^6	1.60×10^5	4.06×10^4	8.10×10^{16}
3 (ID00188110CM1)	48.76	1.93×10^6	2.14×10^5	5.80×10^4	9.48×10^{16}
4 (ID00141910CM1)	54.75	2.37×10^6	2.47×10^5	6.17×10^4	1.15×10^{17}
5 (ID00647210CM1)	49.34	2.05×10^6	2.34×10^5	5.88×10^4	1.01×10^{17}
Note: Canister #2 contained no sample and was the experiment control. Note: Uranium 238 and 235 values were less than 1.00×10^{02} pCi/g					

The design basis for this work was based on the assumption that the hydrogen generation rate would be low. It was estimated that the sludge was approximately one third to one half Texaco Regal oil with the balance being inert solidifying agents such as gypsum and calcium silicate. Previous studies on the radiolysis of Texaco Regal oil have shown upper G-values in the range of 3-molecules H_2/100 eV(2). Given that the sludge was approximately 50% Texaco Regal oil, G-values for the sludge were expected to range from 1 to 1.5. For the samples selected, the energy deposition rate averaged approximately 1×10^{17} eV/day/gram sludge. The activity in a 50-gram sample would deposit approximately 3.3×10^{20} eV over a 60-day testing period. This would produce approximately 5×10^{18} molecules of H_2 assuming a G-value of 1.5-molecules H_2/100 eV. If the test canisters were approximately one liter in volume, then the H_2 concentration would be approximately 250 parts per million (ppm). Given that the sludge contained halogenated solvents, lower hydrogen concentrations were expected due to the competitive formation of hydro-halogenated compounds such as hydrogen fluoride and hydrogen chloride. After accounting for estimated the hydrogen production and halogen scavenging, the 700-cm³ test canisters were expected to contain approximately 150-ppm H_2 at the end of the 60-day test.

Given the high diffusivity of hydrogen, the potential for hydrogen loss due to leakage in the test container is high. A leak rate of 1×10^{-7}-standard cubic centimeters of helium per second (scc He·s^{-1}) is equivalent to 2.68×10^{12}-molecules He·s^{-1}. Given that a 60-day test is equivalent to 5.184×10^6 s, if one assumes that

hydrogen has a similar diffusivity to He and the hydrogen preferentially leaks over other gases in the test container then this would represent 1.4×10^{19} molecules of hydrogen that would be lost (the entire mass of hydrogen produced). Therefore, a leak rate less than 1×10^{-7}-scc·s⁻¹ He was imposed to maintain the integrity of the test. As such, stainless steel high vacuum components, bellows sealed valves and VCR- type metal gasket fittings were selected for the materials of construction. The sludge samples were kept in the sampling jars to minimize interactions with the materials of the vacuum vessels. This eliminated the possibility of corrosion of the vessel and minimized the quantity of plutonium-contaminated mixed waste at the end of the experiment.

Five test canisters were constructed from stainless steel to house the four samples and a blank. One of these is shown in Photograph 1. The lid of each canister was constructed from a 3.5-in. "Conflat" blank vacuum flange (Varian Vacuum Products). The base assembly of each vessel consisted of a 3.5-in. i.d. tube (0.125-in. wall thickness) that was seal-welded to a mating vacuum "Conflat" flange. A 0.125-in. circular base plate was welded to the tube. A copper gasket was used to seal the base to the top flange. Sixteen stainless steel ¼-28 bolts were used to securely fasten the top to the base assembly. The internal volume of each canister was approximately 700 cm³.

Photograph 1. Test Container.

Two VCR-type, face seal, weld stubs provided penetrations through the lid. A pressure transducer (model PX-811-020AV, Omega) was connected to one of the VCR penetrations using a VCR female connector (model SS-4-VCR-7-4, Cajon). A high-vacuum epoxy (Torr-Seal,Varian Vacuum Products) was used to seal the pipe thread connections on the pressure transducer to the female connector. Two bellows-seal valves were connected in series to provide redundant sealing to the vessel through the second penetration.

Gases were introduced into each test canister using a gas fill manifold. The gas-fill manifold provided a connection to the test canister, a standard gas cylinder or helium gas cylinder, a SUMMA passivated gas sampling canister (3) (for VOC analysis by infrared spectrometry) and the mechanical vacuum pump. The pressure of the manifold was monitored using a vacuum pressure transducer (senTorr, Varian Vacuum Products). The vacuum gauge registered pressures that ranged from 1×10^{-3} to 760 torr.

Gases for chromatographic analysis were sampled from each canister using a gas sampling manifold. The manifold consisted of a gas sampling cylinder, a vacuum pressure transducer (senTorr, Varian Vacuum) and a mechanical vacuum pump (model D-16C Maxima, Fischer Scientific) All connections to the manifold were VCR-type, metal face seals. A bellows-seal valve (model SS-4BK-V51, Nupro) provided isolation between the vacuum pump and the manifold. Single-ended, stainless steel gas sampling cylinders (model SS-4-CS-TW-25, Whitey Co.) were welded to a bellows-seal valve. The internal volume of each sampling bulb was approximately 27 cm^3. The vacuum gauge registered pressures that ranged from $1x10^{-3}$ to 760 torr.

Each sludge sample contained milligram quantities of Pu. Thus, efficient filtration was required to insure that Pu contaminated particulate would not be removed from the test container during sampling. A high efficiency, sintered nickel metal filter (GasShield®, model GSG-V4-1-2U, Mott) was placed between the pressure transducer and each canister. The Mott filters provide greater than 99.9999999% removal of all particles down to a particle size of 0.01 μm. An additional Mott GasShield® filter was inserted into the gas fill and gas sampling manifolds to filter the gases extracted from the vessel during sampling and loading of the canister.

