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TRUPACT-II Hydrogen G-Value Program Test Plan

Revision 0

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TRUPACT-II Hydrogen G-Value Program Test Plan

Revision 0

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ABSTRACT

This test plan describes the objectives, scope, participants, and components of the Transuranic Package Transporter-II (TRUPACT-II) Hydrogen G-Value Program (GH2P). The GH2P builds on the experience, results, and experimental setup of the TRUPACT-II Matrix Depletion Program (MDP) to establish effective hydrogen G-values (G-values) for additional waste matrices. This plan details the experimental design and test matrices for experiments to measure the G-value for additional waste matrices, including first- and second-stage sludges at the Idaho National Engineering and Environmental Laboratory, and molten salt extraction residues with varying amounts of residual moisture (i.e., unbound water). Data collected from the GH2P will be used to support an application to the U.S. Nuclear Regulatory Commission for G-values and corresponding wattage limits for the TRUPACT-II payloads containing these waste matrices. The testing will also evaluate the ability to determine G-values on a waste stream basis.

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ACRONYMS AND ABBREVIATIONS

ALARA	as low as reasonably achievable
ASME	American Society of Mechanical Engineers
CAO	Carlsbad Area Office
CBC	chemically bonded ceramics
CFR	*Code of Federal Regulations*
CH	contact-handled
DOE	U.S. Department of Energy
DQO	data quality objective
EPA	U.S. Environmental Protection Agency
GH2P	TRUPACT-II Hydrogen G-Value Program
GGTP	TRUPACT-II Gas Generation Test Program
IDC	item description code
INEEL	Idaho National Engineering and Environmental Laboratory
LANL	Los Alamos National Laboratory
MDP	TRUPACT-II Matrix Depletion Program
MS	mass spectrometer
MSE	molten salt extraction
NRC	U.S. Nuclear Regulatory Commission
PC	personal computer
PE	polyethylene
PVC	polyvinyl chloride
QA	quality assurance
QAO	quality assurance objective
QAPjP	*TRUPACT-II Hydrogen G-value Program Quality Assurance Project Plan* (LANL 1998b)
QAPP	*TRUPACT-II Hydrogen G-Value Program Quality Assurance Program Plan* (LANL 1998a)
QC	quality control
RFETS	Rocky Flats Environmental Technology Site
SARP	*Safety Analysis Report for the TRUPACT-II Shipping Package* (NRC Current Revision)
SOP	standard operating procedure
TARMATDEP	target matrix depletion model
Test Plan	*TRUPACT-II Hydrogen G-Value Program Test Plan*
TGA	thermogravimetric analysis
TRU	transuranic
TRUPACT-II	Transuranic Package Transporter-II
UCL_{95}	95% upper confidence limit
UTL_{95}	95% upper tolerance limit

1.0 HYDROGEN G-VALUE PROGRAM TEST PLAN

This *Transuranic Package Transporter-II (TRUPACT-II) Hydrogen G-Value Program Test Plan* (Test Plan) describes the experimental design and test matrices for the Hydrogen G-Value Program (GH2P). The GH2P builds on the experience, results, and experimental setup of the TRUPACT-II Matrix Depletion Program (MDP) (INEEL 1998) to establish effective hydrogen G-values (G-values) for additional waste matrices. Specifically, this plan provides the program objectives, scope, participants, and components. The plan details the integration of results from all components for the purpose of arriving at G-values for Idaho National Engineering and Environmental Laboratory (INEEL) first- and second-stage sludges (IDC001), and for Rocky Flats Environmental Management Site (RFETS) molten salt extraction (MSE) salt residues with varying amounts of residual moisture (i.e., unbound water). The experimentally determined G-values and corresponding wattage limits will be used in preparing an application for a revision to the *Safety Analysis Report for the TRUPACT-II Shipping Package* (SARP) (NRC Current Revision) for payloads containing these waste matrices. The testing will also evaluate the ability to determine G-values on a waste stream basis.

1.1 Background

A substantial fraction of the nation's inventory of contact-handled (CH) transuranic (TRU) waste cannot be shipped to the Waste Isolation Pilot Plant because it exceeds a wattage limit (from radioactive decay) imposed by the SARP to ensure that the hydrogen concentration in the drum does not exceed the lower flammability limit of 5% (by volume) in any layer of confinement (NRC Current Revision). From experimental and empirical results available prior to the MDP, it was known that matrix depletion decreases the rate of hydrogen gas generation inside CH TRU waste containers (Kazanjian 1976; Kosiewicz 1981; Zerwekh 1979; Zerwekh and Warren 1986; Zerwekh et al. 1993; and Smith et al. 1997). Matrix depletion is the reduction in the radiolytic gas generation potential, or effective G-value, of a target material. The MDP was established as a joint venture of the U.S. Department of Energy (DOE) National TRU Program and the DOE Mixed Waste Focus Area, with the objective of investigating the phenomenon of matrix depletion and arriving at dose-dependent G-values for CH TRU waste material types (INEEL 1998). The adoption of substantially lower G-values translates into higher allowable wattage limits. To confirm earlier reports of the dose dependency of G-values, the following three major elements comprised the MDP:

- Laboratory experiments for the assessment of G-value as a function of dose for several matrices and the effects of experimental conditions, including isotope and heating
- Measurements of G-values and hydrogen concentrations in actual waste and comparisons with MDP G-values
- Theoretical analyses using a numerical model that calculates G-value as a function of dose by explicitly incorporating fundamental nuclear and molecular mechanisms that result in the generation of hydrogen

Matrix depletion experiments were conducted at the Los Alamos National Laboratory (LANL). Envirostone was tested to determine a G-value for one type of waste material present in Waste Type I wastes. Polyethylene (PE) and polyvinyl chloride (PVC), the two most common packaging materials, were tested to establish a dose-dependent G-value for Waste Type II wastes. Wet and dry cellulose matrices were also tested to ensure that dose-dependent G-values would be obtained for all materials that have a high potential for radiolytic hydrogen gas generation and that may be present in Waste Type III wastes. The MDP was successful in quantifying the dose-dependent G-values for these materials.

The MDP testing focused on determining dose-dependent G-values for Waste Types II and III. However, the MDP did not establish a G-value for Waste Material Type I.2 (soils, solidified particulates, or sludges formed from precipitates). Based on evaluations at the INEEL, approximately 38% of the first- and second-stage sludge waste containers exceed the wattage limit for Waste

Material Type I.2 waste containers. The wattage limit for these containers is based on the G-value of water of 1.6 molecules and the assumption that the radionuclides are present in the form of particles such that the effective G-value is 1.3 molecules/100 eV (0.82 x 1.6 molecules/100 eV).

The feed solution from which the sludge is formed may contain up to 1 ppm Pu and up to 4,000 ppm U. The sludge produced by the waste treatment process contains about 20 ppm Pu and up to 80,000 ppm U. Both Pu and U are co-precipitated with $Fe(OH)_3$. The large range of uranium concentration in the sludge may affect the potential for hydrogen generation from this material. Therefore, the G-value of the INEEL sludge will be evaluated in both the presence and absence of uranium in the simulated feed solution.

Sampling of RFETS MSE salt residues in containers that have been in storage at the RFETS has indicated that some salts have absorbed environmental moisture at up to 10.5 weight percent unbound water. Because radiolysis of the unbound water may generate hydrogen, the G-value for these salt waste matrices will be quantified as part of the GH2P.

Americium (Am-241) is a major constituent in both the sludge and salt residue waste matrices. Although this isotope has nuclear properties (half-life, decay modes), different from either Pu-238 or Pu-239, Am-241 will not be included in the simulated GH2P waste matrices for the following reasons:

- MDP testing showed that there was no statistically significant difference in the G-values for waste materials containing Pu-238 (5.5. MeV) or Pu-239 (5.2 MeV). This indicates that neither the small-energy difference, nor the large difference in specific activities for these two isotopes affects the G-value. The Am-241 alpha particles have energy of 5.5 MeV and, thus, are not significantly different than the energy of alpha particles of Pu-238. Any specific activity of Am-241 is intermediate between that of Pu-238 and Pu-239.

- The decay Am-241 differs from that of Pu-238 and Pu-239 in that ~35 percent of its decays by alpha emission are accompanied by a 0.060-MeV gamma emission. However, the amount of hydrogen generated by gamma emission is negligible. The linear energy deposition (eV absorbed per cm) for a 0.060-MeV gamma is about 12 percent of that of a 5.5-MeV alpha particle. A significant fraction of the 0.060-MeV gammas are not absorbed in the waste matrix and will escape without resulting in any hydrogen generation. Even assuming a total absorption of 5.5 MeV and its accompanying 0.060-MeV gamma results in an negligible ~1-percent increase in the total absorbed energy dose.

A number of investigators have performed radiolysis experiments of solidified aqueous wastes (e.g., sludges, concretes, and gel-like or monolithic structures) that contain varying amounts of residual moisture. In general, the presence of nitrates in sludges decreases the rate of radiolytic hydrogen generation. Decreasing the water content of the sludge decreases the rate of gas generation. Bibler (Appendix 3.6.8; NRC Current Revision) conducted a series of experiments to study alpha radiolysis of CH TRU wastes immobilized in concrete, especially incinerator ash. Drying the concrete at 200°C reduced the water contet from 35 to 7.4%, with a reduction in the G-value from 0.38 to 0.0002 molecule/100 eV. The water remaining was thought to be involved in hydration reactions and not easily degraded. Zagorski (Appendix 3.6.8; NRC Current Revision) observed very low G-values from irradiation of water present as hydrate in crystals. The water in the hydrates appears to exhibit the property of an energy sink. This has been attributed to the presence of a hydrated electron that can absorb energy by changing its state. Zagorski found that irradiation of $KOH \cdot 0.5H_2O$ did not produce any hydrogen, oxygen, or hydrogen peroxide.

More recently, radiolytic gas generation measurements were performed on acid-base cements (also called chemically bonded ceramics [CBC]) that contained Pu-containing residues and various amounts of water ranging from 18 to 23 weight percent (Barber 1998). The testing demonstrated that there was no hydrogen production below 16 weight percent added water (i.e., the reaction stoichiometry proportion). Statistical analyses indicated that the G-value is linear with weight

percent water added in excess of stoichiometric requirements. The G-value increased by 0.024 molecule/100 eV for each weight percent of added water (relative to final monolith mass) in excess of stoichiometric requirements.

1.2 Objectives

The GH2P builds upon the experience, results, and experimental setup of the MDP to establish G-values for additional waste matrices. The GH2P has two primary objectives:

- Establish a mean G-value and associated statistics for simulated INEEL first- and second-stage sludges
- Establish mean G-values for simulated RFETS MSE salt residues at three levels of residual moisture content (i.e., 0, 5, and 11% unbound water)

Secondary objectives of the GH2P testing are:

- Evaluate whether the presence and interactions of uranium in the feed solution effect the G-value for simulated INEEL first- and second-stage sludges
- Establish a relationship for simulated RFETS MSE salt residue G-value as a function of residual moisture content (i.e., unbound water)

The *TRUPACT-II Hydrogen G-Value Program Quality Assurance Program Plan* (QAPP) (LANL 1998a) defines the quality assurance (QA) objectives (QAOs) associated with these experiments in terms of precision, accuracy, representativeness, completeness, and comparability. The QAPP also discusses sampling and analysis procedures that are to be used to meet the QAOs set for the program.