Accurate monitoring of the test canister pressure was necessary to calculate the volume of the headspace in the each test canister before and after sampling. The strain gage type pressure transducer was interfaced to a digital panel meter that displayed the output in millivolts. The output of each pressure transducer was calibrated versus a NIST traceable calibrated pressure gage at room temperature and at 44 °C.

Each container was lined with a polyethylene bag to minimize the contamination of the internal surface. Samples of sludge were delivered in 250-ml glass jars, each with a plastic lid and Teflon liner. Clean lids were substituted for the contaminated lids. Each clean lid had eight 1-mm diameter holes drilled through the lid. In addition, a 1-in. diameter section of the Teflon liner was removed to permit gases to freely migrate between the test container and glass jar containing the sludge. A small piece of monofilament was used to lower each jar, the sludge and new lid into the test container. A saran wrap apron was used to prevent contaminated particulate from contacting the vacuum flange or copper gasket during canister loading.

After assembly and prior to sample loading, each vessel was leak tested using a mass spectrometer leak test apparatus (model 17AB, Veeco Instruments) and bell jar to insure the integrity of all mechanical and welded seals. The leak rate of each vessel was quantified prior to being placed in service. In all cases the helium leak rate was less than $1x10^{-7}$ scc·s^{-1}. After loading and sealing each vessel, the atmosphere was evacuated to 6 psia and filled with helium gas to 12 psia. This process was repeated five times. This provided a concentration of helium equivalent to approximately 97%. The vessel was then sealed and placed in a bell jar that was maintained in vacuum. The helium leak rate was measured using a helium leak tester. The leak rate of all five canisters placed in service was less than $4x10^{-8}$ scc·s^{-1}.

Samples of gas were extracted at two points during the overall experiment for the qualitative identification of volatile organic compounds using a Fourier transform infrared (FTIR) spectrometer. Sampling occurred prior to the 60-day test after the He leak test and between the 60-day and 25-day tests. The samples were collected using gas sampling SUMMA canisters and the gas fill manifold. Each SUMMA canister was evacuated to $<1x10^{-2}$ torr, then connected to the gas filling manifold via a quick disconnect fitting. The manifold was evacuated to $<1x10^{-3}$ torr prior to sampling.

The IR system was constructed from an FTIR spectrometer (model 7020, Mattson Instruments) that was interfaced to a 10-m gas cell (Nicolet Instrument Corp.). The cell was heated to 150 °C. Spectra were obtained with a spectrometer resolution of 0.5 cm^{-1}.

Ultra-zero air (UZM®, Scott Specialty Gas) was used as the baseline canister atmosphere for these tests. Ultra-zero ambient air was selected because it is hydrocarbon free. Atmospheric air initially was

detyermined to be unsuitable due to anthropogenic sources of methane. The atmospheric air may vary. The average concentration of methane was 1.7 ppm and was reported to be increasing at a rate of 1% per year (4). Fluctuations in the background concentration of methane would add to the measurement uncertainty for this experiment. In order to remove the residual helium to less than 0.1%, each canister was evacuated to 6 psia and filled to approximately 12 psia with ultra-zero air. This process was performed ten times in succession. After filling, each canister was placed in an oven that was maintained at 135 °F for the duration of the test. After the first 60-day test, methane was not detectable, and the use of zero air was not deemed necessary.

Two trace hydrogen gas standards, containing 25- and 100-ppm H_2 in a balance of UZM® air (Scott Specialty Gas), were used to calibrate the gas chromatograph for hydrogen measurements. When hydrogen concentrations were found in excess of expectations during the experiment, a check of the hydrogen calibration was done with 50-ppm H_2 in a balance of argon. A standard containing 500-ppm methane in air was used to construct a single point calibration plot for methane.

Gas standards containing chlorinated volatile organic compounds were obtained (Scott Specialty Gases) for calibration of the FTIR. Two standards were obtained that contained 10 and 100 ppm each of carbon tetrachloride (CCl4), 1,1,1 trichloroethane (TCA), tetrachloroethylene (PCE), trichloroethylene (TCE), and 5-ppm sulfur hexafluoride in a balance of nitrogen.

The gases He, H_2, O_2, CO_2 , N_2 and CH_4 were analyzed by gas chromatography. A gas chromatograph (model 5890, Hewlett Packard), described elsewhere (5), was equipped with a micro-thermal conductivity detector and two mega-bore columns: a 25-m length, 0.53-mm i.d. molecular sieve column and a 25-m length, 0.53-i.d. Pore Plot Q column. The GC was cooled to 250 K with liquid nitrogen for the separation of helium and hydrogen. Argon was used as the carrier gas. Chromatographic conditions are provided in Table II. The output of the thermal conductivity detector was amplified and digitized using a chromatographic integrator (model 3396, Hewlett Packard). Chromatograms were processed to obtain integrated peak areas using the Chromperfect Software Package. The reported peak areas have units of mV·s, and are referred to as area units.

Table II. Chromatographic Operating Parameters

Reference Gas Flow Rate (ml/min)	0.75
Column, Aux and Detector Gas Flow Rate (ml/min)	20
Detector Temperature (°C)	225
Injection Volume (ml)	0.2
Injection Temperature (°C)	110
Split Flow Rate (ml/min)	16.3
Initial Column Temperature (°C)	-23

An automated sample injection system was used for gas injection. A 0.2-ml sample loop is connected in series to a gas manifold. Prior to sample introduction the manifold and sample loop are evacuated to a pressure < $1x10^{-3}$ torr. Then, the manifold and loop were filled with the sample or standard gases. As such, the pressure within the sample loop is sub-atmospheric. The pressure and temperature of the sample loop are recorded and the measured peak areas are corrected to standard temperature and pressure.