1.3 Activities

The following key activities will be undertaken under the GH2P:

- Preparation of GH2P simulated test matrices - Test matrices described in this plan will be prepared in accordance with procedures prepared for the program. All plutonium operations will be performed in a glove box to contain the plutonium and ascribe to as low as reasonably achievable (ALARA) guidelines
- GH2P sampling and data collection - Sampling and data collection will be performed using the experimental apparatus and equipment developed for the MDP (Connolly et al. 1997)
- Data validation and reduction to determine the G-value for each test cylinder at each sampling cycle.
- Statistical analyses will be performed to determine the mean G-value, the standard deviation of the G-value, the standard error of the mean, the 95% upper confidence limit (UCL_{95}) of the mean G-value, the 95^{th} percentile G-value, and the 95% upper tolerance limit (UTL_{95}) for each waste matrix tested.
- Model predictions of G-values for the test matrices - The target matrix depletion model (TARMATDEP), a computer model developed under the MDP, will be enhanced to analyze radiolytic gas generation from matrices tested under the GH2P.
- Coordination and interfacing with other transportation and gas generation initiatives - During the duration of the GH2P, participants will interface extensively with each other, as well as with participants in other TRU transportation program initiatives. GH2P personnel will participate in meetings on TRUPACT-II transportation initiatives, including the annual TRUPACT-II Gas Generation Test Program (GGTP) meeting.

- Preparation of GH2P documents to support an application to the NRC - Documents will be prepared, reviewed, and approved for the GH2P (specific documents are documented in Section 3.0 of this test plan).

The following decision points will be incorporated in the GH2P experiments:

- The G-value for each test cylinder at each sampling cycle will be evaluated to identify outlier values and anomalous behavior. A meeting of Program participants will be convened to develop a path forward for anomalous data.
- The mean G-value and associated statistics will be derived for each waste matrix after 20 sampling cycles. The data will be evaluated for adequacy, and a decision will be made at that time to either terminate or continue testing, or to evaluate additional waste matrices.
- A leaking cylinder will be removed from the test rack, and the fittings and valves either will be repaired or replaced. The cylinder will then be replaced on the test rack and testing will continue on that cylinder.

2.0 PROGRAM PARTICIPANTS AND RESPONSIBILITIES

The participants in the GH2P are the DOE Carlsbad Area Office (CAO), where overall program management will take place; the INEEL and the RFETS, the two sites with the waste in question; and LANL, the DOE site that will perform sampling, analytical, experimental, and modeling analyses. The following sections provide a breakdown of the responsibilities.

2.1 Carlsbad Area Office

CAO is responsible for the overall management of the GH2P, as well as funding of this program. CAO is also responsible for performing audits of GH2P activities at LANL. The National TRU Program manager at CAO will review and approve program documents, including this test plan. The National TRU Program manager is also responsible for preparation of TRUPACT-II SARP amendment applications.

2.2 Idaho National Engineering and Environmental Laboratory and the Rocky Flats Environmental Technology Site

The INEEL site has containers of the sludge matrix that will be simulated in the GH2P testing. RFETS is the DOE site with containers of the MSE salt residues that will be simulated. The specific responsibilities of the two sites include the following:

- Providing the appropriate recipes for the simulated waste matrices to be tested
- Reviewing all data, reports, and other documents resulting from the GH2P
- Participating in discussions with the GH2P coordinator at LANL to help resolve technical issues and assist in determining future research needs

2.3 Los Alamos National Laboratory

The GH2P coordinator, located at LANL, is responsible for providing technical direction and coordination for the GH2P. The GH2P coordinator reports to the manager of packaging and transportation at CAO. GH2P coordinator responsibilities include the following:

- Reviewing all data, reports, and other documents resulting from the GH2P
- Periodically assessing the status of the GH2P, including QA Program implementation
- Resolving technical issues
- Determining the future direction of the GH2P
- Forwarding recommendations and conclusions to CAO, as necessary
- Preparing the simulated waste matrices
- Conducting GH2 testing of the test matrices and data collection
- Performing data validation, reduction, and statistical determinations of the effective GH2 values for the test matrices
- Developing and applying predictive computer models of the hydrogen generation process at the microscopic level
- Developing a justification to submit to the NRC for revising TRUPACT-II wattage limits
- Preparing documentation to support an application to the NRC for revised TRUPACT-II wattage limits

- Coordinating and interfacing with other transportation and gas generation initiatives

3.0 PROGRAM DOCUMENTS

The GH2P activities will implement this test plan and comply with requirements of various documents, which are described in Sections 3.1 through 3.3 of this test plan. These documents include this test plan, the *GH2P Quality Assurance Program Plan* (LANL 1998a), the *GH2P Quality Assurance Project Plan* (LANL 1998b), and various site-specific implementing procedures.

3.1 TRUPACT-II Hydrogen G-Value Program Test Plan

This test plan will provide the technical basis for the GH2P in terms of its objectives. Specifically, this test plan establishes the scope of the GH2P; defines the different components of the GH2P and the relationship between these components; describes the selection of the parameters and design for the experiments; and documents the integration of results of the different components to arrive at data to support an application for revised G-values for use in the SARP.

3.2 GH2P Quality Assurance Program Plan

GH2P activities will be conducted under the requirements of an approved QAPP (LANL 1998a). The QAPP includes the performance-based QA/QC requirements that must be met by LANL. The GH2P QAPP, with respect to waste parameters that must be characterized, analytical methods, calibrations, and administrative QC measures, is identical to the *TRUPACT-II Matrix Depletion Program Quality Assurance Program Plan* (QAPP) (INEEL 1997). LANL will develop and implement work instructions (e.g., standard operating procedures [SOPs]) for quality-related activities. These work instructions will be approved, distributed, and controlled in accordance with the requirements detailed in the QAPP (LANL 1998a).

The QAPP satisfies the requirements of the *Transuranic Waste Characterization Quality Assurance Program Document* (DOE Current Revision), which includes all the requirements of 10 CFR §830.120. Because DOE facilities are managing the nuclear materials contained in TRU waste, the QAPP also addresses applicable quality elements in the American Society of Mechanical Engineers (ASME) *Quality Assurance Program Requirements for Nuclear Facility Applications* (ASME 1989).

3.3 GH2P Quality Assurance Project Plan

LANL will conduct hydrogen gas G-value experiments in accordance with the QA/QC requirements in the *TRUPACT-II Hydrogen G-Value Program Quality Assurance Project Plan* (QAPjP) (LANL 1998b). The QAPjP is based on the QAPjP that was prepared for MDP testing at LANL (LANL 1998c). The QAPjP provides the requirements for performing the G-value experiments and references site-specific SOPs that detail the implementation of the experiments.

4.0 HYDROGEN G-VALUE PROGRAM

The GH2P will be implemented by the LANL to evaluate G-values for INEEL first- and second-stage sludges, and for MSE pyrochemical salts with varying amounts of residual moisture content. The results of the program will support an application to the NRC for TRUPACT-II wattage limits for the waste matrices tested.

The GH2P will include 10 stainless steel test cylinders that are , filled with either simulated first- or second-stage sludge or simulated MSE salts with varying residual moisture content. The matrices will be impregnated with a Pu-239 radioactive source material to determine G-values.

Water that is added to the matrices may be present in several different forms that range from free water molecules to water molecules loosely bound by surface charges, to water molecules tightly bound within crystal lattices. In general, the tendency for a water molecule to be affected by radiolysis is some inverse function of the strength of the bond that holds the water molecule in place. The water molecules bound to these various minerals have distinct bond energies and, as such, will react differently in a radiation field.

A standard technique for identifying the relative distribution of bond energies of water molecules in a sample containing hydrated minerals is thermogravimetric analysis (TGA). TGA monitors the change in the mass of a sample as a function of temperature or time while the sample is subjected to a controlled temperature program. As a sample is slowly heated from room temperature, free water will be gradually lost, resulting in a decrease in sample weight, which is continuously monitored by a balance. All free water will be lost when the boiling point of the water reaches near 100°C. Bound water will be lost at higher temperatures corresponding to the strength of the bonds. A plot of sample mass (y-axis) versus temperature (x-axis) will show a series of inflection points and plateaus if multiple hydrated minerals are present. The amount of water lost at each step is quantified by the decrease in weight.

TGA will be performed on a cold sample (i.e. without radioactivity) of each waste matrix tested to determine the distribution of bound and unbound water. G-value results can then be evaluated to determine whether G-values correlate most closely with free water, free plus partially bound water, or total water.

Testing will be conducted for a total of 20 sampling cycles. Appendix A provides the justification for the required number of cycles. Gas samples will be withdrawn from the test cylinders every day, initially decreasing in frequency to no less than one sample every 10 days. G-values will be determined for each cylinder at each sampling cycle.

Sections 4.1 through 4.3 present detailed information regarding the actual GH2P experimental procedure. Emphasis is placed on a discussion of the test matrix (breakdown of the cylinder inventory and preparation of the simulated waste matrices), test apparatus, test methodology, QA, and records management and data reporting. The QAPP (LANL 1998a) presents further details concerning the DQOs and test methodology, and separate SOPs present details concerning the GH2P.

4.1 Test Matrix

4.1.1 Preparation of Simulated Sludge

Four test cylinders containing simulated INEEL sludge will be prepared. Two cylinders will include both uranium and plutonium in the sludge and two will have only plutonium. The following recipe for the preparation of simulated first- and second-stage sludges is derived from information provided by the INEEL and RFETS. The simulated feed stream solution approximates that composition of the waste stream to be treated.

Simulated Feed Stream Solution Recipe

1. The target concentration of PuO_2 in the feed solution is 0.001 g/l in a solution that is approximately 0.5 to 1.0 M HNO_3. The amount of uranium in the feed solution will be at least 20 times greater (i.e., at least 0.02 g/L). The necessary amount of plutonium oxide and uranium will be dissolved in concentrated nitric acid and 0.1 M HF. The solution will be diluted to 1M HNO_3.

2. The compounds listed in Table 4-1 will be added to one liter of the feed stream solution to simulate the presence of other materials in the feed stream.

Table 4-1. Compounds added to the simulated feed stream solution.

Compound	Chemical Formula	Mass	Comment
Sodium Nitrate	$NaNO_3$	49 g	From INEEL recipe
Potassium Nitrate	KNO_3	18 g	From INEEL recipe
Aluminum Nitrate	$Al(NO_3)_3*9H_2O$	28 g	From INEEL recipe
Sand		0.4 g	From INEEL recipe
Activated Carbon		0.1g	From INEEL recipe

Simulated Treatment Solutions Recipes

From data supplied by the RFETS, the reagents listed in Table 4-2 will be used to prepare simulated treatment solutions that were used to treat the waste feed stream.

Table 4-2. Reagents in simulated treatment solutions.