Results and Discussion
In order to calculate the number of molecules of hydrogen generated over each test interval, the headspace volume must be known. The volume of the headspace in each canister was determined by expanding the gas into an evacuated reservoir of known volume and monitoring the pressure before and after the expansion. The reservoir consisted of a 27-ml sample cylinder and gas sampling manifold and the volume

between the bellow-seal isolation valves. The volume of manifold was measured to be 24.7 ml. The volume between the bellows-seal isolation valves was measured to be 2.3 ml. The volume of each sample cylinder was measured and provided in Table III. The resulting volume of the headspace of each of the four test containers containing the TRU sludge is also provided in Table III.

Table III. Volumes of Sample Cylinders, Test Canisters (with Samples) and Associated Headspcae Sampling Equipment.

Test Equipment	Free or Headspace Volume (ml)
Sample Cylinder #1	27.25
Sample Cylinder #2	27.71
Sample Cylinder #3	27.55
Sample Cylinder #4	27.01
Sampling Manifold	24.72
Valve 1 - Valve 2 Void	2.30
Test Canister #1 Containing Sample ID00173810CM1	638
Test Canister #3 Containing Sample ID00188110CM1	647
Test Canister #4 Containing Sample ID00141910CM1	637
Test Canister #5 Containing Sample ID00647210CM1	656

The pressure in each canister was monitored at random intervals over the 60-day test to detect gross changes in the atmosphere in each test canister due to chemical reaction of gases, or detect the presence of a leak in the canister. The pressure of each canister as a function of time is shown in Figure 1. Note that all canisters, with the exception of the control, show a steady decrease in pressure. This was not surprising as previous studies have shown that the canister environments containing organic systems become anoxic over time. Subsequent analysis verified removal of oxygen from the headspace.
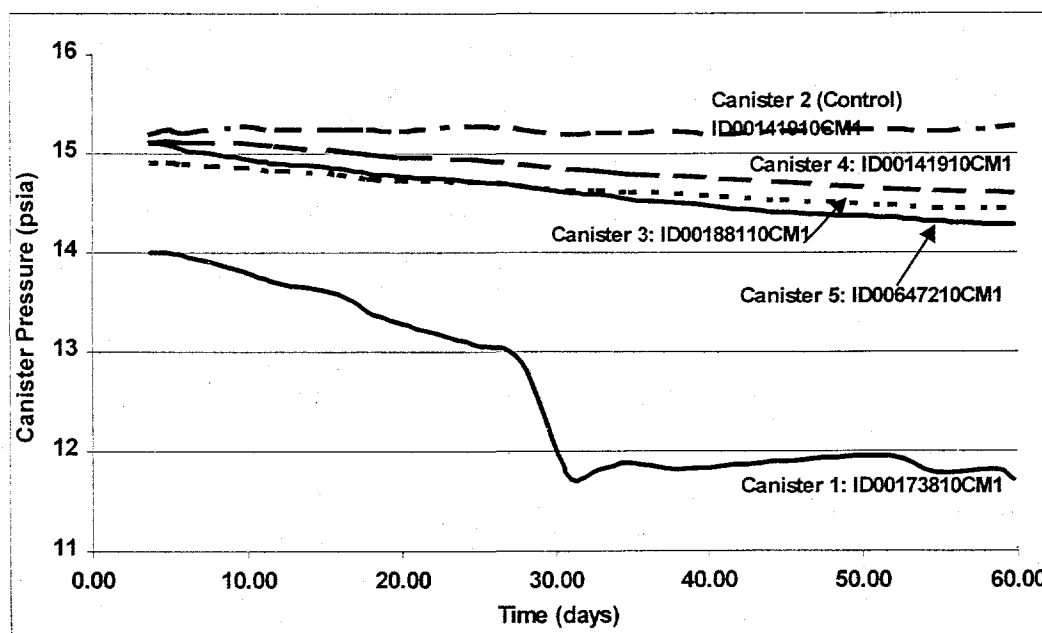

Figure 1. Test Canister Pressures During the 60-Day, 135 °F Test Period.

Examination of the pressure plot for canister 1 (sludge sample 1738) in Figure 1, shows a catastrophic failure in the seal of the test canister after approximately 30 days. It was hypothesized that the organic solvents in the headspace - namely carbon tetrachloride - dissolved a seal in the pressure transducer. The transducer response for the experiment control (canister 2) shows the pressure remained constant over the duration of the experiment at 15.25 psia. The pressure transducer response for test canisters 3, 4 and 5 indicated a steady decrease in pressure.