Compound	Chemical Formula	Concentration	Comment
Magnesium sulfate solution	$MgSO_4*7H_2O$	103 g/L	
Calcium chloride solution	$CaCl_2*2H_2O$	219 g/L	
Ferric sulfate solution	$Fe_2(SO_4)_3*9H_2O$	150 g/L	
Sodium hydroxide solution	NaOH	50% weight % (19N [Normal])	
Flocculent	Dow Purifloc A-23	0.5 g/L	May have to find an equivalent substitute (such as Betz Polymer 1110)
Trisodium phosphate solution	$Na_3PO_4*12H_2O$	0.1 g/L	From INEEL recipe

Addition of Simulated Treatment Solutions to Simulated Feed Stream Solution

To one liter of the simulated feed stream solution (from the RFETS procedure) the following sequence of activities will be carried out:

1. Addition of 33 ml of the magnesium sulfate solution
2. Addition of 33 ml of the calcium chloride solution
3. Addition of 50 ml of the ferric sulfate solution
4. Mixing for 5 minutes
5. Addition of 2.6 g of diatomaceous earth (SiO_2) to simulate the use of this material as a filtration aid on the filter wheel
6. Slow addition of 100 ml of the trisodium phosphate solution while stirring vigorously to simulate the presence of phosphates in the feed solution. It should be noted that the procedure received from the INEEL indicated that trisodium phosphate should be added at this point in the procedure rather than earlier in the preparation of the feed solution (presumably to prevent "premature precipitation" by the addition of the basic trisodium phosphate solution.) Alternatively, it might be possible to simulate presence of phosphates in the acidic feed solution by addition as phosphoric acid rather than as trisodium phosphate.
7. Continuation of stirring and the precipitation through the addition of sodium hydroxide until the pH of the suspension reaches 11 (as measured by pH indicator strips). This may require about 15 ml of the NaOH solution.
8. Continuation of stirring and completion of precipitation through the slow addition of 6 ml of the Purifloc A-23 solution. At least one hour will be allotted for the precipitation to be complete (with occasional stirring) before proceeding to the filtration step.
9. Filtration of the precipitate cake (sludge) from the solution using Buchner funnel vacuum filtration system with 25-micron filter paper. The precipitate cake will be removed from the filter paper, and the precipitate will be loaded into a test cylinder. The supernate will be retained for quantitative analysis of unprecipitated Pu and U and estimation of Pu in the sludge by difference.

The water content of the resulting sludge will be measured using sludges prepared as above, but without any Pu or U. These "cold" sludges will then be dried in an oven and the water content determined by weight loss.

4.1.2 Preparation of Simulated MSE Salts

The intent of the test is to measure hydrogen generation rate from the worst-case salt insofar as hydrogen generation is concerned. The salts in question are mixtures of NaCl, KCl and MgCl2. The nominal salt composition is equimolar amounts of NaCl and KCl plus 30 mole % $MgCl_2$. The salt residues typically contain about 10% Pu. As part of the GH2P duplicate test cylinders will be prepared containing simulated MSE salt residues with 0, 5, and 11% added water, for a total of six test cylinders (see Table 4-3). It should be noted that the proposed waste matrix , which is based on mechanical mixing of the salts, does not simulate the pyrochemical process that results in the final RFETS MSE salt residues, but rather a worse-case waste matrix that will maximize the contact of plutonium with water and, thus, maximize radiolysis.

Table 4-3. Matrix of MSE salt test cylinders.

Mass Percent Unbound Water	Number of Test Cylinders
0%	2
5%	2
11%	2
Total	**6**

Hydrogen can be generated by radiolysis of water that may be present in the salt matrix. Water can be present in the salts in two forms. It may be present in the crystal structure of the salt as chemically bound water. While the crystal structures of neither NaCl or KCl include water, $MgCl_2$ is known to have a hexahydrate form. There is no information as to the extent of the occurrence of $MgCl_2 \cdot 6H_2O$ in the salt residues. Other workers have shown that water incorporated into the crystalline structure of a material are not very susceptible to hydrogen generation by radiolysis.

Water can also be present simply as absorbed water on the surfaces of the salt crystals or within pores. The source of this water is most likely atmospheric water vapor. The results of analyses suggest that the amount of absorbed water is typically less than 1% but values as high as 10.5% have been measured. The expectation, based on reports in the literature, is that this form of water is more susceptible to hydrogen generation by radiolysis.

Therefore, the worst-case salt insofar as hydrogen generation is concerned is one that contains the hexahydrate form of $MgCl_2$ and has up to 11% residual moisture (i.e., unbound water). The following recipe for the preparation of Pu-spiked pyrochemical salt residues was developed in collaboration with RFETS personnel.

1. Dissolve 1 gram of PuO_2 in concentrated nitric acid and 0.1 M HF. Keep solution volume at a minimum (<10 ml).
2. To a small glass beaker, add 2.5 g NaCl (0.043 mole), 3.2 g KCl (0.043 mole) and 4.3 g $MgCl_2$ (0.045 mole).
3. Add the Pu solution to the salt mixture and mix thoroughly.
4. If necessary, add deionized water in small increments until a fully wetted salt slurry is achieved.
5. Evaporate excess water by placing the beakers in 103 to 105°C oven. Continue evaporation until weight loss of subsequent weightings is less than 1%. This mixture simulates a Pu-containing salt residue with all of the $MgCl^2$ in the hydrated form with no absorbed water. (NOTE: the Merck Index indicates that the hexahydrate form of $MgCl_2$ is deliquescent and will lose two waters of hydration upon heating at 100 °C, and at 110°C will begin to lose some chlorine as it becomes converted to an oxychloride.)
6. Samples of simulated salt residues containing 5 and 11% residual moisture content (i.e., unbound water) can be prepared by spraying 0.5 and 1.1 ml of water onto 9.5- and 8.90-gram salt samples, respectively, prepared as described above. Mix salt with a stirring rod to aid in the distribution of water onto salt surfaces.
7. The salt will then be transferred to small glass vials and closed with screw caps containing a septum. The septa will be of a material that will keep the moisture content of the salt within the vial constant, yet permit hydrogen to pass into the test cylinder for sampling. Candidate materials for septa that will pass hydrogen are rubber, silicone, Teflon, and tedlar.

4.2 Test Apparatus

Two components comprise the apparatus for conducting the G-value determination, which is the same as used for the MDP: (a) a series of 1-L test cylinders that is designed to contain the test

matrix of interest and that has been contaminated with sufficient quantities of a plutonium source material to cause breakdown of the matrix by radiolysis; and (b) a series of valves, tubing, and measurement apparatus that is designed to sample the generated gases and quantitatively measuring the constituents.

The test cylinders will be placed in support racks that are mounted firmly on the floor. The entire apparatus will be controlled by a single IBM-compatible personal computer (PC) through LabVIEW software. The PC will be configured as a server to allow full remote access by other selected PCs. The system will be set up to provide alert messages via electronic mail if over-pressure or other system faults requiring immediate attention occur. This software/hardware configuration has already been developed, installed, tested, and documented as part of the MDP.

4.3 Test Methodology

The sampling and analysis phase will begin after the test preparation and setup phase, and is planned to be conducted for at least 20 sampling cycles. During the duration of the testing, gas samples will be withdrawn from the test cylinders every day, initially decreasing in frequency to no less than one sample every 10 days. Three replicates of the flammable gas (i.e., hydrogen) concentration within each test cylinder at each sampling period will be collected. The final replicate concentration will be used in calculations of the G-value.

4.4 Quality Assurance

The following measurements will be made:

- Absolute pressure measurements in each test cylinder at each sampling episode before and after withdrawing a gas sample to determine concentration. The pressure will be monitored in each test cylinder for safety purposes. Pressure measurements before and after gas sample withdrawal are needed to quantify the number of moles of gas taken from the test cylinder for sampling to calculate the G-value
- Temperature measurements at each sampling episode for use in calculating the G-value
- Concentration measurements of hydrogen, oxygen, argon, and/or nitrogen within each test cylinder at each sampling episode using a gas chromatograph. Hydrogen and oxygen concentrations will be established periodically using a mass spectrometer. This information will be used in calculating the G-values, validating gas chromatography results, and supporting mass balance and cylinder leakage evaluations
- Void volume estimations within each test cylinder after placement of the target and radioactive source materials to calculate the effective G-value
- Radioactive source material measurements to establish for each test cylinder the mass of radioactive source material and its isotopic ratio to calculate the effective G-value

The QAPP for the GH2P will define the QAOs associated with these experiments in terms of precision, accuracy, representativeness, completeness, and comparability. Sampling and analysis procedures will also be discussed in the QAPP and will meet the QAOs set for the program. Specific QA measures will also be followed for sample custody, calibration of equipment, data reporting, and data reduction.

4.5 Records Management and Data Reporting

Sample data from the analysis will be stored on the computer hard disk immediately following data acquisition. The ambient temperature and pressure will be recorded and backed up on a network server. A meeting will be convened periodically to analyze the data and investigate any discrepancies or deficiencies within the data. Samples will be analyzed by gas chromatography. Verification samples will be analyzed by mass spectrometry. If the two sets differ by more than the expected error, the discrepancy will be investigated immediately. All records will be filed at the Records Management Document Control.

5.0 DATA MANAGEMENT AND ANALYSIS

Data management and analysis involves several key elements. First, data obtained in each portion of the GH2P must be validated to ensure that QA requirements have been met and that the data are suitable for use in the GH2P. Second, individual G-values must be calculated from raw data collected in the G-value experiments. Third, the individual G-values must be summarized appropriately to formulate G-value statistics for each test matrix. Fourth, the experimentally derived G-values will be compared to available actual drum measurements and the results of predictive modeling using the TARMATDEP computer code.

5.1 Data Validation

Data collected from the LANL experimental apparatus must be validated prior to data reduction. Data validation for the GH2P must be performed in accordance with QAPP (LANL 1998a) and as further explained in the QAPjP (LANL 1998b).

5.2 Data Reduction

Data collected in the experiments will be reduced to derive G-values for each test matrix. This first involves calculating G-values for each sampling cycle and test cylinder. Second, individual G-values will be analyzed and used to derive mean G-values and associated statistics for each test matrix. The following paragraphs discuss these data reduction steps.

The G-value will be calculated for each cylinder and each cycle using the measured hydrogen concentration from each sampling cycle:

(5-1)

where

G_i	=	G-value of target waste matrix at sampling period ***i*** (molecules/100 eV)
$)n$	=	moles of hydrogen generated during the time period t_{i-1} and t_i (mole)
N_A	=	Avogadro's number (6.022045×10^{23} molecules/mol)
m	=	mass of radioactive source material (g)
k	=	conversion factor ($1 \text{ eV}/1.602 \times 10^{-19}$ Ws)
$)t$	=	$t_i - t_{i-1}$ = elapsed time between successive sampling periods (s)
DH_{avg}	=	average decay heat of the Pu-239 radioactive source material. Because the Pu-239 radioactive source material is a blend of plutonium isotopes, an average decay heat for the blend must be estimated based on assay results. Specifically, the average decay heat for the radioactive source material isotopic blend will be calculated as follows:

(5-2)

where

$f_{M,Pu-i}$ = mass fraction of plutonium isotope ***i*** in the radioactive source material

DH_{Pu-i} = decay heat of plutonium isotope ***i*** in the radioactive source material (W/g).