Helium, hydrogen, oxygen, carbon dioxide, nitrogen and methane were eluted from the column in order. The retention time and peak integration times are provided in Table IV for each gas. The separation between hydrogen and helium was approximately 0.3 minutes. Hydrogen can be effectively separated from helium provided that the concentration of helium is not large. However, there was a concern on the accuracy of the determination given the potential interference from helium. Figure 2 is a chromatogram that shows the separation of 100-ppm hydrogen and 1.5% helium in air. The hydrogen peak can be

Table IV. Chromatographic Retention Times and Integration Windows

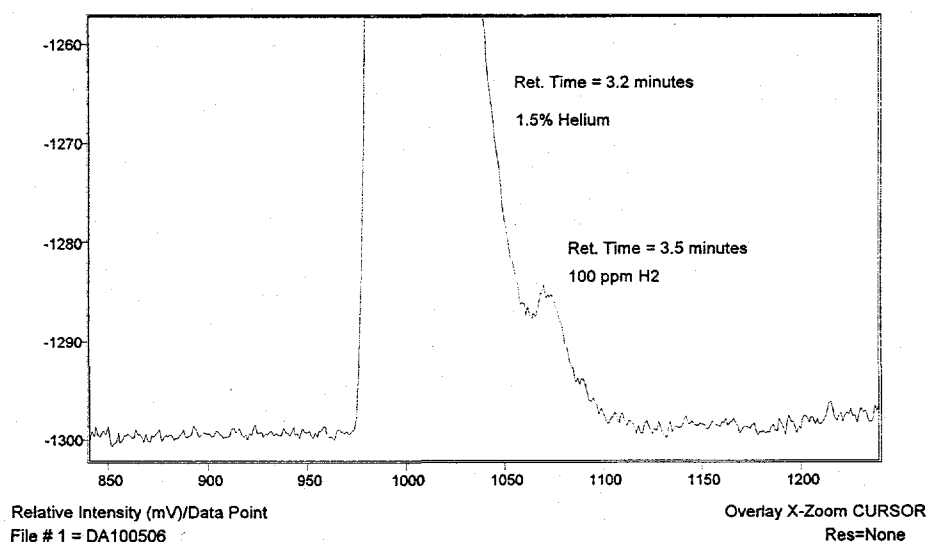| Compound	Retention Time (min)	Beginning Integration Time (min)	Ending Integration Time (min)
He	3.22	3.11	3.44
H2	3.50	3.40	3.74
O2	6.39	6.24	7.02
CO2	10.1	na	na
N2	13.6	13.8	14.9
CH4	17.1	16.9	17.6

Figure 2. Chromatogram for a Mixture of 100-ppm Hydrogen in the Presence of 1.5% He. Note: The Unit Associated with the Ordinate is Data Point Number. Data was Collected at 5 Hz.

observed on the tail of the helium peak. The helium interferes with the accurate integration of the area of the hydrogen peak. The resulting hydrogen concentration was estimated to be 30 ppm. The 100-ppm H_2 gas standard was blended with approximately 0.1% helium. A chromatogram showing the separation of 100-ppm H_2 from 0.1% He is shown in Figure 3. The concentration of hydrogen measured was 86± 4 ppm which was determined to be an acceptable recovery level. Therefore, the targeted residual helium concentration was determined to be 0.1%. The helium concentration in the headspace of each canister after the leak test was reduced by evacuating the canister to 6 psia and backfilling to 12 psia with Ulta-zero air. This process was repeated 10 times to reduce the He concentration below 0.1%.
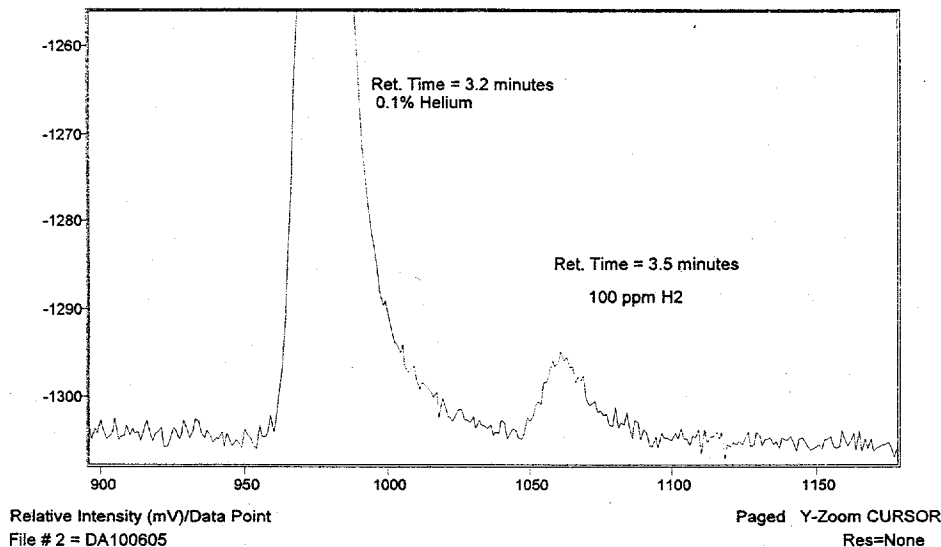

Figure 3. Chromatogram detailing the separation of 100-ppm H_2 from 0.1% He. Note: The Unit Associated with the Ordinate is Data Point Number. Data was Collected at 5 Hz.

Six measurements of the 25-ppm H_2 standard and seven measurements of the 100-ppm H_2 standard in air were measured on separate days. In addition a 199-ppm H_2 standard in argon was measured six times as an independent check of the calibration. The precision, as expressed as a percent relative standard deviation (%RSD), for the 25-ppm standard was 11% RSD. The relative standard deviation is synonymous with the coefficient of variation (6)and is expressed in terms of one standard deviation. The precision of the determination of the 100-ppm standard was also 11% RSD. The 199-ppm check standard was determined to be 200 ppm with a %RSD equal to 9%. The measured integrated peak areas for five determinations of the 199-ppm check standard have been superimposed on the calibration plot shown in Figure 2. The equation for the regression was Y = 1.41X + 1.05, where Y is the baseline corrected peak area that was corrected for variations in the sampling pressure (corrected to standard temperature and pressure, STP) and X is the hydrogen concentration in parts per million. The linear dynamic range of the calibration plot for hydrogen was checked by estimating the concentration of a 5.02% H_2 standard using the calibration data. The measured value was 5.01%.