Table 5-1 lists the characteristics of the Pu-239 radioactive source material.

Table 5-1. Characteristics of the Pu-239 radioactive source material.

Plutonium Isotope	Decay Heat (W/g)	Mass Fraction Isotope in Source Material
Pu-238	5.73×10^{-1}	0.000154
Pu-239	1.95×10^{-3}	0.937605
Pu-240	7.16×10^{-3}	0.059445
Pu-241	3.31×10^{-3}	0.002237
Pu-242	1.17×10^{-4}	0.000559
Totals	**$DH_{avg} = 2.35 \times 10^{-1}$**	**1.000000**

Various G-value statistics will be derived from the G-value for each waste matrix. These statistics will include the number of observations, the mean G-value, the standard deviation of the G-value, the standard error of the mean, the UCL_{95} of the mean G-value, the 95th percentile G-value, and the UTL_{95}. For each waste matrix, the UCL_{95} of the mean G-value will be calculated as follows:

(5-3)

where

$t_{\alpha,n-1}$ = the 95th percentile for a t distribution with ***n-1*** degrees of freedom

n = the number of G-value observations for the waste matrix being examined

s and x = the associated standard deviation and mean.

The standard deviation and mean are estimated as follows:

(5-4)

and

(5-5)

respectively, where x_i is the ith calculated G-value and i is an index from 1 to n.

The statistical tests described above are based on the assumption that the observed G-values for each matrix are normally distributed. All G-values for waste matrices tested under the MDP were normally distributed. In the unlikely event that G-values for the waste matrices that will be tested under the GH2P are not normally distributed, a transformation that results in a normal distribution will be necessary. Standard statistical textbooks may be consulted for transformations and tests of normality. If a transformation is required, the calculations described above will be performed using transformed G-values.

For each test matrix, the UTL_{95} will be calculated as follows (U.S. Environmental Protection Agency [EPA] 1989):

(5-6)

where

K = one-sided normal tolerance factor that is a function of the desired percent coverage (i.e., 95%), the desired tolerance coefficient (i.e., 95%), and the number of samples. Appendix B provides a look-up table of appropriate K values.

5.3 Comparisons with Actual Waste Drums and Theoretical Predictions

The experimentally determined G-values will be compared to available actual drum measurements. Actual drum measurements are being performed as part of the GGTP at the INEEL and the RFETS (Westinghouse 1995, 1996). The GGTP testing procedure is described conceptually in Appendix 1.3.7 of the SARP (NRC Current Revision). The GGTP consists of performing controlled tests with actual containers of CH TRU waste to quantify the gas generation properties of the waste under simulated transportation conditions. Whether or not containers of CH TRU waste are tested is based on their hydrogen gas generation potential. Containers of CH TRU waste that can be shipped without the need for testing are qualified for shipment based on set decay heat limits determined from theoretical worst-case calculations, as required by the TRUPACT-II SARP (NRC Current Revision).

In addition to actual waste drum measurements, the GH2P will include theoretical analyses using the TARMATDEP code to evaluate whether theoretical predictions yield results that are consistent with experimental measurements. The TARMATDEP code will be enhanced to analyze radiolytic gas generation from matrices tested under the GH2P. The TARMATDEP was developed as part of the MDP to theoretically analyze hydrogen gas generation in TRU waste and predict G-value as a function of dose by explicitly incorporating fundamental nuclear and molecular mechanisms that result in the generation of hydrogen. The model tracks alpha radiation propagation through source and target materials and determines the effects on target molecules. Based on user-input dimensions and initial energies, TARMATDEP determines the alpha energy loss profile in two PuO_2 source materials: (a) Pu-238, and (b) Pu-239, as well

as in five candidate target materials, simulating the contents of TRU waste: PE, PVC, wet and dry cellulose, and cement. The program calculates the instantaneous number of hydrogen bonds broken, running sum of hydrogen bonds broken, and absolute G-value. The model allows for user specification of both the total duration of modeling and the time interval between recording of the calculated data. The code provided a series of predictive G-values that (a) matched very well the experimental MDP data, and (b) indicated the behavior of G-value versus time, dose, Pu loading, and other parameters.

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APPENDIX A

STATISTICAL DETAILS OF EXPERIMENTAL DESIGN

A.1 Sample Size for Simulated RFETS MSE Salt Residue Waste Matrix Testing

This appendix documents the estimation of the minimum number of sampling cycles (G-value measurements) to be collected from each of the test cylinders under the GH2P. Previous testing (documented in Section 1.1 of this test plan) has shown a linear relationship between the G-value and residual moisture content. Based on the G-value of water of 1.6 molecules/100eV and planned testing at 0, 5, and 11% residual moisture content levels in simulated salt residue matrices, the estimated G-values are 0, 0.08, and 0.18 molecule/100eV, respectively. The MDP determined a mean G-value of 0.25 ± 0.18 molecule H_2/100 eV for the Envirostone waste matrix, which most nearly approximates the MSE salt residue waste matrix. The experimentally determined G-value for the Envirostone waste matrix was approximately one-third of the theoretical G-value based on the product of the residual moisture content of the Envirostone and the G-value of water.

The design of the simulated MSE salt residue experiment is a two-way, fixed-effects analysis of variance. Measurements of the G-value will be made over time in cylinders with 0, 5, and 11% moisture content in the simulated MSE salt residue waste matrix. Two cylinders will be assigned to each residual moisture content level. Table A-1 lists the design layout.

Table A-1. Two-way ANOVA G-values for MSE salt residue.