The limit of detection (LOD) was calculated using three times the standard deviation of the low standard of the calibration plot, divided by the slope of the calibration plot as determined by a linear least squares regression fit. The LOD for hydrogen was determined from six measurements of the 25-ppm standard. The standard deviation from the six measurements was 3.9 area units. The slope was calculated using a linear regression from six measurements of a 25-ppm standard and five measurements of a 100-ppm standard and was equal to 1.41 and the LOD was estimated to be 9-ppm H_2.

The gas chromatographic response for methane was calibrated using a single point calibration. A 500-ppm methane standard in air was measured five times. The response was 0.564 corrected area units per part per million methane. The precision for the five measurements was approximately 5% RSD. A limit of detection was estimated for methane to be 70 ppm.

Recovery studies were performed with a 500-ppm methane gas standard prepared in a balance of air. An evacuated test canister was filled with the standard and sampled three times. The measured methane concentrations in the three samples were 570, 466, and 533 ppm respectively. The average recovery was calculated to be 523 ± 53 ppm. This is an equivalent recovery of 105%. Methane recoveries were acceptable with a %RSD of 10%. The linear dynamic range for the methane calibration was checked by measuring a standard containing 5% methane. The measured concentration was 6.2% and the expected concentration was 6.17%.

Oxygen and nitrogen were estimated using single point calibrations based on the measurement of an air standard. The slope of the response for oxygen was 2322 corrected area units per percent oxygen, where the area units were corrected to STP. Likewise, the response for nitrogen was 1894 corrected area units per percent nitrogen. The oxygen and nitrogen concentrations were estimated to be $20.9 \pm 0.2\%$ and $78.7 \pm 0.5\%$, respectively. Oxygen and nitrogen concentrations were within 1% of accepted values for air with a relative standard deviation less than 1%.

Gas samples were analyzed over a four month period using the above calibration data. A calibration check standard for hydrogen was measured with each set of samples to insure that the instrument response remained constant. The average concentration was 96 ± 6-ppm H_2.

The volume expansion measurement is dependent upon measuring the difference in pressure resulting from expanding the volume of a 700-ml canister (as an example that is representative of the canisters used in this experiment) into the gas sampling manifold and sample cylinder. The final volume of the manifold, sample cylinder and test canister was approximately 755 ml. The pressure change during sampling was approximately 1 to 1.5 psia. The manufacturers specification for the readout accuracy is 0.5% full scale or 0.1 psia for the pressure transducers with a full scale readout of 20 psia and 0.15 psia for the pressure transducers with a full scale readout of 30 psia. A rigorous calculation was performed to propagate the errors in the estimates for the pressure and volume of the components used in the gas expansion. The result of the calculation predicted the volume measurement for this experiment to be within 15%. For example, the volume in canister 4 that contained the sludge and jar was estimated to be 656 ± 95 cm^3.

The accuracy of the volume determination of the headspace was physically checked by comparing the volume of a canister that was measured with an independent gas expansion system that utilized a certified expansion volume calibrated to 0.1 ml and a NIST-certified pressure gage. The independent system measured the volume to be 699 ml. The volume measured by expansion into the 27-ml sample cylinder, manifold and void between valves resulted in an estimated volume equal to 706 ml. Thus the volume of the test canister measured with the respective pressure transducer was within 1% of the volume estimated using laboratory certified calibrated volume.

Error propagation calculations were performed to estimate the error in the number of molecules of hydrogen predicted in subsequent measurements. The total molecules of gas in the headspace can be calculated using the ideal gas law. Given that the volume of the canister is known to 15%, the canister pressure is known to 1%, and hydrogen can be measured at the 200-ppm level with an error of 10%, the estimated number of molecules of hydrogen can be predicted within 20%. Similarly, the error in energy deposition was known (typically to 8%) for consideration in subsequent g-value calculations. For example, for canister 4 the total number of molecules of hydrogen generated over the 60 day test was $4.64 \times 10^{18} \pm 8.07 \times 10^{17}$ (an error of 17%). The error in the alpha energy deposition was reported to be 8%. Thus, the reported G-values had an error of 18%. This magnitude of error was typical for the other canisters.

Residual helium remaining from the leak test was observed in all samples. Due to the similarities in the size and diffusion constants between He and H_2, the residual He signal can be used as a monitor of the leakage of H_2 from each test container. Chromatograms for the 0- and 60-day samples from canister 5 have been superimposed in Figure 4 and show the elution of helium and hydrogen. The chromatograms have a slight off set that is believed to be due to changes in the pressure of the samples. Notice, that the helium peak area remained constant over the 60-day test. The stability of the He peak was similar for the remaining canisters (with the exception of canister 1 that failed catastrophically) and for the remaining shorter duration tests. This confirmed that the integrity of the test containers was maintained throughout the duration of the testing and that the decrease in pressure was due only to the consumption of oxygen. The decrease in oxygen was clearly observed in the chromatogram for the O_2 peak (that eluted from the GC column at 6.5 minutes as shown in Figure 4). The stability of the helium signal and subsequent ingrowth of hydrogen is clearly shown in the chromatograms. It is speculated that the slight increase in helium was due to an initial adsorption of He into the sludge matrix (from leak testing) that slowly desorbed from the sludge into the atmosphere over the duration of the test. Helium was not detected in test canister 1 due to the leak that developed in the test canister.
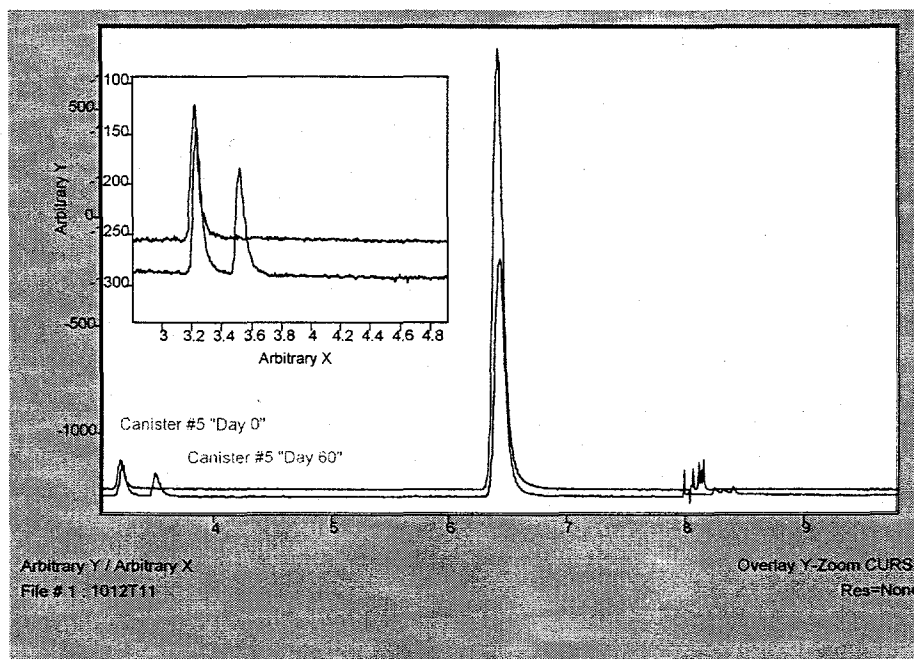

Figure 4. Overlay of Chromatograms from "Day 0" and "Day 60" Samples Obtained from Canister #5 (Inset shows Expanded He and H_2 Peaks). The Ordinate has Units of Minutes and the Abscissa has Units of Relative Intensity.

Qualitative FTIR spectra were obtained for the 0-day headspace gases after the helium leak test. All the samples contained the same components but in different concentrations. All contained large concentrations of carbon tetrachloride. Three of the four samples had a large concentration of 1,1,1-trichloroethane (TCA) in the headspace. The headspace in test canister 1, which later lost its seal, had a low concentration of TCA and was predominantly carbon tetrachloride. Of the remaining three test canisters, canister 4 had the highest concentration of C-Cl and C-F chemical bonds; while, Canisters 3 and 5 had headspace gases that had the most C-H bonds.

The concentration of hydrogen in canisters 3,4 and 5 was measured at Day 0 and Day 60. Duplicate samples were obtained from canisters 3 and 5. The concentrations of hydrogen, oxygen and nitrogen in each sample are shown in Table V. The hydrogen concentration of canisters 3, 4, and 5 was measured to be approximately 430, 340 and 1300 ppm, respectively. The quantities of hydrogen released from the IDC

003 sludge ranged tremendously from sample to sample. The difference in the rate of hydrogen accumulation in canister 5 is remarkably greater than in canisters 3 and 4. The minimum rate measured was approximately 6-ppm H_2 per day. The maximum rate was approximately 22-ppm H_2 per day. The corresponding G-values were calculated for the three samples and were found to be 2.5 ± 0.3, 4.8 ± 0.6 and 13.0 ± 1.7 molecules $H_2/100$ eV, respectively.

Table VI. 60-Day, 135 °F Results.

Gas	Day 0	Day 60
Canister 3 (Sample # ID00188110CM1)		
He (Area Units)	4035	4423
H2 (ppm)	0	430
O2 (%)	20.80	15.3
N2 (%)	79.20	80.8
Canister 4 (Sample # ID00141910CM1)		
He (Area Units)	2972	3831
H2 (ppm)	0	339
O2 (%)	20.80	14.8
N2 (%)	79.20	82.2
Canister 5 (Sample # ID00647210CM1)		
He (Area Units)	1854	2389
H2 (ppm)	0	1300
O2 (%)	20.80	12.7
N2 (%)	79.20	84.7

The concentration of oxygen in each canister was measured in the 0-day and 60-day samples. The concentration of oxygen in each canister decreased over the test period. Test canister number 5 had the largest decrease in oxygen, changing from 19% to 13%. The concentration of oxygen in test canister 3 changed from 20% to 16%. The concentration of oxygen in test canister 4 changed from 19% to 15%. The measured concentration of oxygen in each of the "Day 0" samples was less than 21%. This was potentially due to dilution of the headspace gases by volatile organic compounds that desorbed from the sludge and the analytical uncertainty of the oxygen measurement.

The concentration of nitrogen was measured to estimate the total composition of the gas in each canister. Nitrogen was measured in test canisters 3, 4 and 5 in the 60-day samples and was approximately 81%, 82% and 85% respectively. The percentage of nitrogen did not increase substantially though oxygen was depleted implying that other gases such as the organic solvents, carbon dioxide and carbon monoxide may have made up the balance of the gas in the headspace. Evaluation of the chromatograms indicated that the change in concentration of carbon dioxide was not detectable. Carbon monoxide was detected but not quantified. Methane was not detected in any of the samples by gas chromatography.