	Percent Moisture Content			
Cylinder	0%	5%	11%	Cylinder mean
I	I, 0%	I, 5%	I, 11%	
II	II, 0%	II, 5%	II, 11%	
Mean % Moist				Grand mean

The null and alternate hypotheses are:

$$H_o: \mu(G_{0\%}) = \mu(G_{5\%}) = \mu(G_{11\%})$$

$$H_a: \mu(G_{0\%}) < \mu(G_{5\%}) < \mu(G_{11\%})$$

The primary effect that is being tested is residual moisture content. Two cylinders per level will be used to increase precision and to ensure useable data in case a test cylinder fails. The model that will be tested is:

$$TSS = SSMoisture + SSCylinder + SSMC + SSE$$

The minimum sample size, shown in Table A-2, for this experiment was approximated on the basis of expected theoretical differences in the G-values at the predetermined residual moisture content levels and the standard deviation based on the Envirostone waste matrix results from the MDP testing. The type I error, α, was specified as 0.10 and the type II error, β, was specified as 0.10. The minimum number of observations per waste matrix (i.e., simulated MSE salt residue and either 0, 5, or 11% residual moisture content level) is calculated through the following equation:

Table A-2. ANOVA Summary for MSE salt residue experiment.

Source	Number	d. f.	Sum Squares	Mean Square	F

Cylinder	2	1	SSCylinder	X	X
Moisture content	3	2	SSMoisture	SSMoisture /2	MSMoisture/MSE
CM interaction		2	SSCM	SSCM/2	MSCM/MSE
Error		114	SSError	SSE/114	
Total	120	119			

(A-1)

where

$Z_{1-\alpha}$ = 1.28

$Z_{1-\beta}$ = 1.28

σ = 0.18

Δ = 0.08 (smallest expected difference).

The calculation yields approximately 40 samples (i.e., G-value measurements) per residual moisture content level, which will be divided between two cylinders in each treatment group. Thus, 20 sampling cycles are adequate for the GH2P testing of the simulated MSE salt residue waste matrix. The coefficient of variation (standard deviation/mean) in the MDP experiments was less than used to estimate sample numbers; therefore, the estimated sample number is believed to be conservative. Table A-2 shows the ANOVA summary table. Residual moisture levels will be randomly assigned to test cylinders. Test cylinders will be randomly assigned to slots on the test rack.

A.2 Sample Size for Simulated INEEL Type I and Type II Sludges (IDC 001) Testing

The purpose of this experiment is to compare G-values for simulated sludge waste containing plutonium and plutonium plus uranium. Theoretical calculations indicate expected values of 0.96 molecule H_2/100 eV for both sources. Previous experiments using an Envirostone waste matrix have shown observed plutonium concentrations to be approximately one-third of the theoretical value. The effect of combining uranium plus plutonium on G-values is unknown.

The experimental design is a one-way analysis of variance. Measurements of the G-value will be made from test cylinders containing plutonium and plutonium plus uranium radioactive source material. Two cylinders will be assigned to each treatment group. The null and alternate hypotheses are:

$$H_o: \quad \mu(G_{Pu}) = \mu(G_{Pu+U})$$

$$H_a: \quad \mu(G_{Pu}) \neq \mu(G_{Pu+U})$$

The sample size for this experiment was estimated using Equation A-1 with type I and type II error rates set to 0.025 ($\alpha/2$), and a capability of detecting a difference in the population mean G-value of ±0.25 molecule/100 eV. The population standard deviation was estimated as 0.18 molecule H_2/100 eV based on the results of MDP testing of the Envirostone waste matrix. Thus for this experiment, the parameter values for Equation A-1 are:

$Z_{1-\alpha}$ = 1.96

$Z_{1-\beta}$ = 1.96

σ = 0.18

Δ = 0.25

The estimated minimum sample size is 8 G-value measurements per matrix tested, or four per cylinder. Because this experiment will be done in conjunction with the MSE salt residue testing, 20 sampling cycles will be completed as part of the GH2P testing (i.e., five times more than what is required as a minimum for the simulated sludge waste matrix). Table A-3 shows the ANOVA summary table. Simulated waste matrices will be randomly assigned to test cylinders. Test cylinders will be randomly assigned to slots on the test rack.

Table A-3. ANOVA Summary table for G-values from two sludge types.

Source	d.f.	Sum Squares	Mean Square	F
Sludge	1	SSSludge	SSSludge/1	MSS/MSE
Cylinder	1	SSCylinder	SSCylinder/1	
Within	37	SSError	SSE/37	
Total	39			

APPENDIX B

TOLERANCE FACTORS (K)

Table B-1. Tolerance factors (K) for one-sided normal tolerance intervals with probability level (confidence factor) Y = 0.95 and coverage P = 95%.

n	K	n	K	n	K
3	7.655	25	2.292	475	1.766
4	5.145	30	2.220	500	1.763
5	4.202	35	2.166	525	1.760
6	3.707	40	2.126	550	1.757
7	3.399	45	2.092	575	1.754
8	3.188	50	2.065	600	1.752
9	3.031	75	1.972	625	1.750
10	2.911	100	1.924	650	1.748
11	2.815	125	1.891	675	1.746
12	2.736	150	1.868	700	1.744
13	2.670	175	1.850	725	1.742
14	2.614	200	1.836	750	1.740
15	2.566	225	1.824	775	1.739
16	2.523	250	1.814	800	1.737
17	2.486	275	1.806	825	1.736
18	2.543	300	1.799	850	1.734
19	2.423	325	1.792	875	1.733
20	2.396	350	1.787	900	1.732
21	2.371	375	1.782	925	1.731
22	2.350	400	1.777	950	1.729
23	2.329	425	1.773	975	1.728
24	2.309	450	1.769	1000	1.727