A test at 68°F (room temperature) for 25 days followed immediately after the 60-day test. After the VOC sample was obtained for FTIR analysis, each canister was backfilled with ambient air. Samples were taken at the new 0-day and 25-day for GC analyses. Results of the analyses are show in Table VI. For all canisters, the helium concentrations remained stable. Hydrogen increased in all canisters but at a rate much less than observed previously in the heated 60-day test; this was the first indication of a temperature dependent affect on the hydrogen measurement. As in the previous test, the hydrogen content in canister 5

increased the greatest: from 349 to 433 ppm. The corresponding G-values were calculated for canisters 3, 4 and 5 to be 1.8-, 1.2-, and 2.3- molecules $H_2/100\,eV$, respectively. The rate at which oxygen decreased in each canister was much less then observed in the previous 60-day test at 135°F, providing further indication of some type of temperature dependent affect on these systems.

Results from a 13 day test at 135 °F, that immediately followed the room temperature test, are shown in Table VII. The rates of hydrogen release from the sludge increased with respect to the previous room temperature test, but were not as high as measured in the initial 60-day test. The hydrogen increased from 196 to 288 ppm in canister 3, from 180 to 299 ppm in canister 4 and from 433 to 593 ppm in canister 5. The corresponding G-values were calculated for canisters 3, 4 and 5 to be 3.3-, 3.1-, and 5.4-molecules $H_2/100\,eV$, respectively. Similar to the previous tests, O_2 was consumed. The rate of oxygen consumption increased from that of the 25-day room temperature test to a rate that was equivalent to the initial 60-day 135 °F test. He remained constant.

Table VI. 25-Day, 68 °F Results.

Gas	Day 0	Day 25
Canister 3 (Sample # ID00188110CM1)		
He (Area Units)	1242	1261
H2 (ppm)	132	196
O2 (%)	20.02	19.60
N2 (%)	78.30	77.80
Canister 4 (Sample # ID00141910CM1)		
He (Area Units)	1172	1123
H2 (ppm)	116	180
O2 (%)	19.60	19.10
N2 (%)	79.10	78.00
Canister 5 (Sample # ID00647210CM1)		
He (Area Units)	610	592
H2 (ppm)	349	433
O2 (%)	19.40	18.70
N2 (%)	79.30	78.80

A final test was conducted at 135°F for an additional 9 days. Hydrogen increased in canister 3 from 288 to 390 ppm. The concentration of hydrogen in canister 4 increased from 299 to 341 ppm; in canister 5 hydrogen increased from 593 to 730 ppm. The G-values for canisters 3, 4 and 5 were 6.4-, 1.7-, and 8.1-molecules $H_2/100\,eV$, respectively. The results do not correlate well with the previous results obtained at 135°F. Oxygen decreased from 18.3% to 17.4% in canister 5, from 18.2% to 17.5% in canister 4 and from 18.8% to 18.2% in canister 3.

Rate data from the four sets of experiments is collected in Table VIII. In summary, hydrogen accumulation was much greater than expected and poorly correlated to energy deposition. Furthermore, the G-values ranged dramatically both within and between experiments. Finally, both hydrogen accumulation and oxygen consumption appeared to be temperature dependent, increasing at elevated temperatures. This affect indicates that more than simple real-time radiolysis was occurring in these experiments.

Table VII. 13-Day, 135 °F Results.

Gas	Day 0	Day 13
Canister 3 (Sample # ID00188110CM1)		
He (Area Units)	1261	1253
H2 (ppm)	196	288
O2 (%)	19.60	18.80
N2 (%)	77.80	79.00
Canister 4 (Sample # ID00141910CM1)		.
He (Area Units)	1123	1154
H2 (ppm)	180	299
O2 (%)	19.10	18.20
N2 (%)	78.00	79.00
Canister 5 (Sample # ID00647210CM1)		
He (Area Units)	592	665
H2 (ppm)	433	593
O2 (%)	18.70	18.30
N2 (%)	78.80	79.60

Table VIII. Summary of Hydrogen Generation Rates, Effective Hydrogen G-Values and Oxygen Consumption Rates.

Sample ID	Test Canister	1st 60 day 135 °F	2nd 25 day 68 °F	3rd 13 day 135 °F	4th 9 day 135 °F
Average Hydrogen Production Rates (molecules H_2 liberated to the headspace per day).					
ID00141910CM1	4	6.6×10^{16}	3.2×10^{16}	8.4×10^{16}	4.6×10^{16}
ID00188110CM1	3	8.6×10^{16}	3.2×10^{16}	5.9×10^{16}	1.2×10^{17}
ID00647210CM1	5	2.5×10^{17}	4.4×10^{16}	1.0×10^{17}	1.6×10^{17}
Hydrogen G-values (molecules H_2/100 eV sample absorbed dose).					
ID00141910CM1	4	2.4	1.2	3.1	1.7
ID00188110CM1	3	4.8	2.8	3.3	6.4
ID00647210CM1	5	13	2.3	5.4	8.1
Experiment-Average Oxygen Consumption Rates (molecules O_2 taken from headspace per day).					
ID00141910CM1	4	1.3×10^{19}	2.0×10^{18}	2.0×10^{19}	1.0×10^{19}
ID00188110CM1	3	1.3×10^{19}	1.3×10^{18}	2.0×10^{19}	9.6×10^{18}
ID00647210CM1	5	1.8×10^{19}	3.3×10^{18}	1.5×10^{19}	1.4×10^{19}

Because of the disparate and unexpected hydrogen G-values observed in the series of four experiments, incorrect activity concentration in the sludge samples was noted as the most checkable cause. All four

sample canisters (including the vented canister 1) were placed atop a well counter system for counting of the Am-241 59.7-keV gamma-ray. This exercise assumed similar geometry and attenuation effects across the group. No attempt was made to estimate actual activity concentrations. Rather, relative activity ratios were sought for comparison against relative activity ratios of the INTEC data. The results confirm that activity ratios are similar enough, despite geometry and attenuation effects, to confirm that the INTEC alpha spectroscopy data was accurate at least in relation between samples. Therefore, the wide range of G-values seen could not be attributed to incorrect activity concentration data.

One interesting correlation is shown in Figure 5, which plots the twelve G-values against the headspace carbon tetrachloride concentration which was quantified from the sample drawn from each canister at the end of the first experiment. The hollow triangle data are those from the room-temperature experiment (experiment 2, 68 °F), all solid diamond data points are from the 135 °F experiments. This plot may indicate a system that has a tendency (through as yet unknown mechanisms) to exhibit high G-values (recall Rocky Flats Plant work mentioned in Reference 1, in which IDC 003 drum scale work measured G-values of 15- and 22-molecules H_2/100eV). Further, the hydrogen produced may be scavenged by the presence of halogens (e.g., to form HCl). This effect may be specific to the species of halogenated compounds in the system. For instance, a analogous plot of G-values versus TCA concentration did not show a similar trend. Another possible inference may be that the higher carbon tetrachloride content may indicate lower Regal Oil content. Assuming the oil has some capacity to store and release hydrogen, the unexpected hydrogen accumulations at elevated temperatures may be due to the release of long stored hydrogen. This storage and release effect would be more pronounced for sludge with a higher oil content.
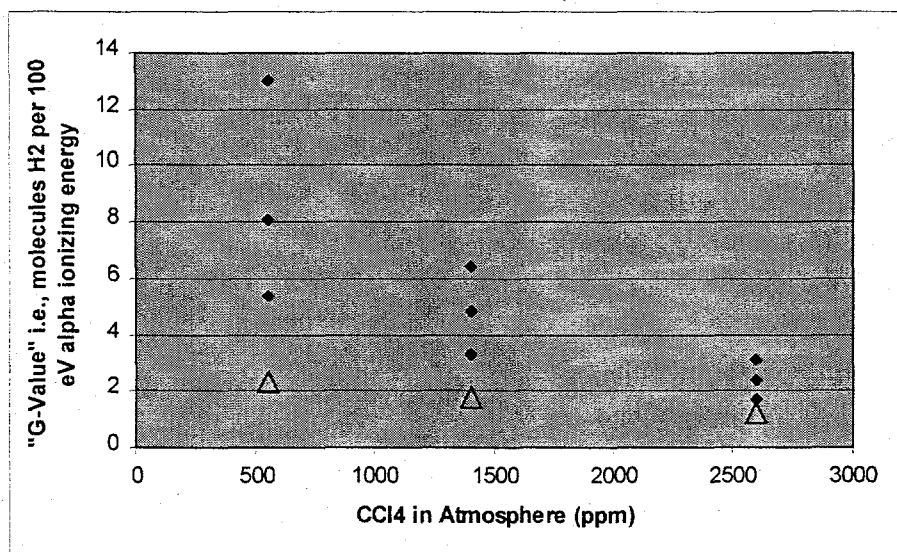

Figure 5. Correlation of G-Value with Carbon Tetrachloride Content. The Diamonds are for G-values Obtained at 135 °F. The Triangles Denote G-values Obtained at 68 °F.

Conclusions
The test containers and sampling system designed for the experiments described performed satisfactorily with the exception of one failed canister. Monitoring the concentration of residual helium in the canisters proved useful in assessing possible leakage from the canisters. No detectable change in helium was observed for four test canisters (three samples and one control) over the total 100-day testing period. The sampling and analysis system provided more than adequate sensitivity and precision to determine reliable G-values. The reported G-values had a precision better than 20% RSD. G-values could be assessed in a time period as short as 9 days for the 50-g samples of IDC 003 Organic Setup sludge.

The effective measured G-values exceeded those expected from radiolysis mechanisms. The average G-value (at 135 °F) for canister 3 was 4.8 ± 1.5-molecules $H_2/100$ eV. The average G-value for canister 4 was calculated to be 2.4 ± 0.7-molecules $H_2/100$ eV. The average value for canister 5 was 8.8 ± 3.9-molecules $H_2/100$ eV. The G-value pooled over all samples and 3 test series at 135 °F was 5.4 ± 3.5-molecules $H_2/100$ eV. The spread of G-values well exceeded the error in the determination. The high G-values are on the order of magnitude of those reported previously for this sludge type. While previous work suspected drum corrosion as a contributing factor to the previously observed high G-values (7), this work found indications of complex radiochemistry and/or questions pertaining to the solubility of hydrogen in the sludge. The temperature-dependent rates of oxygen consumption indicate the role of chemical reactions. The gas generation rates in all four experiments had larger spreads than can be attributed to the absorbed doses within the group. More to the point, the hydrogen generation rates and oxygen consumption rates have not corresponded to the measured alpha activity.

As the subsequent experiments generally did not produce hydrogen G-values greater than those measured in the first experiment, there seems to be some validation of a storage term effect. Certainly, the potential for the release of stored hydrogen upon initial heating may be a safety concern and should be monitored closely in any future work with IDC 003 sludge.

References

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